**Atmospheric
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Discussions**

Interactive comment on "Observations of sulfur dioxide uptake and new particle formation in a midlatitude cumulus cloud" *by* J. R. Peter et al.

Anonymous Referee #2

Received and published: 17 August 2006

Review of Peter et al, "Observations of sulfur dioxide uptake Ě"

1. Recommendation. In this study, the authors revisit the somewhat dormant topic of particle production in clouds, dealing specifically with chemical production, i.e., nucleation (the SO2 uptake analysis is clearly ancillary to this topic, though of some interest in its own right). As they point out, the relatively sparse literature on such production is due, at least in part, to the troublesome issue of artifact particle production caused by droplet shattering on intake probes. To address this issue, the authors have adopted a different measurement strategy. They examine CN concentrations in air detraining from cumulus clouds and compare it with entrained air, taking into account both mixing and the lose of particles to the cloud drops via Brownian diffusion. This approach has its attractions and certainly avoids the artifact shattering issue, but has its drawbacks as

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well. The chief such drawback is that particle production must be estimated from comparison of the predictions of a model of cloud/aerosol interactions with observations of detrained particles, rather than from observations alone. There are many sources of uncertainty in such an approach and it is my view that the authors have not provided a sufficiently credible error analysis to establish that the observed CN concentrations in the detraining air are significantly higher than what might be expected if no particle production had occurred. Hence, while I found the analysis innovative, I cannot recommend publication until such an error analysis has been successfully completed. My specific comments in support of this, together with some comments on other less acute issues, are given below.

2. Comments. 2.1 Page 7473, line 25. Another approach to estimating sulfate production in clouds, of which the authors seem to be unaware, is to use an appropriate chemical tracer. The work of Husain and his colleagues, using Se as a tracer, is an excellent example of this approach and should be cited (cf., Husain et al, J. Geophys. Res., 96, 18789-18805, 1991).

2.2 Page 7474, line 12. Some mention should also be made here of ternary nucleation with NH3 as the third component. Numerous studies on this topic are available.

2.3 Page 7475, line 8. It is not quite clear here whether the ASASP and FSSP sizing is given in terms of radius or diameter. The authors have previously used radius for the CN sizing but particle spectrometer specifications are commonly given in diameter (for some reason) and the size ranges given could be either one given the multiple gain settings of both instruments. Perhaps the authors could simply note at some point early on that all sizes are radii (assuming such is the case).

2.4 Page 7475, lines 12-15. Neither the ASASP nor the pulsed-fluorescent SO2 analyzer is a 64 Hz instrument - this figure must refer to the data acquisition rate of the aircraft data system. The SO2 analyzer is not even a 1 Hz instrument. To get to the sub ppbv levels indicated in Table 1, at least 1 minute averages would be necessary in my

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experience - and I have used 43's and 43s's for many years. At the airspeed of a King Air (~80 m s-1 unless something highly abnormal is happening), this translates into a spatial resolution (assuming a straight flight track, of course) of ~ 4.8 km, rather poor for looking at detrainment from Cu. How do the authors ensure that they are looking at just detrained air? The authors must explain how they made the measurements they say they made. Certainly they must clarify that they do not have instruments that actually measure at 64 Hz, or even 1 Hz in the case of the SO2 analyzer.

2.5 Page 7476, section 3.1. Using conserved variable mixing analysis is an innovative approach to assessing chemical cloud processing and I do find it attractive. However, it is not without its problems and I think the authors have not adequately dealt with them. Unlike its more normal application, use of conserved thermodynamic variables as, essentially, tracers requires a much more quantitative analysis. The authors use F, for example, in predicting what CN and SO2 concentrations to expect, and then compare these with measurements to reach their conclusions regarding the impact of cloud processing. But, to assess the significance of any observed/predicted anomaly, the uncertainty in F must be propagated into the predictions and I do not see this in the analysis. This uncertainty can be estimated from the uncertainty in the regression mixing line and the departures of the in cloud points from the mixing line. This must be done.

2.6 Page 7478, line 14. Speaking of uncertainties, an apparent specific anomaly pops up here. The predicted SO2 concentration is given as 5.81 ś 0.17 mg m-3 while that observed is 4.57 ś 0.12. The difference of 1.24 should have an uncertainty (square-root of the propagated variance) of 0.21, not 0.17. This apparent error is not of great moment in this instance but it does not inspire confidence in the significance of the authors' findings.

2.7 Page 7479, line 5. I rather doubt that the data derived from the authors' analytical approach would have anything like the precision or accuracy of laboratory rate data. The uncertainties in, for example, parcel residence time, gas partial pressures, tem-

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perature of droplets, droplet pH's, etc. would overwhelm the calculation. The authors must be more circumspect here. Similarly, residence times calculated from chemical species decay rates will also be burdened with large uncertainties, though perhaps less so than actual kinetic rate estimates. In principle this is a good idea but its practical feasibility is highly suspect.

2.8 Page 7480, line 1. The authors here attribute the reduction of CDNC with altitude to entrainment. Fair enough, but on the next page (7481) they also discuss collision/coalescence as a lose mechanism for CDNC/CCN. Possibly (indeed. likely) both processes were occurring but, if so, they both must be taken into account in derivative calculations since their impacts are somewhat different and there is no indication that the authors have done this. Furthermore, collision/coalescence suggests precipitation, and in fact "mild" precipitation is included in Figure 2. However, appreciable precipitation will invalidate the conserved variable analysis. Clarification (and perhaps justification) is badly needed here.

2.9 Pages 7482-7485, section 3.3. The analysis of possible CN production in cloud is novel and interesting - and highly problematic. Conceptually, there is nothing wrong with the analysis. The devil, as they say, is in the details. It is important to remember that the actual observed concentrations of detrained CN are lower than those of entrained air for any plausible values of F. Hence, the conclusion that CN production has occurred is based entirely on a model prediction. The model assumes that the main sink for CN is Brownian diffusion to cloud drops, presumably followed by internal aggregation of some sort (depending on solubility) so that residual nuclei after evaporation of detraining drops are far fewer in concentration than the entrained CN (the latter issue is not discussed but numerous plausible mechanisms could be invoked). Problems arise here. The authors do not have detailed size distribution measurements in the nuclei range, their two "size bins" being 1.3 to 6 nm and (apparently) 6-65 nm. They analyze, understandably, only the former range and display the results in Figure 4. However, the diffusivity of CN is highly size dependent, especially in the range of

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1-10 nm where it varies by an order of magnitude. Presumably, this is the cause of the monotonic increase with size in the predicted to observed CN ratios in the figure (if not this, for what reason are the ratios increasing with size - it is not discussed). Because, except for the 1-minute in cloud curves (which the authors plausibly discount), all of the ratios, it is asserted, are much below unity, the authors conclude that the diffusional sink was so large that negligible particles are to be expected unless in-cloud production has taken place. It is not clear this is the case. For example, using the 5 minute in-cloud time period - a quite reasonable estimate - the predicted/observed CN ratio is ˜ 0.5 if we assume that the particles have a radius of ˜ 6 nm - and there is no way of telling if they are ˜ 6 nm or, say, 4 or 3. The issue is then, is this value significantly below unity? To assess this, we need vertical error bars in Figure 4, and they are conspicuously absent. If one takes into account all of the uncertainties that propagate through the calculations (e.g., in CN number concentrations, in cloud drop number and size, particle diffusivity, F, sticking coefficient, pressure, etc.), I would be surprised if this ratio significantly differed from unity. Perhaps I will be surprised, but not until such a calculation is made.

2.10 Page 7497, Figure 5. The figure I have is so small that it is very hard to read and I have had to essentially take the authors' word as to what is in the figure. This should be rectified.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 7471, 2006.

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