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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 #3 (Comments):

Aerosol particles play an important role in atmospheric chemistry and physics. They have an impact on the Earth's radiation budget and thus on climate both on regional and global scales. The various direct and indirect sources of these particles, their complex composition and the change of composition - associated with that their chemical and physical properties - during atmospheric transport and aging makes it extremely difficult to assess their impact quantitatively. To improve our knowledge in this respect and to develop appropriate mitigation strategies the sources and composition of aerosol particles have to be investigated using sophisticated approaches. The paper reports investigations of aerosol particles from filter samples taken at the Gosan site on Jeju island. The authors provide a conclusive study on the origin of aerosol particles combining the information of chemical composition, stable carbon isotope ratios and thermal characteristics. They combine these different measurements with backward trajectories and satellite remote sensing data. This is a laborious but excellent approach to gather the necessary information of aerosol composition and source attribution. The paper contains new and interesting results and certainly merits publication in ACP. However, major revisions are needed before publication. In many chapters the paper contains a lot of information and a lot of data which makes it a bit hard to read and to follow the arguments. Although I have presently no good idea how to do that, I suggest to improve the structure of the paper, maybe by presenting some of the information using additional Figures or Tables. English is not my native language, but to my mind the paper should be necessarily corrected by a native speaker.

Major comments

The abstract is too long and contains too much details. I suggest to shorten and rewrite the abstract describing the problem, the main approach, then highlighting one or two important results and the main conclusions.

Response: The abstract has been shorten and revised as suggested by the reviewer as follows. Please see the revised abstract in the revised MS.

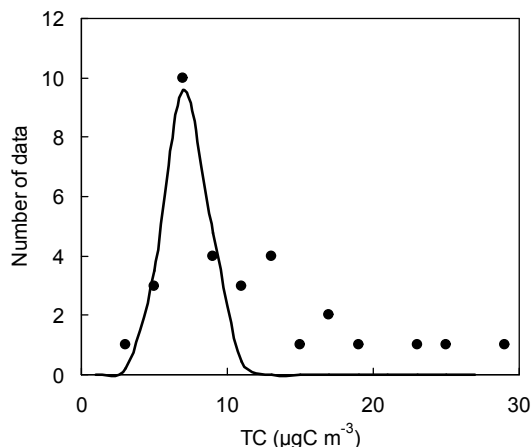
“In order to investigate the emission of carbonaceous aerosols at the Gosan background super-site (33.17 °N, 126.10 °E) in East Asia, total suspended particles (TSP) were collected during spring of 2007 and 2008 and analyzed for particulate organic carbon, elemental carbon, total carbon (TC), total nitrogen (TN), and stable carbon isotopic composition ($\delta^{13}\text{C}$) of TC. The stable carbon isotopic composition of TC ($\delta^{13}\text{C}$) was found to be lowest during pollen emission episodes (range: -26.2% to -23.5% , avg.: $-25.2 \pm 0.9\%$), approaching those of the airborne pollen (-28.0%) collected at the Gosan site. Based on a carbon isotope mass balance equation, we found that $\sim 42\%$ of TC in the TSP samples during the pollen episodes was attributed to airborne pollen from Japanese cedar trees planted around tangerine farms in Jeju Island. A negative correlation between the citric acid-carbon/TC ratios and $\delta^{13}\text{C}$ was obtained during the pollen episodes. These results suggest that citric acid emitted from tangerine fruit may be adsorbed on the airborne pollen and then transported to the Gosan site. Thermal evolution patterns of organic carbon during the pollen episodes were characterized by high OC evolution in the OC2 temperature step (450 °C). Since thermal evolution patterns of organic aerosols are highly influenced by their molecular weight, they can be used as additional information on the formation of secondary organic aerosols and the effect of aging of organic aerosols during the long-range atmospheric transport and sources of organic aerosols.”

How is a “carbon episode” defined. From Figure 2 it is not very clear how the authors distinguish between the different episodes. The differences are not really recognizable. Since obviously TC is used, what is the threshold and what is the reason for that?

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 $\text{TC} > 10 \mu\text{gC m}^{-1}$.”

Following figure has been added in Fig. 2.



There is a significant difference between the pollen episodes in 2007 and 2008. What justifies this differentiation?

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

Actually, the separation into the different episodes is the weakest point of the whole paper and the main target for criticism. Reading the paper raised a number of questions concerning this point (not necessarily in the correct order).

Response: 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.”

The HYSPLIT trajectories give only a rough estimate of the origin of air masses. Usually, it is difficult to calculate trajectories within the PBL. The measurements were done at the ground. I do not know the conditions at the site, but what were the local effects that can significantly alter the composition of an air mass?

Response: Following sentences have been added. Please see lines 254-256 in the revised MS.

“Up to 20% errors of the traveled distance are typical for those trajectories computed from analyzed wind fields (Stohl, 1998). Thus, calculated air mass pathways indicate the general airflow pattern rather than the exact pathway of an air mass.”

A reference has been added in the reference section.

“Stohl, A.: Computation, accuracy and applications of trajectories: A review and bibliography, *Atmos. Environ.*, 32, 947–966, 1998.”

Following sentences have 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.”

Following sentences have been added. Please see lines 261-264 in the revised MS.

“Because the Gosan site is located at the western edge of Jeju Island and there are no high mountains within several kilometers of the site, local geographical conditions rarely affect the backward trajectory calculation.”

Looking at Figure 4, the trajectories look very similar for the different episodes. For which dates are the trajectories calculated? For instance, some of the red and white trajectories also pass over the Nei Mongol desert. Is there no advection of dust particles in these cases? How did you rule that out?

Response: Backward trajectories were calculated everyday and plotted in the revised Fig. 4 according to each episode.

The trajectories during the pollen and non-episodes have been added in the revised Fig. 4c,d.

Following sentences have been added. Please lines 362-364 and 376-378 in the revised MS.

“Air mass backward trajectories during the pollen episodes mainly originated from the northern part of China and the western North Pacific Ocean (Fig. 4c).”

“Air mass backward trajectories during the non-episodes mainly originated either from the northern part of China or the western North Pacific Ocean (Fig. 4d).”

Mass concentrations of PM₁₀ and nss-Ca²⁺ and Ångström exponent were used to track the dust episode.

Samples were collected over several days. How did the back trajectories change during the sampling period? How did local effects such as local winds influence the samples? Is the strict separation into these episodes justified looking at an ensemble of back trajectories for that period?

Response: The carbon episodes were further subdivided based on precursor compounds such as citric acid, sulfate, nitrate, and calcium, which were described in lines in the revised MS. Backward trajectories were used to track the source regions of each episode. All daily trajectories were computed and updated in the revised Fig. 4.

Following sentence has been added. Please see lines 319-320 in the revised MS.

“The air mass backward trajectories generally showed similar transport pattern during each sampling period.”

The plots given in Figure 3 give the MODIS data for two specific days to show the difference of the LTP and AD episodes. Do these data (AOT and Angstrom exponent) look the same for all days during these episodes?

Response: AOT and Angstrom exponent from MODIS data showed similar pattern during the LTP episodes.

Two more examples for the LTP and AD-LTP episodes have been added. Please see Figs. 5c,d and Figs. 5g,h for the LTP and AD-LTP episodes, respectively.

Are any of the back trajectories shown in Figure 4 for these days?

Response: Following sentence has been added. Please see lines 315-319 in the revised MS.

“Air mass backward trajectories for the KOS606 and KOS614 samples during the LTP episodes are shown as yellow trajectories in Fig. 4a, implying that air masses for the KOS606 and KOS614 samples mainly originated from the eastern part of China and migrated to the sample site.”

How did the MODIS data and the back trajectories look like during the pollen episodes?

Response: MODIS data and air mass backward trajectories during the pollen episodes have been added in Figs. 5i,j and Fig. 4c, respectively.

Following sentences have been added. Please see lines 358-364 in the revised MS.

“Since it was cloudy during most of the pollen episodes (Jung and Kawamura, 2011), only a few MODIS images are available. MODIS AOT and α values during the selected day (19 April 2008) of the pollen episodes showed relatively low aerosol loadings over Korean peninsula (Figs. 5i,j). Air mass backward trajectories during the pollen episodes mainly originated from the northern part of China and the western North Pacific Ocean (Fig. 4c).”

What exactly is the difference between the EC and NEC episodes? The back trajectories in both cases start somewhere in Mongolia. What parameters justify this distinction?

Response: We have merged the LTP_EC and LTP_NEC episodes to the LTP episodes in the revised MS and discussed accordingly.

What justifies the distinction between the weak AD episode and the LTP episode? In the text the authors state that the trajectories originate in NEC in this case.

Response: MODIS AOT and Angstrom exponent during the weak AD+LTP episode (25 May 2007) have been added. Please see the revised Fig. 5g,h.

Very low Ångström exponent in the haze plume indicates the presence of dust particles. High $n_{ss-Ca^{2+}}$ further supported the presence of dust particles in the TSP sample. Please see lines 326-339 in the revised MS.

I suggest, the pollen episodes describe very local phenomena? What was the meteorological situation in these cases? What specifies a pollen episode?

Response: Following sentences have been added. Please see lines 539-543 in the revised MS.

“The cultivating area of tangerines in Jeju Island is $\sim 209 \text{ km}^2$, which accounts for $\sim 11\%$ of the total area of the island. In order to dissipate the strong winds from the Pacific Ocean, all tangerine farms are surrounded by Japanese cedar trees. Pollen in the air on Jeju Island in April was mainly from the Japanese cedar trees (Agricultural Research Institute in Jeju special self-governing province, personal communication).”

Pollen episodes were identified as follows. Please see lines 348-350 in the revised MS.

“Identification of pollen episodes was based on daily human observation of pollen blowing and the microscopic image of pollens collected in the TSP samples (Jung and Kawamura, 2011).”

Following sentence has been added. Please see lines 114-116 in the revised MS.

“Measurements of wind direction and wind speed at 10 m above ground level were obtained from the Korea Meteorological Administration at the Gosan Observatory.”

Following sentences have been added. Please see lines 364-367 in the revised MS.

“Dominant wind directions during the pollen episodes were northerly and southeasterly. Relatively low wind speed was observed for southeasterly winds with a median of 5.1 m sec^{-1}

(range: 0.3 – 13.4 m sec⁻¹) compared to northerly winds with a median of 7.1 m sec⁻¹ (range: 0.7 – 20.5 m sec⁻¹).”

Did you sample only pollen during these episodes? Or was it a mixture with a large contribution of pollen?

Response: Pollen samples mean pollen enriched total suspended particulate (TSP) samples. Please see lines 340-367 in the revised MS.

Are the corresponding data given in Table 2 really only pollen?

Response: The data in Table 2 represent chemical compositions and stable carbon isotopic composition in the TSP samples during the AD+LTP, LTP, and pollen episodes.

Please see the Table 2 caption.

How did you separate the pollen from other particles?

Response: Following sentences 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.”

What was the fraction of pollen during the other episodes?

Response: Almost no pollens were observed in the TSP samples during the other episodes. Temporal variation of citric acid as an indicator of pollens in the TSP samples represents negligible fraction of pollens in the TSP samples during the other episodes. Following sentences have been added. Please see lines 371-374 in the revised MS.

“Mass concentrations of citric acid during the non-episodes (range: 0.17 – 18 µg m⁻³) were several dozen times lower than the pollen episodes (range: 20 – 320 µg m⁻³) and almost no pollen grains were observed from the microscopic image of the TSP samples.”

The conclusion given in the abstract (page 13868, lines 19-21) and also in the conclusion „The negative correlation ... These results suggest ...“ is not clear to me.

Response: This result was explained in detail as follows. Please see lines 554-565 in the revised MS.

“It was clearly evident that the $\delta^{13}C_{TC}$ decreased as citric acid-C/TC mass ratios increased. Because the airborne pollen showed much lower $\delta^{13}C_{TC}$ values than the LTP particles (Tables 2-3), the decrease of $\delta^{13}C_{TC}$ with an increase of citric acid-C/TC ratio demonstrates an

increased contribution of airborne pollen to aerosol TC. These results indicated the positive correlation between citric acid and airborne pollen concentration, suggesting that citric acid emitted from tangerine fruit might be adsorbed on airborne pollen and then transported to the Gosan site. Divergence of the $\delta^{13}C_{TC}$ values at a certain level of the citric acid-C/TC ratios as shown in Fig. 10 may be explained by different adsorption efficiencies of citric acid on different pollen and different emission fluxes of citric acid from tangerine fruit over time. The divergence of the $\delta^{13}C_{TC}$ values also can be explained by the variability of the $\delta^{13}C_{TC}$ of non-pollen carbon.”

If 45 % of the TC was due to pollen, what was the rest?

Response: Following sentence has been added. Please see lines 531-532 in the revised MS.

“The rest of TC can be explained by long-range transported anthropogenic OC and EC.”

The authors should specify what “authentic standard pollen” is? How is it prepared? How representative is it?

Response: Authentic standard pollens were purchased from the WAKO Chemical Co. Please see lines 119-122 in the revised MS as follows.

“Two authentic standard pollen samples from Japanese cedar (Pollen_cedar) and Japanese cypress (Pollen_cypress) were obtained from the WAKO Chemical Co. (product No. 168-20911 for Japanese cedar and 165-20921 for Japanese cypress).”

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 $\delta^{13}C_{TC}$ values between the Pollen_Gosan and the authentic standard pollens may be explained by the different geographical conditions.”

What is the origin of oxalic acid on these pollen, the stable carbon isotope ratio of which is given in Table 3?

Response: The origin and stable carbon isotope ratio of oxalic acid on the authentic standard pollens are discussed in lines 582-589 in the revised MS as follows.

“The elevated $\delta^{13}C$ 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 $\delta^{13}C$ values of oxalic acid can be explained by the adsorption of aged oxalic acid on pollen before becoming air borne. The $\delta^{13}C$ 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.”

Can you give any information about the origin of the air masses outside of the “carbon episodes”? The carbon isotope ratios shown Figure 6a for the non-episode samples seem to indicate aged particles or aged organic compounds on these particles during these episodes.

Response: Air mass backward trajectories during the non-episodes have been added. Please see Fig. 4d in the revised MS.

d) Non-episode



Following sentence has been added. Please see lines 376-378 in the revised MS.

“Air mass backward trajectories during the non-episodes mainly originated either from the northern part of China or the western North Pacific Ocean (Fig. 4d).”

I do not understand the interpretation on page 13879 regarding the TC/TN ratios as well as on page 13883 regarding citric acid and the respective carbon isotope ratios. I have the impression that there is a lot of speculation and there might be either a lot of other possible reasons to explain the observed data. For instance, how large is the adsorption efficiency of citric acid? Is there any information available?

Response: Following sentence in lines 1-2 in page 13879 in the original MS was deleted.

“Excellent correlation ($R^2 = 0.98$) was obtained between TC and TN mass concentrations in the Asian continent (Fig. 6b).”

Following sentences in lines 5-9 in page 13879 in the original MS were deleted.

“About twice lower TC/TN mass ratios at the Gosan site suggested that the formation mechanisms of aerosol phase nitrogen and secondary organic aerosols are quite different during the long-range atmospheric transport. Different dry and wet deposition rates between nitrogen containing particles and organic aerosols may also be attributed to these differences.”

Temporal variation of mass concentrations of citric acid has been added. Please see Fig. 3.

The reference “Jung and Kawamura (2011)” has been updated in the reference section 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.”

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

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

Is it ever possible to load pollen or other particles with this compound during the last minutes or hours of transport to the measurement site? What is the distance of the tangerine plantation to the site and what is the transport time? How large is the plantation and how long are the „contact times“ for citric acid to stick on the particles at the observed wind speeds? Is that a realistic explanation?

Response: Following sentences have been added. Please see lines 539-546 in the revised MS.

“The cultivating area of tangerines in Jeju Island is $\sim 209 \text{ km}^2$, which accounts for $\sim 11\%$ of the total area of the island. In order to dissipate the strong winds from the Pacific Ocean, all tangerine farms are surrounded by Japanese cedar trees. Pollen in the air on Jeju Island in April was mainly from the Japanese cedar trees (Agricultural Research Institute in Jeju special self-governing province, personal communication). Because tangerines are widely cultivated in the coastal areas of Jeju Island, the distance of the nearest tangerine farms to the sampling site is between several hundred meters to several tens of kilometers, depending on the wind direction.”

Summarizing all these points I think the conclusions drawn from the results are not always comprehensible. Since the focus of this paper is an identification of the origin and composition of aerosol particles, it is absolutely necessary to clarify the distinction of the different episodes.

Response: The conclusion section has been modified as suggested by the reviewer. Please the modified conclusion section.

Minor points that should be clarified:

Figure 1 is not cited in the text.

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

Page 13873. lines 19-21: What type of standard was used? On page 13874 a C13 standard is mentioned, on page 13875 a mixture of alkanes. Which was used for what? What is an appropriate amount? What was the „theoretical“ value the measurements were compared with

and how was it obtained?

Response: An acetanilide standard was used for the calibration of the EA-irMS. 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 $\delta^{13}C_{TC}$ of -27.26‰.”

A C^{13} alkane was used for the internal standard of each sample for the GC-irMS. Following sentences have been added. Please see lines 235-237 in the revised MS.

“The $\delta^{13}C$ values of free organic acids were then calculated by an isotopic mass balance equation using the measured $\delta^{13}C$ of the derivatives and the derivatizing agent (1-butanol) (Kawamura and Watanabe, 2004).”

A mixture of alkanes was used to check the performance of the GC-irMS prior to actual sample analysis. Following sentence has been added. Please see lines 241-245 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 $\delta^{13}C$ ranged from -33.24‰ to -28.49‰ (<http://php.indiana.edu/~aschimme/n-Alkanes.html>). In this paper we report $\delta^{13}C$ values for oxalic and citric acids.”