

Interactive comment on “Characterization and source apportionment of submicron aerosol with aerosol mass spectrometer during the PRIDE-PRD 2006 campaign” by R. Xiao et al.

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Response to Reviewer #1's Comments:

Comment #1a: It is noted that compared to SV-OOA, LV-OOA is more oxygenated and more aged and that SV-OOA evolves to LV-OOA. What is the evidence in this data that LV-OOA is more regional in nature? It apparently is more water-soluble, consistent with being more oxygenated and thus has a clear diurnal peak during daytime, but how does that make it regional? Is this conclusion based solely on the correlation to sulfate? As a background site in which local events have been removed from the data set, what does regional mean? It is not clear to me what regional means in the context

C3619

of this study.

Response to Comment #1a: The objective of this study is to characterize the air mass in the PRD region. Back Garden site was chosen for this purpose as it is a rural site in the PRD region of south China, which is located about 50 km northwest of the Guangzhou urban center (Miyazaki et al., 2009). This site is surrounded by forest (20 km²) and lake (about 2.7 km²) with much less population and insignificant vehicular emissions (Hua et al., 2008). Occasionally this site could be impacted by some biomass burning in the afternoon and cable burning in the evening. However, these local events have been removed from the data analysis in this study. Therefore, the data used in this analysis could represent the general characteristics of air mass in the PRD region. The paper published in Science by Jimenez et al. (2009) stated that “LV-OOA is likely regional and more aged OA while SV-OOA is likely less-photochemically aged OA, but the relative contributions of the two OOA subtypes depend on both ambient temperature and the extent of photochemical transformation”. We found from our study that LV-OOA contains more m/z 44 than SV-OOA (13.5% compared to 8.5%), suggesting LV-OOA is more aged. We intend to cite their work to support our finding that LV-OOA is more aged. To avoid confusion, we revised this statement as follows: “LV-OOA is more aged OA while SV-OOA is likely less-photochemically aged OA, but the relative contributions of the two OOA subtypes depend on both ambient temperature and the extent of photochemical transformation (Jimenez et al., 2009).”

Comment #1b: Along this line, some clarification is needed regarding the aging of the aerosol (Page 1904 and 1905, eg 1904 line 23 - 24). Are the authors suggesting that SV-OOA evolves with minimal mass increase into LV-OOA? This is my impression. It is not clear that the data shows that. For example, why does LV-OOA peak during the day? If no mass of SOA is being formed during this time, then one would conclude that changes in the concentration of LV-OOA are just due to changes in air mass age (ie, just recording the passage of different aged air masses). Why not make a plot similar to Miyazaki et al., JGR 2009 Fig 9, that shows changes in SV- and LV-OOA with

C3620

photochemical age, his could be very insightful and it seem much of the analysis (eg, data segregation) has been done.

Response to Comment #1b:

It has been shown in the MILAGRO campaign that SV-OOA evolving into LV-OOA is one of the major pathways of LV-OOA formation (DeCarlo et al., 2008). However, there are other possible pathways as well. For example, LV-OOA could be formed by 1) the oxidation of VOCs followed by condensation on existing particles and/or formed through nucleation process (Zhang et al., 2004) and 2) the passage of different aged air masses through transport (Sun et al., 2010). Figure 11 shows that LV-OOA dominates OOA, which increases during daytime while SV-OOA stays low. LV-OOA increased from 4.0 ug m⁻³ at 10:00 LT to 7.1 ug m⁻³ at 16:00 LT. It is more likely that in this study the increased LV-OOA was a combination of the above three formation mechanisms. As we intend to focus on the source apportionment of submicron organic aerosol in the PRD region in this study, future study would involve a quantitative estimate of their relative contribution

Comment #2: It was not clear how these results fit in with the early publication by the same authors (Miyazaki et al., JGR 2009). Ie, how does LV- and SV-OOA relate to HULIS? This is an interesting aspect of the data set and more analysis or discussion should be added, if possible (no one else has this kind of data!). The issue relates to hydrophilic WSOC (WSOC-hpi) and hydrophobic WSOC (WSOC-hpo) versus SV-OOA and LV-OOA. Here is what I found puzzling about the results presented.

Based on the correlation analysis near the end of the paper, it appears that the authors believe LV-OOA is mostly related to WSOC-hpi since the r^2 is 0.71. There is a low correlation between SV-OOA and WSOC-hpo, so it is not clear what SV-OOA is associated with. (Maybe SV-OOA is associated with both and so combined with the observation that only 65% is water-soluble, the r^2 is low for both SV-OOA to WSOC-hpi and SV-OOA to WSOC-hpo). It would be nice to know what the correlation was between

C3621

WSOC-hpo and LV-OOA. (Note, it would be most informative to include WSOC-hpi and WSOC-hpo in the regression Table 3). The authors also argue that LV-OOA is more aged as it has a spectra similar that of fulvic acid. This seems contradictory since one may expect fulvic acid (or HULIS) to be correlated with WSOC-hpo since the solid phase resin (XAD-8 or DAX-8) used to isolate fulvic acid is the same used to quantify WSOC-hpo (see Miyazaki et al., JGR 2009). Maybe the difference is that fulvic acid is isolated from natural surface water. Without knowing all the correlations between, LV-OOA, SV-OOA, WSOC-hpi, and WSOC-hpo, it is hard to come to a conclusion, but I suggest the authors make an attempt. One guess is that it may be that each of LV-OOA and SV-OOA have components of both WSOC-hpi and WSOC-hpo, that would be interesting.

Response to Comment #2: Based on the reviewer's suggestion, we make the following plots to show all the correlations between, LV-OOA, SV-OOA, WSOC-hpi, and WSOC-hpo. It can be seen that LV-OOA correlates with both WSOC-hpi (r^2 as 0.71) and WSOC-hpo (r^2 as 0.49). As the spectra of LV-OOA is similar to that of fulvic acid and the solid phase resin used to isolate fulvic acid is the same as that to quantify WSOC-hpo, LV-OOA does show correlation with WSOC-hpo though its correlation coefficient is lower than WSOC-hpi. Therefore, it is not contradictory. We have added these two plots below in the revised manuscript (Figure 17). However, it is apparent that SV-OOA is not associated with both (WSOC-hpi, and WSOC-hpo).

Scatter plots of WSOC-hpi, WSOC-hpo versus LV-OOA, SV-OOA.

Comment #3: It would be very interesting if the authors could explore the possible roles of cloud chemistry versus clear air. Interesting data is shown that sulfate and the OOA is bimodal suggesting these two formation routes were occurring. Can this be expanded? For example can the size distributions of SV-OOA and LV-OOA be determined in any way? Can any tracer be used for droplet and condensation modes and then correlations between SV-OOA, LV-OOA, WSOC-hpi, and WSOC-hpo explored? Maybe this could be done by looking at the air mass origins, comparing LV-OOA/OOA

C3622

and SV-OOA/OOA for southeast-south air masses versus southwest and north (the former are biomodal, the latter are not). I raise this issue since there is some speculation that LV-OOA is more likely cloud processed.

Response to Comment #3: The size distributions of SV-OOA or LV-OOA are not available in this analysis. SV-OOA and LV-OOA components are resolved from PMF analysis of AMS data. AMS original data contain size distribution information, but all data are pooled together in the PMF analysis to obtain robust statistical results. As the chemical components from AMS analysis in this paper include major components such as ammonium, nitrate, sulfate, chloride, organics (see Table 2), therefore, size distributions of specific tracers are not available as well.

Specific Questions:

Comment #4: Page 1893 line 4, change “summer reason” to “summer season”.

Response to Comment #4: This change has been made in the revised manuscript.

Comment #5: Page 1896, lines 20 to 22. If you are going to refer to other data collected during this study, but not discussed in this paper, can references to publications be provided?

Response to Comment #5: On Page 1896, we have changed the following sentence “Specific measurements at the BG site included the study of chemical composition, size distribution, hygroscopic properties and optical properties of aerosol, various gaseous pollutants, and oxidants (e.g. hydroxyl radicals, hydrogen peroxide).”

to

“Specific measurements at the BG site included the study of chemical composition and size distribution (Yue et al., 2010), hygroscopic properties (Rose et al., 2010) and optical properties of aerosol (Garland et al., 2008), various gaseous pollutants (Li et al., 2010; Shao et al., 2011), and oxidants (e.g. hydroxyl radicals, hydrogen peroxide) (Hofzumahaus et al., 2009; Hua et al., 2008; Lou et al., 2010).”

C3623

Comment #6: Pg 1897 line 9, Not sure what is meant by an inlet T of 40C. Is this heated sample line external to the AMS? Apparently this was done to dry the particles. What about loss of semi volatile species (eg nitrate SV-OOA)?

Response to Comment #6: Yes, it means that the temperature of the sample line external to the AMS is 40 oC. As the residence time of the sampled air in the heated sample line is ~1.5 s, here we assume that evaporation of particulate materials is insignificant at this short residence time.

Comment #7: Pg 1899, lines 15 and so on throughout the paper. Be careful, comparisons are being made to what was measured by an AMS, not necessarily the same thing as the total submicron aerosol mass.

Response to Comment #7: We have already changed “total submicron mass” to “the sum of sulfate, ammonium, nitrate, chloride and organics” on page 1899.

Comment #8: Eq 1, (lognormal distribution) is missing a square bracket at the end.

Response to Comment #8: We added a square bracket “]” at the end.

Comment #9: In Fig 4 and text, these units are commonly written as micro equivalence per m3.

Response to Comment #9: These units have been changed in the revised manuscript.

Comment #10: Pg 1900 and 1901: I suggest referring to this as apparent acidity, you are not measuring H+, or pH, but only roughly estimating acidity indirectly assuming the only missing component from the ion balance is H+.

Response to Comment #10: “particle acidity” has been changed to “apparent acidity” (Lines 14, 18, 25 on Page 1900 in the original manuscript).

Comment #11: Page 1901, line 7 and Fig 5, is local time and Beijing time the same?

Response to Comment #11: Yes, local time and Beijing time are the same.

C3624

The following changes have been made (lines and page refer to those in the original manuscript): Page 1901 line 7: When “local time (LT)” first appear, we clarify it as “local time (LT, Beijing time)”.

Comment #12: Page 1902 and 1903 discussion of Fig 8. I understand the how SOA (eg, m/z 44) can be in the smaller and larger modes of fig 8, but POA (m/z 57) also has a significant fraction in the larger mode (eg, $0.08/(0.08+0.14)=36\%$). How is that explained?

Response to Comment #12: It is true that certain fraction of POA in this study is found in the large mode. m/z 57 is a marker of hydrocarbon-like aerosol (Takegawa et al., 2009), which is often used as an indicator of the primary combustion-related emissions. For example, Takegawa et al (2009) showed in their Figure 5c that the size distributions of m/z 43 (similar to m/z 57 with $R^2=0.72$) during a large enhancement event in the early morning (0410–0650 LT) and during the daytime (1000–1800 LT). The size distribution of m/z 43 during this event showed bimodal peaks at D_{va} ~200 nm and ~500 nm. The presence of small-mode particles indicates that the aerosols were relatively fresh, because the contributions of small-mode particles tend to decrease in aged air [e.g., Alfarra et al., 2004]. Conversely, the monomodal size distribution of m/z 43 during the daytime suggests that the air masses were not largely affected by local emission sources. In our case, the large mode of m/z 57 may indicate the air mass we sampled was relatively aged. The manuscript has been modified accordingly.

A figure in Takegawa et al., 2009 (Figure 5c).

Comment #13: Page 1905 line 17, if LV-OOA is regional why does it have a clear diurnal profile with maximum during the day, in stark contrast to SV-OOA? I would interpret this that LV-OOA is more closely linked to photochemistry compared to SV-OOA, which may be more closely linked to primary emissions. This is consistent with SV-OOA being roughly 40% non-water soluble species.

Response to Comment #13: we agree with the reviewer that the clear diurnal profile

C3625

suggests that LV-OOA is more linked to photochemistry relative to SV-OOA. According to this comment, we have made a change as shown in Response to Comment #1a, and: at Page 1905 line 22: We changed “0.5 ug m⁻³ h⁻¹. The mass concentration of...” to “0.5 ug m⁻³ h⁻¹. LV-OOA is closely linked to photochemistry. The mass concentration of ...”

Comment #14: Page 1906 line 9, how was the number 1.1 = POC/EC determined?

Response to Comment #14: The data between 01:00-07:00 Beijing time of each day were used to estimate the primary OC/EC ratio. The (m/z 44)/(m/z 57) ratios were usually low and remained stable for these data points, indicating these periods were dominated by primary emissions. A linear regression by least squares minimization was fitted to these data points and its slope (1.1) represented the primary OC/EC ratio in this study.

Comment #15: Page 1906 line 23, Can you give an example of oxygenated primary species (biomass burning?).

Response to Comment #15: Examples include levoglucosan, syringol etc. which have been found abundantly in fireplace source tests of woods in the southern United States (Fine et al., 2002).

Comment #16: Page 1907 lines 22-23, change was very trace to was at trace levels throughout the study period.

Response to Comment #16: “was very trace” has been changed to “was at trace levels throughout the study period” in the revised manuscript.

Comment #17: Page 1908 line 19 to 20, I would put brackets around LV-OOA and SV-OOA (it looks like subtraction) in the WSOC fit equation.

Response to Comment #17: The equation has been changed from “WSOC=0.42·LV-OOA + 0.38·SV-OOA + 0.29” to “WSOC=0.42*(LV-OOA) + 0.38*(SV-OOA) + 0.29”.

C3626

Comment #18: Page 1909 line 1: Is it true (ie has it actually been measured by AMS or other MS approach) that WSOC-hpi is more oxygenated (eg, higher O/C) than WSOC-hpo?

Response to Comment #18: Actually this sentence is cited from Miyazaki et al., 2009. Hydrophilic organic compounds are highly oxygenated, with low molecular weights, typically with a number of carboxyl, carbonyl, or other groups per molecule. These compounds tend to be highly soluble in water. Hydrophobic organic compounds tend to be longer in carbon chain length, and less hygroscopic. However, based on our data, O/C ratio for WSOC-hpi and WSOC-hpo cannot be directly determined.

Comment #19: Why in Fig 10 is LV-OOA + SV-OOA plotted with the sum of sulfate and nitrate? Wouldn't it be better to plot just OOA, I assume that LV-OOA and SV-OOA must be fairly close to OOA.

Response to Comment #19: we define OOA as "OOA=LV-OOA + SV-OOA", please see page 1905 line 1.

Comment #20: Fig 13, This figure could be made more informative by also showing the subdivision of OOA into SV- and LV-OOA.

Response to Comment #20: We have modified Fig. 13 based on the reviewer's suggestion.

References

1. Fine, P.M., Cass, G.R., and Simoneit, B.R.T. (2002) Chemical characterization of fine particle emissions from the fireplace combustion of woods grown in the southern United States, *Environmental Science and Technology* 36, 1442-1451.

2. Miyazaki, Y., Kondo, Y., Shiraiwa, M., Takegawa, N., Miyakawa, T., Han, S., Kita, K., Hu, M., Deng, Z. Q., Zhao, Y., Sugimoto, N., Blake, D. R., and Weber, R. J.: Chemical characterization of water-soluble organic carbon aerosols at a rural site in the Pearl River Delta, China, in the summer of 2006, *J. Geophys. Res.*, 114 (D14208),

C3627

doi:10.1029/2009JD011736, 2009.

3. Hua, W., Chen, Z. M., Jie, C. Y., Kondo, Y., Hofzumahaus, A., Takegawa, N., Lu, K.D., Miyazaki, Y., Kita, K., Wang, H. L., Zhang, Y. H., and Hu, M.: Atmospheric hydrogen peroxide and organic hydroperoxides during PRIDE-PRD'06, China: their concentration, formation mechanism and contribution to secondary aerosols, *Atmos. Chem. Phys.*, 8, 6755-6773, 2008.

4. Jimenez J. L., Canagaratna M. R., Donahue N. M., Prevot, A. S. H., Zhang, Q., Kroll, J. H., DeCarlo, P. F., Allan, J. D., Coe, H., Ng, N. L., Aiken, A. C., Docherty, K. S., Ulbrich, I. M., Grieshop, A. P., Robinson, A. L., Duplissy, J., Smith, J. D., Wilson, K. R., Lanz, V. A., Hueglin, C., Sun, Y. L., Tian, J., Laaksonen, A., Raatikainen, T., Rautiainen, J., Vaattovaara, P., Ehn, M., Kulmala, M., Tomlinson, J. M., Collins, D. R., Cubison, M. J., Dunlea, E. J., Huffman, J. A., Onasch, T. B., Alfarra, M. R., Williams, P. I., Bower, K., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Salcedo, D., Cottrell, L., Griffin, R., Takami, A., Miyoshi, T., Hatakeyama, S., Shimono, A., Sun, J. Y., Zhang, Y. M., Dzepina, K., Kimmel, J. R., Sueper, D., Jayne, J. T., Herndon, S. C., Trimborn, A.M., Williams, L. R., Wood, E. C., Middlebrook, A. M., Kolb, C. E., Baltensperger, U., and Worsnop, D. R.: Evolution of organic aerosols in the atmosphere, *Science*, 326, 1525. DOI: 10.1126/science.1180353, 2009.

5. Yue, D.L., Hu, M., Wu, Z. J., Guo, S., Wen, M. T., Nowak, A., Wehner, B., Wiedensohler, A., Takegawa, N., Kondo, Y., Wang, X. S., Li, Y. P., Zeng, L. M., Zhang, Y. H.: Variation of particle number size distributions and chemical compositions at the urban and downwind regional sites in the Pearl River Delta during summertime pollution episodes, *Atmos. Chem. Phys. Disc.*, 10, 14611-14637, 2010.

6. Rose, D., Nowak, A., Achtert, P., Wiedensohler, A., Hu, M., Shao, M., Zhang, Y. , Andreae, M. O., and Pöschl, U.: Cloud condensation nuclei in polluted air and biomass burning smoke near the mega-city Guangzhou, China-Part 1: Size-resolved measurements and implications for the modeling of aerosol particle hygroscopicity and

C3628

7. Garland, R.M., Yang, H., Schmid, O., Rose, D., Nowak, A., Achtert, P., Wiedensohler, A., Takegawa, N., Kita, K., Miyazaki, Y., Kondo, Y., Hu, M., Shao, M., Zeng, L. M., Zhang, Y. H., Andreae, M. O., Poschl, U.: Aerosol optical properties in a rural environment near the mega-city Guangzhou, China: implications for regional air pollution, radiative forcing and remote sensing, *Atmos. Chem. Phys.*, 8, 5161–5168, 2008.
8. Li, X., Brauers, T., Shao, M., Garland, R.M., Wagner, T., Deutschmann, T., and Wahner, A.: MAX-DOAS measurements in southern China: retrieval of aerosol extinctions and validation using ground-based in-situ data, *Atmos. Chem. Phys.*, 10, 2079–2089, 2010.
9. Shao, M., Huang, D. K., Gu, D. S., Lu, S. H., Chang, C. C., Wang, J. L.: Estimates of anthropogenic halocarbon emissions based on its measured ratios relative to CO in the Pearl River Delta, *Atmos. Chem. Phys. Discuss.*, 11, 2949–2989, doi:10.5194/acpd-11-2949-2011, 2011.
10. Hofzumahaus, A., Rohrer, F., Lu, K., Bohn, B., Brauers, T., Chang, C. C., Fuchs, H., Holland, F., Kita, K., Kondo, Y., Li, X., Lou, S., Shao, M., Zeng, L. M., Wahner, A., Zhang, Y. H.: Amplified Trace Gas Removal in the Troposphere, *Science*, 324, 5935, 1702–1704, doi: 10.1126/science.1164566, 2009.
11. Lou, S., Holland, F., Rohrer, F., Lu, K., Bohn, B., Brauers, T., Chang, C. C., Fuchs, H., Haseler, R., Kita, K., Kondo, Y., Li, X., Shao, M., Zeng, L., Wahner, A., Zhang, Y., Wang, W., Hofzumahaus, A.: Atmospheric OH reactivities in the Pearl River Delta – China in summer 2006: measurement and model results, *Atmos. Chem. Phys.*, 10, 11243–11260, doi:10.5194/acp-10-11243-2010, 2010.
12. Takegawa, N., Miyakawa, T., Watanabe, M., Kondo, Y., Miyazaki, Y., Han, S., Zhao, Y., Pinxteren, D., van, Bruggemann, E., Gnauk, T., Herrmann, H., Xiao, R., Deng, Z., Hu, M., Zhu, T., and Zhang, Y.: Performance of an aerodyne aerosol mass spectrometer (AMS) during intensive campaigns in China in the summer of 2006, *Aerosol Sci. Technol.*, 43, 189–204, 2009.

C3629

eter (AMS) during intensive campaigns in China in the summer of 2006, *Aerosol Sci. Technol.*, 43, 189–204, 2009.

13. Alfarra, M. R., Coe, H., Allan, J. D., Bower, K. N., Boudries, H., Canagaratna, M. R., Jimenez, J. L., Jayne, J. T., Garforth, A., Li, S. M., and Worsnop, D. R.: Characterization of urban and regional organic aerosols in the lower Fraser Valley using two Aerodyne Aerosol Mass Spectrometers, *Atmos. Environ.*, 38, 5745–5758, 2004.
14. DeCarlo, P. F., Dunlea, E. J., Kimmel, J. R., Aiken, A. C., Sueper, D., Crounse, J., Wennberg, P. O., Emmons, L., Shinozuka, Y., Clarke, A., Zhou, J., Tomlinson, J., Collins, D. R., Knapp, D., Weinheimer, A. J., Montzka, D. D., Campos, T., and Jimenez, J. L. (2008) Fast airborne aerosol size and chemistry measurements above Mexico City and Central Mexico during the MILAGRO campaign, *Atmos. Chem. Phys.*, 8, 4027–4048.
15. Sun, J., Zhang, Q., Canagaratna, M. R., Zhang, Y., Ng, N. L., Sun, Y., Jayne, J. T., Zhang, X., Zhang, X., and Worsnop, D. R. (2010) Highly time- and size-resolved characterization of submicron aerosol particles in Beijing using an Aerodyne aerosol mass spectrometer, *Atmos. Environ.*, 44, 131–140.
16. Zhang, Q., Stanier, C. O., Canagaratna, M. R., Jayne, J. T., Worsnop, D. R., Pandis, S. N., and Jimenez, J. L. (2004) Insights into the chemistry of new particle formation and growth events in Pittsburgh based on aerosol mass spectrometry, *Environ. Sci. Technol.*, 38(18), 4797–4809.

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 11, 1891, 2011.

C3630

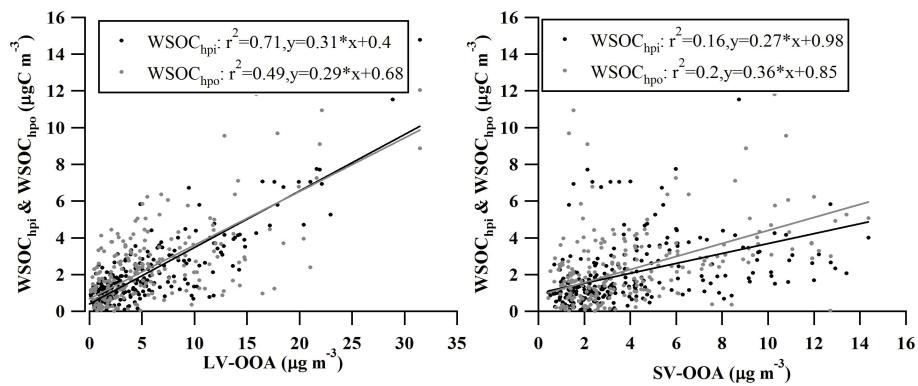


Fig. 1. Scatter plots of WSOChpi, WSOChpo versus LV-OOA, SV-OOA.

C3631

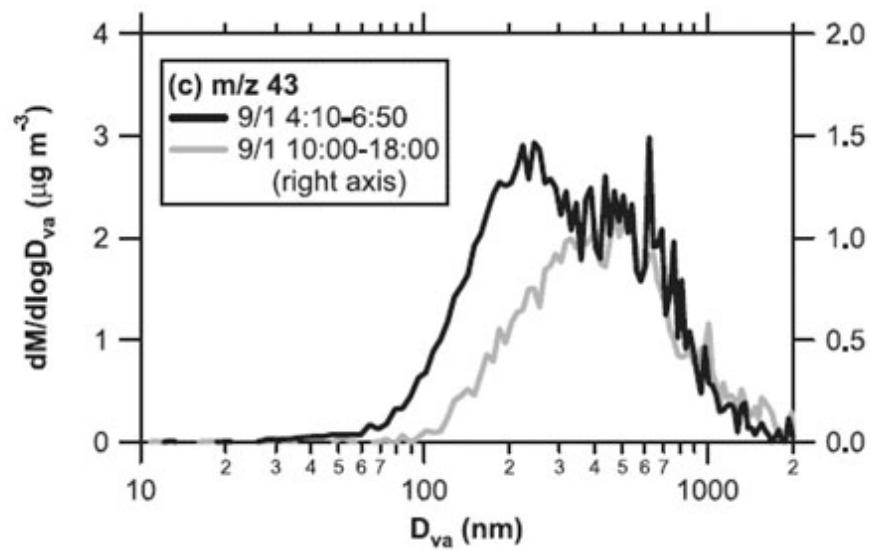


Fig. 2. A figure in Takegawa et al., 2009 (Figure 5c).

C3632