Source apportionment of PM_{10} in a North-Western Europe regional urban background site (Lens, France) using Positive Matrix Factorization and including primary biogenic emissions

A. Waked[1], O. Favez[2], L.Y. Alleman[3,4], C.Piot[5], J.-E. Petit[2,6], T. Delaunay[7], E. Verlinden[7], B. Golly[5], J.-L. Besombes[5], J.-L. Jaffrezo[1] and E.Leoz-Garziandia[2]

[1] {Université Grenoble 1-CNRS, LGGE, F-38041 Grenoble, France}

[2] {INERIS, DRC/CARA/CIME, F-60550 Verneuil-en-Halatte, France}

[3] {Université Lille Nord de France, F-59000 Lille, France}

[4] {Mines Douai, CE, F-59508 Douai, France}

[5] {Université de Savoie, LCME, F-73376 Le Bourget du lac, France}

[6] {Université Versailles Saint-Quentin-CNRS-CEA, LSCE, F-91198 Gif-Sur-Yvette, France}

[7] {Atmo Nord-Pas de Calais, F-59044 Lille, France}

Correspondence to: A. Waked (antoine.waked@lgge.obs.ujf-grenoble.fr) and O. Favez (Olivier.favez@ineris.fr)

Supporting Information

Chemical composition of the profiles of sources

The composition of the traffic (exhaust) factor is dominated by EC and OC* representing together 68% of the total mass of the factor (Figure S3, supporting information). The EC/OC* mass ratio is about 1.55, in general agreement with the ratio of 2.0 from vehicular emissions measured in a French tunnel (El Haddad et al., 2009). Conversely, this factor contains about 19% by mass of nitrate most probably from secondary origin, while such mass fraction is lower than 1% in vehicular emissions measured in the same tunnel study (El Haddad et al., 2009). Therefore, this traffic factor is influenced by other sources than direct vehicular emissions, including secondary processes and possibly resuspension bringing a significant contribution of calcium and trace elements (12% together).

The organic fraction largely dominates the composition of the biomass burning factor (49% from OC* together with 7% of levoglucosan), with an EC/OC ratio of 0.23 in line with that observed in the literature for wood combustion (Fine et al., 2002); the OC/Levoglucosan ratio of 7.04 is in total agreement with the value of 7.35 largely used in the literature (value from Fine et al., 2004 used for example in Europe by Puxbaum et al., 2007). However, the proportion of nitrate is higher than those generally observed in the source chemical profile of biomass burning emissions, with a nitrate/OC ratio in the factor of 0.38 while it is about 0.01 for direct emissions of wood combustion (Fine et al., 2002).

OC* also represents the major fraction in the primary biogenic factor with a contribution of 63% to the total mass. Inorganic species, particularly the sum of nitrate, sulfate and ammonium contributes for 17% only. This fraction is however an indication of secondary aerosols formation, suggesting that the biogenic emission factor do not encompass just primary emissions. Further, the rather large and unexpected proportion of EC (11% of the mass of the factor) is also an indication that this factor may be a mix issued from other processes, or that the PMF procedure is not optimal for solving this factor.

The chemical profile of the mineral dust factor is very different from those from mineral dust like Saharan dust. The high proportions of calcium and metals are clear indicators of dust but the very high fraction of OC* is again indicative of further mixing of sources, or processing of mineral particles during transport, including secondary production. The same comments also apply to the heavy oil combustion factor, which is characterized by large proportions of OC* and EC, together with secondary ionic components dominated by sulfate. This proportion is indicative of combustion processes related mainly to industrial premises because of the important contribution for sulfate.

The sea-salt factor is well characterized by a large mass fraction of Cl and Na (55% and 23 %, respectively, of the total mass). The Cl/Na ratio is 2.45 and is larger than that of sea salt (1.8 ; data from DOE, 1994). The aged marine aerosols profile is very different from that of the sea-salt factor. While the proportion of Na is in the same order of magnitude (17%), Cl is fully depleted due to its replacement by strong acids, with nitrate and sulfate representing 41% and 34% of the mass of the factor, respectively. Therefore, the important fraction of sulfate and nitrate in the source profile of this factor is a clear sign of aging of the air mass and of secondary processing.

Finally, the two factors of secondary inorganic aerosols (Nitrate-rich and Sulfate-rich) are mostly composed of inorganic species with contributions of nitrate in the nitrate-rich factor up to 69% and of sulfate in the sulfate-rich factor up to 53%. The Nitrate/Ammonium ratio in the nitrate-rich factor is 3.2 and is consistent with the chemical equilibrium allowing the formation of ammonium-nitrate (ratio of 3.4 by mass). The Sulfate/Ammonium ratio in the sulfate-rich factor is 2.5 while the chemical equilibrium between sulfate and ammonium is characterized by a ratio between the two compounds of 5.3. This factor probably contains other sources than just secondary sulfate aerosols. Notably, OC contributes to 24% of the mass, while its fraction is negligible in the nitrate-rich factor.

References

1. DOE. Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water ; version 2, A. G. Dickson & C. Goyet, eds., ORNL/CDIAC-74, 1994.

2. El Haddad, I., Marchand, N., Dron, J., Temime-Roussel, B., Quivet, E., Wortham, H., Jaffrezo, J. L., Baduel, C., Voisin, D., Besombes, J. L. and Gille, G.: Comprehensive primary particulate organic characterization of vehicular exhaust emissions in France, Atmospheric Environment, 43(39), 6190–6198, doi:10.1016/j.atmosenv.2009.09.001, 2009.

3. Fine, P.M., Cass, G.R., Simoneit, B.R.T., 2004. Chemical Characterization of Fine Particle Emissions from the Fireplace Combustion of Wood Types Grown in the Midwestern and Western United States. Environmental Engineering Science 21, 387-409.

4. Fine, P. M., Cass, G. R. and Simoneit, B. R. T.: Chemical Characterization of Fine Particle Emissions from the Fireplace Combustion of Woods Grown in the Southern United States, Environ. Sci. Technol., 36(7), 1442–1451, doi:10.1021/es0108988, 2002.

5. Puxbaum, H., Caseiro, A., Sánchez-Ochoa, A., Kasper-Giebl, A., Claeys, M., Gelencsér, A., Legrand, M., Preunkert, S. and Pio, C.: Levoglucosan levels at background sites in Europe for assessing the impact of biomass combustion on the European aerosol background, J. Geophys. Res., 112(D23), D23S05, doi:10.1029/2006JD008114, 2007.

Tables

Table S1. Bootstrap results for the best provided solutions from 8 to 10 factors.

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Factor 7	Factor 8	Unmapped
Boot Factor 1	100	0	0	0	0	0	0	0	0
Boot Factor 2	0	88	2	0	0	0	0	0	10
Boot Factor 3	0	4	90	0	0	0	2	0	4
Boot Factor 4	0	0	0	100	0	0	0	0	0
Boot Factor 5	0	0	0	0	100	0	0	0	0
Boot Factor 6	0	0	0	0	2	98	0	0	0
Boot Factor 7	0	0	0	0	0	0	100	0	0
Boot Factor 8	0	0	0	0	0	0	0	100	0

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Factor 7	Factor 8	Factor 9	Unmapped
Boot Factor 1	100	0	0	0	0	0	0	0	0	0
Boot Factor 2	0	94	0	1	0	1	0	0	0	4
Boot Factor 3	0	0	100	0	0	0	0	0	0	0
Boot Factor 4	0	0	0	100	0	0	0	0	0	0
Boot Factor 5	0	0	0	0	100	0	0	0	0	0
Boot Factor 6	0	0	0	0	0	100	0	0	0	0
Boot Factor 7	1	0	0	0	0	0	99	0	0	0
Boot Factor 8	0	2	0	1	1	0	1	92	0	3
Boot Factor 9	0	0	0	0	0	0	0	0	100	0

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Factor 7	Factor 8	Factor 9	Factor 10	Unmapped
Boot Factor 1	100	0	0	0	0	0	0	0	0	0	0
Boot Factor 2	0	100	0	0	0	0	0	0	0	0	0
Boot Factor 3	1	0	99	0	0	0	0	0	0	0	0
Boot Factor 4	0	0	0	96	0	0	0	1	0	0	3
Boot Factor 5	0	0	0	0	100	0	0	0	0	0	0
Boot Factor 6	0	0	0	0	0	100	0	0	0	0	0
Boot Factor 7	0	0	0	0	0	0	100	0	0	0	0
Boot Factor 8	0	0	0	0	0	0	0	97	0	0	3
Boot Factor 9	0	0	0	0	0	0	0	0	100	0	0
Boot Factor 10	10	0	27	0	1	8	5	2	0	33	14

Table S2. Q robust and Q true for the best provided solutions from 8 to 10 factors.

Solution	Q robust	Q true
8 factor solution	**2135.5**	**2135.7**
9 factor solution	**1722.2**	**1722.3**
10 factor solution	**1411.4**	**1411.6**

Figures

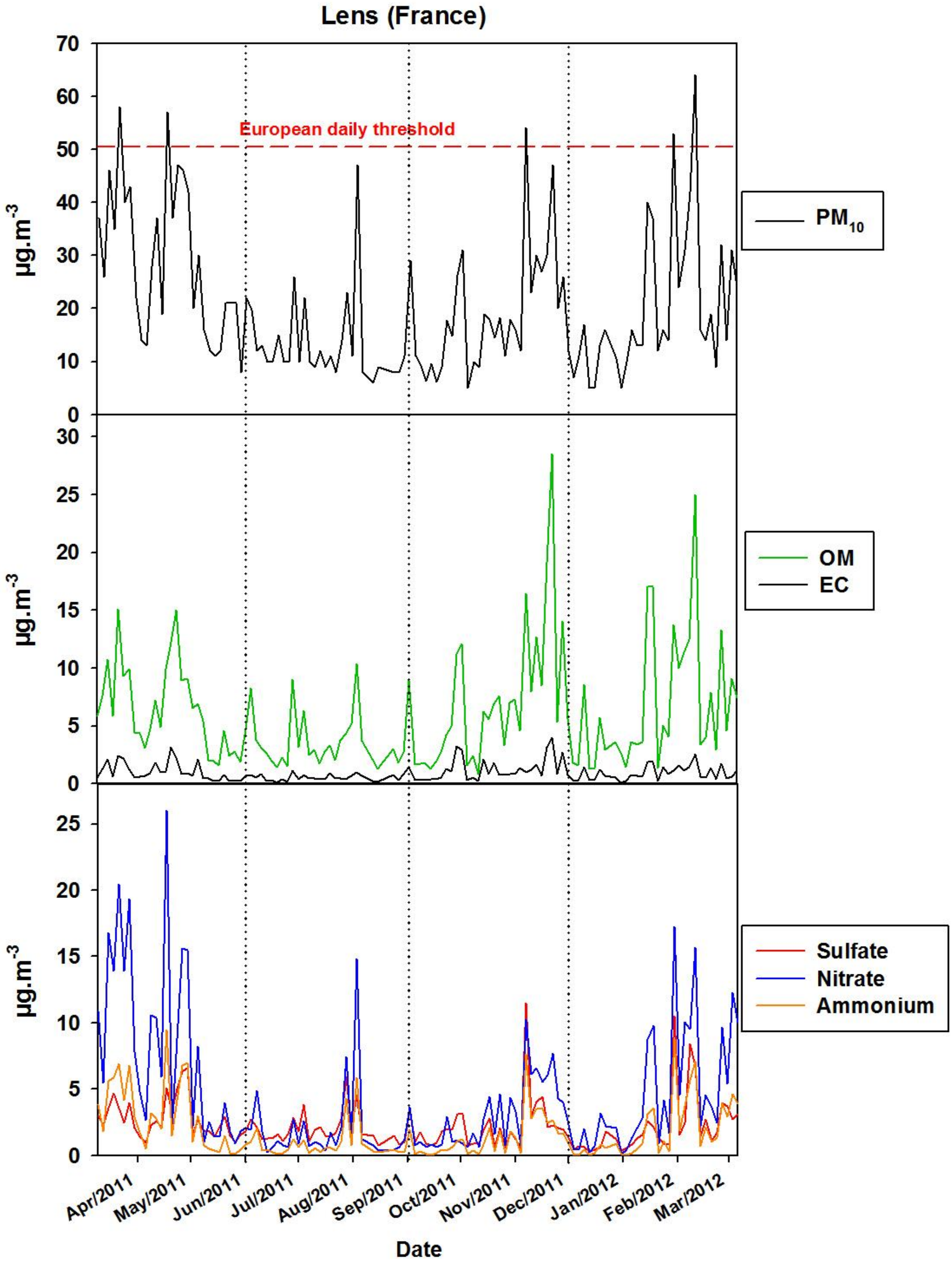

Figure S1 : Annual evolutions of concentrations (in $\mu g.m^{-3}$) of PM_{10}, OM, EC, Sulfate, Nitrate and Ammonium in Lens, France in 2011-2012.

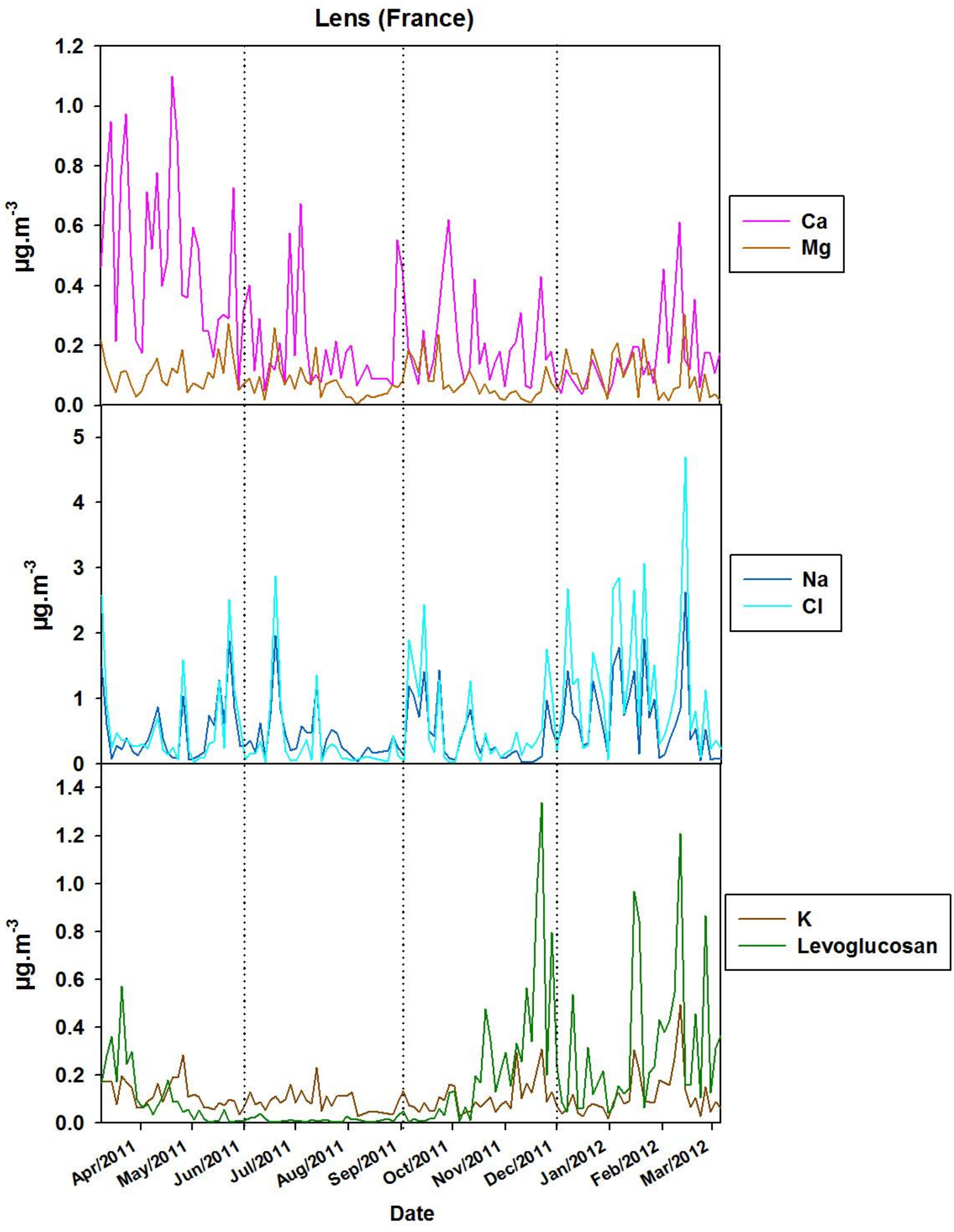

Figure S2 : Annual evolutions of concentrations (in $\mu g.m^{-3}$) of Ca, Mg, Na, Cl, K and Levoglucosan in Lens, France in 2011-2012.

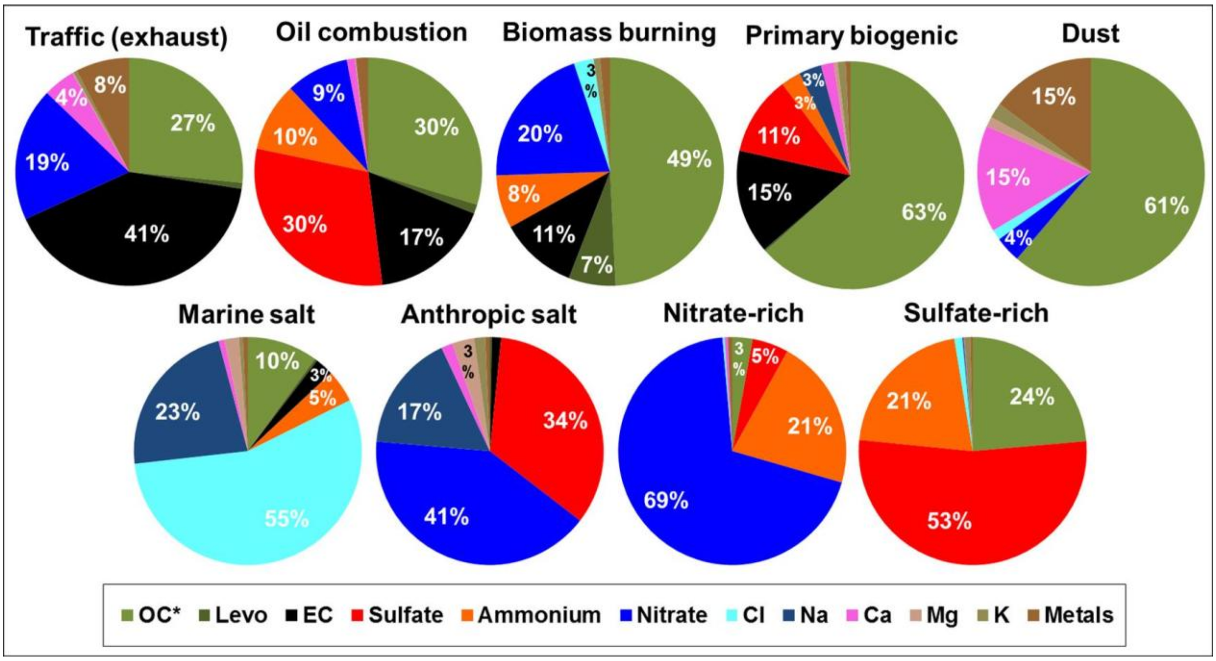

Figure S3 : Chemical composition of each factor (in %)

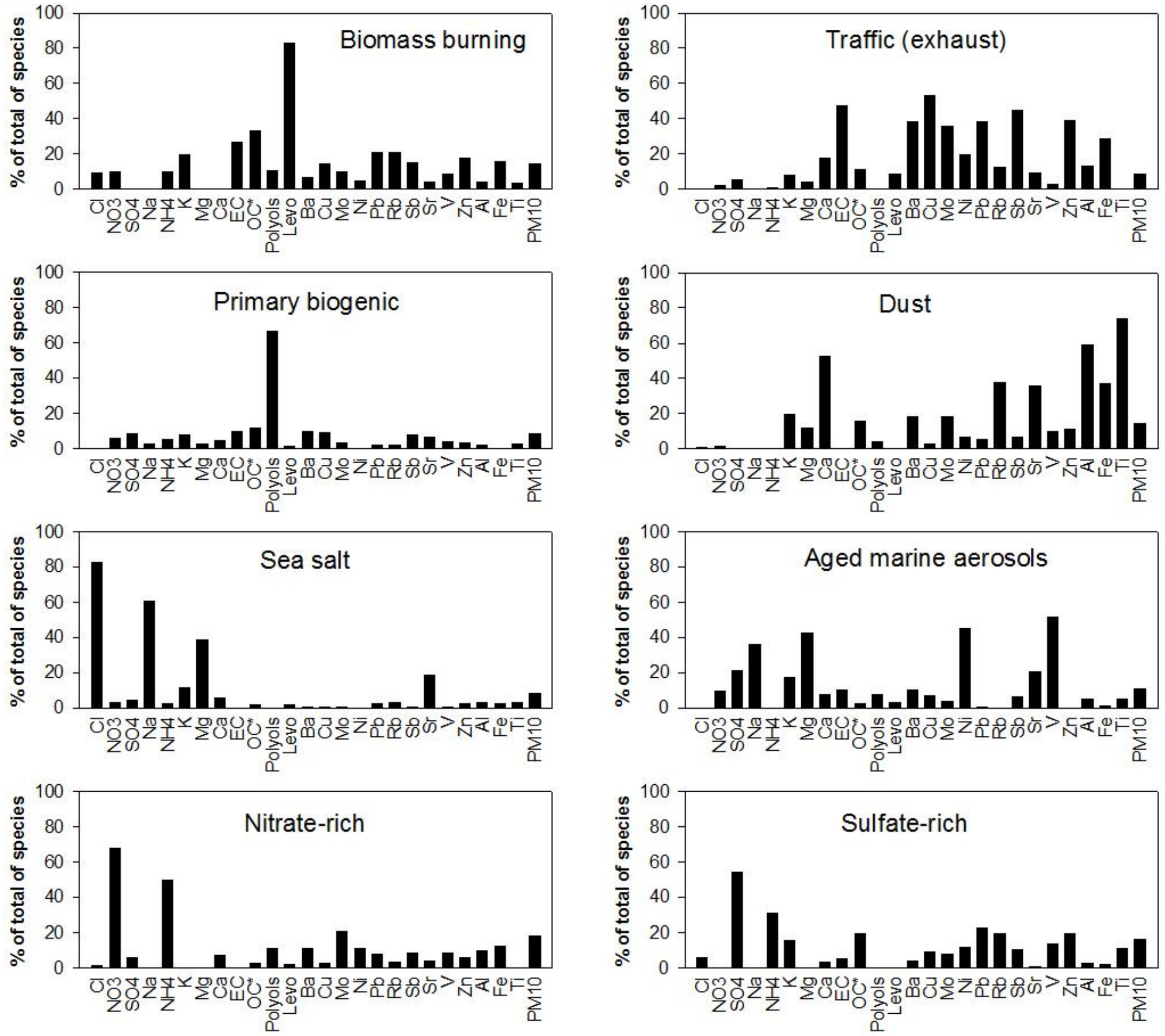

Figure S4 : Source profiles for the 8 factors solution.

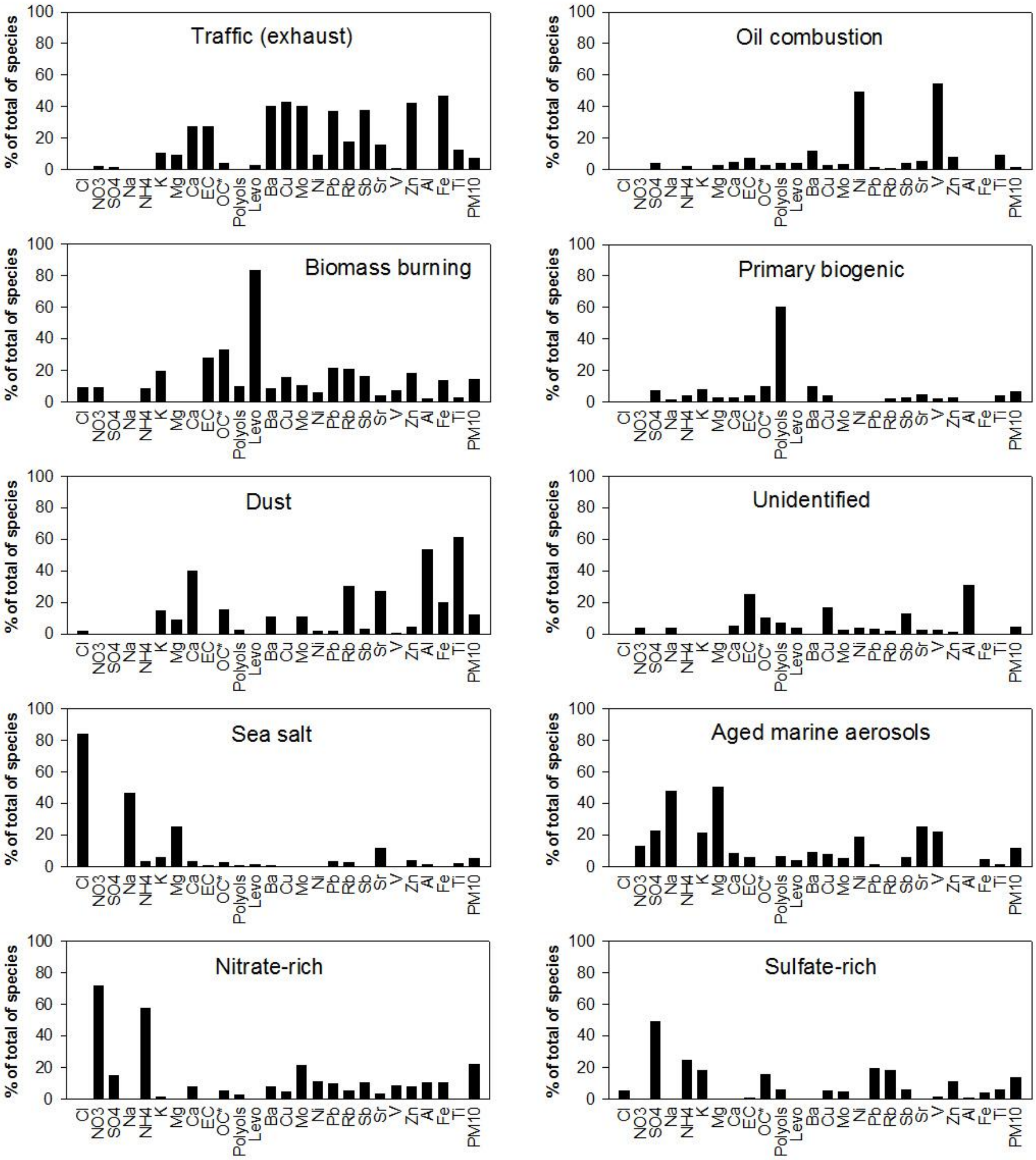

Figure S5 : Source profiles for the 10 factors solution.

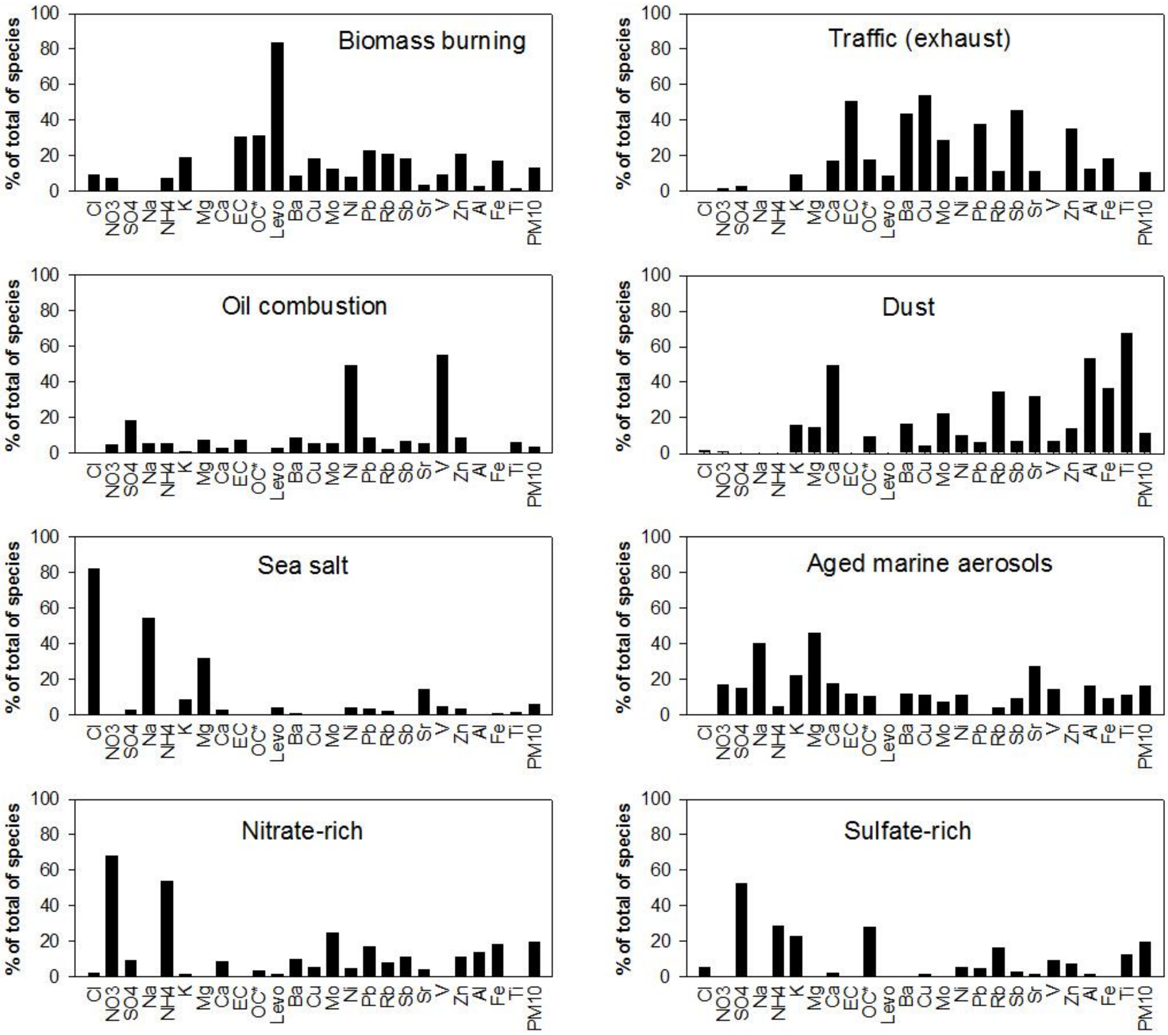

Figure S6 : Source profiles for the 8 factors solution with the exclusion of Polyols* specie.

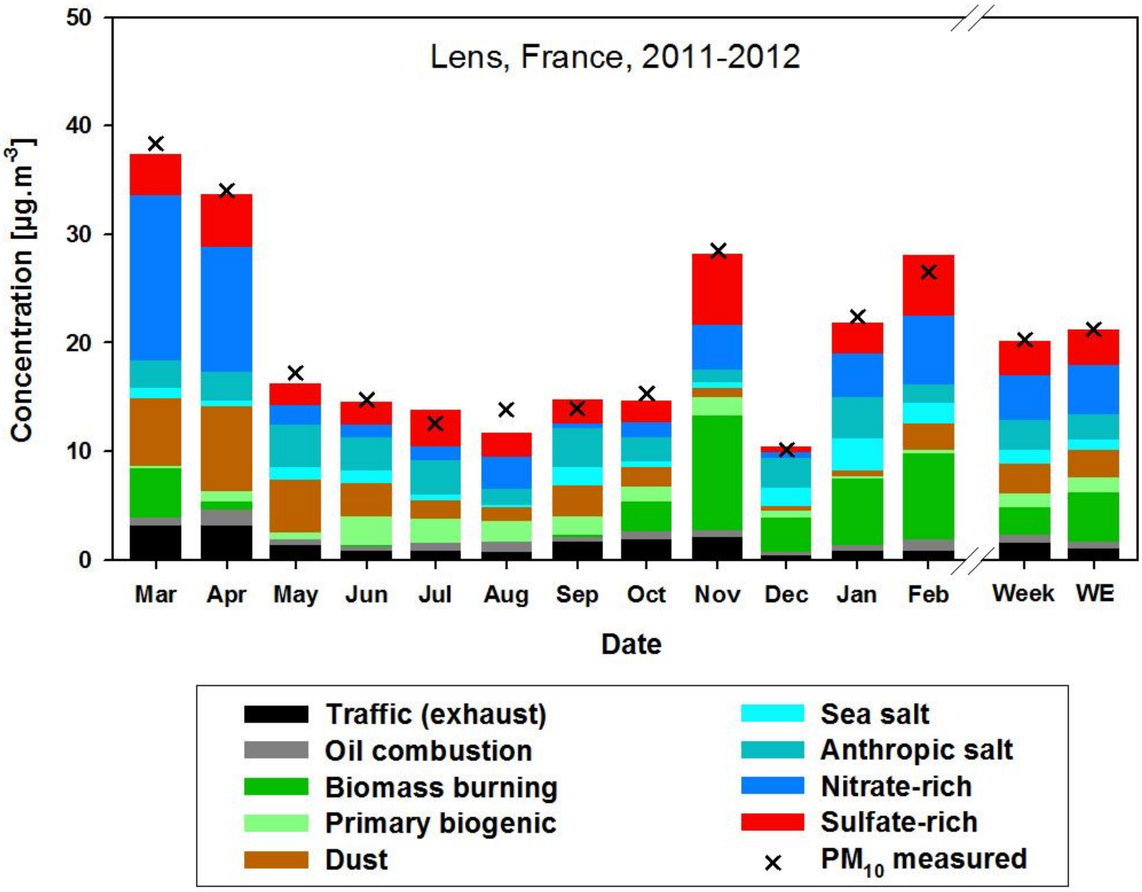

Figure S7 : Contributions of the identified sources to total PM_{10} on a monthly basis and comparison to the measured PM_{10} values

Table S3. Rotational ambiguities for the 9 factor solution

Peak	Strength	Q(Robust)	Q(True)	Converged	Steps
1	-0.3	1786.6	1729.0	Yes	620
2	-0.1	1731.1	1724.2	Yes	769
3	0.1	1735.5	1725.3	Yes	1525
4	0.2	1773.2	1729.1	Yes	1104
5	0.4	1926.1	1736.0	Yes	852