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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Single particle characterization of black carbon aerosol in the Northeast Tibetan Plateau, China" *by* Q. Y. Wang et al.

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Anonymous Referee #1

1. About the MAC calculation and the interpretation of Aeth data. First of all, this part of abstract is not quite pleasant to read: the abstract line 15-18, after you have just stated that "the Aeth data is not reliable", how could you use Aeth to derive MAC? I kind of understand what you mean, the Aeth is not suitable for BC mass determination but only used for absorption measurement (even the absorption data you have used may be wrong as well), but please state these more carefully and logically in the abstract.

Reply: We agree with the Reviewer that overall the discussion of the Aethalometer data

was not consistent. We have revised the abstract and text to make a consistent and logic argument. Our original usage of MAC, although with precedents, is not the most appropriate. Instead of deriving a new MAC number, we have now provided a scaling factor that will effectively convert the Aethalometer data into correct rBC loadings.

For the Aeth data interpretation, you used an attenuation coefficient (σ) which is manufacture defined, to derive the Aeth BC mass. Firstly, this value could be wrong, we can't just use the same value under different atmospheric conditions, because the MAC of BC will be influenced by many factors in the real atmosphere as you have stated, but you have just made a self-conflict after you have made these statements: in Fig. 7A the Aeth BC mass is compared with SP2 BC mass, this will absolutely confuse the reader as the Aeth BC itself is wrong. It is not a good idea to use anything about Aeth BC given you are talking about the MAC in this paper, the better approach for Fig. 7 is to plot the Aeth absorption VS SP2 rBC, then apply for a linear fitting to get the least square fitted MAC (=absorption/mass).

Reply: We agree with the Reviewer that the factory-provided MAC is not universal. The approach the Reviewer suggests is essentially what we have done. Perhaps the Reviewer was confused because we did not make a consistent argument. We realize that MAC is a confusing term used in this paper, and different values for the MAC make the situation worse. Therefore, as mentioned above, we have chosen to leave the factory-provided MAC alone, and instead provide a scaling factor that can be used to correct the Aethalometer output.

And definitely you should discuss in more details where the difference of MAC may result from, between the urban environment Xi'an and this site QHL, but you haven't explained these at all, just simply listed the values from other literatures.

Reply: Clearly, the data set available does not allow direct evaluation of the aerosol composition affecting the MAC as determined by the Aethalometer and SP2. However, we have expanded discussion of this issue with inclusion of the following sentence

in Lines 365 to 371 in the text: “This discrepancy may result from the different aerosol sources and varying mixing state of rBC. For example, rBC at Xi’an site were dominated by fresh vehicular exhausts and coal combustion (Cao et al., 2005, 2009b), which typically exhibit external mixed BC, while both the sources (strong contributions from open burning of biofuel) and aging timescales at QHL could contribute both to a greater degree of internal mixing of OC with BC, and larger OC burdens that could affect the Aethalometer measurement.”

Secondly, it seems that the Aeth data has not been interpreted properly. You claimed “BC concentrations there derived from Aethalometers may also need careful examinations and possibly new interpretations”. Please do it, please do not just use the directly measured attenuation from Aeth, the non-absorbing particles will surely contribute to the total light extinction/attenuation, there is no doubt that this will overestimate the “absorption”. We should at least correct for the aerosol scattering properties (There are so many literatures discussing this correction I am not going to list here). You have just duplicated claiming this truth at many places but have not corrected for it. Given the MAC value is one of the main conclusions, we can’t use this extinction-derived “MAC” and even put this wrong MAC into the abstract.’

Reply: As mentioned above, we have now made our interpretation more consistent. Our statement the Reviewer quotes is for datasets collected at Waliguan GAW station. These datasets are not ours and we don’t know their experiment and data reduction details. Their paper (Ma et al., 2003) did not mention any correction to their Aethalometer data. Therefore we are not able to do what the Reviewer suggests and can only provide a caution/speculation. We disagree with the Reviewer’s statement that we did not correct the scattering effect. Using the new MAC (or the scaling factor used in the revised manuscript) is our correction method. There are different ways of correcting the Aethalometer data as the Reviewer mentioned. With no simultaneous scattering measurements, none of the published methods can be used for our dataset. We instead use the SP2 measurements to derive a simple scaling factor.

2. The SP2 data has not been fully analysed. Have you done the LEO fitting for the scattering signal of BC? We can’t use the raw scattering signal of BC as in Fig.2. I know the approach in Fig. 2 is from Schwarz’s paper 2006, but that is one of the earliest SP2 papers, there are so many updates since then, we are not currently only relying on that plot to derive the “internally mixed” fraction.

Reply: Unfortunately, the SP2 is still not a turn-key instrument. In the case of the Qinghai measurements, a problem with the sampling nozzle (we believe) led to substantially increased variability in particle speed across the laser beam beyond what is typically seen. Experimentation with increased buffer volumes to reduce pressure pulsations in the sheath flow due to the SP2 pump did not improve this issue. Hence, LEO fitting, although calculated, gave only unusable results (due to the excessively large scatter in results). For this reason, we presented a simpler analysis of BC coating state as has previously been carried out. Although Schwarz et al., 2006 was cited, very similar analyses have been carried out much more recently, indicating the continued value of this approach. For example, Subramanian et al. (ACP, 10, 219-237, 2010, www.atmos-chem-phys.net/10/219/2010) used essentially this analysis plotting lag time (as in our Figure 2) against BC mass (shown by color in Figure 2). Further, Perring et al. (GRL, 38, L17809,doi:10.1029/2011GL048356, 2011) used essentially the same analysis, citing Moteki and Kondo, 2007. As part of that work (not published), Perring et al. found that this technique correlated very well with the more sophisticated approach used in Schwarz et al., 2008 (which included identifying reductions in scattering cross section before the onset of BC incandescence). Hence, the use of this simplified analysis is well justified.

About the SP2 calibration, you used fullerene, please also state how you get the single particle mass from modality diameter.

Reply: For the SP2 calibration, the mass-mobility relationship of Moteki and Kondo, AS&T, 2010 was used. We have clarified the text in response to this point. As shown in Lines 139 to 145 in the text: “The fullerene soot was size selected by a differential mo-

bility analyzer (DMA) over a range corresponding to rBC of ∼0.8 – 20 fg mass, based on the mass-mobility relationships for this material in Moteki and Kondo (2010). This mass range corresponds to ∼90 – 270 nm VED, over which the calibration was close to purely linear, and the various determinations of the mass – to mobility relationship for this material are in good agreement (Moteki and Kondo, 2010; Gysel et al., 2011)."

In Fig.2, you set an arbitrary threshold of delay time above which the incand/scatter signal looks large variation however the delay time varies little, but it has not been physically clearly explained why this arbitrary delay time value should be selected. From the image coloured by the single particle mass, it can be seen that the above 2us delay time is mainly composed if smaller particles, it means by this method, you have just selected the smaller BC particle to be "internally mixed" whereas the majority of the larger particles are externally mixed? It is not true in the real atmosphere.

Reply: As discussed above, the analysis for rBC mixing state is quite common, and we have added the relevant citations to the manuscript, as appropriate. To clarify the use of 1.2 μs lag time (updated from 2 μs) as the discriminator between "thickly" and "thinly" coated BC, a side panel has been added to Figure 2 showing a histogram of lag time and clearly identifying 1.2 μs as separating these two populations. As noted in Perring et al., 2011, this measure of coated fraction is largely insensitive to BC mass over the BC mass range where the vast majority of BC-containing particles exist, so the bias to small BC appearing coated identified by the reviewer is entirely negligible; most BC-containing particles have BC mass < 5 fg at Qinghai lake. The change in lag-time discriminator value has only a negligible impact on our results.

More importantly, would you like to explain more precisely your definition of "internally" or "externally" mixing?-Chemically based or size/physically based? Again, please refer to the recent methodology to determine the "thickly coated" fraction from SP2 measurements.

Reply: The SP2 determination of rBC mixing state is based on optical signals associ-

ated with non-BC material being vaporized before the rBC is heated to its vaporization temperature. We have added a sentence in the text stating this. As shown in Lines 158 to 164 in the text: "The delay time between the peaks in the scattered light signal and the incandescence signal, and the ratio of their intensities (Scattered light intensity/incandescent intensity: S/I) were used as an indicator of the amount of non-BC material internally mixed with individual rBC masses (loosely referred as rBC coating thickness hereafter) (Schwarz et al., 2006; Moteki and Kondo, 2007). This is a commonly used approach to distinguish "thinly" and "thickly" coated rBC masses, and is sensitive to optically significant amounts of non-BC material". We are using recent methodology, although it is not possible to perform meaningful LEO analysis.

3. About the BC mass loading the conclusion in page 21953: "These comparisons suggest that the values found at the rural QHL site are well above background values and, hence, are very likely influenced by local rBC sources."1) There is no point to compare this plateau environment (over 3000m a.s.l.) with the urban studies, the urban is certainly more polluted;

Reply: We have removed this comparison in the revised text.

2) You compared the SP2 results with the Aeth data from many other sites, it is making large confusion to compare the BC mass from different instruments (given you have got Aeth BC as well, why not directly compare using the same instrument);

Reply: We see the Reviewer's point. However, Aethalometer measurements need correction, while SP2 measurements appear robust. Since most of the papers quoted here did not mention an Aethalometer correction, just comparing Aethalometer data does not make more sense. Therefore, we opt to still use our directly measured rBC mass from the SP2 to compare to different BC measurements in other studies but clearly list instruments used in individual studies.

3) It may be worthwhile to compare the BC mass at this plateau site with the other measurements which were also conducted at a high altitude station, but you should list

a table clearly stating the altitudes, instrumentation, experimental periods (seasons), local influence at al. You have not stated anything about the measurements from the other sites as you have referenced for comparisons, like Jungfraujoch, GAW etc. , have they been influenced by local source or not? You can't conclude that "because of this, the site is likely influenced by local. . ." what "local" is it?

Reply: A table (Table 2) has been added per the Reviewer's suggestion. BC source attributions from these papers are listed in the table. The entire section has been rewritten. The conclusion the Reviewer mentioned has been removed. Back trajectories at 3 levels are calculated and shown. The term "local" has been defined.

4) The definition of the "background" is far too subjective, what background is it, the troposphere, at which altitude, at what season, the regional or global or just around this site? Because it is above "background", then indicates from "local", I am not with your discussions here.

Reply: Agreed. The section has been rewritten with clearer definition and discussion of local vs regional sources.

4. About the diurnal variation The conclusion in page 21954: "The strong diurnal rBC variation shown in Fig. 4 further suggests that the QHL basin is heavily influenced by local rBC sources." First of all, I would suggest to plot the median and percentiles as well in these diurnal figures, especially for the BC mass. From these diurnal plots, I can't see any apparent "local" influence on BC mass, you have claimed that (and it is even not true) there was only a very slight peak around 8am, but based on this you conclude "heavily" influenced by local? In the abstract "The high rBC values and their diurnal behaviour strongly suggest that the QHL area was heavily influenced by local rBC sources." There are no apparent 8am rBC peak in Fig. 4, it may be the simple truth that the "background " level BC mass has been diluted by the boundary layer rise in the daytime but was trapped due to the largely decreased temperature in the night. There are no indications of "local" influence from this simple analysis. How could the

"heavily" and "strongly" in the abstract come?

Reply: We have updated the diurnal variation figure to the statistical box figure including median and 25/75 percentiles (see Figure 4 in the revised text). We regret that the Reviewer missed the large midnight peak and instead focused on the small peak at 8 AM. As we argue in the manuscript, the midnight peak is due to the trapping of local pollution when the boundary layer is lower than the surrounding mountains. The small peak at 8 AM is attributed to local cooking and heating. We have revised the text (Section 3.1 and Conclusions) to clarify the discussion.

Moreover, even if there is no data available for source attributions, you should at least point out or estimate where the pollution may come from, by combining with the local wind and back trajectory analysis, not just simply claim that "local residential activities".

Reply: Back trajectories have been calculated and added to the manuscript (Section 3.1). The back trajectory analysis is consistent with the general concept of nighttime local pollution trapping and daytime influence of long-distance transport from the west.

Once again, there is no point to compare the diurnal trend at this site with the urban study, how could the traffic activities at this plateau site be similar to that in megacity?

Reply: We have removed this comparison in the revised text.

5. I have no idea what is the reason to plot Fig. 6. How could the BC mass loading be necessarily related to mixing state? This figure is kind of misleading at some point. The mixing state of BC could be largely modulated by the meteorological conditions at this remote site, the mass loading is not the main driver. And the mass loading itself cannot indicate the sources at all, so the conclusions on Page 21956: "This large variability is mainly attributable to the local rBC sources" "drop off of diesel traffic in the evenings, combined with the continued contributions of biomass burning for cooking and heating" are not convincible at all, and even you have not convinced readers what the exact BC sources are.

Reply: We have removed Figure 6 from the manuscript.

6. About the BC/CO ratio. The ratio BC/ΔCO should be normally used rather than the BC/CO, because we need to get rid of the fairly large background of CO (which is around 150ppb in this study).

Reply: We have changed the BC/CO ratio to BC/delta-CO ratio in the revised text. As shown in Lines 400 to 407 in the text: "Since the atmospheric lifetime of CO is much longer than BC, the BC/CO ratios should be considered after correcting for CO background, and while recognizing that the ratio at the time of emission is at its highest value. In this study, the background CO values was estimated to be $\sim$114 ppb based on the mean of the lowest frequency peak of the CO distribution from a histogram of data collected during the sampling period. The background-corrected CO (ΔCO) values higher than 20 ppb were used for the comparison to rBC loadings."

This should also apply to the comparison, please check the other literatures carefully, making sure you are comparing the same thing.

Reply: We have revised these comparisons in the text, which all used BC/delta-CO ratios in the literatures (see Table 3 in the text). The comparison section has also been revised as shown in Lines 420 to 435 in the text: "For further perspective, the rBC/ΔCO ratio derived from this study was compared with other studies. It was within the range (0.8-6.2 ng m-3 ppbv-1) measured in the boundary layer over Europe (McMeeking et al., 2010). Subramanian et al. (2010) found rBC/ΔCO ratios were ranged from 2.2 to 3.3 ng m-3 ppbv-1 in aged urban plumes over Mexico, which was similar-to-higher than at QHL. The rBC/ΔCO in biomass burning plume can increase to 8.5 ng m-3 ppbv-1 (Kondo et al., 2011b), which is 5.5 times the ratio at QHL. Although high rBC/ΔCO ratios were found from biomass burning, there is a lack of research about combustion products from the burning of yak and sheep dung. Kondo et al. (2011b) reported rBC/ΔCO ratios from biomass burning were lower during smoldering (1.7 ng m-3 ppbv-1) than in flaming phases (3.4 ng m-3 ppbv-1). Since yak and sheep dung burning at

Tibetan Plateau are likely in the smoldering phase (Kang et al., 2009), they likely lead to the slightly low rBC/ΔCO ratio compared to other regions. The rBC/ΔCO ratio at QHL was also lower than those observed in urban air, such as Beijing (3.4-5.8 ng m-3 ppbv-1; Han et al., 2009), Guangzhou (7.9 ng m-3 ppbv-1; Andreae et al., 2008), California (3.1 ng m-3 ppbv-1; Kondo et al., 2011b), and Tokyo (5.7 ng m-3 ppbv-1; Kondo et al., 2006)."

The discussions in page 21958-21959 are a bit superficial: an rBC/CO ratio as derived from the whole dataset, comparing with the other literatures, then claim just because of this combined sources are indicated, I think further analysis is essential to make the conclusion solid: 1) how the BC/ΔCO ratio varies with different air masses 2) how could this ratio be influenced by meteorological conditions including the precipitations? 3) how could the BC/CO related to the ageing time of BC, i.e. the mixing state of BC, as the lifetime of BC is mostly shorter than CO, the BC/CO ratio could be modified during transport.

Reply: We appreciate Reviewer #1's point. In the revised text, we discussed the BC/ΔCO ratio from different time of the day and a single snowfall event. As shown in Lines 407 to 419 in the text: "Figure 8 presents the relationship between ΔCO and BC concentrations during Time I and II. A relatively tight relationship between ΔCO and rBC is shown when air mass influenced by local sources (Time II), with a correlation coefficients of 0.87. However, rBC exhibits less dependence on the ΔCO concentration (r=0.71) when air masses are influenced by regional rBC sources (Time I). The derived rBC/ΔCO ratios were 1.17 ng m-3 ppb-1 for Time I and 1.64 ng m-3 ppb-1 for Time II, which may represent regional and local mixed emissions at QHL during the measurement cycle, respectively. As shown in Figure 8, the correlation coefficient of rBC and ΔCO was reduced (r=0.61) when air masses reaching the site have been influenced by wet deposition, and the rBC/ΔCO ratio was 1.16 ng m-3 ppb-1. This was associated with the different atmospheric removal mechanisms of rBC and CO. The sink of BC is dominated by wet deposition (Textor et al., 2006), while the lifetime of CO

is controlled by oxidation via OH (Holloway et al., 2000)."

A few more points should be addressed: 1. At least the back-trajectory data analysis needs to be done to get the idea where the BC is from.

Reply: We have added back trajectory analysis.

We need to investigate how the BC mass, size and mixing state, BC/CO vary with different air mass origins.

Reply: The discussion about BC mass and BC/delta-CO ratio can be seen in Replies 4 and 6, respectively. The discussion about BC size has been added in the revised text as shown in Lines 301 to 325, and the discussion about BC mixing state is shown in Lines 336 to 339 in the text, respectively: "A two-mode lognormal function fits the data well between 0.07 and 1.0 μm. A two-mode mass size distribution for BC was first observed in the Pearl River Delta, and is likely associated with mixed fossil and bio-fuel emissions (Huang et al., 2011). The size distributions between Time I and II have similar primary mode mass median diameters at $\sim$175 nm with a geometric standard deviation, σ, of 2.49 for Time I and 2.51 for Time II, respectively, which is within the range of 150-230 nm reported by previous SP2 studies (Huang et al., 2012, and references therein) assuming the same rBC density of 2 g cm-3 for valid comparison. Different emission sources produce rBC size distributions with different mode peaks. McMeeking et al. (2010) found an rBC peak diameter of $\sim$165 nm in the urban plume from Liverpool/Manchester, while the peak in a Texas urban plume was $\sim$170 nm (Schwarz et al., 2008). In addition, the rBC peak diameter in a biomass burning plume in Asian was reported to be $\sim$210 nm (Kondo et al., 2011b), which is also similar to a biomass burning plume in Texas ($\sim$210 nm) (Schwarz et al., 2008). The mass median diameter of the secondary mode, which is similar to the one reported by Huang et al. (2011), showed some variability with different time of the day, ranging from $\sim$470 nm from Time II when local pollution trapping, and likely aged, to $\sim$500 nm from air coming from Time I when influenced by regional sources. In contrast, measurements made during snow

fall reveal that the amplitude of the secondary mode (MMD: 460 nm), was reduced by one-half with respect to the primary mode (MMD: $\sim$175 nm VED). The statistical uncertainty of this reduction was small, about an eighth of the change. Assuming that the air mass, before snow fall, was consistent with the others observed during the series, this suggests that the larger secondary mode rBC particles were more efficiently removed by snow fall than the primary mode."; "The number fraction of coated rBC ranged from 25.9-67.8%, with an average of 50.5%. As shown in Table 1, the number fraction of thickly coated rBC was $\sim$10% higher in Time I (54.1%) than Time II (48.8%)."

2. The analysis on source attribution should be robust, not just simply "guess" what are the possible sources. The local wind data along with the backtrajectory data should be combined to investigate if the pollutants are local or regional. The current analysis cannot pronouncedly conclude the spatial scale of the pollutants.

Reply: Agreed. As discussed above, we have added back trajectory analysis.

3. The final conclusion should be upgraded to be a scientific level, to state why these dataset is important rather than just listing the results.

Reply: We agree with this point, and have reformed the conclusion section to make the points that these measurements provide first constraints on the rBC concentration and microphysical state in this remote region of Asia, that they will help constrain model predictions of BC in this region, which is of particular interest because of its proximity to major BC sources in Asia, and that, additionally, the measurements contribute to our understanding of the secondary mode of BC mass observed at large sizes, as well as recent results about size dependent removal of BC by precipitation.

4. After all of the above points are addressed, the abstract of this paper needs to be revised carefully.

Reply: We have rewritten the Abstract in light of the extensive changes to the manuscript.

Technical: Page 21950 line 11-15: please state clearly what is the altitude (above sea level) of the experimental site

Reply: The altitude of the experimental site is $\sim$3200m (amsl). We have added this in the new text.

Page 21951: Line 12: could you explain how you get the 25Line 15 and 16: please rewording this sentence

Reply: Because we wanted to see if the dust at QHL influenced the Aethalometer measurements, we chose to vary the cut-off point, finding that there was nearly no difference between the Aethalometer and SP2 results for PM1.0 and PM2.5. A sentence has been added as shown in Lines 384 to 387 in the text: "The Aethalometer data didn't show any change compared to the SP2 data when the inlet cyclone cutoff diameter was varied between 1.0 and 2.5 μm, suggesting that ambient particles in the diameter range of 1.0 to 2.5 μm did not affect the Aethalometer measurements."

Page 21954 line 18: "in contrast"? How could it be in contrast? The peak all occurs around 8.

Reply: The discussion has been removed per the Reviewer's suggestion.

I am not commenting too much on the technical issues/typos, given many places of this manuscript needs to be rewritten.

Reply: The manuscript has been rewritten and edited.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 21947, 2012.