

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

Anonymous Referee #1

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General Comments:

The authors have generated an interesting multiphase data set for soluble gases in clouds and interpreted the results in terms of thermodynamic and kinetic controls on phase partitioning and associated aqueous chemical transformations. These results are appropriate for publication in ACP.

As indicated below, however, I found the interpretations to be overly descriptive in many respects and the terminology often confusing and/or ambiguous. The text also contains several erroneous statements and, in my view, is unnecessarily long and occasionally redundant. I encourage the authors to consider revising to address the specific points indicated below and also to shorten the text substantially (e.g., 25% to 30%) by tightening the discussion, consolidating sections, and eliminating redundancy. For example,

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the Results and Discussion sections could be combined and the two basic issues addressed in the paper [1) Thermodynamic versus kinetic controls on in-cloud phase partitioning and 2) implications of repartitioning with "residual" aerosols after drying] discussed in a more integrated fashion. Tables 3 through 6 could also be combined into a single table, which would facilitate comparisons between phases. In addition, a number of technical points require correction or clarification.

I recommend that the manuscript be returned to the authors for major revision.

Specific Comments:

Table 1. Presumably the reported +/- values refer to standard deviations. This should be specified. If H^+ was calculated, the table should so indicate. In addition, the species used to calculate H^+ should be specified in the text and the associated combined uncertainties reported. Given its fundamental importance for this study, it is surprising and unfortunate that H^+ was not measured directly. Why is this? The 'h' in pH should be capitalized.

Page 482, lines 1-3. The terminology here is confusing. If the cloud droplets are in "equilibrium" (presumably with respect to ambient water vapor), what is driving "growth"? In addition, droplet "growth" due to condensation of water results in low (not "large") solute concentrations relative to the original aerosol solution. Against what reference are these solute concentrations characterized as "large"?

Page 482, lines 19-20. Sampling cloud water during temporary clear-air breaks (which are common features of many clouds) results in evaporation of cloud water within samplers, and thus positive bias in solute concentrations. As discussed in some of the cited literature, this is a common cause for apparent but artifact supersaturation of cloud water with respect to the gas phase and should probably be mentioned explicitly in this context. This effect (i.e., sampling during "non-cloud conditions") and the associated problems are distinct from those involving "long integration times," "droplet heterogeneity," or "cloud dynamics" that are mentioned in the manuscript.

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Page 483, lines 22-23. This statement basically repeats material contained the preceding section and appears out of place in the methods section. I recommend that the authors consider dropping it.

Page 484, lines 3-4 (and elsewhere in the paper). The terminology is confusing. "Aerosols" are also "condensed material." I recommend that the authors adopt more explicit terminology such as "gases, aerosols, and cloud droplets." In this regard, it would be helpful to briefly specify the operational size discrimination between aerosols and cloud droplets [e.g., "aerosols (<?? um diameter) and cloud droplets (>?? um diameter)"]. Most aerosols within clouds exist as deliquesced droplets. Discrimination is by size not state.

Page 484, lines 5-24. Since the phase partitioning of gases with aerosols and cloud droplets are functions of water content (and thus, temperature, relative humidity, and pressure), pH, thermodynamic properties (function of temperature), and kinetics, it is not clear from these descriptions that the original phase partitioning or the modified phase partitioning (i.e., after droplet dehydration) for compounds of interest would be conservative for this suite of measurement techniques. This issue should be briefly addressed. Are the data representative of ambient conditions?

Figure 1. This depiction strikes me as potentially confusing. For instance, the description of the CVI in the text refers to both scavenged gases and aerosols but the figure indicates scavenged aerosol. A table summarizing the major components of the multiphase system that are quantified by each device would be more explicit and, thus, easier to understand and cross-reference.

Page 485, lines 18-26. It appears that the two mist chambers were positioned in tandem. If so, this should be indicated explicitly or otherwise clarified.

Page 487, lines 10-13. Reliable quantification of SO₂ sampled in deionized water requires that mist solutions be treated with Na₂CO₃ and H₂O₂ and incubated prior to analysis to ensure that S(IV) is completely oxidized to S(VI) (e.g., Talbot et al., 1997).

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Was this done? If so, the details should be added to the paper. If not, the SO₂ data should be reported as lower limits. In addition, the implicit but unstated assumption that all Cl⁻ in mist solutions originates from HCl should be justified. Available evidence suggests that soluble Cl gases other than HCl exist at significant concentrations in the troposphere. The text should be clarified in this regard.

Page 487, lines 16-21. I do not understand the statement concerning precision. Relative precision varies among analytes and, consequently, one generic range (i.e., "10% for samples ten times the detection limit") will not be relevant for all analytes. How exactly was precision determined? How were the blanks generated and how many were analyzed? It would be helpful if the estimated precision for each analyte was added to Table 2.

Table 3 (4, 5, 6, and 8). To provide additional context, it would be useful to add ranges or standard deviations to provide an indication of variability in cloud-water composition (and other characteristics of the system reported in the subsequent tables). The inferred concentrations of H⁺ should also be added.

Page 489, line 25. Based on data in Table 1, it does not appear that LWCs varied by large factors during most events. In addition, average LWCs (Table 1) varied by a factor of <3 between events. In contrast, average concentrations of, for example, SO₄²⁻ (Table 3) varied by a factor of 20. This suggests that variability in the aqueous concentrations was more important than variability in LWC in driving inter-event variability in these data. The text should be revised to clarify this point.

Page 490, lines 9-11, and elsewhere in the text. It unreasonable to assume that all Na and Cl at a high elevation site 250 km from the ocean originated from the surface ocean. Significant sources of crustal dust (with distinct Na/Cl ratios) and anthropogenic emissions of volatile Cl complicate evaluation of sea-salt species at inland locations (e.g., Graedel and Keene, 1995, GBC; and references therein). Note in this regard that, later in the manuscript, high NH₃ concentrations are attributed to extensive agriculture

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in the region. Agriculture can also be an important regional source of atmospheric dust. Consequently, the interpretation of Cl cycling based on the assumption that it originates exclusively from sea salt is highly suspect.

Page 491, lines 5 to 14. This discussion seems overly descriptive. The phase partitioning of HNO₃ and HCl are defined by their Henry's Law and acid dissociation constants. It is evident from thermodynamic relationships that HNO₃ and HCl will evaporate from dehydrating droplets. These observations should be interpreted in terms of the underlying controls.

Page 492, Section 4.4 and Table 6. Presumably, these data correspond to the summed concentrations over all impactor stages. This should be indicated. How were the DLs for the samples estimated. Given that low concentrations of particulate species in each sample were distributed over 12 different impactor stages, it would appear that at least some individual stages for most (perhaps all) samples were <DL, yet significant concentrations are reported for many samples. How were values below detection limits for individual stages incorporated into these sums and the corresponding precisions and detection limits?

Table 8, legend. The discussion of theoretical phase partitioning is confusing. The theoretical equilibrium phase partitioning of these gases is defined by Henry's Law, acid dissociation, and solution H⁺ (i.e., the effective or pseudo Henry's Law constant). The method used to calculate the "theoretical values" should be described in the text. The reported values do not correspond to " $H^+/(1+H^+)$ ".

Page 492 to 494, Section 5.1. This discussion seems overly descriptive and it is not clear why the interpretations are based on average values. Given the inherent variability in these data (noted previously by the authors) and the nonlinear nature of phase partitioning, it would seem most prudent to base interpretations on the ensemble of individual paired observations. For instance, a plot of the individual experimentally determined versus theoretical values for Log KH* (log of the effective Henry's Law constant)

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as a function of solution pH would provide very useful context for this discussion.

Page 494, line 16 through the end. In and of itself, an ion such as SO_4^{2-} cannot be evaluated in terms of saturation state. Are the authors referring to S(IV) or to H_2SO_4 in this context. It is not clear how these measurements can be used to distinguish between the two. I suggest that the thermodynamic properties of H_2SO_4 be added to Table 7 and considered as part of the evaluation. Very high solution acidities are required to sustain significant gas-phase mixing ratios of H_2SO_4 .

Page 495, last couple lines, page 496, first couple lines. I do not understand this point. Given the large changes in phase partitioning between cloud droplets and residual aerosols reported by the authors (e.g., 30% to 100% losses of volatile constituents from dried cloud droplets) coupled the reported measurement uncertainties, it appears that the differences in gas phase concentrations for most species during droplet dehydration would be significant and quantifiable. The methods section (bottom of page 484 through top of page 485) indicates that these paired data provide "access to the amount of dissolved gases." Why are they subsequently ignored? A comparison of the gas-phase data measure by MCs downstream of the RJ1 and WJ1 inlets would provide independent quality constraints on the magnitude of changes inferred from ratios of condensed constituents relative to Na. I encourage the authors to consider reporting and interpreting these data as part of the analysis. Alternatively, discussion of gases sampled through the WJ1 should be deleted since they are not reported.

Page 496, lines 5 to 11 including equation 2b. This equation is not used to interpret results and, along with the associated text, could be dropped.

Page 497, lines 4-5. As written, this statement is confusing. It appears that the authors are referring to the fact that virtually all condensed HCOOH and CH_3COOH in a cloud evaporates during the dehydration of cloud droplets to aerosols. The text should be clarified.

Page 497, lines 9-14. These data do not demonstrate that Cl is lost in the form of

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HCl. Other soluble volatile Cl gases exist in air. I suggest that "HCl" be changed to "volatile inorganic Cl." In addition, the interpretation is vague. To what "cloud reactor" are the authors referring and how does this reactor "favour ... chloride depletion." The underlying acid-displacement reactions should be discussed explicitly in terms of thermodynamic controls on HCl phase partitioning.

Page 497, lines 15-22. The discussion of oxalic acid is confusing. Oxalic acid is described as having "low solubility." In fact it is highly soluble (e.g., Table 7), which accounts for its almost complete partitioning into aerosol solutions in ambient air. Based on its high solubility relative to other compounds that are efficiently sampled by mist chambers (e.g., HCOOH and CH₃COOH), it is reasonable to expect that any oxalic acid vapor present in sample air would be scavenged completely by deionized water mist.

Page 497, last few lines. Again, this interpretation is overly descriptive and confusing. NH₃ partitions with cloud droplets and aerosols based on its Henry's Law and dissociation constants and solution pH. Significant NH₃ vapor exists in equilibrium with highly acidic aerosol in most of the troposphere. Evaporation of NH₃ from an acidic, dehydrating cloud droplet is predicted based on its thermodynamic properties. It is not clear why the authors describe this observation as "surprising." In addition, NH₃ phase partitioning is a function of H⁺ not SO₄²⁻ (see equations in Table 7). Consequently, the assessment of NH₄⁺/SO₄²⁻ ratios strikes me as rather peripheral to the primary issue. Assessment of thermodynamic controls on NH₃ phase partitioning should focus on the direct effects of solution H⁺.

Page 498, line 20. The phase partitioning characterized by the authors is specific to the study site and, to prevent confusion, should probably not be characterized as a "global view." In particular, the phase partitioning for some of these compounds in marine air is quite different.

Page 499, lines 5-6 (and elsewhere in this section). It is not clear how the observed

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phase partitioning of carboxylics in clouds relates to their "wet deposition." Data for the corresponding composition of precipitation are not reported in the paper. Wet deposition is influenced by both in-cloud and below-cloud processes.

Page 499, last couple lines and top of page 500. Potential sampling artifacts involving MCs should be mentioned in the methods section and possible measurement biases considered as part of data interpretation. It does not seem particularly helpful to mention these potential problems in the last paragraph of the discussion.

Page 500, lines 15-19. Contributions of different compounds to cloud-droplet composition cannot be directly related to the "scavenging efficiency" of aerosols. The water context of aerosols are orders of magnitude lower and corresponding H⁺ concentrations typically orders of magnitude higher. Both water content and H⁺ influence equilibrium phase partitioning. Consequently, significant fractions of some compounds (e.g., HCOOH and CH₃COOH) partition into cloud water whereas, under most conditions, virtually none would partition into aerosol solutions in clear air.

Page 500, lines 20-25. At thermodynamic equilibrium, most HCOOH and CH₃COOH in most clouds partition in the gas phase (see several of the cited papers). The dominance of gas-phase partitioning for these compounds in clouds should not be attributed exclusive or primarily to kinetic effects.

Technical Comments:

Page 480, line 11. For consistency, recommend specifying "... carboxylic, nitric, and hydrochloric acids ..." rather than a mixture of acids for some species and ions for others.

Page 480, line 13 (and elsewhere in the text). To minimize confusion, "reduced nitrogen species" should be changed to "NH₃". Only one reduced N compound was evaluated.

Table 2. "Gas" is misspelled.

Page 487, line 13. Oxalate should be C₂O₄²⁻.

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Page 487, line 14. Since they were apparently used to estimate H⁺ concentrations via ion-balance calculations, I recommend that all the analytes be specified. What "other ions" were measured.

Page 487, line 14. "drive" should be "derive".

Page 489, lines 3-4. Are these percentage contributions based on mass, moles, or something else?

Page 489, last few lines, and elsewhere in the text. I recommend against repeating in the text ranges in data that appear in a table. Simply refer readers to the appropriate table. For example, "Concentrations varied over large ranges (Table 3)."

Page 492, line 20. This should be "molar" partitioning.

Table 8 is mentioned before Table 7 in the text. The tables should be renumbered.

Table 8. Values for measurements that are reported as 100% should be changed to greater than the appropriate percentage based on the detection limit (i.e., >95%).

Fig 3, legend. HCL should be HCl.

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

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