Author response to referees comments

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Sources and light absorption of water-soluble organic carbon aerosols in the outflow from northern China

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We are grateful to all reviewers for their engaged, constructive and overall positive evaluation of our study. We particularly value the many thoughtful comments, which allowed us to improve the manuscript substantially. There are two major efforts/changes with the revised paper, both inspired by review comments. First, we have performed a substantial number of new experimental tests to find the optimal acidification procedure for both the bulk TOC and the WSOC fraction. Our standard approach of acid fumigation of the aerosol filters prior to water extraction, work-up and analysis (i.e., "pre-acidification" as in our isotope-WSOC methods papers, Kirillova et al 2010 *Analytical Chemistry*) was confronted by instead removing carbonate fraction by a mild acidification in situ to the Ag capsules at the end holding the water-extracted, freeze-dried sample prior to isotopic analyses (i.e, "post-acidification"). Results showed no difference in d13C for TOC whereas a slight but consistent depletion in d13C of the post-acidification samples were recorded. This slight method improvement did not affect any general conclusions but the results were slightly changed accordingly throughout the ms text and figures.
The second major test/improvement concerned the estimation of the relative direct radiative forcing of WSOC vs EC. To afford a first rough estimation of whether WSOC had an effect on the scale of EC, in the originally submitted ms, the solar radiation spectrum had overly simplistically (i.e., faulty) been approximated by a black body radiation model. In the revised paper, we have now implemented the AM1GH model (Levinson et al., 2010 Solar Energy), which accounts for the important absorption of the solar radiation by tropospheric ozone. This decreases substantially the relative radiative absorption of WSOC relative to EC at the Gosan Observatory to 2-10% of that due to EC. In addition to providing this quantitative estimate of the relative importance of light-absorbing WSOC (e.g. WS - Brown Carbon), the major contributions of the paper, as recognized by the reviewers, are (i) that a substantial fraction of WSOC in the Chinese outflow is of fossil origin (20-50%; established here by the first-ever 14C-WSOC for E Asia) and that aging appears to be a significant process for the WSOC in this region (established by 13C-WSOC data in combination with considering the expected trends from the kinetic isotope effect). We appreciate also the many other insightful review comments; each of these is addressed below in detail.

Referee #1

A nice paper that presents interesting data on the levels of brown carbon measured in aerosols based on spectrophotometric measurements of filter extracts from a region with a range of aerosol sources. The topic is of interest and the paper appropriate for this journal. I suggest publication after some editing to improve clarity (ie, use of terminology) and a more *complete analyses that makes use of more current published work. Issues are discussed in more detail below.*

Response: We are encouraged that the referee finds our data interesting and appropriate for eventual publication in ACP. We also thank the reviewer for the constructive suggestions on the improvement of our manuscript.

The WSOC is referred to sometimes as WS-BrC and at times just WSOC. It is not clear what the difference is. Consistent terminology would be helpful. Also, stating it as WS-BrC suggests that all the WSOC is light absorbing, which seems not true. Is the measured light absorption in the extracts correlated with WSOC concentration? I would think this is an analysis worthy of investigation and discussion.

Response: We agree that WSOC and WS-BrC were frequently used interchangeably with no clear distinctions. In the revised version of the ms the WSOC term is now consistently used throughout and the term water-soluble BrC is only very sparingly used when we specifically discuss the light absorptive properties of WSOC. This latter aspect is given less space in the revised ms, as it turns out to be less important, quantitatively, when using improved solar radiation model.

Also in response to review request, a plot of light attenuation coefficient (ATN at 365nm) vs WSOC concentration was added to the Supplementary Information (Figure S6, see below) including a short discussion in the main text. There is a correlation between the two parameters.

Pg 19629 line 13, was the triplicate analysis just analytical or were three separate sections of the same filter analyzed?

Response: For every triplicate analysis we extracted three different sections of the same filter. Hence, the reported uncertainties include both analytical and sub-filter variance. This is now clarified in the ms.

Section 3.2 is confusing. Rewording, especially the last line, may help clarify things. For example, is the last line of this section stating that recorded WSOC concentrations, averaged over the study, or averaged just during the pollution event were both similar to measurements in Chinese cities?

Response: The section has been edited for clarity (the change highlighted below) and now reads in full:

"During GoPoEx, WSOC contributed ~ 45-47% of TOC (Fig. 2C). When comparing total suspended particles (TSP) with $PM_{2.5}$ size fraction, about 80% of WSOC was found in the fine (<2.5 µm) fraction. The highest concentrations were found during the pollution event (10-12 March, 2.3 $\mu g \cdot m^{-3}$ in $PM_{2.5}$ and 3.5 $\mu g \cdot m^{-3}$ in TSP, Fig. 2), but elevated WSOC concentrations were also observed during the two dust events (15-16 and 21-22 March). The concentrations of WSOC during the GoPoEx period are within the range of what has been observed in China (0.4 – 9.6 $\mu g \cdot m^{-3}$ for $PM_{2.5}$) (Feng et al., 2006; Pathak et al., 2011; Huang et al., 2012; Cheng et al., 2011)."

Section 3.3 on AAE. Various AAE values are reported from other studies, all being filterbased and also all of similar values. However, recent measurements (Zhang, ES&T, 47, pp3685, 2013) show that online systems measure lower AAE values, possibly due to differences in the dilutions used in the extraction/analysis methods. How does this affect the results and subsequent radiative forcing calculations?

Response: We agree that the topic of method intercomparison is interesting and important.

Measurements of light-absorbing properties of WSOC using particle into liquid sampler (PILS) coupled to an online spectrophotometer show differences compared with the water extraction method. One study reported that AAE fitted between 300 and 600 nm is 3.2±1.2 for PILS measurements and 7.6±0.5 for filter extracts (Zhang et al., 2013). In addition, by combing size-resolved solvent extracts with Mie theory, Liu et al. (2013) showed that the absorption of solvent extracts is likely to underestimate the light absorption of WSOC in ambient aerosol by a factor of ~2. Taken together, these observations emphasize the importance of methods intercomparisons to reconcile methods-dependent differences. In particular, it is important to note that ambient carbonaceous aerosol constitute a wide range of compounds with different water solubility. Comparisons of extractions in different solvents, such as water and methanol, indicate that light-absorbing species (‘brown carbon’) tends to be more soluble in less hydrophilic solvents (Chen and Bond, 2010; Zhang et al., 2013; Liu et al, 2013). In a recent theoretical study, Psichoudaki and Pandis (2013) presented the *P*-parameter (=volume extraction solvent/volume air sampled) as a measure for optimal solvent extraction. The *P*-values for the present WSOC extracts range 0.09-1.22 $cm^3 m^{-1}$, and fall well within what is described as the ‘optimal range’ of this parameter.

We have added this discussion to the main text.

Page 19633 discussion of AAE. It is does not seem to be stated how good the fit was for the AAE linear regression. That is, does a power law explain the brnC absorption vs wavelength sufficiently well over the analyzed wavelength range?

Response: The R^2-values of linear fit of log(wavelength) vs log(abs(wavelength)) for the 330-400nm interval were typically >0.99. A comment was added to the main text and a figure S5 was added to the Supp Info (see updated/new figures below).

Page 19633 line 23, what is recipient-intercepted? Also later in the text, the meaning of the term recipient is unclear.

Response: Here we implied receptor-intercepted, meaning that the air mass was intercepted after long-range transport to the KCOG receptor site. This is now corrected in the revised text.

Page 19634. Regarding the arguments relating to possible bleaching versus different MACs for different sources. It is known that different sources have different MACs, as pointed out in the paper, but concluding that the data suggest bleaching is less clear.

For example, the MACs reported by Cheng, as noted in this paper, were 0.7 m2/g within Beijing in summer, somewhat lower than what was observed in the pollution event in air *masses great distances from Beijing (the opposite should be observed if bleaching). Why would that be? Furthermore, lower MACs with aging may simply be due to formation of addition WSOC over time that is not brown and have nothing to do with bleaching. Mixing of air masses with WSOC of lower MACs with the Beijing plume would also lead to lower overall WSOC MAC and not be due to bleaching. The isotope data discussed later in the paper does, in a general sense, indicate that the WSOC is more chemically aged, which is expected, but again this does not prove bleaching. What seems to be needed is some analysis (eg, possibly a correlation) between the isotope data, which indicates aging, and MACs, for particles of roughly the same source and without significant SOA production or dilution during transit, which is just not possible. In summary, bleaching may be possible, but it is not at all clear from this data set.*

Response: We are grateful for this constructive comment and agree that the bleaching is just one out of several possible explanations for the observed variability of the MAC. We do note that the MAC(365 nm) for Beijing in winter is reported at 1.8 m2/g (Cheng et al), which is a season more akin to comparison with the timing of our GoPoEx campaign. Nevertheless, there is no good correlation between stable carbon isotope signature and MAC_{365} values observed (R^2=0.29 for TSP and 0.33 for PM2.5), which shows that bleaching due to aging is not the main mechanism.

In accordance, we have changed the discussion in the main text:

"Samples attributed to the Yellow Sea group are characterized by lower absorbance (MAC) although initially they were influenced by the emissions from Beijing and Liaoning. The relatively lower MAC_{365} for these samples may reflect source-dependent differences, secondary contributions or other effects of atmospheric processing, e.g., bleaching induced by photochemical aging."

Section 3.4, what is meant by biomass carbon? Is this biomass burning, solid particles of plant material, SOA from biogenic VOCs, or all of these? In this section it is also referred to as biomass/biogenic. Please use consistent terminology.

Response: Here we implied all non-fossil possibilities of biomass/biofuel burning and biogenic carbon. It is now clarified in the revised ms.

Pg 19635, line 8, typo in line; except for the dust episodes, when then biomass contribution was larger.

A number of points regarding the radiative forcing calculations. 1) The effects from water-soluble-brown carbon seem reasonable (although this depends on what BC MAC is used), but the water-soluble component of brown carbon is only a fraction of the total brown carbon. Other research shows that it can be roughly one-third the total BrnC.

Including all brown carbon would likely make the prediction of brown carbon forcing relative to BC forcing unrealistically high. Any thoughts on why this would be?

Response: As espoused in detail below, we have now recalculated the radiative effect of WSOC relative to EC using a much more realistic model of the solar spectrum than the overly

simplistic (and faulty) black body radiation estimation used in the original ms. The result is that the light-absorbing effect of WSOC is less. The black body radiation model is flawed mainly due to it overlooking the strong absorption by ozone at wavelengths lower than 300nm. The correct for this we have now instead implemented the AM1GH model (Levinson et al, 2010), which accounts for the absorption by ozone and other contributions. Using this model, we find that the relative WSOC/EC contribution is lower and is now estimated to be in the range of 2-10%. Using this estimate, there is now no apparent contradiction with other estimates for the contribution of WSOC to the total brown carbon.
The main text, figure 3 and supplementary information of the manuscript has been updated accordingly, see updated/new figures below.

2) The calculation uses the MAC, WSOC concentration and AAE for WS-BrC, which all introduces error. Why not just use the actual absorption data for the BrC calculation instead of going in circles, ie use data to estimate MAC and AAE, use MAC and AAE to go back and estimate light absorption? Then the error discussed in Supp. Material on line 103 regarding the applicability of the AAE over a wide wavelength range would not exist.

Response: We agree in principle with the reviewer that ideally one would do this. However, there are several factors that complicates/prevents such a direct approach. Instead, the range between 330 and 400nm was justified by 1. Avoidance of interference by nitrate at ~ 300nm (Cheng et al., 2011). 2. Detailed analysis of wavelengths < 300nm are of lower importance for climate implications, due to the high atmospheric absorbance of ozone in these wavelengths. 3. The low signal-to-noise ratio for wavelengths above 400nm for the currently investigated samples. However, we agree with the reviewers' sentiment that this procedure should introduce additional errors. When comparing the 'direct' method with the one done in the paper there is little difference.
We have added a small discussion on this.

3) What is the justification to assume that the bulk light absorption data (ie, in a filter extract) can be directly applied to calculate light absorption by aerosol particles? Some studies have used small particles limits; more recent work has measured ambient BrnC size distributions.

Response: This is an interesting and valid point, also brought up by referee 3. In recent work by Liu et al (ACPD, 2013), this question was addressed by coupling Mie scattering modeling with size-resolved extractions. For their aerosol matrix it is found that the MAC in water solution is roughly 50% of what is expected for the ambient aerosols. We have added a discussion on this. However, we note that our finding of a relatively small role of water-soluble brown carbon to the total direct light absorption stands unaffected.

Referee #2

The MS is an interesting contribution to the field of water soluble carbon and brown carbon and merits publication. There are a few points, however, that should be addressed before publication. The points are given in their order of occurrence in the text.

Response: We thank Referee 2 for this overall positive assessment.

The statement about the greater contribution of fossil fuel combustion to WC-BrC (p. 19627, lines 22-23) needs more background info. BrC is usually thought to originate mainly from biomass fires, which are definitely non-fossil?

Response: It is true that biomass burning has been widely considered as a major source of WSOC and brown carbon (e.g., Hoffer et al., 2006; Asa-Awuku et al., 2008). However, in this study, the sharp 14C-based soruce apportionment tool is for the first time applied to WSOC from China/East Asia and the results show clearly that a large fraction of WSOC is stemming from fossil fuel combustion (30-50%). This is consistent with some other top-down results showing a large contribution also to other aerosol C fractions from fossil fuel combustion in East Asia relative to in other regions (e.g., Zhang et al., 2009; Ramana et al., 2010; Chen et al., 2013). This is now clarified at the appropriate location.

carbon analysis:

a) please discuss possible losses of OC from filters during the carbonate removal step (acid digestion, drying at 60_C); see also Jankowski et al. 2008, Atmos. Environ. 42, 8055-8064

Response: It is feasible that acidification of the filter may influence the WSOC fraction that is extracted for carbon isotope analysis. Jankowski et al. (2008) reports that the lost OC fraction was the volatile components. Our method of WSOC isolation and measurement of concentrations and isotope signatures is focused on the non-volatile WSOC component (Kirillova et al., 2010 *Analytical Chemistry*). However, it is conceivable that this component can also be affected by the acid vapors.

Inspired by the review comment, we have now performed additional experiments to test for effects on isotope composition of WSOC between pre-acidification (Kirillova et al., 2010) and post-acidification. In the pre-acidification method, the aerosol filters are at onset subjected to acid fumigation (12 N HCl) in an open Petri dishes in a desiccator for 24 hours with subsequent drying at 60ºC for 1 hour. In the alternate method, the filters are forst taken through water extraction and freeze drying and the freeze dried material (containing WSOC and possibly some carbonate carbon) is transferred to Ag capsules in preparation for isotope analysis. A mild (1M HCl) microacidification (150 ul) in situ to the Ag capsules is performed to remove the carbonate-C without leaching losses of any of the WSOC.

The two acidification procedures were also tested for d13C of the bulk TOC.

The tests showed that there was a decrease in the extracted WSOC recovery after acid fumigation step (about 62±4% in TSP and 84±3% in PM2.5 size fractions). In contrast, such loss was not observed for TOC fraction. The acid fumigation pre-treatment method also altered the stable isotope signature of the extracted WSOC as it was enriched by0.9±0.7‰ (n=7) compared to WSOC acidified post-processing in the Ag capsules. No significant difference was observed for TOC measured with two acidification methods neither in the concentration nor the isotope signature.

Based on these obtained results the δ^{13}C values were slightly updated for WSOC in Fig. 4 and Fig. S4 (see below). The methods section was also updated based on these findings.

The results do not change any interpretation or conclusion in the ms.

b) please clarify: "the total carbon method was used on the TOT instrument to isolate the entire TOC for subsequent carbon analysis" (p. 19629, lines 24-25,p. 19639, line 1). If a filter containing total carbon (i.e. organic _and_ elemental carbon) is heated to 870_C in the presence of O2, elemental carbon, too, will be combusted, so the gas stream exiting the Sunset analyzer will contain CO2 both from organic and elemental carbon, and not only from TOC.

Response: In our case, we defined TOC (total organic carbon) =OC+EC-CC, (CC = carbonates). TOC is measured as TC using the NIOSH method, but with the difference that the samples were acidified prior to analysis, which removes the carbonates. TOC thus represents all organic carbon in the *chemical* sense of the word (inorganic carbon ~ carbonates). This is now clarified in the text.

c) both for TOC and WSOC: the description "filter areas corresponding to ... μg TOC / WSOC ..." is unclear. Are these parts of filters containing total aerosol samples (PM2.5, etc.) or was WSOC first extracted and then put on filter segments?

Response: First, we measured the concentration of WSOC or TOC on the filter (μg/cm^2). This value was then used for calculation of the concentration of WSOC or TOC in the air. Then we used this concentration value to estimate how much filter area was needed for isotope measurements based on quantification limit of the Aceelerator MS (AMS) measurements of the radiocarbon isotope (at least 40μg C). Therefore, we used the filter area that corresponded to sufficient loading of WSOC or TOC (preferably 100μg or more) for isolation of these fractions for further analysis at the AMS facility. This procedure was described previously (Kirillova et al., 2010). We have added some clarifications in the text.

There is some confusion about the nomenclature: WSOC and WS-BrC seem to be used interchangeably. Not all WSOC is BrC, although most WSOC might also have some absorption in the UV. BrC, however, also absorbs in the visible part of the spectrum, though of course not as efficiently as in the blue and UV regions.

Response: We agree that WSOC and WS-BrC were sometimes used interchangeably. In the revised version of the ms there is now consistent use of the WSOC term throughout and only rare use of water-soluble BrC when we specifically discuss the light absorptive properties of WSOC.

Angstrom exponent (p. 19633): in this MS, the AAE is obtained from spectrophotometer measurements only in the wavelength range 330 - 400 nm. It is well known that there is a change in AAE over the whole spectral range e.g. from UV to near IR. The AAE obtained for the WSOC in this study are compared to literature values, which were obtained for different wavelength ranges, so a direct comparison is not possible.

Response: The light absorption was measured in the wavelength range from 190 to 1090 nm. The absorbance above 400 nm was negligible for most samples, as is normally reported for WSOC, and this is one of several reasons for calculating the AAE in the wavelength range between 330 – 400nm. Utilizing wider ranges, e.g., 330 – 500, provided very similar AAE estimates, but with worse fittings. Thus, we argue that our estimates are relatively robust and therefore comparable with other estimates. The linear fit to log(wavelength) vs log(absorbance(wavelength)) in the 330-400nm range provided $R^2>0.99$ for all samples. A discussion has been added to the main text, and a figure showing the fits have been added to the supporting information (Fig. S5, see below). We note that the main focus and contribution of the paper is the 14C/13C-based studies of sources and processing/aging of WSOC. The revised paper show that the relative direct effect of light-absorbing WSOC is 2-10% of that due do EC.

"Bleaching" of WS-BrC: without further experimental evidence or theoretical arguments, a lower MAC in some samples should not be explained by bleaching. Different sources emit carbonaceous aerosols with different MAC, and the aerosol arriving at Jeju Island may have more sources than only the Beijing winter aerosol. Aging processes may also change MAC of the aerosol (and WSOC) by admixture of nonabsorbing

material, which is different from a reduction of MAC of the original aerosol.

Response: Again, the light absorption of WSOC is not the central focus of this paper. However, agree with this sentiment, also brought up by reviewer 1: the MAC may be influenced by source-variability, secondary contributions, as well as bleaching through atmospheric processing. We have updated the main text accordingly.

In order to make the MS more accessible to readers, the main findings should be included again in a quantitative way in the "conclusion" section.

Response: The conclusions have been updated, to include the quantitative estimates of the relative source contributions of WSOC from biomass/biogenic vs fossil, the estimated relative radiative forcing and the indication of an important role for aging.

minor points:

please avoid use of acronyms without prior explanation (e.g. BT, page 19628, line 19)

It has been clarified that BT stands for Back Trajectories.

add list of analytes to " the filter samples .... were analyzed for concentrations (of what?), ... (p. 19628, lines 23-25)

It has been edited to the following: “The filter samples (1 – 26) collected during the campaign (Fig. 2, Supplementary Material Table S1) were analyzed for concentrations of WSOC and TOC, their isotope compositions and optical properties of the carbonaceous aerosols.”

missing word: p. 19637, line 8: insert "fuel" between "Fossil" and "combustion"

It has now been corrected.

Referee #3

The manuscript present a novel and interesting assessment of water-soluble brown carbon sources and absorption using a combination of isotopic techniques that have never been used for this purpose. The significance of this work, the better understanding of light-absorption of brown carbon and its contribution to aerosol light absorption is beyond any doubt. However, there is a fundamental aspect that needs to be thoroughly discussed before releasing this publication.

Response: We thank Referee 3 for the encouraging and thoughtful evaluation of this work, including both the novelty of isotope probing of E Asian WSOC as well as detailing the challenges facing aerosol absorption measurements.

My major concern is related to the off-line spectrophotometric measurements of watersoluble brown carbon absorption. While the technique is a standard method admittedly for dilute solutions (and this was checked by the authors in a series of dilution experiments), its application becomes severely limited or even impossible towards very concentrated solutions. I wonder what the authors have in their mind about how water-soluble brown carbon absorbs light in ambient aerosol particles, haze particles or cloud droplets. Can these compounds be solubilized all under ambient conditions in an aerosol or haze particle? The compounds likely responsible for light-absorption are not simple organic molecules but complex macromolecular similar to humic substances. Humic substances are well known to change conformation and consequently all of their properties when the conditions in a solution changes: their colour, solubility, molecular weight, etc. may all change. They are even affected by the presence of other electrolytes (e.g. salting out). It may mean that when we measure optical absorption in dilute solutions, and use the very same results for the calculation of their atmospheric absorption with respect to BC absorption, we make a large error that would render all of our efforts meaningless. Lambert-Beer’s law explicitly sets the conditions of dilute solution even for the simplest inorganic dyes. In concentrated solutions there are effects such as self-absorption, shadowing or scattering that causes that the equation can no longer be used. (To say nothing of the effects detailed above for complex macromolecules that are also concentration dependent.)In contrast, atmospheric BC absorption is a well-established phenomenon that is supported by numerous field, laboratory *and theoretical studies, yet loaded with substantial uncertainties especially in global radiative transfer modeling. As regards atmospheric absorption of water-soluble brown carbon, dry aerosol particles contain about 50 (m/m) % water, haze particles about 90 %, and dilute solutions similar to those in the laboratory experiments only exist in cloud droplets. Thus, how can we extrapolate the atmospheric light-absorption of water-soluble brown carbon under so much different conditions? How can we draw the definitive conclusion that BrC contributes by 13-49 % of BC absorption? In my opinion the overly simplistic approach taken by the authors is not scientifically sound.*

Response: We thank the reviewer for bringing up many important aspects of spectrometric probing of WSOC, also relevant for other aerosol fractions, and for both on-line and off-line measurements commonly utilized in the field.

Fundamentally we recognize that carbonaceous aerosol is an extremely heterogeneous mixture, both in terms of individual molecular composition, but also in terms of their physical mixing state. Thus, assigning only two descriptive values for light absorption, i.e., AAE and MAC, for any sub-component, be it EC or WSOC, is perhaps overly simplistic. Nevertheless, rather surprisingly, it seems to be a reasonable or at least functioning approximation in many cases. To our understanding all studies investigating the light-absorbing properties of aerosols rely on the Lambert-Beer law for computing such quantities, despite the fact that, as pointed out by the reviewer, many of the fundamental assumptions that define the validity of this relation is violated in also on-line filter-based methods (PSAP, aethalometers etc). This explains the relatively large number of empirical correction factors used in such analyzes (shadowing, aerosol mixing, loading effects etc, e.g., Weingartner et al, 2003), as mentioned by the reviewer. For the presently investigated dilute solutions of aerosol it may be argued that we are much closer to the validity range of the Lambert-Beer Law, and that we are likely to explore the intrinsic light-absorbing properties of the molecules in this mixture.

It may be, as also implicit from the reviewer comments, that the intrinsic WSOC absorption properties constrained by our and several similar studies are applicable to these aerosols (only) once they are in (more dilute solutions of) cloud droplets. However, we also agree on the need for a broader recognition that solubilization of these molecules may lead to complications with respect to the interpretation of the light absorbing properties of the ambient aerosol phase. Regarding the water content of the ambient aerosols, what is considered is simply the aerosols defined by the given size cut-offs (PM2.5 and TSP) measured at the measurement site. Thus, we do not know the relative water contents of these particles. Due to the dilute water extraction we argue that what WSOC methods are measuring is related to the intrinsic properties of these compounds, given the nature of the solvent, including ionic strength (most light absorbing molecules have a certain degree of solvent dependence). To examine the difference between aerosols with different water content, including lensing effects, is beyond the scope of this isotope-focused study, but offers interesting future directions for investigations. That is one of the reasons for stressing that the current estimates are ‘simplistic’. However, a recent study by Liu et al. (ACPD 13, 18233-18276) have recently recognized the importance of considering the size distribution of the aerosol phase from which solvent extractions were made. They conclude that, for their investigated aerosol matrix, light absorption in water extracts underestimates the light absorption of the ambient aerosol phase by a fairly robust factor of 2. This correction factor thus gives an estimate for the typical size of the correction needed to account for the physical state of the aerosol, similar to correction factors used for filter-based spectrometric investigations.

Regarding the nature of the molecules extracted using typical WSOC procedures, we emphasize that also the current method (as all experimental methods), provides an operational definition for WSOC. A recent theoretical study (Psichoudaki and Pandis, 2013) examined criteria for 'optimal' solvent extraction. We find that our method (Kirillova et al., 2010) lies well within their recommended range. In general we note that complex macromolecules (excluding e.g., soluble proteins, which have been evolved to be water soluble) are in principle less likely to be dissolved in water than smaller molecules. There are several reasons for this: random chemical chains are less likely to be dissolved based on statistical mechanical properties (e.g., Flory, 'Statistical mechanics of chain molecules', 1969) since they may be sterically hindered to go into solution by the aerosol/filter matrix, and since such molecules will have segments which are largely nonpolar. The latter is evidenced by the typically larger MACs observed in methanol extracts than water extracts (e.g., Chen and Bond, 2010).

As espoused above and also pointed out by reviewer H. Moosmüller, the black body radiation model used in the submitted ms to roughly represent solar radiation is overly simplistic as it does not account for ozone absorption at lower wavelengths. We have redone these calculations by now instead using a more realistic model for solar intensity in the troposphere, by implementing the AM1GH spectrum, from Levinson et al. (2010, Solar Energy 84, 1717-1744). Using this approach our estimates of the forcing of WSOC relative to EC is significantly lower and suggesting a WSOC/EC ratio for relative direct radiative effect of 2-10%. We have updated the manuscript accordingly (see updated/new figures below). We have also added an extended discussion on the possible limitations of the water extraction procedures and its relation to the light-absorbing properties of WSOC:

"Other investigations of the light-absorbing properties of WSOC, e.g., using particle into liquid sampler (PILS) coupled to an online spectrophotometer shows differences compared with the water extraction method: AAE fitted between 300 and 600 nm is 3.2±1.2 for PILS measurements and 7.6±0.5 for filter extracts (Zhang et al., 2013). In addition, by combing size-resolved solvent extracts with Mie theory Liu et al. (2013) showed that the absorption of solvent extracts is likely to underestimate the light absorption of WSOC in ambient aerosol by a factor of ~2. Taken together, these observations emphasize the importance of methods-intercomparisons to reconcile methods-dependent differences. In particular, it is important to note that ambient carbonaceous aerosol constitute a wide range of compounds with different water solubility. Comparisons of extractions in different solvents, such as water and methanol, indicate that light-absorbing species ('brown carbon') tends to be more soluble in less hydrophilic solvents (Chen and Bond, 2010; Zhang et al., 2013; Liu et al, 2013). In a recent theoretical study, Psichoudaki and Pandis (2013) presented the *P*-parameter (=volume extraction solvent/volume air sampled) as a measure for optimal solvent extraction. The *P*-values for the present WSOC extracts range 0.09-1.22 cm^3 m^{-1}, and fall well within what is described as the 'optimal range' of this parameter."

We thank Ref. 3 for his/her mindful comments that are stimulating and critically affecting our thinking about several intricate aspects of absorption measurements in this field or aerosol research.

Following the logic above it is also possible that the harsh treatment (acid fumigation) of the filter before the isotope analysis changes the physical and chemical state of the complex molecules, including their solubilities. These issues must be resolved before publication of the manuscript in ACP.

Response: Inspired by this comment and a related one from Ref.2, we have now performed additional experiments to test effects of different acidification strategies on WSOC isotope results. Here again is the response provided to the closely related question raised by Ref. 2 above:

Inspired by the review comment, we have now performed additional experiments to test for effects on isotope composition of WSOC between pre-acidification (Kirillova et al., 2010) and post-acidification. In the pre-acidification method, the aerosol filters are at onset subjected to acid fumigation (12 N HCl) in an open Petri dishes in a desiccator for 24 hours with subsequent drying at 60ºC for 1 hour. In the alternate method, the filters are forst taken through water extraction and freeze drying and the freeze dried material (containing WSOC and possibly some carbonate carbon) is transferred to Ag capsules in preparation for isotope analysis. A mild (1M HCl) microacidification (150 ul) in situ to the Ag capsules is performed to remove the carbonate-C without leaching losses of any of the WSOC.

The two acidification procedures were also tested for d13C of the bulk TOC.

The tests showed that there was a decrease in the extracted WSOC recovery after acid fumigation step (about 62±4% in TSP and 84±3% in PM2.5 size fractions). In contrast, such loss was not observed for TOC fraction. The acid fumigation pre-treatment method also altered the stable isotope signature of the extracted WSOC as it was enriched by0.9±0.7‰ (n=7) compared to WSOC acidified post-processing in the Ag capsules. No significant difference was observed for TOC measured with two acidification methods neither in the concentration nor the isotope signature.

Based on these obtained results the δ^{13}C values were slightly updated for WSOC in Fig. 4 and Fig. S4, see below. The methods section was also updated based on these findings. The results do not change any interpretation or conclusion in the ms.

Referee H. Moosmüller

This manuscript presents very interesting work that should be published in ACP after the following comments are taken into account:

1) Major Flaw: The radiative forcing calculation assumes a solar black body spectrum. This is wrong for the troposphere as solar radiation below _300 nm is effectively absorbed by the stratospheric ozone layer. As a consequence, the solar spectrum in the troposphere doesn't contain any light below _ 300 nm; it is dark below _ 300 nm. Figure S6 clearly shows that for the solar black body model used here, most of the BrC radiative forcing occurs below 300 nm. Therefore, the calculated ratios of WS-BrC and BC radiative forcing seem completely wrong. Calculations need to be redone with an appropriate solar model that takes ozone absorption into account.

We are encouraged that the reviewer found our work interesting and brought up an important aspect to improve the calculations of the relative radiative forcing of WSOC compared to EC component. This is similar to concern brought up by reviewer above and addressed in detail there.

In short, we agree with the important comment that black body spectrum is not a good approximation for the spectrum in the troposphere. To account for this we exchanged the black body radiation model for a more realistic one, the AM1GH spectrum, from Levinson et al. (2010, Solary Energy 84, 1717-1744). As predicted by the reviewer this significantly lowers the estimated solar energy absorbed by WS-BrC relative to BC from 13-49% to 2-10% (see updated/new figures below).

2) The authors need to clarify the difference between WSOC and WS-BrC!

The term WS-BrC was introduced to emphasize the potentially large light-absorbance of WSOC. Given the new estimates, with the above mentioned model for solar emission, we now have removed the WS-BrC term from most parts of the manuscript, and replaced it with WSOC. The parts where water-soluble BrC is kept, it is explicitly explained.

3) Wavelength dependent absorption spectra should be shown, ideally plotted in loglog space together with the linear (in log-log space) Angstrom coefficient fit to enable the reader to evaluate slope and curvature and SNR of these spectra.

We have plotted log(abs) vs log(wavelength) along with the linear fit in Fig. S6 (see below), the fitting is also discussed in the main text. The linear fit to log(wavelength) vs log(absorbance(wavelength)) in the 330-400nm range provided $R^2>0.99$ for all samples.

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Updated/new figures

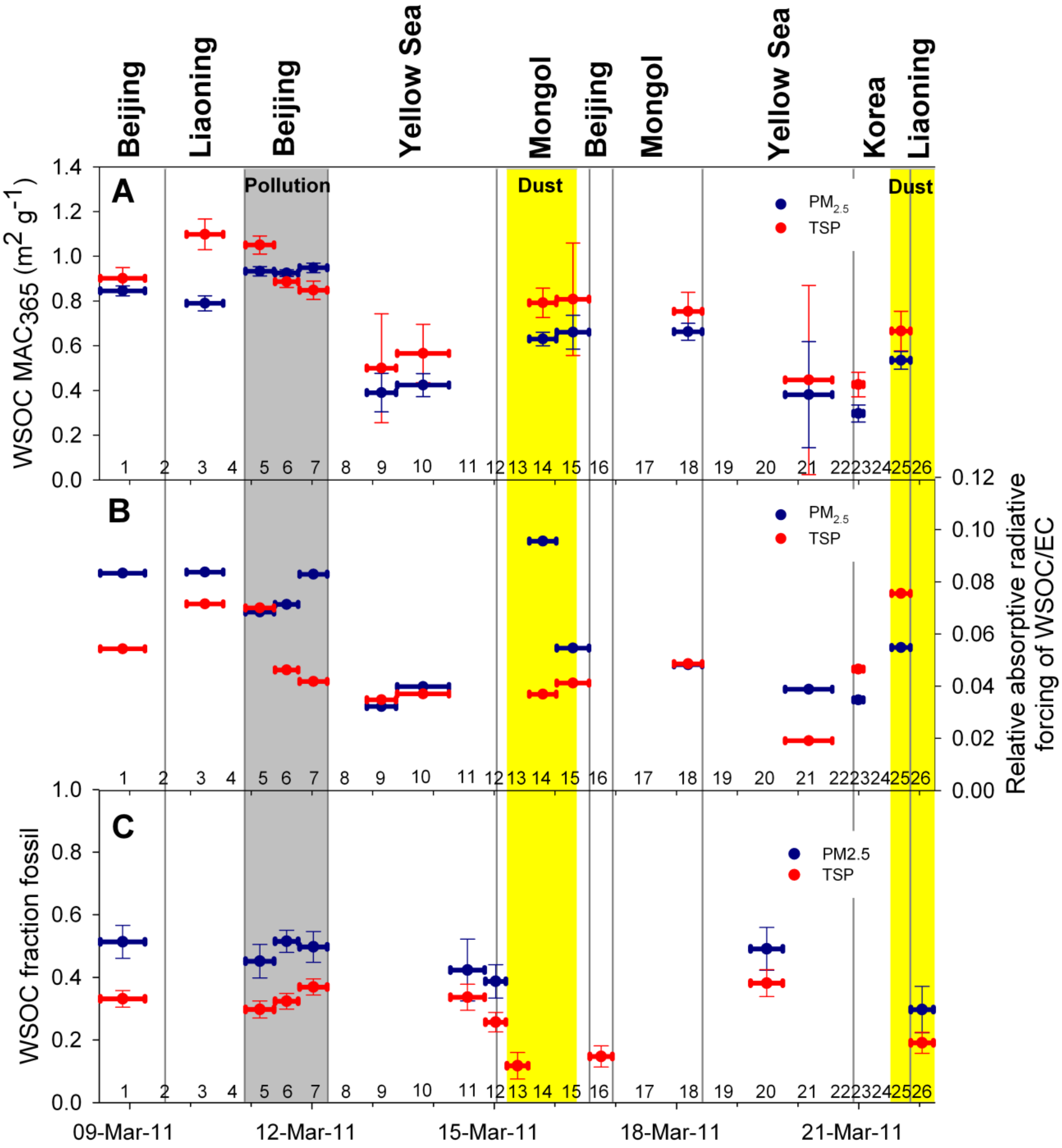

Figure 3. Mass absorption cross section of water-soluble brown carbon (WSOC) at 365 nm (MAC_{365}) (panel A); relative absorptive radiative forcing of WSOC compared to that of elemental carbon (EC) (panel B); radiocarbon-based source-apportionment measurements of fraction fossil in $PM_{2.5}$ and TSP aerosols at KCOG station during the GoPoEx campaign (panel C).

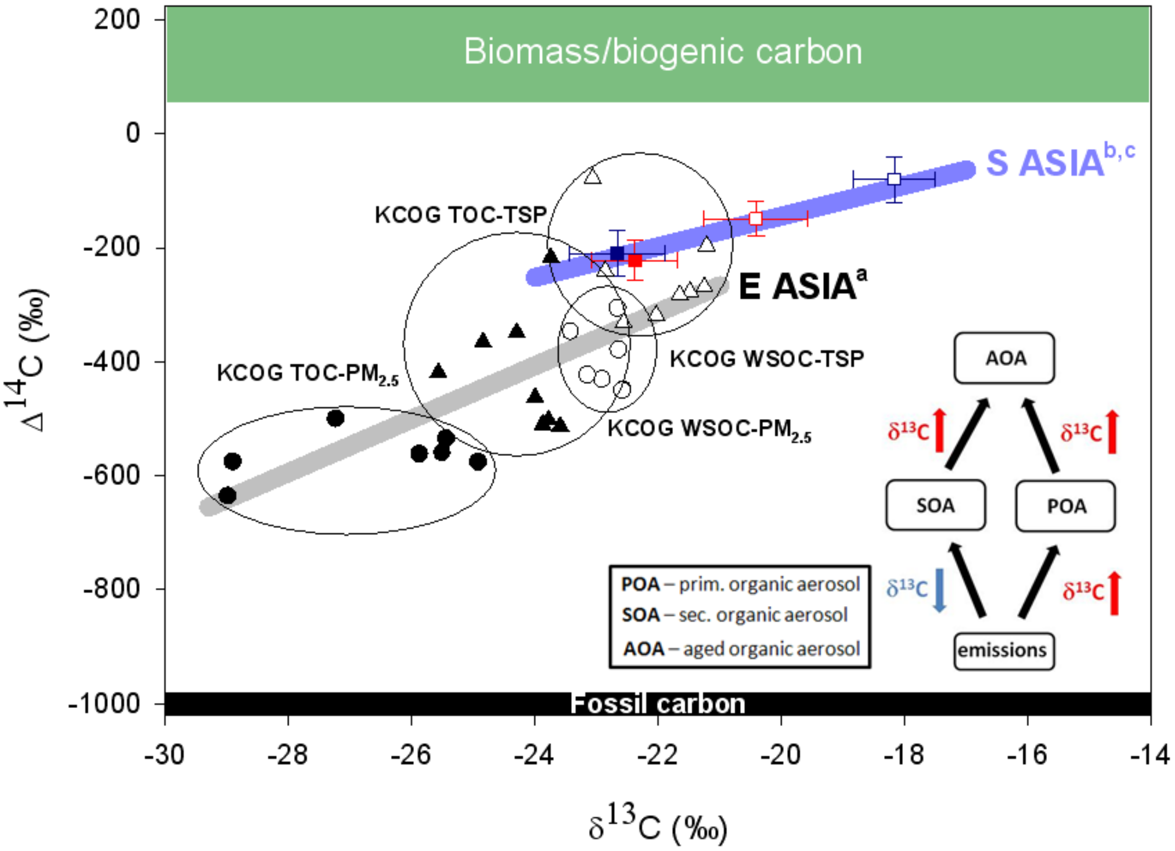

Figure 4. Two-dimensional presentation of dual-isotope (δ^{13}C vs Δ^{14}C) signals of WSOC and TOC in $PM_{2.5}$ and TSP for a. GoPoEx campaign in East Asia (dust-influenced samples are excluded) compared to in South Asia (b. Sheesley et al. (2012) and c. Kirillova et al. (2013) datasets from western-central Indian site of Sinhagad (SINH) and Indian Ocean site on Hanimaadhoo Island, Maldives (MCOH). South Asian data is presented as mean values with standard deviation spread for SINH-TOC (red filled squares), MCOH-TOC (blue filled squares), SINH-WSOC (red open squares) and MCOH-WSOC (blue open squares). Linear fits of TOC and WSOC data are presented as thick light blue line for South Asia and grey line for East Asia. The bottom right inset graphically summarizes the general trends of the influence of atmospheric processing on the δ^{13}C signature of carbonaceous aerosols.

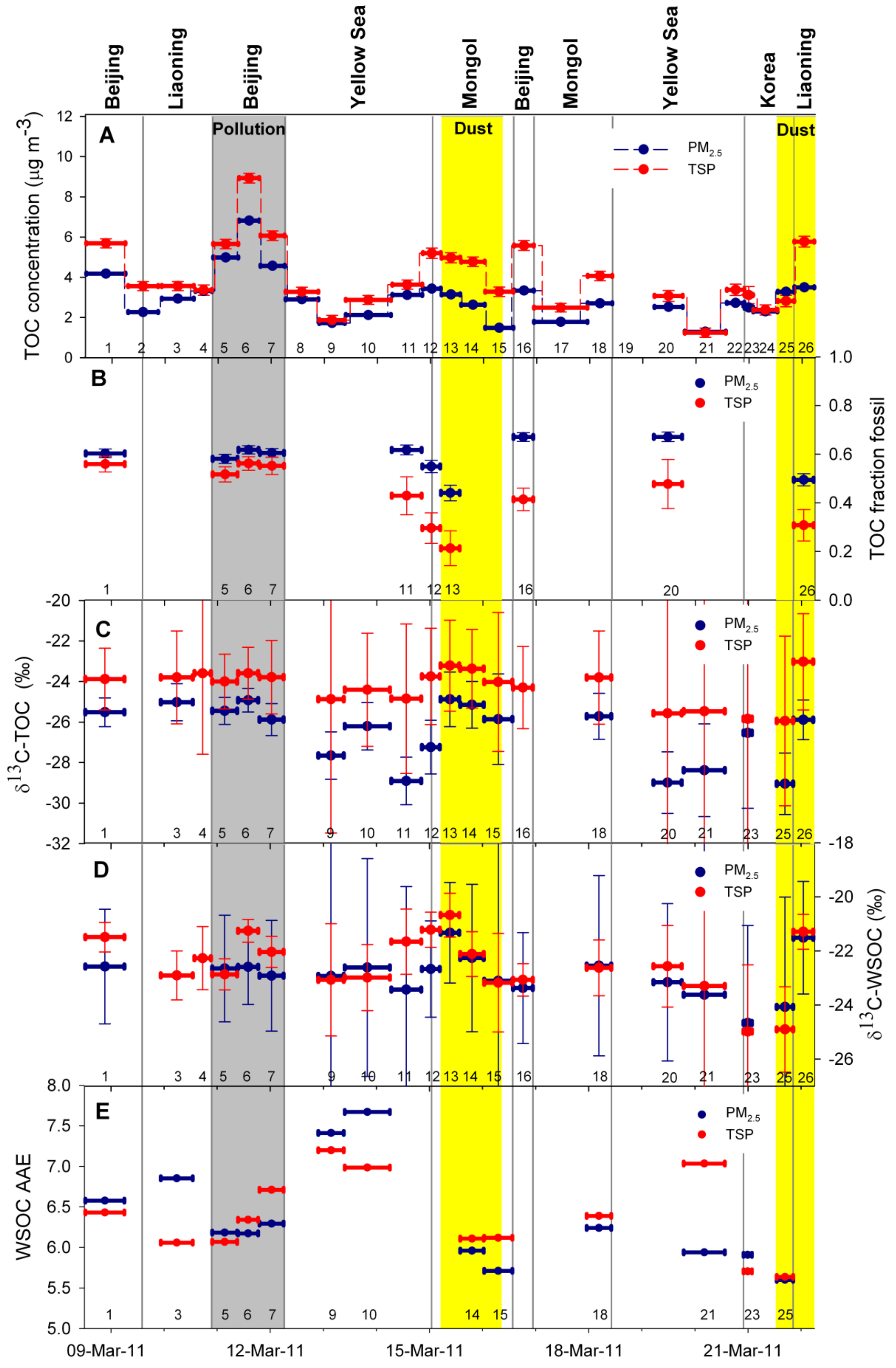

Figure S4. Concentrations of total carbon (TC) (panel A); fraction fossil of total organic carbon (TOC) (panel B); stable carbon ratio in TOC (panel C) and water-soluble organic carbon (WSOC) (panel D); Absorption Ångström Exponents (AAE) for water-soluble organic carbon (WSOC) during GoPoEx campaign (panel E).

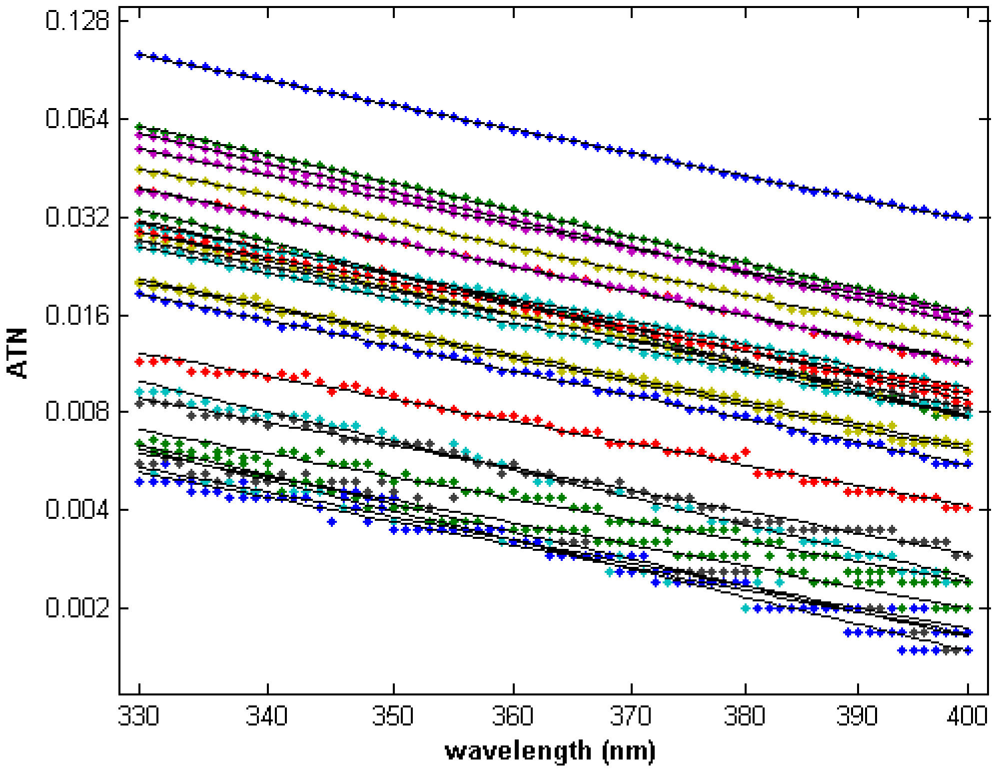

Figure S5. Wavelength dependent absorption spectra with the linear Ångström absorption coefficient (AAE) fitting for 13 TSP and $PM_{2.5}$ samples extracted.

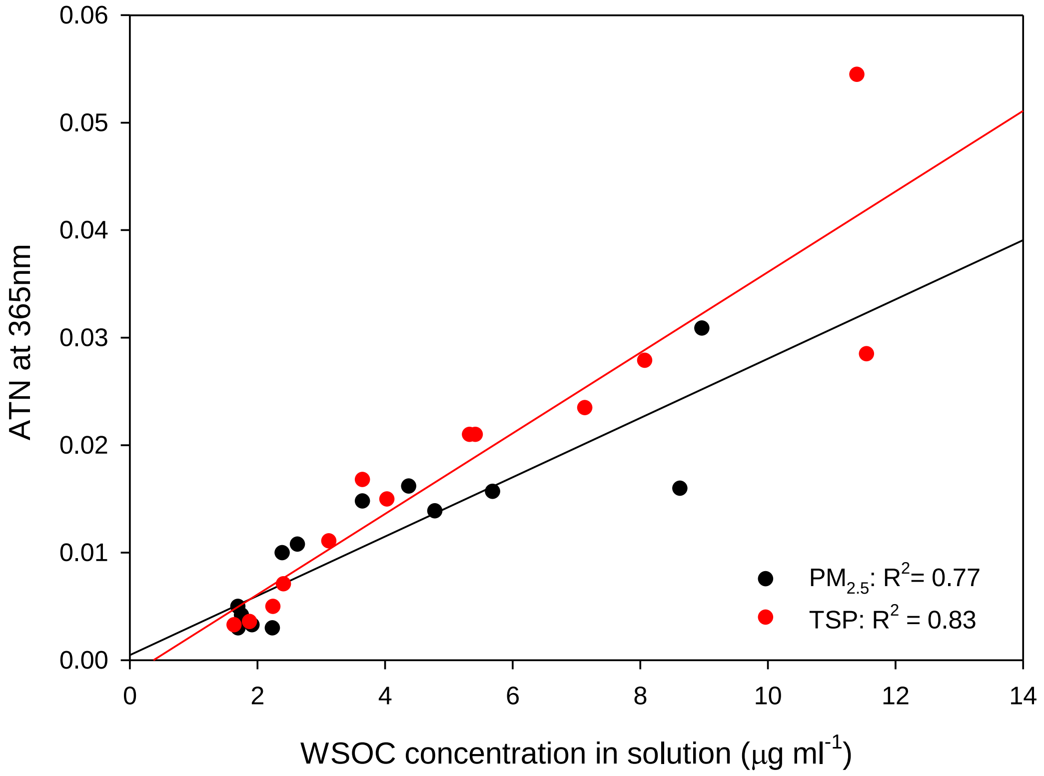

Figure S6. Relationship of the light attenuation coefficient (ATN) at 365 nm of the solution and the concentration of WSOC in the solution for 13 $PM_{2.5}$ and TSP extracts.

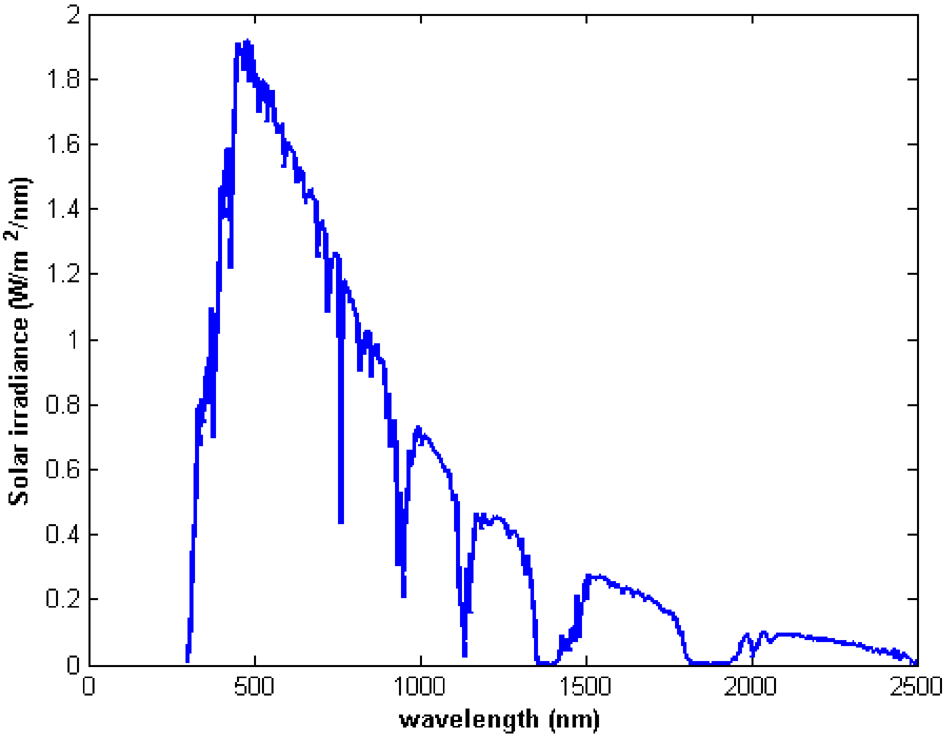

Figure S7. Plot showing the AM1GH model for solar irradiance, used for calculations of the relative radiative forcing model in Equations S1-2 (Levinson et al., 2010).

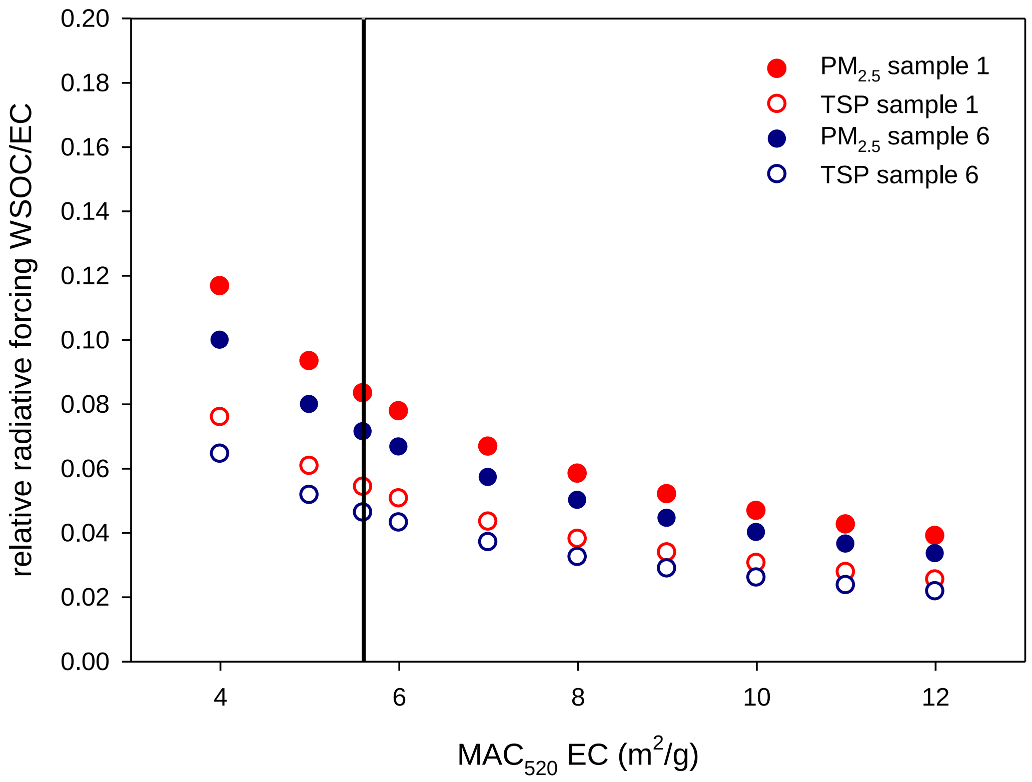

Figure S8. Dependency of the relative radiative forcing WSOC/EC, calculated using Equation (S3), on the value of MAC$_{520,EC}$. Two samples are depicted: sample 6 from the Bejing pollution plume and sample 10 from the Yellow Sea back trajectory cluster, for two size fractions (PM$_{2.5}$ and TSP). The vertical line emphasize $MAC_{520,EC}$ = 5.6 m^2/g (Chung et al., 2012) used in this paper.

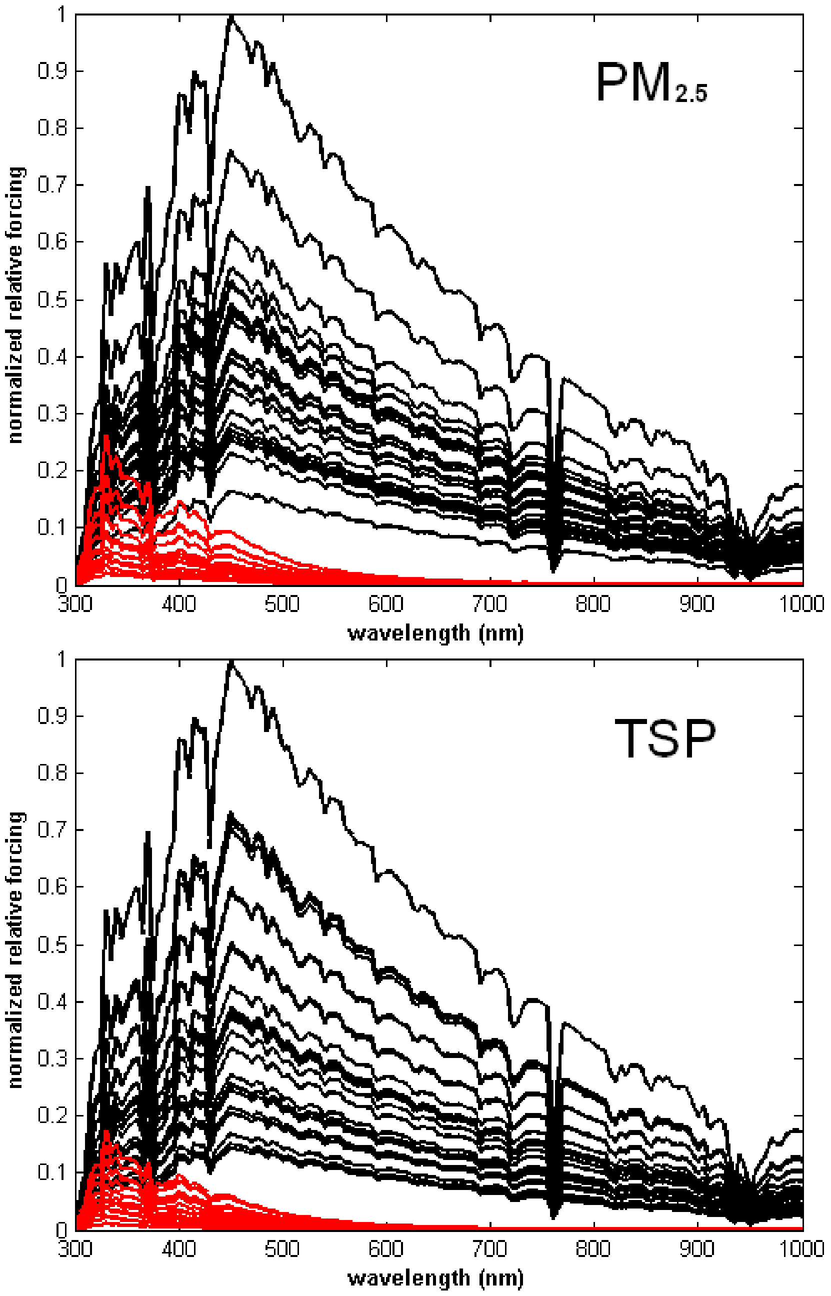

Figure S9. Normalized wavelength-dependence of the absorptive radiative forcing of water-soluble brown carbon (WSOC, red) relative to black carbon (BC, black) for observation of their light absorption in samples of the outflow originating in N China and intercepted during GoPoEx computed using the model outlined in SI Text.