**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Characteristics of size distributions at urban and rural locations in New York" *by* M.-S. Bae et al.

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minsbae@hotmail.com

Characteristics of Size Distributions at Urban and Rural Locations in New York Min-Suk Bae1, James J. Schwab1, Olga Hogrefe1, Brian P. Frank2, G. Garland Lala1, Kenneth L. Demerjian1 1 Atmospheric Sciences Research Center, University at Albany, State University of New York, Albany, New York, USA, 2 Division of Air Resources, New York State Department of Environmental Conservation, Albany, NY, USA

Interactive comment on "Characteristics of size distributions at urban and rural locations in New York" by M.-S. Bae et al. Anonymous Referee 1 Received and published: 27 February 2010

The manuscript describes measurements of aerosol size distribution at three sites:

one urban in New York City and two rural sites in New York State. General characteristics of size distributions and absolute concentrations are discussed. The effect of diffusion loss correction on size distribution and aerosol number concentration is given significant attention. I agree with the authors that diffusion loss correction should be applied to the aerosol size distribution data, but feel that the manuscript does not provide sufficient evidence for the accuracy of the method of correcting the data. While the correlation with the CPC is improved when applying the correction, there are indications that the spectral shapes of the nano-SMPS and long-SMPS in the overlap region do not match after the correction. The paper is rather tedious to read and should be substantially shorted. For example, section 3.2 can be entirely removed, because it has little value: the formulas for the TSI diffusion loss correction can be found in the literature (Reineking and Porstendörfer, 1986; Birmili et al., 1997; Chen et al., 1998).

Thanks for your comments. We address the comments below. Please note that section 3.2 has been moved to the "Supplementary Material" section. We think this best addresses the reviewer's concerns, while at the same time retaining some emphasis on the importance of this adjustment to SMPS data for very small particles. (Author's note: we included the expanded discussion of diffusion loss corrections because, like reviewer 1, we believe that diffusion loss correction should be applied to the aerosol size distribution data. We agree with reviewer 2, and are aware of the fact that "most aerosol scientists" are correcting their data. However, there are also other scientists operating SMPS instruments that are not "trained aerosol scientists" and are less aware of some of these subtleties. We have seen examples of this at meetings and in published papers. Still, the reviewers are entirely correct that there is no new science here. For these reasons we believe that moving section 3.2 to the Supplementary Material section is a good compromise.) Your point about "the spectral shapes of the nano-SMPS and long-SMPS in the overlap region do not match after the correction" is well taken. However, this minor mismatch has nothing to do with the diffusion correction scheme. We would love to say the profiles match perfectly, but alas, that is not the case. Figure 1 shows how well they match, which ranges from pretty well, to a little

better than okay. We could have simply presented the merged data sets, but in the spirit of full disclosure, we present our merging scheme openly. "The paper is rather tedious to read and should be substantially shorted." is also well taken, we shortened the paper significantly. "The paper is rather tedious to read and should be substantially shorted. For example, section 3.2 can be entirely removed, because it has little value: the formulas for the TSI diffusion loss correction can be found in the literature (Reineking and Porstendörfer, 1986; Birmili et al., 1997; Chen et al., 1998)." is well taken, so, the section 3.1 and 3.2 are entirely moved to the Supplementary Material.

Specific comments:

Abstract, lines 14 – 17. The high number concentration events in the urban sites are attributed to primary emissions, while in the rural sites are attributed to nucleation events. Nucleation events have been observed in urban areas. On what basis are the high number concentration events are attributed to primary emissions alone?

We explored that the relationship between the high number concentrations and primary emissions in urban areas. As one example of an extension paper, we plan to use AMS data to explore relationships between paired SMPS size distribution measurements and the " HOA factor" (which tends to be associated with primary emissions) and the "OOA factor" (associated more with secondary organic aerosol). To clarify, we explained the following sentences to the text: "The small particle limit is generally accompanied by observations of low PM2.5 mass, high number concentration, and small median diameter caused by the occurrence of "small fresh particles" associated with two possible processes; 1) recent primary emission (as observed for the QC01 and QC04 campaigns) associated with Black Carbon (BC) or hydrocarbon-like organic aerosol (HOA), 2) particle nucleation and growth associated with sulfate (Jung et al 2006) (as observed for the WFM02 and PSP04 campaigns)." Fig. 1 shows an example the relationship between number concentrations and EC.

Section 2.2. The CPC counts were diffusion corrected (Section 3.4). This needs to be

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mentioned in this section.

Added as suggested by the Editor.

Section 2.3.2. The inclusion of the activation and counting efficiency of the CPC into the total diffusion loss correction is confusing, because these processes have no common physical basis. Why then is the efficiency of bipolar charging not included into the "total penetration"?

The reviewer is correct – activation and optical detection efficiencies are not related to the diffusion losses in any way. These efficiencies and the charging efficiency are important, but unrelated to the diffusion loss correction.

Section 2.4. When discussing the condensation sink, the authors correct the mean free path for the temperature and pressure effects (Eq.6). Were these effects substantial? If so, were the calculations of aerosol size distributions corrected for these effects or were the standard settings of the TSI software used?

These effects are quite small – on the order of 5

Sections 3.2. I do not understand the purpose of this section. Was it to determine the diffusion loss correction by the TSI software? If so, the easiest way would have been to compare the aerosol size distributions obtained with the new and old versions of the TSI software. The formulas for the TSI diffusion loss correction can also be found in the literature (Reineking and Porstendörfer, 1986; Birmili et al., 1997; Chen et al., 1998). What is done, however, is rather confusing and shows a lack of understanding of the SMPS data inversion, which is more complex than a simple factor connecting the CPC counts to the actual size distribution. For example, the authors use "transfer function" to describe a relationship between the raw counts collected by the SMPS and the size distribution reported by the TSI software. This term could be very confusing, because it is usually used to describe the efficiency of particle transfer through the DMA as a function of particle electrical mobility (see Knutson and Whitby 1975, Wang and

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FLagan 1990, etc.). It is also not clear what exactly the "empirical transfer function" incorporates, because the authors do not specify how the "raw" counts per size bin were obtained. The TSI SMPS operates by collecting CPC raw counts at 10 Hz, i.e. the CPC counts are equally distributed in time. On the other hand, the size bins produced by the TSI software are equally distributed in log-size (usually 64 bins per decade of particle size). It is obvious that the raw CPC counts could not correspond to the size bins: different scan rates produce different number of time increments, but the number of size bins remains practically the same. My guess is that the authors used "raw" counts exported by the TSI software, which re-bins the CPC raw counts into size bins, corresponding to the size bins in the inverted size distribution. If my guess is correct, then the "empirical transfer function" includes not only the diffusion correction, but also the charging efficiency correction and all the flow rate effects in the data inversion. Basically, these "empirical transfer functions" are applicable only for the current flow setting (via the ratio of the sample, sheath and CPC flows, and the diffusion broadening of the DMA transfer function). Therefore, these transfer functions are of little use and should be removed from the paper. Another important question is: was multiple charge correction used? Depending on size distribution, it may have a significant effect on what the authors call "empirical transfer function".

Section 3.1 and 3.2 are entirely moved to the Supplementary Material. As noted above, we believe the material in the supplement is of importance for understanding the details of the diffusion correction, especially at 20 nm and below for instrument users. We concede that "empirical transfer function" is not a good term to use for the relationship we show. We now describe it (rather inelegantly, but accurately) as the "function relating the reported raw counts to reported concentrations". The reviewer's guesses are all correct, that we use the "raw" counts re-binned by the TSI software; that charging efficiency and flow rate effects are what give the function its shape in the absence of the diffusion correction. We still contend that comparing this "function" with and without diffusion correction turned on gives a good illustration of the size dependence of the computed diffusion correction. Multiple charge correction was used for all our mea-

surements, but its effects are rather small below 20 nm – the region where diffusion correction is most critical. Also we are aware that the losses depend on flow rate (Frank et al.2008)

Frank, B. P., Saltiel, S., Hogrefe, O., Grygas, J., and Garland Lala, G.: Determination of mean particle size using the electrical aerosol detector and the condensation particle counter: Comparison with the scanning mobility particle sizer, J. Aerosol Sci., 39, 19-29, 2008.

Page 78, lines 9–18. The noise at small sizes is common even when no diffusion correction is made. Yet, the authors present it as if the diffusion correction was the only reason why they have neglected the data below 8 nm. In fact, the diffusion correction is still minor relatively to the other corrections during the inversion, which is apparent from Fig.2. I do not think the noise justifies the removal of data below 8 nm.

Perhaps if the reviewer actually saw the data below 8nm he/she would think differently. The "scale factor" in panel b of Figure 2 (now S-2) shows a large and increasing multiplier for small diameters – due mainly to charging efficiency. Panel c of that figure shows the scaling due only to the diffusion correction – and it is increasing very rapidly below 10nm. When we apply the diffusion correction to data bins at mobility diameters down to 3.1 nm, the combined scale factor, as illustrated in panel a, becomes as large as 30,000! That is, a single particle detected by the CPC gets converted to a reported concentration of 30,000 – due to the combined effects of poor charging efficiency and very large diffusion losses. (In particular, the diffusion loss is not minor compared to the other corrections at 3 nm!) Including this data makes the time series color contour plots very hard to interpret. Averaged over long enough times, the stochastic counts should "balance out", but for the purposes of display and interpretation in this study, we prefer to exclude the data below 8 nm.

Section 3.3. The difference of agreement between Nano-SMPS and LDMA at different sizes in the overlap range raises a question of how accurate/valid the diffusion correc-

tion is. Even though no examples of size distributions measured with the Nano-SMPS and LDMA are given, the size dependence of r2 suggests that the spectra have different shapes. I also doubt that r2 is suitable for judging the agreement. Smaller size bins usually have higher noise due to the weaker counting statistics amplified by the charging and diffusion loss corrections. This would lead to lower r2 at smaller sizes even if the agreement between the two instruments is perfect on average. Would the ratio of concentrations be a better measure? Also, the use of a single size bin for merging seems not very robust statistically; why not compare an average of several bins?

First of all, the diffusion correction has almost no effect on the level of agreement between the Nano and LDMA SMPS's. Note first that the merge points used were between roughly 40 and 60 nm. Next see from panel c of Figure 2 (now S-2) that the diffusion correction is not large at these diameters (1.3-1.5) and it is almost the same for both flow conditions used (3 and 0.3; and 6 and 0.6 li/min). Since both data sets were diffusion corrected, and the diffusion correction is small and nearly the same, the difference cannot be attributed to the diffusion correction itself. Panel b of Figure 3 (now Figure 1) shows pretty tight correlation between the two SMPS systems at the merge point (with more scatter for the QC01 campaign), and pretty good counting statistics (i.e., no strong evidence for excessive noise). Second, an average of several bins would also be a good way to merge the data sets. Our method seems quite reasonable as well, providing a merged data set that is consistent with both Nano and LDMA data sets over the range in question

Page 79, lines 7–9. A different merge point for the PSP04 campaign is explained by "different operation conditions". What are these conditions? If the flow rates are meant, then this raises a question of the accuracy of the diffusion loss correction, because this is probably the only reason why the results would be different.

The truth is that we really don't know the reason our method determined a different merge point for the PSP04 campaign. It was not due to "different operating conditions" as pointed out by the reviewer. We have removed this wording from the manuscript.

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Page 79, lines 10–11 and Table 3. Why would the bins be different in width and size? Does the TSI software not export the data in a standard way?

What is reported in Table 3 are the upper and lower bin diameters as reported by the TSI software. We are not sure why they are not identical for the LDMA – as they are for the Nano. While confusing (and annoying?) these differences are small enough as to be inconsequential.

Section 3.4. Why was the size-dependent counting efficiency of the CPC not taken into account when calculating the CPC-proxy data from the Nano-SMPS distributions? How would the particles smaller than 8 nm, some of which would still be counted by the CPC, affect the comparison? To support the statement about statistical significance of the slope increase, the uncertainty in their values should be provided. How was the statistical significance of the increase in r2 determined?

We first note that the 3022 has a specified efficiency of 50In the figure comparing the CPC and summed SMPS data sets (old figure 2, new figure 4), it is quite clear to the eye that the slopes are "significantly" different. We calculated the slopes and their 95

Page 81, lines 8–9. What is "a much more dynamic situation"?

We agree with the reviewer that the word "dynamic" is a little vague. To clarify this point to the reader, we have changed the following sentence in the text: "This is a significantly lower mode diameter than appears in the distribution prior to diffusion loss corrections, and is consistent with high primary emissions with particle growth at the QC site."

Page 81, lines 17–18. I would recommend applying the diffusion correction, provided it is accurate, not only to urban, but to any data set.

Good point. We have changed the following sentence in the text: "We believe these results show that diffusion loss corrections are always necessary for SMPS data gathered from urban as well as rural locations."

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Page 81, lines 18–20. How the findings presented in this paper can be used to evaluate whether or not reprocessing (any reprocessing?) "extremely large data sets . . . will yield important additional information"? Will small data sets be any different in this respect?

No, certainly any data set can be used, so we have changed the following sentence in the text: "These findings may be useful when evaluating whether reprocessing data sets from rural or urban ambient monitoring sites will yield important additional information."

Page 82, lines 1–4. Why would the slower oxidation of intermediate volatility compounds lead to higher aerosol number concentrations, would it not be the other way around? A more probable reason would be lower mixing heights.

We have removed the phrase about slower oxidation of the IVOC from the text – the reviewer raises a good point, and we can't back up our speculation. We did add a phrase about the lower mixing heights and thank the reviewer for that helpful comment.

Page 83, lines 1–2. The statistical criteria for an outlier need to be specified.

We agree with the reviewer. To clarify this point to the reader, we have changed the following sentence in the text: "when the data is an outlier based on statistical analysis such as extremely high values or zero values compared to before and after scans."

Page 83, second paragraph. The selection of bin boundaries is rather arbitrary and probably is not needed, because practically no critical information is extracted from this binning. Showing average size distributions would have provided all the information (such as the smaller particles dominate the number concentration, for example). In the bin definition, the emissions are attributed to the second and third bins, yet in the following section (p.84, 5–10) the high number concentration events, which are dominated by the first two bins, are attributed to traffic emissions. The definition of "ultrafine mode" given on line 14 contradicts the preceding attribution of the second

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and third bins to the ultrafine mode, because part of bin one and four also fall into this mode. The lower boundary of the accumulation mode is usually attributed to 100 nm, not 67.3 nm.

We agree with the reviewer. In the interest of making the paper shorter and more concise, we have removed this paragraph.

Page 84, lines 10–12. "There is a strong association between CPC and the SMPS size range of 8.35–19.8. . . " This is one of the examples of trivial statements in the paper. The CPC measures the total number concentration (or a close proxy of it), the SMPS measures another proxy of the total number concentration, the two correlate (see section 3.4), the size distribution is dominated by the smallest size range. Is it then surprising that the CPC and the lowest size bins of the SMPS correlate? Of course, not. What new information does this sentence provide?

The reviewer raises a good point. We have removed the offending sentences:

Sections 3.8 and 3.9. I do not understand why the relationship between the ion balance and the number concentration is investigated. Is there any physical or chemical process that would link the two? The discussion of ion balance and chemical composition seems irrelevant to this paper. Unless the authors present a compelling reason why this needs to be discussed, the parts dealing with chemical composition should be removed from the paper.

The discussion of the relationship (or lack thereof) between ion balance and number concentration has been removed from the paper. Interestingly enough, in the expanded discussion of the particle formation events requested by reviewer 2, we see hints of a role that ion balance may play in describing these events. We added the following sentences to the supplementary material: "Particle acidity was examined based on the ratio of measured ammonium concentrations versus the measured sulfate. A value of one suggests that sulfate might be fully neutralized by ammonium in the form of $(NH_4)_2SO_4$. For these events, the aerosol was neutral during the initial stages of

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growth, and became more acidic during the later stages – confirming the role of sulfuric acid in this type of regional growth event."

Page 86, line 24. What is "the small particle limit"?

Thanks for the comment. To clarify this point , we have changed the following sentence: "The low mass loading limiting case is generally accompanied by observations of low PM2.5 mass, high number concentration, and small particle diameter caused by the occurrence of "small fresh particles" associated with two possible processes"

Page 87, lines 7–13. I do not agree with these two sentences: a strong local source, such as a busy roadway, may influence both the number concentration and the PM2.5 mass; regional scale nucleation events may influence urban number concentrations, but not their PM2.5 mass.

Point taken -to clarify this point we have changed the following sentence: "Number concentration is highly sensitive to the fresh vehicle exhaust emissions of ultrafine particles, whereas PM2.5 mass is highly influenced by the aged aerosol linked to the urban background mostly occurring in the accumulation mode due to the atmospheric processing of vehicle emissions and other sources as shown in Fig. 6 - 9."

Page 87, line 25. Indicate the units of CS values.

Indicated as suggested by the Reviewer

Page 88, lines 7–10. The sentence "The stronger relationship. . . " is confusing: what does "dynamic condensation processes from primary particles" mean? If it means that the primary particles contribute to CS, and CS correlates with PM2.5, then it contradicts the statement on p.87, l.7–13 that the primary sources do not contribute significantly to PM2.5.

See the response above – the text has been changed to include the contribution of strong urban sources to the PM2.5 mass.

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Table 1. ASRC and DEC need to be defined. I would also suggest adding time periods for each campaign.

Defined as suggested by the Reviewer

Figure 1. Why are the points not equally spaced along the x axis in the diffusion loss graphs? The SMPS usually exports size distribution data in equally spaced logdiameter size bins.

Sample line diffusion loss caused by particle deposition onto sample lines was computed. The selected sizes for computation were 8, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 200, 300, 400, and 500 nm.

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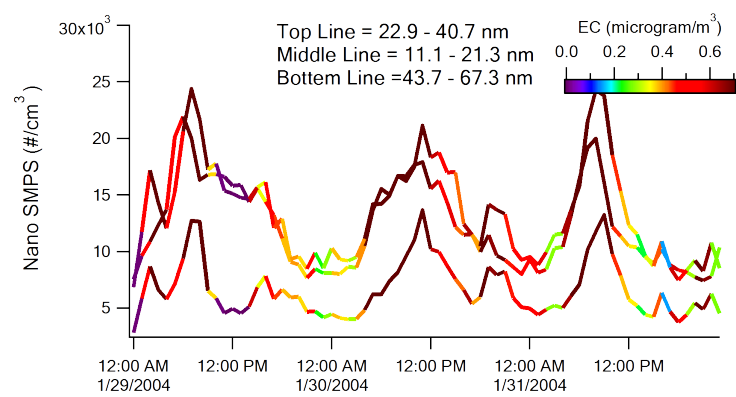
Fig. 1. Time series number concentrations (#/cm3) from Nano SMPS colored by EC concentrations (microgram/m3)

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