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Discussions

Interactive comment on "In-cloud sulfate addition to single particles resolved with sulfur isotope analysis during HCCT-2010" *by* E. Harris et al.

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Harris et al. measure the sulfur isotopic composition of particulate sulfate, H2SO4, and SO2 during 3 cloud events in Germany over a 9 day period in late-September early-October 2010. They measured the "connected flow", in that they sample air before, during and after cloud processing, in order to examine the mechanisms of sulfur oxidation leading to changes in the aerosol size distribution. They conclude that direct uptake of H2SO4(g) and ultrafine particulate sulfate were the most important mechanisms modifying (increasing) the size of ultrafine particles. For the larger particles, aqueous-phase oxidation of SO2 by TMI catalysis and H2O2 were the main processes responsible for sulfate formation.

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Interactive Discussion

Discussion Paper

This paper is novel, produces interesting and important results, and is very well written. I have some important suggestions, mainly regarding clarity, that should be easy for the authors to address but that are important to fix before publication. The lack of clarity in Figure 5 is my biggest concern.

Page 2940 Line 19: The oxidation rate of S(IV) by TMI catalysis is not really pH independent because the concentration of S(IV), on which the rate depends, is pH dependent (increases with increasing pH). The reason that the rate of oxidation of S(IV) by H2O2 is not pH dependent is because although this reaction is acid-catalyzed, the pH dependency of [S(IV)] acts in the opposite direction so that these pH-dependent effects cancel and the overall rate of reaction is pH-independent. It is true that reaction of S(IV) by O2 is not AS pH-dependent as the oxidation by O3, because O3 reacts primarily with SO32-, which is only present in significant quantities above a pH of about 5.5. In contrast, the rate constant for TMI catalyzed oxidation by O2 is assumed to be the same for HSO3- and SO32-, reducing the pH dependence, but not eliminating it. Although I'm not sure that this has been explicitly demonstrated in laboratory studies.

Introduction: You need to mention Criegee chemistry in the intro. You wait until later in the paper (Section 4.3) to discuss it. You are ignoring it, but it is not clear whether or not this is appropriate. Some discussion about its potential impacts on sulfate formation in this location during this time period are warranted. Perhaps you could use the results of the Pierce et al. (2013) modeling paper to examine this.

Section 2: It would be useful to have a table of alpha values for each reaction discussed in the Introduction.

Page 2942 Lines 21-23: It's not clear why isotopic analysis are particularly useful for distinguishing between these two reactions. Perhaps if you include a table as I mention above, this would be clear why.

Page 2954 Line 24: "…but WHAT has a much smaller magnitude than for FCE11.2 and 1.3."? The observed isotopic composition? The fractionation factor?

Figure 5: I cannot evaluate Figure 5 or its discussion, which is central to the paper, because I don't understand it. It appears to be missing parts based on the discussion. For example, on page 2956 line 11, I do not see any green line as is mentioned here. I only see a green and blue dotted line in one of the 8 figures, and it's not clear to me why it's not on all of them. There is a dark blue line in all of them. The "SO2 oxidation by TMI-catalysis" is written in brown but has no label. In the caption it says "Dashed lines follow from upwind to in-cloud to downwind…" but I see no dashed line. I also don't see "fine dashed with circle symbols".

Page 2956 Line 28: What exactly do you mean by "cloud droplet residual particles"? This should be defined. It's the residual part that I don't understand.

Page 2957 line 14: ""During FCE 11.3 the increase in d34S could be due to..". Is the increase in d34S in the fine our coarse particles? Mixed or dust?

Very last sentence of conclusion: Large scale models will never be able to capture the details of these single particle processes. Any ideas for a parameterization? What is the most important thing that models are missing with respect to what you have learned here?

Table 3: Is the oxidation of SO2 on the surface of aerosols (surf) via O3?

Figure 4: Your label "change" is not descriptive enough. The change of what? Please show an equation instead.

Figure 5 caption: "…could BE added…"

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 2935, 2014.