**Atmospheric
Measurement
Techniques
Discussions**

Interactive comment on "Analysis of cloud
condensation nuclei composition and growth
kinetics using a pumped counterflow virtual
impactor and aerosol mass spectrometer" *by*
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Response to Comments by D. Toohey

Comment 1

First, as the authors know, the extent to which the AMS undersamples particles depends on the state (e.g., phase, size, composition) of the particles, and can be as much as 50% (some have reported even lower for some particles). A number of recent studies have examined the issue of the collection efficiency (CE, or 'bounce') and, while

there is still much to understand, clear trends are beginning to emerge. It is important for this paper, the first to describe the use of the AMS in a new application that involves the processing of dissolvable materials, to describe how the observations might be affected by changes in CE due to (1) differences in the relative humidity conditions between the two sample modes ("CCN-active" and "polydisperse") and (2) potential alteration in the physicochemical state of the particles. This is an issue that cannot easily be resolved in one study, but being that this is the first of its kind with the promise of many more to follow, it would be very helpful for the authors to include a new section before the conclusions that discusses the potential complications and limitations of the method that relies on the AMS. With respect to (1), it is important to note whether or not the airstream was dried prior to sampling with the AMS in polydisperse mode. If not, it is useful here to speculate on the potential introduction of biases in the results.

Response

Bounce collection efficiency (E_b)is an important issue for quantitative interpretation of AMS results. Studies of AMS collection efficiency on ambient particles have typically yielded values of ~0.5, with larger values observed for a few specific conditions: (1) high mass fraction of ammonium nitrate, (2) acidic sulfate aerosol, (3) relative humidity > 90%. Laboratory experiments have also shown that organic liquid coatings increase collection efficiency. However, enhancement of collection efficiency by organic liquid has not been demonstrated in ambient data; rather, a recent study shows E_b to be unaffected by organic content (Middlebrook et al., 2011). This is consistent with recent evidence suggesting that many organics may exist in the atmosphere in a glasslike state (Zobrist et al., 2008).

Parameterizations for estimating collection efficiency based on ammonium nitrate content and sulfate acidity can be found in the literature (Middlebrook et al., 2011; Matthew et al., 2008; Crosier et al., 2007; Quinn et al., 2006). These corrections would need to be applied independently to the measured polydisperse and CCN-active composition. The effect of relative humidity is somewhat more complicated. Because the PCVI out-

put flow is dried by replacement of the humid air with dry air at the stagnation plane, the CCN-active distribution is expected to have a collection efficiency of ~0.5, similar to typical results for dried ambient particles, except for the types of particle composition described above. In theory, one could also dry the input flow to the TGDC-PCVI-AMS; however, while this would simplify an E_b-based comparison of the polydisperse and CCN-active aerosol, there is a possibility that it could introduce artifacts into the comparison by changing the phase of the input aerosol, thereby altering the cloud formation process. As discussed in the manuscript, the nature of the TGDC-PCVI-AMS system means that droplet growth kinetics affect which particles are classified as "cloud droplets".

In the present study, the input airstream was not dried. Instead, the polydisperse collection efficiency was estimated by two methods: (1) correlation of single particle mass spectra with optical scattering pulses from a light scattering module incorporated into the AMS, providing a direct measure of E_b for particles with mobility diameters larger than ~215 nm; and (2) comparison with SMPS measurements. These measurements yielded an estimatd E_b of 0.6 +/0.1, and are described in detail in Slowik et al., 2010. The similarity of this value to "normal" dry E_b values, coupled with the lack of compositional changes in CCN-active particle modes (i.e. excluding the small CCN-inactive mode observed in downtown Toronto), suggests that E_b does not cause significant biases in the present study. (We note that the optical scattering/single particle measurements were made for both the CCN-active and polydisperse distributions, however the number of sampled CCN-active particles was too low for the measurement to be useful in constraining E_b.)

References:

Crosier J., Allan, J. D., Coe, H., Bower, K. N., Formenti, P., and Williams, P. I.: Chemical composition of summertime aerosol in the Po Valley (Italy), Northern Adriatic, and Black Sea, Quart. J. Roy. Met. Soc., 133, 61-75, 2007. Matthew, B. M., Middlebrook, A. M., and Onasch, T. B.: Collection efficiencies in an Aerodyne aerosol mass spec-

trometer as a function of particle phase for laboratory generated aerosols, Aerosol Sci. Technol., 42, 884-898, 2008. Middlebrook, A. M., Bahreini, R., Jimenez, J. L., and Canagaratna, M. R.: Evaluation of composition-dependent collection efficiencies for the Aerodyne aerosol mass spectrometer using field data, Aerosol. Sci. Technol., submitted, 2011. Quinn, P. K., Bates, T. S., Coffmann, D., Onasch, T. B., Worsnop, D., Baynard, T., de Gouw, J. A., Goldan, P. D., Kuster, W. C., Williams, E., Roberts, J. M., Lerner, B., Stohl, A., Pettersson, A., and Lovejoy, E. R.: Impacts of sources and aging on submicrometer aerosol properties in the marine boundary layer across the Gulf of Maine, J. Geophys. Res., 111, D23S36, doi:10.1029/2006JD007582, 2006. Slowik, J. G., Stroud, S., Bottenheim, J. W., Brickell, P. C., Chang, R. Y.-W., Liggio, J., Makar, P. A., Martin, R. V., Moran, M. D., Shantz, N. C., Sjostedt, S. J., van Donkelaar, A., Vlasenko, A., Wiebe, H. A., Xia, A. G., Zhang, J., Leaitch, W. R., and Abbatt, J. P. D.: Characterization of a large biogenic secondary organic aerosol event from eastern Canadian forests, Atmos. Chem. Phys., 10, 2825-2845, 2010. Zobrist, B., Marcolli, C., Pedernera, D. A., and Koop, T.: Do atmospheric aerosols form glasses? Atmos. Chem. Phys., 8, 5221-5244, 2008.

Comment 2

With respect to (2), it would be useful to discuss how a particle formed by deliquescence=>activation=>evaporation=>efflorescence may be in a different physical and chemical state, and thus have a different CE, than that of the original particle. Finally, this section would provide a good opportunity to speculate on how ancillary measurements (e.g., SMPS, UHSAS, etc.) might help to constrain this issue. Alternatively, if the authors have other information that they bring to bear on this issue (e.g., SMPS measurements) it would be good to present those here.

Response

E_b-constraining measurements, such as the optical scattering/single particle measurements described above or comparisons with SMPS, UHSAS, PILS, etc.,

would certainly help to constrain this issue. At present, ambient AMS measurements show that particles with a wide variety of compositions, (and, presumably, delicquescence/efflorescence-cycle histories) yield similar E_b values of $\sim$0.5. We are unaware of any ambient measurements indicating such processing significantly affects E_b. As laboratory experiments have demonstrated E_b values significantly below 0.5 for some pure materials, e.g. ammonium sulfate, this may suggest that even "dry" ambient particles tend to retain some water.

Comment 3

Second, it would be very useful to try to place some quantifiable bounds on systematic errors that may arise from potential variations in CE noted above. It appears as though the uncertainties in Tables 1 and 2 are standard deviations only. Would you expect systematic errors to be larger, smaller, or similar to these errors? Can they be neglected, or are they potentially larger than the variations you observed in the data?

Response

As discussed in response to Comments 1 and 2, we do not believe that E_b causes significant systematic errors in the present study. For these measurements, we expect the major uncertainty to be related to signal-to-noise and, most importantly, ambient variability in composition, which are incorporated into the reported errors. However, E_b-related biases could potentially be larger for other sampling locations, and the effect of these errors should be considered separately for each dataset.

Comment 4

Does it make sense to provide a reference to work by K. Noone on the CVI technique?

Response

We have added the following reference: Noone, K. J., Ogren, J. A., Heintzenberg, J., Charlson, R. J., and Covert, D. S.: Design and calibration of a counterflow virtual impactor or sampling of atmospheric fog and cloud droplets, Aerosol Sci. Technol., 8,

235-244, 1988.

Comment 5

Page 291. Can you describe in a bit more detail how you know that transmission is only 50%?

Response

Ideally, the PCVI yields an enhancement in the particle concentration given by the ratio of the input to output flows. During laboratory testing, we introduced NH4NO3 particles with mobility diameter = 350 nm into the TGDC system. A supersaturation and residence time were chosen such that the entire cloud droplet distribution consisted of sizes larger than the PCVI cutpoint. This was confirmed by an aerodynamic particle sizer inserted between the TGDC and PCVI, which also yielded the number concentration of particles entering the PCVI. The AMS, which detects 350 nm NH4NO3 particles with $\sim$100% efficiency, was used to determine the number concentration of transmitted particles. In a second set of experiments, the AMS was replaced with a CPC, which sampled with a diluted flow to preserve the flow conditions within the PCVI. These two tests both indicated that the PCVI operated at $\sim$50% of its ideal transmission.

Comment 6

Page 292, lines 9-10. Assuming the flows are at STP, shouldn't the counterflow be in slight excess over the sum of the pump and sample flows? Otherwise, you will be sampling some ambient air?

Response

The flow balance in the PCVI is as follows: input flow + counterflow = output flow + pump flow. The relationship of the counterflow to the input and pump flows is expected to affect the location of the stagnation plane within the PCVI, but does not greatly affect gas transmission. The counterflow needs to be higher than the output flow to avoid sampling ambient gas. Details of the gas transmission as a function of the counter-

flow/output flow ratio are shown in Fig. 5 of Boulter et al., 2006. For an ideal device, setting counterflow = output flow yields zero transmission of sampled ambient gas. In practice, counterflow/output flow ratios of up to ∼3 were required to remove better than 99 % of the ambient gas. In the present system, a ratio of 5 is used (counterflow = 0.5 L/min vs. output flow = 0.1 L/min).

Reference:

Boulter, J. E., Cziczo, D. J., Middlebrook, A. M., Thomson, D. S., and Murphy, D. M.: Design and performance of a pumped counterflow virtual impactor, Aerosol Sci. Technol, 49, 969-976, 2006.

Comment 7

Page 293, lines 22-25, Page 294 lines 2-6. A style comment - you can probably condense this or delete some text given that you talk about specific figures in the individual sections on the case studies that immediately follow, and you don't necessarily need to note that the figures are coming here.

Response

The section on page 293 has been condensed. We now simply note that the following sections focus on comparisons of CCN-active vs. polydisperse composition and mass distributions.

Comment 8

Page 294. You may want to comment somewhere here about the lack of time for smaller particles to be scavenged by the cloud particles.

Response

Because the residence time in the chamber is so short (maximum residence time of ∼10 s), scavenging is not expected to be significant. This is now stated in the text.

Comment 9

Page 295 and 297. It would be good to report the uncertainties in the quantities listed in the text so that the reader doesn't have to keep referring back to the table.

Response

We agree and have followed this suggestion in the revised manuscript.

Comment 10

Page 296, line 14. "Washington". . .more specifically? Nearby town, part of state, etc. would be helpful.

Response

The measurements were conducted in Richland, WA, USA.

Comment 11

Minor technical issues: Page 289, line 24. ". . .the atmosphere. . ." Page 291, line 22. ". . .particles were produced by atomization. . ." Page 291, lines 22-23. This was meant to be ammonium sulfate, correct? Not $(NH_4)_2$- SO_4 or NH_4NO_3. Page 292, line 6. "4" should be a subscript. Figures 2, 5, and 6. The traces would be easier to see (and colors easier to distinguish) if they were similar in thickness to those in Figures 3 and 4. Page 295, line 7. ". . .the detection limit. . ." Page 299, line 14. ". . .to activate. . ." Page 302, line 18. ". . .composition. . ." IPCC and Solomon references are redundant.

Response

We thank the reviewer for pointing out these issues. All suggestions will be incorporated into the final manuscript.