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Title: Springtime carbon emission episodes at the Gosan background site revealed by total carbon, stable carbon isotopic composition, and thermal characteristics of carbonaceous particles

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Responses to the reviewer's specific comments and questions:

Reviewer #1 (Comments):

This paper reports on the analysis of total suspended matter from filter samples taken in April/May 2007 and April 2008 at the Gosan site on Jeju Island. The samples were analysed with respect to total carbon, organic and elemental carbon, total nitrogen and citric and oxalic acid concentration. The thermal characteristics of organic and elemental carbon are reported for individual filter samples. Furthermore the carbon isotopic composition of total carbon and oxalic and citric acid were measured and used for the interpretation of the aerosol sources. Aerosol particles influence climate and have adverse health effects. Elucidating the source of particles and identifying potential strategies for reducing atmospheric burdens of particles is an up to date topic. A particular challenge in this respect is the organic fraction of aerosols which has a vast variety of sources and is known to change properties and composition upon atmospheric aging. Therefore the paper in principle merits publication in ACP. Unfortunately the paper has several weaknesses which should be corrected before publication.

Major comments

The main issue with the interpretation of these data comes from the classification of individual episodes. It seems from the manuscript that the classification into long range transport, pollen and Asian dust, is based on HYSPLIT backward trajectory analysis. While the sampling was performed 3m above ground level, the backward trajectories were calculated for 500m above ground level. No explanation is given why a trajectory at 500m would be representative of the 3m sampling height in the observation period. This is a crucial point and a proper justification for using backward trajectories at 500m must be given. This is particularly important when taking into account that the filter samples were taken over long averaging times (2 to 6 days). These long averaging times certainly increase the risk that samples can not be unambiguously assign to one air mass origin or episode.

Response: Following sentence has been added. Please see lines 256-261 in the revised MS.

“Because a long-range transported haze layer was frequently observed between ~0.2 km and 3 km elevation over the Korean peninsula (Noh et al., 2009; Yoon et al., 2008), even though aerosol sampling was conducted at ~3 m height above the ground level, backward trajectories that ended at 500 m height were used in this study by assuming complete vertical mixing below a boundary layer height.”

Two references have been added in the reference section.

“Noh, Y. M., Müller, D., Shin, D. H., Lee, H., Jung, J. S., Lee, K. H., Cribb, M., Li, Z., Kim, Y. J.: Optical and Microphysical Properties of Severe Haze and Smoke Aerosol Measured by Integrated Remote Sensing Techniques in Gwangju, Korea, *Atmos. Environ.*, 43, 879–888, 2009.

Yoon, S. C., Kim, S. W., and Kim, M. H.: Ground-based Mie-scattering lidar measurements of aerosol extinction profiles during ABC-EAREX 2005: Comparisons of instruments and inversion algorithms, *J. Meteor. Soc. Japan*, 86, 377-396, 2008.”

In particular the data in table 2 shows, that hardly any difference can be seen between the different classes (see also attached figure). Within the reported standard deviations no difference can be seen between episodes. If at all the main difference between the episodes is seen in d13C.

Response: Mass concentrations of ammonium, nitrate, and sulfate have been added in Table 2. The categorization of the haze episodes for the AD episode has been modified as AD+LTP (Asian dust plus long-range transported pollution).

Following sentences have been added. Please see lines 297-305 in the revised MS.

“Subdivision of the carbon episodes was conducted as follows. Pollen episodes were identified by the elevated concentrations of citric acid and pollen in the TSP samples as described by Jung and Kawamura (2011). Even though the TC value ($7.5 \mu\text{gC m}^{-1}$) for the KOS612 sample during the pollen episodes was lower than the threshold value, we included this sample to the carbon episode for comparison of different episodes. LTP episodes were identified by the elevated concentrations of nitrate and sulfate during the carbon episodes. AD+LTP episodes were identified by the elevated concentrations of Ca^{2+} and low aerosol Ångström exponents as well as the elevated concentrations of nitrate and sulfate during the carbon episodes.”

Following sentence has been added. Please see lines 306-308 in the revised MS.

“Mass concentrations of nitrate and sulfate during the LTP episodes were more than 2 times higher than those during the pollen and non-episodes (Table 2), indicating strong influences of anthropogenic pollutants.”

The sentence beginning “The elevated concentration of nss-Ca^{2+} ...” has been modified as

follows. Please see lines 334-337 in the revised MS.

“The elevated concentrations of nss-Ca^{2+} (avg. $7.5 \pm 0.2 \mu\text{g m}^{-3}$), nitrate (avg. $16.0 \pm 7.6 \mu\text{g m}^{-3}$), and sulfate (avg. $32.5 \pm 15.1 \mu\text{g m}^{-3}$) in the KOS603 and KOS627 filter samples supported the presence of dust particles and anthropogenic pollutants (Tables 1-2)”

On the other hand e.g. the data for the two pollen episodes shown in figure 2 seem to differ substantially in terms of $\delta^{13}\text{C}$ and TC/TN ratio, further raising the question how representative the classification of episodes is.

Response: More severe pollen episodes were observed during 2008 than 2007. This difference caused the elevated mass concentrations of TC during the pollen episodes in 2008. However, stable isotopic composition of TC in TSP samples during the pollen episodes (Figs. 7a and 10) showed similar trend according to pollen strength. Thermal evolution pattern of OC were comparable between 2007 and 2008 (Figs. 11 and 13).

The authors should furthermore provide information on how they accounted for the different number of samples available for the individual episodes. Were the reported values weighted with number of samples or is the difference in data coverage not considered when comparing different episodes?

Response: Following sentence has been added. Please see lines 438-441 in the revised MS.

“Because TC mass weighted average $\delta^{13}\text{C}_{\text{TC}}$ values during the different episodes agreed within 3‰ to the arithmetic means of $\delta^{13}\text{C}_{\text{TC}}$, we used the arithmetic means when comparing different episodes.”

The sampling and methods part of the manuscript lacks detailed information in a number of places, partly making it difficult to assess the validity of data interpretation.

Response: The term “at a flow rate of $50 \text{ m}^3 \text{ hr}^{-1}$ ” has been added. Please see lines 109-110 in the revised MS.

Following sentence has been added. Please see lines 167-171 in the revised MS.

“The nitrate (NO_3^-) and sulfate (SO_4^{2-}) were determined using a Shodex IC SI-90 4E column with 1.8 mM Na_2CO_3 /1.7 mM NaHCO_3 as an eluent (flow rate: 1.2 ml min^{-1} , sample loop volume: 200 μl , time eluted: 15 min). The analytical errors of the water-soluble inorganic ions were less than 1.4% based on the triplicate analyses of filter sample.”

Following sentence has been added. Please see lines 194-196 in the revised MS.

“5 standards ranging from 0.2 mg to 0.6 mg of acetanilide were prepared and analyzed by the EA-irMS. Acetanilide was purchased from Thermo Electron with a $\delta^{13}\text{C}_{\text{TC}}$ of -27.26‰.”

Following sentence has been added. Please see lines 229-235 in the revised MS.

“Peak identification was performed by comparing the GC-irMS retention times with those of authentic standards. Identification of the esters was also confirmed by mass spectra of the sample using a GC-mass spectrometry (Thermo Trace MS) system (Jung and Kawamura, 2011). The $\delta^{13}\text{C}$ values of the esters relative to the PDB standard were calculated from $^{13}\text{C}/^{12}\text{C}$ ratio of the C^{13} standard and its $\delta^{13}\text{C}$. The internal standard was purchased from the WAKO Chemical Co. and its $\delta^{13}\text{C}$ is -27.24‰ (Kawamura and Watanabe, 2004).”

Following sentence has been added. Please see lines 241-244 in the revised MS.

“Around 0.55–2.83 ng of the working standards were injected to the GC-irMS. The working standards were purchased from the biogeochemical laboratories at Indiana University and their $\delta^{13}\text{C}$ ranged from -33.24‰ to -28.49‰ (<http://php.indiana.edu/~aschimme/n-Alkanes.html>).”

For instance the authors need to describe the procedure used to separate pollen from an ambient sample in much more detail and show that this sample contains pollen only.

Response: Following sentence has been added. Please see lines 125-129 in the revised MS.

“An aliquot (15 cm²) of the KOS751 filter sample was placed in a glass vial (50 ml) with a Teflon-lined screw cap and the pollen grains were separated by mild vibration using an automatic vibrator (Iuchi, HM-10) for 5 min. The separated pollen grains were then transferred to a pear shape flask for chemical analysis.”

Also the standard pollen samples used need to be further specified, in particular with respect to the author’s statement on page 13882, line 4 that $d13\text{C}$ of pollen samples may depend on geographical location. Table3 shows a much lower (-28‰ $d13\text{C}$ for the pollen in the ambient sample than measured for the standard pollen (-25.4 and -23.3‰ for cedar and cypress pollen, respectively).

Response: Following sentences have been added. Please see lines 501-505 in the revised MS.

“The Pollen_Gosan was produced on Jeju Island, Korea while the authentic standard pollens were produced on Japan (personal communication to Wako Chemical Co.). Thus, the differences of $\delta^{13}\text{C}_{\text{TC}}$ values between the Pollen_Gosan and the authentic standard pollens may be explained by the different geographical conditions.”

Also the huge differences in the $d13\text{C}$ of the water soluble fraction, especially of oxalic acid is not well explained, probably due to the small number of samples (here only one ambient pollen sample is discussed).

Response: $\delta^{13}\text{C}$ values of oxalic acid in the different types of pollens were explained in the original MS as follows. Please see lines 582-589 in the revised MS.

“The elevated $\delta^{13}\text{C}$ values of oxalic acid were obtained for the authentic standard pollen

samples; -5.0‰ for the Pollen_cedar and 1.0‰ for the Pollen_cypress. These high $\delta^{13}\text{C}$ values of oxalic acid can be explained by the adsorption of aged oxalic acid on pollen before becoming air borne. The $\delta^{13}\text{C}$ value of oxalic acid in the Pollen_Gosan was higher than those in the tangerine peel and the KOS751 sample. Jung and Kawamura (2011) reported similar amounts of oxalic and citric acids in the tangerine peel, suggesting that not only aged oxalic acid but also directly emitted oxalic acid from the tangerine peel may be adsorbed on the Pollen_Gosan and transported together.”

The term “C2” in the original Ms has been changed to “oxalic”. Please see lines 582-589 in the revised MS.

In several parts of the manuscript the discussion remains very speculative and is in this reviewers' opinion not sufficiently underpinned by the data. For instance on Page 13883 line 23 the authors interpret a “divergence of the $d13\text{C}$ values at a certain level of citric acid-C/TC ratio” as due to “different adsorption efficiency of citric acid on pollens and different emission strength of citric acid from tangerine fruit”. This is certainly not the only possible explanation, e.g. mixed air mass influence on some of the samples, other sources of citric acid, fractions of carbon with low $d13\text{C}$ other than pollen etc. could all lead to the same observation.

Response: Following sentence has been added. Please see lines 564-565 in the revised MS.

“The divergence of the $\delta^{13}\text{C}_{\text{TC}}$ values also can be explained by the variability of the $\delta^{13}\text{C}_{\text{TC}}$ of non-pollen carbon.”

Similarly the authors interpret the difference of $d13\text{C}$ of citric acid in the ambient sample and the $d13\text{C}$ of citric acid in tangerine peel as due to the kinetic isotope effect. This is highly speculative. To this reviewers knowledge no data on KIE of citric acid in atmospheric reactions is available in the literature. In any case the presence of a KIE and its influence on observed $d13\text{C}$ in citric acid would imply a chemical loss process of citric acid. This would at the same time mean that no robust correlation between citric acid content of a sample and e.g. $d13\text{C}$ of total carbon can be expected.

Response: Sentences beginning “Laboratory ...” in lines 6-15 in page 13884 in the original MS were deleted.

Following sentences have been added. Please see lines 571-577 in the revised MS.

“The pollen-enriched TSP samples were collected during spring of 2007 and 2008 whereas tangerine fruit was produced during early winter of 2010. Thus, these differences can be partially explained by seasonal and annual variations of $\delta^{13}\text{C}$ of citric acid in the tangerine peel. The $\delta^{13}\text{C}$ values of *n*-alkanes for individual lipids from the leaves of *Quercus castaneifolia* showed ~ 2.5 and 5.2‰ differences for C_{29} and C_{31} *n*-alkanes, respectively, in autumn leaves

compared with leaves sampled at the start of the growing season (Lockheart et al., 1997).”

A reference has been added in the reference section.

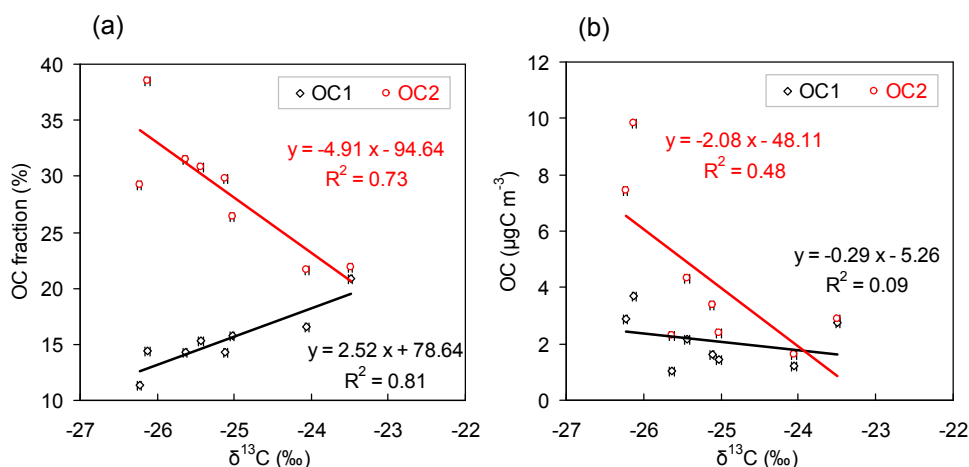
“Lockheart, M. J., Van Bergen, P. F., and Evershed, R. P.: Variations in the stable carbon isotope compositions of individual lipids from the leaves of modern angiosperms: implications for the study of higher land plant-derived sedimentary organic matter, *Org. Geochem.*, 26, 137–153, 1997.”

Similarly the discussion of thermally resolved OC components and their changing abundance during long range transport (page 13887 line 10 and following) remains very vague and speculative. In the discussion of the dependence of $\delta^{13}C$ on thermally evolved OC fractions, it seems that the main fractions OC1 and OC2 have to show the observed behaviour. Since both fractions are normalized by total OC, if one increases, the other will necessarily decrease. An anti-correlated dependence of $\delta^{13}C$ on OC1 and OC2 therefore seems to provide no information on the source or characteristics of the aerosol.

Response: The sentences beginning “The OC1 and OC2 ...” in line 21 in page 13887 to line 2 in page 13888 in the original MS have been modified as follows. Please see lines 653-665 in the revised MS.

“The OC1 and OC2 fractions normalized by total OC mass showed good correlations with $\delta^{13}C_{TC}$ with R^2 of 0.81 and 0.73, respectively, during the pollen episodes (Fig. 13a) whereas a moderate correlation was observed between OC2 mass concentration and $\delta^{13}C_{TC}$ with $R^2 = 0.48$ (Fig. 13b). However, almost no correlation was observed between the OC1 mass concentration and $\delta^{13}C_{TC}$ (Fig. 13b). Because the Pollen_Gosan had low $\delta^{13}C_{TC}$ of -28.0‰ (Table 3), the negative correlations of the normalized OC2 mass fraction and OC2 mass concentration with $\delta^{13}C_{TC}$ indicated that a large fraction of the pollen-enriched TSP samples evolved at the OC2 temperature step (300 – 450 °C). Almost no correlation between OC1 mass concentrations and $\delta^{13}C_{TC}$ indicated that the positive correlation between the normalized OC1 fraction and $\delta^{13}C_{TC}$ was mainly attributed to a relative decrease in OC1 fraction to total OC as OC2 fraction increases during the pollen episodes.”

Scatter plot of OC mass concentrations versus stable carbon isotopic composition has been added in the Fig. 13b as follows.



Minor and technical points:

Figure 1 is not referred to in the text.

Response: The term “(Fig. 1)” has been added. Please see line 106 in the revised MS.

“Carbon episodes” as used in the title and throughout the manuscript is not a well defined term.

Response: Following sentences have been added. Please see lines 288-294 in the revised MS.

“The frequency distribution of TC mass concentrations at $2 \mu\text{gC m}^{-1}$ increments is shown in Fig. 2 with a peak value in the range of $6\text{--}8 \mu\text{gC m}^{-1}$. Gaussian fit of the frequency distribution showed a peak center at $7.2 \mu\text{gC m}^{-1}$ with the width of $3.1 \mu\text{gC m}^{-1}$, representing background TC mass distributions during the entire sampling periods. The Gaussian fit was clearly separated from the total TC distribution with a threshold value of $10 \mu\text{gC m}^{-1}$ (Fig. 2). Thus, this study defined the carbon episode as an average mass concentration of $\text{TC} > 10 \mu\text{gC m}^{-1}$.”

Page 13869 line 8: sentence not clear

Response: Following sentence has been added. Please see lines 48-52 in the revised MS.

“Novakov and Penner (1993) determined the relative contributions of sulfate and organic aerosols to cloud condensation nuclei (CCN) concentrations at a marine site known to be influenced by anthropogenic emissions, and found that organic aerosols account for the major part of both the total aerosol number concentration and the CCN fraction.”

Page 13879 line 4: sentence not clear. More detailed information on aerosol sampling should be provided. For instance what was the cut-off size of the sampling set-up, which sampling flows were used?

Response: The sentence begging “TC and TN concentrations ...” in line 22 in page 13878 in the original MS has been modified as follows. Please see lines 407-412 in the revised MS.

“TC and TN concentrations were obtained from the Hua mountain site in China in winter (size cut: PM₁₀, sampling flow rate: 100 l min⁻¹, integration time: 10 hr) (Li et al., 2011) and three cities in China; Shanghai in winter and spring (PM_{2.5}, 0.4 l min⁻¹, weekly) (Ye et al., 2003), Nanjing in winter (PM_{2.5}, 1110 l min⁻¹, 12 hr) (Yang et al., 2005), Baoji in spring (PM₁₀, 100 l min⁻¹, 8 hr) (Wang et al., 2010).”

Page 13871 line 24: what was the tangerine fruit prepared for?

Response: Following phrase has been added. Please see lines 129-130 in the revised MS.

“In order to track the sources of the dicarboxylic acids and related compounds and airborne pollen,”

Following phrase has been added. Please see lines 131-133 in the revised MS.

“and analyzed for dicarboxylic acids and related compounds (Jung and Kawamura, 2011) and for carbon isotopic compositions of total carbon, oxalic acid, and citric acid.”

Filter areas used for individual analysis are given surprisingly exact. How well determined is the filter area use?

Response: Following phrase has been added. Please see line 182 in the revised MS.

“cut using a circular cutter with a diameter of 1.6 cm”

Page 13874 line 15: were blank measurements for this procedure performed?

Response: Following sentences have been added. Please see lines 217-219 in the revised MS.

“The blank level of TC mass was less than 2.0% of the measured mass. The $\delta^{13}C_{TC}$ values reported here were corrected against the blank using isotope mass balance equations (Turekian et al., 2003).”

Page 13876 line 7: starting from here results are presented.

Response: The title of section 3 has been changed to “Air mass backward trajectories and aerosol optical thickness (AOT)”. Please see line 247 in the revised MS.

The paragraphs starting from line 7 in page 13876 in the original MS has been moved to section 4 and named as “4.1 Categorization of the carbon emission episodes”. Please see line 287 and below in the revised MS.

Page 13880 line 21: removed_C is not the abbreviation used in figure 6.

Response: The terms “removed_C” and “remained_C” in section 4.3 have been changed to “RMD-C” and “REM-C”, respectively.

Following sentence has been added. Please see line 464 in the revised MS.

“where REM-C represents the remaining carbon after the HCl fume treatment.”

Page 13881 top paragraph: some explanation could be provided why carbonate C is expected to have high $\delta^{13}\text{C}$.

Response: Following sentences have been added. Please see lines 465-468 in the revised MS.

“Isotope equilibrium exchange reactions within the inorganic carbon system “atmospheric CO_2 – dissolved bicarbonate – solid carbonate” lead to an enrichment of ^{13}C in carbonates (Hoefs, 1996). Thus, carbonate carbon is isotopically heavy, with $\delta^{13}\text{C}$ values of around 0‰ (Hoefs, 1996; Kawamura et al., 2004).”

A reference has been added in the reference section.

“Hoefs, J.: *Stable isotope geochemistry*, Springer, New York, 1997.”

Discussion of citric acid in pollen samples (page 13883): the cited reference (Jung and Kawamura 2011) is not available and the conclusions are therefore difficult to assess.

Response: The cited reference “Jung and Kawamura (2011)’ has been published recently in *Atmospheric Environment*.

The reference has been modified as follows.

“Jung, J. and Kawamura, K.: Enhanced concentrations of citric acid in spring aerosols collected at the Gosan background site in East Asia, *Atmos. Environ.*, 45, 5266–5272, 2011.”

Table3: sum formulas of oxalic acid and citric acid could be provided

Response: Following phrases have been added in the Table 3. Please see the annotation in the Table 3 in the revised MS.

“Oxalic acid: $(\text{COOH})_2$, Citric acid: $\text{C}_3\text{H}_5\text{O}(\text{COOH})_3$ ”

Figure 10: Why is it that for most of the data the signal at times 0 and 1000 is >0 ? If this is an issue of offsetting the data for visualization, a better way of presentation should be chosen.

Response: Since it is difficult to show multiple peaks at one figure panel, base line of each thermogram was shifted 0.5 toward the Y-axis for better visualization. Following sentence has been added in Fig. 11 caption.

“Base line of each thermogram was shifted 0.5 toward the Y-axis to better visualization of overlaying thermograms.”

Figure 11: this again shows how little difference between episodes is seen in some of the aerosol features: LTP_NEC is equal to pollen events in terms of OC1 and OC2 characteristics.

Response: LTP_NEC and LTP_EC episodes have been merged in the revised MS.

Following sentence has been added. Please see lines 628-630 in the revised MS.

“Thermal evolution patterns of OC during the LTP episodes showed relatively constant OC2 mass concentrations but strongly variable OC1 mass concentrations (Fig. 12).”