9-year trends of PM₁₀ sources and oxidative potential in a rural background site in France

Supplementary information

5 **Table of Contents**

- 6 S1. Calculation of major chemical components of PM₁₀
- 7 S2. PMF model description
- 8 **S3.** Summary of PMF-resolved sources

10 S1. Calculation of major chemical components of PM₁₀

11 Organic matter (OM) is calculated by multiplying OC mass concentrations by a factor 1.8 based on 12 findings obtained from previous studies (Favez et al., 2010; Putaud et al., 2010). Sea salt sulfate (ss-13 sulfate) is calculated by multiplying the mass concentration of sodium by a factor of 0.252. The non-sea 14 salt sulfate (nss-sulfate) corresponds to the sea salt sulfate subtracted from the total mass of sulfate using 15 the factor from Seinfeld and Pandis (1998). Sea salt is estimated based on the mass concentrations of 16 sodium chloride (Putaud et al., 2010). Dust is calculated based on calcium of non-sea-salt origin, 17 following the empirical expression in (Putaud et al., 2004).

19 $[PM_{10}] = [OM] + [EC] + [nss - sulfate] + [nitrates] + [ammonium] + [sea salt] + [dust] +$ [non - dust]20

 $[nss - sulfate] = [SO_4^{2-}] - 0.252[Na^+]$

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

 $[dust] = 5.6 * [nss - Ca^{2+}]$ [nss - Ca²⁺] = [Ca²⁺] - [Na⁺]/26

- 22 (Eq. S1)
- 23 24 where:
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30 S2. PMF model description

The PMF model is based on a factorial analysis that takes into account the evolution of the concentration 31 32 of the measured chemical species and gathers, in the same factor, the fractions of the species evolving 33 in the same way. Each factor will then be assigned to a source by the user based on literature data and 34 geochemical knowledge of source characteristics in terms of trace chemical species.

35 The application of this model does not require prior knowledge of the chemical profiles of the sources, 36 but its application must be performed on a large dataset (many chemical species, including in particular 37 tracers and indicators of major sources) and on a large time series of samples. This is particularly the 38 case for this study, to our knowledge among the largest datasets in the Europe. The general equation 39 used in this PMF model is the following: 40

$$x_{ij} = (\sum_{k=1}^{p} g_{ik} \times f_{kj}) + e_{ij}$$
(Eq. S2)

- 41 Where x_{ij} : species concentration *j* for sample *i* 42
 - g_{ik} : factor contribution k for sample i
 - f_{kj} : factor contribution k from the specie j
 - e_{ii} : specie contribution *j* for sample *i* not explained by the model
- 46 This can be expressed in a matrix form simply by Eq. S3: 47

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

48 The model seeks to minimize the matrix E weighted by the matrix S containing the measurement

49 uncertainties, i.e. Q=E/S. The S-matrix is calculated using Eq. S4 proposed by (Gianini et al., 2013):

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$$s_{ij} = \sqrt{(DL_j)^2 + (CV_j \times x_{ij})^2 + (CV_{PM} \times x_{ij})^2}$$
(Eq. S4)
51 Where : DL_i : the limit of detection for species *j* (2 times the standard deviation of blanks)

- Where : DL_j : the limit of detection for species j (2 times the standard deviation of blanks)
- CV_j : the coefficient of variation of specie j (calculated from several successive 52 53 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., 2013).

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:

$$PD = 1 - r^2$$
, where r is the Pearson coefficient (Eq. S5)
$$\frac{\sqrt{2}}{\sum_{i=1}^{n} \frac{|a_i - b_i|}{|a_i|}}$$
(Eq. S6)

$$\frac{\sqrt{2}}{n} \sum_{i=1}^{n} \frac{|a_i - b_i|}{a_i + b_i}$$

where a and b are the relative mass to PM₁₀ of two different factors and n is the number of common species in a and b.

S3. Summary of PMF-resolved sources

Table S1. The PMF-resolved sources and their specific tracers

Identified factors	Specific tracers	
Biomass burning	Levoglucosan, mannosan	
Nitrate-rich	NO_3^- , NH_4^+	
Sulfate-rich	SO4 ²⁻ , NH4 ⁺	
Mineral dust	Ca ²⁺ , Al, Ti, Fe, Cu, Zn	
Fresh sea salt	Na^+ , Cl^- , Mg^{2+}	
Aged sea salt	Na^+ , Mg^{2+}	
Primary biogenic	Polyols	
MSA-rich	MSA	
Traffic	EC, Cu, Sb, Sn	

96 Table S2: Summary of the tested chemical constraints on source-specific tracers in the PMF factor profiles.

Factor profile	Element	Туре	Value	Used in the final model
Biomass burning	Levoglucosan	Pull up maximally	(% dQ 0.50)	Yes
Biomass burning	Mannosan	Pull up maximally	(% dQ 0.50)	Yes
Primary biogenic	Levoglucosan	Set to zero	0	No
Primary biogenic	Mannosan	Set to zero	0	No
Primary biogenic	Polyols	Pull up maximally	(% dQ 0.50)	No
Primary biogenic	EC	Pull down maximally	(% dQ 0.50)	No
MSA-rich	MSA	Pull up maximally	(% dQ 0.50)	Yes
MSA-rich	Levoglucosan	Set to zero	0	Yes
MSA-rich	Mannosan	Set to zero	0	Yes
MSA-rich	Polyols	Pull down maximally	(% dQ 0.50)	No
MSA-rich	EC	Pull down maximally	(% dQ 0.50)	No
Nitrate-rich	Levoglucosan	Set to zero	0	No
Nitrate-rich	Mannosan	Set to zero	0	No
Mineral dust	Ti	Pull up maximally	(% dQ 0.50)	Yes
Primary traffic	Levoglucosan	Set to 0	0	Yes
Primary traffic	Mannosan	Set to 0	0	Yes
Primary traffic	Cu/Fe	Set to value	0.046 (% dQ 0.50)	No
Primary traffic	Cu/Sn	Set to value	5.6 (% dQ 0.50)	No
Primary traffic	Cu/Sb	Set to value	12.6 (% dQ 0.50)	No
Primary traffic	Cu/Mn	Set to value	5.7 (% dQ 0.50)	No
Primary traffic	OC*/EC	Set to value	0.44 (% dQ 0.50)	No



116117Figure S1: Chemical profile and temporal evolution with error estimates of the biomass burning factor



120 Figure S2: Chemical profile and temporal evolution with error estimates of the nitrate-rich factor

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124125Figure S3: Chemical profile and temporal evolution with error estimates of the sulphate-rich factor



128129Figure S4: Chemical profile and temporal evolution with error estimates of the mineral dust factor



133 Figure S5: Chemical profile and temporal evolution with error estimates of the fresh sea salt factor

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137138 Figure S6: Chemical profile and temporal evolution with error estimates of the aged sea salt factor



141142Figure S7: Chemical profile and temporal evolution with error estimates of the primary biogenic factor



146 Figure S8: Chemical profile and temporal evolution with error estimates of the MSA-rich factor



150151 Figure S9: Chemical profile and temporal evolution with error estimates of the traffic factor

STL deconvolution of PM10



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Figure S10: The Season-trend (STL) deconvolution of contributions of PM_{10} from year 2012 to 2020.

STL deconvolution of the EC source



Figure S11: The Season-trend (STL) deconvolution of contributions of EC to PM₁₀ from year 2012 to 2020.

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160	Table S3: Comparison of the PMF-resolved source contributions (in terms of µg m ⁻³ and percentage) to PM ₁₀ betwee
161	daily and weekly samples

Source	24-hr samples (<i>n</i> =253)		7-day samples $(n=181)$	
	Contribution (µg m ⁻³)	Percentage contribution (%)	Contribution (µg m ⁻³)	Percentage contribution (%)
Sulphate-rich	1.5	15.1	1.9	19.7
Primary biogenic	0.6	6.2	1.2	12.4
Aged sea salt	0.9	8.8	0.6	6.2

Nitrate-rich	2.3	22.6	1.7	18.2
Fresh sea salt	0.5	4.6	0.4	4.2
MSA-rich	0.3	3.3	0.5	5.1
Traffic	1.6	15.7	0.9	9.8
Mineral dust	1.2	12.1	1.3	13.8
Biomass burning	1.2	11.7	1.0	10.7



Figure S12: 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

166 percentage (%) contribution of each specie to total reconstructed PM₁₀.





170 percentage (%) contribution of each specie to total reconstructed PM₁₀.



Figure S14: 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 PM₁₀.





176 Figure S15: Comparison of PMF-resolved chemical profiles between the weekly (February 28, 2012 to December 28, 177 2015) and daily (January 12, 2016 to December 22, 2020) samples for the mineral dust factor. The bars represent the 178 percentage (%) contribution of each specie to total reconstructed PM₁₀.



180 Figure S16: Comparison of PMF-resolved chemical profiles between the weekly (February 28, 2012 to December 28, 181 2015) and daily (January 12, 2016 to December 22, 2020) samples for the MSA-rich factor. The bars represent the





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188 Figure S18: Comparison of PMF-resolved chemical profiles between the weekly (February 28, 2012 to December 28, 189 2015) and daily (January 12, 2016 to December 22, 2020) samples for the sulphate-rich factor. The bars represent the 190 percentage (%) contribution of each specie to total reconstructed $PM_{10}\!.$



193 194 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 primary biogenic factor. The bars represent

the percentage (%) contribution of each specie to total reconstructed PM₁₀.



197 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 traffic factor. The bars represent the percentage (%) contribution of each specie to total reconstructed PM₁₀.