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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 #2

Major concerns: 1. While the authors stated in the abstract that QHL is affected by the East Asian summer monsoon, Indian summer monsoon, winter monsoon, and the westerly jet stream, indicating that the meteorology there is unique, there is really litter discussion about how the meteorology affected the observation results?

Reply: Qinghai Lake is situated in the northeast of the Qinghai-Tibetan Plateau. Its size and proximity to the junction of three major climate systems (the East Asian monsoon, the Indian monsoon, and the Westerly) make it sensitive to climate changes (An et

al., Scientific Reports, 2012; http://www.ncbi.nlm.nih.gov/pmc/ articles/PMC3431539/). Because of its unique geographical position, we introduced background environmental configuration at the preface. In the revised text, we have added the discussion about the influences of local meteorology and long range transport.

How is this dataset in a short campaign representative for the general situation at QHL?

Reply: The work environment in the Tibetan Plateau region is not conducive to long term measurements with limited resources. Therefore, we choose the SP2, which has high sensitivity and resolution, to measure BC in this important rural area for a limited time. In our intensive observation, we acquired enough BC data, which can represent the general characteristic of BC in this area. We will continue to get more data about BC in this region with SP2 in the future.

Why is this dataset important scientifically? This is one of the key issues for the current manuscript.

Reply: The atmosphere in Tibetan is prone to influenced by human activities during autumn (Cao et al., AE, 2009; http://www.sciencedirect.com/science/article/pii/S1352231009005263). Our observations in this season can be used to identify the contribution of natural or human activities, and the influence of local sources or long range transport. Furthermore, our measurement is the first observation in this area. We began to measure BC in autumn to fill this gap in northeast Tibetan. These measurements provide first constraints on the BC concentration and microphysical state in this remote region of Asia, and 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. Finally, our present observation can also provide a background for understanding the data of paleoclimate, since we have climatic records before 200 and 10000 years ago.

In addition, the meteorology should be well discussed in order to examine the features of the regional or long range transport of aerosol at this special site.

Reply: We have performed, and included in the manuscript, back trajectory analysis which we link to our measurements as a function of time of day (and hence, mixed layer depth). We have added significant discussion using these analyses of the data.

2. Line 21 and the following, page 21950. How was this SP2 configured for the scattering and incandescent detectors? The detectors decide the detection ranges of BC particles and mixing state.

Reply: We have clarified the description of the SP2 setup to address this. Some sentences in the revised text to explain this. As shown in Lines 120 to 131 in the text: "The operating principles of the SP2 have been described in detail elsewhere (Schwarz et al., 2006; Liu et al., 2010; Moteki and Kondo, 2010). Briefly, the SP2 measures rBC mass in individual rBC-containing particles using intense, intracavity YAG laser light at a wavelength of 1064 nm. When an rBC-containing particle passes through the laser beam, the rBC component is heated to its vaporization temperature and emits incandescent light. The intensity of the incandescence signal is linearly related to the rBC mass and independent of the particle morphology or mixing state over most of the rBC mass range typically observed in the accumulation mode (Slowik et al., 2007). Here, the rBC mass in the range $\sim$0.4–1050 fg, equivalent to 70–1000 nm diameter volume equivalent diameter (VED) assuming 2.0 g cm-3 void-free density was quantified. This range provided coverage of >90% of the rBC mass in the accumulation mode."

3. Line 7, page 21951. Why was the calibration conducted over a range of 125–400 nm mobility diameter? As it is feasible to select particles with a size less than 100 nm by DMA, the higher minimum size used would affect the measured SP2 detection limits in this campaign. What are the measured detection limits in this campaign? In Figure 5, the BC data below 100 nm were presented. It is a little bit confused and should be clarified.

Reply: Calibration of the SP2 is a topic that has been addressed elsewhere extensively. As the purpose of this manuscript is not to present the SP2, but rather it's scientific

products at Qinghai Lake, we decline to expand discussion of the instrumentation excessively. However, here it is apparent that Reveiwer # 2 has become confused by the difference between the mobility diameter selected for a calibration, and the volume-equivalent diameter of rBC that this corresponds to (which depends on the choice of calibration material). Hence we have harmonized the use of rBC mass and volume-equivalent diameter to make these issues transparent to the reader, and we include additional citations that contain the details of the recommended SP2 calibration approach. As shown in Lines 139 to 145 in the text: "The fullerene soot was size selected by a differential mobility analyzer (DMA) over a range corresponding to rBC of $\sim$0.8 – 20 fg mass, based on the mass-mobility relationships for this material in Moteki and Kondo (2010). This mass range corresponds to $\sim$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)."

4. Line 11, page 21951. "The uncertainty in the rBC mass determination is $\sim$25% due to uncertainties in the rBC mass calibration, sample flow measurement, and estimation of rBC mass outside of SP2 detection range." How was 25% calculated? As this uncertainty is campaign-dependent, the process to obtain this specific value should be provided with some details.

Reply: The uncertainty of $\sim$25% was estimated from the square root of uncertainties in each part. As shown in Lines 150 to 154 in the text: "The total uncertainty in the rBC mass determination was $\sim$25%, estimated from the square root of uncertainties in the rBC mass calibration including possible variability in SP2 response to ambient rBC mass ($\sim$20%, Moteki and Kondo, 2010; Laborde et al., 2012), sample flow measurement ($\sim$10%), and estimation of rBC mass outside of SP2 detection range ($\sim$10%)." We note that the uncertainty is not necessarily campaign dependent, and is dominated by uncertainty (determined by only two publications, Moteki and Kondo, AS&T 2010, and Gysel et al, 2011) in the variability of the SP2 response to ambient rBC mass.

5. Line 17 and the following, page 21951. As to the method to identify BC mixing state, although the “time delay” method was previously used by Schwarz et al., 2006, there are new (and possibly better) methods also used by Schwarz et al. (2008). Why was the old method chosen by the authors (including Schwarz)? The threshold of 2 us seemed not to be a clear criterion from Figure 2. Also, to my knowledge, SP2 cannot identify mixing state for all BC-containing particles. What was the detection range for mixing state in this campaign and how are the current results representative for all the BC particles. As SP2 detects particles one by one, it is possible to see the distribution of BC mixing state versus BC particle size, which will be helpful to address the above issue.

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. 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.

6. Page 21953. It is better for the authors to make a clear table for the comparison of BC concentrations, with necessary sampling information for the other sites.

Reply: We have added a new table in the revised manuscript (see Table 2 in the text), and the comparison section in the text has also been revised. As shown in Lines 277 to 295 in the text: “Table 2 shows the comparison of measured mean rBC concentration at QHL with other measurements of BC from selected remote rural and high alpine areas. The average rBC concentration at QHL was comparable or lower than BC in southeast Tibet and the central Himalayas (0.34-0.99 μg m-3) (Cao et al., 2010; Dumka et al., 2010; Engling et al., 2010; Qu et al., 2009), where high BC concentrations were mainly influenced by long-range transport and regional anthropogenic emissions. The concentration measured at QHL was $\sim$2-7 times higher than several sites located in Central Tibet (Ming et al., 2010), Southern/Western Himalayas (Babu et al., 2011; Marinoni et al., 2010), and Western China (Cao et al., 2009a; Zhao et al., 2012), where high BC concentrations were influenced by regional emissions. Our averaged rBC value is $\sim$34% higher than BCAeth measured in Waliguan using an Aethalometer (Ma et al., 2003), the highest Global Atmospheric Watch (GAW) station, which is about 130 km southeast from the sampling site (see Figure 1). Considering that the BCAeth values from an Aethalometer might be too high in this region, the actual BC value at Waliguan may be even lower. The high BCAeth concentrations at Waliguan were attributed to air masses from northeastern cities (Ma et al., 2003). This is different from QHL, where the higher rBC concentrations are likely caused by local pollution

trapping. Therefore, although QHL and Waliguan are close to each other, the different local geographies likely cause different BC loadings at these two sites."

7. Lines 10-22, page 21954. As to the diurnal variation, I did not see apparent high concentrations around 08:00 LST corresponding to local residential activities as the authors stated, especially when considering the uncertainties of the hourly averages. The authors should also avoid using the wording "heavily influenced by local rBC sources", because they actually did not have enough evidence to say that.

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). The median values were used to illustrate the diurnal variation, and there is also a slight peak around 8am, which indicated local influence. This small peak is visible in the median values, yet is quite minor. We have revised the text to avoid overstating these observations.

8. Lines 17-19, page 21955. How was the 30-nm layer estimated for this campaign? While the authors citing Schwarz et al. (2008) is fine, it may not be good for this campaign, because of the different instrumental configuration and mixing state identifying methods.

Reply: The 30-nm value is a rough estimate based on Schwarz et al, 2008, and was found to be independent of the analysis approach (between the Schwarz et al., 2008 analysis, and the simpler analysis shown here; unpublished work by A. Perring as part of her 2011 GRL paper). Because LEO data were of insufficient quality, we are not aware of any other approach to determining the sensitivity. However, we have added a sentence clarifying that the absolute value of the internally mixed number fraction is not as significant as its relative value between different air masses.

9. Figure 6. I do not think there is useful information as the authors discussed, as the regression is really too weak. The interpretation of this figure in the aspect of sources is too arbitrary and without effective support. The text between lines 9-15, page 21956 is only kind of assumption.

Reply: We have deleted Figure 6 and revised the associated discussion in the new text.

10. Lines 21-29, page 21957. The calculation of MAC in this part is of little significance. Firstly, the authors should very clearly state that the MAC talked about in this paper refers to the MAC of BC on an aethalometer filter, not the true MAC in the real atmosphere. While the authors already concluded that "non-BC aerosol species strongly affect the Aethalometer at QHL" in line 11, they then made a contradictory assumption that "assuming that rBC is the only absorbing component in the ambient aerosol" in line 25. Therefore, the MAC calculated here is useless in terms of reflecting the BC property in the air. Actually, the MAC here should be only regarded as a correction factor for aethalometer measurement.

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 logical 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 to correct rBC loadings as measured by the SP2 for the Qinghai lake region.

11. Lines 7-18, page 21959. Since CO is a long life-time species, the background level of CO would largely determine the BC/CO ratios, which should be talked about.

Reply: We have added discussion about background level of CO in the new text and converted all our results using delta-CO (i.e., CO concentration with the background removed). 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."

In terms of identifying sources using BC/CO ratios, I believe that BC/delta-CO is more frequently used in the literature as it can exclude the influence of the background CO.

Reply: We agree with Reviewer #2, and have revised this section using the BC/delta-CO ratio in the text and in calculations.

The authors should carefully go through the literature and select effective index. Also, the authors should make a table to clearly list the relevant results in the literature for better comparison, with necessary information included, like sampling time, site, method, etc.

Reply: We have added a new comparison table with necessary information in the revised text (see Table 3). 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)."

Minor concerns: 1. Line 14, page 21949. condensation of emitted gases => condensation of emitted semi-volatile gases.

Reply: We have made this change as shown in Lines 63 and 66 the text: "As emissions age, BC becomes more internally mixed through a variety of mechanisms including condensation of emitted semi-volatile gases or those produced in photochemical oxidation processes (Oshima et al., 2009; Petters et al., 2006)."

2. Line 16, page 21951. "entering the instrument to below either 1.0-μm or 2.5-μm diameter depending on setup." When for 1.0 and when for 2.5? Why? How would this strange setup affect the results?

Reply: We do not believe this setup is strange – impactors are often used to restrict sampled aerosol to the fine mode. However, because we wanted to see if the dust at QHL influenced the BC observed by the SP2 and Aethalometer measurements, we chose to vary the cut-off point, finding that there were nearly no differences between the Aethalometer and SP2 results for PM1.0 and PM2.5. We have added some sentences to discuss this setup as shown in Lines 384 to 390 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. A priori, we would expect that if dust aerosol were contributing strongly to the Aethalometer scaling factor, then the change in sampling would, in fact, result in a shift. Hence dust likely is not a strong contributor to total aerosol absorption in the QHL boundary layer in this season."

3. Line 7, page 21953. The QHL conc. was compared with an urban atmosphere, Shenzen. How far between the two sites? Any significance for such a comparison? There are also similar problems in the other parts. Any comparison should produce some scientific information, not just list data.

Reply: Shenzhen is an urban city located in the southeast China, which is about 3000 km away from QHL. We have changed these comparisons to some high altitude stations to make the comparison more relevant (see Table 2 in the revised text). Also, we note that the contrast between BC mixing state and concentration from urban sources and the sources in Qinghai Lake is intrinsically interesting.

4. Line 10, page 21955. Any more explanation for the small second mode?

Reply: We do not have concrete information about the source of this mode However, the persistent secondary mode may be associated with the atypical emission sources and combustion conditions found in the Qinghai regions (i.e. yak dung and other biofuel combusted at high altitude). Testing this assumption would require direct research into rBC mass size distributions generated from these sources/conditions.

5. Lines 26-28, page 21955. "Variability in this metric was larger during the day than at night, suggesting that nighttime aerosol was less influenced by individual sources for short times." This sentence should be rephrased to make the point clear.

Reply: The sentence has been modified to read: "The variability in rBC mixing state was observed to be larger during the day than at night, suggesting that nighttime aerosol was less influenced by contributions from the presumably more varied individual sources that appear, from the diurnal cycle, to be sampled during the day."

6. Lines 15-20, page 21957. Since the BC at QHL has been found significantly influenced by local sources, it is not safe for the authors to state that the GAW site, 130 km away, has a similar situation for aethalometer measurement. This statement should be removed.

Reply: Reviewer #2's point is well taken. We have revised this discussion to clarify that our conclusions about the Aethalometer data at GAW (other than our concerns about its uncertainties) are largely speculative.

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