Atmos. Chem. Phys. Discuss., 14, C10390–C10392, 2014
www.atmos-chem-phys-discuss.net/14/C10390/2014/

Atmospheric Chemistry and Physics
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Discussions

Interactive comment on "A critical evaluation of proxy methods used to estimate the acidity of atmospheric particles" *by* C. J. Hennigan et al.

Anonymous Referee #2

Received and published: 20 December 2014

Within the manuscript entitled "A critical evaluation of proxy methods used to estimate the acidity of atmospheric particles" by Hennigan et al. the authors compare different approaches to estimate solution pH of atmospheric aerosols. The acidity is an important property influencing the physical and chemical behavior of particles. Several proxy methods for the estimation of the acidity are used in a huge number of publications, e.g. to explain the formation of SOA. However, up to now, these methods are not critically evaluated and compared with each other. Therefore, this very important and ambitious work is more than worth to be published by ACP.

A nice and and extensive review was already done by referee No.1, who addressed major issues within this manuscript. Once his and the comments below are taken into account, I recommend the publication by ACP. Basically, I agree with most of the

comments given by referee No.1, especially with the following:

- The ion-balance- and molar-ratio method are deriving from the same information and should be treated in this way.

- The use of the terms (free/strong/total) acidity should be rivised as pointed out by referee No.1.

- Regarding the "Achilles heel" (see referee No.1 comment): At many points in the manuscript, a critical view was set on a H+ signal range, where the signal to noise is likely in general rather low. As already written by referee No.1, no time series of either basic species data or corresponding ratios, e.g. calculated with equations 2, 3, 4 or 5, are given. That makes it difficult for the reader to keep in mind that the analytical uncertainty is a key limitation for every approach. This should be addressed more explicitely.

- I am also confused why the partitioning of HNO_3 was mentioned in section 2.4 as an example, while later the results from these data were not shown in section 3.4, but only from the partitioning of NH_3. Also, as denoted by the authors on page 27598, lines 9-13, the partitioning of HNO_3 can also be used in case of low NH_3 concentrations. An additional comparison using the HNO_3 partitioning would potentially emphasize the recommendation to use the phase partitioning approach.

- It is often not clear which part of the MILAGRO dataset was used in the different comparisons and why. This should be revised.

Besides, I have some other comments:

Page 27591, line 22: Here and also on page 27595, line 20 and 24, correlation coefficients are given. As already pointed out by referee No.1, an explanation on which method was used to calculate these coefficients, should be given. In addition, implications and judgments should be done carefully. On page 27595, both R^2 coefficients are called "high values", although a R^2 value of 0.47 should not be considered as "high", especially when a value of 0.80 is also called "high".

Minor comments:

Page 27588, line 23: the active term using "we" should be converted to a passive term, as was used in the whole manuscript.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 27579, 2014.