

Comment on Hennigan et al. (2014)

This paper addresses the estimation of aerosol pH from several different methods. This is an important topic in atmospheric chemistry, which is receiving increasing attention recently due to proposals of important reactions such as IEPOX uptake that may be a function of pH. The work is interesting and timely, and highlights important uncertainties when doing these kind of analyses that are not yet fully appreciated by the community. There are however some issues with the way the results are presented, in my opinion, which I address below.

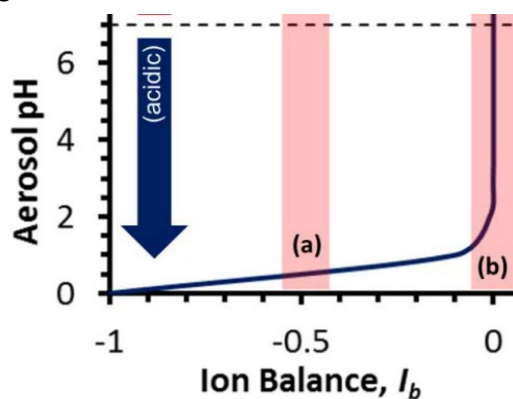
(1) Some conclusions may be generalized too widely or presented too strongly, and some finer nuances may be needed. In particular the end of the abstract states: “Furthermore, neither the ion balance nor the molar ratio can be used as surrogates for aerosol pH, and published studies to date with conclusions based on such acidity proxies may need to be reevaluated. Given the significance of acidity for chemical processes in the atmosphere, the implications of this study are important and far reaching.” Thus most readers would conclude that *the molar ratio method never works, and that studies using it are wrong and should be ignored.*

It seems that the conclusion that is supported by the results in the paper is a narrower one: the molar ratio method has a very large uncertainty *when the acids in the aerosol are completely neutralized by ammonia, i.e. when the molar ratio ~ 1* (within the uncertainties of the measurements). This result had already been presented at several conferences by Jennifer Murphy’s group, based on the CalNex-LA 2010 results, see e.g. this abstract from Fall AGU 2011 (that happens to include some common coauthors with this paper):

<http://adsabs.harvard.edu/abs/2011AGUFM.A32A..01M>

Quoting from that abstract: “It is challenging to measure aerosol pH directly, but it is possible to combine measurements of particle composition, relative humidity and temperature with calculations from aerosol thermodynamics algorithms to calculate the bulk pH. **While this approach is relatively straightforward in environments with high levels of strong acidity ($> 20 \text{ neq m}^{-3}$), it produces a high level of uncertainty ($> 6 \text{ pH units}$) in more neutral conditions.** We demonstrate that simultaneous measurements of gas phase NH_3 offer a powerful additional constraint that can reduce the calculated pH uncertainty by an order of magnitude.”

Thus, unlike the abstract of this paper, the Murphy et al. work more clearly states that the molar ratio method does work for sufficiently acidic aerosols, and that it is only for neutral (or close to neutral) conditions that the large uncertainty on pH arises. This is actually consistent with the results of the current paper, e.g. Figure 8:

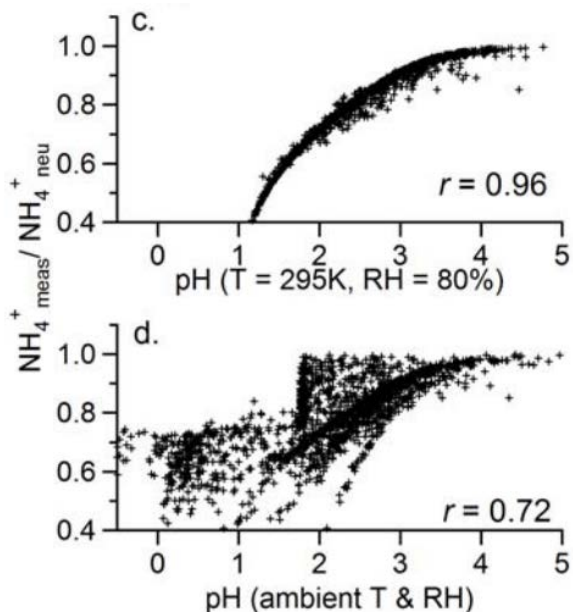


I.e. there is a clear relationship between both parameters for acidic aerosols and not for neutralized ones. As an aside, the way Fig 8 is shown in ACPD may give the wrong impression about the uncertainty, since pHs beyond 7 or 8 are not thought to occur in the atmosphere. It seems that the inset of the figure as shown above shows the more relevant information for the atmosphere, so I suggest that the figure is updated accordingly for the ACP version.

One would expect the $\text{NH}_3(\text{g})$ concentration to be low under acidic conditions, since the uptake coefficient of $\text{NH}_3(\text{g})$ is high for acidic conditions [Swartz et al., 1999]. Thus applying the molar ratio method or the method that uses $\text{NH}_3(\text{g})$ should give similar results as long as aerosol concentrations are not very low.

(2) An important detail is that although the pH value cannot be determined accurately with the molar ratio method for neutralized aerosols, *a lower limit of the pH can nevertheless be derived*, e.g. $\text{pH} > 1$ or so for the figure above. This is very useful information, as some chemical processes may need lower pH to proceed quickly, and thus the information from the molar ratio method may still be able to establish whether some chemical processes can / cannot be active.

(3) On a narrower topic, I was surprised to see the paper conclude that “Similarly, no relationship is observed between the cation / anion molar ratio and predicted aerosol pH.” We had done similar work before based on the Pittsburgh 2002 AMS measurements (where aerosols were often very acidic) [Zhang et al. 2007] and we had shown that as long as T & RH are kept constant, the molar ratio and AIM-estimated pH are tightly correlated, see panel (c) below from Figure S1 in that paper:



As panel (d) shows, a large amount of scatter appears only when the instantaneous T & RH are used in the calculation. A question then arises on what is more relevant for a given application of estimated pH, the estimates under constant T & RH or the ones under the instantaneous T & RH. This will depend on the timescale of the process of interest. For processes with a timescale of a day or longer one can argue that the pH estimated under constant T & RH may be a better surrogate of the pH that those aerosols have experienced over the last few days. This is relevant to e.g. IEPOX uptake to make IEPOX-SOA over

the SE US, as the concentration of IEPOX-SOA observed at a given site likely has been formed over a period of several days.

(4) Partially some of the confusion may arise because only the Mexico City MILAGRO dataset from T1 has been used here. There are two features of that dataset that may make the analysis more difficult than elsewhere:

(a) the aerosols during MILAGRO were almost always neutralized within experimental error due to very high emissions of NH_3 . At least this was the case at the nearby T0 site (see Fig S6 of Aiken et al. [2009]). Thus some of the nominally acidic conditions in this dataset may have a substantial influence from the measurement uncertainties (also see (b) below). Thus much of the data used in this paper is in the regime where the molar ratio method does not work, and this may be part of the explanation for the low correlations observed.

(b) There were substantial dust concentrations during MILAGRO, and especially the T1 site was described by the researchers there as very dusty. This may lead to complexities in the measurements, their interpretation, and the modeling. E.g. as was concluded by a previous MILAGRO paper "The bulk equilibrium approach fails to reproduce the observed coarse nitrate and overpredicts the fine nitrate" [Karydis et al., 2011]. Thus even if the mineral ions are included in the equilibrium model, they likely have not had time to reach equilibrium in the real atmosphere, potentially leading to model-measurement deviations.

Given (a) and (b), it does not seem possible to draw near universal conclusions (as certainly the end of the abstract sounds like) from a limited dataset that may not span the dynamic range observed over wider regions of the atmosphere.

(5) It would have been desirable that the authors also include another dataset in which acidic conditions were prevalent in this paper, which would allow a fairer and more complete evaluation of the methods. I understand that is too much to ask for the revision of this paper, but I do hope that either the authors or others in the community perform and present such work in the future. We note that the relevant datasets including NH_3 , HNO_3 , and aerosol composition are likely available e.g. for some campaigns of the NOAA P3 (see <http://www.esrl.noaa.gov/csd/field.html>), and likely for other campaigns as well.

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