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Atmospheric Chemistry and Physics Discussions



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

**E. Harris et al.**

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We thank the anonymous reviewer for providing helpful and constructive feedback on the manuscript. All the suggestions for change will be incorporated into the final paper. The comments are addressed pointwise below in the order they appear in the review. Page and line numbers refer to the discussion paper prior to the changes.

1. *On how many particles in total is this analysis based? ...How representative is the particle collective of what is going on in these clouds?*

   A total of 128 particles (54 for FCE 11.2 and 74 for FCE 11.3) were analysed, with at least five particles analysed on each of the 8 individual filters for each

event (coarse and fine; upwind, downwind, cloud droplet residual and interstitial). Particles with enough sulfate for isotopic analysis were chosen at random from the thousands of particles on each filter. We now mention this point in the text (P2955 L24):

'A total of 128 particles, 54 from FCE 11.2 and 74 from FCE 11.3, were analysed to investigate the changes in isotopic composition between the measurement stations. At least five particles on each of the eight filters (upwind/downwind/interstitial/cloud droplet residual; coarse/fine) were analysed. Particles were chosen at random from the thousands of particles present on the filter, therefore there is no apparent bias and despite the small sample size inherent in this technique, the results are expected to be representative.'

2. P2493 L11: The reviewer requests that more detail is added to the section referring to connected flow calculations, particularly regarding the coefficient of divergence. We have added more detail into the text (P2493 L9-17):

   '...the local meteorological conditions were stable.

   Connected flow between sites was investigated with ozone concentration profiles, ozone cross correlations, and hydrodynamic flow analysis, as ozone is quasi-chemically-inert and relatively insoluble in water with no significant primary sources (Tilgner et al., 2014). The coefficients of divergence (COD) for several aerosol particle bins and ozone concentrations were also calculated to characterise connected flow conditions. The COD is a statistical measure of temporal similarities between the concentrations measured at the different stations; lower COD values indicate very similar concentration profiles, and a COD of $<$0.1-0.2 can be used as an indication of homogeneity between sites (Tilgner et al., 2014; USEPA, 2004). In addition, connected flow between the sites was periodically measured with tracer experiments following the release of an inert gas ($SF_6$) at Goldlauter, with measurements at 5-minute intervals at nine sites including the in-cloud and downwind stations. The connected flow analyses are discussed in



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detail in a companion paper in this special issue of *Atmospheric Chemistry and Physics* (Tilgner et al., 2014).'

3. Figure 3: We thanks the reviewer for pointing out that the abbreviation 'PBA' used in the figure was not defined. We have added to the figure caption: '...are shown on the right-hand axis. PBA = Primary Biological Aerosol, OA = Organic Aerosol, IA = Inorganic Aerosol.'

   The reviewer also wonders how soot, coated soot and mixed OA/IA are differentiated without SEM analysis. We have clarified now in the text that the combination of ratios is critical for distinction: in at least one ratio each particle used was able to be distinguished. At P2950 L6-7: '...it was possible to distinguish the different particle types from a NanoSIMS isotopic analysis without a corresponding SEM image. The distinction between OA/IA, soot and coated soot is challenging as there is a high degree of overlap in most ratios; however, when all the ratios are used in combination all the particles used for isotopic analysis were able to be definitively categorised. Ratios $X_O$, $X_C$ and $X_S$ are particularly useful to distinguish between mixed OA/IA and coated soot.'

4. Table 1: Reviewer 2 mentions that some of the processes defined as occurring on solid particles can actually also occur on liquid particles, ie. CON, SCAV and COAG. The lines between various processes are blurry as particles are not simply 'liquid' or 'solid', but rather occur across a continuum from, for example, truly solid mineral dust through OA/IA which covers a range of viscosity states to cloud droplets which are true liquids. We have amended the table to reflect this more clearly:

   - COND refers to solid and semisolid (ie. OA) particles in this paper; once a particle crosses the bounday to liquid, the process become dissolution. This is of course a simplified distinction; for most particles which are semisolid,



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gases may first 'condense' on the surface and then be very slowly mixed through the particle in a delayed 'dissolution'.

- SCAV and COAG could occur for both solid and liquid particles as mentioned by the reviewer.

The revised version of Table 1 is attached to this comment.

5. Figure 5 (caption): The missing word 'be' was added to the caption following the review by Becky Alexander. In addition, we have now added a reference to Table 3 (Table 4 in the revised manuscript) as requested by the reviewer: 'Straight thick lines (blue, green and brown) show the isotopic composition of sulfate that could be added to particles in the cloud from different sources according to the legend, and the dashed dark blue line shows the sulfate that would have been added from the $SO_2$ removal ($\alpha_{\text{cloud}}$) as discussed in Harris et al. (2013) (values given in Table 4). '

6. Conclusions: The reviewer mentions that it would be useful to give the modelling community a guide as to how wrong their answer may be if they do not account for the variation in particle composition when modelling sulfate production. *'For example, can you compared the estimated sulfate production within the cloud assuming an internal mixture for the particle population to the sulfate production based on different particle types'?*

   A comparison as suggested by the reviewer would require a complex model treatment and is, as such, beyond the scope of this paper. There are a number of non-linear factors and feedbacks that complicate a quick assessment of how much this may affect a model; for example, particle lifetimes, CCN number concentration and the non-linear relationship to cloud droplet number concentration, the pre-existing particle population... We have therefore provided a few guideline examples of situations where a large effect may be expected and a hypothesis of



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what the effects may be (at the end of the Conclusions; see the response to B. Alexander for changes already made to the conclusions):

'...even when it is not the most important process on a total mass basis. These effects will be most important in environments such as Asia, where $SO_2$ and dust concentrations may be very high, and in areas where water vapour concentrations are higher so that clouds are more sensitive to increases in CCN number concentration. Under these two cases, we would expect that models in which sulfate addition is not resolved for particle type may overestimate and underestimate the cooling effect and lifetime of sulfate aerosol respectively. Future model studies considering the potential role of these processes first on a smaller scale, as in the black carbon case, and then on a regional scale in sensitive areas, will help to parameterise these effects to improve modelling of $SO_2$ and sulfate in global-scale studies.'

7. Conclusions: The reviewer mentioned that a significant amount of organic matter is produced in clouds, and wonders if it may be possible to apply this technique to investigate this problem. We have added to the conclusions:

'The results demonstrate the potential of sulfur isotope measurements for investigating $SO_2$ oxidation, particularly when single-particle isotope ratios are measured with NanoSIMS. The application of this technique to other systems, for example, the formation of nitrate and other nitrogen compounds in clouds, may show similar behaviour to the sulfate system and be an ideal topic for NanoSIMS investigation. Organic matter production in clouds accounts for a large amount of mass gain. A NanoSIMS study of OA formation could yield exciting results although it may be challenging compared to the simpler sulfate case. Investigatory studies looking at the variation in carbon isotopic composition between characteristic SOA types or important precursor compounds, as well as an study of the behaviour, matrix effects, and precision of $^{13}C$ measurements in aerosol particles with NanoSIMS, would provide an idea of the feasibility of a study of this type.'



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## References

Harris, E., Sinha, B., van Pinxteren, D., Tilgner, A., Fomba, W., Schneider, J., Roth, A., Gnauk, T., Fahlbusch, B., Mertes, S., Lee, T., Collett, J., Foley, S., Borrmann, S., Hoppe, P., and Herrmann, H.: Enhanced role of transition metal ion catalysis during in-cloud oxidation of SO2, Science, 340, 727–730, doi: 10.1126/science.1230911, 2013.

Tilgner, A., Schnoene, L., Brauer, P., van Pinxteren, D., Hoffmann, E., Spindler, G., Mertes, S., Birmili, W., Otto, R., Merkel, M., Weinhold, K., Wiedensohler, A., Deneke, H., Haunold, W., Engel, A., Weber, A., and Herrmann, H.: Critical assessment of meteorological conditions and airow connectivity, Atmospheric Chemistry and Physics Discussions, HCCT Special Issue, 1861- 1917, 2014.

USEPA: Air Quality Criteria for Particulate Matter, Report No. EPA/600/P-99/002aF and EPA/600/P-99/002bF, Tech. rep., National Center for Environmental Assessment, Office of Research and Development, US Environmental Protection Agency, Washington, DC, 2004.

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| Process | Abb. | Description | Effect on: | |
|---|---|---|---|---|
| | | | Number conc. | Mean diameter |
| Condensation | CON | Phase transfer of gaseous $H_2SO_4$ to the solid (particle) or semisolid phase | None | Increase |
| Uptake (dissolution) | DISS | Dissolution of $H_2SO_4$ into a cloud droplet or a liquid particle | None | Increase |
| Impaction scavenging | SCAV | Collision and combination of an interstitial particle with a cloud droplet | Decrease | Increase |
| Coagulation | COAG | Collision and combination of two smaller particles to form one larger particle | Decrease | Increase |
| Cloud droplet nucleation | NUC | Formation of a cloud droplet on a CCN, and dissolution of CCN components (eg. sulfate) | None | None |
| Aqueous oxidation | AQOX | Dissolution and oxidation of $SO_2$ in the aqueous phase (cloud droplet) | None | Increase |

**Table 1 (revised):** Definitions and abbrevations ('Abb.') for processes involving modification of particulate by sulfur species observed at HCCT-2010, after Seinfeld and Pandis (1998), p.933. For in-cloud processes, effects on number concentration and mean diameter refer to the effect on the particle population following evaporation after an air particle leaves the cloud, ie. downwind vs. upwind of a cloud. Processes CON, DISS, COAG and SCAV collectively involve direct transfer of sulfate from the gas-phase and ultrafine particle into a larger particle mode, and will be referred to as 'direct uptake', which can occur both in and out of a cloud.

**Fig. 1.** Table 1 (revised)



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