

Interactive comment on “Contribution of gaseous and particulate species to droplet solute composition” by K. Sellegri et al.

K. Sellegri et al.

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General Comments:

Following comments from reviewer 1, text has been by 30 % shorten, which hopefully makes it more clear and easy to follow. However, I found it difficult to address the two basic issues [1) Thermodynamic versus kinetic controls on in cloud phase partitioning and 2) implications of repartitioning with "residual" aerosols after drying]. Indeed, thermodynamic versus kinetic controls that we observed are consequences of the repartition of compounds and thus both issues can not be differentiated. Result and Discussion sections have been merged. Also, Tables 3 through 6 have been combined into a single table.

Specific Comments:

Table 1. The reported +/- values were specified to refer to standard deviations and pH

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were also indicated to be derived from calculated H^+ . The species used to calculate H^+ have been specified in the text. It is indeed unfortunate that H^+ was not measured directly, this is due to instrumental disfunctionment that we noticed only later.

Page 482, lines 1 to 3. The terminology has been corrected.

Page 482, lines 19 to 20. Sampling cloud water during temporary clear sky episodes has been added as an additional source of bias in solute concentrations.

Page 483, lines 22 to 23 dropped.

Page 484, lines 3 to 4 (and elsewhere in the paper). The terminology of "gases, aerosols, and cloud droplets" has been adopted through the text, operational size discrimination has been specified in the text and in the revised figure1.

Page 484, lines 5 to 24. Phase partitioning of gases with aerosols and cloud droplets is respected through the sampling process, and is representative of the ambient conditions. The process of evaporation of cloud droplets in the CVI is, however, less representative since the droplets are evaporated at a higher temperature and also in a clean carrier gas. Nevertheless, on this last statement, we have checked that the sum of (CVI&cascade impactor) + (RJI&cascade impactor) was fitting to the (WAI&cascade impactor) showing that being evaporated in a clean carrier gas or in atmospheric air did not influence the evaporating process of the droplets.

Figure 1. Has been revised to be more explicit.

Page 485, lines 18 to 26. Mist chambers were specified to be positioned in tandem.

Page 487, lines 10 to 13. The oxidation of S(IV) to S(VI) is already discussed p494 lines 16 to 25 and SO₂ concentrations specified to be lower limits. This issue has been moved to the experimental section. I agree with that the assumption that all CI in mist solutions originates from HCl is not justified. Thus, as suggested, HCl has been replaced by soluble volatile chloride.

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Page 487, lines 16 to 21. The precision which is given here stands for the Ion Chromatography analysis. Thus, relative precision does not vary among analytes, and is given by the quality of the analytical water and the stability of the standards, which were prepared every day (i.e. the detection limit of the instrument), compared to the analysed concentrations. This point was indeed confusing in the text and has been clarified.

Table 3 (4, 5, 6, and 8). Standard deviations have been added for CDI and MC samples.

Page 489, line 2 to 5. The text has been revised to clarify variability of LWC.

Page 490, lines 9 to 11, and elsewhere in the text. All discussions on the modification of sea salt through the Cl/Na ratios have been dropped.

Page 491, lines 5 to 14. Although it may appear evident from thermodynamic relationships that HNO₃ and HCl will evaporate from dehydrating droplets, in situ measurements of the degassing are rare in the literature and therefore of interest. In fact, providing the fraction of material that is degassing is of great interest to cloud modellers. We therefore feel that the discussion, although rather descriptive, both relates observations and provide a first explanation to the processes that are observed. It was therefore left unchanged.

Page 492, Section 4.4 and Table 6. The data do correspond to the summed concentrations over all impactor stages, as now indicated in the text and in the caption of Table 3. DL per impactor stage are estimated as the blank level plus standard deviation. After subtracting this value to each impactor substrate (or set the concentration to zero if the impactor stage is lower than detection limit) we add all stages concentrations. Moreover, an additional check was done. Impactor data are convenient to tell if the bulk concentration are above detection limit or not, thanks to the size distribution. When no clear distribution of the compound is observed over the aerosol sizes ("flat size distribution"), we took it as a "below detection limit sample", even if each individual stage could be slightly above the calculated detection limit for "static" blank values

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(which had not run with 20 hours of atmospheric vapors through it, as regular samples had).

Table 8, legend. The "theoretical values" are calculated as $H^*/(1+H^*)$ (and not $H^+/(1+H^+)$) where H^* is the effective Henry's Law constant, which do take into account acid dissociation, and solution H^+ .

Page 492 to 494, Section 5.1. R_x is calculated from mist chamber data and cloud droplet impactor data. Although both devices were run during the same cloud event, they were not always simultaneous, partly because their sampling durations are different. Consequently, it is not possible from our data set to perform individual paired observations. Our intention was not to study a time evolution of the partitioning in cloud, which is not suitable for orographic clouds anyway (because the life time at which we look at the cloud is more or less constant in this case), but our goal was rather to provide a global view of the phase partitioning.

§For instance, a plot of the individual experimentally determined versus theoretical values for $\text{Log } KH^*$ (log of the) as a function of solution pH would provide very useful context for this discussion." The dependence of partitioning with pH has been discussed in a number of papers from Po Valley, Chemdrop, GDF, Kleiner-feldberg experiments and also from the theoretical work of Pandis. Our opinion is that, for gases which are present predominantly in one phase, the variation with pH only reflects the theoretical pH dependency of the equilibrium which changes significantly. A proportion of 0.1% or 0.0001% expected in the liquid phase lead to a different deviation although the measurements are not able to get to this precision. See Ricci et al., 1998 Contribution to Atmospheric Physics for a discussion on that subject. We therefore choose not to present the results in that way.

Page 494, line 16 through the end. H_2SO_4 has never been measured. However, based on measurements performed at high altitude sites, (150 ppq), we expect H_2SO_4 to be present a very limited concentrations. Thus the hypothesis that it is not contributing to

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the major part of dissolved S-species seems appropriate.

Page 495, last couple lines, page 496, first couple lines. Gases measured in the WAI are significant, and by comparing WAI[gas] wint RJI[gas] we find a good agreement with the results from CDI-CVI as calculated in equation 2b. This is true for organic gases (we find 99, 99 and 60 % of degassing Acetic, formic and oxalic acids during droplet dehydration), and also for chloride for which we find 77% of it degassing but it is more difficult to evaluate for NO₃ and SO₄, because of the sticky property of NO₃ interfering in the MC sampling and because of the oxidation of SIV to SVI problem. For NH₄, we found 31% of it degassing, but with a large variation amongst samples. Overall, we found that the CDI-CVI method was more reliable than the MC(WAI)-MC(RJI) method, and thus decided to use preferably the first one. Consequently, as suggested, measurement in the WAI are dropped.

Page 496, lines 5 to 11 equation 2b is kept in order to check (for consistency) with equation 3b (both calculations are in Table 8).

Page 497, lines 4 to 5. The text has been clarified.

Page 497, lines 9 to 14. The "reactor favouring chloride depletion" referred to the fact that reactions such as NaCl+HNO₃ forming HCl +NaNO₃ are favoured in presence of a liquid phase. However, all discussion concerning sea salt has been dropped.

Page 497, lines 15 to 22. The discussion of oxalic has been corrected.

Page 497, last few lines. I agree that evaporation of NH₃ from an acidic, dehydrating cloud droplet is predicted based on its thermodynamic properties. However, it could seem surprising from a logical point of view. The use of NH₄⁺/SO₄²⁻ ratios aims to study the effect of (NH₄)₂SO₄ salt formation effect on each compound evaporation but going too far into the thermodynamics of the (NH₄)₂SO₄ is beyond the scope of this paper.

Page 498, line 20. The phase partitioning characterized in this paper has been specif-

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ically attributed to the site.

Page 499, lines 5 to 6 (and elsewhere in this section). The term of "wet deposition" is only used here to imagine what the consequences of such results could have on modelling. The sentence has been clarified.

Page 499, last couple lines and top of page 500. Potential sampling artifacts involving MCs have been moved to the methods section.

Page 500, lines 15 to 19. Contributions of different compounds to cloud droplet composition is not exclusively related to the "scavenging efficiency" of aerosols in the text. What we wanted to point out is that, once dissolved, aerosol contribution to the droplet concentration should not be neglected in thermodynamics equilibrium.

Page 500, lines 20 to 25. Only the subsaturation of the liquid phase was meant to be attributed exclusive or primarily to kinetic effects. This has been corrected.

All technical comments have been corrected according to the referee suggestions.

Interactive comment on Atmos. Chem. Phys. Discuss., 3, 479, 2003.

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