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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Characteristics and mixing state of amine-containing particles at a rural site in the Pearl River Delta, China" *by* Chunlei Cheng et al.

Anonymous Referee #2

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This paper reports on field measurements of small amines in atmospheric aerosols by single particle mass spectrometry. The collected information is used to infer the amine and particle sources and also to shed some light on the particle chemistry. The study is timely. Overall, the paper is clearly written, but several important issues need to be resolved before it can be published. I suggest a major revision.

An in-depth discussion of the three particle categories is in order. It must be told to the reader that these categories are defined operationally, based on the analysis technique. The categories do not necessarily correspond to the particle types utilized by the atmospheric aerosol community. The categories are not exclusive - a nitrate

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particle may contain a strong ECOC signature, and so on. All this must be kept in mind when interpreting the particle compositions based on these three operationally defined categories.

The statement of the low ammonium ion abundance in lines 261 and 269 is in contradiction with the information given later in line 321 and also in Figure 6. This also calls for several other questions: - What is the relationship between the peak area and actual abundance of a chemical species? Is it indeed one-to-one? If not, did you perform any calibrations? Did you perform tests and calibrations for single-component particles or for mixtures? - Does the detection of ammonium depend on the particle composition/acidity? For instance, is peak area same for the particles containing same amounts of ammonium, but in the forms of ammonium nitrate, ammonium bisulfate, and ammonium sulfate? - The replacement of ammonia by amines is indeed possible. However, how realistic is it to expect that most of the ammonium will be replaced, considering that amines are an order of magnitude less atmospherically abundant than ammonia? - Similarly, how likely is it that most of chloride has been evicted from the sea-salt particles by the aging process? Could the lack of detected chloride be traced down to some other reason, such as the detection technique itself? Any calibrations with authentic chloride aerosols? What about the presence of NaCl2- clusters? Is it where all of the chloride go?

The authors must be very careful when referring to the particle mixing state. It appears that they confuse the abundances of different particles with the abundances of different chemicals in the same particle. For instance, in Line 314, do they imply that nitrate and sulfate were present in the same particles and were elevated during summer or that sulfate- and nitrate-containing particles had a high occurrence during summer? Similarly, if I am interpreting the text and Figure 6 correctly, the figure caption should not be the 'mixing state', but the fraction of particles containing different components.

As written, it appears that the authors do not treat the charge balance (ion equivalency) correctly when calculating the relative acidity. One cannot simply add the peaks of

nitrate and sulfate because the former corresponds to monoprotic and the latter to diprotic acid, respectively. Also, are peak intensities proportional to actual abundancies of chemical species?

Figure 5 is problematic. Does 'size' refer to the radius or diameter? If the y-axis is the particle count, then the plotted curves cannot be size distributions. A size distribution is expressed as dCount/dSize, but shown are apparently counts for different size bins. Those must be presented are individual points or bars, not a continuous curve. What is the bin size?

What is the shape of the particle transmission function of the aerodynamic lens? Have plots shown in Figure 5 been corrected for the size-dependent particle transmission? Frankly, I do not expect the abundance of amine-containing particles to taper off at the smaller sizes. In fact, an opposite should be true. It takes significantly less time to enrich the smaller particles with amines through the substitution reaction than to enrich the larger particles.

L175 and everywhere: replace 'm/zs' with 'm/z' L175-180: I suggest placing this information in a table L188-191: provide a reference to the processing method

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