

# Supplementary material for: Source apportionment of the carbonaceous aerosol in Norway – Quantitative estimates based on $^{14}\text{C}$ , thermal-optical and organic tracer analysis

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## Contents

The supplementary material consists of:

- **Appendix S1:** - provides general comments on some LHS issues.
- **Tables S1 – S5.** Table S1 provides concentrations of sugars and sugar-alcohols observed for the Oslo and Hurdal sites during the summer and winter campaigns. Tables S2–S5 provide the results of the LHS source-apportionment in terms of carbon contributions ( $\mu\text{gC m}^{-3}$ ). These data are the same as those used in Tables 6–9 in the main manuscript, except that the latter use percentage contributions.
- **Figure S1: Alternative LHS calculation**

As discussed in section 3, we have conducted a second set of source-apportionment calculations, in which wider uncertainty ranges have been utilized for the key  $(\text{OC}/\text{TC})_{\text{bb}}$  factor. These alternative calculations use a central estimate of  $(\text{OC}/\text{TC})_{\text{bb}} = 0.82$ , and low and high values of 0.66 to 0.95. This alternative is presented partly to illustrate what happens with other sets of assumptions, and partly to demonstrate the robustness of the source-apportionment methodology. The results illustrated in Fig. S1 can be compared with Fig.1 of the main manuscript.

## Appendix S1: General Comments on LHS issues

A few issues commonly arise when discussing the LHS-based source-apportionment methodology as used here, which can be summarised:

- i) omission of negative solutions may bias the results
- ii) the ‘flat’ distribution functions used are unrealistic
- iii) a Monte-Carlo methodology might produce different results

These concerns are understandable, but we believe unfounded. Some of these complexities behind our views are outlined below, but it is important to realise that the main purpose of the LHS approach is to show which solutions are consistent with the observations, and the elimination of negative solutions is a key part of this process.

First, we give some background to the LHS methodology, and reasons for the deliberate rejection of standard (e.g. Gaussian) approaches to the specification of possible emission ratios. The use of the LHS approach was started by one of us (DS) as part of the source-apportionment analysis of the CARBOSOL project (Gelencsér et al., 2007), partly in response to the fact that it was so hard to decide on best-estimate emission ratios. In CARBOSOL we found several examples where the initial best estimate of some experts lay outside the range of values first suggested by other groups. Subsequent requests for 'best-estimate' ratios and ranges from colleagues in several studies (Szidat et al., 2009; Genberg et al., 2011, and this work) have produced similar differences of opinion - there is in fact no 'best' estimate for many of the ratios we are dealing with. Such differences reflect the widely varying ratios found in the literature, and the differing experiences and backgrounds of those involved. These exercises illustrate that source-apportionment exercises need to be approached with a large degree of pragmatism, and the LHS assumptions reflect this.

The LHS approach is thus not primarily designed to give a 'best'-estimate, it is designed to show which solutions are possible. One of the encouraging and important findings of these LHS studies has been that one can allow very wide ranges of emission ratios, and still end up with quite similar general findings - the impossible combinations are excluded by the requirement that all solutions are positive.

Some complexities of source-apportionment for organic aerosol are also very relevant:

1. Although we have some estimates of precision of some emission rates, we generally know very little about accuracy. For example, the biomass burning ratio  $(TC/LG)_{bb}$  depends on appliances, maintenance standards, type of wood, dampness, and a host of other factors (e.g. Puxbaum et al., 2007). The average ratio will likely change a lot with time-of-year (from residential to agricultural burning), season, and distance from source (e.g. Hoffmann et al., 2010). This also makes  $(TC/LG)_{bb}$  dependent on wind-direction for example, even for the same season and sites. We can roughly take care of the range of such estimates, but we cannot assign a proper statistical distribution.
2. Much of the literature uses different analysis techniques, e.g. to get EC/OC ratios. Again, we can specify a loose range, but cannot assign a proper statistical distribution to this.

In analysis of some environmental variables (e.g. concentrations) inclusion of negative measurements is necessary in order to exclude a positive bias (random noise in a measurement will produce both positive and negative deviations from the true value, and all data are needed to estimate the true mean). However, the main reason behind negative solutions in our LHS is not some effect of random noise, but that a combination of factors being tested is not consistent with the amounts of carbon present on the filter. For example, we do allow the possibility of very high  $(TC/LG)_{bb}$  ratios, as such ratios might arise as a result of loss of LG (levoglucosan) as an air parcel moves along. On many occasions though, such high ratios will result in an unrealistically high contribution of biomass-burning to both the  $F^{14}C$  and  $OC_{bb}$ ,  $EC_{bb}$  components. The measured values of  $F^{14}C$  and other compounds will often exclude that such high biomass-burning contributions are possible. Indeed, excluding 'impossible' solutions is one of the points of the exercise. With this in mind, it would be wrong to accept negative solutions to LHS. Such solutions represent not just acceptable errors caused by normal-distribution type problems, but also represent unacceptable solutions.

Considering Monte-Carlo (MC) versus LHS methods, then this difference is of very minor importance. As discussed in e.g. McKay et al. (1979), LHS provides essentially the same results as MC at significantly less cost. Considering the very significant uncertainties in other aspects of source-apportionment, there would be no advantage in using MC over LHS, and indeed it would be harder to explore the same number of input parameters.

Table S1: Concentrations of sugars and sugar-alcohols in PM<sub>10</sub> (ng m<sup>-3</sup>), for the Urban site (U: Oslo) and the rural site (R: Hurdal). Samples are either day (D), night (N) or 24h.

| PM <sub>10</sub> | Arabitol   | Mannitol   | Trehalose  | Inositol | Erytritol | Sucrose    | Fructose   | Glucose    | Ribose     |
|------------------|------------|------------|------------|----------|-----------|------------|------------|------------|------------|
| Summer           |            |            |            |          |           |            |            |            |            |
| U D              | 20 ±10     | 24 ±8      | 10 ±3      | 2.0 ±0.6 | 3.3 ±2.5  | 5.7 ±3.0   | 4.7 ±1.4   | 20 ±7      | 1.5 ±0.5   |
| U N              | 20 ±9      | 26 ±6      | 11 ±5      | 1.6 ±0.6 | 1.9 ±1.9  | 3.6 ±1.9   | 3.4 ±1.4   | 17 ±8      | 2.4 ±1.1   |
| U 24h            | 20 ±9      | 25 ±8      | 10 ±4      | 1.8 ±0.7 | 2.5 ±2.3  | 4.6 ±2.7   | 4.0 ±1.5   | 19 ±8      | 1.9 ±0.9   |
| R D              | 25 ±7      | 28 ±10     | 18 ±7      | 2.3 ±0.9 | 3.2 ±1.6  | 24 ±22     | 5.2 ±1.4   | 32 ±18     | 0.6 ±0.7   |
| R N              | 40 ±14     | 64 ±21     | 32 ±12     | 1.8 ±0.7 | 8.2 ±6.6  | 2.0 ±0.6   | 4.5 ±1.3   | 25 ±9      | 2.8 ±1.6   |
| R 24h            | 32 ±13     | 45 ±24     | 25 ±12     | 2.0 ±0.6 | 5.6 ±5.3  | 13 ±19     | 4.9 ±1.4   | 29 ±15     | 1.7 ±1.6   |
| Winter           |            |            |            |          |           |            |            |            |            |
| U D              | 2.7 ±1.1   | 3.2 ±0.8   | 6.0 ±2.9   | 1.0 ±0.7 | n.d.      | 2.8 ±1.1   | 3.5 ±2.2   | 7.0 ±2.4   | 1.4 ±0.4   |
| U N              | 2.7 ±1.0   | 2.6 ±1.9   | 3.7 ±2.1   | 0.6 ±0.6 | n.d.      | 2.8 ±1.0   | 2.3 ±1.0   | 6.1 ±1.9   | 0.9 ±0.4   |
| U 24h            | 2.7 ±1.0   | 2.9 ±1.4   | 4.9 ±2.7   | 0.8 ±0.6 | n.d.      | 2.8 ±1.0   | 2.9 ±1.7   | 6.6 ±2.1   | 1.2 ±0.5   |
| R D              | 0.77 ±0.48 | 0.78 ±0.42 | 1.73 ±0.92 | n.d.     | n.d.      | 1.52 ±0.97 | 1.02 ±0.79 | 1.70 ±0.99 | 0.25 ±0.05 |
| R N              | 0.71 ±0.45 | 0.53 ±0.38 | 1.11 ±0.52 | n.d.     | n.d.      | 0.89 ±0.64 | 0.53 ±0.21 | 1.26 ±0.50 | 0.60 ±0.44 |
| R 24h            | 0.74 ±0.45 | 0.65 ±0.40 | 1.42 ±0.79 | n.d.     | n.d.      | 1.20 ±0.85 | 0.78 ±0.61 | 1.48 ±0.79 | 0.43 ±0.35 |

Table S2: Calculated contributions to total carbon (μgC m<sup>-3</sup>) from LHS analysis, PM<sub>10</sub>, Summer sampling (19th June – 15th July 2006). C.E. is central estimate (50th percentile), range is 10th-90th percentiles of LHS results.

|                    | Hurdal-24h |             | Oslo-24h |             | Oslo-Day |             | Oslo-Night |             |
|--------------------|------------|-------------|----------|-------------|----------|-------------|------------|-------------|
|                    | C.E.       | Range       | C.E.     | Range       | C.E.     | Range       | C.E.       | Range       |
| EC <sub>bb</sub>   | 0.03       | (0.02–0.04) | 0.12     | (0.08–0.15) | 0.09     | (0.05–0.11) | 0.16       | (0.10–0.21) |
| EC <sub>ff</sub>   | 0.25       | (0.20–0.32) | 0.50     | (0.28–0.70) | 0.51     | (0.30–0.70) | 0.49       | (0.26–0.69) |
| OC <sub>bb</sub>   | 0.10       | (0.07–0.12) | 0.42     | (0.28–0.51) | 0.30     | (0.20–0.37) | 0.56       | (0.37–0.67) |
| OC <sub>ff</sub>   | 0.19       | (0.10–0.28) | 0.68     | (0.46–0.90) | 0.69     | (0.47–0.90) | 0.70       | (0.47–0.94) |
| OC <sub>POA</sub>  | 0.12       | (0.06–0.19) | 0.28     | (0.13–0.48) | 0.29     | (0.13–0.49) | 0.28       | (0.12–0.48) |
| OC <sub>ASOA</sub> | 0.07       | (0.01–0.16) | 0.39     | (0.09–0.72) | 0.40     | (0.10–0.72) | 0.42       | (0.10–0.77) |
| OC <sub>BSOA</sub> | 1.65       | (1.45–1.86) | 1.40     | (1.13–1.65) | 1.63     | (1.36–1.88) | 1.13       | (0.87–1.42) |
| OC <sub>PBAP</sub> | 0.70       | (0.53–0.88) | 0.59     | (0.42–0.77) | 0.61     | (0.42–0.84) | 0.52       | (0.38–0.66) |
| OC <sub>pbs</sub>  | 0.53       | (0.39–0.66) | 0.28     | (0.20–0.35) | 0.23     | (0.16–0.29) | 0.33       | (0.23–0.42) |
| OC <sub>psc</sub>  | 0.17       | (0.09–0.27) | 0.31     | (0.16–0.49) | 0.39     | (0.20–0.61) | 0.20       | (0.10–0.31) |

Table S3: Calculated contributions to total carbon ( $\mu\text{gC m}^{-3}$ ) from LHS analysis,  $\text{PM}_{10}$ , Winter sampling (1st-8th March 2007). C.E. is central estimate (50th percentile), range is 10th-90th percentiles of LHS results.

|                           | Hurdal-24h |             | Oslo-24h |             | Oslo-Day |             | Oslo-Night |             |
|---------------------------|------------|-------------|----------|-------------|----------|-------------|------------|-------------|
|                           | C.E.       | Range       | C.E.     | Range       | C.E.     | Range       | C.E.       | Range       |
| $\text{EC}_{\text{bb}}$   | 0.11       | (0.08–0.14) | 0.29     | (0.22–0.37) | 0.31     | (0.21–0.41) | 0.29       | (0.23–0.35) |
| $\text{EC}_{\text{ff}}$   | 0.15       | (0.05–0.23) | 0.53     | (0.24–0.80) | 0.57     | (0.25–0.85) | 0.47       | (0.20–0.72) |
| $\text{OC}_{\text{bb}}$   | 0.39       | (0.31–0.47) | 1.03     | (0.81–1.24) | 1.09     | (0.77–1.40) | 1.01       | (0.86–1.17) |
| $\text{OC}_{\text{ff}}$   | 0.29       | (0.20–0.39) | 0.89     | (0.61–1.20) | 1.05     | (0.76–1.38) | 0.76       | (0.49–1.03) |
| $\text{OC}_{\text{POA}}$  | 0.09       | (0.03–0.17) | 0.31     | (0.11–0.56) | 0.35     | (0.12–0.65) | 0.26       | (0.09–0.47) |
| $\text{OC}_{\text{ASOA}}$ | 0.20       | (0.06–0.35) | 0.58     | (0.16–1.05) | 0.70     | (0.23–1.21) | 0.49       | (0.12–0.91) |
| $\text{OC}_{\text{BSOA}}$ | 0.12       | (0.02–0.23) | 0.35     | (0.06–0.66) | 0.40     | (0.04–0.83) | 0.24       | (0.05–0.45) |
| $\text{OC}_{\text{PBAP}}$ | 0.09       | (0.05–0.14) | 0.08     | (0.05–0.11) | 0.08     | (0.06–0.12) | 0.08       | (0.05–0.11) |
| $\text{OC}_{\text{pbs}}$  | 0.01       | (0.00–0.01) | 0.03     | (0.02–0.03) | 0.03     | (0.02–0.04) | 0.02       | (0.01–0.03) |
| $\text{OC}_{\text{pbc}}$  | 0.08       | (0.05–0.14) | 0.06     | (0.03–0.09) | 0.05     | (0.03–0.08) | 0.06       | (0.03–0.09) |

Table S4: Calculated contributions to total carbon ( $\mu\text{gC m}^{-3}$ ) from LHS analysis,  $\text{PM}_1$ , Summer sampling (19th June – 15th July 2006). C.E. is central estimate (50th percentile), range is 10th-90th percentiles of LHS results.

|                           | Hurdal-24h |             | Oslo-24h |             | Oslo-Day |             | Oslo-Night |             |
|---------------------------|------------|-------------|----------|-------------|----------|-------------|------------|-------------|
|                           | C.E.       | Range       | C.E.     | Range       | C.E.     | Range       | C.E.       | Range       |
| $\text{EC}_{\text{bb}}$   | 0.03       | (0.02–0.04) | 0.13     | (0.09–0.16) | 0.09     | (0.07–0.12) | 0.17       | (0.12–0.21) |
| $\text{EC}_{\text{ff}}$   | 0.17       | (0.11–0.24) | 0.29     | (0.14–0.40) | 0.21     | (0.10–0.30) | 0.34       | (0.16–0.50) |
| $\text{OC}_{\text{bb}}$   | 0.08       | (0.06–0.09) | 0.31     | (0.23–0.38) | 0.23     | (0.17–0.27) | 0.42       | (0.31–0.50) |
| $\text{OC}_{\text{ff}}$   | 0.18       | (0.11–0.26) | 0.59     | (0.46–0.74) | 0.63     | (0.52–0.74) | 0.55       | (0.38–0.73) |
| $\text{OC}_{\text{POA}}$  | 0.09       | (0.04–0.14) | 0.18     | (0.07–0.35) | 0.14     | (0.05–0.28) | 0.20       | (0.08–0.36) |
| $\text{OC}_{\text{ASOA}}$ | 0.09       | (0.01–0.18) | 0.41     | (0.16–0.65) | 0.48     | (0.29–0.68) | 0.35       | (0.09–0.63) |
| $\text{OC}_{\text{BSOA}}$ | 1.18       | (1.11–1.24) | 0.89     | (0.77–1.02) | 0.98     | (0.89–1.08) | 0.79       | (0.65–0.96) |
| $\text{OC}_{\text{PBAP}}$ | 0.03       | (0.02–0.04) | 0.02     | (0.01–0.03) | 0.03     | (0.02–0.03) | 0.01       | (0.01–0.02) |
| $\text{OC}_{\text{pbs}}$  | 0.02       | (0.01–0.02) | 0.01     | (0.01–0.01) | 0.01     | (0.01–0.02) | 0.01       | (0.01–0.01) |
| $\text{OC}_{\text{pbc}}$  | 0.01       | (0.01–0.01) | 0.01     | (0.00–0.01) | 0.01     | (0.01–0.02) | 0.01       | (0.00–0.01) |

Table S5: Calculated contributions to total carbon ( $\mu\text{gC m}^{-3}$ ) from LHS analysis,  $\text{PM}_{10}$ , Winter sampling (1st-8th March 2007). C.E. is central estimate (50th percentile), range is 10th-90th percentiles of LHS results.

|                           | Hurdal-24h |             | Oslo-24h |             | Oslo-Day |             | Oslo-Night |             |
|---------------------------|------------|-------------|----------|-------------|----------|-------------|------------|-------------|
|                           | C.E.       | Range       | C.E.     | Range       | C.E.     | Range       | C.E.       | Range       |
| $\text{EC}_{\text{bb}}$   | 0.15       | (0.11–0.18) | 0.36     | (0.28–0.44) | 0.35     | (0.27–0.44) | 0.37       | (0.30–0.44) |
| $\text{EC}_{\text{ff}}$   | 0.10       | (0.02–0.17) | 0.35     | (0.10–0.57) | 0.39     | (0.13–0.62) | 0.31       | (0.08–0.52) |
| $\text{OC}_{\text{bb}}$   | 0.36       | (0.29–0.44) | 0.88     | (0.73–1.04) | 0.86     | (0.67–1.04) | 0.92       | (0.78–1.05) |
| $\text{OC}_{\text{ff}}$   | 0.28       | (0.20–0.36) | 0.76     | (0.53–1.01) | 0.92     | (0.68–1.19) | 0.59       | (0.37–0.83) |
| $\text{OC}_{\text{POA}}$  | 0.07       | (0.01–0.13) | 0.21     | (0.05–0.42) | 0.25     | (0.07–0.50) | 0.18       | (0.04–0.34) |
| $\text{OC}_{\text{ASOA}}$ | 0.22       | (0.09–0.34) | 0.54     | (0.17–0.94) | 0.66     | (0.25–1.10) | 0.41       | (0.10–0.77) |
| $\text{OC}_{\text{BSOA}}$ | 0.12       | (0.02–0.24) | 0.26     | (0.04–0.49) | 0.27     | (0.04–0.54) | 0.23       | (0.05–0.43) |
| $\text{OC}_{\text{PBAP}}$ | 0.03       | (0.02–0.04) | 0.02     | (0.02–0.03) | 0.04     | (0.02–0.05) | 0.01       | (0.01–0.01) |
| $\text{OC}_{\text{pbs}}$  | 0.01       | (0.01–0.02) | 0.01     | (0.01–0.01) | 0.01     | (0.01–0.02) | 0.01       | (0.01–0.01) |
| $\text{OC}_{\text{pbc}}$  | 0.02       | (0.01–0.03) | 0.01     | (0.01–0.02) | 0.02     | (0.01–0.03) | 0.00       | (0.00–0.01) |

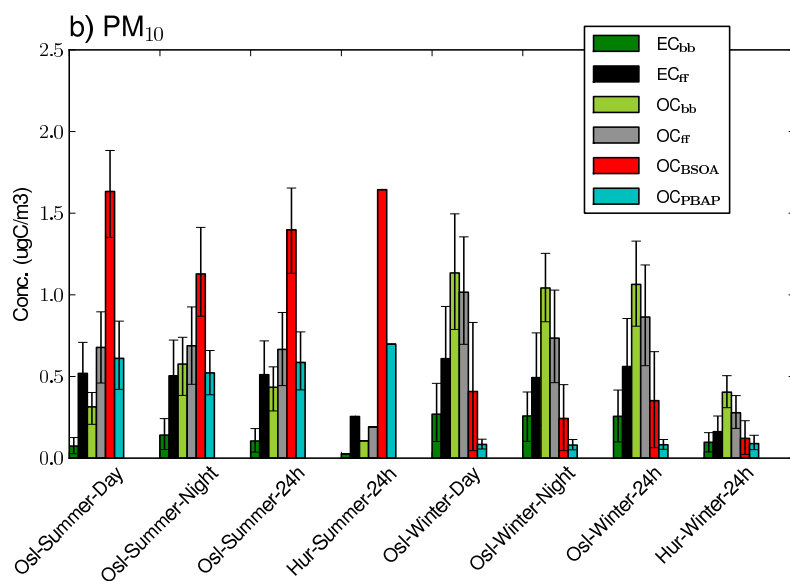
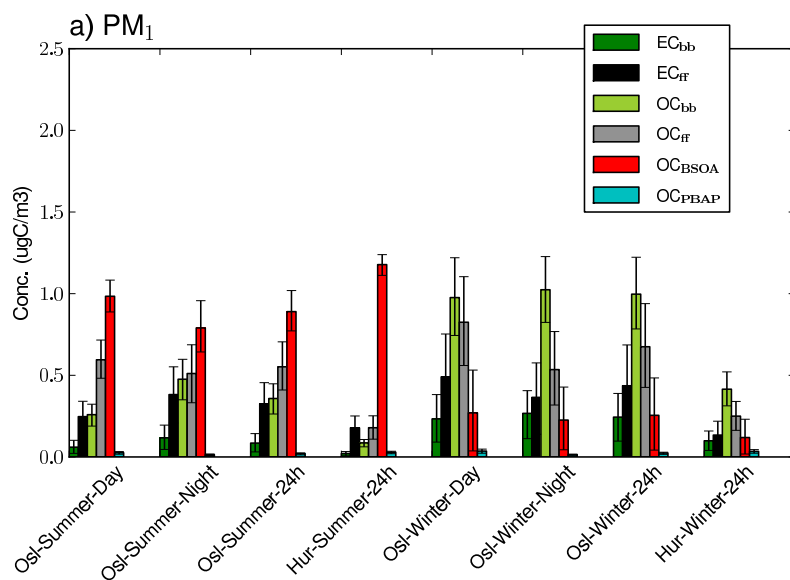


Figure S1: Alternative calculation of best estimate concentrations ( $\mu\text{gC m}^{-3}$ ) of different carbonaceous particle fractions for the SORGA samples. Uncertainty bars represent 10 and 90 percentiles from LHS calculations. These estimates use the wider uncertainty range for some parameters.

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