An apportionment method for the Oxydative Potential to the atmospheric PM sources: application to a one-year study in Chamonix, France. Suplementary Informations

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SI 1   Sources profiles from the PMF

Biomass burning is a profile highly represented by biomass burning proxy: the levoglucosan and the methoxyphenols. The BC_{bb} and OC* are also mainly in this factor. Associated with it, some potassium and rubidium are also present in this source. These proxy are well-known to be tracers of biomass burning activities (Godoy et al., 2005; Jordan et al., 2006; Nava et al., 2015; Puxbaum et al., 2007)

Vehicular emissions are associated to a very large contribution of metals (Cu, Mo, Pb, Sb, Fe, Zr, Ti) and a significant amount of carbonaceous matter (mainly BC_{ff}) and organic compound (HOP). The two sources from vehicle' traffic which are "exhaust" (i.e. fuel combustion (Allen et al., 2001; Hu et al., 2009; Viana et al., 2008)) and "non-exhaust" (i.e. road abrasion, brake wear, etc. (Sanders et al., 2003; Sternbeck et al., 2002)) are mixed in this profile.

Primary biogenic emissions are identified thanks to the presence of polyols (sum of arabitol, sorbitol and mannitol) coming from the biogenic activity (fungi, pollens and bacteria) (Bauer et al., 2008) or from vegetal debris (Yttri et al., 2007). The temporal contribution of this factor (mainly during summer) also pledges in favour of the biogenic activity.

Secondary biogenic emissions are dominated by the MSA (methane sulfonic acid), product by the oxidation of the DMS (dimethyl sulfate). The DMS is well-known for being emitted by marine algae (Saltzman et al., 1983; Zhang et al., 2014) or vegetation and soil micro-biology (Jardine et al., 2015).

Crustal dust is characterized with a high predominance of Mg^{2+}, Ca^{2+}, Ti, Mn, Fe, which are elements of the terrestrial crust. We identified this source as re-suspension of soil or rock dust (Almeida et al., 2005; Dall'Osto et al., 2013; Moreno et al., 2011; Putaud et al., 2004).

Sea/road salt shows a high proportion of Na^+ and Cl^-, but also Mg^{2+}. These ions are proxy of sea salt (Belis et al., 2013; O'Dowd et al., 1997; Pio et al., 2007) as well as road salt, especially during winter in the Alps region (Air Rhne-Alpes, 2012).

Nitrate rich with a high concentration of nitrate ions (NO_3^-) associates with ammonium (NH_4^+). It indicates the presence of ammonium nitrate NO_3NH_4.

Sulfate rich with a high concentration of sulfate ions (SO_4^{2-}) associates with ammonium (NH_4^+). It indicates the presence of ammonium sulfate $SO_4(NH_4)_2$.

Table 1: Concentration of species in $1\,\mu$g of PM for each source attributed by the PMF model.

specie	Primary biogenic	Sea/road salt	Secondary biogenic	Crustal dust	Vehicular	Biomass burning	Nitrate rich	Sulfate rich
	ng/μg							
OC*	412.86	228.75	733.01	180.92	301.20	401.67	225.14	249.95
BC_{bb}	15.37	19.29	22.65	4.35	24.69	72.99	10.96	6.91
BC_{ff}	160.58	72.08	116.95	8.35	295.70	0	63.05	0.48
MSA	0.27	0	18.38	0	0.07	0	0.37	0.09
Cl^-	0	36.48	0	0	0	4.74	4.35	0
NO_3^-	4.58	0	71.42	102.12	0	9.41	427.27	18.97
SO_4^{2-}	26.33	20.65	37.48	72.18	0	39.76	0	302.41
Na^+	3.07	62.22	21.23	0.09	2.80	1.52	0	0.62
NH_4^+	11.47	4.25	0	0	6.02	8.82	86.69	108.24
K^+	9.11	3.96	10.18	3.70	2.21	9.53	3.33	3.33
Mg^{2+}	0.15	0.68	2.86	4.43	0	0.39	0	0.52
Ca^{2+}	0	0	11.74	115.47	5.62	3.07	8.54	11.97
Levoglucosan	8.07	21.00	2.37	0	13.77	107.71	32.88	4.64
Σpolyols	14.55	0	3.27	1.09	0	0.64	0.43	1.66
Σmethoxy	0	0	0	0.60	0	11.34	0	0
Fe	12.14	21.73	8.04	38.82	42.06	1.02	0	1.00
	pg/μg							
As	16.16	2.32	55.47	37.70	64.14	0.00	12.97	16.55
Cu	552.51	421.26	908.64	261.28	1147.23	247.42	0	92.72
Mn	150.02	146.43	381.62	1224.90	495.22	21.15	4.25	140.64
Mo	17.22	16.99	39.99	13.09	82.84	0	0	13.62
Ni	4.17	21.56	0.13	106.58	46.94	0	0	18.64
Pb	75.42	0	119.94	156.67	380.18	0	99.35	113.36
Rb	11.03	18.15	0	69.91	34.72	27.09	0	0
Sb	25.32	28.88	27.92	0	80.69	0	6.15	3.11
Ti	308.11	135.57	253.05	1754.87	291.41	0	42.31	101.03
V	28.44	21.14	31.64	92.69	0	0	0	14.14
Zn	377.67	225.73	1240.86	548.98	2091.33	139.94	602.30	373.39
Zr	45.51	11.33	16.67	34.12	52.09	6.24	6.56	0
σHOP	0	145.45	4.77	8.66	140.33	0.00	34.46	0

Table 1 summaries the factor profiles in $1\,\mu$g of PM of each source while Fig. 1 presents the fraction of each species associated with each source.
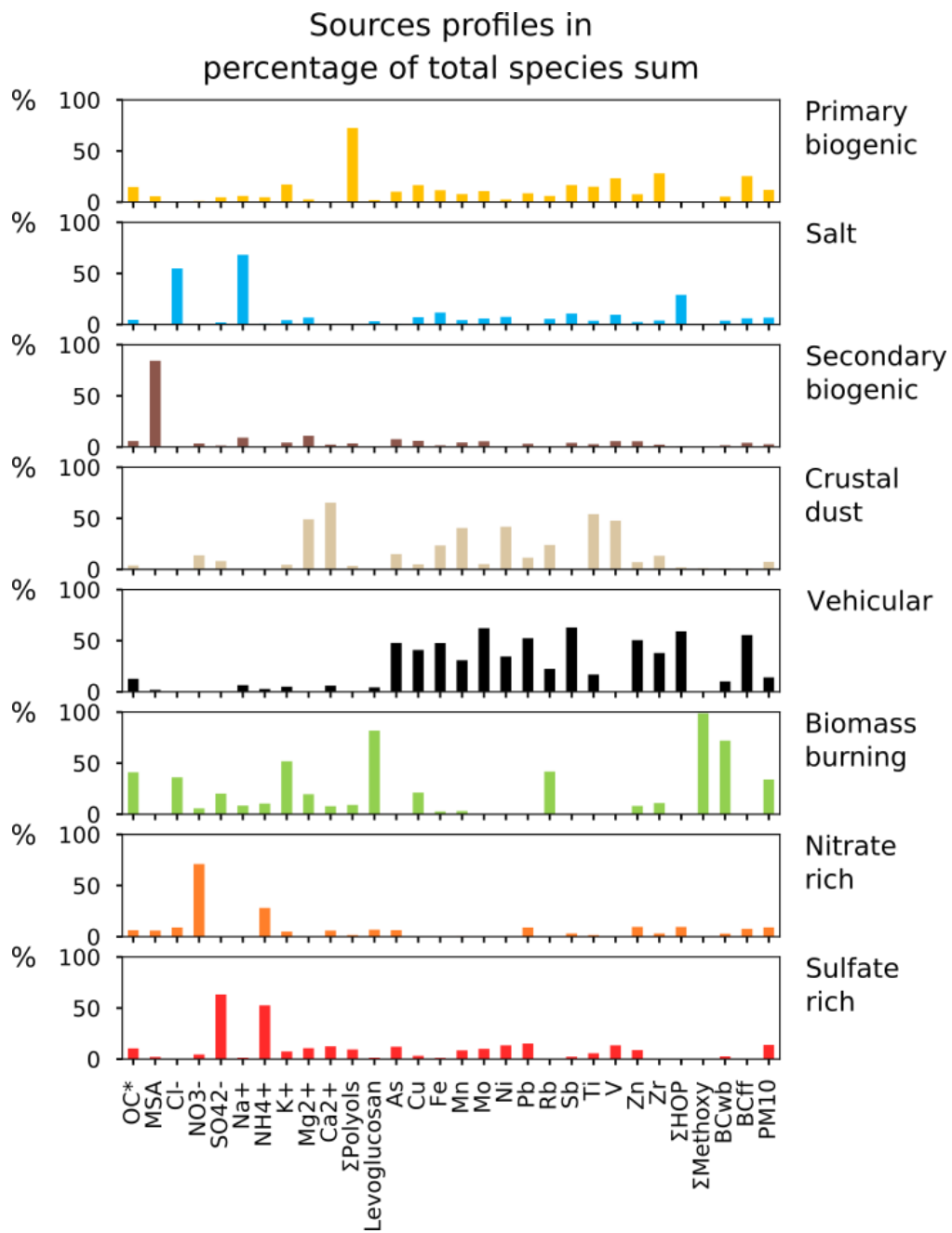
Figure 1: Percentage of the ambient species concentration apportioned in each factor attributed by the PMF model.

SI 2   Correlation between OP and chemical species, and OP and sources

The univariate correlation on an annual basis between the OP values and the concentrations of chemical species was first investigated and is presented in Fig. 2. We see a strong relationship between some of the organic species and the OP (levoglucosan, methoxyphenol) as well as the carbonaceous matter (OC and BC) for both tests. It suggests important contributions of biomass burning source and fossil fuel burning activities to the OP's. The metals Cu, Rb, and Sb appear highly correlated to the OP, but Ni, Ti and V do not. The results for the ions indicate weak positive correlations with both OP only. We also note that the polyols and MSA show a tendency with anti-correlations with both OPs. Most of these results are strongly affected by the really high changes in concentrations during the winter and the summer periods, in part related to the local impact of meteorology and inversion layers in winter (Calas et al., 2018).
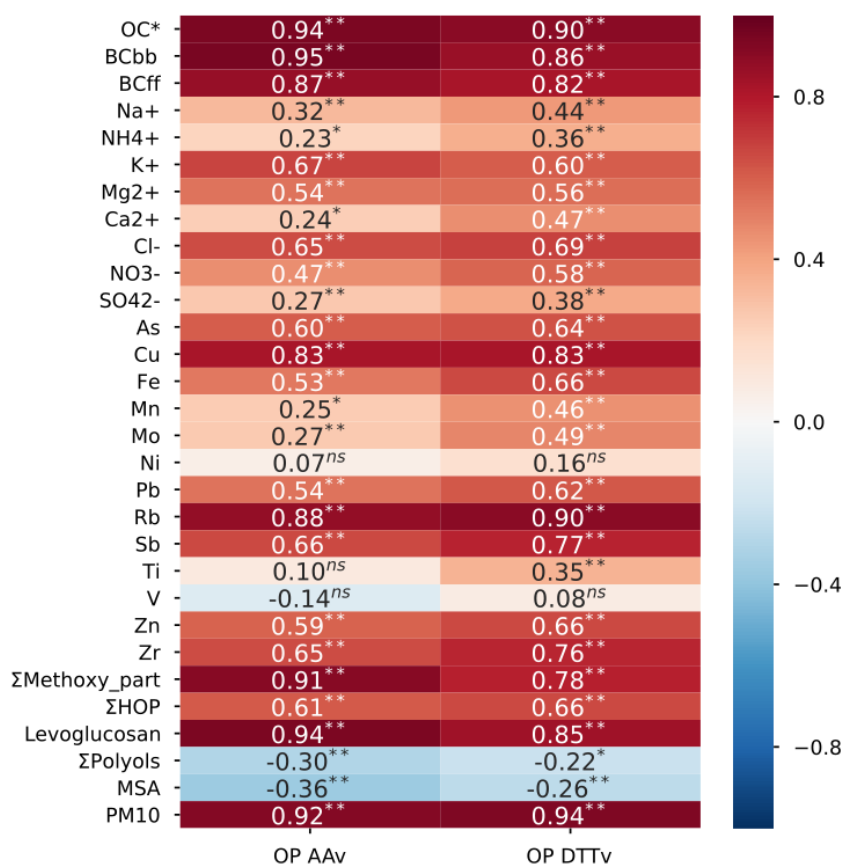
Figure 2: Pearson's correlation coefficient between the concentrations of the species and the OP AA_v and OP DTT_v activity from the 2, November 2013 to the 31, October 2014 (97 samples). **: p-values <0.01, *: p-value <0.05, ns: p-value >0.05.

The univariate-correlation between the contributions of the sources of PM deduced from the PMF and the OPs is presented Fig. 3. It emphasized the hypothesis of the high contribution of the biomass burning and vehicular sources to the OP of the PM_{10}. We do not see very large differences between the two tests, expect for the crustal dust source (no correlation with the OP AA_v but a positive one for the OP DTT_v).
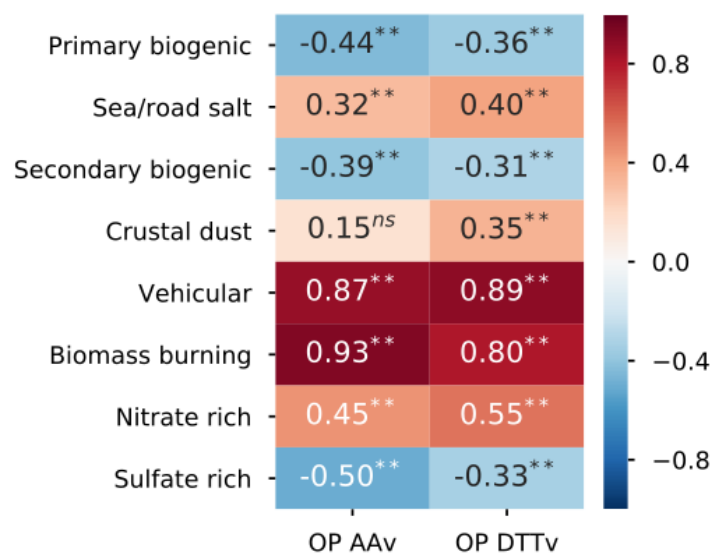
Figure 3: Pearson's correlation coefficient between the PM concentrations of the sources from the PMF and the OP AA_v and OP DTT_v activity from the 14, November 2013 to the 31, October 2014 (85 samples). **: p-values <0.01, *: p-value <0.05, ns: p-value >0.05.

SI 3   Additional reference

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