Supplement of

Nine-year trends of PM$_{10}$ sources and oxidative potential in a rural background site in France

Lucille Joanna Borlaza et al.

Correspondence to: Lucille Joanna Borlaza (lucille-joanna.borlaza@univ-grenoble-alpes.fr)
and Jean-Luc Jaffrezo (jaffrezo@univ-grenoble-alpes.fr)

The copyright of individual parts of the supplement might differ from the article licence.
Table of Contents
S1. Calculation of major chemical components of PM$_{10}$
S2. PMF model description
S3. Summary of PMF-resolved sources

S1. Calculation of major chemical components of PM$_{10}$
Organic matter (OM) is calculated by multiplying OC mass concentrations by a factor 1.8 based on findings obtained from previous studies (Favez et al., 2010; Putaud et al., 2010). Sea salt sulfate (ss-sulfate) is calculated by multiplying the mass concentration of sodium by a factor of 0.252. The non-sea salt sulfate (nss-sulfate) corresponds to the sea salt sulfate subtracted from the total mass of sulfate using the factor from Seinfeld and Pandis (1998). Sea salt is estimated based on the mass concentrations of sodium chloride (Putaud et al., 2010). Dust is calculated based on calcium of non-sea-salt origin, following the empirical expression in (Putaud et al., 2004). Non-dust elements correspond to the sum of the other common measured trace elements other than geological ones (Salameh et al., 2015).

\[
[PM_{10}] = [OM] + [EC] + [nss - sulfate] + [nitrates] + [ammonium] + [sea salt] + [dust] + [non - dust]
\]

(Eq. S1)

where:

\[
[nss - sulfate] = [SO_{4}^{2-}] - 0.252[Na^{+}]
\]

\[
[sea salt] = [Cl^{-}] + 1.47[Na^{+}]
\]

\[
[dust] = 5.6 \times [nss - Ca^{2+}]
\]

\[
[nss - Ca^{2+}] = [Ca^{2+}] - [Na^{+}]/26
\]

\[
[non - dust] = [Cu] + [Ni] + [Pb] + [V] + [Zn]
\]

Table S1. Summary of quantification limits (QL) of each chemical specie measured in the OPE site.

<table>
<thead>
<tr>
<th>Specie</th>
<th>Unit</th>
<th>Quantification limit (QL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OC</td>
<td>µg m$^{-3}$</td>
<td>0.096</td>
</tr>
<tr>
<td>EC</td>
<td>µg m$^{-3}$</td>
<td>0.002</td>
</tr>
<tr>
<td>TC</td>
<td>µg m$^{-3}$</td>
<td>0.094</td>
</tr>
<tr>
<td>Cellulose</td>
<td>ng m$^{-3}$</td>
<td>6.500</td>
</tr>
<tr>
<td>MSA</td>
<td>ng m$^{-3}$</td>
<td>0.227</td>
</tr>
<tr>
<td>Cl$^{-}$</td>
<td>ng m$^{-3}$</td>
<td>4.451</td>
</tr>
<tr>
<td>NO$_{3}^{-}$</td>
<td>ng m$^{-3}$</td>
<td>24.820</td>
</tr>
<tr>
<td>SO$_{4}^{2-}$</td>
<td>ng m$^{-3}$</td>
<td>5.027</td>
</tr>
<tr>
<td>Na$^{+}$</td>
<td>ng m$^{-3}$</td>
<td>4.805</td>
</tr>
<tr>
<td>NH$_{4}^{+}$</td>
<td>ng m$^{-3}$</td>
<td>13.342</td>
</tr>
<tr>
<td>K$^{+}$</td>
<td>ng m$^{-3}$</td>
<td>1.628</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>ng m$^{-3}$</td>
<td>0.344</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>ng m$^{-3}$</td>
<td>5.014</td>
</tr>
<tr>
<td>Arabinol</td>
<td>ng m$^{-3}$</td>
<td>0.554</td>
</tr>
<tr>
<td>Sorbitol</td>
<td>ng m$^{-3}$</td>
<td>0.337</td>
</tr>
<tr>
<td>Mannitol</td>
<td>ng m$^{-3}$</td>
<td>0.356</td>
</tr>
<tr>
<td>Levoglucosan</td>
<td>ng m$^{-3}$</td>
<td>1.351</td>
</tr>
<tr>
<td>Mannosan</td>
<td>ng m$^{-3}$</td>
<td>0.352</td>
</tr>
<tr>
<td>Al</td>
<td>ng m$^{-3}$</td>
<td>25.440</td>
</tr>
<tr>
<td>As</td>
<td>ng m$^{-3}$</td>
<td>0.013</td>
</tr>
<tr>
<td>Ba</td>
<td>ng m$^{-3}$</td>
<td>1.708</td>
</tr>
<tr>
<td>Ca</td>
<td>ng m$^{-3}$</td>
<td>110.347</td>
</tr>
<tr>
<td>Cd</td>
<td>ng m$^{-3}$</td>
<td>0.023</td>
</tr>
<tr>
<td>Ce</td>
<td>ng m$^{-3}$</td>
<td>0.045</td>
</tr>
<tr>
<td>Co</td>
<td>ng m$^{-3}$</td>
<td>0.020</td>
</tr>
</tbody>
</table>
S. PMF model description

The PMF model is based on a factorial analysis that takes into account the evolution of the concentration of the measured chemical species and gathers, in the same factor, the fractions of the species evolving in the same way. Each factor will then be assigned to a source by the user based on literature data and geochemical knowledge of source characteristics in terms of trace chemical species.

The application of this model does not require prior knowledge of the chemical profiles of the sources, but its application must be performed on a large dataset (many chemical species, including in particular tracers and indicators of major sources) and on a large time series of samples. This is particularly the case for this study, to our knowledge among the largest datasets in the Europe. The general equation used in this PMF model is the following:

\[ x_{ij} = \sum_{k=1}^{n} g_{ik} \cdot f_{kj} + e_{ij} \] (Eq. S2)

Where \( x_{ij} \): species concentration \( j \) for sample \( i \)

\( g_{ik} \): factor contribution \( k \) for sample \( i \)

\( f_{kj} \): factor contribution \( k \) from the species \( j \)

\( e_{ij} \): species contribution \( j \) for sample \( i \) not explained by the model

This can be expressed in a matrix form simply by Eq. S3:

\[ X = G \cdot F + E \] (Eq. S3)

The model seeks to minimize the matrix \( E \) weighted by the matrix \( S \) containing the measurement uncertainties, i.e. \( Q=E/S \). The S-matrix is calculated using Eq. S4 proposed by (Gianini et al., 2012):

\[ s_{ij} = \sqrt{(DL_j)^2 + (CV_j \times x_{ij})^2 + (CV_{PM} \times x_{ij})^2} \] (Eq. S4)

Where \( DL_j \): the limit of detection for species \( j \) (2 times the standard deviation of blanks)

\( CV_j \): the coefficient of variation of species \( j \) (calculated from several successive analyses of the same sample)
CV_{PM} : the additional coefficient of variation representing additional uncertainties by chemical species category

For some species, it was necessary to use an expanded uncertainty that takes into account analytical error and sampling error, which can be used instead of the methodology proposed by (Gianini et al., 2012). An uncertainty of \( \frac{5}{6} \times DL \) was used for values <DL and the uncertainties that are four times the specie concentration geometric mean were attributed to missing or replaced values.

The robustness of the final PMF solution was evaluated using various statistical parameters based on the European guide on air pollution source apportionment with receptor models (Belis et al., 2014) and the geochemical soundness of the solution. In brief, the parameters are listed as follows:

- Evolution of the ratio Qtrue/Qrobust (<1.5)
- The weighted residuals are normally distributed for most of the species and between ±3 which should indicate good model results of most variables
- Evaluation of the statistical robustness of the optimal solution (sensitivity to noise and any random data point) using a bootstrap test (BS) for 100 successive iterations of the model and for a minimum correlation (r²) of 0.6
- Evaluation of the geochemical soundness of the PMF-resolved factor profiles based on a priori knowledge of the chemical footprints of the sources, their specific tracers, the temporal variability (daily, weekly and seasonally), and the characteristics of the site studied
- Statistical evaluation and precision for constrained solutions using BS for 100 successive iterations of the model and for a minimum correlation (r²) of 0.6
- There is no added extra uncertainty to the whole dataset

The Pearson distance and the Similarity Identity Distance (PD-SID):

To evaluate the stability of the chemical profile obtained in the OPE site against other sites in France, the Pearson distance (PD) and the Similarity Identity Distance (SID), following Belis et al. (2015), was used to perform a similarity assessment. The PD and SID defined by Eq. S5 and Eq. S6:

\[
PD = 1 - r^2, \quad \text{where} \quad r \quad \text{is the Pearson coefficient} \quad \text{(Eq. S5)}
\]

\[
\frac{\sqrt{2}}{\pi} \sum_{i=1}^{n} \frac{|a_i - b_i|}{a_i + b_i} \quad \text{(Eq. S6)}
\]

where a and b are the relative mass to PM_{10} of two different factors and n is the number of common species in a and b.

### S3. Summary of PMF-resolved sources

Table S2. The PMF-resolved sources and their specific tracers

<table>
<thead>
<tr>
<th>Identified factors</th>
<th>Specific tracers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biomass burning</td>
<td>Levoglucosan, mannosan</td>
</tr>
<tr>
<td>Nitrate-rich</td>
<td>NO\textsubscript{3}, NH\textsubscript{4}+</td>
</tr>
<tr>
<td>Sulfate-rich</td>
<td>SO\textsubscript{4}²⁻, NH\textsubscript{4}+</td>
</tr>
<tr>
<td>Mineral dust</td>
<td>Ca\textsuperscript{2+}, Al, Ti, Fe, Cu, Zn</td>
</tr>
<tr>
<td>Fresh sea salt</td>
<td>Na\textsuperscript{+}, Cl\textsuperscript{-}, Mg\textsuperscript{2+}</td>
</tr>
<tr>
<td>Aged sea salt</td>
<td>Na\textsuperscript{+}, Mg\textsuperscript{2+}</td>
</tr>
<tr>
<td>Primary biogenic</td>
<td>Polyols</td>
</tr>
<tr>
<td>MSA-rich</td>
<td>MSA</td>
</tr>
<tr>
<td>Traffic</td>
<td>EC, Cu, Sb, Sn</td>
</tr>
</tbody>
</table>
Table S3: Summary of the tested chemical constraints on source-specific tracers in the PMF factor profiles.

<table>
<thead>
<tr>
<th>Factor profile</th>
<th>Element</th>
<th>Type</th>
<th>Value</th>
<th>Used in the final model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biomass burning</td>
<td>Levoglucosan</td>
<td>Pull up maximally</td>
<td>(% dQ 0.50)</td>
<td>Yes</td>
</tr>
<tr>
<td>Biomass burning</td>
<td>Mannosan</td>
<td>Pull up maximally</td>
<td>(% dQ 0.50)</td>
<td>Yes</td>
</tr>
<tr>
<td>Primary biogenic</td>
<td>Levoglucosan</td>
<td>Set to zero</td>
<td>0</td>
<td>No</td>
</tr>
<tr>
<td>Primary biogenic</td>
<td>Mannosan</td>
<td>Set to zero</td>
<td>0</td>
<td>No</td>
</tr>
<tr>
<td>Primary biogenic</td>
<td>Polyols</td>
<td>Pull up maximally</td>
<td>(% dQ 0.50)</td>
<td>No</td>
</tr>
<tr>
<td>Primary biogenic</td>
<td>EC</td>
<td>Pull down maximally</td>
<td>(% dQ 0.50)</td>
<td>No</td>
</tr>
<tr>
<td>MSA-rich</td>
<td>MSA</td>
<td>Pull up maximally</td>
<td>(% dQ 0.50)</td>
<td>Yes</td>
</tr>
<tr>
<td>MSA-rich</td>
<td>Levoglucosan</td>
<td>Set to zero</td>
<td>0</td>
<td>Yes</td>
</tr>
<tr>
<td>MSA-rich</td>
<td>Mannosan</td>
<td>Set to zero</td>
<td>0</td>
<td>Yes</td>
</tr>
<tr>
<td>MSA-rich</td>
<td>Polyols</td>
<td>Pull down maximally</td>
<td>(% dQ 0.50)</td>
<td>No</td>
</tr>
<tr>
<td>MSA-rich</td>
<td>EC</td>
<td>Pull down maximally</td>
<td>(% dQ 0.50)</td>
<td>No</td>
</tr>
<tr>
<td>Nitrate-rich</td>
<td>Levoglucosan</td>
<td>Set to zero</td>
<td>0</td>
<td>No</td>
</tr>
<tr>
<td>Nitrate-rich</td>
<td>Mannosan</td>
<td>Set to zero</td>
<td>0</td>
<td>No</td>
</tr>
<tr>
<td>Mineral dust</td>
<td>Ti</td>
<td>Pull up maximally</td>
<td>(% dQ 0.50)</td>
<td>Yes</td>
</tr>
<tr>
<td>Primary traffic</td>
<td>Levoglucosan</td>
<td>Set to 0</td>
<td>0</td>
<td>Yes</td>
</tr>
<tr>
<td>Primary traffic</td>
<td>Mannosan</td>
<td>Set to 0</td>
<td>0</td>
<td>Yes</td>
</tr>
<tr>
<td>Primary traffic</td>
<td>Cu/Fe</td>
<td>Set to value</td>
<td>0.046 (% dQ 0.50)</td>
<td>No</td>
</tr>
<tr>
<td>Primary traffic</td>
<td>Cu/Sn</td>
<td>Set to value</td>
<td>5.6 (% dQ 0.50)</td>
<td>No</td>
</tr>
<tr>
<td>Primary traffic</td>
<td>Cu/Sb</td>
<td>Set to value</td>
<td>12.6 (% dQ 0.50)</td>
<td>No</td>
</tr>
<tr>
<td>Primary traffic</td>
<td>Cu/Mn</td>
<td>Set to value</td>
<td>5.7 (% dQ 0.50)</td>
<td>No</td>
</tr>
<tr>
<td>Primary traffic</td>
<td>OC*/EC</td>
<td>Set to value</td>
<td>0.44 (% dQ 0.50)</td>
<td>No</td>
</tr>
</tbody>
</table>
Figure S1: Chemical profile and temporal evolution with error estimates of the biomass burning factor
Figure S2: Chemical profile and temporal evolution with error estimates of the nitrate-rich factor
Figure S3: Chemical profile and temporal evolution with error estimates of the sulphate-rich factor
Figure S4: Chemical profile and temporal evolution with error estimates of the mineral dust factor
Figure S5: Chemical profile and temporal evolution with error estimates of the fresh sea salt factor
Figure S6: Chemical profile and temporal evolution with error estimates of the aged sea salt factor
Figure S7: Chemical profile and temporal evolution with error estimates of the primary biogenic factor
Figure S8: Chemical profile and temporal evolution with error estimates of the MSA-rich factor
Figure S9: Chemical profile and temporal evolution with error estimates of the traffic factor
Figure S10: The Season-trend (STL) deconvolution of contributions of PM$_{10}$ in µg m$^{-3}$ from year 2012 to 2020.

Figure S11: The Season-trend (STL) deconvolution of contributions of EC in µg m$^{-3}$ to PM$_{10}$ from year 2012 to 2020.
Figure S12: The Season-trend (STL) deconvolution of contributions of EC in µg m\(^{-3}\) to PM\(_{10}\) from year 2012 to 2020.

Table S4: Comparison of the PMF-resolved source contributions (in terms of µg m\(^{-3}\) and percentage) to PM\(_{10}\) between daily and weekly samples

<table>
<thead>
<tr>
<th>Source</th>
<th>24-hr samples (n=253)</th>
<th>7-day samples (n=181)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Contribution (µg m(^{-3}))</td>
<td>Percentage contribution (%)</td>
</tr>
<tr>
<td>Sulphate-rich</td>
<td>1.5</td>
<td>15.1</td>
</tr>
<tr>
<td>Primary biogenic</td>
<td>0.6</td>
<td>6.2</td>
</tr>
<tr>
<td>Aged sea salt</td>
<td>0.9</td>
<td>8.8</td>
</tr>
<tr>
<td>Nitrate-rich</td>
<td>2.3</td>
<td>22.6</td>
</tr>
<tr>
<td>Fresh sea salt</td>
<td>0.5</td>
<td>4.6</td>
</tr>
<tr>
<td>MSA-rich</td>
<td>0.3</td>
<td>3.3</td>
</tr>
<tr>
<td>Traffic</td>
<td>1.6</td>
<td>15.7</td>
</tr>
<tr>
<td>Mineral dust</td>
<td>1.2</td>
<td>12.1</td>
</tr>
<tr>
<td>Biomass burning</td>
<td>1.2</td>
<td>11.7</td>
</tr>
</tbody>
</table>

Figure S13: Comparison of PMF-resolved chemical profiles between the weekly (February 28, 2012 to December 28, 2015) and daily (January 12, 2016 to December 22, 2020) samples for the aged sea salt factor. The bars represent the percentage (%) contribution of each specie to total reconstructed PM\(_{10}\).
Figure S1: Comparison of PMF-resolved chemical profiles between the weekly (February 28, 2012 to December 28, 2015) and daily (January 12, 2016 to December 22, 2020) samples for the fresh sea salt factor. The bars represent the percentage (%) contribution of each specie to total reconstructed PM$_{10}$.

Figure S15: Comparison of PMF-resolved chemical profiles between the weekly (February 28, 2012 to December 28, 2015) and daily (January 12, 2016 to December 22, 2020) samples for the biomass burning factor. The bars represent the percentage (%) contribution of each specie to total reconstructed PM$_{10}$.

Figure S16: Comparison of PMF-resolved chemical profiles between the weekly (February 28, 2012 to December 28, 2015) and daily (January 12, 2016 to December 22, 2020) samples for the mineral dust factor. The bars represent the percentage (%) contribution of each specie to total reconstructed PM$_{10}$.

Figure S17: Comparison of PMF-resolved chemical profiles between the weekly (February 28, 2012 to December 28, 2015) and daily (January 12, 2016 to December 22, 2020) samples for the MSA-rich factor. The bars represent the percentage (%) contribution of each specie to total reconstructed PM$_{10}$. 
Figure S18: Comparison of PMF-resolved chemical profiles between the weekly (February 28, 2012 to December 28, 2015) and daily (January 12, 2016 to December 22, 2020) samples for the nitrate-rich factor. The bars represent the percentage (%) contribution of each specie to total reconstructed PM$_{10}$.

Figure S19: Comparison of PMF-resolved chemical profiles between the weekly (February 28, 2012 to December 28, 2015) and daily (January 12, 2016 to December 22, 2020) samples for the sulphate-rich factor. The bars represent the percentage (%) contribution of each specie to total reconstructed PM$_{10}$.

Figure S20: Comparison of PMF-resolved chemical profiles between the weekly (February 28, 2012 to December 28, 2015) and daily (January 12, 2016 to December 22, 2020) samples for the primary biogenic factor. The bars represent the percentage (%) contribution of each specie to total reconstructed PM$_{10}$.

Figure S21: Comparison of PMF-resolved chemical profiles between the weekly (February 28, 2012 to December 28, 2015) and daily (January 12, 2016 to December 22, 2020) samples for the traffic factor. The bars represent the percentage (%) contribution of each specie to total reconstructed PM$_{10}$.