Atmos. Chem. Phys. Discuss., 13, C13179–C13195, 2014
www.atmos-chem-phys-discuss.net/13/C13179/2014/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Quantifying black carbon from biomass burning by means of levoglucosan – a one year time series at the Arctic observatory Zeppelin" *by* K. E. Yttri et al.

K. E. Yttri et al.

key@nilu.no

Received and published: 30 March 2014

Reply to general comment by referee #1:

In his general comment, Referee #1 points to emission ratios as a major point of uncertainty when it comes to transforming observed ambient concentrations of levoglucosan to concentrations of aerosol particles from biomass burning, to which we agree.

Further, Referee #1 claims that the variability in the emission ratio is "much-much greater than that represented in Table 2" and applied in the current study.

We agree that emission ratios reported for levoglucosan in various studies vary

substantially and that this reflects variability in burning conditions and type of wood/vegetation burnt, and for ambient measurements, also potential degradation, e.g. by OH. However, the total range of emission ratios observed and reported in the scientific literature cannot be expected to be applicable for all cases. E.g. emissions ratios derived from prescribed fires in different continents (e.g. USA) or from laboratory burn experiments using vegetation from Western and Southeastern USA, as reported by e.g. Sullivan et al. (2008), are thus not particularly relevant for the Arctic and sub-Arctic regions studied in the current paper and thus accounting for such data is not apparent, at least not when better alternatives exist. In the current study, we have made an effort to select emission ratios that are derived from the region that we are studying and hence of relevance for the current study, i.e., both with respect to emissions from agricultural/wild fires and residential wood burning. We recognize, though, that emission ratios for levoglucosan wrt to EC, OC and TC are not abundant for the actual region and that we thus might miss parts of the total range, but expanding the range based on ratios from prescribed fires or laboratory burn tests involving vegetation from totally different parts of the world is scientifically hard to justify.

Referee #1 points to the emission ratios derived from the study of Saarikoski et al. (2007) used for wild and agricultural fires in the present study, claiming that it is mostly relevant for wild fires in Western Russia and that "it is highly probable that wild/agricultural burning of many different fuel types from different regions impacted the measurements across the entire year". Further, he points to the fact that this was a single event, lasting for 12 days, and that levoglucosan most likely had undergone some degradation during long-range transport (at least several hundred kilometers) from the emissions in western Russia until it reached Helsinki.

In our opinion, the emission ratios derived from Saarikoski et al. (2007) appear to be a very good choice for a number of reasons. The vegetation type burnt was a mix of different land cover types (See Table 1 in Stohl et al. (2007), including cropland, and the area burnt was vast (20 000 km2). The vegetation type is likely to be repre-

sentative for a major part of the region considered to be the footprint of the Zeppelin Observatory (See Figure 3 in the current paper). Using these ambient data provides a good method of averaging the variability observed for emission ratios when burning only one tree/vegetation type. In addition, major changes in the burning conditions is likely to occur over a period of 12 days, which also is accounted for in the emission ratios derived.

Concerning degradation of levoglucosan, we cannot neglect that this might have taken place during the episode from which the emission ratios were derived; but to what extent? The current FLEXPART simulation of the episode (See .ppt file: FLEXPART_SIMULATION_2006_EPISODE_ACPD_882) shows that the transport time from the areas burnt and to Helsinki was in fact rapid; i.e., typically less than 24 hours and occasionally no more than 6 hours. In the study by Saarnio et al. (2010) a transport time of 24 – 100 hours is listed for the actual episode. This then suggest that the moderate variability observed for the derived emission ratios during this episode (See Table 2) could be a result of rapid transport (as predicted by FLEXPART) and hence little time for degradation, or that degradation plays a smaller role than expected for transport times ranging from 24 - 100 hours. In either case, this governs the use of the derived emission factor and range.

Referee #1 points to the emission factors used for residential wood burning in the current study stating that they are representative of the fuels and appliances in Norway, and that it is likely that residential wood burning from other areas (especially Northern Russia) had as much or more impact on the measurements over the course of the study. Residential wood burning emission ratios of levoglucosan for the region defined by FLEXPART to be the footprint of Zeppelin (during winter) are scarce. The emission ratio range that we have applied in the current study (OC/levoglucosan = 8 – 15; derived from Table 2 in the current study) does however include the ratio reported by Saarikoski et al. (2008) (OC/levoglucosan = 9.2) for the urban area of Helsinki, Finland. Saarikoski et al. (2008) also applied the same analytical approach as that of Yttri et al. (2009 and

2011), which further improves the comparability. Residential wood burning emission ratios of levoglucsoan for Northern Russia would indeed be desirable, but do not exist to our knowledge.

Referee #1 would like to see the uncertainties associated with the levoglucosan emission ratios applied in the current study brought into the interpretation of the results to a broader extent than at present, and he points to two issues discussed in the text where this might seem appropriate:

1) Could the employed emission ratios impact the apparent underprediction of residential burning emissions from northern Russia during winter?

In section 4.4 of the revised paper we have stated that: “we consider OH degradation of levoglucosan, levoglucosan emission ratios and uncertainties in the emissions to be the most important reasons for the observed deficit between the modeled and observational derived mean ECbb.” Hence, we cannot exclude that the at least part of the underestimation can be attributed to the emission ratio. However, the statement concerning the underestimation heavily relies on the information about the emissions and the FLEXPART footprint for Zeppelin. Figure 4 shows that there is no overlap between the area with known BC emissions, and the footprint for Zeppelin when there is a strong levoglucosan episode observed at Zeppelin. In more detail; In the emissions shown in Figure 4 panel a) there is no emissions present in north-east of Russia for March 2008. However, there is a strong episode with high levoglucosan concentrations at Zeppelin starting on the 27th March, and combining this with the Zeppelin footprints shown in panel b) and c) for this period the air is coming from this region.

2) During the Jan-Feb-March sampling, levoglucosan appears to be very well correlated with EBC (though with the resolution on Fig. 2 it is a little hard to tell). Nevertheless, it is surprising to see this level of structure in both traces, and yet the apportionment method only estimates 9-45

The correlation between EBC (or σap) and levoglucosan is thoroughly discussed in the

paper (page 31981 ln 19 – page 31982 ln2). In brief; One cannot conclude whether the high correlation observed between EBC and levoglucosan (R2 = 0.84) is attributed to either biomass burning being the major source of EBC or whether thorough mixing of aerosol particles from all sources entering the polar dome during the Arctic Haze period is the reason. The full text on this topic as stated in the paper is given below.

No pronounced correlation was observed between the absorption coefficient (σap) and levoglucosan on an annual basis; hence BC from other sources than biomass burning was likely the major contributor to the observed absorption coefficient values. From January 2009 higher correlation between σap and levoglucosan was observed, and for the last 40 days of sampling (25 of January – 7 of March 2009) R2 = 0.84. Although this was the time period during which the highest concentrations of levoglucosan were observed, one cannot exclude that the high correlation was a result of the Arctic Haze phenomenon causing thorough mixing of aerosol particles from all sources entering the polar dome during this time of the year, rather than biomass burning (here: residential wood burning) being the major source of BC. No pronounced correlation was observed when correlating major inorganic aerosol constituents and SO2 with σap, except for SO42- (R2 = 0.74). Consequently, we cannot point to either of the two suggested reasons explaining the high correlation observed between levoglucosan and σap.

To account for the general comment made by referee #1, focusing on the uncertainty associated with the range of emission ratios for levoglucosan applied in the current study, we have included parts of the answers given above into the paper.

Added to section 2.6 of the revised paper:

The choice of emission ratio is critical for the EC derived from biomass burning (ECbb) emissions. Thus, we have made an effort to select emission ratios from the geographical region being the source region of the Zeppelin Observatory, both with respect to emissions from agricultural/wild fires and residential wood burning. Emission ratios for levoglucosan wrt to EC, OC and TC are not abundant for the actual region and we

recognize that we thus potentially could might miss parts of the total range. However, expanding the range based on ratios from prescribed fires or laboratory burn tests involving vegetation from other parts of the world is scientifically hard to justify.

Added to section 4.4 of the revised paper

We consider OH degradation of levoglucosan, levoglucosan emission ratios and uncertainties in the emissions to be the most important reasons for the observed deficit between the modeled and observational derived mean ECbb.

It should be noted though, that a part, yet unknown, of the underestimation could be attributed to uncertainties in the emissions, as well as the levoglucosan emission ratio

Reply to specific comments by referee #1:

Pg. 31983, line 17-18: This finding could indicate something about the lifetime of levoglucosan. But what if the assumed levoglucosan and BC emission ratios were off during this period (see above comment)? That could greatly impact the interpretation of the findings as well.

Answer:

The two following sentences have been added to section 4.4 to account for the referees comment:

We consider OH degradation of levoglucosan, levoglucosan emission ratios and uncertainties in the emissions to be the most important reasons for the observed deficit between the modeled and observational derived mean ECbb.

It should be noted though, that a part, yet unknown, of the underestimation could be attributed to uncertainties in the emissions as well as the levoglucosan emission ratio.

Comment from ref #1: For the model-measurement comparisons and discussion, a scatter plot would greatly help. As it is, the resolution in Fig. 2 makes it very hard to compare.

Answer: We will ask ACP/ACPD editorial office to enlarge Figure 2 for the final version of the paper to ease the comparison between modelled and observed values.

Comment from ref #1: Figure 5 (the only figure that plots the ECbb/ECB ratio) shows the values assuming no degradation of levoglucosan (monthly mean values of only 2-16

Changes have been made to the caption of Figure 5 to account for the comment made by referee #1:

Fig. 5. The blue bars show the monthly mean relative contribution of elemental carbon from biomass burning (ECbb) to total equivalent black carbon (EBC) at Zeppelin for the time period March 2008–February 2009 (left axis). Standard deviations are included. These values are lower estimates as degradation of levoglucosan are not accounted for. The light blue curve is the monthly mean ambient concentration of elemental carbon from biomass burning (ECbb), whereas the red curve is that of equivalent black carbon (EBC) for the same period (right axis).

Reply to general comment by referee #2:

General comment:

"There was only 1 major issue that I had with the methods of the paper – 2 field blanks for 73 filters measured by thermal optical analysis is insufficient."

Answer:

Of the 12 field blanks sampled during the sampling period, only 7 were available for Thermal-Optical analysis. This is because some of the field blanks were entirely consumed for the levoglucosan analysis, leaving none for TOA. Reanalysis was only possible for one of the two field blanks reported in the submitted paper. The results show showed that the mean $\pm$ SD carbon content of the field blanks was 1.0 $\pm$ 0.3 μg C cm$-$2. The carbon content was entirely attributed to OC; i.e., no EC was observed on the field blanks. For the field blank being reanalyzed, the concentration increased from

0.1 μg C cm$-$2, which is below the instrument's analytical detection limit, to 0.73 μg C cm$-$2, strongly suggesting that the field blanks have picked up organic material during its 5 years of storage in the freezer at minus 18 °C.

The following text have been added to the revised paper:

Field blanks (n = 2) analyzed within 10 months after the sampling period was ended, showed remarkably low carbon concentrations; i.e., < 0.2 μg C cm$-$2, being the analytical LOD of the TOA instrument. The carbon content of field blanks (n = 6) analyzed after 5 years, was 1.0 $\pm$ 0.3 μg C cm$-$2. For the one field blank for which reanalysis was possible, the concentration increased from 0.1 μg C cm$-$2, which is below the instrument's analytical LOD, to 0.73 μg C cm$-$2, strongly suggesting that the field blanks have picked up organic material during 5 years of storage in the freezer at -18 °C. For all field blanks, the carbon content was entirely attributed to OC; i.e., no EC was observed on the field blanks. The sampling approach did not allow for addressing positive and negative artefacts associated with sampling of OC.

Reply to specific comments by referee #2:

Specific comments:

Abstract: line 10: this is a blanket statement for Europe – would it be better to be more specific? I.e. High density wood burning areas?

Answer:

The objective for addressing the impact from residential wood burning emissions by means of levoglucosan can vary substantially between studies, and it need not necessarily be that this is due to anticipated high levels. Further, which criteria would qualify to define an area as a "high density wood burning area" and how would this be documented? The urban sites listed in Table 5 in the paper by Szidat et al. (2009) includes sites situated widely across Europe and cannot as a whole be categorized as high density wood burning areas. The same argument can be used for the rural background

sites addressed by Puxbaum et al. (2007) and Yttri et al. (2013). Hence, we think that the statement should be as it is without any further specification about its quality.

Ln 14: how long were the elevated episodes?

Answer:

Episodes of elevated concentrations lasted from 1-6 days.

The following text has been added to the revised paper:

Episodes of elevated levoglucosan concentration lasting from 1 - 6 days were more frequent in winter than in summer and peak values were higher, exceeding 10 ng m-3 at the most.

Ln 27-28: this is an overstatement that the model compared relatively well. The following statements just illustrate that the model fell within the large range provided by the ECbb and ECbb*.

Answer:

The phrase stated in the paper and which the referee points to ("Calculations using the Lagrangian particle dispersion model FLEXPART show that the seasonal variation of the modelled ECbb (ECbb,m) concentration compared relatively well with observationally derived ECbb from agricultural/wild fires during summer, and residential wood burning in winter.") merely states that the seasonal variation compares well between the model and that observed, and do not relate to the quantitative aspect of the comparison between the model and the observations, which is addressed in the following sentence in the paper.

P31968 ln1: awkward phrase: "highly absorbing species black carbon"

The actual sentence has been rephrased:

Consequently, it can be argued that the largest uncertainties when studying the

aerosols' impact on climate in the Arctic are attributed to black carbon (BC)1, which is generated by incomplete combustion of fossil fuel and biomass.

P31969 ln 4: need a ref for 20-30% BC

Answer:

The following reference has been included:

Yttri, K.E., Dye, C., Braathen, O.-A., Simpson, D., Steinnes, E. Carbonaceous aerosols in Norwegian urban sites. Atmos. Chem. Phys., 9, 2007-2020, 2009.

P31970 ln 2: should be "confirmation of"

Answer:

Changed accordingly.

Section 2: you need to clarify that the QA for the methods is included in one section – I had questions throughout that were then answered in section 3.

The following text has been added to section 2.2 in the revised paper:

Quality assurance of the aerosol filter sampling, as well as the chemical analysis performed is presented in section 3.

P31972 ln 12: are these stable carbon or deuterated standards? Give molecular formula and source of standard.

The following amendments have been made to the text to account for the referee's request:

Levoglucosan, mannosan, and galactosan were identified and quantified on the basis of retention time and mass spectra of authentic standards (Sigma). 13C labeled levoglucosan ($C_6H_{10}O_5$) and galactosan ($C_6H_{10}O_5$), purchased from Cambridge Isotope Laboratories, Inc., were used as internal standards. This approach accounts for any potential loss of the native compounds during the sample preparation.

P31973 ln 17: delete obviously

Answer:

Changed accordingly.

P31973 ln 22: give n for residential and wildfire/ agricultural emission sources that were averaged to create the emission factors used here.

Answer:

See comments made to general comment by referee #1.

P31973 ln 26-27: delete this sentence

Answer:

Done

Equation 4: what is the r2 for this relationship between _ (sigma) and EC for Zeppelin?

Answer:

r2 equaled 0.77. This information has been added to the text in section 2.7 of the paper.

P31977 ln 10: I'm not familiar with this schedule – can you explain the 2+2+3?

The following amendment was made to the text to account for the referee's request:

Moreover, during occasions when the Digitel sampler was not operational due to e.g. maintenance, filter samples were obtained from a co-located high volume sampler, with a sampling time of 2 (Monday – Wednesday and Wednesday - Friday) and 3 (Friday - Monday) days pr week.

Ln 28: Is this the precision of the standards? The recovery is needed for the levoglucosan analysis during this particular study.

The following amendment was made to the text in section 2.3 to answer to the referees questions:

The precision reported is that of authentic standards. The use of 13C isotope labeled standards of levoglucosan (C6H10O5) and galactosan (C6H10O5) as internal standards, accounted for the recovery.

The following amendment was made to the text to improve its clarity:

Levoglucosan, mannosan, and galactosan were identified and quantified on the basis of retention time and mass spectra of authentic standards (Sigma). 13C labeled levoglucosan (C6H10O5) and galactosan (C6H10O5), purchased from Cambridge Isotope Laboratories, Inc., were used as internal standards. This approach accounts for any potential loss of the native compounds during the sample preparation.

P31978 ln10: This is a VERY low n for field blanks. Appropriate QAQC would be field blank analysis for 1 in 10 samples. You cannot get good statistical information from 2 field blanks. The authors really need to go back and analyze a couple more field blanks to fill out this QAQC. This is a sticking point for the paper, but the importance of field blank analysis cannot be overstated.

Answer:

See answer made to the general comment put forward by referee #2.

P31978 ln 24: are these comparison values for Zurich? Please include the city, country.

Answer:

Table 5 in Szidat et al. (2009) provides a list of 12 studies including 15 sites in 10 different European cities, and thus detailed information on city and country cannot be listed in the text in the current paper.

P31983 ln10-15: this discussion becomes difficult to follow. Edit for clarity.

The following changes were made to the text to improve its clarity:

When using chemical half-life times of levoglucosan ranging from 3 – 4 days for the winter time period, including the τ1/2 values suggested for winter by Hoffmann et al. (2010), ECbb is underestimated by a factor of 5 – 7, corresponding to an ECbb* concentration ranging from 20 – 28 ng m-3. When using chemical half life times of levoglucosan ranging from $\frac{1}{2}$ - 2 days, which includes the τ1/2 values suggested for summer by Hoffmann et al. (2010), ECbb is underestimated by a factor of 130 - 4000. This in turn corresponds to an ECbb* concentration range which far exceeds that of the summer time mean EBC concentration, and thus is unlikely.

P31986 ln 12-14: once the model for estimating halflife is shown to be inaccurate, it would seem to be more appropriate to report a range than to merely adjust the half-life until a "reasonable" percentage is obtained. In this case reasonable just means <100%, there needs to be better justification for choosing 4 days again.

The following text has been added to the paper to account for the comment made by referee #2.

Consequently, a reliable upper estimate of ECbb* to EBC for summer cannot be provided based on the chemical life times suggested for levoglucosan by Hoffmann et al. (2010).

Ln 22-23: this sentence is awkward.

The following text has been added to the paper to account for the comment made by referee #2:

No statement can be made whether fossil fuel or biomass burning sources dominated during the warm season, as no reliable upper estimate of ECbb* to EBC could be provided for summer based on the chemical life times suggested by Hoffmann et al. (2010).

Ln 28-3 (next page): this sentences need to be clarified and/or saved for the conclu-

sion, as they are repeated later. This is an important clarification, so the authors should take care to word these sentences very clearly and carefully. Please edit.

Answer:

The sentence has been clarified and saved for the conclusion as suggested by referee#1. See answer made to comment Ln 27 -3 (next page) by referee #2.

P31987 ln 25-26: add "annual" before Arctic EBC and delete "totally"

Answer:

Done.

Ln 27 -3 (next page): this is copied directly from the previous page. It is awkward and also should not be copied directly.

The following changes have been made to the text to increase its clarity:

Note though, that the annual Arctic EBC loading is dominated by the wintertime sources, thus focus should be to understand these in more detail for a successful mitigation. On the other hand, winter values are not as important as summer values from a radiative forcing (climate) perspective, although they do lead to BC deposition on snow and ice, which leads to a reduction of the snow/ice albedo, which may persist into spring/summer.

Figure 1: need to include labels. At a minimum, the Arctic Circle should be labeled. Answer:

The figure has been corrected in accordance with the suggestion made by the referee.

Figure 3: The source regions defined by FLEXPART for the annual sensitivity seems to be very dispersed. What does this tell us? Is FLEXPART not ideal for long-term averaging?

Answer: Figure 3 shows the source regions averaged over summer and winter and this

includes many different periods (meteorological conditions) with very different transport patterns. While the region with high emission sensitivity for an individual episode may be quite well defined and relatively small, seasonal averaging leads to a much larger region with high emission sensitivity. This is not at all specific to FLEXPART but would be obtained in a very similar manner with any other model and reflects reality. For instance, see the trajectory statistics plots shown by Eleftheriadis et al. (2009).

Figure 5: the blue ECbb line cannot be seen at all. The figure needs to be adjusted with lighter color for the bars.

The Figure has been adjusted in accordance with the suggestion made by the referee.

References:

Eleftheriadis, K., Vratolis, S., and Nyeki, S.: Aerosol black carbon in the European Arctic: Measurements at Zeppelin station, Ny-Ålesund, Svalbard from 1998–2007, Geophys. Res. Lett., 36, L02809, doi:10.1029/2008GL035741, 2009.

Hoffmann, D., Tilgner, A., Iinuma, Y., and Herrmann, H.: Atmospheric stability of levoglucosan: a detailed laboratory and modeling study, Environ. Sci. Technol., 44, 694–699, doi: 10.1021/es902476f, 2010.

Puxbaum, H. Caseiro, A., Sánchez-Ochoa, Kasper-Giebl, A., Claeys, M., Gelencsér, A., Legrand, M., Preunkert, S., and Pio, C.A.: Levoglucosan levels at background sites in Europe for assessing the impact of biomass combustion on the European, aerosol background, J. Geophys. Res., 112, D23S05, doi: 10.1029/2006JD008114, 2007.

S. Saarikoski, H. Timonen, K. Saarnio, M. Aurela, L. Järvi, P. Keronen, V.-M. Kerminen, and R. Hillamo Sources of organic carbon in fine particulate matter in northern European urban air. Atmos. Chem. Phys., 8, 6281-6295, 2008

Saarnio K., Aurela M., Timonen H., Saarikoski S., Teinilä K., Mäkelä T., Sofiev M., Koskinen J., Aalto P.P., Kulmala M., Kukkonen J. and Hillamo R. (2010) Chemical composition of fine particles in fresh smoke plumes from boreal wild-land fires in Europe.

Sci. Total Environ. 408, 2527–2542, doi:10.1016/j.scitotenv.2010.03.010.

Stohl, A., Berg, T., Burkhart, J. F., Fjæraa, A. M., Forster, C., Herber, A., Hov, Ø., Lunder, C., McMillan, W. W., Oltmans, S., Shiobara, M., Simpson, D., Solberg, S., Stebel, K., Ström, J., Tørseth, K., Treffeisen, R., Virkkunen, K., and Yttri, K. E.: Arctic smoke - record high air pollution levels in the European Arctic due to agricultural fires in Eastern Europe, Atmos. Chem. Phys., 7, 511–534, doi:10.5194/acp-7-511-2007, 2007.

Sullivan, A.P., Holden, A.S., Patterson, L.A., McMeeking, G.R., Kreidenweis, S.M., Malm, W.C., Hao, W.M., Wold, C.E., and Collett Jr., J.L.: A method for smoke marker measurements and its potential application for determining the contribution of biomass burning from wildfires and prescribed fires to ambient PM2.5 organic carbon, J. Geophys. Res., 113, D22302, doi:10.1029/2008JD010216, 2008.

Szidat, S., Ruff, M., Perron, N., Wacker, L., Synal, H.-A., Hallquist, M., Shannigrahi, A.S., Yttri, K.E., Dye, C., and Simpson, D. Fossil and non-fossil sources of organic carbon (OC) and elemental carbon (EC) in Göteborg, Sweden. Atmos. Chem. Phys., 9, 1521-1535, 2009.

Yttri, K.E., Dye, C., Braathen, O.-A., Simpson, D., Steinnes, E. Carbonaceous aerosols in Norwegian urban sites. Atmos. Chem. Phys., 9, 2007-2020, 2009.

Yttri, K.E., Simpson, D., Stenström, K., Puxbaum, H., Svendby, T. (2011) Source apportionment of the carbonaceous aerosol in Norway - quantitative estimates based on 14C, thermal-optical and organic tracer analysis. Atmos. Chem. Phys., 11, 9375-9394. doi:10.5194/acp-11-9375-2011, 2011a.

Yttri, K.E., Simpson, D., Nøjgaard, J.K., Kristensen, K., Genberg, J., Stenström, K., Swietlicki, E., Hillamo, R., Aurela, M., Bauer, H., Offenberg, J.H., Jaoui, M., Dye, C., Eckhardt, S., Burkhart, J.F., Stohl, A., Glasius, M. Source apportionment of the summertime carbonaceous aerosol at Nordic rural background sites. Atmos. Chem. Phys.,

11, 13339-13357. doi:10.5194/acp-11-13339-2011, 2011b.

Yttri, K.E. et al. Source apportionment of the carbonaceous aerosol in the European regional background environment - Impact of anthropogenic sources (In prep.).

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/13/C13179/2014/acpd-13-C13179-2014-supplement.zip

---

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 31965, 2013.