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# *Interactive comment on* "Incomplete sulfate aerosol neutralization despite excess ammonia in the eastern US: a possible role of organic aerosol" *by* Rachel F. Silvern et al.

**Anonymous Referee #2**

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The authors present data suggesting that the sulfate in the Eastern US is not fully neutralized by ammonia despite the availability of the latter in the gas phase and argue that this could be due to mass transfer delays between the gas and particulate phase caused by organics. This is clearly an important issue that has received a lot of attention in the literature during the last few years. The paper is well written, however, the evidence provided to support its major conclusion is rather weak and it neglects other simpler explanations. It also neglects important work that has been published recently explaining similar observations with existing aerosol thermodynamics models. These problems are discussed below.

(1) Evidence that the aerosol is in equilibrium in the Southeast US The authors con-

clude from their data analysis that the aerosol in the eastern US is not in equilibrium probably due to limitations of the mass transfer of ammonia due to the organics. However, they neglect at least two studies that have used high quality gas-phase ammonia measurements in the same area and season to investigate this issue and reached the opposite conclusion. Weber et al. (2016) showed that the measured gas-phase ammonia was in equilibrium with the particulate phase during SOAS (see for example Figure 1 in that paper). They used 1-hr as averaging time therefore the equilibration timescale should be much less than this. If there was a significant delay in the mass transfer of ammonia between the two phases there should be significant observed discrepancies. Similar conclusions were reached by Nowak et al. (2006) for the 2002 ANARChE study in Atlanta. They concluded that the agreement between the measured and predicted ammonia within the uncertainties suggests that the assumption of thermodynamic equilibrium on the 7.5 min timescale is appropriate for most of the ANARChE data examined here.

(2) Alternative explanations Weber et al. (2016) have argued that the incomplete neutralization of sulfate in the southeast US and the corresponding changes during the last 15 years are in general consistent with our current understanding of inorganic aerosol thermodynamics. They did not need to invoke delays in mass transfer and lack of equilibrium between the two phases. The authors appear to try something similar in Figure 3 but in a rather convoluted way using wet deposition data (please see comment 6 below).

(3) Model evaluation The use of GEOS-Chem to test the hypothesis of delays in the mass transfer of ammonia is the most original aspect of the current work. However, the evaluation of the corresponding GEOS-Chem predictions is rather superficial given the availability of the SOAS measurements during the same summer. The ability of GEOS-Chem to reproduce observed gas-phase ammonia concentrations is critical for the authors' argument. For example, the problems of the base case simulation could be due to the overprediction of ammonia availability (e.g., due to errors in ammonia

emissions) and the assumed delay in mass transfer could be correcting one error by introducing another.

(4) Terminology and details about calculated quantities I found the terminology used in the paper quite confusing. For example, the terms “sulfate neutralization” and “aerosol neutralization” are used throughout the paper instead of the ammonium to sulfate molar or equivalent ratio. Sometimes the nitrate is also used sometimes it is not. In all cases the other cations that could, in principle at least, be neutralizing sulfate are not included in this neutralization ratio.

It is not clear if the different ratios shown throughout the paper correspond to PM1, PM2.5, PM10 or something else. This detail is critical given the importance of calcium, magnesium, etc., for the coarse particles.

It is also not clear how the authors estimate the averages of the different ratios. Do they average the concentrations and then estimate the ratios or do they estimate the ratios with some averaging time (daily?) and then average them?

(5) Originality of hypothesis The same hypothesis regarding the organic aerosol role in mass transfer of ammonia in the southeast US has been presented Kim et al. (ACP, 2015) with a number of common authors in the two studies. This should be discussed in the introduction of the paper.

(6) Use of wet deposition data The authors use wet deposition measurements as practically a surrogate of total (gas and particulate) ammonia. This is rather tricky given that rainfall takes place during specific meteolorogical conditions, clouds can produce sulfate, and there are of course different wet removal efficiencies for ammonia and sulfate. Despite these problems, the paper does not address the potential biases that could be introduced in the analysis because of the use of these data. This could be one of the reasons for the differences between the conclusions here and those of other studies. I realize that gas-phase ammonia measurements exist only during specific field campaigns, but there are enough of them available both in the US and Europe.

Use of these measurements is clearly preferable to the wet deposition data.

(7) Role of organosulfates and crustal elements Some additional information is needed regarding the potential role of organosulfates and crustal elements for the present analysis. The authors appear to assume that they are negligible for the purposes of this work. However, some quantitative arguments are needed taking for example advantage of the SOAS measurements.

(8) Some additional minor points:

Page 2, lines 2-4. This is clearly not true when there are other cations present.

Figure 2a is rather misleading given that most of the sulfur dioxide is emitted by point sources. It should probably be replaced with a table with the emissions in different regions of the US (e.g., southeast, northeast, etc.).

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Discussion paper