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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Sulphuric acid closure and contribution to nucleation mode particle growth" *by* M. Boy et al.

Anonymous Referee #2

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This paper provides some new insight into the processes that controll sulfuric acid concentration in the atmosphere. It includes a photochemical model to determine OH concentrations, which can be combined with measurements of SO2 to generate a H2SO4 production rate. A condensational sink term is then determined from particle size and number distributions using a Fuchs-Sutugin type relation. The resulting calculated sulfur concentration is then compared to the measured sulfuric acid concentrations. The results obtained over this nearly month long study provide some limited insight into why modeled results sometimes fit well with measured values and other times show poor agreement. The overall concept being presented is sound. The significance of the results is, however, being overstated. The paper should contain a more complete analysis of uncertainties, because the uncertainties in calculating sulfuric concentration are probably very large, and the sulfuric measurement uncertainty is also fairly significant.

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The total uncertainty between measured and calculated sulfuric acid concentration is probably a factor of 2. It is not clear from this paper what value is used for the accommodation coefficient. Is the accommodation coefficient assumed to be the same for all particles and conditions? Several modeling scenarios are proposed, and the best fit (SC 8) is then used in Figure 8. I don't object to showing the best fit, but I think that using closure in the title is very misleading. It is hard to have a closure experiment when one is using a somewhat free parameter (basically sulfuric production/OH concentration) to provide a best fit. This is also not the first closure measure of this type in the literature, as stated in the introduction of the paper. At least two studies made nearly a decade ago provided a far more direct closure study for sulfuric acid. (F. L. Eisele and D. J. Tanner, Measurement of the gas phase concentration of H2SO4 and methane sulfonic acid and estimates of H2SO4 production and loss, JGR, 98, 9001, 1993; and R.J. Weber, J.J. Marti, P.H. McMurry, F.L. Eisele, D.J. Tanner and A. Jefferson, Measurements of new particle formation and ultrafine particle growth rates at a clean continental site, JGR, 102, 4375-4385, 1997.) In both cases, OH was measured directly by the same instrument that measured sulfuric acid, thus dramatically minimizing the uncertainty in their ratio. These studies also obtained good agreement, but with only the sulfuric acid accommodation coefficient as a possible free parameter. This parameter was also subsequently measured in the laboratory. (A. Jefferson, F. Eisele, P. Ziemann, J. Marti, R. Weber and P. McMurry, Measurements of the H2SO4 mass accommodation coefficient onto polydisperse aerosol, JGR, 102, 19,021, 1997.) The contribution of sulfuric acid to growth rates was also calculated where growth rates "were estimated visually". This estimate should be discussed in more detail. A factor of two uncertainty is suggested for these growth rates but certainly some days must have provided more uniform air masses than others. Thus, some growth rates may be somewhat better than a factor of two and provide a good factional growth rate while others might be nearly meaningless. Were NMHC and HCHO particulary high when sulfuric acid made up the smallest fraction of particle growth? Is there any chemical or physical data (volatility or H2O update etc.) to support the idea that sulfuric acid can

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Interactive Comment

make up as little as 3-4% of the aerosol mass. There should be some discussion of at least a few sample days, i.e., in Figure 8 some days show good agreement while others show quite poor agreement. Do the authors have any additional insight that would shed some light on these differences?

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 6341, 2004.