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The hygroscopicity parameter (κ) of ambient organic aerosol at a field site subject to biogenic and anthropogenic influences: Relationship to degree of aerosol oxidation

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Abstract

Cloud condensation nuclei (CCN) concentrations were measured at a rural site in Ontario, Canada during the spring of 2007. The CCN concentrations were compared to values predicted from the aerosol chemical composition and size distribution using κ-Köhler theory. The hygroscopicity of the organic component was characterised by two methods, both of which are based on the aerosol's degree of oxygenation as determined by the mass spectra measured with an Aerodyne aerosol mass spectrometer. The first approach uses a statistical technique, positive matrix factorization (PMF), to separate hygroscopic and non-hygroscopic factors while the second uses the O/C, which is an indication of the aerosol's degree of oxygenation. In both cases, the hygroscopicity parameter (κ) of the organic component is varied so that the predicted and measured CCN concentrations are internally consistent and in good agreement. By focussing on a small number of organic components defined by their composition, we can simplify the estimates needed to describe the aerosol's hygroscopicity. We find that κ of the oxygenated organic component from the PMF analysis is 0.20±0.03 while κ of the entire organic component can be parameterized as κ_{org}=(0.30±0.05)×(O/C).

1 Introduction

Aerosols can affect climate directly by scattering and absorbing incoming solar radiation, or indirectly by acting as cloud condensation nuclei (CCN), which form clouds and in turn can reflect light (Twomey, 1977). The efficiency of aerosols as CCN also affects both aerosol particle and cloud droplet lifetimes (Albrecht, 1989). It is well recognized that these effects represent one of the largest uncertainties in assessing the changes in radiative forcing from pre-industrial times to the present (IPCC, 2007). As such, understanding the hygroscopic properties of aerosols and the processes that govern cloud droplet activation are important.

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Köhler theory has been used to predict the CCN-activity of inorganic compounds for many years (Köhler, 1936). In the last decade, the focus has turned to the prediction of the CCN-activity of organic compounds in atmospheric particles. Laboratory studies have shown that the CCN-activity of organic, inorganic, or mixed aerosol systems can be predicted as long as the composition of the particles is well-characterised and their properties known (Abbatt et al., 2005; Bilde and Svenningsson, 2004; Broekhuizen et al., 2004a; Raymond and Pandis, 2002, 2003). However, ambient aerosols are composed of numerous organic compounds that are difficult to identify and quantify (Jacobson et al., 2000; Saxena and Hildemann, 1996), therefore complicating the prediction of the CCN-activity of those ambient particles. The organic fraction comprises a significant fraction of the aerosol at many locations in the Northern Hemisphere (Zhang et al., 2007), highlighting the need to study organic aerosol hygroscopicity. In this study, we test our ability to predict the CCN-activity of ambient aerosols at a continental site by conducting an aerosol-CCN closure study, in which we compare CCN concentrations measured using a CCN counter with those predicted using modified Köhler theory. We then vary the hygroscopicity of the organic aerosol component in the model to obtain the best degree of closure.

Two unique strategies are used in this paper to simplify the experimental approach to studying this aerosol property. These strategies reflect recent major developments in the aerosol field. First, field observations of the organic aerosol made by an Aerodyne aerosol mass spectrometer (AMS) are characterised by the degree of oxygenation. Of late, this has been accomplished by factor analysis techniques (Zhang et al., 2005, 2007) including, more recently, positive matrix factorization (PMF) (Lanz et al., 2007; Ulbrich et al., 2009). Here aerosol mass spectra, which contain signal from hundreds if not thousands of organic molecules, are described as a linear combination of a few characteristic factors relating to emission sources, atmospheric processing, etc. This approach characterises the overall organic composition in terms of a sufficiently small number of factors that might match the number of organic aerosol species specified in climate and air quality models, such as the hydrophilic and hydrophobic organic

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fractions found in some global models (Chung and Seinfeld, 2002; Cooke and Wilson, 1996; Lohmann et al., 1999). A combination of AMS measurements (Zhang et al., 2007) and the subsequent application of PMF (Ulbrich et al., 2009) is now a common approach used in the organic aerosol community. This study also uses the O/C to directly determine the aerosol's degree of oxygenation.

The second simplifying advance that we take advantage of is to describe the organic hygroscopicity using the κ-Köhler method (Petters and Kreidenweis, 2007, 2008). Specifically, this expression of the Köhler model groups the properties of each compound present in the aerosol that affects its hygroscopicity into a single variable, κ. Thus, knowledge of the individual molecular solubilities, surface tension properties and molecular weights, which are largely unknown in ambient aerosol, is obviated. And so, the overall goal of this work is to determine the hygroscopic properties, expressed as the κ parameter, for the small number of PMF factors that can now be used to describe organic aerosol composition, as well as in relation to the degree of oxygenation as determined from the O/C.

An extensive review of early aerosol-CCN closure studies that had limited information about the organic component of the aerosol can be found in Broekhuizen et al. (2006). However, with the recent widespread use of the AMS and following the initial study of Broekhuizen et al. (2006), a few closure studies have since been conducted in which the aerosol chemical composition is highly time resolved and the organic fraction quantified. These studies from the field achieved closure by determining the hygroscopicity of either the entire aerosol by assuming an average chemical composition in continental China (Rose et al., 2008), or the entire organic component by assuming that the hygroscopicity in the organic component was constant at rural locations (Chang et al., 2007; Medina et al., 2007; Stroud et al., 2007), in the Amazon (Gunthe et al., 2009; Roberts et al., 2002), at cloud level (Wang et al., 2008), as well as sites that are removed from major source areas (Ervens et al., 2009). A general conclusion is that the organic fraction is hygroscopic. This contrasts with urban closure studies indicating insoluble organics (Lance et al., 2009), especially at small sizes (e.g. Broekhuizen

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et al., 2006; Cubison et al., 2008; Quinn et al., 2008), although this can also be true for remote locations (Ervens et al., 2007). Here we provide the first characterisation of varying hygroscopicity of the organic component based on its degree of oxygenation. This study builds on the results from previous closure studies conducted in our group at urban and rural sites (Broekhuizen et al., 2006; Chang et al., 2007).

2 Experimental method

The Egbert 2007 study took place between 14 May and 15 June 2007, at Environment Canada's Centre for Atmospheric Research and Experiment (CARE). This rural site, situated at Egbert, Ontario, Canada (44.23 N, 79.78 W, 251 m above sea level), is approximately 70 km north of Toronto, is surrounded by farmland, and experiences relatively minimal influences from local sources. The actual sampling location is 125 m from the main CARE building and the nearest road, 75 m away, is used by only a few vehicles per hour. The site is often impacted by polluted urban outflow from the populated and industrialized regions of Southwestern Ontario and mid-western United States, as well as cleaner continental air from the north (Rupakheti et al., 2005).

The main goal of Egbert 2007 was to improve our understanding of the sources and hygroscopicity of organic aerosols. To this end, recent publications from this campaign have shown that the oxidation state of the aerosol correlates with the photochemical age of the air (Vlasenko et al., 2009), significant secondary organic aerosol mass can be formed from monoterpene oxidation (Slowik et al., 2009a), oxygenated organic aerosols from anthropogenically-influenced air could have primary and secondary sources, while biogenically-influenced air only had secondary sources (Chan et al., 2009), and aerosols from anthropogenically-influenced air showed a delay in cloud droplet activation compared to biogenically-influenced air (Shantz et al., 2009). The present study focusses on the hygroscopicity of the organic component of the aerosol by performing an aerosol-CCN closure experiment alongside measurements of the organic component of the gas and particulate phases, so as to best define the

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source of air sampled at CARE. A wide variety of instruments were deployed during the study, but only those of direct relevance to this analysis are described here.

2.1 Scanning mobility particle sizer

A scanning mobility particle sizer (SMPS, TSI 3071, 3081, 3080) measured aerosol size distributions between 10 nm and 420 nm in diameter every 15 min with a sample to sheath flow ratio of 1:6, where the sheath flow was dried with silica gel. All instruments sampled from the roof of the building, with intakes ≈5.5 m above ground. The main inlet was a PVC pipe (0.2 m inner diameter), lined with aluminium tape to decrease electrostatic deposition, where the residence time was ≈1 min. The SMPS sampled from the centre line of the main inlet in stainless steel tubing with a residence time of the secondary lines of ≈1 s.

2.2 CCN counter

The CCN concentration was measured at a constant supersaturation using a parallel-plate continuous flow thermal gradient diffusion chamber that was previously used in a closure study at the same site (Chang et al., 2007). This instrument, built at the University of Toronto, is a more portable and automated version of the design described by Pradeep Kumar et al. (2003). It consists of two parallel aluminium plates held at different temperatures, which results in a supersaturation forming at the centre of the chamber (Saxena et al., 1970). A sheath flow (1.8 L min^{-1}) keeps the sample aerosol flow (0.2 L min^{-1}) at the centre of the chamber such that particles that are CCN-active at that supersaturation activate and are counted by an aerodynamic particle sizer (TSI 3320) as they exit the chamber. The cooler bottom plate was maintained at room temperature while the warmer upper plate was heated with a resistive heating pad (Omega) to the temperature required for the desired supersaturation. Like the chamber described by Pradeep Kumar et al. (2003), this instrument has a movable injector that allows the

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residence time to vary from 9 to 21 s. For most of this study, the residence time of the chamber was 19 s where the highest concentration of CCN was measured.

The CCN counter was calibrated four times throughout the study using monodisperse ammonium sulphate particles to determine the size at which 50% of the aerosols activated. Based on these calibrations, the effective supersaturation in the chamber was determined to be 0.42±0.03%. This instrument also sampled from the main inlet with a residence time in its secondary line of <6 s.

2.3 Proton-transfer-reaction mass spectrometer

Volatile organic compounds (VOCs) were measured using a proton-transfer-reaction mass spectrometer (PTR-MS, Ionicon Analytik). The details of this method and its application to ambient air sampling have been described elsewhere (de Gouw and Warneke, 2007). A description of the instrument performance during this particular study can be found in Vlasenko et al. (2009). In brief, ambient air was sampled at 4.4 L min^{-1} through a 7.5 m long PFA tube with 0.48 cm inner diameter whose inlet was 2 m from the main aerosol inlet. The PTR-MS sampled 0.2 L min^{-1} from the main flow through a heated 0.2 cm outer diameter silocosteel line. Protonated VOC species were recorded in scanning mode from *m/z* 21 to 160 on a 140 s time interval. The system was calibrated by standard addition using commercial custom-made gas mixtures (Apel-Riemer Inc. and Scott Specialty Gases). In addition, background measurements were made by installing a charcoal cartridge (Supelco) upstream of the PTR-MS inlet line.

2.4 Aerosol mass spectrometers

A time-of-flight aerosol mass spectrometer (C-ToF AMS, Aerodyne) measured the aerosol chemical composition that was non-refractory at 870 K and 10^{-7} torr. The operation of the AMS has been described elsewhere (Drewnick et al., 2005; Jayne et al., 2000; Jimenez et al., 2003) and the specific operation of this instrument for this study

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is described by Slowik et al. (2009a). This AMS sampled off a separate stainless steel and copper inlet ≈3 m from the main inlet with a residence time of ≈15 s. AMS mass concentration measurements are complicated by uncertainties in collection efficiency due to the possibility of particle bounce at the vaporizer surface. However, this does not affect the analysis below, which only uses the fractional composition and assumes an internally mixed particle ensemble.

The PMF receptor modelling technique uses multivariate statistical methods to represent an input data matrix as a linear combination of a set of factor profiles (mass spectra, for AMS data) and their time-dependent intensities (Paatero, 1997; Paatero and Tapper, 1994). Application of PMF to AMS datasets have previously been discussed (Lanz et al., 2007; Slowik et al., 2009b; Ulbrich et al., 2009; Allan et al., 2009), as has the PMF analysis for the present study (Slowik et al., 2009a). In the present study, four factors were resolved for the organic component: a hydrocarbon-like organic aerosol (HOA) component correlating with tracers for primary anthropogenic emissions (e.g. NO_x and benzene); a biomass burning organic aerosol (BBOA) component; and two oxygenated organic aerosol components (OOA-1, OOA-2), where OOA-1 is more oxygenated than OOA-2. OOA-1 correlates with tracers for long-range transport (e.g. particulate sulphate), while OOA-2 correlates with VOCs measured by the PTR-MS at *m/z* 71 (ion $C_4H_6OH^+$) which is thought to arise from products of photochemistry (e.g. methacrolein and methyl vinyl ketone). The reader is directed to the publication by Slowik et al. (2009a) for further detailed information on the PMF solution. The important point for the current analysis is the differentiation between the oxygenated (OOA and BBOA) and unoxygenated (HOA) components of the organic aerosol.

A high-resolution time-of-flight AMS (HR-ToF AMS) was also deployed at the site. The mass resolution of the W-ToF AMS, (3000–5000), means that fragments of nominally the same *m/z* can be quantified separately, and hence the total molar ratio of oxygen to carbon (O/C) can be determined. The application, accuracy, precision and limitations of the HR-ToF AMS in quantifying total C and O have been discussed previously (Aiken et al., 2007, 2008). Although the absolute accuracy of determining O/C

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for ambient aerosols using an AMS is not well established, it can be used as a tracer for atmospheric oxidation. High resolution data analysis for this study was completed using a custom algorithm, which incorporated a peak fitting procedure, typical AMS correction factors and a correction for the O/C as suggested by Aiken et al. (2008) to account for discrepancies between AMS derived O/C and that derived from laboratory standards. While the subsequent calculations and results are from the C-ToF AMS, they will be compared with O/C results from the HR-ToF AMS in Sect. 4.2.

3 Methodology for determining the hygroscopicity parameter

Data were averaged into 15 min intervals and using the chemical composition measured by the C-ToF AMS, the activation diameter for a dry particle at the supersaturation of the CCN chamber (0.42%) was calculated using κ-Köhler theory (Petters and Kreidenweis, 2007, 2008), where Köhler curves were generated for increasing particle sizes until the critical supersaturation of the initial dry particle was less than or equal to the supersaturation of the CCN counter. The aerosol size distribution, as measured by the SMPS, was then integrated for all dry particle sizes greater than the activation diameter to arrive at the predicted CCN concentration. The hygroscopicity parameter of the aerosol's organic component (κ_{org}) was then iteratively varied (changing the activation diameter and thus the predicted CCN concentrations) to yield predicted CCN concentrations consistent with those measured by the CCN counter. The rest of this section describes in detail how the activation diameter was calculated and the assumptions made in order to determine κ_{org}.

κ-Köhler theory (Petters and Kreidenweis, 2007, 2008) simplifies the Köhler equation by combining all the compound-specific variables (e.g. molecular weight, density, van't Hoff factor) into a single parameter κ, as shown in Eq. 1:

$$S = \frac{D^3 - D_i^3}{D^3 - D_i^3(1-\kappa)} \exp\left(\frac{4\sigma M_w}{\rho_w \mathrm{RTD}}\right), \quad (1)$$

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where D and D_i are the droplet wet diameter and initial dry diameter, respectively, σ is the droplet surface tension (0.072 N m^{-2} initially), M_w is the molecular weight of water, ρ_w is the density of water, R is the universal gas constant and T is the temperature. In this equation, the overall κ of the aerosol is calculated as the volume-weighted average of the κ of the components, which assumes that the total volume of the water content can be calculated by adding the water contents of the individual components (Petters and Kreidenweis, 2007), i.e.

$$\kappa = \sum_i \varepsilon_i \kappa_i, \quad (2)$$

where ε_i and κ_i are the volume fraction and κ of the i^{th} components of the aerosol. For a soluble compound, κ_i can be calculated as:

$$\kappa_i = \frac{i_i \rho_i M_w}{\rho_w M_i}, \quad (3)$$

where i_i, ρ_i, and M_i are the van't Hoff factor, density and molecular weight, respectively, of the compound.

Measurements of ammonium, nitrate and sulphate from the AMS were grouped together and assumed to behave as ammonium sulphate, with a κ of 0.61 and density of 1770 kg m^{-3} (Petters and Kreidenweis, 2007; Windholz, 1983). The errors associated with this assumption are not large since the aerosol was not acidic during the study and the κ and density of ammonium nitrate are 0.67 and 1730 kg m^{-3}, respectively, which are close to the values for ammonium sulphate. In this analysis, the bulk aerosol mass spectrum was used, which means that the aerosol is assumed to be internally mixed with a constant chemical composition and degree of oxygenation at all sizes. These assumptions are justified by the lack of local sources, and the observation that the aerosol mass distribution, in both the SMPS and AMS, was mostly unimodal with little mass at particle sizes less than 70 nm, the upper bound of the typical activation diameter, suggesting that the sampled aerosols were well processed and hence internally mixed. The sensitivity of our results to the presence of black carbon is discussed

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in Sect. 4.3 and the contribution of mineral dust to the aerosol submicron fraction is considered negligible at this site.

There are numerous approaches in representing κ_{org}. However, in this analysis we will focus on two methods, both of which are based on the degree of oxygenation of the organic component as determined from AMS measurements. We generally assume that a more oxygenated organic aerosol is more polar and therefore more soluble and hygroscopic than a less oxygenated organic aerosol. This is supported by laboratory studies that have found that oleic acid aerosols that have undergone ozonolysis have significantly increased CCN-activity (Broekhuizen et al., 2004b; Shilling et al., 2007), chamber studies that show that aging secondary organic aerosols can also increase their CCN-activity (Duplissy et al., 2008; Petters et al., 2006), and ambient observations that have found air masses with more OOA-rich aerosols to be more hygroscopic (McFiggans et al., 2005). In contrast, the more hydrocarbon-like component of the aerosol is non-polar and therefore less hygroscopic. Thus, there is an expectation that the degree of oxygenation will dictate the aerosol's hygroscopicity.

The first approach to representing κ uses the factors from the PMF analysis grouped into two components: a non-hygroscopic, unoxygenated component consisting of the HOA factor, whose κ (κ_{unox}) is approximated by 0, and a hygroscopic component, consisting of the oxygenated factors OOA-1, OOA-2 and BBOA. This oxygenated component is assumed to have a single hygroscopicity, with a κ (κ_{ox}) that was varied until the predicted CCN number concentrations were in good agreement with the measured concentrations (the criteria for this will be described in Sect. 4.1.1). The oxygenated factors were grouped together because our model was not sensitive enough to elucidate separate hygroscopicities for each factor. In this approach, Eq. 2 can be rewritten as:

$$\kappa_{org} = \varepsilon_{ox} \times \kappa_{ox} + \varepsilon_{unox} \times \kappa_{unox} = \varepsilon_{ox} \times \kappa_{ox}, \quad (4)$$

where the volume fractions are calculated by assuming that the density of the oxygenated component is that of adipic acid (1360 kg m^{-3}). The overall aerosol chemical

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density is calculated assuming a density for ammonium, nitrate, sulphate, and organic of 1760, 1730, 1770 and 1200 kg m^{-3}, respectively.

The second approach assumes a direct relationship between the organic aerosol's degree of oxygenation and its hygroscopicity. The simplest relationship is a linear one, so that

$$\kappa_{org} = a \times (O/C), \quad (5)$$

where O/C, the mole ratio of atomic oxygen to atomic carbon, is a measurement of the organic aerosol's degree of oxygenation and can be estimated from the fraction of the total organic signal occurring at *m/z* 44 measured by the C-ToF AMS, as described by Aiken et al. (2008). In Eq. 5, a is the value of κ_{org} when the O/C is one and is varied until the predicted CCN concentrations are in good agreement with measured concentrations. This relationship between the organic aerosol's O/C and hygroscopicity may not be linear and more complicated relationships between the two quantities will exist that may be more accurate, but for the purposes of this initial attempt, we start with the simplest functionality.

Using either approach, κ for the entire aerosol can be calculated from Eq. 2 combined with either Eq. 4 or Eq. 5, and then the activation diameter calculated from Eq. 1 for the supersaturation of the CCN counter (0.42%).

4 Results and discussion

4.1 Calculations using PMF factors

4.1.1 Results from the entire study

The relative contribution of the organic component to the hygroscopicity of the ambient aerosol at Egbert depends on the overall chemical composition, and more specifically the inorganic fraction (Chang et al., 2007), i.e. for inorganic-rich particles, the

hygroscopicity of the organic fraction becomes unimportant in assessing the overall hygroscopicity of the particle. As such, the ratio of CCN concentrations predicted using the κ-Köhler model to CCN concentrations measured with the CCN counter (R_{CCN}) for the entire study is plotted as a function of aerosol inorganic fraction in Fig. 1. Figure 1a shows that R_{CCN} is dependent on composition when the organic component is assumed to be non-hygroscopic (i.e. $\kappa_{unox}=\kappa_{ox}=0$), with the organic-rich data points being underpredicted ($R_{CCN}=0.892\pm0.008$) compared to the inorganic-rich data points (1.14 ± 0.01), where the uncertainty given is the standard error.

Allowing the oxygenated OOA and BBOA components to be hygroscopic with a κ_{ox} of 0.20 (Fig. 1b) reduces the difference between the mean R_{CCN} of the organic-rich data points and the inorganic-rich data points (mean R_{CCN} are 1.23 ± 0.01 and 1.22 ± 0.01, respectively). For a Köhler model that predicts with a consistent accuracy for all chemical composition, R_{CCN} should be independent of composition. If the mean R_{CCN} of the organic-rich data points is lower than that of the inorganic-rich data points, then the hygroscopicity of the organic component needs to be increased until R_{CCN} is independent of composition by increasing κ_{ox}. Conversely, if the mean R_{CCN} is higher for the organic-rich data points, then κ_{ox} is too high and needs to be decreased.

In order to assess this systematically, the data points were split into two equal populations based on the magnitude of their inorganic fraction and their mean R_{CCN} was then compared. κ_{ox} for the entire data set was varied until the means of the two halves were no longer significantly different (two-tailed t-test, unequal variances, significance level of $p<0.05$). Since aerosols with a high inorganic fraction are less sensitive to changes in the hygroscopicity of the aerosol's organic component (see Broekhuizen et al., 2006; Chang et al., 2007), the mean of the more inorganic half of the population was used as a reference. Using this method, κ_{ox} for the entire study was found to be 0.20 ± 0.03.

This method of internal comparison was chosen because both measured and predicted CCN concentrations are precise but not necessarily fully accurate due to experimental uncertainties, such as different line losses to the SMPS and CCN counter,

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errors in the sizing of the SMPS and counting errors in both systems, as well as uncertainties in model assumptions, such as mixing state, particle sphericity, density, etc. As such, the criterion for the best value of κ_{ox} is a consistent R_{CCN}, whether over or underpredicted, regardless of composition. Although the overprediction from this calculation is approximately 20%, a linear regression of the predicted and measured CCN concentrations results in a slope of 1.02 (see Fig. 2), which suggests that the model is appropriate and is comparable to other field studies (Broekhuizen et al., 2006; Chang et al., 2007; Medina et al., 2007; Wang et al., 2008).

4.1.2 Results from select time periods

Because local sources were not prominent during the study, it was possible to characterise regional air masses during which the organic aerosol composition was assumed to be more uniform. From this analysis, we can assess the uncertainty that arises from assuming that the organic components have the same hygroscopicity regardless of source. The study was broken down into four air regimes based on aerosol chemical composition, the characteristics of the organic component (based on the PMF factors), local wind direction and wind speed, the photochemical age of the air from the ratio of toluene to benzene (de Gouw et al., 2005; Roberts et al., 1984), and back trajectories. The four periods are described below and illustrated in Fig. 3 with typical back trajectories calculated using HYSPLIT (Draxler and Rolph, 2003; Rolph, 2003) shown in Fig. 4. All dates and times are local, eastern daylight savings time.

1. For this study, periods of high anthropogenic influence were characterised by both high sulphate and organic aerosol mass loading. The toluene/benzene was often high, suggesting a shorter photochemical age, and back trajectories show that the air masses originated from populated regions to the south (the red trace in Fig. 4). These periods are referred to as “Anthropogenic”, while recognizing that aerosol precursors will not be exclusively anthropogenic.

2. Two of the Anthropogenic periods were preceded by times when the local winds were from the southeast and the aerosol was mostly organic (specifically high HOA and OOA-1, as opposed to the Anthropogenic period which had more OOA-2) with very little sulphate. The back trajectories, however, tended to be from the northwest to northeast, suggesting that these air masses did not originate from highly populated or polluted regions (purple trace in Fig. 4). However, because the toluene/benzene was high (suggesting that the photochemical age was short), it would appear that the aerosols during these times were from clean continental air but were influenced by more local anthropogenic sources (e.g. a highway 10 km to the east). These periods are referred to as "Pre-Anthropogenic".

3. Continental air, characterised by low sulphate loadings, a low toluene/benzene (suggesting enhanced photochemical processing) and higher organic mass fractions, was associated with trajectories from the mostly forested north (green trace in Fig. 4). The earlier episode (19–21 May) was colder and expectedly less influenced by biogenics whereas the episode near the end of the study (8–13 June) was characterised by warmer temperatures and high organic mass loadings mostly from biogenic sources (Slowik et al., 2009a). These periods are referred to as "Biogenic" for this analysis. Measurements during the second biogenic period were interrupted by a failure in the CCN counter, as well as a period (11 June, 18:15–12 June, 18:30) during which the air was elevated in SO_2 and particulate sulphate concentrations. The majority of the sulphur in the latter case is suspected to have originated from smelters in the Sudbury region based on the back trajectories (not shown); such an observation at Egbert is not uncommon (Rupakheti et al., 2005).

4. At the end of the study, after the second Biogenic period, the winds shifted from the north to the east and the air was characterised by a high toluene/benzene as well as a higher HOA fraction (compared to the Biogenic period). Back trajectories show the air originating from the east (blue trace in Fig. 4), suggesting that it is

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different from the Biogenic period. This period will be referred to as "Easterly Flow".

The composition of the aerosol during the Anthropogenic period was dominated by the inorganic fraction, which in turn, dominates the hygroscopicity of the entire aerosol. This means that these aerosols are much less sensitive to changes in the hygroscopicity of the organic component (Chang et al., 2007). This can be seen in Fig. 1, which shows that R_{CCN} for the Anthropogenic period (in red) is dominated by inorganics and is less sensitive to an increase in κ_{ox} compared to the Biogenic period (in green). As such, the mean R_{CCN} of the Anthropogenic period was used as a reference, and, in an approach similar to that described in the previous section, it was compared to the mean R_{CCN} of the other time periods as κ_{ox} was varied. The final value of κ_{ox} for a time period was determined when its mean R_{CCN} was no longer significantly different than that of the Anthropogenic period (two-tailed t-test, unequal variances, significance level of $p<0.05$) with the same κ_{ox}. Table 1 shows κ_{ox} found for the different time periods and the uncertainties denote when the means of the two populations became significantly different.

For the Biogenic and Easterly Flow times, κ_{ox} are the same, suggesting that the hygroscopicity of the organic component can be characterised in the same manner. They are also similar to the value of 0.20 that was found from the earlier analysis for the whole study period. However, the Pre-Anthropogenic period had a lower κ_{ox} than the rest of the study, suggesting that during this time, the oxygenated components are not contributing significantly to the hygroscopicity of the aerosol. At this point we can only suggest reasons why this behaviour was observed. In particular, noting that the HOA component of the aerosol is high, it is possible that the HOA plays a role in suppressing CCN-activity, perhaps through an effect on the mass accommodation coefficient for water uptake, similar to the observations by Shantz et al. (2009). However, this is only speculation and we have no firm evidence that this is the case.

Figure 5 shows plots of predicted to measured CCN concentrations for the different time periods assuming κ_{ox}=0 (black points) and κ_{ox}=0.20 (red points). As expected,

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we see that during the Anthropogenic time (Fig. 5a), the predicted CCN concentrations do not change significantly compared to the Biogenic and Easterly Flow times (Fig. 5c and d), as well as the Pre-Anthropogenic time, which is even overpredicted (Fig. 5b).

4.2 Results from the entire study using O/C

A similar analysis to that described in Sect. 4.1.1 was performed on the entire data set by dividing the population into two equal populations based on the inorganic fraction and comparing their R_{CCN}. However, κ_{org} was calculated from the O/C using Eq. 5, and not the PMF factors derived from the AMS spectra. By varying the value of κ_{org} for an organic component with an O/C of one (a in Eq. 5), the relationship

$$\kappa_{org}=(0.30\pm0.05)\times(O/C) \quad (6)$$

was found to give an internally consistent result, where the uncertainties are values for which the means of the two halves of the population are not significantly different (two-tailed t-test, unequal variances, significance level of $p<0.05$). As mentioned previously, the O/C was estimated from the fraction of the organic signal at m/z 44, directly from the C-ToF AMS mass spectra, which, on average, is 6% higher than that calculated from the HR-ToF AMS. The grey trace in the top panel of Fig. 3 shows the time series for κ_{org} calculated using the PMF factors, assuming $\kappa_{ox}=0.2$ and $\kappa_{unox}=0$, while the black and red traces are from Eq. 6, using O/C estimated from the C-ToF and HR-ToF AMSs, respectively. We see that all three estimates of κ_{org} yield similar results. This is not completely unexpected since both the PMF and O/C approaches incorporate the degree of oxygenation of the organic component calculated using different analyses. In essence, this shows that the O/C of the entire aerosol can be reasonably expressed as a linear combination of the O/C of the PMF factors.

Putting the results from the O/C analysis into context with those obtained from the PMF factors, Table 2 shows κ calculated for the PMF factors from their O/C using Eq. 6. Values for the two OOA components are consistent with $\kappa_{ox}=0.20$ determined from Sect. 4.1.1, while the HOA kappa confirms that characterising it as non-hygroscopic

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is reasonable. The BBOA κ, 0.05, is low compared to that of the biomass burning marker levoglucosan (κ=0.21, Petters and Kreidenweis, 2007), suggesting that there are components to the BBOA that are not as hygroscopic as levoglucosan. This is supported by the biomass burning experiments performed by (Petters et al., 2009), in which the lower limit that was measured (κ=0.05) is thought to be representative of the organic component in their experiments.

The advantage of the described method is that κ_{org} is calculated from the degree of oxygenation of the organic component of the aerosol as deduced from aerosol mass spectra and does not depend on the PMF analysis, which involves a stage of statistical analysis. It is unclear whether this approach can be generalized to other aerosol types as the range in the O/C for this study was limited to 0.3 to 0.6. As such, further analysis of ambient aerosols with a wider range of oxygenation should be studied in order to determine whether this simple relationship between hygroscopicity and aerosol oxygenation can be applied widely.

4.3 Uncertainties

Table 3 shows the sensitivity of our results to different uncertainties. Systematic uncertainties in the chamber supersaturation (±0.03% supersaturation, Case 1) and SMPS diameter sizing (±5%, Case 2) are quantified for both calculation methods in Table 3. Other uncertainties pertain to the aerosol chemical composition and attempts to quantify uncertainties in the overall aerosol density (Case 3) as well as the density of the oxygenated component (Case 4), both of which affect the calculation of the volume fraction in Eq. 4. If the BBOA component is considered as insoluble (Case 5), the results for κ_{ox} are 0.05 higher. Results from Chan et al. (2009) for Egbert 2007 found that the ratio of elemental carbon to organic matter (EC/OM) for the study was 0.2 except for the final Biogenic period, during which it decreased to 0.15. Case 6 considers the average case in which the ratio is 0.2 and the extra EC mass is assumed to be non-hygroscopic with a density of 1800 kg m^{-3}. Finally, Cases 7 and 8 show the sensitivity

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of the results to a decrease in the surface tension of the droplet by 10% and 20%, respectively, which has the greatest effect on the predicted values.

With the exception of surface tension lowering effects, the uncertainties are individually similar to the uncertainty determined statistically for κ_{ox} and a, although the cumulative effects of multiple cases occuring at once are not quantified. Reductions in the droplet surface tension result in the greatest uncertainty since they affect the exponential term in Eq. 1. However, the κ-Köhler model usually uses the surface tension of water and κ is varied to account for aerosol properties (Petters and Kreidenweis, 2007). As such, the uncertainties in Cases 7 and 8 are presented to gain general understanding in the sensitivity of our results.

4.4 Comparison with literature values

For a theoretical compound that has a van't Hoff factor of one, a molecular weight of 150 g mol^{-1} and a density of 1500 kg m^{-3}, κ is calculated to be 0.18 from Eq. 3. This is consistent with the 0.2 calculated for κ_{ox}, suggesting that its hygroscopicity could be explained by these reasonable assumptions in physical properties.

Studies of secondary organic aerosols (SOA) formed in smog chambers with monoterpene VOC precursors have measured the κ of the entire aerosol to be in the range of 0.04–0.14 (Duplissy et al., 2008; Engelhart et al., 2008; Prenni et al., 2007; Wex et al., 2009) as compared to the values of roughly 0.2 for the OOA factors measured in this study. However, chamber-generated aerosols are typically less oxidized than the OOA components of ambient aerosols (in particular, the OOA-1 component) in part due to higher precursor concentrations, perhaps arising from increased particle-phase partitioning of the more volatile, less oxygenated and hygroscopic components that can arise at high mass loadings frequently used in chamber experiments (Duplissy et al., 2008; Kostenidou et al., 2009; Shilling et al., 2009). The difference could also arise from the limited number of SOA precursors being used in the chamber experiments. Finally, it may not be entirely valid to compare the κ for OOA factors for aerosol measured in the field to that of lab aerosol, since the latter may not be a fully

oxygenated aerosol, i.e. it may have some saturated hydrocarbon functional groups that lower its hygroscopicity. As such, it is not surprising that the ambient data are somewhat more hygroscopic than the results from the chamber studies.

For example, and to be more specific, in an OH oxidation study performed by Duplissy et al. (2008), κ for the entire aerosol was found to be 0.12 for initial precursor concentrations of 10 ppb for α-pinene and 3.8 ppbv NO_x. The fraction of the organic signal at *m/z* 44 was approximately 0.12, which would result in a κ of 0.16, calculated using Eq. 6. Similarly, in an ozonolysis study of α-pinene by George (2009), the ratio of *m/z* 44 to total organic ranged from 0.046 to 0.069, corresponding to a range of κ for the entire aerosol from 0.08 to 0.1. In all cases, the resulting κ for the entire aerosol is consistently lower than the 0.2 found for the OOA components in this study, where the *m/z* 44 to total organic fraction was 0.10 to 0.19.

Other studies that have attempted to quantify κ_{org} in the field found that using a value of 0.1 can adequately describe the CCN-activity of the aerosol at cloud-level (Wang et al., 2008) and in the Amazon rainforest (Gunthe et al., 2009). This is comparable to the campaign-wide average for this study of 0.14 for κ_{org}, calculated using both Eqs. 4 and 6.

Others have simplified aerosol hygroscopicity even further by using a single κ for the whole aerosol over an entire study. If we do this, we find that the average κ of 0.30 is consistent with the 0.3 value that was found in continental China (Rose et al., 2008). However, we find that if we apply this constant κ to all data, we significantly overpredict CCN numbers when the aerosol is dominated by the organic-rich fraction (R_{CCN}=1.37±0.01) compared to times when the aerosol is mostly inorganic (R_{CCN}=1.14±0.01) (Fig. 6). This indicates that more chemical information is needed in order to accurately predict the CCN-activity of ambient aerosols, as opposed to the simplistic approach of assuming that the chemical composition is constant and that one value for κ can be applied to all aerosol types. The approach taken in this paper is to ascribe a specific κ to the two groups of AMS PMF factors.

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In summary, while our overall results match average κ values derived for bulk ambient aerosols, average κ_{org} from ambient aerosols, as well as smog chamber studies, we find that information about the degree of oxygenation of the organic component improves our ability to predict a particle's hygroscopicity.

5 Conclusions

In this analysis we use the degree of oxygenation of the organic fraction of continental aerosol to determine its overall hygroscopicity. Two methods are used to determine the degree of oxygenation, factors elucidated from PMF analysis and from the values of O/C, both of which yield a similar result in terms of the overall κ_{org}. Analysis of the entire study found that a κ_{ox} of 0.20±0.03 is suitable if we assume that the unoxygenated HOA component is non-hygroscopic, and that this overall value is similar to those for most of the specific time periods for the study. However, there are select occasions, such as the Pre-Anthropogenic period, when the organic component does not contribute signicantly to the overall hygroscopicity and we can only speculate that this may have been due to a surface coating or oligomerization process that inhibited water uptake.

The hygroscopicity of the organic component was also found to be related to the O/C through the proposed equation κ_{org}=(0.30±0.05)× (O/C), although the degree of oxygenation of the aerosol in this study was limited in range and further studies in locations with aerosols of different degrees of oxygenation are needed to see if this relationship is more widely applicable.

With the wide-spread use of the AMS and subsequent PMF analysis to characterise ambient aerosol composition, these results are especially relevant in light of the limitations inherent to climate models that can only incorporate a limited number of aerosol components. Specifically, these models frequently only incorporate a hydrophobic and a hydrophilic organic aerosol species, similar in nature to the HOA and OOA AMS factors. By associating specific κ to these two aerosol types, as derived from analyses of

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the type presented in this paper, an empirically-based hygroscopicity constant for the climate model organic aerosol component can be determined.

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Table 1. κ_{ox} for select time periods.

Time Period	κ_{ox}
Biogenic	0.26±0.06
Easterly Flow	0.26±0.03
Pre-Anthropogenic	0.06±0.03

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Table 2. κ calculated for the PMF factors of the organic aerosol component.

Factor	*m/z* 44/Total Organic	O/C	κ
OOA-1	0.19	0.81	0.24
OOA-2	0.10	0.46	0.14
BBOA	0.025	0.17	0.05
HOA	8×10^{-8}	<0.08	<0.02

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Table 3. Sensitivity analysis for potential uncertainties in the two calculaton methods.

Case	Description	Uncertainty in κ_{ox}	Uncertainty in slope of O/C
1	0.03% uncertainty in supersaturation	±0.04	±0.07
2	5% uncertainty in SMPS size	±0.04	±0.06
3	10% uncertainty in overall density	±0.05	±0.01
4	10% uncertainty in density of oxygenated component	±0.05	N/A
5	BBOA as insoluble	+0.05	N/A
6	EC/OM ratio =0.2	+0.05	+0.09
7	10% decrease in surface tenstion	−0.07	−0.18
8	20% decrease in surface tenstion	−0.15	−0.22

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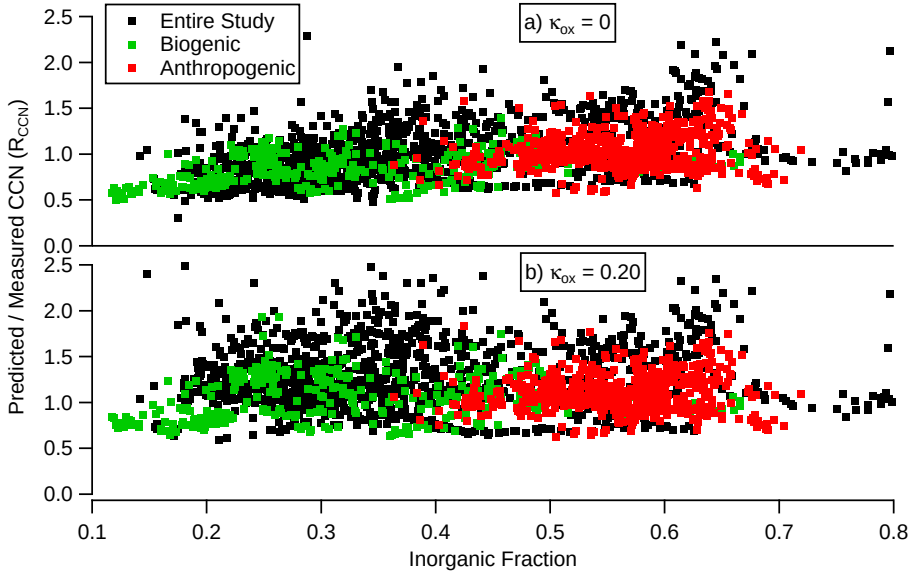

Fig. 1. Ratio of predicted to measured CCN concentrations plotted against aerosol inorganic fraction. Panel **(a)** shows the case in which all of the organic component is assumed to be non-hygroscopic (κ_{org}=0) while **(b)** shows the case in which only κ_{ox}=0.20. Red and green points refer to data from the Anthropogenic and Biogenic periods, respectively (see Fig. 3), while the black points are for the entire study.

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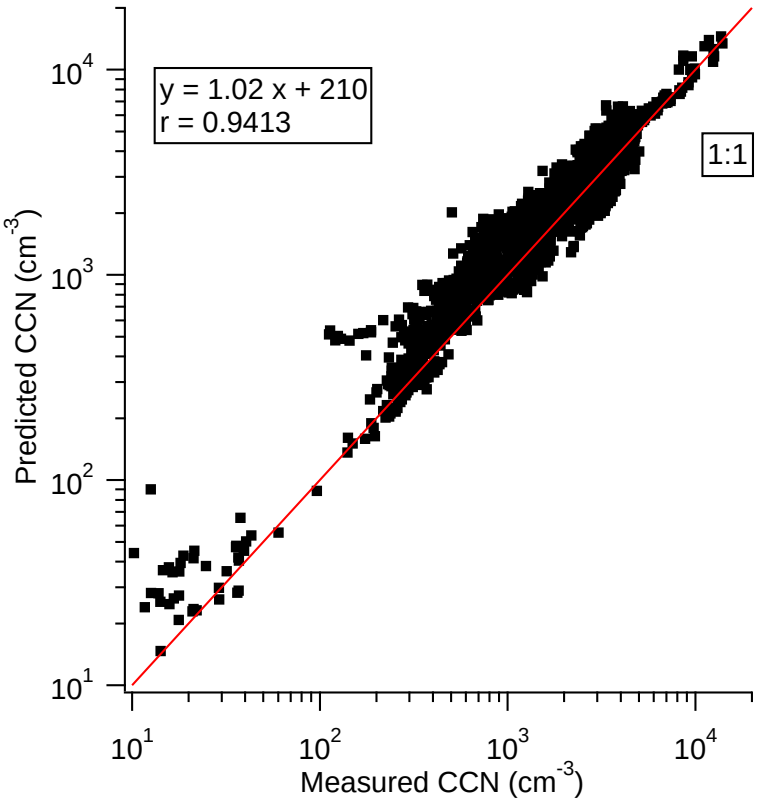

Fig. 2. Comparing predicted and measured CCN concentrations for the entire study assuming that κ_{ox}=0.20. The red line is the 1:1 line.

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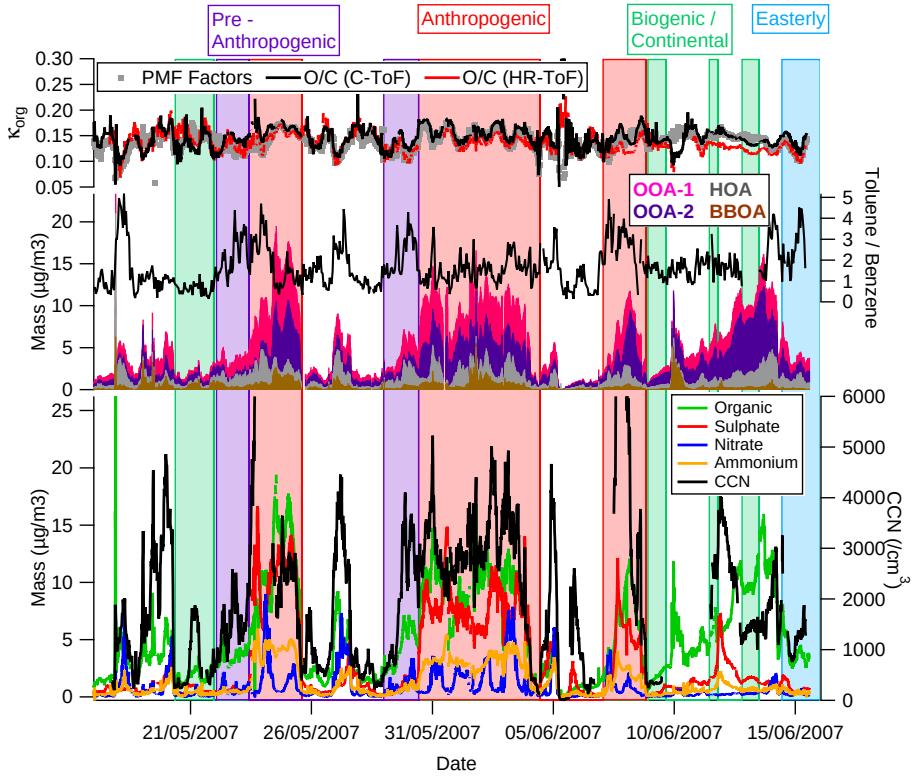

Fig. 3. Time series in local time of κ_{org} calculated from PMF factors and O/C (top panel, see text for more detail), toluene/benzene (black trace in middle panel), PMF factors (middle panel, note that these are cumulative), and aerosol chemical measurements measured by the AMS and CCN concentrations (bottom panel).

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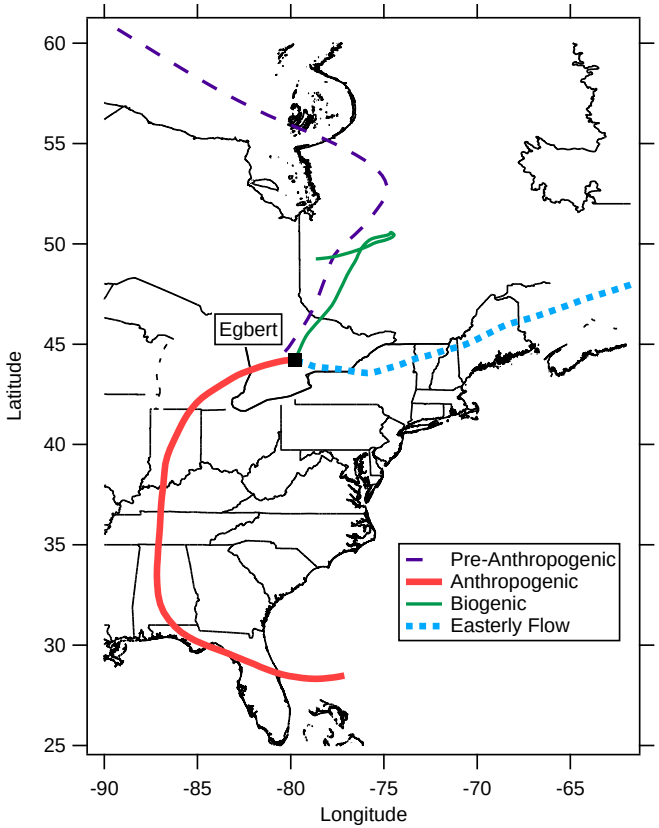

Fig. 4. 72 h back trajectories for 22 May 2007 (Pre-Anthropogenic), 2 June 2007 (Anthropogenic), 13 June 2007 (Biogenic) and 15 June 2007 (Easterly Flow). Trajectories were produced using NOAA HYSPLIT (Draxler and Rolph, 2003; Rolph, 2003).

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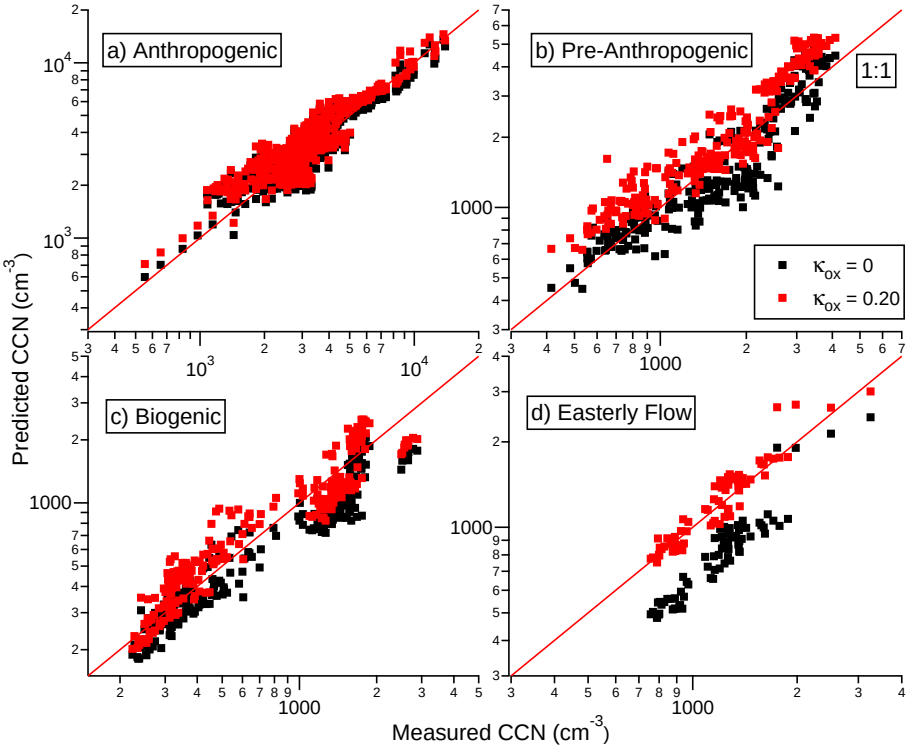

Fig. 5. Comparison of predicted and measured CCN concentrations for different time periods (see Fig. 3) when κ_{ox}=0 (black) and 0.20 (red). The lines are 1:1 lines.

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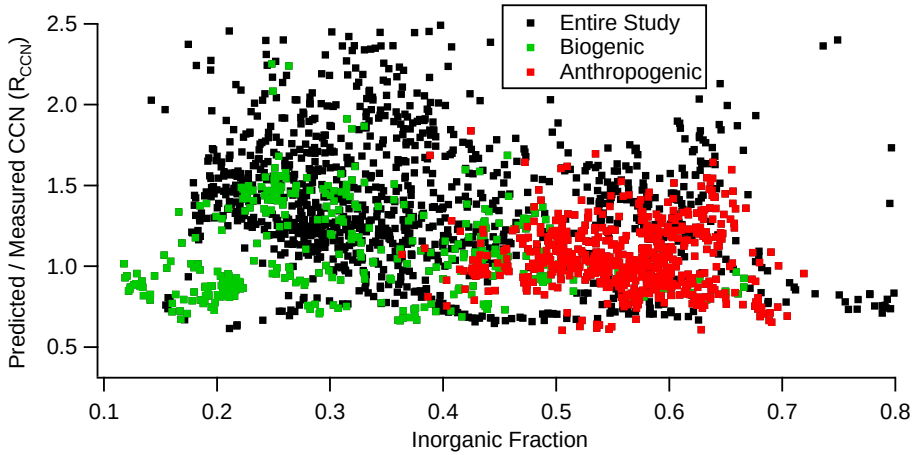

Fig. 6. Ratio of predicted to measured CCN concentrations plotted against inorganic fraction for a constant κ for the entire aerosol of 0.30. Red and green points refer to data from the Anthropogenic and Biogenic periods, respectively while the black points are for the entire study.

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