Response to reviewers

We thank the reviewers for their thorough reading of our manuscript and their comments, which have been helpful for improving the manuscript. Please find below our replies to each of the comments (original comments shown in italics).

Response to Anonymous Referee #1 (CALLED #2 in ACPD web-site!)

This work presents a source apportionment analysis of carbonaceous aerosols in 4 Nordic rural background sites. The dataset is interesting, as it includes resuls on organosulphates and nitrooxyorganosulphates, which are rare in the literature. The approach used by the authors is not highly novel given that it has also been applied at Norwegian monitoring stations in a piece of work which is currently under review in this same journal. The introduction and methodology sections are very thorough, which is positive as the work may be used as reference for a review on organic aerosol sources.

Specific comments:

- page 2, line 4: "accounting for 4-12% of TCp", this sentence is misleading, it may seem to the reader that FF=4-12% of EC,which is incorrect.Please rephrase to avoid this.

Reply: We have rephrased the text to :
Fossil fuel sources totally dominated the ambient EC loading, **which accounted** for 4-12% of TCp, whereas <1.5% **of EC** was attributed to combustion of biomass.

- page 2, ine 1: "3-7% was explained by combustion of biomass":what would the authors expect to obtain in winter? How would this picture change?
Reply: The contribution from biomass combustion is expected to be higher during winter due to emissions from residential wood combustion. In order to keep the abstract as concise as possible, we prefer not to include a discussion of expected, but not studied, changes during other seasons in the abstract.

- Page 6, line 13: what is the vehicle flow/day at the A6?

Reply: 15,800 vehicles pr day in 2009. We have now included this information

- *section 2.2: there are two limitations which should be discussed: (1) the authors state they use Whatman filters, which are known to have high Na-contents and therefore tend to frost the combustion oven in the Sunset analyser, reducing the laser signal transission. How do the authors detect this degradation of the laser signal, and correct for it? (2) QBQ setup:the authors should mention the limitations of this approach, whereby gas phase organics may not have time enough to reach equilibrium and condense/adsorb onto the backup filter, therefore underestimating the positive artefact.*

Reply (1):
The Whatman QM-A filters are known to contain a certain amount of sodium (Na). At high concentrations, Na has the potential to frost the combustion oven of the instrument, causing a deteriation of the laser transmission signal.

Blank level concentrations of Na in Whatman QM-A filters (47 mm) are found to be 34 µg pr filter. This in turn corresponds to 2.8 µg pr cm-2 for a filter with an exposed area of 12 cm2, which is not particularly high. For a sampling period of one week, this Na filter loading would correspond to an ambient Na concentration of 89 ng m-3 when using the kleinfiltergerät LVS samplers. Further, it should be kept in mind that it is only *four* front- and *four* backup Whatman QM-a filters which have been analyzed from each of the four sites, and that these have been analyzed in four different instruments. Consequently, the actual amount of Na that the combustion ovens have experienced during the analyses of these filters is rather limited. By visual inspection, none of the ovens were affected by frosting.

The EC/OC instruments used in the current study are operated, inspected and maintained according to the laboratories instrument SOP, including regular change of oven in order to avoid interference of various sorts.

Reply (2):
Section 2.2 contains a description of the sampling approach used, whereas section 2.11, Quality assurance, addresses the quality assurance of the sampling methodology and the various analytical methods used in the study.

In section 2.11, we state that the QBQ approach provides a quantitative *estimate* of the positive sampling artifact. In addition, we refer to the papers of McDow and Huntzicker (1990) and Turpin et al. (1994), which describes the performance and limitations of tandem filter sampling for subsequent analysis of OC in detail. We do not think that listing all their pro and con arguments in the current paper would be appropriate. Even more important, the one week sampling time used in the present study should should be a fairly good argument to state that saturation has likely been made even for the backup filter. Keep in mind that McDow and Huntzicker (1990) tested for a period of 12, 24 and 48 hours.

- section 2.11: how much do the authors estimate that negative artefacts accounted for? With 1-week exposure their influence should be considerable. Can the authors estimate the contribution from negative artefacts?

Reply:
As already stated, neither the QBQ nor the QBT approach account for any negative artefact. In fact there is no sampling approach at present which to a sufficient level is able to account for both the negative and the positive sampling artefact. While there seems to be an agreement that a denuder in front of a quartz fibre filter, followed by a backup sorbent is the desired

solution, there has been a major challenge to find a backup sorbent which suits the actual purpose. As discussed by Chow et al. (2010), the positive artifact is likely to be bigger than the negative one. We assume this to be true for the Nordic countries as well, and has accounted for this in our calculations; Thus, the true OC should lie between the measured front and back filter values, i.e. between OCF and OCB. Hence, we take this into account in Eq. (2) (See the supplementary part), and have assigned the low, central, and high value of OC to be OCp, OCp+0.2×(OCF−OCB), OCF.

For clarification we have replaced the following sentence in section 2.11
"The rather high filter face velocity (50-54 cm s-1), and the fact that negative artifacts were not accounted for suggests that the corrected levels of OC (OCP) should be considered conservative."

with the following
"The rather high filter face velocity (50-54 cm s-1), and the fact that negative artifacts are not accounted for by this approach, suggests that the corrected levels of OC (OCP) should be considered conservative."

- section 4: line 25, "assumed emission ratios": please provide the ratios used for reference for the reader,even if they are also in Yttri et al 2011. How variable are these ratios? OC/EC may vary lagely from diesel to gasoline.

Reply: The ratios used are identical to those used in the now-published Yttri et al. 2011 (SORGA) paper. We considered adding the table also into the current paper, but doing this raises the need for discussion of both the ratios and the notation used. As both have been discussed extensively in the SORGA paper (and indeed further discussions can be found in related LHS-based studies, see below) we don't feel we can justify the extra text and space needed, and that this would detract from other issues in the paper. We prefer to point the reader to these earlier papers, and hence have made this more explicit in section 4, adding:

Extensive discussion of the choices behind the factors used, and their uncertainties, can be found in earlier related studies: Szidat et al. (2009), Gelencser et al. (2007) and ,for wood-burning emissions, Simpson et al. (2007).

- line 28: TCbb: please add that it also includes primary and secondary particles, as in the case of TCff. - It seems that the SOA tracers (isoprene, etc) were not used in this analysis. Is this correct? - Were potential interactions between C species on the filter accounted for? With such long sampling periods this kind of interaction is rather likely, and it would result in mixed aerosol sources. - Plaease add the detection limits for OC and EC analyses.

Reply:
TCbb: text added to make this clear "; OCbb includes primary and secondary OC"
SOA tracers were not used in the LHS analysis.
Interactions on the filter were not accounted for. Indeed, it is probably a good assumption that

ambient aerosols have very mixed composition, but the tracers we use (14C, levoglucosan, EC, etc.) are not affected by such interactions.
The analytical detection limit of the EC/OC analyses is 0.2 µg C cm-2, which is now stated in the manuscript.

Please find below our reply to a similar question in the initial review process

“3) My main concern regards the detection limit of the Sunset instrument for OC and EC: what were these limits? How were they determined? How do the authors ensure that they are able to report accurately concentrations <0.2 ugOC/m3, or 0.1ugEC/m3?

Answer:
In the current study we have applied the QBQ approach, which is said to provide a quantitative estimate of the positive sampling artifact of OC (or a dynamic blank if you like). Thus, OC on the backup filter should contain the sum of vaporous OC adsorbed during sampling and that native to the filter (not removed during preheating) and in addition, OC which have been adsorbed during storing, transportation, etc. What has been discovered by several researchers over the last years is that the level of OC on a backup filter actually might decrease quite substantially during sampling. This is explained by the fact that air low in vaporous OC and which is drawn through the filter actually might deplete the OC concentration of the backup filter. The level of OC on a backup filter could be reduced by as much as a factor of two when inserted into the sampler and letting particle free air depleted in vaporous OC flow through. *This means that a field blank is not representative when it comes to subtracting its OC level from that of the front filter*. Based on these arguments great caution should be made when using field blanks for correction of data from EC/OC analysis, and when backup filters (dynamic blanks) are available (as in the present study) these should much be preferred over ordinary field blanks.

From the above mentioned it becomes obvious that establishing the detection limit for OC by the common approach; i.e. as the mean concentration of the actual variable on a number of field blanks ± the SD, or as 3 times the SD of the actual variable on a number of field blanks, does not provide a reliable picture of the true detection limit. Further, one should be aware that EC is not present on ordinary field blanks or on dynamic blanks (unless there has been a leakage, and that will be addressed by a dynamic blank as well as an ordinary field blank), thus the detection limit cannot be addressed by the common approach. Hence, the analytical detection limit provided by the manufacturer of the Sunset lab instrument (0.2 µg C cm-2) has to be applied. To give an example of how the detection limit would look like for EC and OC according to the common approach, I have included an example for the Birkenes site:
Mean OC level on ordinary field blank: 1.64 ± 0.48 µg C cm-2
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-2
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-2
Analytical detection limit 0.2 μg C cm^{-2} (Sunset lab instrument)
Exposed filter area: 11.64 cm^2

-2 (Sunset lab instrument)
Exposed filter area: 11.64 cm^2

2
Flow rate: 38 l min^{-1}
-1
Sampling time: 168 hours (= 1 week)
Total air volume: 386.4 m^3
3
Established detection limit OC (3 x SD on ordinary field blanks): 0.044 μg C m^{-3}
-3
Established detection limit EC (based on analytical detection limit): 0.006 μg C m^{-3}
-3
Finally it is questioned *"How do the authors ensure that they are able to report accurately concentrations <0.2 ugOC/m3, or 0.1ugEC/m3?". In addition to what has been described above, it is stated in section 2.11 Quality assurance* that an inter comparison was conducted within the project. The main results from this exercise are provided in the paper and they show that there is a good consistency between the four different laboratories reporting levels of EC and OC. It should also be kept in mind that the samples have been collected over a one week period. Thus, although the levels in terms of μg C m^{-3} are rather low there is in fact quite much OC pr cm^{-2}, as the samplers have been operating at a rather high filter face velocity (50 - 56 cm s^{-1}) (See Table 1 in the paper). E.g. 0.2 μg C m^{-3} corresponds to 6.6 μg C cm^{-2} (which is a factor 4.5 times higher than the detection limit calculated above)."

- line 2 on page 17: "the current study covers one of the longest periods..." this might be true, but it is still a rather short measurement period. - It would be useful to see ratios levoglucosan/ OC, levoglucosan/(mannosan+galactosan) and levl/mannosan, for comparison with the literature and aiming to characterise the type of wood.

Reply:
The interested reader can calculate the actual mean ratios from data in Table 2. The authors find it questionable whether such ratios would be of any use with respect to addressing the type of biomass burned. One reason is that there might be a combination of biomass being burnt; that goes for both wild fires and domestic wood burning. Secondly, only a very few emissions studies are reported for European wood/biomass types, and only one for Northern Europe (Frey et al., 2009). Thirdly, various analytical techniques are in use for the analysis of monosaccharide anhydrides (MA), potentially causing different splits between the three most commonly reported isomers. Although work is in progress to compare the performance of the

various analytical methods used to measure MAs, no such data is currently available.

Frey Anna K.; Tissari Jarkko; Saarnio Karri M.; et al., 2009. Chemical composition and mass size distribution of fine particulate matter emitted by a small masonry heater. Boreal Environment Research 14, 255-271.

Please find below our reply to a related question in the initial review process

“4) For comparison with existing studies, it would be useful to add the ratio levoglucosan/OCtot for days under predominant influence of BB. Also the ratios levoglucosan (Mannos+Galactos) and L/M to see if it is possible to distinguish different biomass burning sources (see Fine et al., 2004; Ward et al., 2006; Engling et al., 2006; Fabbri et al., 2008). For comparison with existing studies, it would be useful to add the ratio levoglucosan/OCtot for days under predominant influence of BB. Also the ratios levoglucosan (Mannos+Galactos) and L/M to see if it is possible to distinguish different biomass burning sources (see Fine et al., 2004; Ward et al., 2006; Engling et al., 2006; Fabbri et al., 2008)

Answer:
As stated in the abstract of the paper, no more than *"3-7% (of TCp) was explained by combustion of biomass (OCbb and ECbb in this late summer campaign i.e. emissions from residential wood burning and/or wild/agricultural fires."* Hence, there are is no week (not "days" as stated by the referee) which is under predominant influence by biomass burning as stated by the referee. Consequently, adding the levoglucosan/OC ratio to the paper is of no use as the OC from biomass burning would totally "drown" in the OC signal from more dominating sources (here: BSOA). Thus, the OC/levoglucosan ratio is not suitable for extraction, comparison and discussion with ratios reported in other studies. Given the minor contribution of the biomass burning source to the total carbonaceous aerosol loading, we do not find it reasonable to elaborate further on this source by also including the isomer splits of the monosaccharide anhydrides for subsequent indications of hardwood versus softwood.

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- figure 3: "agricultural use category": please define, how is this quantified? does the land use change with time? This is unlikely. Figure 3 is rather unclear and would require clarification in the text. Same for "evergreen surface category " in section 6.3, how is this quantified?

Reply: Regarding Figure 3 and the NOAH LSM categories, we feel that to provide detail on the NOAH LSM categories is beyond the scope of the MS. Instead we rely on the reference to Dorman and Sellers, which provides ample details on the categorization of land-use types. We do acknowledge that the agricultural category is in fact not time dependent, and further that the entire LSM is potentially in need of updating -- but to our knowledge it is the currently used standard LSM for models. Furthermore, it is what drives the meteorology models that we used, and thus it is logical to 'peg' our analysis to that input.

We have added the following sentence on page 16385:
“This figure shows the relative **air mass exposure to** each of the surface types for the period of measurement **observation. It should be noted that the NOAH LSM land use categories, used to define the surface types, are static and thus do not include seasonality nor changes over time.”**

- reference Winiwarter 1999 is missing from the reference list.
Reply: We have added the reference (Winiwarter, W.; Haberl, H. & Simpson, D. On the boundary between man-made and natural emissions: Problems in defining European ecosystems J. Geophys. Res., 1999, 104, 8153-8159).

- section 6.5, page 22, line 7: "PBAP sources otherwise introduce uncertainty": some words seem to be missing in this sentence, please revise.

Reply: The sentence has been changed to “PBAB sources that would otherwise...”

- section 6.6, title: please add "aerosol" as "Biogenic aerosol oxidation products"

Reply: Since the manuscript only considers analysis of aerosols, we have found it sufficient to specify this in the beginning of the paragraph.

- Table 2: please add units for F14C TC
Reply: F14C is dimentionless since it is a fraction between two measurements, F14C = A(SN) /A(ON) (normalized activity of the sample and 95% of the normalized activity of the oxalic standard (OxI). It is found in Reimer et al. 2004

- Table 3 header: please add "b.d:below detection"
Reply: Has been added.

Responses to Anonymous Referee #2

The current manuscript adds to a list of recent publications on source apportionment

of carbonaceous aerosols combining molecular and isotopic tracers with Monte-Carlolike solution of complex equation systems. Here, results from Scandinavian rural sites during summer are presented indicating primary and secondary biogenic sources to be dominant, which should be accepted for publication in ACP.
General comment:
I realized that this work applies techniques from Yttri et al. (2011), which is in turn under revision in ACPD at the moment. I expect that acceptance of the present work depends on the decision upon Yttri et al. (2011) and that requested revisions of the technique will be adapted here as well.

Reply: The (SORGA) paper, Yttri et al., 2011, has now been published in ACP (11, 9375-9394, 2011). No major revisions in the LHS methodology were required, but some small improvements (concerning precision) and a bug-fix were applied. The new methodology was used for the current submission.

Specific comments:
The QBQ approach is a nice idea to correct for the positive sampling artifact. I wonder, however, whether it was used in an appropriate way in this work. In Genberg et al. (ACPD 11, 13575-13616, 2011), a correction factor of 2.16 was found for Vavihill using teflon-quartz-quartz stacks in similar sampling systems. This means that the SVOC concentration of the back filter has to be multiplied by this factor to account for the positive artifact on the front filter. As nothing is documented in this work, I assume that such a correction factor has not been applied (although site, season, and contributing authors are identical at least in part). This suggests that the TCp and OCp numbers given in Table 2 are substantially overestimated affecting all source apportionment results of the manuscript, as TCp is their basis. This should be improved.

Reply:

The referee refers to a paper by Genberg et al., (*ACPD 11, 13575-13616, 2011*), in which a factor of 2.16 was observed between a backup Quartz filter in what appears to be a QBT sampling line and a backup Quartz filter from a QBQ sampling line (both collected at the rural background site Vavihill, Sweden). Further, the referee uses this as an argument when stating that the OCp levels presented in Table 2 in the reviewed paper for four different sites in Scandinavia, obtained by QBQ, is substantially overestimated. The authors of the peer reviewed paper disagree with the referee in this statement.

The QBQ and the QBT sampling approach are both based on tandem filter sampling, differing in the quality of the front filter, being Quartz and Teflon quality, respectively. Most studies, starting with McDow and Huntzicker (1990), but see also e.g., Subramanian *et al*., 2004, seem to agree that the QBT approach provides a higher estimate of the positive artifact than the QBQ approach. This also includes studies from the Nordic environment (Yttri et al., 2009). There is, however, no scientific basis for saying that the QBT approach provides a more correct estimate of the positive artifact than that of the QBQ approach, merely because it provides a higher number. We are fully aware of the fact that short sampling time might cause the Quartz backup filter in a QBQ set up not to be fully saturated and thus underestimating the positive artifact. However, in the current study, using a sampling time of one week, this potential problem should be minimized. In addition, the QBQ approach has been found to approach that of QBT with increased sampling time (See e.g. Yttri et al., 2009). In this aspect it is timely to underpin that the results presented in Genberg et al., 2011, is based on *24 hours* of sampling, whereas the current study has a sampling time of *one week*. Consequently, the results presented by Genberg et al. (2011) and in the current study cannot be compared. In fact, it could even be speculated that the quartz back up filter in the QBQ sampling line reported by Genberg et al. (2011) was not saturated, given that the sampling took place in a Scandinavian rural background environment and for 24 hours only. Another factor to account for is the larger pressure drop over the Teflon filter in a QBT sampling line, which might cause volatilization of SVOC from the front filter, consequently increasing the negative artifact. Indeed, Subramanian et al. (2004) reported an overcorrection of 16-20% for the QBT approach compared to that of denuder-based sampling.

McDow, S.R., Huntzicker, J.J., 1990. Vapor adsorption artifact in the sampling of organic aerosol: face velocity effects. Atmospheric Environment 24A, 2563–2571.

Subramanian, R., Khlystov, A.Y., Cabada, J.C., Robinson, A.L., 2004. Positive and negative artifacts in particulate organic carbon measurements with denuded and undenuded sampler configurations. Aerosol Science and Technology 38(S1), 27-48.

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

Sections 2.5-2.10 show limits of detection and/or quantification for the different components in an inconsistent way. Only one term should be used (lod or loq) and levels should be given as ng/cm2 and corresponding ng/m3. All components should be considered (at the moment, such levels are missing in sections 2.7 and 2.9).

Reply: We have added the following information to the manuscript:

2.5 Measurement of levoglucosan, mannosan and galactosan

New text:
The limit of detection for the method at a signal to noise ratio of three ranged from 1.2 - 3.0 ng cm-2 for the individual MAs.

2.6 Measurement of arabitol, mannitol and trehalose

New text:
The limit of detection of the method at a signal to noise ratio of three ranged from 15 – 29 ng cm-2 for the individual sugar-alcohols.

2.7 Measurement of pinic acid, organosulphates and nitrooxy-organosulphates

New text:
The limit of detection of the method was 2 ng cm-2 for pinic acid, organosulphates and nitrooxy-organosulphates.

2.9 Precursor Specific SOA tracers

New text:
The limits of detection range from 6 to 30 ng cm-2 for the precursor specific SOA tracers.

In section 7.4, the use of indicative and subjunctive does not reflect to me the stages of known facts and speculation. It should be adjusted to assured and hypothetical statements, respectively, e.g. as follows: "could be" instead of "was" in line 2, "suggest" instead of "show" in line 6, "shows there are" instead of "could suggest there may be" in line 14.
Reply: We have rephrased as suggested.

Technical comments:

PM10 should be defined at first usage on page 16371, line 4.
Reply: This has been corrected.

The abbreviation LRT should already be introduced on page 16374, line 16 (instead of page 16375).
Reply: This has been corrected

Page 16374, line 26: of anthropogenic
Reply: corrected.

How is it possible to extract 20cm2 from a 47mm filter, which probably has an active sampling diameter of 35mm (page 16377, line 17)?
Reply: has been corrected.

In order to omit ambiguities, "Elemental carbon was" should be substituted by "Solid graphite targets were" or a similar description on page 16377, line 20.
Reply: This has been corrected

The cellulose concentrations on page 16388, line 7 don't fit with the results of Table 2.
Reply:
We have changed the sentence to:
The mean cellulose concentrations observed in the present study, ranging from 89–342 ng m−3, are comparable to those observed for the European rural background

environment by Sanchez-Ochoa et al. (2007).

Table 2: (1) Dividing EC by TCp concentrations does not equal given EC/TCp ratios; (2) the unit of F14C is not %; (3) the term "(MW=264)" is written twice for this organo-sulphate; (4) the value for organo-sulphate (MW=280) for Hyytiälä should read 0.10 0.13.
Reply :

1. The explanation is that the EC/TCp ratio in Table 2 is not based on the mean EC/meanTCp, since we have calculated the mean EC/TCp for n = 4, i.e. resembling the four weeks of sampling at each of the sites. We have presented the average ratio of EC/TCp for each site, not the average EC at each site over the average TCp for each site.
2. This is due to a typesetting error.
3. A typesetting error which should be corrected in the final version.
4. Has been corrected.

Figure 2: The unit in the annotation of the y-axis should read µgC/m3.
Reply: This will be corrected in the final version of the figure.

Figure 4: The caption should read ": : :and Vavihill filter samples (PM10) from LHS analysis.".
Reply: Has been corrected.

Supplementary tables: The captions should read "Calculated contributions to TCp: : :".
Reply: Has been corrected.