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# Closure between measured and modeled cloud condensation nuclei (CCN) using size-resolved aerosol compositions in downtown Toronto

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## Abstract

Measurements of cloud condensation nuclei (CCN) were made in downtown Toronto during August and September, 2003. CCN measurements were performed at 0.58% supersaturation using a thermal-gradient diffusion chamber, whereas the aerosol size distribution and composition were simultaneously measured with a TSI SMPS and APS system and an Aerodyne Aerosol Mass Spectrometer (AMS), respectively. Aerosol composition data shows that the particles were predominately organic in nature, in particular for those with a vacuum aerodynamic diameter of <0.25 $\mu$m. In this study, the largest contribution to CCN concentrations came from this size range, suggesting that the CCN are also organic-rich. Using the size and composition information, a detailed CCN closure analysis was performed. In all analyses, the particles were assumed to be internally mixed, the organic fraction was assumed to be insoluble, and the inorganic fraction was assumed to be ammonium sulfate. The AMS time-of-flight data were used for Köhler theory predictions for each particle size and composition to obtain the dry diameter required for activation. By so doing, this closure analysis yielded an average value of $CCN_{predicted}/CCN_{observed}$=1.04 ($R^2$=0.87). Several other closure analyses were performed to mimic other methods of aerosol compositional analysis. In all cases, by assuming uniform aerosol composition across a wider range of particle sizes, significant overprediction of CCN concentrations resulted.

## 1. Introduction

Aerosols and clouds play vital roles in the climate system, both through direct and indirect radiative forcing. Clouds also impact the hydrological cycle through condensation, transport and precipitation processes. Cloud droplets form when aerosol particles are exposed to conditions of water vapor supersaturation. Particles defined as CCN have sufficient soluble mass to activate, or grow to micron size droplets, at a particular supersaturation. Cloud formation processes are complex and highly dynamic in nature;



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however, in general, the concentration of CCN in an air parcel will impact cloud properties. A higher concentration of CCN at a given supersaturation will lead to more droplets with a small mean droplet diameter. This may lead to a more reflective cloud and is termed the first indirect effect, or Twomey effect (Twomey, 1977). The second indirect effect is related to the inhibition of precipitation in clouds with small mean droplet diameters which affects the extent and lifetime of clouds (Albrecht, 1989).

The impact of anthropogenic emissions on cloud and aerosol properties can be significant. Indirect effects have been documented on a local and regional scale (e.g. Rosenfeld, 1999, 2000; Durkee et al., 2000; Givati and Rosenfeld, 2004; Chung and Ramanathan, 2004); however, the understanding of cloud formation processes and aerosol effects are not sufficient to predict indirect effects on a global scale. To accurately understand the indirect effects on a regional and global scale, a better understanding must be achieved on how cloud properties and formation processes are affected by aerosol chemical and physical properties.

The first step towards this goal is the ability to accurately determine how particles of a defined size distribution and composition will act as CCN. A large number of laboratory studies have investigated the CCN behavior of soluble inorganic species such as ammonium sulfate and sodium chloride (Katz and Kocmond, 1973; Gerber et al., 1977). Recently, significant work has also been done with both soluble and insoluble organic species (Cruz and Pandis, 1997; Corrigan and Novakov, 1999; Giebl et al., 2002; Raymond and Pandis, 2002; Kumar et al., 2003; Broekhuizen et al., 2004a). Examples include low molecular weight dicarboxylic acids, oleic acid, and biogenic secondary organic aerosol (Broekhuizen et al., 2004b; VanReken et al., 2005). These studies focus on single component systems or well defined binary or tertiary mixtures (Raymond and Pandis, 2003; Bilde and Svenningsson, 2004; Abbatt et al., 2005). They have shown that Köhler theory accurately predicts activation behavior for a wide range of species under most conditions. This body of laboratory work gives a solid foundation on which to make predictions. However, atmospheric aerosols are complex mixtures of soluble inorganic and organic species (e.g. Saxena and Hildemann, 1996; Murphy et

al., 1998), as well as insoluble components such as organics, soot, and mineral dust. The particles may contain surface active species (Shulman et al., 1996; Facchini et al., 1999) which lower the surface tension of the droplets, as well as soluble gases which may affect activation (Laaksonen et al., 1998). In short, it may be difficult to predict CCN concentrations due to the highly complex and variable nature of true atmospheric aerosols.

## 2. Background

Aerosol/CCN closure studies involve exposing an atmospheric aerosol population to a particular supersaturation or set of supersaturations under controlled conditions and measuring the CCN concentration. The CCN concentration is compared to Köhler theory predictions based on concurrent measurements of dry particle size distributions and compositions. A successful closure study will accurately predict the concentration of CCN.

Previous closure studies have met with varying amounts of success. A variety of methods were used for both aircraft and ground-based measurements. The first attempts at achieving aerosol/CCN closure included studies by Bigg (1986), Quinn et al. (1993), and Martin et al. (1994). While providing useful CCN and aerosol size and composition information, these studies were largely unsuccessful at achieving closure. In a ground based study at Cape Grim, Tasmania, Bigg (1986) compared measured CCN concentrations with predicted concentrations based on particle size distribution measurements and the assumption that the particles were either composed of ammonium sulfate or sodium chloride. The results agree reasonably well at low particle concentrations ($<300\,cm^{-3}$), but under higher aerosol loading the deviation between observations and measurements is a factor of 3–5. Quinn et al. (1993) did not achieve closure during ground based measurements performed at Cheeka Peak, Washington. Only one measurement was performed at 0.3% supersaturation and the predicted CCN concentration based on an ammonium sulfate assumption was a factor of 2 higher than

measured concentrations. Martin et al. (1993) compares two sets of data from flights over the British isles and the North Sea. Assuming an ammonium sulfate composition, reasonable closure is achieved for a maritime air mass, but not for an air mass with continental origins.

More recent closure studies have had more success in achieving closure with some notable exceptions. Liu et al. (1996) made ground based aerosol and CCN measurements at Chebogue Point, Nova Scotia, during the 1993 NARE campaign. Composition information was derived from filter samples and the particles were divided into soluble and insoluble fractions, of which the soluble was assumed to be ammonium sulfate. There was closure within uncertainties for 10 of the 12 data sets with one overprediction and one underprediction. The aerosol mass loading during this study was strongly inorganic in character with small organic contributions. Covert et al. (1998) and Zhou et al. (2001) both used relative humidity controlled tandem differential mobility analyzers (RH-TDMA) to obtain hygroscopic growth factors. The study by Covert et al. (1998) was a ground based measurement as part of ACE 1, while that of Zhou et al. (2001) was a ship borne measurement as part of AOE-96. In both cases, hygroscopic growth factor derived aerosol compositions were used to predict CCN concentrations. The compositional analysis revealed soluble inorganic sulfate was the dominant mass fraction under most conditions in both studies. Despite this fact, Covert et al. (1998) overpredicted the CCN concentrations by 25% for all data, while Zhou et al. (2001) overpredicted by 30%.

Cantrell et al. (2001) achieved closure during INDOEX at the Kaashidhoo Climate Observatory. Compositional analysis was achieved in five size ranges from 0.056 to 1.0 $\mu$m using microorifice uniform deposit cascade impactors (MOUDIs). A soluble mass fraction, $\varepsilon$, was calculated and utilized in a simplified Köhler theory, assuming the soluble fraction was ammonium sulfate. The soluble fraction, $\varepsilon$, generally varied between about 0.25 and 0.5, and aerosol/CCN closure was achieved in 8 of 10 data sets. The CCN concentrations were overpredicted in both cases where closure was not achieved.

Significant airborne experiments were performed as part of ACE-2. Wood et al. (2000) conducted Lagrangian experiments in the marine boundary layer. The measured CCN spectrum was compared to model predictions for soluble ammonium sulfate with varying amounts of insoluble material. The best fit was for a 5% soluble mass fraction, while fractions of 20%, 50% and 100% overpredicted CCN concentrations. However, ground based composition measurements did not support a 5% soluble mass fraction, so closure was not achieved in this study. Using aerosol composition data based on ground based filter samples collected at Tenerife, Chuang et al. (2000) overpredicted the measured CCN concentrations by a factor of 3–10 and could not explain this discrepancy by the presence of insoluble material, as the sub-micron insoluble fraction was measured to be <3% at Tenerife. In the study of Snider and Brenguier (2000), calculated CCN concentrations based on ammonium sulfate as the soluble fraction were a factor of 2 higher than measured CCN concentrations unless the aerosol insoluble mass fraction was elevated to unreasonable levels. Closure was achieved for two days unaffected by continental pollution when subsequent refinements are made to the Köhler calculations (Snider et al., 2003). Dusek et al. (2003) also made ground based CCN measurements at Sagres, Portugal during ACE-2. CCN concentrations were overpredicted by about 30% on average for all data. A large contribution from organic species is an unlikely source of error, as the sub-micron aerosol carbon mass was generally below 15%.

Two recent studies by Roberts et al. (2002) and VanReken et al. (2003) were successful in achieving aerosol/CCN closure. Roberts et al. (2002) made ground based measurements as part of CLAIRE-98 in the Amazon Basin. CCN concentrations were measured between 0.15% and 1.5% supersaturation. Mass distributions were measured with a MOUDI impactor and size distributions with an SMPS system. Compositional analysis revealed organic mass fractions of nearly 80%, of which half was estimated to be soluble. Ammonium bisulfate constituted about 15% of the remaining aerosol mass. A three component Köhler model was used to predict CCN concentrations and agreed with measurements within uncertainty, although only when the

model assumed that the organic fraction was insoluble. The VanReken et al. (2003) CRYSTAL-FACE study is the first airborne measurement to achieve closure. CCN concentrations were calculated based on the assumption of pure ammonium sulfate using the SMPS aerosol size distributions. This assumption was generally supported by aerosol mass spectrometry (AMS) measurements. There is a systematic overprediction of CCN concentrations of about 5% for the 0.2% supersaturation data and about 20% for the 0.85% supersaturation data.

More recently, Rissman et al. (2005) have found a degree of overprediction when applying Köhler theory to aerosol measurements and comparing with airborne observations of CCN concentrations.

In general, aerosol/CCN closure has been difficult to achieve. This may be due to a number of factors. Many of the studies described above state that incomplete compositional analysis and the unknown effect of organic species or insoluble material limits the success of achieving closure. Measurement biases in the CCN chambers and detectors or in the measurement of particle size distributions may also be a contributing factor. For airborne measurements, spatial and temporal variability aboard a moving platform may also be a contributing factor in the failure to achieve closure. The studies able to achieve closure were generally not influenced by strong anthropogenic sources and were characterized by low concentrations of organic carbon in the aerosol phase. Only the Roberts et al. (2002) study was characterized by high concentrations of organic material (80% by mass), but water-soluble organic compounds comprised about half of the total organic carbon and the site was not influenced by anthropogenic emissions.

Recent analytical advances have made fast time resolved characterization of single aerosol particles or aerosol populations possible. The Aerodyne Aerosol Mass Spectrometer (AMS) has been widely used in this regard, but has not been explicitly used for aerosol/CCN closure to this point. As noted above, there have also been recent laboratory studies on the effect of organic species on CCN activity for single or multicomponent aerosols. While there are many yet unanswered questions, the roles of

solubility, surface tension, and oxidation state in CCN activation are now better understood than for many previous closure studies. These two factors make the possibility of aerosol/CCN closure in a variety of environments possible.

To this end, a CCN chamber, developed at the University of Toronto, was deployed in an urban environment in downtown Toronto in conjunction with measurements of aerosol physical and chemical properties to determine whether aerosol/CCN closure could be achieved in air masses strongly influenced by local and regional anthropogenic emissions. Toronto can be affected by both clean, Arctic air which is has low background particulate and minimal anthropogenic influence and air from the southwest that has been influenced by large urban centers and areas of high sulfur emissions from power generation sources.

## 3. Experimental Description

### 3.1. Sampling Site

The sampling site was located in downtown Toronto, Ontario, Canada on the University of Toronto St. George Campus. Measurements were made over several weeks from 20 August to 25 September 2003 at the Wallberg Building at 184–200 College St. This site is heavily influenced by weekday traffic with a weekday traffic volume of approximately 33 000 vehicles/day (Tan et al., 2002). The duct used for sample collection was approximately 6 m above the ground and 15 m north of College Street. A map of the downtown sampling site is shown in Fig. 1. Detailed analysis of aerosol properties, meteorological data, and source apportionment for this field campaign can be found in Buset et al., 2005[1].

[1]Buset, K. C., Evans, G. J., Leaitch, W. R., Brook, J. R., and Toom-Sauntry, D.: Use of advanced receptor modeling for analysis of an intensive 5-week aerosol sampling campaign, Atm. Environ., submitted, 2005.

### 3.2. Instrumentation

Particle composition was measured by several instruments, including an Aerodyne Aerosol Mass Spectrometer (AMS). The AMS has been widely used in laboratory and field campaigns (e.g. Jayne et al., 2000; Allan et al., 2003; Jimenez et al., 2003; Alfarra et al., 2004). It was operated in two modes. In one mode, average mass concentrations of non-refractory particulate species such as sulfate, nitrate, chloride, ammonium, and organic carbon were measured every 15 min. The AMS has nearly 100% transmission of particles with vacuum aerodynamic diameters in the 0.06 $\mu$m to 0.6 $\mu$m range (Zhang et al., 2004). The oven used for particle vaporization was set to 550°C and the particle collection efficiency was assumed to be 100%. In the second AMS mode, size-resolved compositional analysis was performed for particles between 0.01 $\mu$m and 1.0 $\mu$m in the time-of-flight (TOF) configuration. TOF spectra were collected as hourly averages. For a detailed description of the AMS data collection and calibration, see Buset et al. (2005).

Water soluble inorganic particulate mass was also analyzed using a water Particle-In-Liquid-Sampler (PILS) with two ion chromatographs for inorganic ion analysis. The PILS also collected 15 min average samples to coincide with the AMS and other instrumentation. A correlation plot between $SO_4^{2-}$ from the PILS and $SO_4^{2-}$ from the AMS yielded a slope of 0.97 (Buset et al., 2005), giving credence to the assumption that the collection efficiency of the AMS was near 100%. This correlation was valid for most of the sampling period, during which the mass tended to be dominated by organic material. During the first few days of the study (20–22 August), a regional haze covered the area and the particle composition was dominated by sulfate. During this period early in the study, the PILS was not operational. However, comparisons with mass concentrations from a TEOM and estimated from the integrated size distributions indicated that the AMS collection efficiency was closer to 50%.

Particle size distributions were measured using a Scanning Mobility Particle Sizer (SMPS). The SMPS consisted of a Differential Mobility Analyzer (DMA) (Model 3071,

TSI Inc.) connected to a Condensation Particle Counter (CPC) (Model 3022, TSI Inc.). Large particles (>0.5 $\mu$m) were measured using an Aerodynamic Particle Sizer (APS) (Model 3320, TSI Inc.). Size distributions from 0.01 $\mu$m to 20 $\mu$m were collected as 15 min averages.

CCN concentrations were measured with the University of Toronto thermal gradient diffusion chamber (TGDC). The instrument has been validated through a number of laboratory studies on inorganic, organic, and internally mixed aerosol particles (Kumar et al., 2003; Broekhuizen et al., 2004a, b; Abbatt et al., 2005) and is described in detail elsewhere (Kumar et al., 2003). Briefly, it is a continuous flow chamber consisting of two parallel wetted copper plates held at different temperatures resulting in a supersaturation in the center of the flow. The particle flow (~0.2 LPM) is entrained into the center of the chamber via a humidified sheath flow (~1.8 LPM) and is sampled at the end of the chamber by an APS (Model 3320, TSI Inc.) which pumps at 1.0 LPM. A diaphragm pump (Model 107CEF075, Thomas Industries, Inc.) pumped the remaining chamber effluent (1.0 LPM). Filter paper was used to wet the copper plates and was routinely remoistened to prevent drying and to maintain a constant supersaturation in the chamber. The chamber was operated at 0.58% supersaturation for the entire campaign and was routinely calibrated with monodisperse ammonium sulfate particles to ensure a stable supersaturation. CCN concentrations were collected every minute and were combined into 15 min averages to correspond with the other instrumentation sample times. The raw CCN counts were multiplied by a factor of 10 to account for dilution in the chamber by the particle free sheath flow and then multiplied by 1.4 to account for particle losses in the chamber. This value of 1.4 has been shown to be robust for all particle sizes and compositions in previous laboratory studies with this chamber (Kumar et al., 2003; Broekhuizen et al., 2004a, b; Abbatt et al., 2005) and was verified by calibration with ammonium sulfate. A schematic of the sampling setup is shown in Fig. 2.

Gas-phase measurements were also performed in 15 min sampling intervals. $SO_2$ was measured using a fluorescent $SO_2$ analyzer (Model 100A, API Inc.). Other gas-

phase and particle measurements were used in the receptor modeling study and can be found in Buset et al. (2005).

## 4. Results

### 4.1. CCN and AMS Measurements

CCN measurements were performed on 10 days between 27 August and 17 September 2003. However, on only 4 of the 10 days (27 August, 5 September, 15 September, and 16 September) were the SMPS and AMS instruments also collecting data. All four days were weekdays and therefore influenced by high vehicle traffic loads. CCN concentrations were quite variable, ranging from 144 $cm^{-3}$ on 5 September to 3291 $cm^{-3}$ on 16 September. Table 1 summarizes the results of the CCN measurements over the 4 study days.

The CCN concentrations fall within the values seen in other studies and are representative of concentrations observed in both remote marine environments (e.g. Hegg et al., 1991, 1995; Hudson, 1993) and also those observed under conditions of heavy anthropogenic influence (e.g. Hudson and Frisbie, 1991; Hitzenberger et al., 1999). That the CCN concentrations varied by a factor of 30 over the course of this study allows the closure methodology to be vigorously tested over a variety of conditions.

The AMS data consistently show a large organic fraction for particle sizes less than approximately 0.25 $\mu$m as shown for two sample days in Fig. 3. Figure 4 shows a breakdown of the organic fraction for the same time periods shown in Fig. 3. The organic fraction below 0.25 $\mu$m consistently shows low values for $m/z$=44 ($CO_2^+$) which is a marker for oxidatively processed, or secondary organic species. There are, however, significant levels of $m/z$=57 ($C_4H_9^+$). This suggests a significant local source of hydrocarbon-like organic (HOC) emissions often associated with primary emission sources, such as vehicles. This was independent of air mass history, as shown by the cases of air masses with significant sulfate loading (Fig. 3b) as well as those with

minimal sulfate loading (Fig. 3a). This is important for aerosol/CCN closure because the SMPS derived size distributions show very few particles above 0.25–0.30 $\mu$m for most days. When trying to achieve aerosol/CCN closure, the particle composition must be known in the size range where particle number concentrations are large (below 0.25 $\mu$m in this study). While the total inorganic mass fraction may be large on some days, most of the mass is contained in the 0.25–1.0 $\mu$m mass range where the particle number concentrations are low. Therefore, this inorganic mass will have a minimal effect on CCN. This demonstrates the importance of size resolved mass analysis for sites strongly impacted by local emissions.

### 4.2. Comparison of CCN concentrations to SMPS measurements

The AMS TOF data were used, in combination with the number size distributions measured with the SMPS, to calculate predicted CCN concentrations. Briefly, the AMS compositional data were used to predict an onset activation diameter $D^*$ at the supersaturation used in the CCN measurements. Then the SMPS particle counts were integrated for all sizes greater than or equal to $D^*$. The predicted CCN concentrations are then compared to the measured CCN concentration to determine whether closure is attained.

For each TOF size bin, a soluble volume fraction, $V_{sol}$, was calculated according to Eq. (1)

$$V_{sol} = \frac{m_{sol}/\rho_{sol}}{m_{sol}/\rho_{sol} + m_{org}/\rho_{org}} \quad (1)$$

where $m_{sol}$ and $\rho_{sol}$ are the total inorganic mass and the density of the inorganic fraction, respectively, and $m_{org}$ and $\rho_{org}$ are the organic fraction mass and density, respectively. An organic volume fraction, $V_{org}$, was calculated in a similar fashion. The soluble fraction was assumed to be ammonium sulfate in all cases ($\rho$=1.77 g cm$^{-3}$) and the organic fraction was assumed to be completely insoluble ($\rho$=1.0 g cm$^{-3}$). These are

reasonable assumptions based on the $NH_4^+$-$SO_4^{2-}$ ratio and the nature of the organic fraction below 0.25 $\mu$m. In particular, there is only a small $CO_2^+$ signal in this size region as seen in Fig. 4 and it is difficult to know if this signal corresponds to soluble organic species. Due to our lack of knowledge of the organic speciation, an assumption of complete insolubility remains valid.

The AMS TOF data are collected as a vacuum aerodynamic diameter, $D_{va}$, which must be converted to a mobility diameter, $D_m$, for comparison with the SMPS data. For simplicity, the particles were assumed to be spherical with a bulk density, $\rho_B$, of 1.0 g cm$^{-3}$. This assumption is consistent with the density assumptions made above, given that the sulfate fraction is generally so small that it has almost no impact on bulk particle density. With these assumptions, $D_{va}$=$D_m$.

These volume fractions, $V_{sol}$ and $V_{org}$, were used to calculate the number of moles of soluble material and the diameter of the insoluble core, respectively. These parameters were used in an insoluble core Köhler theory calculation to determine whether each AMS-TOF bin would activate at 0.58% supersaturation according to Eq. (2) (Seinfeld and Pandis, 1998)

$$\ln\left(\frac{p_w(D_p)}{p^\circ}\right) = \frac{4M_w\sigma_w}{RT\rho_w D_p} - \frac{6n_s M_w}{\pi\rho_w(D_p^3 - d_u^3)} \quad (2)$$

where $p_w(D_p)$ is the droplet water vapor pressure, $p^\circ$ is the equilibrium water vapor pressure, $M_w$, $\rho_w$, and $\sigma_w$ are the molecular weight, density, and surface tension of water, respectively, $R$ is the gas constant, $T$ is the droplet temperature, $n_s$ is the moles of solute, $D_p$ is the droplet diameter, and $d_u$ is the insoluble core diameter. The smallest size bin which would activate was designated as the onset activation diameter, $D^*$. In all cases in this study, every aerosol size bin larger than $D^*$ also activated, although it would be possible for particles larger than $D^*$ to be CCN inactive under certain conditions, e.g. very organic rich. The 15 min SMPS averages were integrated for all sizes larger than $D^*$ to obtain the predicted CCN concentration. There is a degree of uncertainty with each point in this calculation due to the fact that the AMS TOF data are

hourly averages rather than 15 min averages, however, there was not a significant difference if hourly CCN and SMPS averages were used instead of 15 min averages. The $D^*$ values for this closure analysis are given in Table 1.

As a final result, Fig. 5 shows that the ratio of $CCN_{predicted}$ to $CCN_{observed}$ is 1.04, which indicates that aerosol/CCN closure was achieved within experimental uncertainties. Error bars were not included for figure clarity, however, the uncertainties in the measured CCN concentrations are estimated to be ±10% based on previous studies (Kumar et al., 2003). The largest uncertainty for the closure analysis is in the predicted CCN concentrations, estimated at ±25% based on uncertainties in the chamber supersaturation used to calculate $D^*$, the SMPS size distributions, the AMS data, and the assumed density and composition of the aerosol particles.

As a test of the closure analysis, several other methods were used to mimic various experimental designs. The first analysis method mimics the results based on a coarse filter sample method. The AMS integrated mass concentrations (0.010 $\mu$m–1.0 $\mu$m) were used, not the TOF data. All particles in this size range (0.010 $\mu$m–1.0 $\mu$m) were assumed to have the same composition, that is, the composition from the AMS measurements. The organic mass fraction and total inorganic mass fraction was used to calculate a soluble and insoluble volume fraction, $V_{sol}$ and $V_{org}$, as above. Köhler theory was used to predict $D^*$ according to Eq. (2). The SMPS size distribution was integrated for all sizes larger than $D^*$ to obtain $CCN_{predicted}$. This value was compared to $CCN_{observed}$ for all data points. The results of this calculation are shown in Fig. 6. The CCN concentration is overpredicted by a factor of ~2 on average.

The second calculation method simulates a cascade-type impactor filter sample with a size resolution of 0.05 $\mu$m–0.30 $\mu$m. The AMS TOF data set was integrated from 0.05 $\mu$m to 0.30 $\mu$m. The composition for each size bin was weighted by the number of particles in that bin and this number weighted composition was averaged across the entire size range. All particles in this size range were assumed to have the same composition, that is, the number weighted average composition. The soluble volume fraction and organic volume fraction were calculated as shown above with the same

assumptions. Again, an insoluble core Köhler theory was used to calculate $D^*$ as above and each 15 min size distribution was integrated for all sizes larger than $D^*$. In this case, $CCN_{predicted}$ is about 25% higher than $CCN_{observed}$ on average for the four days as shown in Fig. 6. There was no significant difference in the results between 15 min and hourly SMPS averages. While this calculation method achieves closure within experimental uncertainty, the fact that the CCN concentrations are systematically overpredicted as in other closure studies that use cascade impactors, suggests that the greater size resolution provided by the AMS is needed to achieve closure.

To test the assumption of an internally mixed aerosol population, we performed the closure calculation again, this time assuming a completely externally mixed aerosol population. Each SMPS size bin was weighted by its representative AMS TOF mass fraction. In this way, the size distribution was divided into pure ammonium sulfate particles and pure insoluble organic particles. The ammonium sulfate particles larger than $D^*$ for pure ammonium sulfate at 0.58% supersaturation were integrated and compared to $CCN_{observed}$. The CCN concentrations using this method were underpredicted by a factor of 4 on average. This discrepancy between predicted and observed CCN concentrations still can not be resolved by the fact that the ammonium sulfate was associated with some nitrate. The possibility remains that a fraction of the organic material was soluble, and the aerosol was externally mixed and yielded aerosol/CCN closure. However, this scenario is unlikely and this result gives us confidence in our assumptions that the particles are internally mixed and also suggests that the CCN are predominantly organic particles with a small sulfate component that drives the activation.

## 5. Discussion

The aerosol mass concentrations in downtown Toronto can vary widely (Table 1), but were often characterized during this study by high concentrations of primary organic emissions in the size range below 0.25 $\mu$m. CCN concentrations were also highly

variable, ranging from approximately 100 $cm^{-3}$ to 4000 $cm^{-3}$. Aerosol/CCN closure has been achieved for the entire range of CCN concentrations using size-resolved particle mass concentrations measured with the Aerodyne AMS. This is, to our knowledge, the first aerosol/CCN closure study which has been able to achieve closure for an aerosol population that is strongly influenced by anthropogenic emissions and it is the first to directly use AMS size-resolved composition data to study aerosol/CCN closure.

Previous laboratory studies (e.g. Bilde and Svenningsson, 2004; Broekhuizen et al., 2004a) have shown that, for a relatively insoluble organic particle, small amounts of a highly soluble inorganic species such as ammonium sulfate or sodium chloride have a large effect on the particle dry diameter needed for activation. In fact, a particle with a mass fraction of only 15–20% ammonium sulfate can be reasonably modeled under the assumption that it is pure ammonium sulfate. Furthermore, recent studies (Broekhuizen et al., 2004b; Abbatt et al., 2005) have shown that while organic particle oxidation can affect CCN activation, significant organic surface tension effects have not yet been demonstrated in the laboratory, especially when highly soluble species are also present. Solubility appears to be the driving force behind CCN activation in most cases.

The aerosol/CCN closure studies which have been successful in achieving closure (Liu et al., 1996; Cantrell et al., 2001; Roberts et al., 2002; VanReken et al., 2003) have seen high levels of sulfate, generally larger than 50% by mass. Only the Roberts et al. (2002) study saw significant organic mass fractions (approx. 80%), half of which were estimated to be water soluble. Their CCN concentrations were well modeled using a three-component model; however, the model assumed a completely insoluble organic fraction. In these studies, data for which closure was not achieved were often characterized by large anthropogenic contributions or high organic mass loading.

To further aid the interpretation of the present closure study, back trajectory calculations were performed for the four sample days using the National Oceanic and Atmospheric Administration's (NOAA) Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (http://www.arl.noaa.gov/ready/hysplit4.html, NOAA Air Re-

sources Laboratory, Silver Spring, Maryland). Ground-level, 48-h back trajectories were calculated at noon for each of the four sample days using the CDC1 global reanalysis meteorological data. As seen in Fig. 7, the days which experienced low CCN concentrations, 27 August and 5 September, had air mass origins in northern Michigan and northern Ontario, respectively. This was evidenced by low sulfate and nitrate particulate mass loading, and low $SO_2$ concentrations. The particulate mass on those two days was extremely organic-rich and was likely the result of fresh local emissions only. 15 September saw air masses from southern Ontario, and Cleveland, Ohio, while 16 September showed trajectories from Detroit, Michigan and Chicago, Illinois. These two days had elevated $SO_2$ gas-phase concentrations, higher sulfate and nitrate particulate mass loading, high CCN concentrations and significant upwind and local anthropogenic influence. The AMS TOF size spectra show that most of the sulfate and nitrate mass, however, was still contained in particles with diameters larger than 0.25 $\mu$m. The majority of the particles were below 0.25 $\mu$m and showed strong signatures of local primary anthropogenic organic emissions (Fig. 4b). The organic-rich, locally derived particles were likely influenced by the elevated upwind anthropogenic emissions, leading to higher CCN concentrations. Using the closure methodology described above, CCN concentrations were accurately predicted for all four days, regardless of air mass history or CCN concentrations.

Few other ground based studies and almost no airborne studies have achieved closure, and most have overpredicted CCN concentrations. It is difficult to assess the reason for these discrepancies; however, airborne CCN measurements are more difficult and may be subject to measurement errors related to rapidly changing conditions and insufficient time or spatial resolution. Incomplete or missing composition information is often cited as a reason for overprediction as well. The recent advances in high time-resolution aerosol mass spectrometric techniques such as AMS or ATOFMS and the increasing ability to measure the composition of single aerosol particles may allow aerosol/CCN closure to be achieved in a wider variety of conditions and experimental platforms. This has been nicely demonstrated in the Fall 2003 University of Toronto

Intensive Campaign. Organic mass concentrations often exceeded 80% for the entire size range. The inorganic mass fractions for the size range 0.05 $\mu$m–0.30 $\mu$m rarely exceeded 10%, with a maximum of 16% on 16 September 2003. The dry activation diameters for particles in this range of inorganic mass fractions have been shown in the laboratory to vary considerably as a function of inorganic mass fraction (Raymond and Pandis, 2003; Broekhuizen et al., 2004a; Bilde and Svenningsson, 2004). Therefore, it is clear that detailed, size-resolved mass fractions are required to achieve closure under these conditions.

## 6. Conclusions

Aerosol/CCN closure has been achieved using an insoluble core Köhler model based on size resolved AMS TOF particle mass concentrations and SMPS derived size distributions. This is the first study to explicitly use the AMS TOF data to achieve aerosol/CCN closure and is also the first study to achieve closure under conditions of high anthropogenic emissions. This study has provided further evidence that small amounts of soluble inorganic material such as sulfate can drive the CCN activity of organic rich particles. Furthermore, it has been shown that closure was unlikely to have been achieved using conventional filter methods to derive aerosol mass concentrations.

Clearly, more laboratory and field work is needed to ascertain the impact of oxidation on the organic rich particles seen in urban environments or near biomass burning sites. The impact of surface tension also needs to be further elucidated. However, the increasing use of particle mass spectrometry in field and laboratory studies and the increasing development of quantitative single particle techniques shows great promise in allowing aerosol/CCN closure to be achieved on both ground based and airborne platforms.

Cloud droplet formation is a complicated process involving many chemical, physical, and dynamic factors, but the ability to achieve aerosol/CCN closure is a very important

step in the goal of incorporating accurate and detailed cloud formation parameters into global climate models.

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**Table 1.** Summary of the results from the four sample days, including the gas-phase $SO_2$ concentration, $D^*$, particulate sulfate concentration, and particulate organic concentration.

| Date | Number of 15 min averages | Measured CCN concentration $cm^{-3}$ | | Predicted CCN concentration $cm^{-3}$ | | $(SO_2)$ ppbv | | $D^*$ $\mu$m | | Particulate $(SO_4^{2-})$ $\mu g\ m^{-3}$ | | Particulate (organic) $\mu g\ m^{-3}$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Range | Mean | Range | Mean | Mean | Peak | Range | Mean | Range | Mean | Range | Mean |
| 27 Aug. | 11 | 467–1247 | 814 | 515–1142 | 762 | 1.28 | 1.8 | 0.118–0.128 | 0.122 | 0.09–0.52 | 0.27 | 3.8–6.5 | 5.1 |
| 5 Sept. | 30 | 144–635 | 301 | 106–1096 | 407 | 1.33 | 2.0 | 0.117–0.217 | 0.150 | 0.00–0.28 | 0.06 | 2.2–24.6 | 6.2 |
| 15 Sept. | 13 | 856–1418 | 1231 | 1026–1744 | 1319 | 1.22 | 2.3 | 0.094–0.111 | 0.101 | 1.7–4.5 | 3.5 | 4.9–9.5 | 6.9 |
| 16 Sept. | 20 | 1311–3291 | 2299 | 1245–4100 | 2514 | 2.11 | 3.5 | 0.091–0.130 | 0.109 | 0.78–2.2 | 1.6 | 6.3–41.1 | 14.5 |

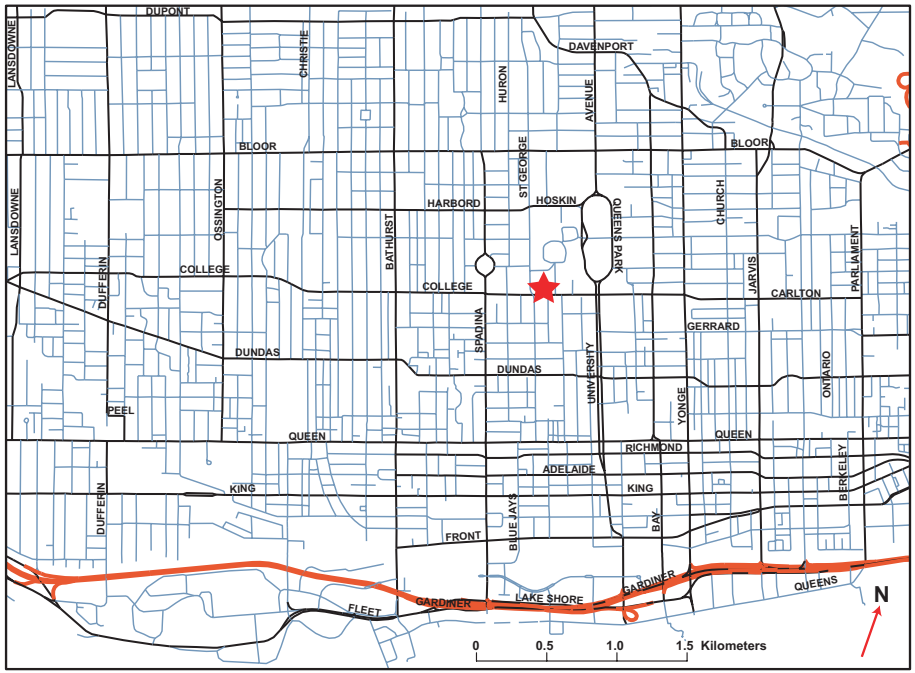


**Fig. 1.** Map of downtown Toronto showing the sample site (red star) at 184–200 College St. The map was created with CanMap Route Logistics Ontario (v8.2), DMTI Spatial Inc.



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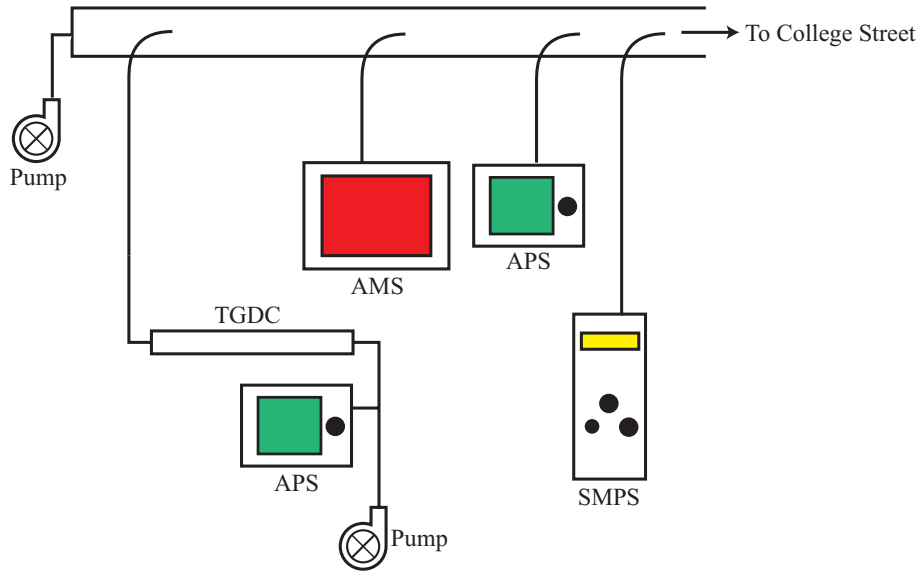


**Fig. 2.** Schematic of the experimental setup.

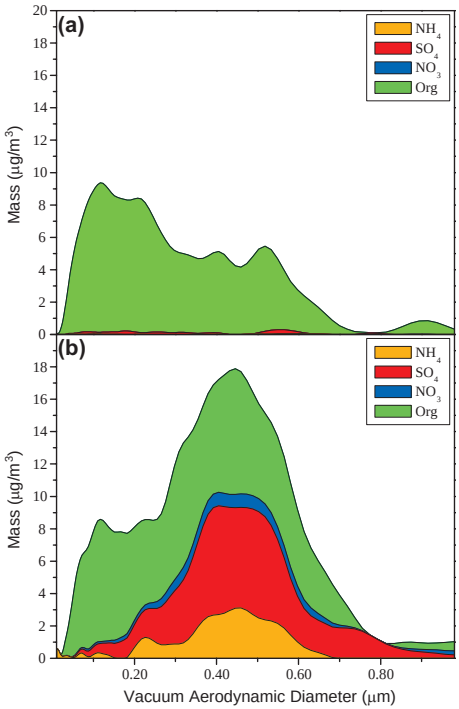


**Fig. 3.** AMS TOF spectra for two days showing mass concentrations vs. vacuum aerodynamic diameter. Green represents the organic fraction, red represents sulfate, blue represents nitrate, and orange represents ammonium. For example, the organic fraction in (b) at 0.5 $\mu$m is approximately 7 $\mu$g/m$^3$, not 17 $\mu$g/m$^3$. **(a)** 20:00–21:00 UTC, 5 September 2003. **(b)** 16:00–17:00 UTC, 15 September 2003.



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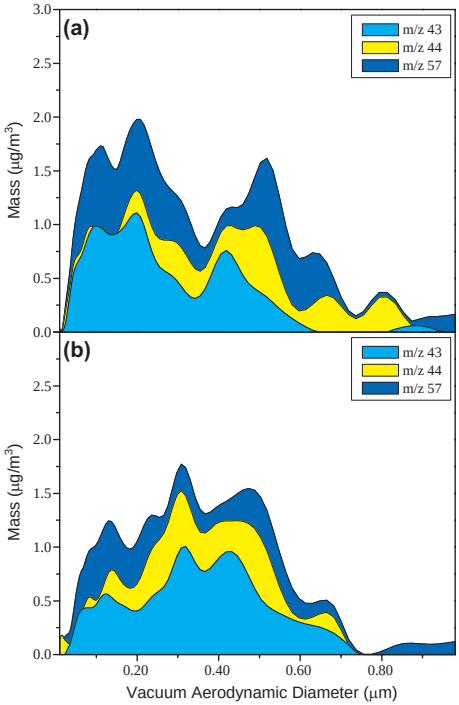


**Fig. 4.** AMS TOF spectra for two days showing key peaks in the organic mass fraction vs. vacuum aerodynamic diameter. The mass peak ($m/z$=44 amu) is representative of aged organics, while the peak ($m/z$=57 amu) is representative of primary emissions. The light blue represents $m/z$=43, the yellow represents $m/z$=44, and the dark blue represents $m/z$=57. **(a)** 20:00–21:00 UTC, 5 September 2003. **(b)** 16:00–17:00 UTC, 15 September 2003.

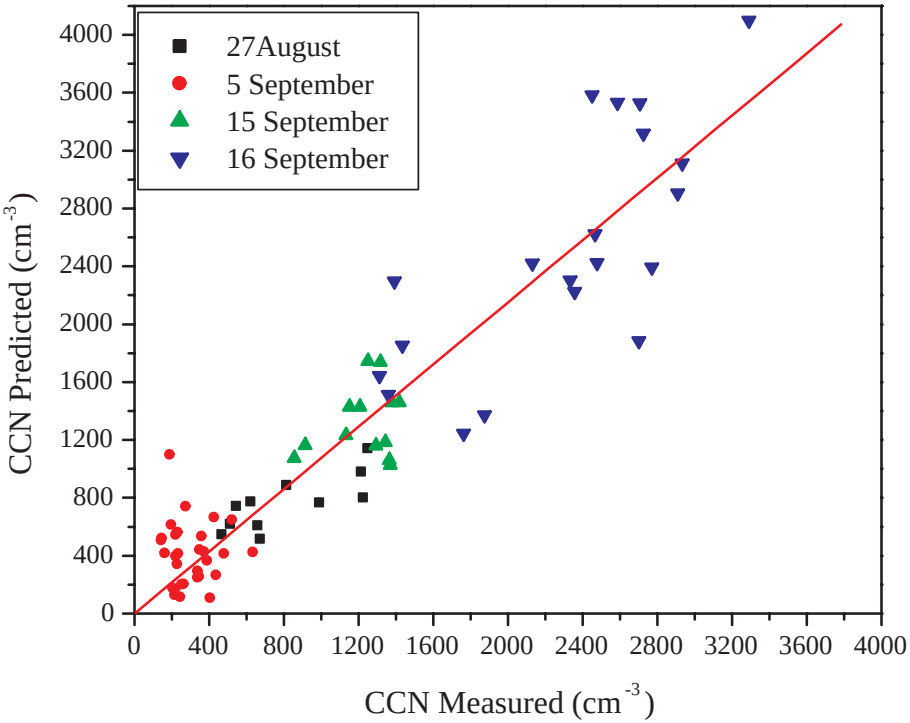


**Fig. 5.** Predicted CCN concentration vs. measured CCN concentrations for the four sample days. The CCN concentrations are predicted based on a bin by bin analysis of the AMS TOF data (see text). The red line is a linear least squares fit to all the data (slope=1.04, $R^2$=0.87).



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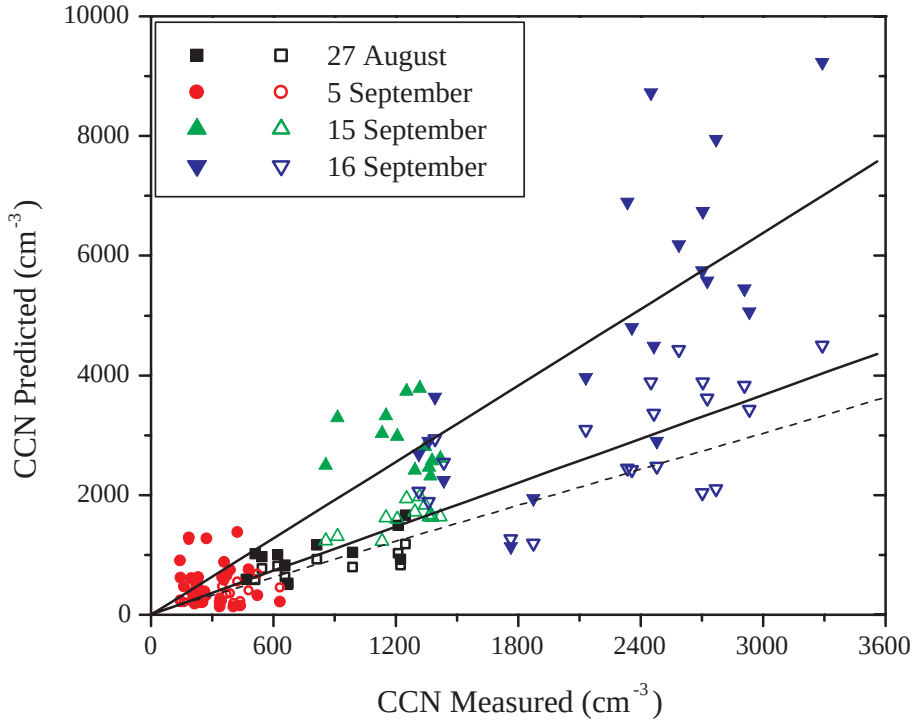


**Fig. 6.** Predicted CCN concentration vs. measured CCN concentrations for the four sample days. The filled symbols are for predicted CCN concentrations based on a simulated coarse filter sample method (see text). The open symbols are for predicted CCN concentrations based on a simulated filter sample method for particles with diameters between 0.05 and 0.30 $\mu$m (see text). The black lines are linear least squares fits of the two data sets (slope=2.13, $R^2$=0.81; slope=1.22, $R^2$=0.85), and the dashed line is the 1:1 line.

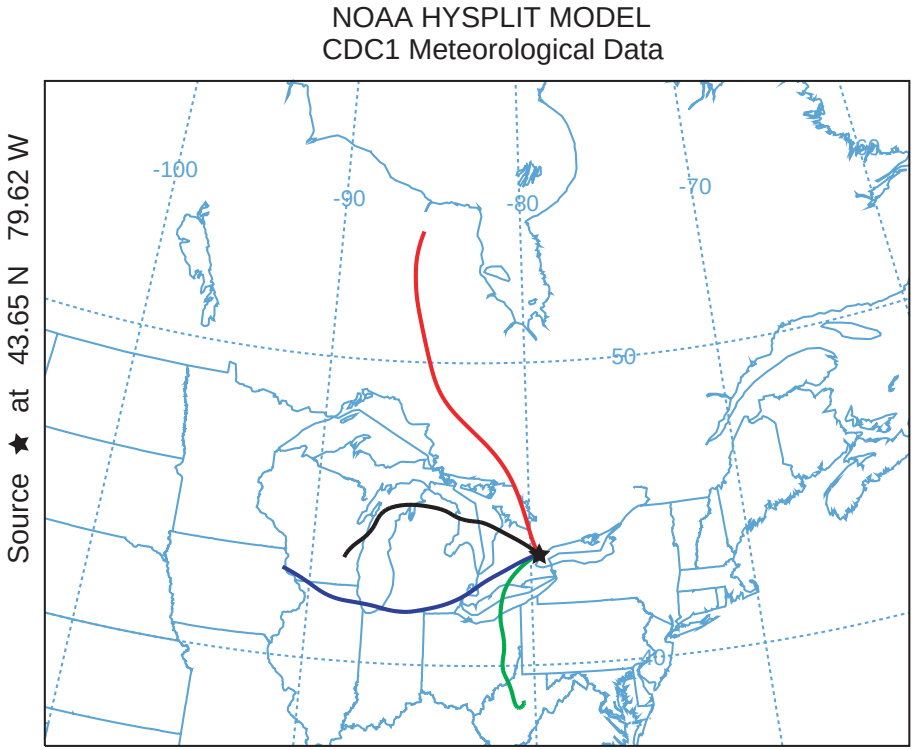


**Fig. 7.** Simulated 48 h back trajectories for the four sample days. The sample trajectories end at 16:00 UTC for all four days. (black line) 27 August; (red line) 5 September; (green line) 15 September; (blue line) 16 September. This plot is a product of the NOAA Air Resources Laboratory HYSPLIT model.



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