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Polyols and glucose particulate species as tracers of primary biogenic organic aerosols at 28 French sites

Abdoulaye Samaké et al.

Correspondence to: Abdoulaye Samaké (abdoulaye.samake2@univ-grenoble-alpes.fr) and Jean-Luc Jaffrezo (lean-luc.laffrezo@univ-grenoble-alpes.fr)

Table SI-1: Characteristics of sampling sites (including altitude, site typology) and number of analyzed samples.

Sampling site	Altitude (m)	PM fraction	AASQA* in charge of sampling sites	Number of Samples	Sugar compounds analyzed by	PMF analysis	Typology
OPE-ANDRA	293	PM_{10}	OPE-ANDRA	266	IGE		Rural
OPE-ANDRA	293	$PM_{2.5}$	OPE-ANDRA	310	IGE		Rural
Peyrusse Vieille	175	PM_{10}	ATMO Occitanie	59	IGE		Rural
Revin	395	PM_{10}	ATMO Grand-Est	168	LSCE	+	Rural
Revin	395	$PM_{2.5}$	ATMO Grand-Est	162	IGE		Rural
Dieulefit	550	$PM_{2.5}$	ATMO AuRA	56	IGE		Rural
Verneuil	180	$PM_{2.5}$	LIG'AIR	60	IGE		Rural
Chamonix	1035	PM_{10}	ATMO AuRA	120	IGE	+	Urban
Marnaz	504	PM_{10}	ATMO AuRA	203	IGE	+	Urban
Passy	588	PM_{10}	ATMO AuRA	344	IGE	+	Urban
Lanslebourg	1400	PM_{10}	ATMO AuRA	82	IGE		Urban
Grenoble_LF	214	PM_{10}	ATMO AuRA	714	IGE	+	Urban
Grenoble_CB	212	PM_{10}	ATMO AuRA	72	IGE		Urban
Grenoble_VIF	310	PM_{10}	ATMO AuRA	72	IGE		Urban
Gap	743	PM_{10}	AIR PACA	125	IGE		Urban
Lyon	160	PM_{10}	ATMO AuRA	172	IGE	+	Urban
Marseille	64	PM_{10}	AIR PACA	255	IGE	+	Urban
Gardanne	212	PM_{10}	AIR PACA	88	IGE		Urban
Meyreuil	235	PM_{10}	AIR PACA	91	IGE		Urban
Mallet	200	PM_{10}	AIR PACA	96	IGE		Urban
Port-de-Bouc	1	PM_{10}	AIR PACA	242	IGE	+	Urban
Aix-en-Provence	188	PM_{10}	AIR PACA	177	IGE	+	Urban
Nice	9	PM_{10}	AIR PACA	228	IGE	+	Urban
Talence	20	PM_{10}	ATMO Nouvelle-Aquitaine	159	IGE	+	Urban
Poitiers	0	PM_{10}	ATMO Nouvelle-Aquitaine	134	IGE	+	Urban
Lens	47	PM_{10}	ATMO Hauts-de-France	118 169	IGE LSCE	+ +	Urban Urban
Nogent	47	PM_{10}	ATMO Hauts-de-France	155	LSCE	+	Urban
Rouen	6	PM_{10}	ATMO Normandie	168	LSCE	+	Urban
Roubaix	10	PM_{10}	ATMO Hauts-de-France	159	LSCE	+	Traffic
Strasbourg	139	PM_{10}	ATMO Grand-Est	120	IGE	+	Traffic

**AASQA: Officially-approved French Air Quality Monitoring networks which instrument and maintain the sampling sites, and handle the filters. The AASQA follow the well-defined criteria for the classification (typology) of all sites in France. The description of the monitoring sites can be accessed by clicking on the AASQA designation. Symbol (+) indicates cases where PMF analysis was performed.*

**Except PM_{10} collected at OPE-ANDRA (sampled on weekly basis with low volume sampler operating at a flow rate of 1 $m^3.h^{-1}$), all others PM samples were collected on daily basis, using high volume samplers operating at a flow rate of 30 $m^3.h^{-1}$.*

Table SI-2 : Yearly average mass concentrations of polyols and glucose according to the sampling site typologies. Concentration values are expressed in ng.m^{-3}.

	All sampling sites	Rural	Urban	Urban in Alp valley environment	Traffic
Polyols	33.2 ± 33.5	34.6 ± 45.4	28.1 ± 28.4	38.7 ± 35.1	24.7 ± 25.0
Glucose	20.4 ± 15.6	21.5 ± 26.8	17.1 ± 16.8	24.2±18.4	13.6 ± 12.6
Polyols-to-OM (%)	0.59 ± 0.69	0.95 ± 0.93	0.52 ± 0.55	0.65 ± 0.75	0.37 ± 0.36

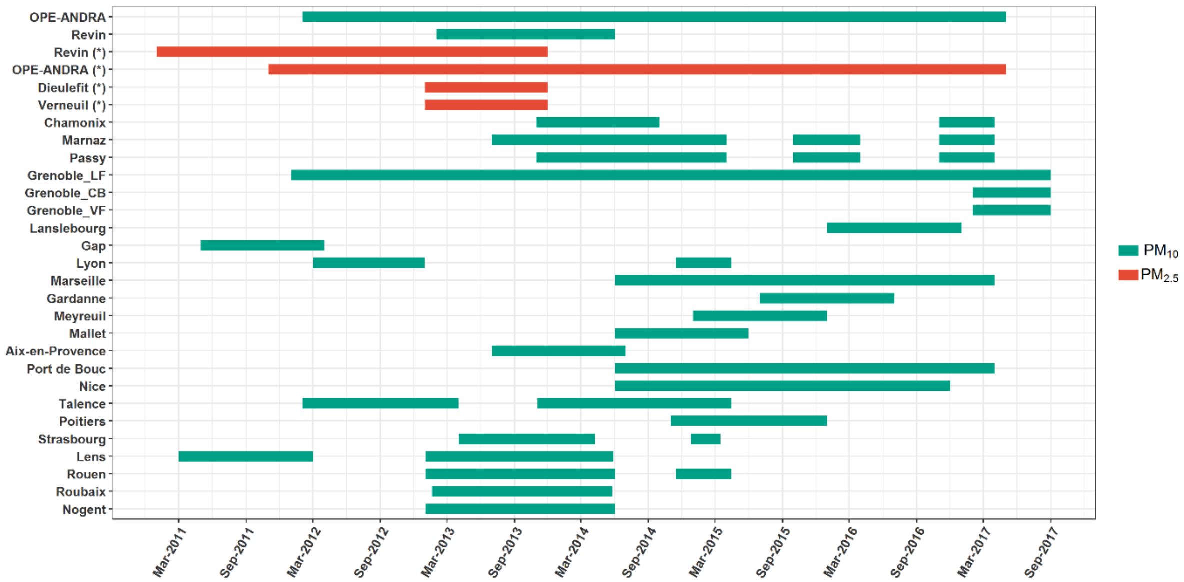

Figure SI-1: Timeline of Particulate matter (PM) sampling campaign periods for each studied site.

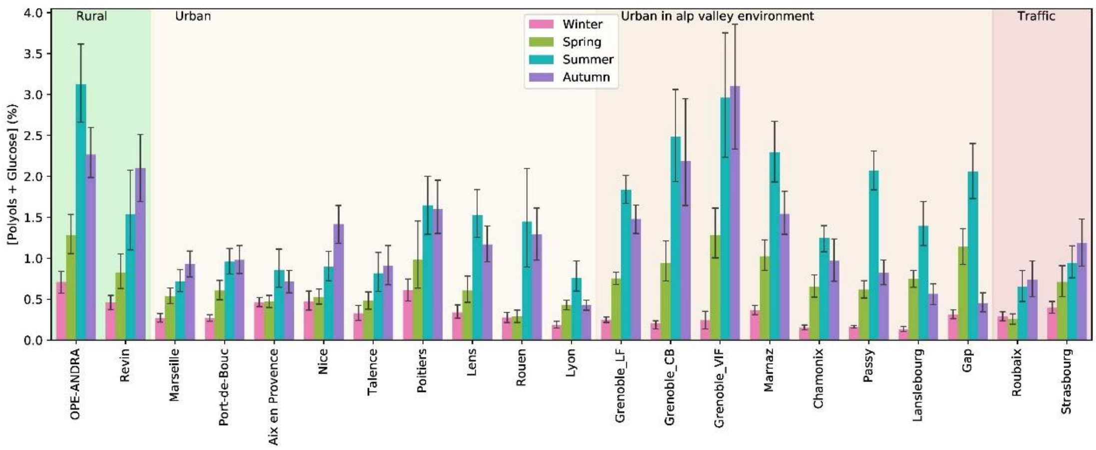

Figure SI-2: Spatial and seasonal average contributions of the sum of dominant polyols (arabitol + mannitol) and glucose to total organic (OM) aerosols at various sites in France.

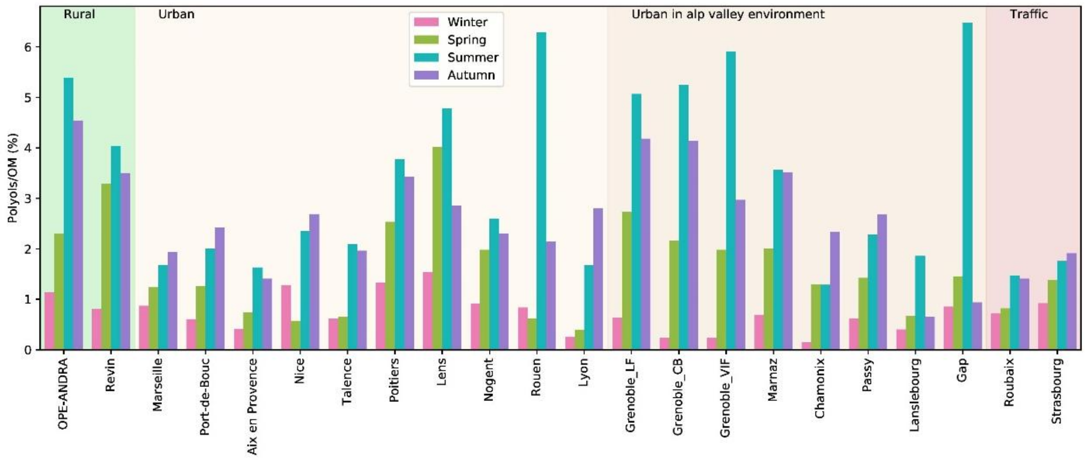

Figure SI-3 : Maximum seasonal contributions of dominant polyols to total organic aerosols (OM) at various sites in France.

Description of the Positive Matrix Factorization (PMF) analyses

PMF model

The PMF (Positive Matrix Factorization) is an algorithm that solves the following equation:

$$X = G \times F + E$$

In the field of atmospheric science, if the X matrix is the concentration of species at a given receptor-site, the G matrix may be interpreted as the contribution of a "source" factor, and the F matrix the chemical profile of this factor. In this study, we use the EPA PMF5 software to solve the PMF problem (US EPA, 2015). We also use the ability of the ME-2 algorithm to add constraints in the selected base solution.

Input matrices

Table SI-3 summarizes the different species used as input in the PMF runs. The uncertainties are given thanks to Gianini et al. (2012):

$$\Upsilon = \sqrt{(x \times CV)^2 + (DL)^2 + (x \times a)^2}$$

Where x is the concentrations of species, CV the coefficient of variation, DL is the detection limit and a is a factor accounting for additional sources of errors. OC* refer to the OC mass minus the carbon mass of the organic species considered in the PMF matrix (namely MSA, polyols, levoglucosan, mannosan, hopanes, methoxyphenol). The variables with a weak signal-to-noise ratio ($0.2 < S/N < 2$) were downweighed (3 times their uncertainties) and the ones with $S/N < 0.2$ were discarded. Values lower than the detection limit (DL) were set to DL/2 with uncertainties equal to 5/6 × DL.

Table SI-3 : Input chemical species and uncertainties in the PMF run.

	Carbonaceous	Water-soluble ions	Organic markers	Metals
Species	OC*, EC^s, BC_{wb}^d, BC_{ff}^d	MSA, Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, K^+, Mg^{2+}, Ca^{2+}	Polyols, Levoglucosan, $Mannosan^s$, $Methoxyphenol^d$, $Hopanes^d$	Al^s, As, Ba^s, Cd, Co, Cr^s, Cs^s, Cu, Fe, La^s, Mn, Mo, Ni, Pb, Rb, Sb, Se^s, Sn^s, Sr, Ti, V^s, Zr^s, Zn
Uncertainties	Gianini, et al. (2012)			
factor "a"	0.03	0.05	0.01	0.15

^{s}*: only in the SOURCES research program,*
^{d}*: only in the DECOMBIO research program.*

Set of constraints

The specific set of constraints is given in the following Table SI-4:

Table SI-4: Summary of the applied specific chemical constraints on source-specific tracers in the PMF factor profiles.

Factor profile	Element	Type	Value
Biomass burning	Levoglucosan	Pull up maximally	(% dQ 0.50)
Biomass burning	Mannosan	Pull up maximally	(% dQ 0.50)
Road traffic	Levoglucosan	Set to 0	0
Road traffic	Mannosan	Set to 0	0
Primary biogenic	Levoglucosan	Set to 0	0
Primary biogenic	Mannosan	Set to 0	0
Primary biogenic	Polyols	Pull up maximally	(% dQ 0.50)
Primary biogenic	EC	Pull down maximally	(% dQ 0.50)
Secondary biogenic	Levoglucosan	Set to 0	0
Secondary biogenic	Mannosan	Set to 0	0
Secondary biogenic	Polyols	Pull down maximally	(% dQ 0.50)
Secondary biogenic	MSA	Pull up maximally	(% dQ 0.50)
Secondary biogenic	EC	Pull down maximally	(% dQ 0.50)
HFO combustion	Levoglucosan	Set to 0	0
HFO combustion	Mannosan	Set to 0	0
HFO combustion	Polyols	Set to 0	0
HFO combustion	MSA	Set to 0	0
Sea-salt	Mg^{2+}/Na^{+}	Set to Value	0.119 (% dQ 0.50)

Selection of the solutions

The PMF runs for the DECOMBIO and SOURCES projects were performed in the following manner:

- a base run with geochemical factor link to specific sources;
- a base validation thanks to bootstrapping the solution with bootstrap mapping > 70%;

- a constrained run with specific constraints on species tracers of sources;
- and finally, a constrained bootstrapping and displacement validation.

Only the solutions obtained from constrained runs are presented in this study.

The criteria for a valid solution were the recommendations of the Joint Research Community (JRC) report (Belis et al., 2014):

- Q_{true}/Q_{robust} <1.5. In this study, the ratio is close to 1 (no outliers issue),
- weighted residual are normal and between ±4,
- evaluation of geochemical meaning of the factors,
- error monitored thanks to bootstrap and displacement.

Overview of source contributions

The source identification was done thanks to specific marker of emission sources, summarized in Table SI-5 and their respective relative contribution in Fig. SI-4. Briefly, we observed common sources all over the regional territory, namely the biomass burning, the road traffic, the sulfate and nitrate rich, the primary biogenic and secondary biogenic factors. We also found local sources such as Industrial at specific sites. Overall, we clearly identified the large influence of biomass burning and road traffic sources as well as the nitrate and sulfate rich factor on a yearly mean contribution. We also noted the presence of the primary biogenic source at each site, with varying proportions (see the main text for detailed discussion).

Table SI-5: Characteristic marker species for identifying PMF factors.

Identified factors	Specific markers
Biomass burning	Levoglucosan, mannosan, K^+, OC, EC
Road traffic	EC, OC, Ba, Cr, Co, Cu, Fe, Mo, Pb, Sb, Sn, Zn
Nitrate rich	NO_3^-, NH_4^+
Sulfate rich	SO_4^{2-}, NH_4^+, Se, OC
Primary biogenic	Polyols
Secondary biogenic	MSA
Dust	Ca^{2+}, Al, Ba, Co, Cu, Fe, Mn, Pb, Sr, Ti, Zn
Salt	Na^+, Mg^{2+}, Ca^{2+}, Cl^-
Aged salt	Na^+, Mg^{2+}, NO_3^-, SO_4^{2-}
Industrial	As, Cd, Cr, Cs, Co, Ni, Pb, Rb, Se, V, Zn
Heavy fuel oil (HFO)	V, Ni, SO_4^{2-}, EC

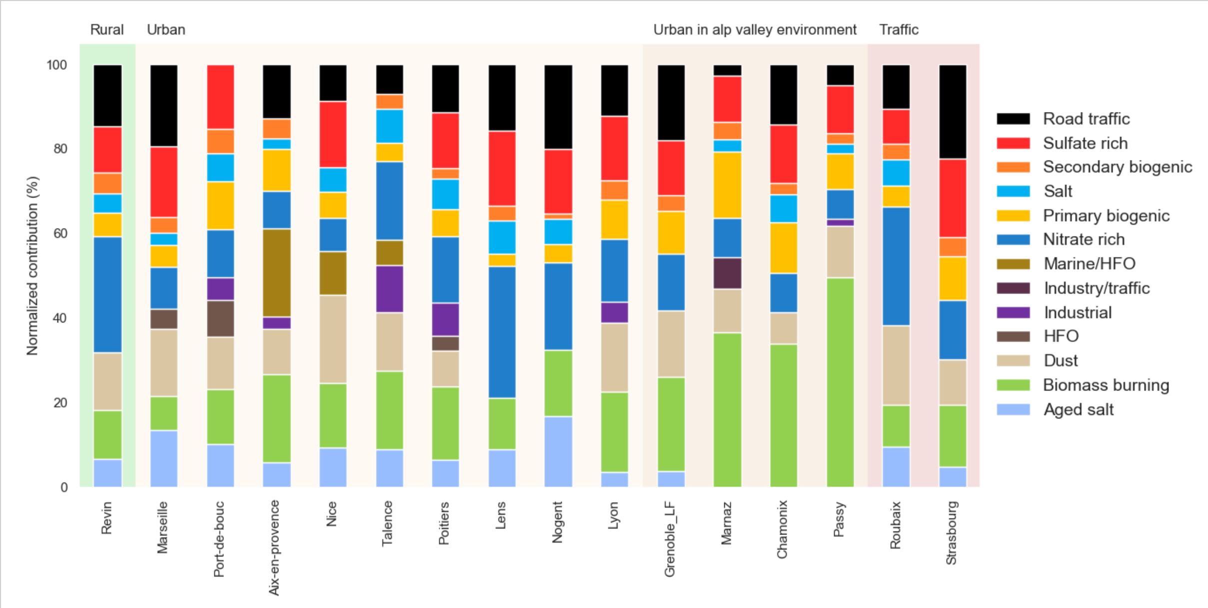

Figure SI-4: Normalized contributions of the different sources to the PM mass found in the DECOMBIO and SOURCES research program for the annual sampling period (HFO: heavy fuel oil).

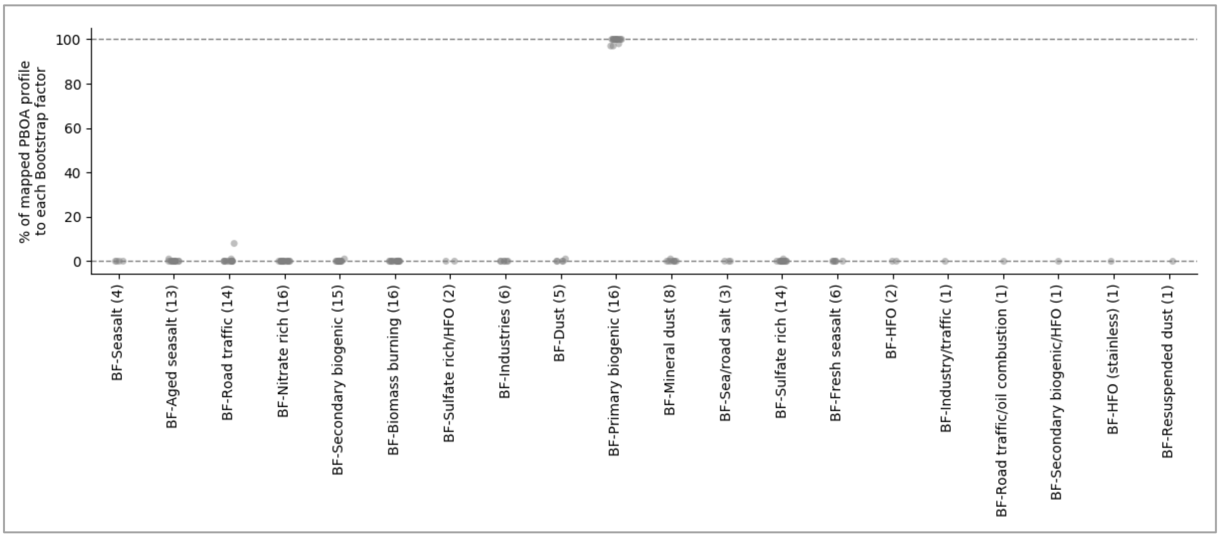

Figure SI-5: Mapping of the PBOA factor in the 16 PMF runs, according to bootstrap analysis (n=100 resampled runs). The number in parenthesis indicates the number of site where this factor was identified. BF stands for "Bootstrap factor".

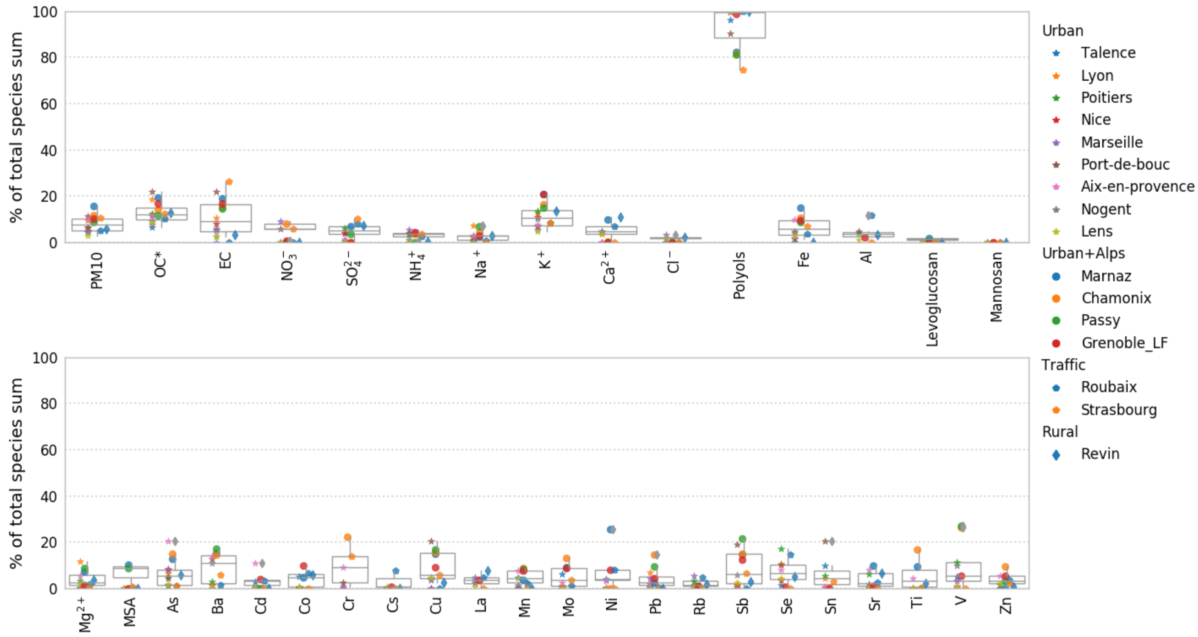

Figure SI-6: Percentage of each species apportioned by the PBOA profile from PMF studies. Values lower than a few pg µg^{-1} are not displayed on purpose. For each boxplot, the top, middle and bottom lines of the box represent the 75th, median and 25th percentile, respectively. The whiskers at the top and bottom of the box extend from the maximum to the minimum.

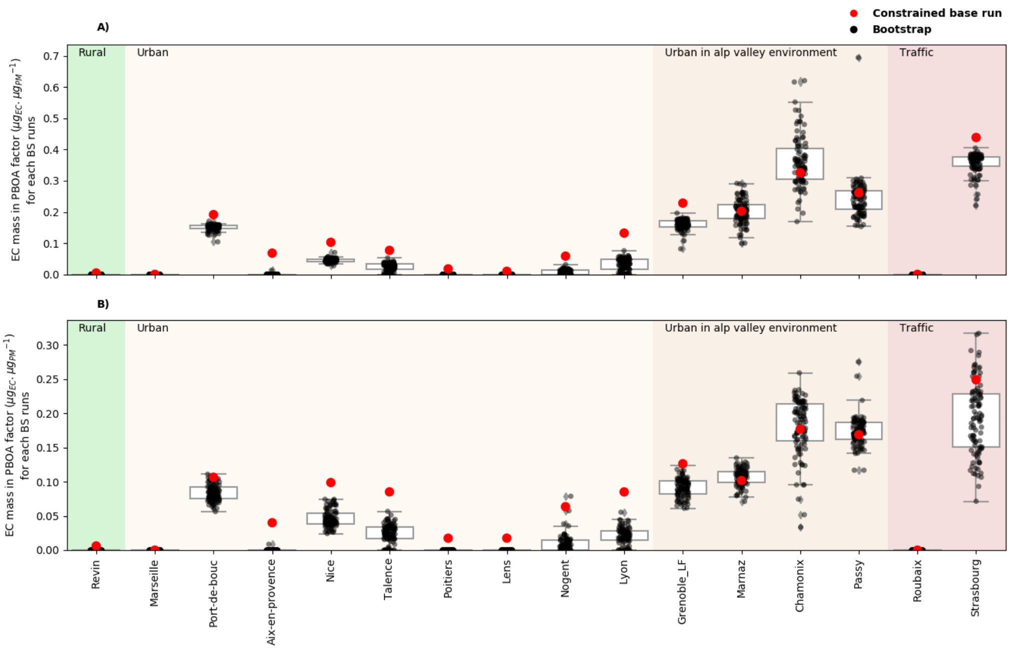

Figure SI-7: Constrained base run value and variability of EC apportioned by the PBOA factor, thanks to bootstrap analysis (n=100 resampled runs). The BS stands for "Bootstrap solution". (A) Yearly average of EC mass apportioned by the PBOA ($\mu g_{EC}.m^{-3}$) and (B) mass-contribution of EC to PBOA mass ($\mu g_{EC}.\ \mu g_{PM}^{-1}$).

Table SI-6: PBOA average factor profile (in fraction of PM mass) identified in the DECOMBIO and SOURCES programs.

Chemical species	Mean (ng µg^{-1})	Standard deviation (ng µg^{-1})
OC*	394	51
EC	81	68
Cl^-	3.9	6.8
NO_3^-	22	49
SO_4^{2-}	55	61
Na^+	4.6	5.2
$NH4^+$	13	14
K^+	9.5	3.2
Mg^{2+}	0.75	0.86
Ca^{2+}	5.6	6.3
MSA	0.12	0.32
Polyols	25	10
Levoglucosan	0.5	1.5
Mannosan	0	0
Fe	9.0	6.2
Al	3.1	2.5
	(pg µg^{-1})	(pg µg^{-1})
As	21	19
Ba	209	153
Cd	1.8	3.2
Co	3.2	4.7
Cr	107	182
Cs	0.6	1.5
Cu	351	298
La	5.4	4.8
Mn	115	130
Mo	11	11
Ni	31	57
Pb	75	80
Rb	7	10
Sb	29	26
Se	45	54
Sn	43	45
Sr	31	36
Ti	64	111
V	32	33
Zn	333	484

OC corresponds to the bulk organic carbon fraction minus the carbon in the characterized organic species.*

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