Atmos. Chem. Phys. Discuss., 11, C1905–C1916, 2011
www.atmos-chem-phys-discuss.net/11/C1905/2011/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Scavenging of biomass burning refractory black carbon and ice nuclei in a Western Pacific extratropical storm" *by* J. L. Stith et al.

J. L. Stith et al.

stith@ucar.edu

Received and published: 16 April 2011

Response to General Comments.

We thank this referee for the detailed comments on our paper. This referee suggests that the main conclusion of our paper is that refractory black carbon and organic-rich aerosol emitted from biomass burning are scavenged by cirrus crystals and that the present manuscript does not present a scientifically relevant case that was not covered by an earlier manuscript by Baumgardner et al. (2008). While it is true that our study

does not refute the results by Baumgardner et al. (2008), that study did not include the measurements of Ice Nuclei (IN), their comparison with ice particle concentrations, and compositional/morphological analysis which is presented here. This referee concludes that the only additional scientific conclusion here is that not only black carbon aerosol but also organic-rich biomass burning aerosol are scavenged. While the above finding is certainly part of our study, it is not the main conclusion or even the most important result from our study.

PACDEX was a proof-of-concept study with the G-V research aircraft that explored the impact of Asian aerosol particles on clouds over the Pacific Ocean. This paper represents the results from a first effort employing new techniques for sampling different regions within extratropical cyclones downwind of the Asian continent. The variety of aerosol source regions likely produce not only CCN, but IN, and their impact on clouds over the Pacific is unknown. As this referee points out, measuring IN from cloud residuals is a powerful approach to studying nucleation scavenging, and these are very challenging measurements to make. One of the important results of our study is that on average, multiple residual particles were produced for each ice crystal entering the CVI in such an extratropical storm system. This was identified by referee #1 (Jensen, 2011) as one of the most interesting results from our study and one that would have relevance for other studies that use the CVI to study IN. We also provide relevant estimates concerning the sizes of crystals that are likely to shatter in the CVI inlet used in this study (those above about 70 microns). Clouds that produce precipitation via the ice phase contain ice particles larger than this size and are of considerable interest in cloud physics. While further details of this process will be described in future work, we feel that it is important to include this limitation of the technique in our paper, and that it will be of interest to readers of this journal. We add to this discussion other possible influences on the CVI data (such as the effects of the lower limit size cutoff, the interactions with the wall of the inlet, and the enhancement factor) as recommended by referee #2 and discussed below. The ice crystal concentrations may also be influenced by ice particles shattering on the tip of the 2DC instrument, this is discussed below.

Despite these potential limitations, a major result of our study is that IN concentrations from the CVI residuals correlated (nearly one-to-one in some regions) with ice concentrations. The CFDC concentrations should match up with ice crystal concentrations if a single IN was present in each crystal nucleated by an IN particle, if ice initiation occurred in regions similar to the operating conditions of the CFDC (which was operated near and above water saturation) and if the residual particle survived the shattering intact to be detected by the CFDC. Since we do not have enough information available to prove that these conditions existed in the storm, we must assume that conditions similar to this were likely to be present in the storm (or come up with another explanation for the results). With this assumption, the concentration of ice in the midlevels of the sampled storm can be attributed to heterogeneous freezing through the known nucleation processes which are measured by the CFDC. Understanding and predicting the concentration of ice in clouds has been remarkably difficult (e.g. Cantrell and Heymsfield, 2005), so these results, which do not require the presence of ice multiplication to explain the observed ice concentrations, are of interest (e.g. Jensen 2011). We add text to the paper to better clarify the above points.

The purpose of the discussion about the composition of the CVI residual particles is to contrast the compositional and morphological characteristics of the CFDC particles with other particles in the residuals, i.e. to try and ascertain what was "different" about the IN. A second objective of this section is to better identify the types of particles that were likely to be detected by the SP2. We have not eliminated the possibility of non-biomass particles in the samples. Given the trajectory of the airmass, there are likely to be multiple sources of aerosol in the samples as suggested by referee #2; however, based on both the number of upwind fires and the nature of the aerosol, particles with a biomass origin appear to be a major component of the residuals. We have rewritten this section to be clearer and to address the concerns of this reviewer which are discussed in more detail below.

We modify the abstract and introduction to better reflect the above points and we modify

the discussion on particle composition to be clearer. We adopt a new title, "Observations of ice nuclei and heterogeneous freezing in a Western Pacific extratropical storm" to better reflect the major focus of the paper.

Response to Major Points:

1a) CFDC. We discuss the counting uncertainties and provide a reference for the CFDC in the paper.

1b) CVI. Concerning the uncertainty introduced by the CVI enhancement factor, this is relatively small since enhancement factor is a function of true airspeed and sample volumetric flow rate, which are readily measured and calibrated quantities. The "approximately a factor of 25" in the text was not meant to convey an uncertainty in knowledge of the enhancement factor itself, only to give a sense of its magnitude. In fact, the enhancement factor varies over time within a single flight (due to airspeed changes and flow rates in instruments sampling off the CVI at any given time, all of which are carefully tracked). For this PACDEX flight, due to the high airspeed of the G-V aircraft, the enhancement factor actually ranged between about 35 and 55, but was always well known. We have changed the sentence "The subisokinetic nature of the CVI provides for an enhancement by approximately a factor of 25 for the residual particles" to "The subisokinetic nature of the CVI provides a substantial enhancement in number concentration of the residual particles; this enhancement factor varies with airspeed and sample flow rate and its uncertainty is estimated to be about 8% (Twohy et al., 2003). Thus uncertainty in CVI enhancement factor is not significant for the measurements presented.

The counterflow characteristics of the CVI mean its transmission efficiency is relatively sharp; see for example, Schwarzenböck and Heintzenberg (2000). Their calibration using glass beads yielded 84% collection efficiency of particles 25-30% larger than the cut size. This corresponds to between 6 -7 μm diameter for a nominal 50% cut size of 5 μm as used in PACDEX. In our study, only 2DC particles that image three pixels (75

microns) or greater are included, well above the size where CVI collection efficiency should be a factor. Additionally, concentrations from the CDP suggest that crystals smaller than 75 microns are present in concentrations too low to affect the results significantly (see Fig 6 in paper). We have added to the paper "Given the small CVI cut size relative to the measured ice crystal size distribution, CVI aspiration efficiency is expected to be approximately 100% for ice crystal sizes."

Collection efficiency for glass beads used in the calibration studies may be higher than for droplets and ice due to their tendency to bounce off inlet surfaces. However, Glantz et al. (2003) showed that CVI residual number concentrations in stratocumulus cloud were within 75% of droplet concentrations measured by an FSSP when most of the droplets were larger than the CVI cut size and when drizzle was not present. Measurements with our inlet yield similar results.

1c) 2DC The under-wing location of the 2DC on the G-V is far enough forward and below the wing surface that contamination from wing surfaces is unlikely. Shattering on the probe tips can be a factor when large particles are present. To account for this possibility, we have rerun the data using the shattering correction method from Field et al. (2006). This reduces the 2DC concentrations somewhat, as expected, resulting in slightly better agreement with the IN concentrations in the latter half of the main sampling pass, and somewhat higher IN concentrations than 2DC in the other portions. Interestingly, examination of the 2DC images in regions where the IN concentrations were higher than the 2DC suggests the presence of aggregated ice crystals, which would be expected to release multiple IN upon evaporation (since they are composed of multiple single crystals). Thus, even in the region where shattering on probe tips occurred the data qualitatively support the observations of heterogeneous freezing occurring on IN. We thank the reviewer for spurring this exercise that has produced an interesting additional result. A complete size distribution is now presented.

2a) Shattering effects on IN concentrations. Concerning the comments from the referee about reliance on processes that are not well understood or characterized, several

points are worth noting. First we have made it clear that particles larger than about 70 microns (which includes the ice crystals we measured with the 2DC) are likely to shatter in the CVI and produce multiple fragments of ice before evaporating. If each IN that nucleated a single crystal survived the fragmentation intact and if heterogeneous nucleation was responsible for the observed ice crystals, we would expect there to be a one-to-one correspondence between the observed IN concentrations and the observed ice crystal concentrations, provided the nucleation of the crystals in the natural cloud occurred at temperatures and saturation conditions similar to those in the CFDC and through the nucleation processes which are represented in the CFDC. Under this scenario, one would also expect aggregates of ice crystals to produce multiple IN particles upon breakup and evaporation, which appears to be the case (which has become evident as we added the corrections for probe tip shattering). The observed agreement between IN and ice particles supports the above scenario. Other explanations for the correspondence between IN and ice particles might be possible, but we don't know what they might be and would welcome suggestions from this reviewer for alternate explanations of this result. We will remove the sentence discussing the CFDC operating at colder temperatures than ambient giving higher IN concentrations due to crystal shattering. We believe that this effect is due to a combination of colder temperatures in the CFDC and aggregation of ice particles (which is described in the revised paper).

It would certainly be helpful if the shattering/breakup of particles in the CVI or on the tips of cloud probes were better characterized. This is an area of active research. We have begun to model these processes within the NCAR CVI inlet using computational fluid dynamical modeling in conjunction with aerodynamic breakup theory. In future work, these results will be compared with observations or residual number in this and other field projects. We also wish to caution that shattering results using this particular CVI inlet are not necessarily transferable to other CVI inlets with different geometries. In particular, the NCAR CVI inlet is routinely used for measurements of total condensed water content (liquid plus ice). Since we wish to retain large ice that can provide a substantial fraction of total condensed water, this CVI inlet does not employ a "waste

flow" at the back of the inlet to remove large crystals that may survive intact. Such a geometry has been employed and discussed by Ström et al. (1999), and may reduce the shattering effect.

2b) Inlet artifacts Ice crystals hitting inlet surfaces at high speed may ablate inlet material, as discussed by Murphy et al. (2004). The G-V CVI inlet was made entirely of commercially pure, grade 2 titanium in order to more easily identify inlet material. To test for possible secondary particles generated from ablation of the inlet, 7168 particles sampled downstream of the CVI in this case study were analyzed by scanning electron microscopy and X-ray analysis. Particles with high enough titanium levels to potentially be from the inlet were 4.1% of the total number. For the total population of analyzed CVI particles with an approximate lower detection limit of 200 nm, the median geometric diameter was 0.62 microns, while titanium particles had a median diameter of 1.2 microns. So, unlike the results for Murphy et al. which showed no substantial size-dependence for inlet metals vs. other detected particles, titanium particles ablated from the CVI inlet tended to be about twice as large as the general residual population. The Ti-bearing particles constituted 8.4% of particles larger than 1000 nm in size, 3.1% of particles 500 to 1000 nm in size, and only 1.9% of particles between 200 and 500 nm in size.

While IN tend to be larger particles in the atmosphere and only a special subset of those (DeMott et al., 2010), we do not believe titanium from the inlet affected the IN measurements. The particle types collected downstream of the CFDC on this day that nucleated ice did not contain titanium. Additionally, in many years of collecting IN samples from the CFDC in the field, only one particle containing titanium has been identified, and that appeared to be a spherical aggregate of TiO2 from industrial processes (DeMott et al, 2004).

Whether or not titanium metal particles will incandesce in the SP-2 is unknown, as this composition has not been tested in the laboratory. Due to this uncertainty, the CVI/SP2 data should be considered an upper limit for rBC in the CVI samples. We plan future

tests with Ti in the SP2 to better understand its response to this metal. While we cannot state with certainty that the measured rBC concentrations were not affected by titanium from the inlet to some extent, we don't believe they were a large fraction of the concentration measured for the following reasons. First, as we note below (2d), we have SP2 samples in the warm sector ambient air (out of cloud in relatively dust-free air) through a different, non titanium, inlet. These revealed a greater percentage of rBC as a fraction of total scattering particles than did the samples that were taken in cloud through the CVI in the warm sector air. This is not what you would expect if the SP2 signal for rBC in the CVI samples was due to Ti from the inlet. Second, a fraction of these Ti-bearing particles may have been present naturally in the residuals. X-ray analysis of samples taken in the cool sector air outside of cloud and also though a non-titanium inlet indicated the percent of titanium particles was about 0.25% by number in that region of the air near the storm. Although this was a different airmass than the warm sector, it suggests the presence of Ti in the atmospheric aerosol.

2c), Scavenging of rBC and other particles. Concerning the comments from the referee on the number of particles of rBC and other particles found per ice crystal sampled and the scavenging calculations: We discussed possible explanations for how particles might be produced from multiple fragments of ice particles (p 577, 11) and scavenging was included as one of several possibilities. Since we are not able to test all of the possible explanations, the main result of this section of our paper is that multiple particles are produced when the ice particles shatter/evaporate and that the IN (and to a lesser extent, the rBC) in the residuals appear to be a small subset of the total aerosol contained in the ice crystal. We have however ruled out ablation of inlet materials as a major contribution to the high concentrations of total residuals observed. The particles that we measured in the CVI represent primarily the residuals from the shattered/evaporated ice particles. Of these particles, the number of IN appears similar to the number of single ice crystals in the clouds, suggesting that the IN survived the inlet intact in a likely heterogeneous freezing environment. rBC particles seen by the SP2 appear somewhat more numerous than IN and particles that are neither IN

or rBC predominate, a conclusion that, at least qualitatively, is supported by the electron microscope analysis that suggests the predominate particles in the residue were not rBC or IN. The observation that the IN are a small subset of the total aerosols released when the ice particles evaporates argues against nucleation scavenging as the primary source of the particles in the residuals (i.e. in agreement with Baumgardner et al., 2008), so another explanation (577, 11-24) including non-nucleation scavenging seems likely. Precise non-nucleation scavenging calculations are not possible due to uncertainties in the size distribution of interstitial aerosol and the residence time of crystals within the cloud. However, simple calculations indicate the numbers of residuals are not inconsistent with non-nucleation scavenging. Some basic details are now briefly discussed in the paper. Additionally, while number concentrations and rBC concentrations in cloud residuals were higher than residual IN concentrations, they were generally lower than the concentrations of these particles measured out of cloud in the region (see below for further information).

2d) Relationship of rBC in and out of cloud. In response to the queries from the referee: "...does the SP2 incandescence signal within cloud differ from clear air sampling? And can the authors demonstrate a contrasting case within a cloud containing similar size ice crystals where residuals did not show a large BC increase?" An out of cloud sample (not using the CVI, but our HIML inlet) in the warm sector air for the SP2 was available between 6:21 and 6:25 in the extreme southeast leg of the sampling area at the same altitude as the cloud leg in Fig. 7 (8.5 km). The CVI/SP2 data in the warm sector cloud showed a gradient of number concentration in the SP2 data from the west to the east, with higher concentrations in the west (Figs. 1 and 7-top). Concentrations in the clear air between 6:21 and 6:25 averaged 3.3 cm-3 and 1.4 cm-3 for the SP2 total scattering and rBC concentrations, respectively. The nearest in cloud sample from the CVI in the eastern portion of the warm sector cloud around 5:56-5:57 indicates a residual number concentration of approximately 0.1 cm-3 and 0.01 cm-3 for the SP2 total scattering and rBC concentrations, respectively (Fig. 7). These data suggest that the in cloud CVI residues in the eastern part of the leg upon evaporation produced only a small

fraction of the aerosol number density that was present in the clear air. Thus, here we have a decrease in rBC in the cloud, not an increase as suggested by the second question from the referee.

Only a brief sample of clear air in the warm sector in the western sampling regions is available between 2:23 and 2:25, just above the cloud between 9.9 and 8.5 km altitude, which exhibited SP2 concentrations of 2.5 cm-3 and 0.83 cm-3, respectively. In cloud on the western part of the sampling leg, SP2 concentrations from the CVI residue ranged from about 0.1 to 10 cm-3 and 0.01 to 0.2 cm-3 for the total scattering and rBC concentrations, respectively (Fig. 7). Thus, SP2 concentrations from the CVI residue in the western part of the sampling area appear to be closer to ambient values for the total scattering signal and somewhat less than ambient for the rBC signal.

It appears that the ice particle residuals in the western sector of the sampling leg contained more aerosol compared to ambient values, than did those in the eastern section. According to the size distributions and the particle imagery we show in the revised paper, ice particles in the western sector were significantly larger than those in the eastern section, which would favor more non-nucleation scavenging, through longer growth times and more surface area available for scavenging.

3. Concerning the concern from the referee that we did not demonstrate that the collected cloud residuals originated from a biomass burning source, we modify that section to clarify. In particular, the intent of this section is to describe the characteristics of the aerosols acting as IN and to determine what differences in either composition or morphology distinguish the IN from the other aerosol. Our intent is not to prove that all the aerosols in the CVI residue were from a biomass burning source and, as the referee points out, given the trajectory of the air, other aerosols in the mix are certainly possible. However, the morphology and composition of the thousands of aerosol particles that we have examined is remarkably similar and suggests a biomass burning source, although more chemical measurements (such as acetonitrile or HCN, which are not available) would certainly be helpful in confirming this result.

Minor points.

We rewrite the composition section of the paper to be clearer. The 2DC with the processing used in the revised paper covers particles from 75 microns to over 3 mm, using a circle fit technique, which allows sizing of particles larger than the diode array width. This is described in the revised paper and covers the hydrometeor size range adequately. Concerning the figure showing the IN (and SP2) correlation with the CWC, we included that since the CWC is from a different instrument than the 2DC (e.g. which measures total condensate from both shattered and un-shattered particles, if any). It is not critical to the paper and can be omitted.

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