Reply to review comments

Reviewer #1:

This paper characterizes the Absorption Ångström exponent (AAE) values of aerosols at urban and rural site in the PRD region of China based on the measurements using a three-wavelength photoacoustic spectrometer and reports the AAE values for pure black carbon (BC) and contributions of light absorption by brown carbon (BrC). This manuscript includes sufficient originality, and the topic seems to fit the journal. I recommend publication to ACP after the points below have been addressed.

Major comments:

Question 1 The evaluation of accuracy for the measurement of absorption coefficients is critically important in this study. Therefore, more detailed information on the calibration procedure and uncertainties for the measurements of absorption coefficients at each wavelength should be added. What kind of particles did you use for calibrations? How the theoretical value of 1 was determined? If the authors used similar methods with those used in the previous studies (e.g., Arnott et al. 2010, Nakayama et al. 2015), it would also be better to refer them.

REPLY:

1) More detailed calibration information has been added into section 2.3, as below:

"The calibrations of PASS-3 for flow rate, laser power, and absorption were conducted following the standard procedures provided by the operational manual, which were also applied in relevant previous studies (Arnott et al., 2000; Lan et al., 2013; Nakayama et al., 2015). Firstly, the flow rate of sample air was calibrated by a soap film flow meter, with the results shown in Table 1; secondly, the laser power for each wavelength was calibrated by a laser power meter and the error in Table 1 indicated the reading difference between the laser power meter and the laser detector inside the instrument; thirdly, the light absorption calibration was performed by measuring highly absorbing NO_2 (200 ppm) at 532 nm. Then a good linear regression (with R^2>0.99) of the calculated extinction coefficient of NO_2 and the measured light absorption was established. Since the scattering of gas is negligible, the extinction of NO_2 should be very close to the absorption of NO_2, and thus the slope of the fitting curve should be very close to 1, as shown in Table 1. The detection limit of aerosol light absorption with 2 s time resolution was 10, 10, and 3 Mm^{-1} at 405, 532, and 781 nm, respectively."

2）More description of uncertainty calculation has been added into section 2.4, as below:

"The uncertainty of the absorption measurement at a wavelength (U_{Abs_λ}) includes the fit to the absorption calibration slope, the electronic noise within the instrument (Lack

et al., 2012a), as well as the drift correction of signals, and can be expressed as below:

$$\Delta X = \sqrt[2]{(\Delta X_{\text{calibration}})^2 + (\Delta X_{\text{noise}})^2 + (\Delta X_{\text{drift}})^2} \quad (5)$$

$$U_{\text{Abs}\_\lambda} = \Delta X / \text{Abs}_\lambda \quad (6)$$

Where $\Delta X_{\text{calibration}}$ is derived from the uncertainty of the regression slope under a 95% confidence level (p); ΔX_{noise} can be calculated through uncertainty propagation of noise equivalent absorption measured by PASS-3 every 2 minutes; ΔX_{drift} is the standard deviation of the averaged baseline absorption of filtered air. Finally, ΔX is divided by Abs_λ to get the corresponding relative uncertainty (U_{Abs_λ}). In result, the relative uncertainties of the absorption measurements at the three wavelengths were ~1.2% for the campaign of urban$_{\text{-winter}}$, 0.8–0.9% for the campaign of urban$_{\text{-fall}}$, and 1.5–1.6% for the campaign of rural$_{\text{-fall}}$."

Question 2 It is also unclear what do the values of error in the laser powers and slopes in Table 1 mean and how did you decide these values. In addition, it is amazing that the all values for Rural$_{\text{_fall}}$ and Tunnel is same in Table 1. How many times did you calibrate the instrument?

REPLY: Clarification has been made in the revised section 2.3 as in the reply to Question 1. The same calibration values of tunnel and rural$_{\text{_fall}}$ were a copy-paste error, which has been corrected now. Calibrations were conducted both at the beginning and at the end of a field campaign in our study.

Question 3 If you used the soot particles for calibration, the systematic uncertainties of the calibration factors for scattering measurements also influence to the determination of calibration factors for the absorption measurements. The estimated systematic uncertainties of the calibration factors for absorption measurements at each wavelength are needed to be taken into account to estimate the uncertainties for AAE and AAE_BC, as well as for the light absorption and contributions of BrC. In addition to the systematic uncertainties, influence of drift of the signals in 30 min should also be added in eq. (5).

REPLY:

1) The author used highly absorbing NO_2 (200 ppm) for absorption calibration and scattering of gas was negligible and thus needs not to be considered.

2) The influence of drift has been added in the total uncertainty calculation as suggested. The details are given in the reply to Question 1.

Question 4 In section 3.2 and 3.3, the authors reported that the linear relation between AAE and r_org/bc was obtained for all cases. However, I think the linear relation between AAE and r_org/(bc+org) may be expected, if a simple mixing rule is assumed.

REPLY: Firstly, the authors think that the meaning of the linear relation between AAE and r_org/bc is very similar to that between AAE and r_org/(bc+org). When org=0, they all get an intercept representing the AAE for pure BC. Secondly,

converting the absorption at 781 nm to the mass concentration of BC will introduce additional uncertainties because mass absorption efficient (MAE) needs be assumed. Thirdly, the ratio of OC and EC was also used to explore the correlations with ambient AAE values in a previous study (Utry et al., 2014), and proved to be a good index of the relative amount of OC and EC. Therefore, we believe that using r_org/bc is a better choice.

Question 5 The plot between AAE and OC/EC was used in Utry et al. (2014). I recommend to adding some information and discussion in the introduction and discussion sections.

REPLY: The following discussion has been added into the text as recommended.

1) In the introduction: "Some previous studies showed that ambient AAE was significantly affected by aerosol OC/EC (organic carbon/elemental carbon) ratio, suggesting a potentially important role of organic matter in aerosol light absorption (Utry et al., 2014)."

2) In section 3.2: "Utry et al. (2014) also revealed a strong correlation between AAE and aerosol OC/EC at an urban site in Hungary, where OC was mainly emitted from wood burning and contained a large amount of BrC"

Question 6 In section 3.2, the authors reported the difference in AAE_BC values at SZ site and those at HS site and pointed out the difference of sources (fuel combustion and biomass burning) as a source of the difference of AAE_BC. Although it is interesting findings, more detailed discussion on the relationship between source (size, shape, and mixing state of BC) and AAE_BC value should be added.

REPLY: More discussion about the difference of $AAE_{\_BC}$ between the urban and rural sites has been added as below:

"In PRD, Lan (2013) ever found that the BC diameters of both vehicular exhaust and biomass burning were generally above 100 nm, using a single particle soot photometer to measure, and the BC diameters of vehicular emissions were even larger. On the other hand, Gyawali et al. (2009) found that the AAE value would decrease as the BC diameter increases in the range of 0.1–1 μm by theoretical modeling. Therefore, the larger $AAE_{\_BC}$ obtained at the rural site could be a result of the smaller BC diameters of biomass burning in PRD."

Question 7 In section 3.4, the authors reported that "BrC could play a more important role under polluted condition". I recommend to adding some discussions on the source of BrC in SZ site in winter. It seems to be nice to calculate the AAE values for BrC for the discussion of the source of BrC.

REPLY: The following relevant information and discussion has been added into section 3.4 as recommended.

1) "The higher BrC contribution in the $urban_{\_winter}$ campaign than that in the $urban_{\_fall}$ campaign suggested that BrC could play a more important role in polluted continental air mass, since Shenzhen had a higher frequency of continental air mass from the

north than that of marine air mass from the south in winter."

2) "On the other hand, the highest BrC contribution at 405 nm in the rural$_{-fall}$ campaign could be attributed to the influence of biomass burning in the farmland nearby, which was supported by the biggest difference of BrC absorption between 405 and 532 nm: the AAE_{405_532} of BrC was calculated to be 1.7, 2.5, and 4.3 for the campaigns of urban$_{-winter}$, urban$_{-fall}$, and rural$_{-fall}$, respectively. High AAE_{405_532} was found to be a feature in the biomass burning simulation experiments, as in Table 4. Especially strong absorption at 404 nm of biomass burning-emitted BrC was also found by Lack et al. (2012b). The lowest AAE_{405_532} of the urban$_{-winter}$ campaign indicated that fossil fuel combustion, rather than biomass burning, seemed to be the major source of BrC in Shenzhen in winter."

Question 8 As authors suggested, in addition to BrC, size distribution, mixing state, and fractal dimension of BC particles can affect to the observed AAE values. Because all of the size distributions, mixing state, fractal dimension, and r_org/bc can vary depending on sources of BC, the effect of size distribution, mixing state, and fractal dimension on AAE value may depend on r_org/bc. In this case, the intercept values of the AAE vs. r_org/bc do not represent the typical AAE values for BC. I would like ask to consider this point.
REPLY: This point has been clarified in the revised text in section 3.2, as below:
"It should be noted that previous studies showed that AAE of ambient aerosol can also be influenced by a couple of other factors, such as size distribution, mixing state, and fractal dimension of BC particles (Levin et al., 2010; Gyawali et al., 2009; Scarnatol et al., 2013; Bond et al., 2006), but it is quite complicated and almost impossible to consider the influence of all these factors simultaneously. Scarnato et al. (2013) also pointed out that it is very difficult to clarify the relationship between AAE and aerosol morphology and mixing state due to quite complicated mechanisms in real cases. In this study, this issue was just simplified using a univariate regression analysis to explore the relationship between ambient AAE and organic aerosol. In result, the good correlations obtained in Fig. 2 indicated that BrC itself could be the dominant factor leading to the variation of AAE, and thus the extrapolated intercept was a good surrogate for $AAE_{\_BC}$. The influence of other factors could be partly reflected by the error bars of the data points in Fig. 2 and the estimated uncertainty of the intercept (i.e., U_{AAE_BC})."

Minor comments:
Question 1 Page 28454, lines 12-13 and page 28466 lines 17-18: I think it better to revised the sentence from ".. AAE values … at 405 nm, and … at 532 nm" to ".. AAE values … between 405-781 nm, and … between 532-781 nm".
REPLY: The suggestion was taken and the sentences have been modified.

Question 2 Page 28459, lines 12-13: Are these detection limit values for 2min data?

REPLY: These detection limit values are for 2s data, which has been stated in the revised sentence.

Question 3 Page 28461, lines 20-22: Please add the uncertainties and their definition.
REPLY: The sentences have been revised as below:
"The campaign-average ambient AAE_{405_781} values (± relative uncertainties) were calculated to be 1.05 (±0.01%), 0.92 (±0.10%), and 1.22 (±0.002%), respectively, for the $urban_{\text{-winter}}$, $urban_{\text{-fall}}$, and $rural_{\text{-fall}}$ campaigns, while those of AAE_{532_781} were 0.98 (±0.01%), 0.82 (±0.05%), and 1.00 (±0.001%), respectively. The corresponding uncertainties in the brackets were calculated through the uncertainty propagation of the absorption measurement uncertainties based on Equation 1. The relatively higher values of AAE_{405_781} and AAE_{532_781} in the $rural_{\text{-fall}}$ campaign might be related to the biomass burning in the farmland surrounding the HS site."

Question 4 Page 28466 line 16: "the absorption of pure BC" => "the AAE of pure BC"?
REPLY: Corrected.

Reviewer #2:

A three-wavelength photo-acoustic soot spectrometer, an aerosol mass spectrometer, and an aerosol chemical speciation monitor were used to measure and show the relationship between the relative abundance of organic aerosol to black carbon and its relationship to the Absorption Angstrom Exponent (AAE) in ambient samples collected in urban and rural areas in the Pearl River Delta region of China. Since the AAE is widely used in attributing the light absorption of brown carbon at shorter wavelengths, the method was improved by statistical analysis and applied to the collected data. The findings from this study are relevant to the readers of ACP as well as the air pollution and aerosol communities. The manuscript includes enough discussions of the limitations and implications of the study. Therefore, I recommend publication of this manuscript upon consideration of the suggested revisions listed below.

General Comments
- Be consistent in the use of brown carbon or BrC, and Absorption Angstrom Exponent or AAE.
- Better tie results with what they mean. It is difficult to follow when several numbers are listed in a long sequence.
- Choose words that are more descriptive of what is being said, or follow up with a brief explanation. Some choices are vague and leave the reader to wonder in what context they are being applied, or are being related to. Example: levels, comparatively, and convenient.
-Remove words that do not add any significance to the text.

- Be consistent with tenses.
- Check for the proper use of “in”, “by”, “on”, etc.
- Cross-referencing different sections within the text makes it for a difficult read.

REPLY: The above suggestions were all taken and the relevant sentences have been carefully modified in the revised manuscript.

Specific Comments (by line)

- 55, Unclear when said that, “BrC aerosol could contribute more than 65 and 15% light absorption at 370 nm”

REPLY: The sentence has been rephrased in the revised text as below:

“BrC aerosol could contribute more than 65% of light absorption at 370 nm and 15% at a mid-wavelength (Favez et al., 2009).”

- 60, Related to line 45, but too far apart.

REPLY: The relevant sentences have been moved closely to each other in the revised text.

- 63, The authors could expand on why East Asia in one of the five regions of atmospheric brown clouds.

REPLY: The suggestion was taken and the sentences have been modified in the revised text as below:

“South and East Asia are typical regions of atmospheric brown clouds (ABC) (Alexander et al., 2015). Biomass burning has been recognized as a significant contributor to ABC, including forest burning, crop waste burning, traditional religious activities and residential burning in those countries like India, China, Thailand, etc. (Venkataraman et al., 2006; Yan et al., 2006; Chakrabarty et al., 2013; Chakrabarty et al., 2014; Huang et al., 2012). ”

- 75, What is it meant by universal?

REPLY: It has been revised to “widely used”.

- 110, What type of “little local emission”

REPLY: It has been revised to “little local fossil fuel combustion emission nearby”

- 117, It is stated that tunnel experiments were performed three times. Does that mean measurements were done three times inside each tunnel? I only see two tunnels, the Tanglanshan and the Jiuweiling tunnel. Is there another one? Please reword this sentence.

REPLY: The sentence has been modified in the revised text as below:

“We performed tunnel experiments three times in Shenzhen urban areas: twice in the Tanglangshan tunnel (TL) and once in the Jiuweiling (JW) tunnel.”

- 128, Rearrange order of the sentence to better describe why biomass burning simulation experiments were done in the combustion laboratory. Although it is known that biomass burning is a great source of BrC, as it is, it appears that biomass burning experiments were done without a purpose.

REPLY: The relevant sentences have been modified in the revised text as follows:

"Moreover, since biomass burning is recognized as an important source of BrC (Ramanathan, et al., 2007) and is a popular source in rural areas in PRD, especially during the harvest season (He et al., 2011; Zhang et al., 2013), we performed biomass burning simulation experiments in a combustion laboratory to study the spectral dependence of aerosol light absorption in biomass burning smoke."

- 138,139, Why was the water boiling test protocol developed by the University of California used?

REPLY: We just refer to the protocol to make our burning processes normalized and more reliable.

- 152, Please clarify how the data was processed and how AMS data was related to PASS-3 data. Remove "in the later data analysis and discussion."

REPLY: The data processing has been clarified in the revised text as below:

"Then, we processed the 2 min time resolution data of absorption at three wavelengths for half hour averages and made further data analysis based on the half hour time resolution datasets. On the other hand, we also processed the 10 min time resolution data of organic aerosol derived from AMS or ACSM for half hour averages to explore the relationship with the absorption datasets."

- 163, Expand on how the ACSM is a convenient version of the HR-ToF-AMS.

REPLY: The relevant sentences have been expanded and rearranged in the revised text as below:

"An aerosol chemical speciation monitor (ACSM) (Aerodyne Research, MA, US) was used at the HS site and in the tunnel experiments with a time resolution of 10 min. In comparison with HR-ToF-AMS, ACSM was smaller and more convenient to be transported to field sampling sites and setup in a monitoring car with limited space. The detailed description of ACSM was given by Ng et al. (2011)."

- 169-171 What are satisfied results. Please also reword this sentence.

REPLY: The words "satisfied results" were removed and the sentences have been reworded as below:

"The calibrations of PASS-3 for flow rate, laser power, and absorption were conducted following the standard procedures provided by the operational manual, which were also applied in relevant previous studies (Arnott et al., 2000; Lan et al., 2013; Nakayama et al., 2015). Firstly..."

- 178, Table 1. I see how the calibration adds to the validity of the data, but I would

consider adding such information to a supplement and not to the main text.
REPLY: As reviewer #1 cared about the calibration information very much, the authors think it is better to keep the calibration part in the main text.

- 224, Please explain unfavorable meteorological conditions in PRD.
REPLY: The reasons have been added into the revised text as below:
"The higher aerosol pollution observed in the winter could be attributed to the unfavorable meteorological conditions in PRD in the winter, when the air mass came from the polluted northern continent with a overwhelming frequency and the atmospheric boundary layer became shallower due to lower ambient temperatures (Huang et al., 2014)."

- 226, Please consider a better location to compare the data with. I do not see how Denver, CO relates to the PRD region.
REPLY: The comparison with Denver has been deleted in the revised text. No comparable study has been found in the literature currently and thus better comparison cannot be made.

- 231, Reword this sentence – "suffering from the severe polluted outflow air from its northeastern the Guangzhou..."
REPLY: The sentence has been modified in the revised text as "suffering from the polluted air outflow from the northeast, where the megacity of Guangzhou was located, during the fall and winter seasons (Gong et al., 2012)."

- 233, Refer to HS again, if this is the place you are still talking about.
REPLY: The suggestion was taken and the sentence has been modified in the revised text as "The relatively higher values of AAE_{405_781} and AAE_{532_781} in the $rural_{-fall}$ campaign might be related to the biomass burning in the farmland surrounding the HS site."

- 246, Clarify if dust events happened. It is mentioned that there were no dust events, but the authors follow to say that they scarcely happened.
REPLY: The sentence has been modified in the revised text as "there was no dust event during the three campaigns"

- Fig. 1, Explain why there are gaps in the data in Urban-winter (January) and Urban-fall (September).
REPLY: The data missing was due to the failure of power supply or pump repairmen.

- 260 - 271, Seems to be redundant information. The information was already stated previously.
REPLY: The first sentence has been removed in the revised text, while other sentences are remained because in the previous part, the authors just gave a brief introduction of our method.

- 299, This is the third time it has been stated that the assumption of AAE = 1 for BC is not reasonable. I believe this point has been made.
REPLY: The sentence has been deleted in the revised text.

- 328-344, Please reword.
REPLY: We have modified this paragraph to make it clearer.

- 350-359, Data is too sporadic. It is difficult to follow what set of data goes with what site or wavelength.
REPLY: The relevant sentences have been modified in the revised text as below:
"In result, the average light absorption of BrC at 405 nm was 3.0, 1.4, and 3.9 Mm^{-1} in the $urban_{-winter}$, $urban_{-fall}$, and $rural_{-fall}$ campaigns, respectively, contributing 11.7%(±5%), 6.3%(±4%), and 12.1%(±7%) of the total aerosol light absorption, respectively. Here, the values in the brackets were the relative uncertainties calculated through Equation 4. The average light absorption of BrC at 532 nm was 1.9, 0.7, and 1.2 Mm^{-1} in the $urban_{-winter}$, $urban_{-fall}$, and $rural_{-fall}$ campaigns, respectively, contributing 10.0%(±2%), 4.1%(±3%), and 5.5%(±5%) of the total aerosol light absorption, respectively."

- 363, What is it meant by level?
REPLY: The word has been modified as "fraction"

Technical Comments
- Figure 2, Any reason why when r_org/bc reach 2 the AAE's drop for all cases?
REPLY: The authors do not see the drop for all cases, although there are a few dropping points, which are believed to be influenced by random errors in this study. More measurements are needed to explore whether the dropping points represent some special mechanisms.

- How many points were used for the figures?
REPLY: For each field campaign, we processed the original data to half hour averages and thus have at least 700 data points of light absorption at each wavelength. Based on these data, further data analysis was made, including plotting the figures. This information has been added into section 2.2 in the revised text.

- Table 4, Please specify the burning modes for all biomass types. My understanding from looking at the table is that only the modes for Peanut stalk and Short straw are specified. Perhaps arranging the AAE's in ascending or descending order would make it easier for the reader to compare results.
REPLY: We have specified burning mode for each biomass type and the data in the table was arranged in descending order according to the $AAE_{405\text{-}532}$ values.