



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

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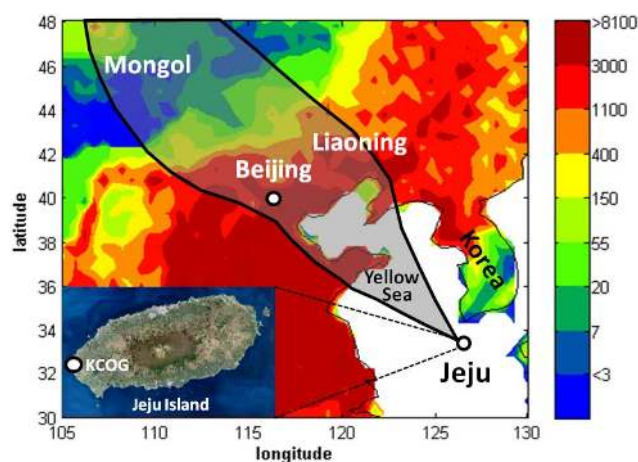
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**Abstract.** High loadings of anthropogenic carbonaceous aerosols in Chinese air influence the air quality for over one billion people and impact the regional climate. A large fraction (17–80 %) of this aerosol carbon is water-soluble, promoting cloud formation and thus climate cooling. Recent findings, however, suggest that water-soluble carbonaceous aerosols also absorb sunlight, bringing additional direct and indirect climate warming effects, yet the extent and nature of light absorption by this water-soluble “brown carbon” and its relation to sources is poorly understood. Here, we combine source estimates constrained by dual carbon isotopes with light-absorption measurements of water-soluble organic carbon (WSOC) for a March 2011 campaign at the Korea Climate Observatory at Gosan (KCOG), a receptor station in SE Yellow Sea for the outflow from northern China. The mass absorption cross section at 365 nm ( $MAC_{365}$ ) of WSOC for air masses from N. China were in general higher ( $0.8\text{--}1.1\text{ m}^2\text{ g}^{-1}$ ), than from other source regions ( $0.3\text{--}0.8\text{ m}^2\text{ g}^{-1}$ ). However, this effect corresponds to only 2–10 % of the radiative forcing caused by light absorption by elemental carbon. Radiocarbon constraints show that the WSOC in Chinese outflow had significantly higher fraction fossil sources (30–50 %) compared to previous findings in S. Asia, N. America and Europe. Stable carbon ( $\delta^{13}\text{C}$ ) measurements were consistent with aging during long-range air mass transport for this large fraction of carbonaceous aerosols.

## 1 Introduction

High emissions of anthropogenic carbon aerosols from highly industrialized and populated northern and eastern China (Fig. 1) greatly influence the regional climate and air quality of the whole East Asian region. The water-soluble organic carbon (WSOC) is a substantial component of East Asian aerosols with concentrations spanning from 17 to 80 % of the total organic carbon (TOC) (Feng et al., 2006, 2007; Duvall et al., 2008; Pathak et al., 2011; Huang et al., 2012). WSOC may influence regional climate through several mechanisms. WSOC affects the particle’s hygroscopicity and hence the ability of aerosol particles to act as cloud condensation nuclei (CCN) thus contributing to the indirect aerosol climate effects (e.g., Charlson et al., 2001; Svenningsson et al., 2006; Asa-Awuku et al., 2008). It has recently been found that WSOC exhibits light-absorbing (“brown carbon” BrC) properties (Cheng et al., 2011, Zhang et al., 2011). This water-soluble BrC thus potentially contributes both a direct climate forcing (Chung et al., 2012; Bahadur et al., 2012; Jacobson, 2012) and a semi-direct climate effect through heating and evaporation of clouds (Jacobson, 2012).

There is a need to better understand the sources, properties and atmospheric processing of WSOC. It has been suggested that WSOC in atmospheric particles may come from a wide range of primary and secondary sources (e.g., Decesari et al., 2007; de Gouw et al., 2008). A few initial studies with direct measurement of the natural abundance radiocarbon content of WSOC appears promising to constrain the sources of this large aerosol carbon fraction. Short-term radiocarbon-based studies of WSOC in North America and Europe suggest



**Fig. 1.** Map depicting bottom-up emission inventory estimates of anthropogenic total organic carbon (TOC) estimated as the sum of black carbon (BC) and organic carbon (OC) in tons  $\text{yr}^{-1}$  per  $0.5^\circ \times 0.5^\circ$  grid in year 2006 (Zhang et al., 2009). The five main geographical source regions from back trajectories (BTs) analysis for the present March 2011 campaign (GoPoEx – Gosan Pollution Experiment) are indicated: Beijing, Liaoning, Mongol, Yellow Sea and Korea. The shaded sector between the black lines show the predominant range of BTs of the Chinese outflow for the study period. The location of the Korean Climate Observatory at Gosan (KCOG) on Jeju Island is shown in the inset satellite image, provided by NASA (<http://earthobservatory.nasa.gov/IOTD/view.php?id=35900>).

an overwhelming contribution of modern carbon sources to WSOC in both rural and urban environments (Szidat et al., 2004; Weber et al., 2007; Wozniak et al., 2008, 2012a, b; Kirillova et al., 2010). Recent year-round  $^{14}\text{C}$ -WSOC campaigns at two regional background sites constrained a 20% fossil contribution in South Asia (Kirillova et al., 2013). A larger contribution of fossil fuel combustion to elemental carbon (EC) was found in East Asia compared to South Asia (Zhang et al., 2009; Ramana et al., 2010; Chen et al., 2013). To test the postulation that biomass burning is the predominantly largest source of WSOC and water-soluble BrC (e.g., Hoffer et al., 2006; Asa-Awuku et al., 2008), a radiocarbon-based investigation of WSOC sources over the East Asia was performed.

Furthermore, the stable carbon isotope signal ( $\delta^{13}\text{C}$ ) can be used to differentiate not only the sources but also the atmospheric processing of the carbonaceous aerosols as it additionally reflects kinetic isotope effects (KIE) induced by transformation reactions during both primary aerosol and precursor emissions as well as during atmospheric transport (Anderson et al., 2004; Widory, 2006; Aggarwal and Kawamura, 2008; Das et al., 2010; Iannone et al., 2010; Kirillova et al., 2013).

In this paper we present carbon isotope-constrained source apportionment and light-absorbing properties of WSOC from the Gosan Pollution Experiment (GoPoEx), performed

at the Korea Climate Observatory at Gosan (KCOG), Jeju Island, SE Yellow Sea, in March 2011. The findings quantify the light absorption effect and establish that, contrary to other regions, fossil sources are important for WSOC in the Chinese outflow.

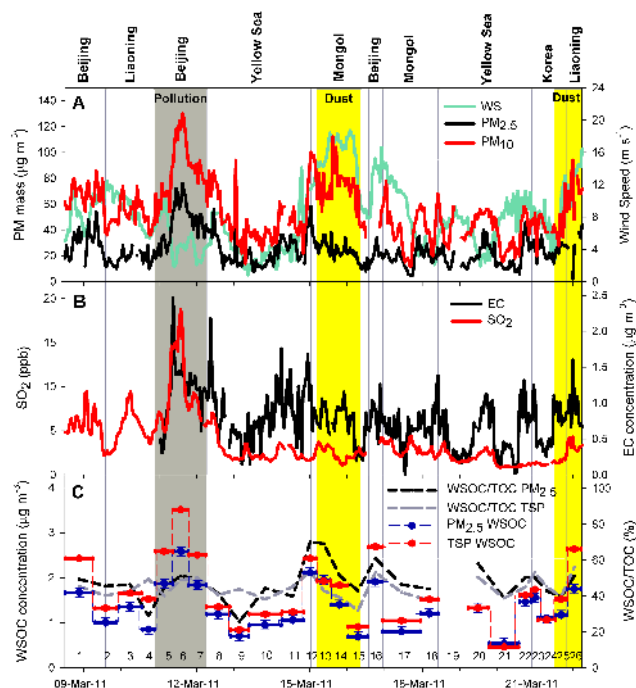
## 2 Materials and methods

### 2.1 Sampling site and sampling program

The Gosan Pollution Experiment (GoPoEx) was conducted at the Korea Climate Observatory at Gosan (KCOG, 72 m a.s.l.,  $33.17^\circ\text{N}$ ,  $126.10^\circ\text{E}$ ) during 8–27 March 2011. KCOG is located in a rural area at the western tip of Jeju Island, 100 km south of the Korean peninsula (Fig. 1), and is a part of The Aerosol Characterization Experiments (ACE) Asia (Huebert et al., 2003), Advanced Global Atmospheric Gases Experiment (AGAGE, <http://agage.eas.gatech.edu/>), Global Atmosphere Watch (GAW) program ([www.wmo.int/pages/prog/arep/gaw/gaw\\_home\\_en.html](http://www.wmo.int/pages/prog/arep/gaw/gaw_home_en.html)), and the International Atmospheric Brown Cloud (ABC) project ([www.rrcap.unep.org/abc/](http://www.rrcap.unep.org/abc/)). During GoPoEx, measurements of gaseous components (e.g., CO and SO<sub>2</sub>) and bulk particulate parameters (e.g., PM<sub>2.5</sub>, PM<sub>10</sub>, elemental carbon (EC)) as well as meteorology descriptors were collected at high frequency (averaged to  $\leq 1$  h, Fig. 2). These measurements, in conjunction with HYSPLIT forecast back trajectories (BTs) and weather maps from the Korean Meteorological Association (KMA) were used to guide the high-volume filter sampling, with the aim of obtaining geographical source-region specific filter collections. Aerosols were collected on pre-combusted quartz-fiber filters using high volume PM<sub>2.5</sub> (model DH77, Digital A.G., Switzerland) and TSP samplers. The filter samples (1–26) collected during the campaign (Fig. 2, Supplement Table S1) were analyzed for concentrations of WSOC and total organic carbon (TOC), their isotope compositions and optical properties of the carbonaceous aerosols.

### 2.2 Analysis of carbonaceous aerosol fractions

The aerosol total organic carbon (TOC) concentrations were measured with a thermal-optical transmission (TOT) analyzer (Sunset Laboratory, Tigard, OR, USA) using the standard NIOSH 5040 method (Birch and Cary, 1996) but with the difference that the samples were acidified prior to analysis (by fumigation in open glass Petri dishes held in a desiccator over 12 M hydrochloric acid for 24 h and subsequently dried at  $60^\circ\text{C}$  for 1 h) to remove the carbonates. TOC thus represents all organic carbon in the chemical sense of the word (inorganic carbon is equal to carbonates), thus also including elemental carbon (EC). TOC concentration values were blank corrected and the field blank input was on average 10% ( $1.19 \pm 0.34$  SD,  $\mu\text{g cm}^{-2}$ ;  $n = 4$ ) for TSP and 11% ( $0.74 \pm 0.08$  SD,  $\mu\text{g cm}^{-2}$ ;  $n = 4$ ) for PM<sub>2.5</sub>. The



**Fig. 2.** Pollutant tracers and water-soluble organic carbon concentrations during the March 2011 GoPoEx campaign at KCOG: ambient air particulate mass (PM<sub>2.5</sub> and PM<sub>10</sub>) and wind speed (A); concentrations of SO<sub>2</sub> provided by South Korean National Institute of Environmental Research (NIER) and semi-continuously measured elemental carbon (EC) (B); concentrations of water-soluble organic carbon (WSOC) and WSOC to total organic carbon (TOC) ratio (C) in both ambient total suspended particles (TSP) and PM<sub>2.5</sub> fractions at KCOG during the GoPoEx campaign. The relation between pollutant tracers and back trajectory source regions are marked at the top. The pollution event is marked in grey and the dust events in yellow.

average relative standard deviation of triplicate analysis was 7% for TSP and 11% for PM<sub>2.5</sub>. WSOC was extracted by ultrasonication and quantified by a high-temperature catalytic instrument (Shimadzu-TOC-V<sub>CPH</sub>, Japan) as described previously (Kirillova et al., 2010). All WSOC results were blank corrected by subtracting an average field blank value. The WSOC field blanks corresponded to an average 6% ( $0.30 \pm 0.06$  SD,  $\mu\text{g cm}^{-2}$ ;  $n = 3$ ) for TSP and 7% ( $0.20 \pm 0.01$  SD,  $\mu\text{g cm}^{-2}$ ;  $n = 3$ ) for PM<sub>2.5</sub> of the field sample loading. Triplicate analysis was done on three TSP and four PM<sub>2.5</sub> filters by extracting three different sections of the same filter in order to estimate both analytical and sub-filter variance. The average relative standard deviation of these triplicate analyses was 4% for TSP and 6% for PM<sub>2.5</sub>.

### 2.3 Carbon isotope analysis

Ten samples were chosen for carbon isotope analysis based on an air mass origin from China and sufficient carbon loadings as described in Supplement.

#### 2.3.1 TOC

The carbon aerosol TOT analyzer was slightly modified for online isolation of CO<sub>2</sub> produced during the combustion of a sample for further measurements of <sup>13</sup>C and <sup>14</sup>C. First, a filter area containing at least 100  $\mu\text{g}$  TOC according to the concentration measurements for each sample was acidified by fumigation (as described in Sect. 2.2). The total carbon method was used on the TOT instrument to isolate the entire TOC for subsequent radiocarbon analysis. During this method a 1.5 cm<sup>2</sup> subsample was heated at the two ramps to 870 °C in the atmosphere of helium (98%) and oxygen (2%) during 110 s and remained to be exposed to the temperature of 870 °C for 190 s until all the TOC was oxidized to CO<sub>2</sub>.

The CO<sub>2</sub> produced by the TOT analyzer was purified through magnesium perchlorate and silver wool traps to remove water and halogen-containing gases, correspondingly. Subsequently, it was cryotrapped in liquid N<sub>2</sub> and sealed in the glass ampoules. Further, the CO<sub>2</sub> was reduced to graphite, and the carbon isotopic composition was measured at the US NSF National Ocean Science Accelerator Mass Spectrometry (NOSAMS) facility (Woods Hole, MA, USA).

This acid fumigation method was compared with an alternative protocol (“in situ micro-acidification”), in which 150  $\mu\text{L}$  1 M HCl was added to the filter subsamples packed into silver capsules, with subsequent drying at 60 °C for 3 h. Then the concentration of TOC and stable carbon isotope composition were measured at the Stable Isotope Laboratory (SIL) of the Department of Geological Sciences at Stockholm University (Stockholm, Sweden). The instrumental method employed sample combustion with a Carlo Erba NC2500 analyzer connected via a split interface to reduce the gas volume to a Finnigan MAT Delta V mass spectrometer. The differences in TOC mass and stable carbon isotope signature between the two acidification techniques were within the uncertainty estimates for TOC.

#### 2.3.2 WSOC

For <sup>13</sup>C and <sup>14</sup>C analysis a filter area corresponding to at least 150  $\mu\text{g}$  WSOC based on concentration measurements for each of 10 chosen samples was acidified by fumigation as described above and extracted as described previously (Kirillova et al., 2010). However, the acid fumigation method described above was compared with an alternative protocol using milder in situ micro-acidification: addition of 150  $\mu\text{L}$  1 M HCl to the freeze-dried water extracts, followed by drying at 60 °C for 3 h. When comparing the  $\delta^{13}\text{C}$  signature of the samples using the two acidification methods, the samples analyzed using the in situ micro-acidification protocols were uniformly shifted by  $-0.9 \pm 0.7\text{‰}$  ( $n = 7$ ) compared with the original method. Thus, enrichment in  $\delta^{13}\text{C}$  is induced by the original method. This correction was applied uniformly to all samples. Since the  $\Delta^{14}\text{C}$  metric is reported relatively to a  $\delta^{13}\text{C}$  standard (i.e.,  $-25\text{‰}$ ), these isotope effects do not

influence the reported  $\Delta^{14}\text{C}$  values. Stable carbon isotope ( $\delta^{13}\text{C}$ -WSOC) measurements were performed at the Stable Isotope Laboratory (SIL) of the Department of Geological Sciences at Stockholm University (Stockholm, Sweden). The radiocarbon measurements of the freeze-dried WSOC isolates were performed at the US-NSF NOSAMS facility as described previously (McNichol et al., 1992; Pearson et al., 1998; Kirillova et al., 2010).

## 2.4 Uncertainty estimation

The overall precision of TC and WSOC concentrations and isotopic signatures was estimated based on uncertainties from several different sources, including the precision of concentration estimation (estimates from triplicate analysis), mass contributions from field blanks (estimates from several blanks), as well as precision of isotope characterization (instrument precision) and the isotope signature of the field blanks (Supplement). To properly account for all uncertainties, we employed an error propagation scheme based on a Monte Carlo strategy as described previously (Kirillova et al., 2013).

## 2.5 Light absorption by WSOC

Light extinction of 13 WSOC samples (both TSP and  $\text{PM}_{2.5}$ ) was measured using a Hitachi U2010 spectrophotometer, using the wavelength range of 190–1100 nm. No acidification was implemented to the filters or WSOC extracts utilized for spectroscopic measurements. The mass absorption cross section (MAC) was computed according to the Lambert–Beer law:

$$\text{MAC} = \frac{-\ln \left| \frac{I}{I_0} \right|}{C \cdot L} = \frac{A}{C \cdot L}, \quad (1)$$

where  $I$  denote light intensity,  $C$  is the concentration of WSOC in solution,  $L$  is the light path length (i.e., 1 cm, for the currently used quartz cuvettes) and  $A$  is the absorbance (assuming that the scattering contribution to extinction is low). For comparison with previous results, the MAC was computed for 365 nm (Cheng et al., 2011). Equation (1) predicts a linear relation between absorbance and concentration. This prediction was tested by dilution experiments, and was found to agree well within the currently investigated concentration/wavelength range (data not shown).

The wavelength ( $\lambda$ ) dependence of the WSOC absorption was investigated by fitting the absorption Ångström exponent (AAE) using the following relation:

$$\frac{A(\lambda_1)}{A(\lambda_2)} = \left( \frac{\lambda_2}{\lambda_1} \right)^{\text{AAE}}. \quad (2)$$

AAE were fitted within the range 330–400 nm. This range is justified by (1) avoidance of interference by nitrate at  $\sim 300$  nm (Cheng et al., 2011). (2) Detailed analysis of wave-

lengths  $< 300$  nm are of lower importance for climate implications, due to the high atmospheric absorbance of ozone in this wavelength range. (3) The low signal-to-noise ratio for wavelengths above 400 nm for the currently investigated samples. The linear fits of  $\log(\lambda)$  vs.  $\log(A(\lambda))$  data (where the slope = AAE) showed good correlations, with  $R^2 > 0.99$  for all investigated samples in the 330–400 nm range (Supplement Fig. S5).

## 3 Results and discussion

### 3.1 Meteorological setting and air mass characterization

The climate of Jeju Island is driven by the Asian monsoon system. In late winter and spring, the air masses arriving at KCOG are largely influenced by the anthropogenic activities in China and Korea, and by Asian dust storms (e.g., Carmichael et al., 1996; Huebert et al., 2003; Sahu et al., 2009). The major objective of the Gosan Pollution Experiment (GoPoEx), carried out at KCOG on 8–23 March 2011, was to intercept aerosols from the northern China outflow to study their sources and properties.

To examine the geographical source regions of the air masses during GoPoEx, five-day back trajectories (BTs) were generated at three arrival heights (100, 500 and 850 m a.g.l.) for every 6 h using NOAA HYSPLIT software v4 (<http://www.arl.noaa.gov/ready/hysplit4.html>). Consideration of both path and heights of the BTs allowed us to determine five main source areas: Beijing, Liaoning, Yellow Sea, Mongol (Mongolia and the Nei Mongol province of China) and the Korean peninsula (Fig. 1, Supplement, Fig. S1–3). The air in the Yellow Sea category circulated for extended times at high altitude over the Jeju region before descending to KCOG, whereas air mass transfer over the other source regions occurred at low altitudes.

Three episodes of elevated pollutant loadings were observed during the high-intensity campaign (Fig. 2): (1) a pollution event was observed from 10:00 p.m. LT of 10 March to 06:00 a.m. of 12 March (filter samples 5–7) with air masses originating from the Beijing area, which was characterized by high loadings of  $\text{PM}_{2.5}$ ,  $\text{PM}_{10}$ , EC and  $\text{SO}_2$ . (2) An Asian dust episode was observed from 05:00 a.m. of 15 March to 09:00 a.m. of 16 March (filter samples 13–15), originating from the Mongol source sector, which was characterized by high  $\text{PM}_{10}$  low  $\text{PM}_{2.5}$  and pollution tracers and high wind speeds ( $13\text{--}16 \text{ m s}^{-1}$ ). (3) A second dust event combined with rain was observed from 01:00 p.m. of 21 March to the end of campaign (filter samples 25 and 26).

### 3.2 WSOC abundance and distribution

During GoPoEx, WSOC contributed  $\sim 45\text{--}47\%$  of TOC (Fig. 2c). When comparing total suspended particles (TSP) with  $\text{PM}_{2.5}$  size fraction, about 80 % of WSOC was found in

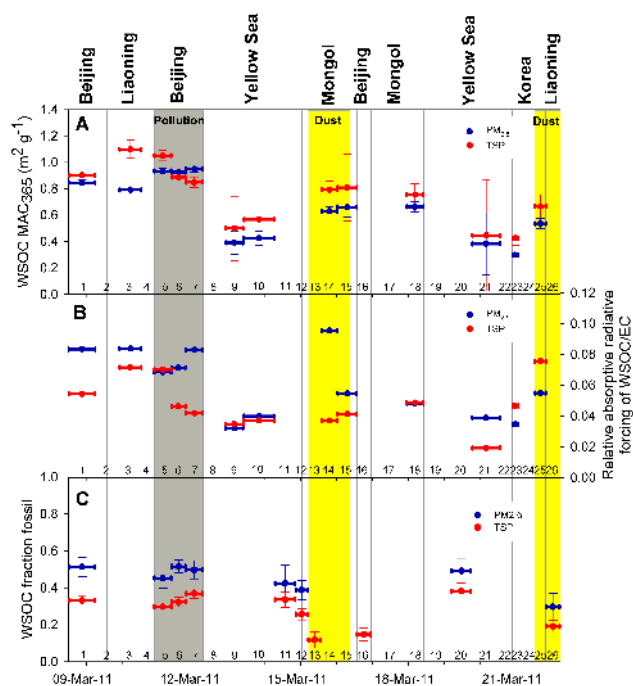


the fine ( $<2.5\ \mu\text{m}$ ) fraction. The highest concentrations were found during the pollution event (10–12 March,  $2.3\ \mu\text{g m}^{-3}$  in  $\text{PM}_{2.5}$  and  $3.5\ \mu\text{g m}^{-3}$  in TSP, Fig. 2), but elevated WSOC concentrations were also observed during the two dust events (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 ( $0.4\text{--}9.6\ \mu\text{g m}^{-3}$  for  $\text{PM}_{2.5}$ ) (Feng et al., 2006; Pathak et al., 2011; Huang et al., 2012; Cheng et al., 2011).

### 3.3 Light absorption of water-soluble organic carbon (WSOC) in outflow from northern China

Black carbon (BC) is frequently referred to as the major light absorbing aerosol species (e.g., Ramanathan and Carmichael, 2008; Bond et al., 2013). However, other carbonaceous aerosols may also absorb light, but typically with a more pronounced wavelength dependence – “brown carbon” (Andreae and Gelencsér, 2006). For the GoPoEx, the light absorption of WSOC was found to have a wavelength dependence reflected in an absorption Ångström exponent (AAE) ranging between 5.6 and 7.7 ( $6.4 \pm 0.6$ , Supplement Fig. S4). In comparison, the AAE for BC is typically 1 (Hecobian et al., 2010; Cheng et al., 2011; Kirchstetter and Thatcher, 2012). The WSOC AAE for GoPoEx is comparable with observations, using similar extraction protocols, near Beijing, China of 7.2 in summer and 7.5 in winter (Cheng et al., 2011), values of 6.2–8.3 in SE USA (Hecobian et al., 2010), 7.1 over the Amazonas (Hoffer et al., 2006). Similarly, the current range of the receptor-intercepted WSOC mass absorption cross-section values at 365 nm ( $\text{MAC}_{365}$ ) (Fig. 3a) were  $0.3\text{--}1.1\ \text{m}^2\ \text{g}^{-1}$  ( $0.7 \pm 0.2\ \text{m}^2\ \text{g}^{-1}$ ), which compares with Beijing source area during winter ( $1.8 \pm 0.2$ ; Cheng et al., 2011), Beijing in summer ( $0.7\ \text{m}^2\ \text{g}^{-1}$ ; Cheng et al., 2011) and with SE USA ( $0.3\text{--}0.7\ \text{m}^2\ \text{g}^{-1}$ ; Hecobian et al., 2010). A broad relationship exists between the WSOC light absorption at 365 nm and WSOC concentration (Fig. S6), with  $R^2 = 0.77$  for  $\text{PM}_{2.5}$  and 0.83 for TSP. This may be related to different light-absorbing properties of samples from different source areas and/or different degree of atmospheric processing during long-range transport.

One investigation of light-absorbing properties of WSOC using a particle into liquid sampler (PILS) coupled to an online spectrophotometer shows differences when compared with the water extraction method: AAE fitted between 300 and 600 nm is  $3.2 \pm 1.2$  for PILS measurements and  $7.6 \pm 0.5$  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 may underestimate the light absorption of WSOC in ambient aerosol by a factor of  $\sim 2$ . Taken together, these observations emphasize the importance of methods-intercomparisons to reconcile methods-dependent differences. In particular, it is important to note that ambient



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

carbonaceous aerosols 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 (i.e., volume extraction solvent/volume air sampled) as a measure for optimal solvent extraction. The  $p$  values for the present WSOC extracts range  $0.09\text{--}1.22\ \text{cm}^3\ \text{m}^{-1}$ , and fall well within what is described as the “optimal range” of this parameter.

Higher  $\text{MAC}_{365}$  values were observed for samples of Chinese origins (Beijing and Liaoning), including the Beijing area pollution plume, than for Mongol and Korea source regions and dust events (Fig. 3a). 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  $\text{MAC}_{365}$  for these samples may reflect source-dependent differences, secondary contributions or other effects of atmospheric processing (e.g., bleaching induced by photochemical aging).

To estimate the relative range of direct climate warming effects due to light absorption of WSOC compared to EC, a simplistic calculation of absorption-based radiative

forcing was employed (Supplement for details). The relative absorption-based radiative forcing was calculated as the wavelength-dependent integrated product of solar emission and WSOC light absorption attenuation divided by the analogous integral for EC (Supplement Fig. S9). The amount of solar energy absorbed by WSOC relative to EC was 2–10% during the GoPoEx (Fig. 3b). It should be emphasized that this estimate is a first order approximation; including several simplifying assumptions (see Supplement for further discussion). For instance, the light-absorption by solvent extracts may not reflect the absorption of ambient aerosols, considering the size distribution of the aerosol, the water contents and the effects of internal mixing and their effects on absorption/scattering. However, given its limitations, this estimate indicates that the direct absorption climate effect by WSOC contributes with only a minor climate warming effect. Still this effect offsets some of the expected net cooling due to the indirect effect expected from WSOC, in particular when including additional climate effects such as indirect cloud burn-off effects (Jacobson, 2012).

### 3.4 Sources and atmospheric processing of WSOC

Radiocarbon ( $\Delta^{14}\text{C}$ ) has recently been shown to be a powerful technique for differentiating biomass/biofuel burning and biogenic emissions vs fossil sources for different components of Asian carbonaceous aerosols (e.g., Gustafsson et al., 2009; Sheesley et al., 2012; Kirillova et al., 2013). For GoPoEx, radiocarbon measurements of WSOC show that the fossil contribution is as large as the biomass/biogenic contribution in the  $\text{PM}_{2.5}$  fraction (Fig. 3c). These values are much higher than what has previously been reported for WSOC in Europe and USA, showing the much larger influence of fossil sources to this large component of aerosol carbon in the northern China outflow. For TSP, the fossil contribution was somewhat lower, showing a large influence from biomass/biogenic coarse mode water-soluble particles. Little variation in time was found during the present campaign, except for the dust episodes, when the biomass/biogenic contribution was larger.

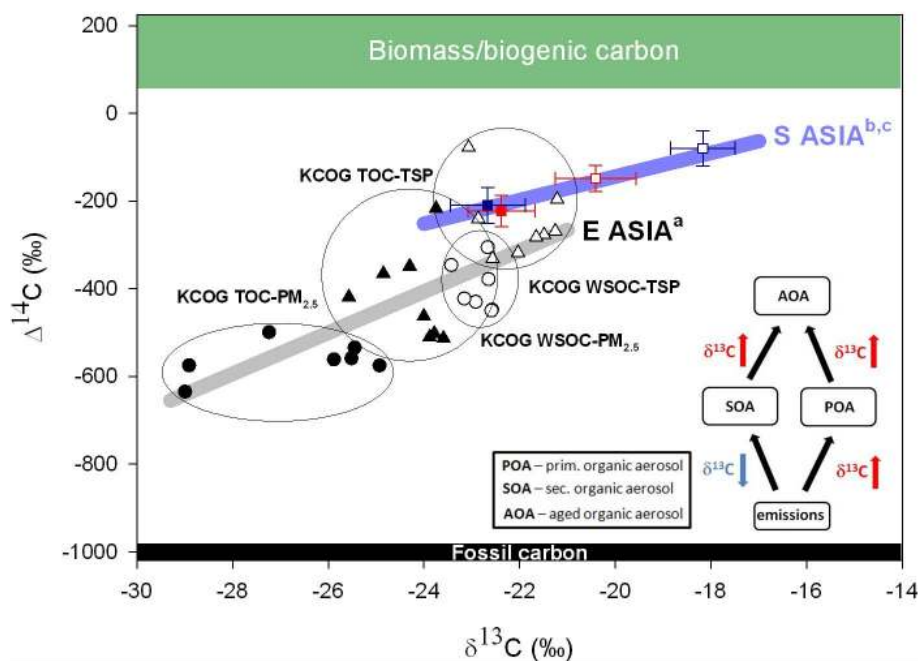
By combining the  $\Delta^{14}\text{C}$  with the stable carbon isotope ( $\delta^{13}\text{C}$ ) composition, it is possible to examine the dual effects of source variability and atmospheric processing of WSOC as well as of TOC (Kirillova et al., 2013). Since the  $\Delta^{14}\text{C}$  parameter is reported relative to a stable carbon standard, this parameter is only sensitive to emission source (biomass burning/biogenic vs fossil) variability. In contrast,  $\delta^{13}\text{C}$  is sensitive to both variability of different emissions sources (e.g., coal, petroleum, wood combustion and marine sources) and to atmospheric processing due to the kinetic isotope effect. By considering the two-dimensional  $\Delta^{14}\text{C}$ – $\delta^{13}\text{C}$  signal for the GoPoEx campaign, four clusters appear in the following order (from lower left to top right along the E. Asia continuum in Fig. 4): TOC  $\text{PM}_{2.5}$ , TOC TSP, WSOC  $\text{PM}_{2.5}$  and WSOC TSP. The four populations are distributed along a

straight line, which is similar to our previous findings for the South Asian outflow (Fig. 4: S. Asia continuum line, Kirillova et al., 2013). Comparison of the East Asian and South Asian data sets show three consistent trends: (1) higher fossil contribution in both WSOC and TOC in E. Asia than in S. Asia; (2) WSOC is more modern (i.e., “younger”  $^{14}\text{C}$  signal) and more enriched in  $^{13}\text{C}$  compared to TOC in both size fractions for both E. and S. Asia; (3) Coarse particles are more modern and enriched in  $^{13}\text{C}$  compared to  $\text{PM}_{2.5}$  for both WSOC and TOC.

The enrichment in  $^{13}\text{C}$  of WSOC relative to TOC in both East and South Asia may reflect either difference in sources or in atmospheric processing. Particulate emission sources cover a wide range of  $\delta^{13}\text{C}$  values: on average  $-13\text{‰}$  for C4 plants,  $-22$  to  $-18\text{‰}$  for marine sources,  $-23$  to  $-21\text{‰}$  for coal,  $-34$  to  $-25\text{‰}$  for C3 plants,  $-29$  to  $-24\text{‰}$  for liquid petroleum and  $-40$  to  $-28\text{‰}$  for gaseous petroleum (e.g., Miyazaki et al., 2007, 2011; Kawashima and Haneishi, 2012; Anghitori et al., 2011; Widory, 2006). For Chinese outflow, C4 plants (e.g., maize and sugar cane) are not expected to be a large contribution. By combining the isotope data with ratios of inorganic ions isolated from the same filters, marine sources are not expected to have a major influence on WSOC during the GoPoEx (Fig. S10).

The  $\delta^{13}\text{C}$  value is also influenced by atmospheric processing (Fig. 4 inset). During formation of secondary organic aerosol (SOA), molecules depleted in heavy isotopes are expected to react faster, leading to depletion in  $^{13}\text{C}$ . This prediction is supported by laboratory studies (e.g., Iannone et al., 2010; Anderson et al., 2004). In contrast, during atmospheric aging (here meaning reactions with reactive species such as the hydroxyl radical) molecules with lighter isotopes react faster, forming gaseous species such as CO,  $\text{CO}_2$  and volatile organic carbon (VOC). This leads to an enrichment of  $^{13}\text{C}$  in the residual carbon in the aerosol phase, which has also been supported by laboratory and field studies (Aggarwal and Kawamura, 2008; Smith et al., 2009). In addition, aging may also involve rearrangement within the aerosol phase (e.g., condensation reactions), without production of gaseous substances (Kalberer et al., 2004; Zahardis et al., 2006; Nguyen et al., 2011). Since there is then no net transfer of carbon, these reactions do not affect  $\delta^{13}\text{C}$  signature of the aerosol TOC, but may change the signature of a subpopulation such as of the WSOC. Semivolatile organic compounds partition between gas and particulate phases causing enrichment of heavier isotopes in the particulate phase. However, laboratory studies indicate these effects are likely to have only a minor effect on the  $\delta^{13}\text{C}$  signature (Harrington et al., 1999; Wang and Kawamura, 2006).

Both SOA formation and aging leads to production of more polar compounds, such as WSOC. The higher  $\delta^{13}\text{C}$  values ( $^{13}\text{C}$  enrichment) of WSOC compared with TOC either indicates differences in sources or processing. Excluding the less likely candidates C4 plants and marine contributions, it is unlikely that the observed difference between TOC and



**Fig. 4.** Two-dimensional presentation of dual-isotope ( $\delta^{13}\text{C}$  vs.  $\Delta^{14}\text{C}$ ) signals of WSOC and TOC in  $\text{PM}_{2.5}$  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) data sets from western-central Indian site of Sinhadag (SINH) and Indian Ocean site on Hanimaadhoo Island, Maldives (MCOH). South Asian data are 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 a thick light blue line for South Asia and a grey line for East Asia. The bottom right inset graphically summarizes the general trends of the influence of atmospheric processing on the  $\delta^{13}\text{C}$  signature of carbonaceous aerosols.

WSOC reflects source differences. Instead, the more probable explanation is that this difference is determined by atmospheric processing/aging since enrichment in  $^{13}\text{C}$  is observed (Kirillova et al., 2013). This hypothesis is consistent with the fact that the same TOC vs WSOC trend is observed at all three sites (KCOG, MCOH and SINH) and for two size fractions ( $\text{PM}_{2.5}$  and TSP) (Fig. 4), as well as WSOC being more polar than TOC in general. The more enriched  $^{13}\text{C}$  values observed at MCOH (S. Asia receptor), compared with SINH and KCOG, are likely to reflect a longer source-receptor transport time.

The enrichment in  $^{13}\text{C}$  observed in WSOC relative to TOC is for the currently examined data sets always correlated with higher biomass ( $\Delta^{14}\text{C}$  value) contents. Fossil fuel combustion in general occurs at higher temperatures/pressures than biomass burning. This means that fossil sources of carbonaceous aerosols are more recalcitrant to further chemical oxidation than products of biomass burning and biogenic origins (Elmqvist et al., 2006). This observation thus offers an explanation why “aging” (here in the meaning of reactive transformations) of carbonaceous aerosols is preferential for more  $^{14}\text{C}$ -modern (i.e., biomass) components. In addition, atmospheric processing also offers an explanation why  $\text{PM}_{2.5}$  particles are more depleted in  $^{13}\text{C}$  than TSP: SOA formation produces particles that rarely grow larger than  $2.5\ \mu\text{m}$  (Se-

infeld and Pandis, 1998). The lower  $\delta^{13}\text{C}$  of  $\text{PM}_{2.5}$  for both TOC and WSOC are thus expected to reflect larger relative contributions from SOA to the WSOC in  $\text{PM}_{2.5}$  than in the TSP pool.

#### 4 Conclusions

Radiocarbon ( $^{14}\text{C}$ ) constraints of carbonaceous aerosols in Chinese outflow show that up to half of water soluble organic carbon (WSOC) (26–49 % in  $\text{PM}_{2.5}$  and 12–38 % in TSP) is of fossil origins. This contribution is significantly larger than what has been observed in South Asia, Europe and USA. The direct light absorptive properties of WSOC were found to range 2–10 % relative to that of the main light absorptive aerosol component, elemental carbon. Thus, even though WSOC typically absorb sunlight to some extent, the net climate effect of WSOC during GoPoEx campaign is expected to be cooling. Stable carbon isotope analysis show that the WSOC from the Chinese outflow observed at the Yellow Sea receptor site is subject to aging during long-range transport.

**Supplementary material related to this article is available online at <http://www.atmos-chem-phys.net/14/1413/2014/acp-14-1413-2014-supplement.pdf>.**

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