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Interactive comment on "Closure between measured and modeled cloud condensation nuclei (CCN) using size-resolved aerosol compositions in downtown Toronto" *by* K. Broekhuizen et al.

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The manuscript presents an interesting attempt to reconcile the composition of ambient atmospheric aerosol particles with their measured ability to act as cloud condensation nuclei. The study is based on a range of detailed in situ measurements using state-of-the-art instrumentation. The subject area is one of current significance and very active research.

The working hypothesis, though unstated explicitly, appears to be that the activation behaviour of a measured aerosol distribution as measured by a CCN spectrometer at a single supersaturation may be adequately described by the use of the equilibrium Kohler equation assuming that only the inorganic components contribute to the solute term and that the Kelvin term uses the surface tension and density of water.

The testing of the hypothesis appears to have been central to the experimental design and in addition, the measurement methodology, techniques and instrumentation are all appropriate so far as they go and appear well-executed.

The manuscript is clearly-written and provides a useful background to the study with a thorough overview of the limitations and successes of previous CCN closure studies.

However, there are a few problems that will impact on the attempted closure. These are wrapped up in teh fact that the closure is an underconstrained problem using the available measurements. This is based on several assumptions made in the exercise.

Firstly, as has been correctly identified, the frequent (indeed nearly ubiquitous) observation using AMS in a wide range of locations is that the m/z 57-dominated smallest particle AMS (Aitken) mass mode which is found close to source, is dominated by organic material. However, this mode is generally entirely decoupled from the main sulphate (Accumulation) mass mode and may be considered externally mixed from it. It is therefore likely that, particularly in the region which is most important in determining cloud droplet number (around the threshold activation dry size), there may be a significant contribution from both modes (with a significant contribution to the sulphate mass at a given size contributed from the smaller tail of the accumulation mode). Such a splitting of modes by hygroscopicity is always identified when conducting HTDMA measurements in urban locations. That this is the case in Toronto is fairly obvious from figure 3 b). The main sulphate mass mode has a mass modal diameter of around 450 nm. This appears internally mixed with the organic, nitrate and ammonium mass in the accumulation mode (all components have the same mass distribution shape). This mode has large and small tails, including all components. Superimposed on this distribution there is a predominantly organic mode at smaller sizes. The particles in this mode should therefore not be assumed to comprise internally-mixed organic and sulphate at the ensemble mass loadings at any given size. It is likely that the nature of the organic material will also be externally-mixed to some degree where there is a contribution from both modes, with the tail of the larger mode containing more oxidised older material (probably containing more CO2+) and the smaller mode comprising 57-dominated material, contributed by local emissions.

It is necessary to assume a mixing state in order to conduct CCN closure for a particle of a given size. To correctly assess the mixing state it would be necessary to use a quantitative single particle composition instrument. Since such an instrument does not exist, an instrument which probes physical property by number (and hence mixing state of physical property), such as a HTDMA or VTDMA should be employed. An alternative would be to use the CCN spectrometer and AMS in series. The assumption in the current study is that the particles are internally-mixed. As has been argued above, I believe this is a significant and incorrect assumption in downtown Toronto.

Following this assumption, the soluble material is assumed to be ammonium sulphate, with the appropriate bulk properties, and the organic is assumed insoluble. However, the statement on p 11 that "Due to our lack of knowledge of the organic speciation, an assumption of complete insolubility remains valid" cannot be made reliably. Even if the soluble material were to be ammonium sulphate, the further assumption, made for simplicity, that vacuum aerodynamic and mobility diameter are equal is frequently violated and will introduce errors in the insoluble volume fraction calculation. I therefore contend that the closure exercise makes too many assumptions to reliably make the conclusions in the paper. Indeed, the fact that there are a number of potentially counteracting effects is summarised in the statement at the bottom of page 13 that "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". I do not agree that some degree of external mixing is unlikely - and this will affect the closure exercise. I therefore do not believe that the following statement "... this re-

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sult 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" can be made, based on the closure exercise.

I certainly agree that the deployment of combinations of modern state-of-the-art instruments will provide us with a much better chance to close composition and CCN activation - however, I don't believe the experiment as described in the paper provides sufficient constraint to make conclusions about the quantitative degree of closure or to elucidate the roles of particular aerosol components in cloud activation. Given the above, I cannot recommend publication in its current form. Significantly rephrased discussion and conclusion sections and a more extensive sensitivity and uncertainty analysis must be carried out to ensure that the study is more rigorous and conservative in its conclusions.

More minor points:

It is stated on page 7 that "the roles of solubility, surface tension and oxidation state in CCN activation are now better understood than for many previous closure studies". Unfortunately, this greater understanding appears relatively unexploited in the current manuscript (organics are assumed fully insoluble and no sensitivity to this is carried out, no sensitivity to surface tension effects is carried out and the organics are assumed entirely unoxidised - or at least not sufficiently oxidised to show any solubility) and cannot be propounded as a motivation for the attempted closure in this case.

On the bottom of page 8, a discussion of the AMS collection efficiency is made suggesting that, for sulphate mass, the efficiency changed from around 50% under sulphate-dominated conditions to around 100% when there was a high organic loading. Firstly, for the earlier period when the efficiency was estimated by comparison with the TEOM and integrated SMPS / APS, were the measurements from the different instruments remapped onto a common diameter scale prior to integration to account for density fluctuations (since they measure on mobility, vacuum aerodynamic and transition regime aerodynamic scales)? Secondly, for the latter period when the collection efficiency was estimated by comparison with the PILS instrument, were the TEOM and size distribution measurements used for consistency to cross-check how the collection efficiency inferred by this method compared with that during the earlier period? If not, this should be done and the results reported.

Whilst, as I have stated, I do not believe the manuscript should be published in its present form, the measurements are able contribute significantly to the available aerosol and CCN database. I would encourage the co-authors to resubmit the findings with less emphasis on the attempted closure.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 6263, 2005.