

Correspondence to Referee # 4

Thank you very much for your constructive comments. The general comments are overlapped with specific comments, for which responses are given below.

1. Page 20522, Lines 15-18. “Our measurements of EC confirmed the definition of EC1 as char-EC emitted from smoldering combustion and EC2+3 as soot-EC generated from higher-temperature combustion such as motor vehicle exhaust and coal combustion.” I know that this is from Han et al.’ study. I think that here the references should be cited.

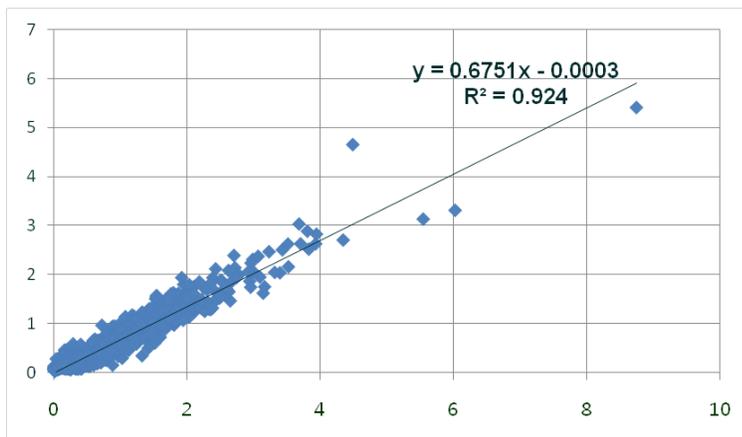
Han et al. (2007) will be added to the abstract.

2. Page 20524, Line 19, “Therefore, BC is considered as light-absorbing EC and is generally lower in concentration than EC.” I cannot agree with this point. BC and EC are just two terms that should be used to define the same material in the atmosphere. The difference used in the literature comes just from the methods that used for the quantification of this kind of material.

As you mentioned, BC and EC call the same material but were defined differently based on different quantification methods: BC by optical method and EC by chemical method. Therefore, we could get different values for EC and BC, even though we run two instruments side by side.

There is detailed explanation regarding this matter in the manual of aethalometer that has been most widely used for BC measurement (Magee Scientific, http://mageesci.com/support/downloads/Aethalometer_book_2005.07.03.pdf).

Also, attached is a figure showing continuous measurements of EC at Gosan from October 2009 to January 2010. The measurement was done by Sunset instrument (Model 4), which reports two types of EC: “thermal EC” and “optical EC”. The linearity (r^2) is excellent between “optical EC” and “thermal EC” but the slope was not unity. The disagreement is greater for higher EC concentrations. If matrix effect is removed, the agreement between BC and EC would be much improved.



This sentence was reworded as follows: **“Therefore, BC and EC may show slightly different concentrations due to their different quantification techniques.”**

3. Page 20526, Line 20, “most of these studies : : :...were conducted during a specific season, such as spring (Lee et al., 2007; Shen et al., 2007), spring and early summer (Aggarwal and Kawamura, 2009), or fall and winter (Cao et al., 2005).” This seems not the case. Lots of studies in northeast Asia have been done not just during a specific season but from whole year or several year observations.

The paragraph of the line 14-25 in page 20526 will be rewritten with more references as follow:

In recent decades, carbonaceous aerosols, both EC and OC, have been measured in many regions of Northeast Asia, including South Korea, China, and Japan (Ohta et al., 1998; Kim et al., 2000; *He et al., 2001*; Park et al., 2001; *Ye et al., 2003*; Cao et al., 2005; Hagler et al., 2006; Lee et al., 2007, 2008, 2009; Shen et al., 2007; *Zhang et al., 2007*; Moon et al., 2008; Aggarwal and Kawamura, 2009). The areas covered have included urban areas (*He et al., 2001*; Park et al., 2001; *Ye et al., 2003*; *Zhang et al., 2007*; Lee et al., 2009), developing regions (Hagler, 2006), and sandlands (Cao et al., 2005; Shen et al., 2007). *Most* of these studies focused on *PM_{2.5} through a year (He et al., 2001; Ye et al., 2003) and PM_{2.5} or PM₁₀ during* a specific season, such as spring (Lee et al., 2007; Shen et al., 2007), spring and early summer (Aggarwal and Kawamura, 2009), fall and winter (Cao et al., 2005), *or winter (Zhang et al., 2007)*. There have been few year-round studies of both fine and coarse aerosols, particularly at a site where it is feasible to monitor long-range transport and the atmospheric processes involving air pollutants emitted from the Asian continent.

Ye, B., Ji, X., Yang, H., Yao, X., Chan, C. K., Cadle, S. H., Chan T., Mulawa, P.A. : Concentration and chemical composition of PM_{2.5} in Shanghai for a 1-year period, Atmos. Environ., 37, 499-510, 2003.

Zhang, R., Cao J., Lee S., Shen Z., Ho K. : Carbonaceous aerosols in PM₁₀ and pollution gases in winter in Beijing, Journal of Environmental Sciences, 19, 564–571, 2007.

He, K., Yang, F., Ma, Y., Zhang, Q., Yao, X., Chan, C. K., Cadle, S., Chan, T., Mulawa, P. : The characteristics of PM_{2.5} in Beijing, China, Atmos. Environ., 35, 4959–4970, 2001.

4. Page 20529, Line 18, “A considerable fraction of mass other than water-soluble ions, OC, and EC was possibly due to trace metals and silica, which were not measured.” I would like to see a reference here.

A reference was added to this sentence:

“A considerable fraction of mass other than water-soluble ions, OC, and EC was possibly due to trace metals and silica, which were not measured (*Moon et al., 2008*).”

5. Page 20529, Line 25. “The difference in OC/EC ratios is likely due to relatively higher EC concentration than OC in this study area.” It seems that this sentence is meaningless. Compared with other studies, the EC concentration in this area is not very high.

This sentence will be cut out in the manuscript.

6. Page 20532, Line 19. “Charred EC” should be “char EC”.

Line 28: It will be corrected to “char EC”.

7. Page 20534, Line 13, “It is likely due to the formation of secondary organic aerosols from biomass burning.” However, EC is not influenced by the formation of SOA. In addition, where is the biomass burning? Local or regional?

The paragraph of the line 9-16 in page 20534 will be rewritten as follows:

In this study, carbonaceous fractions were higher in summer and fall under low mass and sulfate concentrations but lower in winter and spring under high mass and sulfate concentrations. Particularly, the OC and EC fractions of PM1.0 were highest in fall. It is *likely associated with biomass burning from nearby continents*. In spring, biomass burning also takes place but its effect is diluted by high anthropogenic emissions of sulfur and nitrogen. *Furthermore*, most of the fall samples were taken under stable atmospheric conditions with little *precipitation*, which were favorable for the formation and buildup of *EC and secondary OC particles*.

In fall, we often observed enhanced concentrations of aerosols at Gosan, which was influenced by fires mostly from agricultural burnings in China and Korea. The local effect would be much less, but can't be ruled out because there are farming areas close to the station.

8. Page 20534, Lines 21-24, I wonder if there should be an introduction of the Absorption Cross Section Calibration Option. Or there should be a discussion about the Absorption Cross Section Calibration Option.

Absorbance (A) measured by Aethalometer is converted to the amount of black carbon loading on filter [g/m^2] using the following equations:

$$A(\lambda) = C(\lambda) * d(B)$$

$$\sigma(\lambda) = C(\lambda) * 100$$

Specific attenuation cross-section for the aerosol black carbon deposit on the filter [m^2/g]

$$d(B) = A(\lambda) / \sigma(\lambda)$$

Surface loading on filter [g/m^2]

The specific attenuation cross section σ is dependent on wavelength and inversely proportional to the wavelength (λ , nm). Here, we used the “Magee BC calibration” for $\sigma(\lambda)$.

$$\sigma = 14625 / \lambda \text{ [m}^2\text{/g]}$$

For 880 nm, σ is $14625/880 = 16.619$.

Then $d(B)$ is multiplied by aerosol collecting spot area of filter [cm^2] and divided by flow rate of air through filter [l/min] and sampling period [min], resulting in BC concentration [ng/m^3].

These are well documented in Hansen (2005), an operating manual for aethalometer used in the experiment.

The sentence in the line 21 on page 20534 was rewritten with adding the calibration option for 880 nm as follows:

The EC was compared with BC measured by Aethalometer (Fig. 6a). In contrast to EC quantification by thermochemical analysis, BC concentration was obtained by optical analysis, which estimates light absorption of particles and converts it into mass concentration **using a mass specific attenuation cross-section of 16.6 m^2/g at 880 nm (Magee BC calibration, Hansen, 2005).**

Hansen, A.D.H., The Aethalometer TM, Magee Scientific Company, Berkeley, California, USA, 2005.

9. Page 20535, Lines 10-11. I would like to suggest references here.

Two references will be added to the text: Han et al. (2007, 2010).

10. In Sec. 4. (such as Page 20537, Line 13), Han et al. (2009, Atmospheric Environment) have also studied the PM_{2.5} char and soot concentrations in winter and summer from 14 cities in China. I would like to suggest a comparison of char and soot concentrations here. This will give a general picture of the difference in char and soot concentrations between China and South Korea.

The paragraph from the line 25 in page 20536 to the line 21 in page 20537 will be rewritten:

The soot-EC/char-EC ratio depends upon the mixing function of the different sources: motor vehicle emissions and possibly grass burning result in higher soot-EC/char-EC ratios, while wood combustion, particularly biomass burning by smoldering at low temperature, produces lower soot-EC/char-EC ratios (Chow et al., 2004; Chen et al., 2007). In coal combustion, this ratio can be very low or relatively high, depending on the type of coal (Han et al., 2010). To apply the definitions of Han et al. (2010) to our study, we compared seasonal EC₂₊₃/EC₁ ratios (Fig. 7). Seasonally averaged EC₁ concentration was highest in winter and lowest in summer. This order is very well matched with the intensity of continental outflows. In contrast, EC₂₊₃ did not show clear seasonal variation, but the highest concentrations were found in spring and the lowest

concentrations in fall and winter. As a result, the ratios of EC₂₊₃/EC₁ were highest in summer, when **air** masses reached at Gosan from the east passing through South Korea or/and Japan with the least influence by the continent and greater influence by South Korea and Japan (See Fig. 9e). ***In fact, the EC₂₊₃/EC₁ ratio of 1.25 in summer is comparable to the ratio of 1.67 for motor vehicle exhaust (Chow et al., 2004).*** EC₂₊₃ emitted during winter and spring may have remained suspended in the atmosphere due to its smaller size and kept its proportion through increased motor vehicle sources from South Korea and Japan, in spite of the wet scavenging caused by frequent precipitation during summer. Han et al. (2010) collected **PM_{2.5}** EC particles in Xi'an, a sandland in China, of which result **was** consistent with our observation that EC₁ had a minimum level in summer, but in contrast to our observations, the level of EC₂₊₃ was also minimum in summer. Higher EC₂₊₃ concentrations during summer in our data imply increased influence of South Korea and Japan on EC concentrations. Hence, EC₂₊₃ is considerably enhanced, but EC₁ is markedly less because of limited contact with industrial regions in China. ***In other study by Han et al. (2009) that measured PM_{2.5} EC in 14 Chinese cities during summer and winter period, the lower ratios of EC₂₊₃/EC₁ were found at the sites associated with industries in the Eastern coastal region of China, while the opposite trend was observed at the sites in Northern and Southern China with the least industrial effect.*** Therefore, our study supports the classification of char-EC and soot-EC proposed by Han et al. (2010), and the ratio of EC₂₊₃ to EC₁ can serve as an indication of a continental effect.

11. Also in Sec. 4. From Table 2, it seems that soot concentration in PM_{1.0} (0.46 in average) is a little higher than that in PM_{2.5} (0.40) and PM₁₀ (0.30). I think that there should be an explanation for this. In my view, I think that this is associated with the fact that amounts of ions and metal oxides exist in coarse particles, which would influence the carbon and soot energy stability in thermal oxidation. Please refer to Novakov and Corrigan, 1995, *Mikrochim Acta* (association with the metal oxides), and Han et al., 2009, *Chemosphere* (association with ions, perhaps especially with the nitrate in this study).

The reason for higher EC₂₊₃ mean in PM_{1.0} than those in PM_{2.5} and PM₁₀ will be given below the Table 2:

In our measurements, it was observed that averaged EC₂₊₃ in PM_{1.0} (0.46) was a little higher than that in PM_{2.5} (0.40) and PM₁₀ (0.30). It is likely associated with the amount of catalytically active mineral oxides (Fung 1990; Novakov and Corrigan, 1995; Elmquist et al., 2006). In particular, the presence of these components in coarse particles may lead to a catalytically mediated lowering of the activation energy for soot oxidation but not for char (Elmquist et al., 2006).

Fung, K.K. : Particulate carbon speciation by MnO₂ oxidation. *Aerosol Sci. Technol.* 12, 122–127, 1990.

Navakov and Corrigan : Thermal characterization of biomass smoke particles, *Mikrochim. Acta*, 119, 157-166, 1995.

Elmquist, M., Cornelissen, G., Kukulska, Z., and Gustafsson, Ö. : Distinct oxidative stabilities of char versus soot black carbon: Implications for quantification and environmental recalcitrance, *Global Biogeochem. Cycles*, 20, GB2009, doi:10.1029/2005GB002629, 2006.

12. Page 20541, the second paragraph. I cannot understand “OP : : :: : .. is likely a light absorbing aerosol”, as well as other relevant sentences. I think that OP comes from the pyrolysis of organics in carbon analysis process, and thus itself is not a kind of aerosol. For example, water soluble organics and volatile organics can result in more OP in carbon analysis process. However, these materials are not “light-absorbing organic carbon or a strong candidate for brown carbon”. I understand that these materials can come from biomass burning and thus may be associated with HULIS production. “The enhanced absorption of shortwave radiation” may be linked to the HULIS in samples, but not with the OP. Thus, I think that the statement “OP is light-absorbing organic carbon or a strong candidate for brown carbon” is wrong. Please check the manuscript and find the corresponding part associated with the description of OP, and to make sure that all these parts are correct.

Yes, you are right. OP is a sub-component of organic carbon that is a major constituent of aerosol particles. According to your comment, this paragraph was corrected and shortened.

OP is defined as charred OC having characteristics similar to those of EC1 that absorbs light. The BC absorption spectrum measured by Aethalometer revealed different tendencies among 7 wavelengths (Lim et al., 2011), for some of which the absorption of short wavelength (370 nm) was greater than that of longer wavelengths. It is generally known that soot, which is composed of submicron particles of grape-like clusters, exhibits strong light absorption characteristics with little spectral dependence (Schnaiter et al., 2003; Kirchstetter et al., 2004). In the present study, the enhanced absorption of shortwave radiation was clear for samples containing large amounts of OP. Thus, OP is likely to be linked with light-absorbing organic carbon such as HUILIS.

13. When discussing about the seasonal variations of chemical components, I would like to know based on what the seasons are separated. Also, the introduction of local human activities (with or without) would be useful.

We divided the sampling period from August 2007 to September 2008 into four seasons based on meteorological parameters (such as temperature, relative humidity, and wind direction and speed) and backward air mass trajectories: fall (October and November 2007), winter (December 2007 to February 2008), spring (March to May 2008), and summer (August 2007 and June to early September 2008). We used hourly averaged meteorological data and checked all air mass trajectories using NOAA Hysplit model and the Lagrangian particle dispersion model FLEXPART time by time for the whole experiment period. The four seasons were clearly

distinguished by these methods. The monthly variations of meteorological parameters (Figure 4) and selected air mass trajectories (Figure 9) reveal seasonal air mass characteristics: (a), (b), (c) and (d), and (e) are typical air trajectories observed in late fall to early spring, winter, spring, and summer, respectively.