

Reply to Comments of Anonymous Referee # 2

General this is a study of particle organics collected in Fairbanks, Alaska in the summer of 2009. This is now some time ago but if the data obtained are interesting they might merit publication even after one decade. Detailed chemical particle analysis can be tedious and I feel this paper delivers interesting data and their sound interpretation even though the results are not 'real-time'. The paper is beyond standard as it delivers analysis data on lignin and resin products the analysis of which is usually not being done. The same is true for the determination of the phthalate esters.

Overall, I feel the paper is well in the scope of ACP and could be accepted after a revision which is somewhere between minor and mayor.

Reply: We thank the reviewer for the positive comments and very careful reading of the manuscript. We have now taken all of them into account in the revised version of the manuscript. Please refer to the revised manuscript where we highlighted the changes in yellow. We provide here below a reply to the specific comments and modifications made in the revised manuscript.

Details

Abstract, last sentence: Is this sentence needed? How would that connection work? Can you add a few words? See also last comment below here.

Reply: Following the comment of reviewer, we rephrased the sentence at the end of the abstract.

“We propose that PM_{2.5} laden with OAs derived in central Alaska may have a serious impact on the air quality and climate in the Arctic via long-range atmospheric transport.”

Please see lines 29-31 in the revised manuscript.

P6, l 151 ff: It would be great to document all of the individual analysis results, e.g. in a data file as part of the supplement. The information content of Table 1 is a bit sparse.

Reply: We now provided a Table S1 in the supplement with information on the list of all organic compounds measured and their concentrations in all PM_{2.5} aerosol samples collected during the campaign.

P7, l 165 ff: The analysis of these compounds in my view is a highlight of the paper. Maybe it could still be improved in that possible oxidation of the anhydrosugars is included in the discussion and properly referenced. Levoglucosan and the other compounds have been shown to undergo atmospheric oxidation in both the gas phase and the condensed phase and it would be good to include that here.

Reply: We added the following sentences with appropriate references in the revised version about the possibility of oxidation of anhydrosugars and its impact on their concentration levels during the campaign.

“The chemical reaction of anhydrosugars could also influence their concentrations in the atmosphere. Although previous studies have reported that levoglucosan can remain stable in the atmosphere for around 10 days with no substantial degradation (Fraser and Lakshmanan, 2000; Schkolnik and Rudich, 2006), recent findings (Hoffmann et al., 2009; Hennigan et al., 2010; Gensch et al., 2018) reported significant chemical reactivity of levoglucosan and have raised a question over the stability of levoglucosan in the atmosphere. Hennigan et al. (2010) carried out a smog chamber experiment and reported the lifetime of atmospheric levoglucosan to be 0.7 to 2.2 days when exposed to 1×10^6 molecules of OH cm⁻³. This lifetime is within the range of 0.5 to 3.4 days predicted by Hoffmann et al. (2009) using the Spectral Aerosol Cloud Chemistry Interaction Model. Lai et al. (2014) found that the atmospheric lifetime of levoglucosan ranged from 1.2 to 3.9 days by the control experiment integrating OH in a flow reactor under different environmental conditions and different mixing states. Nevertheless, Bai et al. (2013) reported an atmospheric lifetime of levoglucosan to be 26 days under the different variables along with OH level of 2×10^6 molecules cm⁻³ that is much longer than other predictions.

It is notable from the above discussion that the degradation of levoglucosan is mostly induced by the oxidation reaction with OH radicals and photochemical aging during long-range transport. Therefore, the degradation of levoglucosan could be insignificant if the receptor site is close to the source region. As discussed previously, anhydrosugars detected in Alaskan aerosols during the campaign were originated from local and regional BB, we consider that the degradation of anhydrosugars may not be important to contribute the low levels of BB tracers in the samples collected at the beginning and end of the campaign.”

Please see lines 236-257 in the revised manuscript.

Based on the levoglucosan determinations: Can you estimate the PM mass concentration contribution from wood burning? That would be a great additional number and result.

Reply: This is a great suggestion but we do not have a PM_{2.5} mass data for these samples. However, Referee # 3 asked to discuss the contributions of biomass burning and other tracer compounds in organic carbon (OC) in the revised version. Therefore, based on the comment of both the reviewers, we have added a new table (Table 3) and discussed the contribution of tracer compound classes to OC in the revised manuscript as given below.

“3.8 Contributions of compound classes to aerosol organic carbon

The contributions of each compound class to organic carbon (OC) in the Alaskan aerosols are given in Table 3. BB tracers accounted for 1.35 to 8.35 % (ave. 4.40 %) of OC. The contribution of anhydrosugars to OC was substantially high (ave. 4.26 %) than that of lignin and resin acids (ave. 0.14 %). This value from Fairbanks is notably higher than those reported in aerosol samples collected from a round-the-world cruise (ave. 0.15 %) (Fu et al., 2011), Gosan Jeju Island in Korea (ave. 0.29 %), Sapporo (ave. 0.44 %) and Chichijima (ave. 0.06 %) in Japan (Simoneit et al., 2004a), and Chennai in India (ave. 0.59 %) (Fu et al., 2010). The lipid compound classes in Fairbanks samples accounted for 1.16 to 45.8 % (ave. 12.4 %) of OC. *n*-Alkanoic acids contributed on average 7.48 % (0.67 to 15.9 %), which is much higher than those estimated in samples of round-the-world cruise (ave. 0.82 %), Sapporo (ave. 0.62 %) and Chichijima (ave. 0.78 %) (Simoneit et al., 2004a; Fu et al., 2011). The tracers of primary biological aerosol particles accounted for on average 0.85 % (0.17 to 1.50 %), among which comparable contributions of primary sugars (ave. 0.39 %) and sugar alcohols (ave. 0.46 %) to OC were found in Alaskan aerosols. Plastic burning tracer accounted for 0.02 to 1.07 % of OC (ave. 0.14 %), which is lower than those from Sapporo (ave. 1.1 %) and Chichijima

samples (ave. 1.2 %) (Simoneit et al., 2004a) and tropical samples from India (ave. 4.50 %) (Fu et al., 2010). Biogenic SOA tracers contributed 0.18 to 3.99 % of OC (ave. 1.66 %), among which the contribution of isoprene-derived SOA tracers was high (ave. 1.28 %) followed by monoterpene (ave. 0.34 %) and sesquiterpene (ave. 0.03 %) SOA tracers. Other SOA tracers that contribute very less to OC include polyacids (ave. 0.08 %) and aromatic acids (ave. 0.02 %).

With the consideration of water-soluble dicarboxylic acids and related polar compounds measured in the same sample sets as reported in Deshmukh et al. (2018), the total organic compounds identified in the Alaskan aerosols accounted for 6.37 to 59.2 % with a mean of 21.4 % of OC. This result indicates that a substantial portion of OAs studied in the Alaskan site can be identified at a molecular level.

Table 3. Contributions (%) of individual organic compound classes to organic carbon (OC) in PM_{2.5} aerosols from central Alaska.^a

Compound classes	Minimum	Maximum	Mean	Median	Standard deviation
Biomass burning tracers					
Anhydrosugars	1.32	8.12	4.26	3.64	2.13
Lignin and resin acids ^b	0.03	0.51	0.14	0.11	0.13
Subtotal	1.35	8.35	4.40	3.71	2.24
Lipid compounds					
<i>n</i> -Alkanes	0.05	8.53	1.55	0.98	2.19
<i>n</i> -Alkanols	0.40	21.3	3.32	1.82	5.47
<i>n</i> -Alkanoic acids	0.67	15.9	7.48	6.71	4.80
Subtotal	1.16	45.8	12.4	9.20	11.3
Primary biological aerosols					
Primary sugars	0.05	0.85	0.39	0.50	0.26
Sugar alcohols	0.07	0.95	0.46	0.33	0.33
Subtotal	0.17	1.50	0.85	0.74	0.56
Phthalate esters	0.02	1.07	0.14	0.05	0.28
Aromatic acid	0.01	0.09	0.02	0.01	0.02
Polyacids	0.02	0.25	0.08	0.09	0.06
Biogenic SOA tracers					
Isoprene oxidation products	0.07	3.20	1.28	0.83	1.12
Monoterpene oxidation products	0.07	0.75	0.34	0.34	0.20
Sesquiterpene oxidation products	0.02	0.04	0.03	0.03	0.01
Subtotal	0.18	3.99	1.66	1.22	1.29
Dicarboxylic acids and related compounds ^a	1.15	2.97	1.90	1.87	0.58
Total detected organic compounds	6.37	59.2	21.4	16.9	13.8

^aAll the organic compounds quantified were converted to carbon contents and then divided by OC. See Deshmukh et al. (2018) for OC and dicarboxylic acids and related compounds. ^bThe results of lignin and resin acids were combined due to the very low contribution of resin acid to OC.

Please see Table 3 and lines 623-649 in the revised manuscript.

P14, l 410 ff: Can these tracer determinations also be used to estimate a mass or mass fraction contribution of plastic burning to the analysed PM? That would also be interesting.

Reply: Please see our related response above. We have added the following sentences towards the contribution of plastic burning to the analyzed OC in Alaskan samples.

“Plastic burning tracer accounted for 0.02 to 1.07 % of OC (ave. 0.14 %), which is lower than those from Sapporo (ave. 1.1 %) and Chichijima samples (ave. 1.2 %) (Simoneit et al., 2004a) and tropical samples from India (ave. 4.50 %) (Fu et al., 2010).

Please see line 637-640 in the revised manuscript.

P18, l 548 ff: The end of the conclusion is interesting and the thought that these Alaskan BB particles might affect the Arctic (where such particles are also measured) should find its way into the abstract to substantiate its current last sentence.

Reply: We thank the reviewer for appreciating the conclusion of this paper. Reviewer # 3 also suggested revising the atmospheric implications of our results by referring to the existing literature on the biomass burning aerosol burden over the Arctic. Following the comment of both the reviewers, we made a detailed discussion about the implications of the result in the context of Arctic climate. Please see our related reply above for the modification made in the abstract section. We added the following sentences in the section 4 in the revised manuscript.

“The Arctic is a critical region on the Earth with a significant warming and high sensitivity to climate forcing due to a strong effect on an albedo-sea ice feedback system. Our results substantiated that forest fires and plant emissions are important factors controlling the organic chemical composition of fine aerosol particles in central Alaska. The results of Hegg et al. (2009) and Warneke et al. (2009) validate that BB causes a more efficient transport and deposition of BC aerosol in Arctic snow, causing a strong climate forcing in high latitudes. Based on in-situ measurements in the Arctic and a transport model of carbon monoxide (CO), Warneke et al. (2010) proposed that BB plumes transported to the Arctic in spring in 2008 were more than double the Arctic atmospheric burden in other seasons. Biogenic emissions from boreal forest largely increase during the summertime growing season. The year-round measurements conducted at Fairbanks by Haque et al. (2016) have shown that SOA derived from biogenic VOC emissions dominated organic chemical composition of total suspended particles during summer in central Alaska. The measurements of Ward et al. (2012) and Wang and Hopke (2014) demonstrate that Arctic air pollution could be so severe that the city of Fairbanks has been labeled as a serious nonattainment area by the United States Environmental Protection Agency.

It is worth therefore to note from the above discussion that the Fairbanks exemplifies many of the problems of pollution in the Arctic regions. The local and regional BB episodes in warmer season enhanced the atmospheric levels of OAs in central Alaska. Because residence time of fine particles is relatively long in the atmosphere, we propose that OAs of PM_{2.5} at Fairbanks can be subjected to long-range transport to the Arctic causing a significant influence on the air quality and climate in the Arctic region. Although we studied the aerosol samples collected in 2009, further research is needed to characterize the seasonal and interannual trends of OAs using more recent aerosol samples to better evaluate their current impact in the Arctic atmosphere.”

Please see lines 671-695 in the revised manuscript.

References

- Bai, J., Sun, X., Zhang, C., Xu, Y., and Qi, C.: The OH-initiated atmospheric reaction mechanism and kinetics for levoglucosan emitted in biomass burning, *Chemosphere*, 93, 2004-2010, 2013.
- Deshmukh, D. K., Haque, M. M., Kawamura, K., and Kim, Y.: Dicarboxylic acids, oxocarboxylic acids and α -dicarbonyls in fine aerosols over central Alaska: implications for sources and atmospheric processes, *Atmos. Res.*, 202, 128-139, 2018.
- Fraser, M.P., Lakshmanan, K.: Using levoglucosan as a molecular marker for the long-range transport of biomass combustion aerosols, *Environ. Sci. Technol.*, 34, 4560-4564, 2000.
- Fu, P. Q., Kawamura, K., and Miura, K.: Molecular characterization of marine organic aerosols collected during a round-the-world cruise, *J. Geophys. Res.*, 116, D13302, doi:10.1029/2011JD015604, 2011.
- Fu, P. Q., Kawamura, K., Pavuluri, C. M., Swaminathan, T., and Chen, J.: Molecular characterization of urban organic aerosol in tropical India: contributions of primary emissions and secondary photooxidation, *Atmos. Chem. Phys.*, 2663-2689, 2010.
- Gensch, I., Sang-Arlt, X.F., Laumer, W., Chan, C.Y., Engling, G., Rudolph, J., and Kiendler-Scharr, A.: Using $\delta^{13}\text{C}$ of levoglucosan as a chemical clock, *Environ. Sci. Technol.*, 52, 11094-11101, 2018.
- Haque, M. M., Kawamura, K., and Kim, Y.: Seasonal variations of biogenic secondary organic aerosol tracers in ambient aerosols from Alaska, *Atmos. Environ.*, 130, 95-104, 2016.
- Hegg, D. A. et al.: Source attribution of black carbon in Arctic snow, *Environ. Sci. Technol.*, 43, 4016-4021, 2009.
- Hennigan, C.J., Sullivan, A.P., Collett, J.L., and Robinson, A.L.: Levoglucosan stability in biomass burning particles exposed to hydroxyl radicals, *Geophys. Res. Lett.*, 37, L09806, doi:10.1029/2010GL043088, 2010.
- Hoffmann, D., Tilgner, A., Iinuma, Y., and Hermann, H.: Atmospheric stability of levoglucosan: a detailed laboratory and modeling study, *Environ. Sci. Technol.*, 44, 694-699, 2009.
- Lai, C., Liu, Y., Ma, J., Ma, Q., and He, H.: Degradation kinetics of levoglucosan initiated by hydroxyl radical under different environmental conditions, *Atmos. Environ.*, 91, 32-39, 2014.
- Schkolnik, G., Rudich, Y.: Detection and quantification of levoglucosan in atmospheric aerosols: a review, *Anal. Bioanal. Chem.*, 385, 26-33, 2006.
- Simoneit, B. R. T., Kobayashi, M., Mochida, M., Kawamura, K., Lee, M., Lim, H. J., Turpin, B. J., and Komazaki, Y.: Composition and major source of organic compounds of aerosol particulate matter sampled during the ACE-Asia campaign, *J. Geophys. Res.*, 109, D19S10, doi:10.1029/2004JD004598, 2004a.
- Wang, Y. and Hopke, P.K.: Is Alaska truly the great escape from air pollution? Long term source apportionment of fine particulate matter in Fairbanks, Alaska, *Aerosol Air Qual. Res.*, 14, 1875-1882, 2014.
- Ward, T., Trost, B., Conner, J., Flanagan, J., and Jayanty, R. K. M.: Source apportionment of $\text{PM}_{2.5}$ in a subarctic airshed - Fairbanks, Alaska, *Aerosol Air Qual. Res.*, 12, 536-543, 2012.
- Warneke, C. et al.: Biomass burning in Siberia and Kazakhstan as an important source for haze over the Alaskan Arctic in April 2008, *Geophys. Res. Lett.*, 36, L02813, doi:10.1029/2008GL036194, 2009.

Warneke, C et al.: An important contribution to springtime Arctic aerosol from biomass burning in Russia, *Geophys. Res. Lett.*, 37, L01801, doi:10.1029/2009GL041816, 2010.