Long range and local air pollution: what can we learn from chemical speciation of particulate matter at paired sites?

Marco Pandolfi [a,*], Dennis Mooibroek [b], Philip Hopke [c], Dominik van Pinxteren [d], Xavier Querol [a], Herrmann Hartmut [d], Andrés Alastuey [a], Olivier Favez [e], Christoph Hüglin [f], Esperanza Perdrix [g], Véronique Riffault [g], Stéphane Sauvage [g], Eric van der Swaluw [b], Oksana Tarasova [h], and Augustin Colette [e]

[a] Institute of Environmental Analysis and Water Research (IDAEA-CSIC), c/ Jordi-Girona 18-26, Barcelona, Spain

[b] Centre for Environmental Monitoring, National Institute of Public Health and the Environment (RIVM), A. van Leeuwenhoeklaan 9, P.O. Box 1, 3720 BA, Bilthoven, The Netherlands

[c] Center for Air Resources Engineering and Science, Clarkson University, Potsdam, NY, USA

[d] Leibniz Institute for Tropospheric Research (TROPOS), Atmospheric Chemistry Department (ACD), Permoserstr. 15, 04318 Leipzig, Germany

[e] National Institute for Industrial Environment and Risks (INERIS), Verneuil-en-Halatte, 60550, France

[f] Empa, Swiss Federal Laboratories for Materials Science and Technology, 8600 Dübendorf, Switzerland

[g] IMT Lille Douai, Univ. Lille, SAGE – Département Sciences de l'Atmosphère et Génie de l'Environnement, 59000 Lille, France

[h] World Meteorological Organization, Research Department, Geneva, Switzerland

* Corresponding author: Marco Pandolfi (marco.pandolfi@idaea.csic.es)

Table S1: Chemical PM_{10} data sampled at Barcelona (BCN; UB), Montseny (MSY; RB) and Montsec (MSA; CB) (Spain) and used in the PMF model (2010 – 2014). Specie concentrations are reported in $\mu g/m^3$.

Chemical specie	**BCN**			**MSY**			**MSA**			
[$\mu g/m^3$]	mean	SD	median	mean	SD	median	mean	SD	median	
PM_{10}	24.5719	10.1681	23.0796	16.3678	9.2712	15.0258	9.3843	7.8660	7.4151	
Al	0.2611	0.2306	0.1880	0.2773	0.5118	0.1441	0.2493	0.5356	0.1176	
Ca	0.6699	0.4680	0.5431	0.2887	0.3444	0.1937	0.3517	0.4216	0.2049	
K	0.2129	0.1471	0.1915	0.1420	0.1432	0.1060	0.1105	0.1508	0.0863	
Na	0.7847	0.6495	0.6153	0.3048	0.2704	0.2162	0.1711	0.1729	0.1143	
Mg	0.1661	0.0999	0.1389	0.1013	0.1163	0.0724	0.0760	0.1149	0.0476	
Fe	0.5097	0.2823	0.4394	0.2052	0.3401	0.1022	0.1368	0.2874	0.0671	
Mn	0.0101	0.0061	0.0088	0.0040	0.0044	0.0029	0.0041	0.0058	0.0026	
Ti	0.0183	0.0135	0.0148	0.0149	0.0267	0.0076	0.0148	0.0342	0.0066	
V	0.0056	0.0043	0.0046	0.0020	0.0018	0.0015	0.0012	0.0015	0.0007	
Ni	0.0027	0.0023	0.0021	0.0012	0.0015	0.0009	0.0006	0.0011	0.0004	
Cu	0.0189	0.0119	0.0163	0.0029	0.0018	0.0026	0.0011	0.0010	0.0009	
As	0.0004	0.0002	0.0004	0.0002	0.0001	0.0002	0.0001	0.0001	0.0001	
Rb	0.0005	0.0003	0.0004	0.0004	0.0005	0.0002	0.0003	0.0006	0.0002	
Sr	0.0024	0.0020	0.0020	0.0013	0.0021	0.0008	0.0016	0.0025	0.0009	
Sb	0.0024	0.0016	0.0020	0.0003	0.0002	0.0003	0.0001	0.0002	0.0000	
Pb	0.0083	0.0114	0.0061	0.0023	0.0019	0.0020	0.0012	0.0009	0.0009	
SO_4^{2-}	2.6322	1.6846	2.2756	1.8946	1.4842	1.6141	1.3343	1.1454	1.0266	
NO_3^-	2.4192	2.1829	1.7304	1.0455	1.0382	0.7587	0.7540	0.8747	0.4910	
Cl^-	0.6844	0.7647	0.4260	0.2488	0.2979	0.1662	0.1382	0.1762	0.1022	
NH_4^+	0.7736	0.8742	0.4737	0.4976	0.4713	0.3674	0.4482	0.4605	0.2983	
EC	1.1545	0.6589	1.0129	0.2318	0.1291	0.2089	0.1071	0.0811	0.0930	
OC	2.9088	1.4308	2.6011	1.8983	0.8589	1.7894	1.5188	0.8708	1.4112	

Table S2: Chemical PM_{10} data sampled at Zurich (ZUE; UB) and Payerne (PAY; RB) (Switzerland) and used in the PMF model (2008-2009). Specie concentrations are reported in $\mu g/m^3$.

Chemical specie	ZUE			PAY			
[$\mu g/m^3$]	mean	SD	median	mean	SD	median	
PM_{10}	20.41303	11.52026	15.77000	18.45809	11.84675	14.90000	
OC	3.70135	2.14696	3.09000	3.51303	2.23133	3.10000	
EC	1.26427	0.74653	1.06000	0.66292	0.46896	0.55000	
NO_3^-	3.78748	4.30968	1.98800	3.80962	4.64906	1.77700	
SO_4^{2-}	2.36776	1.53784	1.99100	1.91618	1.27660	1.68200	
Na^+	0.15094	0.16235	0.10100	0.12454	0.12452	0.09200	
NH_4^+	1.61817	1.54775	1.06000	1.57806	1.58461	0.92600	
K^+	0.20227	0.19533	0.12400	0.17213	0.16706	0.11100	
Mg_2^+	0.02904	0.02118	0.02400	0.02048	0.01686	0.01800	
Ca_2^+	0.31661	0.28609	0.19600	0.17528	0.13329	0.13800	
Al	0.07053	0.06501	0.04381	0.06521	0.06854	0.04636	
Ti	0.00195	0.00133	0.00158	0.00171	0.00155	0.00124	
V	0.00067	0.00046	0.00058	0.00056	0.00052	0.00039	
Cr	0.00198	0.00161	0.00154	0.00066	0.00071	0.00048	
Mn	0.00537	0.00318	0.00445	0.00264	0.00165	0.00229	
Fe	0.46942	0.27748	0.41346	0.11914	0.07740	0.09687	
Cu	0.02069	0.01165	0.01809	0.00415	0.00272	0.00338	
Zn	0.02849	0.02162	0.02359	0.01958	0.01611	0.01735	
Ga	0.00016	0.00011	0.00012	0.00008	0.00007	0.00006	
As	0.00052	0.00106	0.00032	0.00050	0.00058	0.00037	
Rb	0.00049	0.00042	0.00035	0.00056	0.00040	0.00051	
Sr	0.00076	0.00062	0.00054	0.00051	0.00048	0.00037	
Y	0.00004	0.00003	0.00003	0.00003	0.00003	0.00002	
Mo	0.00116	0.00070	0.00099	0.00024	0.00017	0.00022	
Cd	0.00012	0.00008	0.00010	0.00009	0.00007	0.00007	
Sb	0.00225	0.00129	0.00192	0.00059	0.00040	0.00053	
Ba	0.00370	0.00228	0.00310	0.00162	0.00188	0.00116	
La	0.00008	0.00005	0.00007	0.00005	0.00005	0.00004	
Ce	0.00014	0.00008	0.00013	0.00008	0.00007	0.00006	
Nd	0.00004	0.00003	0.00003	0.00003	0.00003	0.00002	
Pb	0.00533	0.00387	0.00396	0.00383	0.00311	0.00298	

Table S3: Chemical $PM_{2.5}$ data sampled at Schiedam (SCH; UB) and Hellendoorn (HEL; RB) (The Netherlands) and used in the PMF model (2007-2008). The concentration of major elements is reported in mg/m^3 and the concentration of trace elements in ng/m^3.

Chemical specie	SCH		HEL	
[μg/m^3]	mean	SD	mean	SD
$PM_{2.5}$	17.2	11.6	14.0	6.9
OC	2.1	1.1	2.0	0.8
EC	2.2	1.6	1.7	1.1
NH_4^+	1.2	1.5	1.6	1.4
NO_3^-	2.8	3.4	3.7	3.1
SO_4^{2-}	2.6	1.4	2.6	1.8
Cl	0.3	0.3	0.3	0.3
[ng/m^3]				
Al	61.9	131.7	35.6	74.3
As	0.7	0.6	0.4	0.4
Ba	11.0	56.3	5.5	16.5
Ca	87.5	76.8	61.7	55.8
Cd	0.3	0.3	0.3	0.2
Co	0.3	0.2	0.2	0.1
Cr	2.9	1.3	2.7	1.2
Cu	5.5	9.9	2.5	3.3
Fe	115.9	117.5	71.5	76.5
K	134.2	529.5	84.0	124.7
Mg	64.9	86.9	44.6	33.0
Mn	4.0	3.4	2.6	2.3
Mo	0.6	0.4	0.5	0.4
Na	339.9	311.4	173.8	201.0
Ni	5.4	4.0	1.9	1.2
P	90.0	37.7	80.1	36.3
Pb	9.1	11.9	8.3	12.5
Sb	1.0	1.0	0.6	0.5
Se	2.7	5.8	0.8	0.6
Si	93.2	171.3	84.5	12.5
Sn	4.2	11.2	0.9	0.8
Sr	2.2	12.4	0.9	2.2
Ti	2.5	2.9	1.5	2.0
V	9.0	7.7	2.0	1.9
Zn	95.3	36.7	90.5	31.7

Table S4: Chemical PM_{10} data sampled at Lens (LENS; UB) and Revin (REV; UB) (France) and used in the PMF model (2013-2014). Specie concentrations are reported in $\mu g/m^3$.

Chemical specie	LENS			REV			
[$\mu g/m^3$]	mean	SD	median	mean	SD	median	
PM_{10}	20.5193	12.7126	16.0000	16.3038	9.6521	15.0000	
EC	0.6029	0.5851	0.4462	0.1742	0.0993	0.1537	
OC	3.2052	2.6364	2.5157	2.1603	1.2652	1.8912	
Cl -	0.7378	0.9006	0.3797	0.3037	0.5599	0.0777	
NO_3^-	5.0508	5.5206	2.5376	3.2520	4.0694	1.8593	
SO_4^{2-}	2.3309	2.2417	1.6347	2.0347	1.7630	1.5002	
Na^+	0.6213	0.5690	0.4616	0.3787	0.4537	0.2097	
NH_4^+	1.8741	2.1916	0.9945	1.2723	1.4603	0.7491	
K^+	0.1294	0.0982	0.1064	0.0503	0.0413	0.0399	
Mg^{2+}	0.0796	0.0640	0.0611	0.0408	0.0398	0.0278	
MSA	0.0728	0.0805	0.0503	0.0395	0.0508	0.0210	
Levoglucosan	0.1906	0.2729	0.0940	0.1003	0.0994	0.0719	
Polisac	0.0304	0.0684	0.0125	0.0117	0.0143	0.0061	
Alcohols	0.0239	0.0347	0.0116	0.0242	0.0305	0.0126	
Al	0.1566	0.2059	0.0993	0.1192	0.2519	0.0539	
Fe	0.2713	0.2757	0.1696	0.1675	0.1891	0.1108	
Ca	0.3682	0.4660	0.2266	0.2543	0.3906	0.1705	
As	0.0007	0.0008	0.0004	0.0007	0.0007	0.0004	
Cd	0.0002	0.0002	0.0002	0.0002	0.0003	0.0002	
Co	0.0002	0.0002	0.0001	0.0001	0.0001	0.0001	
Cu	0.0121	0.0167	0.0072	0.0045	0.0042	0.0032	
La	0.0002	0.0002	0.0001	0.0001	0.0001	0.0001	
Mn	0.0066	0.0060	0.0045	0.0061	0.0055	0.0042	
Pb	0.0087	0.0092	0.0056	0.0082	0.0061	0.0065	
Rb	0.0005	0.0005	0.0003	0.0005	0.0004	0.0003	
Sb	0.0012	0.0011	0.0009	0.0006	0.0004	0.0005	
Se	0.0011	0.0009	0.0007	0.0012	0.0010	0.0010	
Sr	0.0019	0.0019	0.0015	0.0014	0.0017	0.0011	
Ti	0.0102	0.0107	0.0069	0.0098	0.0121	0.0066	
Zn	0.0302	0.0374	0.0183	0.0363	0.0405	0.0246	

- **Source profiles from multi-site PMF for Spain.**

Figure S1 shows the chemical profiles of the sources detected at BCN, MSY and MSA from the multi-site PMF. A total of 7 common sources were identified at the three sites, namely:

- *Heavy-Oil combustion* (V-Ni), traced mainly by V, Ni and SO_4^{2-} and representing the direct emissions from heavy oil combustion sources, mostly shipping in the area under study during the period considered, but also long range transport. The sulfate associated with this source also includes primary sulfate from shipping (Ref.)

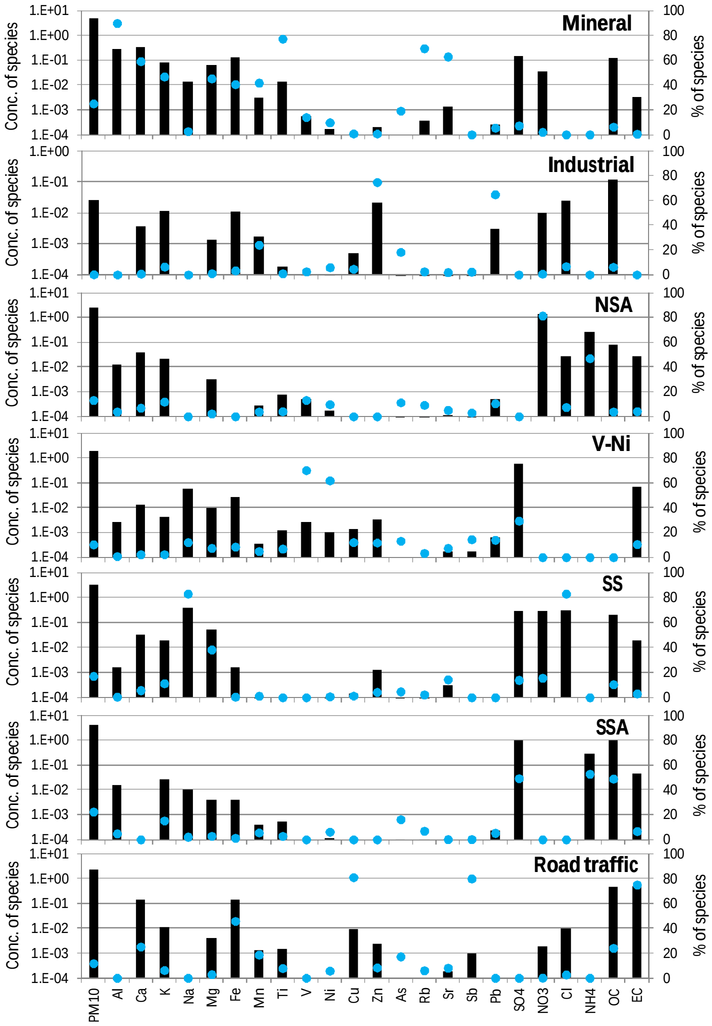

Figure S1: Chemical profiles of the sources detected at Barcelona (BCN; UB), Montseny (MSY; RB) and Montsec (MSA; CB) (Spain).

- *Mineral (MM),* traced by typical crustal elements such as Al, Ca, Ti, Rb, and Sr;
- *Sea salt (SS)*, traced by Na and Cl mainly with contributions from SO_4^{2-} and NO_3^- suggesting some aging of marine aerosols;
- *Secondary sulfate (SSA)*, secondary inorganic source traced by SO_4^{2-} and NH_4^+ with relatively high contents of OC which have been attributed to the condensation

of semi-volatile compounds on the high specific surface area of ammonium sulfate particles (Amato et al., 2009);

- *Primary Industrial (IND)*, traced by Pb and As representing mostly emissions from metallurgy;
- *Primary Road Traffic (RT)*, traced mainly by EC, OC, Cu, Sb and Fe;
- *Secondary nitrate (NSA)*, secondary inorganic source traced by NO_3^- and NH_4^+.

- **Source profiles from multi-site PMF for Switzerland.**

Figure S2 shows the chemical profiles of the sources from multi-site PMF for Switzerland. A total of 6 sources were identified at the two sites. A description of the sources is given below. The number and type of sources is the same as in Gianini et al. (2012):

- *Primary Road Traffic (RT)*, explaining large fractions of EC, OC and of the road traffic related elements (Mn, Cr, Fe, Cu, Mo, Sb);

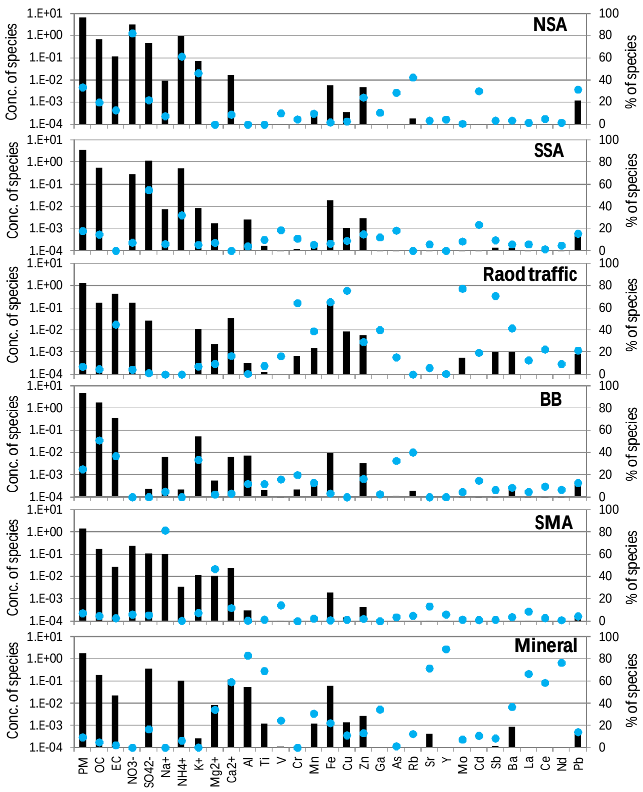

Figure S2: Chemical profiles of the sources detected at Zurich-Kaserne (ZUE; UB) and Payerne (PAY; RB).

- *Mineral (MM)*, dominated by Ca^{2+}, Fe, Al and Mg^{2+}, representing the main components of crustal matter. The mineral dust factors account moreover for a large mass fraction of crustal elements such as Ti, Sr, Y, La, Ce and Nd;
- *Na-Mg rich* (*SS*), contributing to high fractions of Na^+ and Mg^{2+}. The contributions of the *Na-Mg rich* factor did not show a clear annual cycle with elevated values during winter, thus suggesting a low contribution from the de-

icing road salt. This source was mostly related to the transport of sea spray aerosol particles (Gianini et al., 2012).

- *Secondary sulfate* (SSA), characterized by high concentrations of SO_4^{2-} and NH_4^+. Moreover, a relevant fraction of measured OC is also explained by the SSA factors; secondary OC is expected to be in receptor modelling studies largely associated with the secondary SO_4^{2-} because of similar temporal variation of these constituents of atmospheric PM (Kim et al., 2003). Relatively high contents of OC in secondary sulfate factors have been attributed to the condensation of semi-volatile compounds on the high specific surface area of ammonium sulfate (Amato et al., 2009);
- *Secondary nitrate* (*NSA*), secondary inorganic source traced by NO_3^- and NH_4^+;
- *Biomass burning* (*BB*), traced by high concentrations of OC, EC and K^+. This factor also explains a relevant mass fraction of Rb, an element related to biomass combustion emissions (Godoy et al., 2005);

- **Source profiles from multi-site PMF for France.**

Figure S3 shows the chemical profiles of the sources from multi-site PMF for France. A total of 9 sources were identified at the French paired sites. A description of the sources is given below.

- *Sea salt (SS)*, traced by Na^+ and Cl^- this source represents mainly fresh marine aerosols;
- *Land (or Primary) biogenic (LB)*, traced by alcohols (arabitol and mannitol);
- *Secondary sulfate* (*SSA*)*,* secondary inorganic aerosol traced by SO_4^{2-} and NH_4^+;
- *Primary Road traffic (RT)*, traced by EC, OC, Fe, Cu, Sb;
- *Biomass burning (BB)*, traced mostly by levoglucosan and polysaccharides;
- *Secondary nitrate (NSA),* secondary inorganic aerosol traced by NO_3^- and NH_4^+;
- *Marine aged,* representing aged sea salt. Lack of Cl^- in the chemical profiles and presence of Na^+ and NO_3^-;
- *Mineral (MM),* traced mainly by typical crustal elements such as Fe, Ca, Al, Sr and Ti;
- *Marine biogenic (MB),* traced mainly by methane sulphonic acid, a product of DMS oxidation.

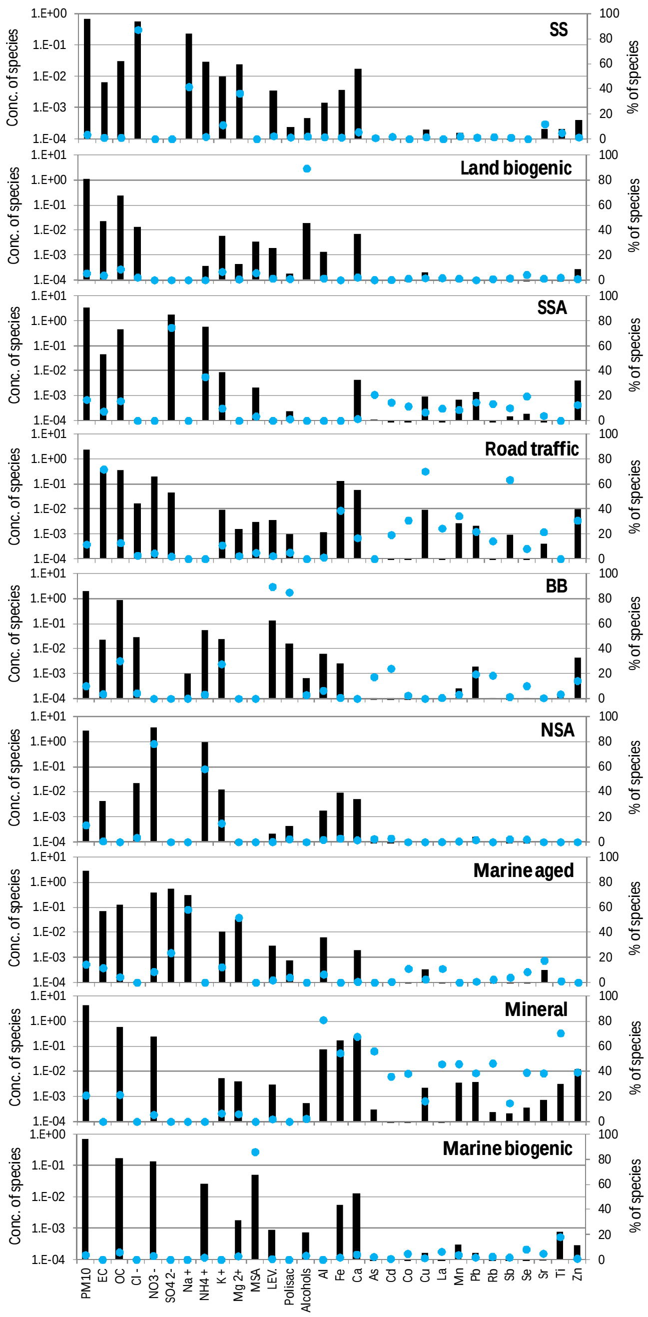

Figure S3: Chemical profiles of the sources detected at Lens (LENS; UB) and Revin (REV; RB).

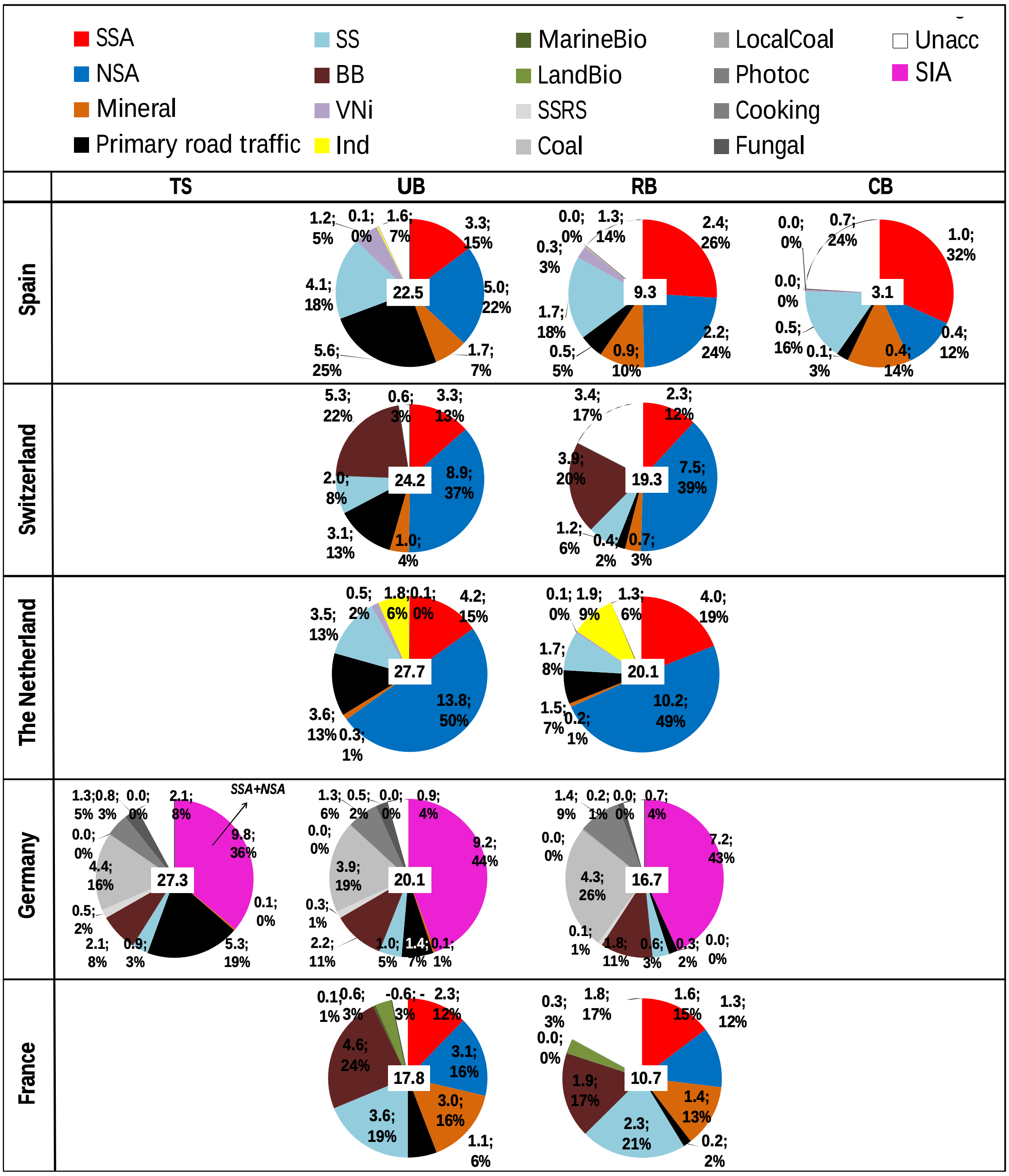

Figure S4: Source contributions to PM_{10} ($PM_{2.5}$ for The Netherlands) in winter (DJF) from the multi-site PMF for each country. The number in the white box at the center of the pie chart is the measured mass of PM (in $\mu g/m^3$). TS: traffic site; UB: urban background; RB: regional background; CB: continental background.

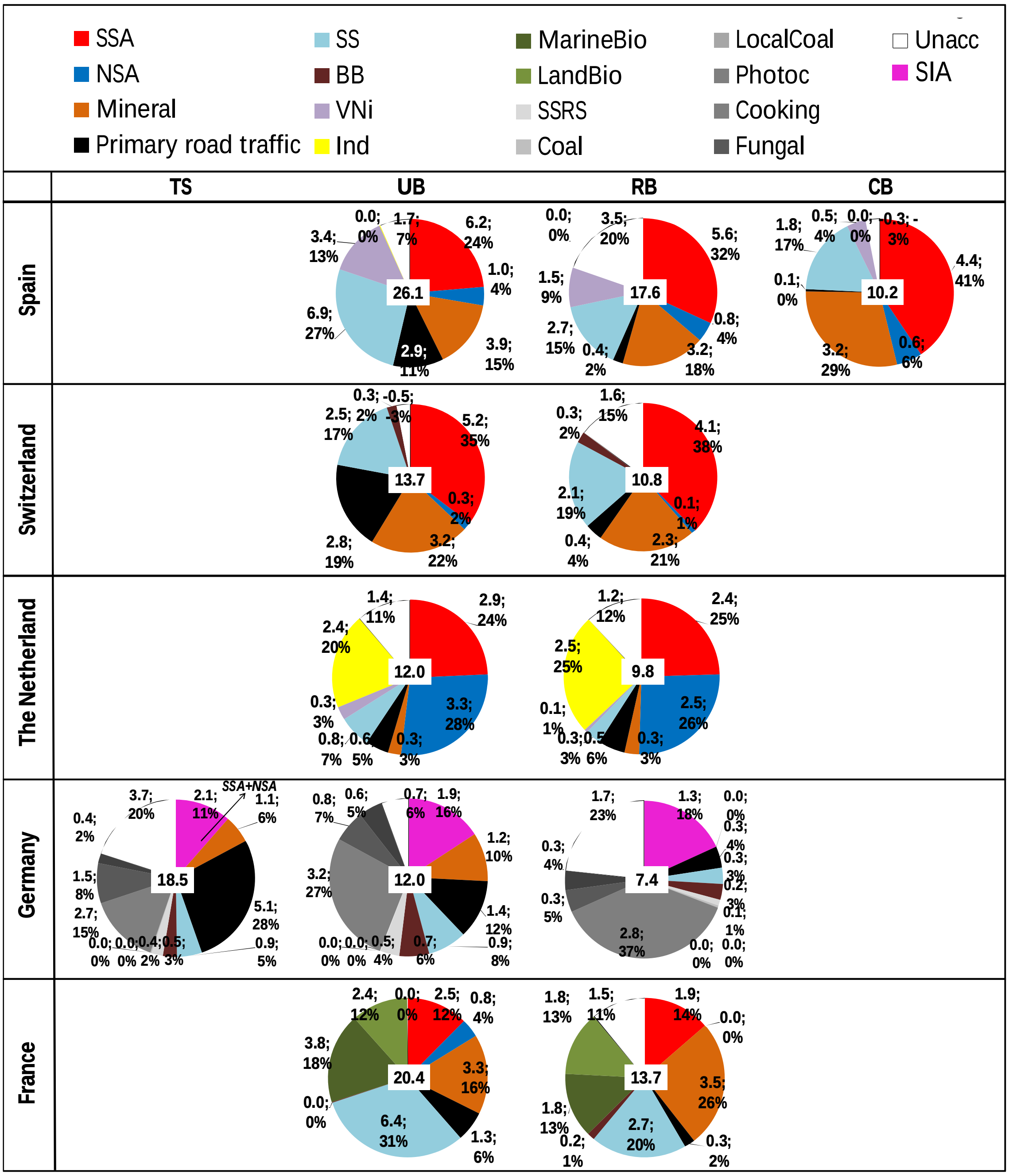

Figure S5: Source contributions to PM_{10} ($PM_{2.5}$ for The Netherlands) in summer (JJA) from the multi-site PMF for each country. The number in the white box at the center of the pie chart is the measured mass of PM (in $\mu g/m^3$). TS: traffic site; UB: urban background; RB: regional background; CB: continental background.

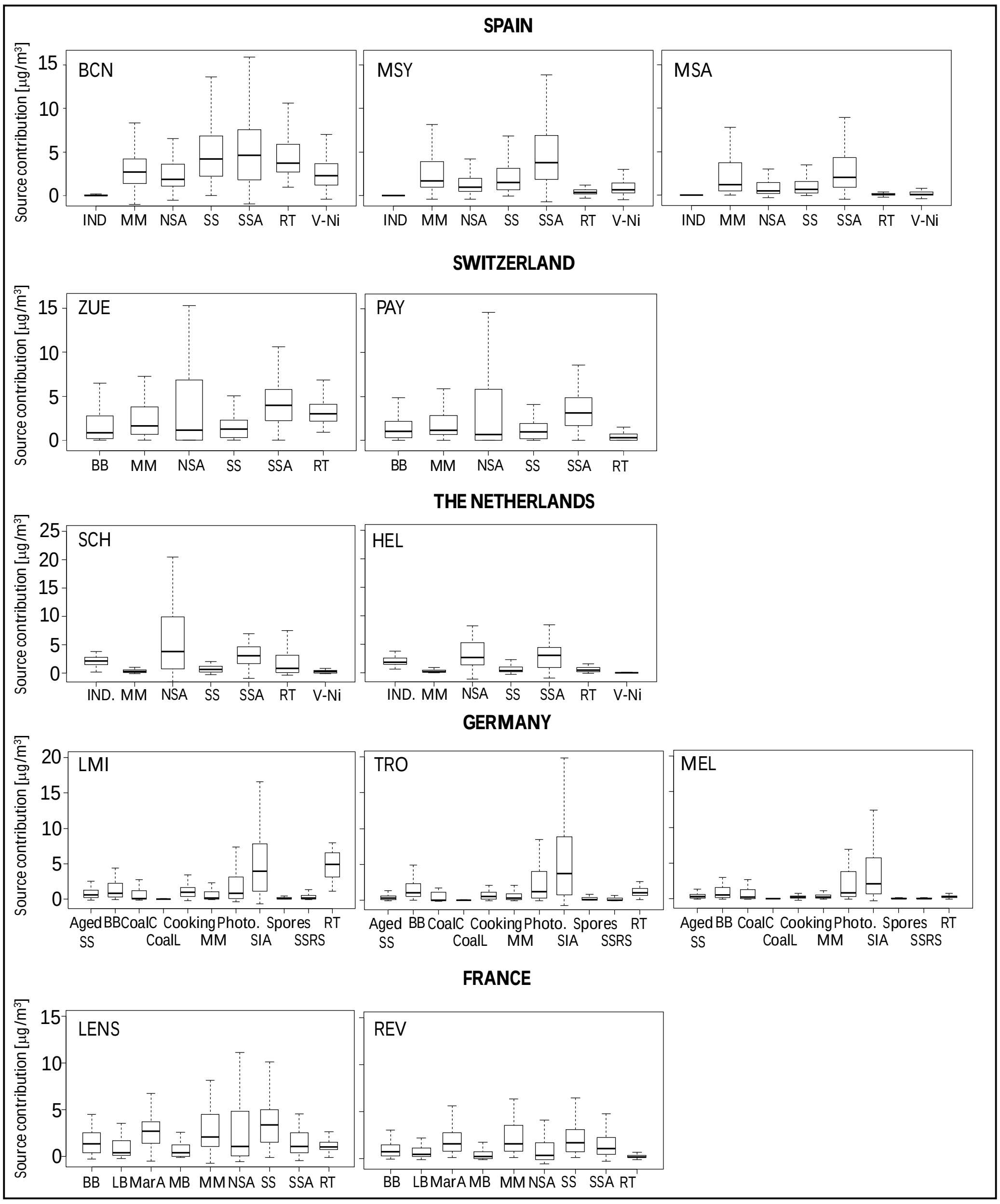

Figure S6: Mean annual source contributions to PM_{10} ($PM_{2.5}$ for The Netherlands) from the multi-site PMF for each site and country. IND: Industrial; MM: Mineral matter; NSA: nitrate-rich particles; SS: Sea Salt; SSA: sulfate-rich particles; RT: Road traffic; V-Ni: Residual oil combustion; BB: Biomass burning; Photo: Photochemistry; CoalL: Coal local; SIA: Secondary inorganic aerosols; SSRS: Sea salt/Road dust; LB: Land biogenic; Mar A: Marine aged; MB: Marine biogenic.

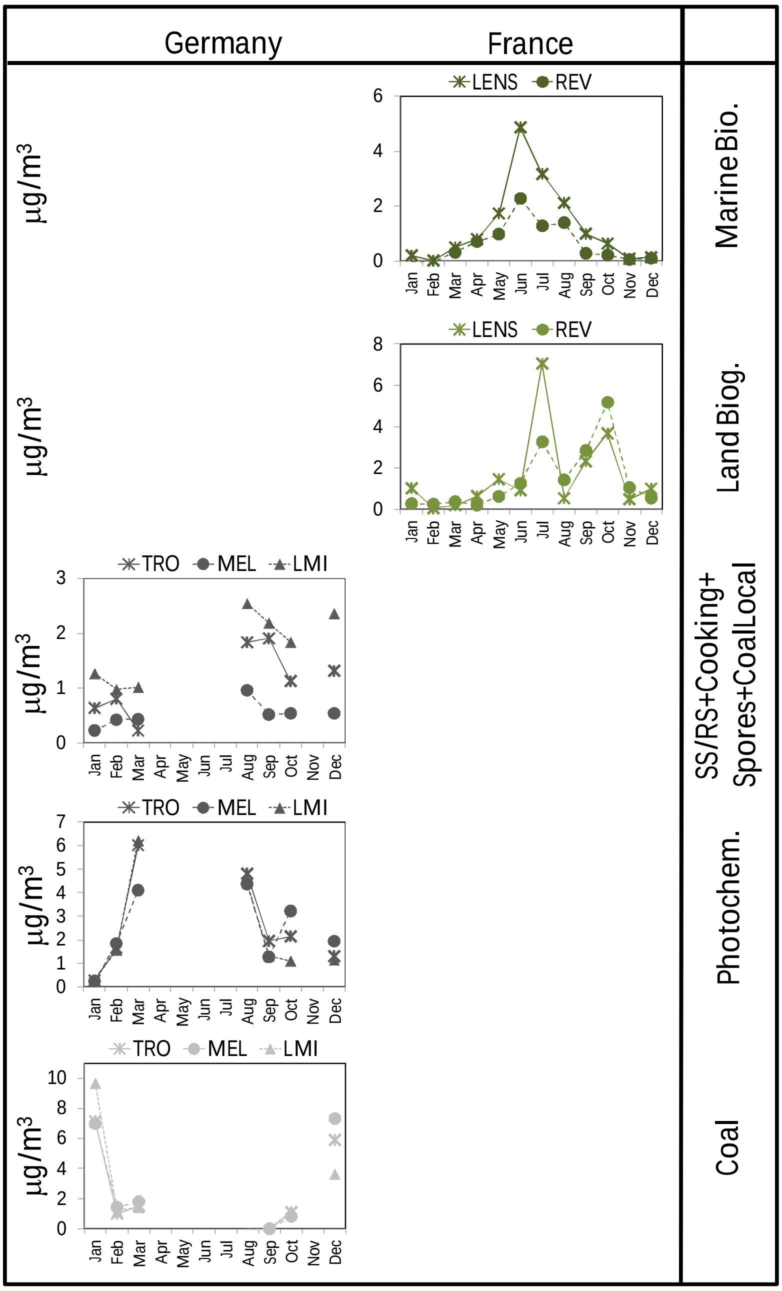

Figure S7: PMF source contributions for those sources only calculated at specific sites: France (*Marine biogenic* and *Land biogenic*); Germany (*SS/RS+cooking+fungal spores+coal local*, *photochemistry*, and *coal*).

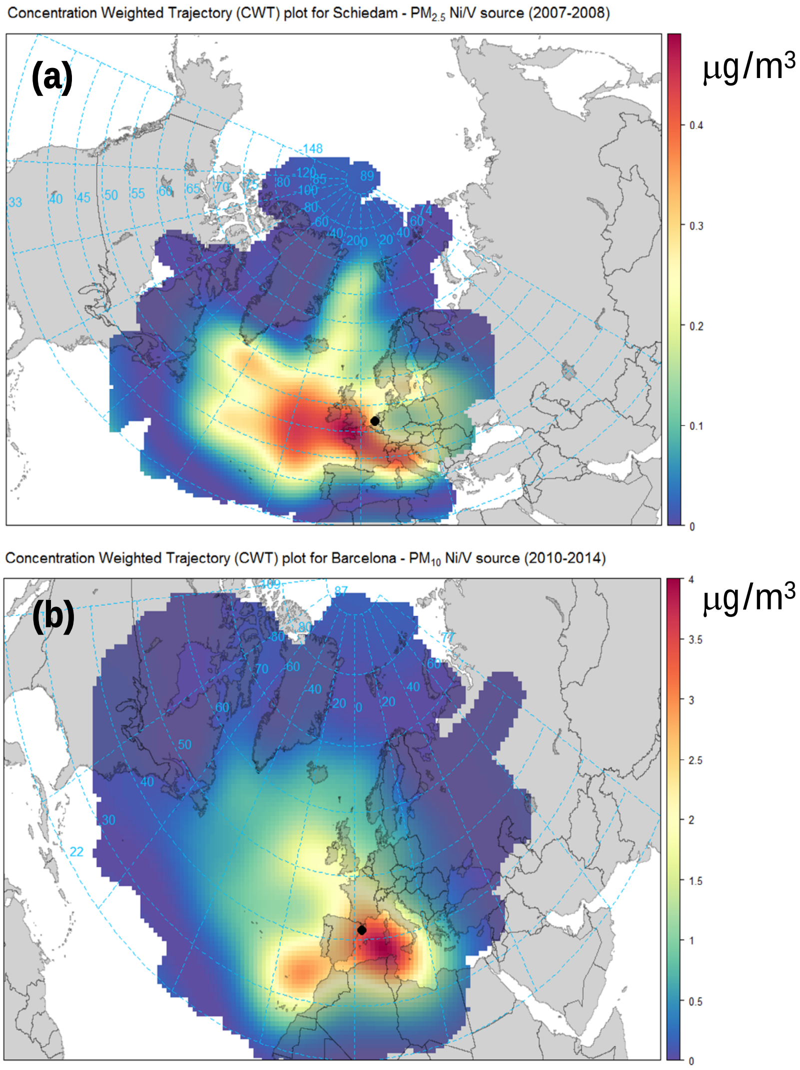

Figure S8: Concentration Weighted Trajectory (CWT) plots of the V-Ni source contributions for: (a) Schiedam (NL; $PM_{2.5}$; 2007-2008) and (b) Barcelona (ES; PM_{10}; 2010-2014).

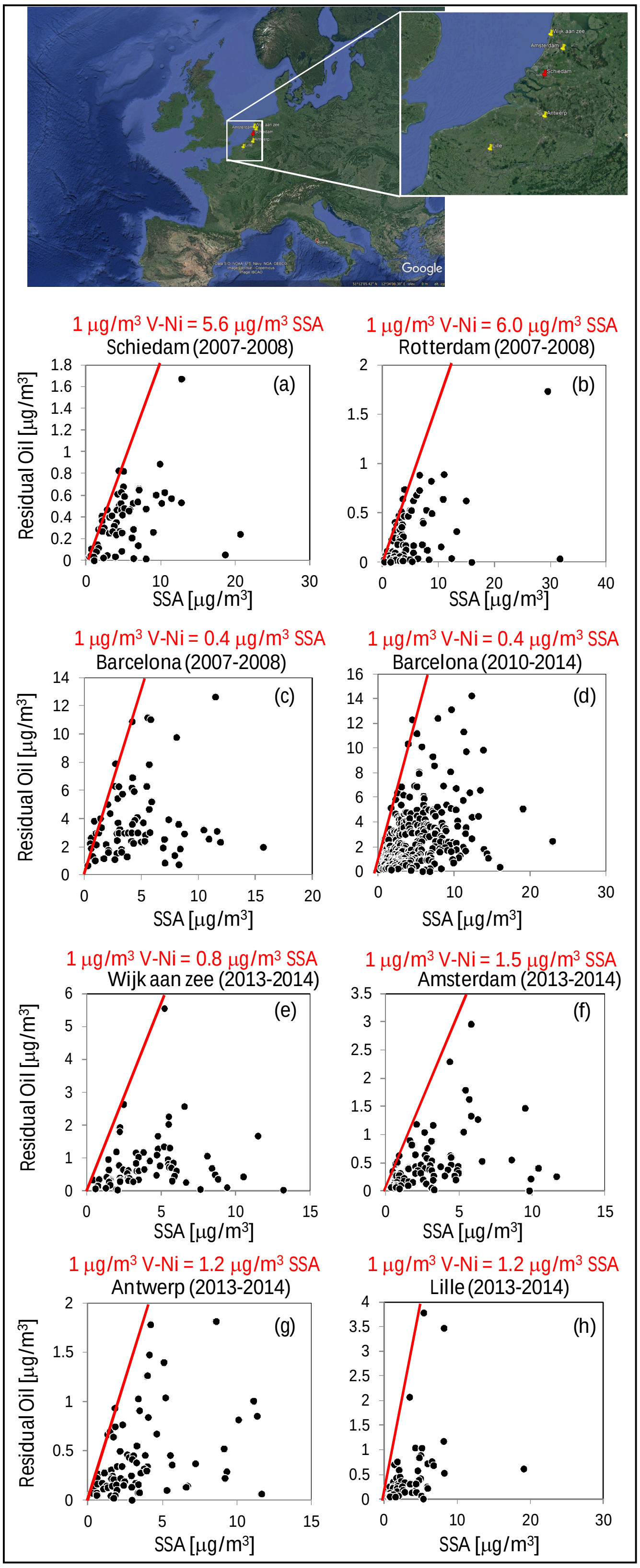

Figure S9: Contributions (µg/m³) of the V/Ni-bearing particles from shipping and SSA particles to PM at Schiedam (a), Rotterdam (b), Wijk aan zee (e), Amsterdam (f) in the Netherlands, Barcelona (c and d; Spain), Antwerp (g; Belgium) and Lille (h; France). The red lines represent the edges of the scatter plots.

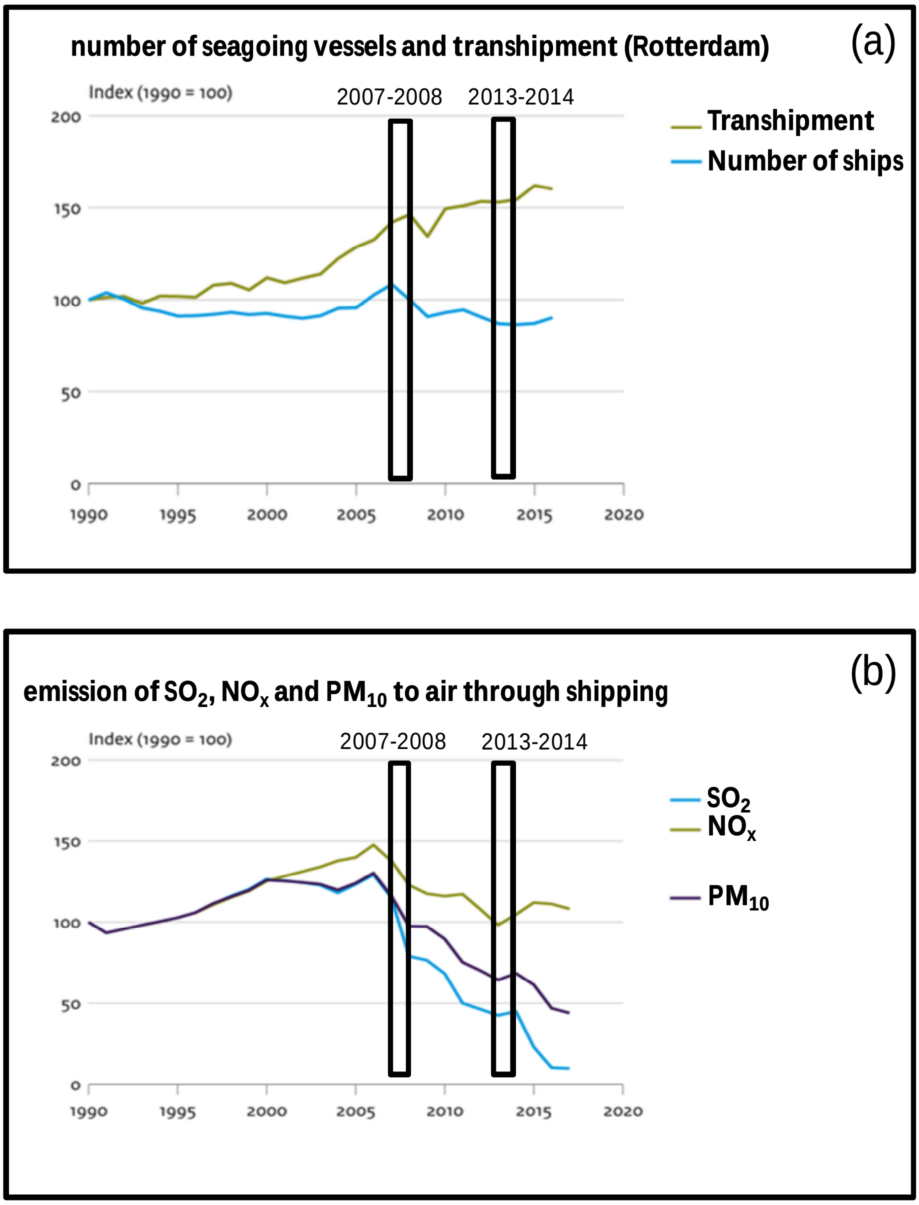

Figure S10: Number of seagoing vessels in Rotterdam (a), and emissions of SO_2, NO_x and PM_{10} through maritime shipping (b) from 1990 to 2017 (adapted from Environmental Data Compendium, Government of the Netherlands, https://www.clo.nl/en.)

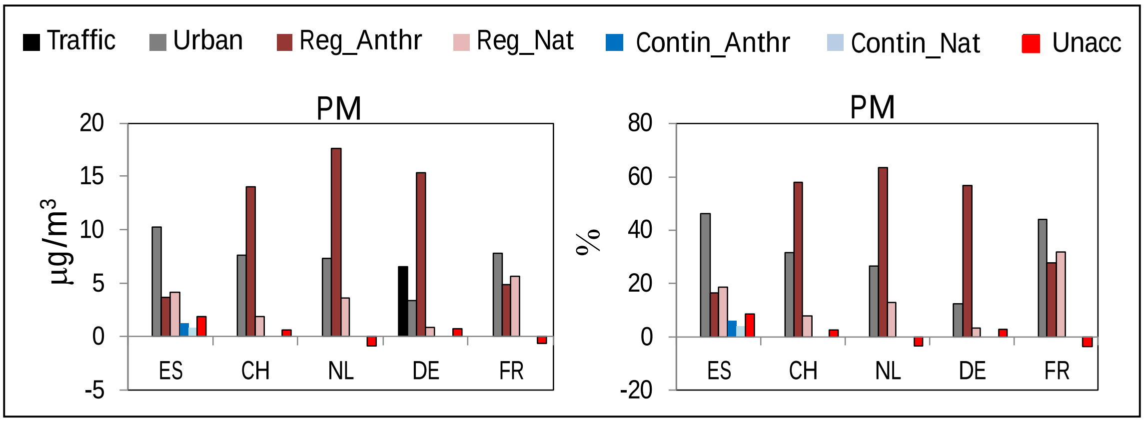

Figure S11: Lenschow's approach applied to the concentrations of PM. Average values for winter (DJF) are reported. ES: Spain; CH: Switzerland; NL: The Netherlands; DE: Germany; FR: France. In all countries with the exception of Spain, Reg_Anthr and Reg_Nat are the sum of regional+continental.

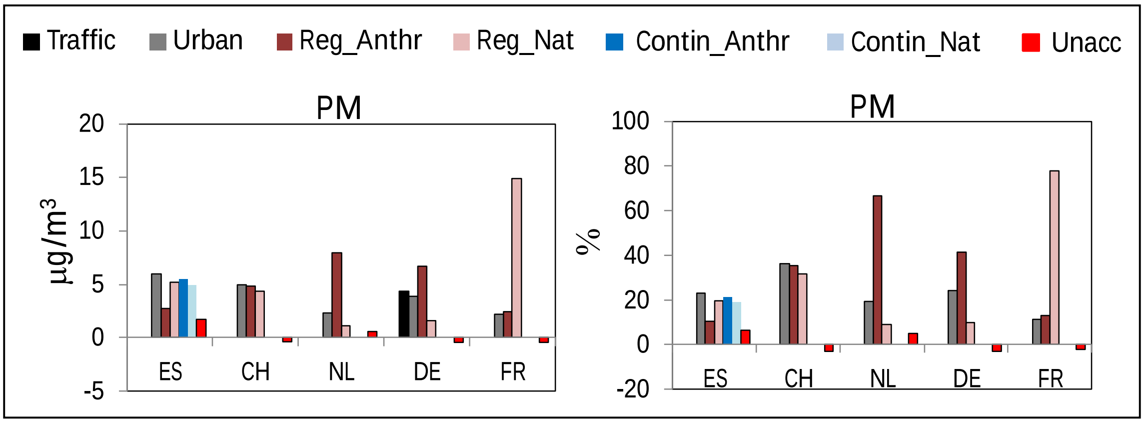

Figure S12: Lenschow's approach applied to the concentrations of PM. Average values for summer (JJA) are reported. ES: Spain; CH: Switzerland; NL: The Netherlands; DE: Germany; FR: France. In all countries with the exception of Spain, Reg_Anthr and Reg_Nat are the sum of regional+continental.

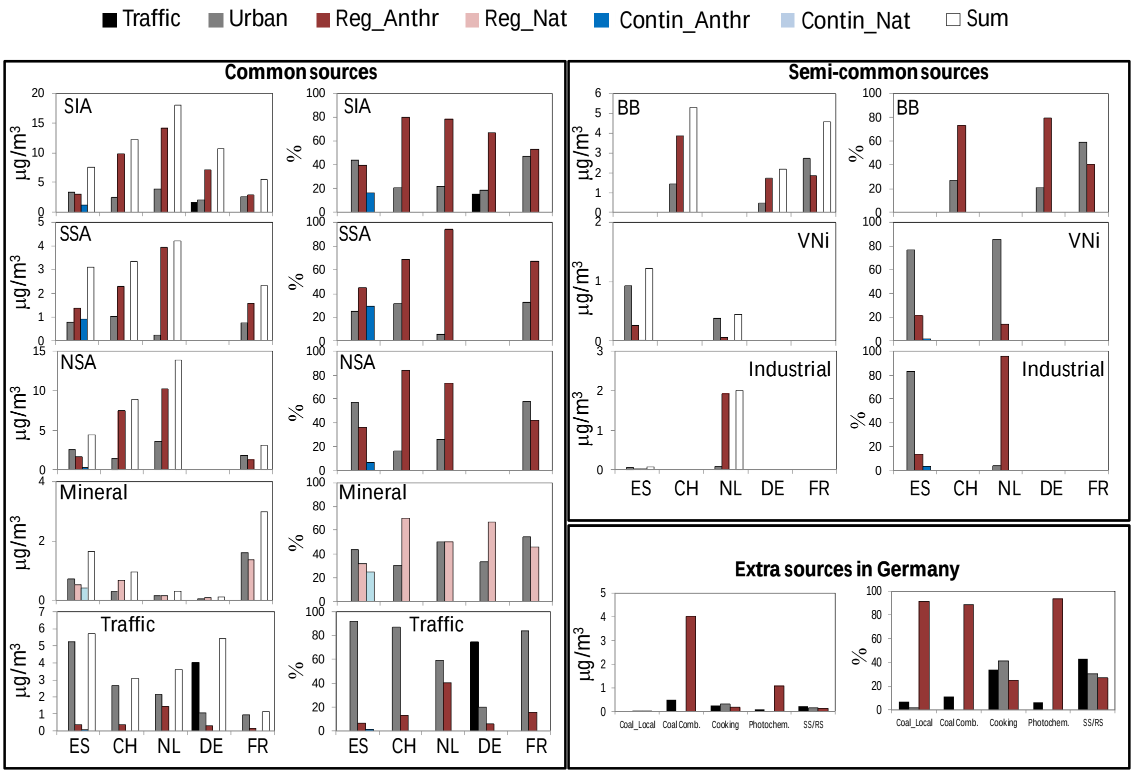

Figure S13: Lenschow's approach applied to the PMF source contributions. Average values for winter (DJF) are reported. ES: Spain; CH: Switzerland; NL: The Netherlands; DL: Germany; FR: France. In all countries with the exception of Spain, Reg_Anthr and Reg_Nat are the sum of regional+continental.

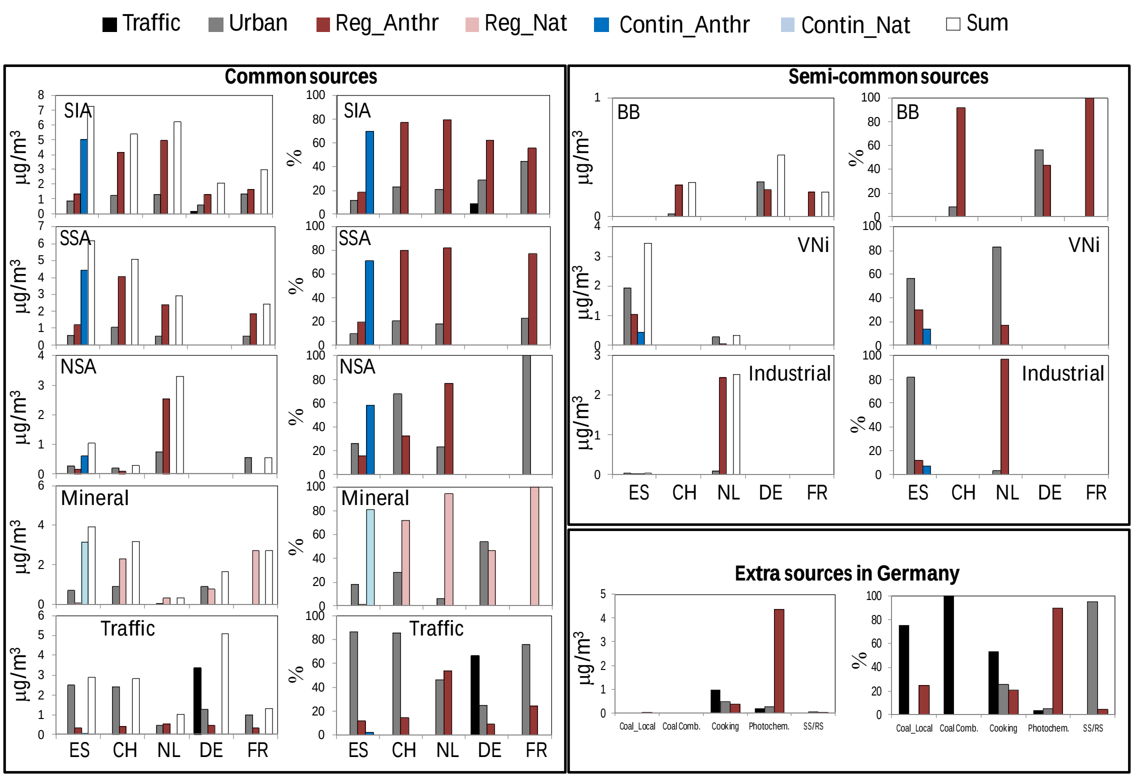

Figure S14: Lenschow's approach applied to the PMF source contributions. Average values for summer (JJA) are reported. ES: Spain; CH: Switzerland; NL: The Netherlands; DL: Germany; FR: France. In all countries, with the exception of Spain, Reg_Anthr and Reg_Nat are the sum of regional+continental.

Table S5: Allocation of PM to different sources and origin in each country. Annual means and winter (DJF) and summer (JJA) averages are reported.

		Annual mean					
Country	Contribution to PM (A) [$\mu g/m^3$; % of PM mass]	Traffic [$\mu g/m^3$; %]	Urban [$\mu g/m^3$; % of PM mass]	Regional [$\mu g/m^3$; % of PM mass]		Continental [$\mu g/m^3$; % of PM mass]	
		Anthr.	Anthr.	Natural	Anthr.	Natural	Anthr.
Spain	24.4; 100		8.5; 35.0	4.6; 18.8	3.4; 13.8	3.3; 13.5	4.3; 17.8
Switzerland	19.3; 100		6.5; 33.7	3.3; 17.0	10.0; 51.9		
The Netherlands	16.8; 100		4.3; 25.5	2.0; 12.1	10.5; 62.1		
Germany	21.6; 100	5.4; 24.8	3.5; 16.3	1.1; 5.0	10.8; 50.0		
France	20.7; 100		6.7; 32.6	9.1; 43.9	4.6; 22.5		
		Winter					
	Contribution to PM [$\mu g/m^3$; % of PM mass]	Traffic [$\mu g/m^3$; %]	Urban [$\mu g/m^3$; % of PM mass]	Regional [$\mu g/m^3$; % of PM mass]		Continental [$\mu g/m^3$; % of PM mass]	
		Anthr.	Anthr.	Natural	Anthr.	Natural	Anthr.
Spain	22.3; 100		10.3; 46.1	4.2; 18.8	3.7; 16.5	0.9; 4.0	1.3; 6.0
Switzerland	24.2; 100		7.6; 31.5	1.9; 7.9	14.0; 58.0		
The Netherlands	27.7; 100		7.4; 26.6	3.6; 13.1	17.6; 63.5		
Germany	27.0; 100	6.6; 24.3	3.4; 12.5	0.9; 3.4	15.4; 56.9		
France	17.8; 100		7.8; 44.0	5.7; 31.9	4.9; 27.6		
		Summer					
	Contribution to PM [$\mu g/m^3$; % of PM mass]	Traffic [$\mu g/m^3$; %]	Urban [$\mu g/m^3$; % of PM mass]	Regional [$\mu g/m^3$; % of PM mass]		Continental [$\mu g/m^3$; % of PM mass]	
		Anthr.	Anthr.	Natural	Anthr.	Natural	Anthr.
Spain	26.1; 100		6.0; 23.1	5.2; 19.7	2.7; 10.4	5.0; 19.1	5.5; 21.2
Switzerland	13.7; 100		5.0; 36.3	4.3; 31.7	4.8; 35.1		
The Netherlands	12.0; 100		2.3; 19.3	1.1; 9.2	8.0; 66.6		
Germany	16.0; 100	4.3; 27.3	3.9; 24.2	1.6; 9.8	6.6; 41.6		
France	19.1; 100		2.2; 11.5	14.9; 77.9	2.5; 12.9		

(A) PM concentrations measured in Barcelona (BCN; Spain), Zurich (ZUE; Switzerland), Schiedam (SCH; The Netherlands), Leipzig-Mitte (LMI; Germany) and Lens (LENS; France).

Table S6: Allocation of PMF source contributions in each country. Annual means are reported.

	Source contribution (A)	**Annual mean**					
	SIA [μg/m^3; % of PM mass]	Traffic [μg/m^3; % of SIA]	Urban [μg/m^3; % of SIA]	Regional [μg/m^3; % of SIA]		Continental [μg/m^3; % of SIA]	
		Anthr.	Anthr.	Natural	Anthr.	Natural	Anthr.
Spain	8.2; 33.6		1.9; 23.8		2.2; 27.4		4.0; 48.8
Switzerland	9.1; 46.9		1.7; 18.6		7.7; 85.4		
The Netherlands	9.8; 58.2		2.1; 21.0		7.7; 79.0		
Germany	6.2; 26.9	0.8; 13.5	1.3; 20.6		4.4; 71.7		
France	5.8; 28.2		2.5; 43.5		3.3; 56.5		
		Annual mean					
	SSA [μg/m^3; % of PM mass]	Traffic [μg/m^3; % of SSA]	Urban [μg/m^3; % of SSA]	Regional [μg/m^3; % of SSA]		Continental [μg/m^3; % of SSA]	
		Anthr.	Anthr.	Natural	Anthr.	Natural	Anthr.
Spain	5.2; 21.4		0.5; 8.7		1.8; 33.8		3.0; 57.5
Switzerland	4.6; 23.7		1.1; 23.7		3.5; 76.8		
The Netherlands	3.6; 21.2		0.7; 18.8		2.9; 81.2		
Germany							
France	2.2; 10.6		0.4; 17.4		1.8; 82.6		
		Annual mean					
	NSA [μg/m^3; % of PM mass]	Traffic [μg/m^3; % of NSA]	Urban [μg/m^3; % of NSA]	Regional [μg/m^3; % of NSA]		Continental [μg/m^3; % of NSA]	
		Anthr.	Anthr.	Natural	Anthr.	Natural	Anthr.
Spain	3.0; 12.2		1.5; 50.3		0.5; 16.1		1.0; 33.6
Switzerland	4.5; 23.2		0.6; 13.5		4.2; 94.2		
The Netherlands	6.2; 36.9		1.4; 22.2		4.8; 77.8		
Germany							
France	3.6; 17.5		2.1; 59.3		1.5; 40.7		
		Annual mean					
	Mineral [μg/m^3; % of PM mass]	Traffic [μg/m^3; % of Mineral]	Urban [μg/m^3; % of Mineral]	Regional [μg/m^3; % of Mineral]		Continental [μg/m^3; % of Mineral]	
		Anthr.	Anthr.	Natural	Anthr.	Natural	Anthr.
Spain	3.3; 13.6		0.7; 20.5	0.4; 13.2		2.2; 66.3	
Switzerland	2.6; 13.4		0.9; 33.1	1.9; 73.7			
The Netherlands	0.5; 3.2		0.1; 27.5	0.4; 72.5			
Germany	0.6; 2.4	0.0; 0.0	0.4; 70.4	0.3; 57.7			
France	5.0; 24.3		1.8; 35.3	3.2; 64.7			
		Annual mean					
	Road traffic [μg/m^3; % of PM mass]	Traffic [μg/m^3; % of RT]	Urban [μg/m^3; % of RT]	Regional [μg/m^3; % of RT]		Continental [μg/m^3; % of RT]	
		Anthr.	Anthr.	Natural	Anthr.	Natural	Anthr.
Spain	4.7; 19.1		4.2; 90.0		0.4; 8.1		0.1; 1.9
Switzerland	3.6; 18.5		3.0; 84.3		0.5; 13.4		
The Netherlands	2.0; 11.9		1.2; 62.2		0.7; 36.1		
Germany	5.2; 22.6	3.8; 73.0	1.1; 20.9		0.3; 6.1		
France	1.2; 5.6		0.9; 79.2		0.2; 20.8		
		Annual mean					
	SS [μg/m^3; % of PM mass]	Traffic [μg/m^3; % of SS]	Urban [μg/m^3; % of SS]	Regional [μg/m^3; % of SS]		Continental [μg/m^3; % of SS]	
		Anthr.	Anthr.	Natural	Anthr.	Natural	Anthr.
Spain	5.2; 21.5			5.2; 100			
Switzerland	1.7; 9.0			1.7; 100			

The Netherlands	1.6; 9.7			1.6; 100			
Germany	0.9; 4.0			0.9; 100			
France	3.7; 17.7			3.7; 100			
		Annual mean					
	Biomass burning [µg/m^3; % of PM mass]	Traffic [µg/m^3; % of BB]	Urban [µg/m^3; % of BB]	Regional [µg/m^3; % of BB]		Continental [µg/m^3; % of BB]	
		Anthr.	Anthr.	Natural	Anthr.	Natural	Anthr.
Spain							
Switzerland	2.3; 12.0		0.6; 25.4		1.8; 78.1		
The Netherlands							
Germany	1.4; 6.0	0.0; 0.0	0.3; 23.2		1.1; 76.9		
France	2.6; 12.8		1.5; 57.6		1.1; 42.4		
		Annual mean					
	V-Ni [µg/m^3; % of PM mass]	Traffic [µg/m^3; % of V-Ni]	Urban [µg/m^3; % of V-Ni]	Regional [µg/m^3; % of V-Ni]		Continental [µg/m^3; % of V-Ni]	
		Anthr.	Anthr.	Natural	Anthr.	Natural	Anthr.
Spain	2.7; 10.9		1.7; 62.9		0.7; 27.5		0.3; 9.6
Switzerland							
The Netherlands	0.3; 1.7		0.2; 83.8		0.1; 16.2		
Germany							
France							
		Annual mean					
	Industrial [µg/m^3; % of PM mass]	Traffic [µg/m^3; % of Ind]	Urban [µg/m^3; % of Ind]	Regional [µg/m^3; % of Ind]		Continental [µg/m^3; % of Ind]	
		Anthr.	Anthr.	Natural	Anthr.	Natural	Anthr.
Spain	0.05; 0.2		0.04; 79.1		0.01; 13.2		0.00; 7.8
Switzerland							
The Netherlands	2.1; 12.7		0.3; 13.6		2.0; 91.3		
Germany							
France							
		Annual mean					
	Germany [µg/m^3; % of PM mass]	Traffic [µg/m^3; %]	Urban [µg/m^3; %]	Regional [µg/m^3; %]		Continental [µg/m^3; %]	
		Anthr.	Anthr.	Natural	Anthr.	Natural	Anthr.
Coal_Local	0.02; 0.09	0.0; 12.6	0.0; 4.9		0.0; 82.5		
Coal	2.3; 10.0	0.3; 11.4	0.0; 0.0		2.3; 98.8		
Cooking	1.1; 5.0	0.5; 44.3	0.4; 32.8		0.3; 22.9		
Photochemistry	2.0; 8.6	0.1; 4.7	0.0; 0.3		1.9; 96.9		
SS/RS	0.5; 2.0	0.1; 20.6	0.3; 55.0		0.1, 24.4		
Fungal spores	0.2; 0.8			0.2; 0.8			
		Annual mean					
	France [µg/m^3; % of PM mass]	Traffic [µg/m^3; %]	Urban [µg/m^3;%]	Regional [µg/m^3; %]		Continental [µg/m^3; %]	
		Anthr.	Anthr.	Natural	Anthr.	Natural	Anthr.
Marine bio	1.0; 4.8			1.0; 100			
Land bio	1.2; 5.7			1.2; 100			

(A) Source contributions calculated for Barcelona (BCN; Spain), Zurich (ZUE; Switzerland), Schiedam (SCH; The Netherlands), Leipzig-Mitte (LMI; Germany) and Lens (LENS; France).

Table S7: Allocation of PMF source contributions in each country. Mean values for the winter period (DJF) are reported.

	Source contribution [A]	**Winter mean**					
	SIA [$\mu g/m^3$; % of PM mass]	Traffic [$\mu g/m^3$; % of SIA]	Urban [$\mu g/m^3$; % of SIA]	Regional [$\mu g/m^3$; % of SIA]		Continental [$\mu g/m^3$; % of SIA]	
		Anthr.	Anthr.	Natural	Anthr.	Natural	Anthr.
Spain	8.3; 37.0		3.3; 40.0		3.0; 36.1		1.2; 14.8
Switzerland	12.2; 50.2		2.5; 20.3		9.8; 80.4		
The Netherlands	18.0; 65.1		3.9; 21.6		14.1; 78.4		
Germany	9.9; 36.1	1.6; 16.0	2.0; 20.1		6.4; 65.3		
France	5.5; 30.6		2.6; 47.1		2.9; 52.9		
		Winter mean					
	SSA [$\mu g/m^3$; % of PM mass]	Traffic [$\mu g/m^3$; % of SSA]	Urban [$\mu g/m^3$; % of SSA]	Regional [$\mu g/m^3$; % of SSA]		Continental [$\mu g/m^3$; % of SSA]	
		Anthr.	Anthr.	Natural	Anthr.	Natural	Anthr.
Spain	3.3; 14.7		0.8; 23.7		1.6; 47.8		0.9; 27.8
Switzerland	3.3; 13.5		1.0; 32.1		2.3; 70.6		
The Netherlands	4.2; 15.2		0.3; 6.1		4.0; 93.9		
Germany							
France	2.3; 13.1		0.8; 32.6		1.6; 67.4		
		Winter mean					
	NSA [$\mu g/m^3$; % of PM mass]	Traffic [$\mu g/m^3$; % of NSA]	Urban [$\mu g/m^3$; % of NSA]	Regional [$\mu g/m^3$; % of NSA]		Continental [$\mu g/m^3$; % of NSA]	
		Anthr.	Anthr.	Natural	Anthr.	Natural	Anthr.
Spain	5.0; 22.3		3.0; 60.9		1.6; 32.4		0.3; 6.2
Switzerland	8.9; 36.8		1.4; 16.0		7.5; 83.9		
The Netherlands	13.8; 50.0		3.6; 26.3		10.2; 73.7		
Germany							
France	3.1; 17.5		1.8; 58.0		1.3; 42.0		
		Winter mean					
	Mineral [$\mu g/m^3$; % of PM mass]	Traffic [$\mu g/m^3$; % of Mineral]	Urban [$\mu g/m^3$; % of Mineral]	Regional [$\mu g/m^3$; % of Mineral]		Continental [$\mu g/m^3$; % of Mineral]	
		Anthr.	Anthr.	Natural	Anthr.	Natural	Anthr.
Spain	1.7; 7.3		0.7; 43.2	0.5; 31.5		0.4; 24.3	
Switzerland	1.0; 4.1		0.3; 28.7	0.7; 66.7			
The Netherlands	0.3; 1.1		0.16; 49.7	0.16; 50.3			
Germany	0.09; 0.3	0.0; 0.0	0.03; 39.9	0.06; 68.3			
France	3.0; 16.7		1.6; 54.1	1.4; 45.9			
		Winter mean					
	Road traffic [$\mu g/m^3$; % of PM mass]	Traffic [$\mu g/m^3$; % of RT]	Urban [$\mu g/m^3$; % of RT]	Regional [$\mu g/m^3$; % of RT]		Continental [$\mu g/m^3$; % of RT]	
		Anthr.	Anthr.	Natural	Anthr.	Natural	Anthr.
Spain	5.6; 25.1		5.2; 92.9		0.4; 7.1		0.1; 1.4
Switzerland	3.1; 12.8		2.7; 86.5		0.4; 12.9		
The Netherlands	3.6; 13.0		2.1; 59.4		1.5; 40.6		
Germany	5.3; 19.2	4.0; 76.2	1.1; 20.5		0.3; 5.9		
France	1.1; 6.3		0.9; 84.0		0.2; 16.0		
		Winter mean					
	SS [$\mu g/m^3$; % of PM mass]	Traffic [$\mu g/m^3$; % of SS]	Urban [$\mu g/m^3$; % of SS]	Regional [$\mu g/m^3$; % of SS]		Continental [$\mu g/m^3$; % of SS]	
		Anthr.	Anthr.	Natural	Anthr.	Natural	Anthr.
Spain	4.1; 18.0			4.1; 100			

Switzerland	2.0; 8.4			2.0; 100			
The Netherlands	3.5; 12.5			3.5; 100			
Germany	0.9; 3.2			0.9; 100			
France	3.6; 20.1			3.6; 100			
		Winter mean					
	Biomass burning [$\mu g/m^3$; % of PM mass]	Traffic [$\mu g/m^3$; % of BB]	Urban [$\mu g/m^3$; % of BB]	Regional [$\mu g/m^3$; % of BB]		Continental [$\mu g/m^3$; % of BB]	
		Anthr.	Anthr.	Natural	Anthr.	Natural	Anthr.
Spain							
Switzerland	5.3; 21.9		1.4; 26.8		3.9; 73.1		
The Netherlands							
Germany	2.1; 7.8	0.0; 0.0	0.5; 21.2		1.7; 77.8		
France	4.6; 25.7		2.7; 59.4		1.9; 40.6		
		Winter mean					
	V-Ni [$\mu g/m^3$; % of PM mass]	Traffic [$\mu g/m^3$; % of V-Ni]	Urban [$\mu g/m^3$; % of V-Ni]	Regional [$\mu g/m^3$; % of V-Ni]		Continental [$\mu g/m^3$; % of V-Ni]	
		Anthr.	Anthr.	Natural	Anthr.	Natural	Anthr.
Spain	1.2; 5.3		0.9; 78.8		0.2; 20.9		0.0; 0.4
Switzerland							
The Netherlands	0.5; 1.6		0.4; 85.6		0.1; 14.4		
Germany							
France							
		Winter mean					
	Industrial [$\mu g/m^3$; % of PM mass]	Traffic [$\mu g/m^3$; % of Ind]	Urban [$\mu g/m^3$; % of Ind]	Regional [$\mu g/m^3$; % of Ind]		Continental [$\mu g/m^3$; % of Ind]	
		Anthr.	Anthr.	Natural	Anthr.	Natural	Anthr.
Spain	0.1; 0.3		0.1; 83.7		0.01; 13.9		0.00; 3.5
Switzerland							
The Netherlands	1.8; 6.3		0.1; 4.5		1.7; 95.3		
Germany							
France							
		Winter mean					
	Germany [$\mu g/m^3$; % of PM mass]	Traffic [$\mu g/m^3$; % of Ind]	Urban [$\mu g/m^3$; % of Ind]	Regional [$\mu g/m^3$; % of Ind]		Continental [$\mu g/m^3$; % of Ind]	
		Anthr.	Anthr.	Natural	Anthr.	Natural	Anthr.
Coal_Local	0.03; 0.12	0.00; 6.6	0.00; 1.6		0.03; 86.7		
Coal	4.4; 15.9	0.5; 11.4	0.0; 0.0		3.9; 90.0		
Cooking	0.8; 2.9	0.3; 33.7	0.3; 41.1		0.2; 24.7		
Photochemistry	1.3; 4.7	0.1; 5.9	0.0; 0.0		1.2; 94.6		
SS/RS	0.5; 1.9	0.12; 44.8	0.2; 31.8		0.1, 28.1		
Fungal spores	0.0; 0.0			0.0; 0.0			
		Winter mean					
	France [$\mu g/m^3$; % of PM mass]	Traffic [$\mu g/m^3$; %]	Urban [$\mu g/m^3$;%]	Regional [$\mu g/m^3$; %]		Continental [$\mu g/m^3$; %]	
		Anthr.	Anthr.	Natural	Anthr.	Natural	Anthr.
Marine bio	0.1; 0.6			0.1; 100			
Land bio	0.6; 3.6			0.6; 100			

(A) Source contributions calculated for Barcelona (BCN; Spain), Zurich (ZUE; Switzerland), Schiedam (SCH; The Netherlands), Leipzig-Mitte (LMI; Germany) and Lens (LENS; France).

Table S8: Allocation of PMF source contributions in each country. Mean values for the summer period (JJA) are reported.

	Source contribution [(A)]	**Summer mean**					
	SIA [$\mu g/m^3$; % of PM mass]	Traffic [$\mu g/m^3$; % of SIA]	Urban [$\mu g/m^3$; % of SIA]	Regional [$\mu g/m^3$; % of SIA]		Continental [$\mu g/m^3$; % of SIA]	
		Anthr.	Anthr.	Natural	Anthr.	Natural	Anthr.
Spain	7.2; 27.7		0.9; 11.9		1.3; 18.7		5.0; 69.4
Switzerland	5.4; 39.5		1.2; 22.7		4.1; 76.5		
The Netherlands	6.2; 51.9		1.3; 20.6		4.9; 79.4		
Germany	2.1; 11.4	0.2; 8.5	0.6; 28.5		1.3; 61.8		
France	3.3; 16.3		1.3; 39.6		2.0; 60.0		
		Summer mean					
	SSA [$\mu g/m^3$; % of PM mass]	Traffic [$\mu g/m^3$; % of SSA]	Urban [$\mu g/m^3$; % of SSA]	Regional [$\mu g/m^3$; % of SSA]		Continental [$\mu g/m^3$; % of SSA]	
		Anthr.	Anthr.	Natural	Anthr.	Natural	Anthr.
Spain	6.2; 23.7		0.6; 9.5		1.2; 19.2		4.4; 71.3
Switzerland	5.2; 37.7		1.0; 20.1		4.1; 78.5		
The Netherlands	2.9; 24.3		0.3; 17.8		2.6; 82.2		
Germany							
France	2.5; 12.5		0.6; 21.9		1.9; 77.3		
		Summer mean					
	NSA [$\mu g/m^3$; % of PM mass]	Traffic [$\mu g/m^3$; % of NSA]	Urban [$\mu g/m^3$; % of NSA]	Regional [$\mu g/m^3$; % of NSA]		Continental [$\mu g/m^3$; % of NSA]	
		Anthr.	Anthr.	Natural	Anthr.	Natural	Anthr.
Spain	1.0; 4.0		0.3; 26.1		0.2; 15.8		0.6; 58.1
Switzerland	0.3; 1.9		0.2; 76.5		0.1; 33.5		
The Netherlands	3.3; 27.5		0.8; 23.1		2.5; 76.9		
Germany							
France	0.8; 3.9		0.8; 100.0		0.0; 0.0		
		Summer mean					
	Mineral [$\mu g/m^3$; % of PM mass]	Traffic [$\mu g/m^3$; % of Mineral]	Urban [$\mu g/m^3$; % of Mineral]	Regional [$\mu g/m^3$; % of Mineral]		Continental [$\mu g/m^3$; % of Mineral]	
		Anthr.	Anthr.	Natural	Anthr.	Natural	Anthr.
Spain	3.9; 15.0		0.7; 18.0	0.1; 1.4		3.2; 80.6	
Switzerland	3.2; 23.1		0.9; 28.4	2.3; 72.1			
The Netherlands	0.3; 2.7		0.02; 6.0	0.3; 94.0			
Germany	1.1; 5.8	0.0; 0.0	1.1; 92.0	0.0; 8.0			
France	3.3; 16.3		0.3; 8.9	3.0; 90.1			
		Summer mean					
	Road traffic [$\mu g/m^3$; % of PM mass]	Traffic [$\mu g/m^3$; % of RT]	Urban [$\mu g/m^3$; % of RT]	Regional [$\mu g/m^3$; % of RT]		Continental [$\mu g/m^3$; % of RT]	
		Anthr.	Anthr.	Natural	Anthr.	Natural	Anthr.
Spain	2.9; 11.0		2.5; 86.5		0.3; 11.7		0.1; 1.8
Switzerland	2.8; 20.4		2.4; 86.6		0.4; 14.5		
The Netherlands	0.6; 4.8		0.5; 88.8		0.0; 11.2		
Germany	5.1; 27.5	3.4; 66.2	1.3; 25.0		0.5; 8.9		
France	1.3; 6.3		1.0; 77.9		0.3; 23.2		
		Summer mean					
	SS [$\mu g/m^3$; % of PM mass]	Traffic [$\mu g/m^3$; % of SS]	Urban [$\mu g/m^3$; % of SS]	Regional [$\mu g/m^3$; % of SS]		Continental [$\mu g/m^3$; % of SS]	
		Anthr.	Anthr.	Natural	Anthr.	Natural	Anthr.
Spain	6.9; 26.5			6.9; 100			

Switzerland	2.5; 18.1			2.5; 100			
The Netherlands	0.8; 6.7			0.8; 100			
Germany	0.9; 5.1			0.9; 100			
France	6.4; 31.5			6.4; 100			
		Summer mean					
	Biomass burning [μg/m^3; % of PM mass]	Traffic [μg/m^3; % of BB]	Urban [μg/m^3; % of BB]	Regional [μg/m^3; % of BB]		Continental [μg/m^3; % of BB]	
		Anthr.	Anthr.	Natural	Anthr.	Natural	Anthr.
Spain							
Switzerland	0.3; 2.2		0.02; 7.8		0.3; 88.2		
The Netherlands							
Germany	0.5; 2.8	0.0; 0.0	0.5; 96.2		0.0; 3.8		
France	0.0; 0.0		0.0; 0.0		0.0; 0.0		
		Summer mean					
	V-Ni [μg/m^3; % of PM mass]	Traffic [μg/m^3; % of V-Ni]	Urban [μg/m^3; % of V-Ni]	Regional [μg/m^3; % of V-Ni]		Continental [μg/m^3; % of V-Ni]	
		Anthr.	Anthr.	Natural	Anthr.	Natural	Anthr.
Spain	3.4; 13.2		1.9; 56.4		1.0; 30.3		0.5; 13.4
Switzerland							
The Netherlands	0.3; 2.9		0.3; 83.0		0.1; 17.0		
Germany							
France							
		Summer mean					
	Industrial [μg/m^3; % of PM mass]	Traffic [μg/m^3; % of Ind]	Urban [μg/m^3; % of Ind]	Regional [μg/m^3; % of Ind]		Continental [μg/m^3; % of Ind]	
		Anthr.	Anthr.	Natural	Anthr.	Natural	Anthr.
Spain	0.03; 0.1		0.03; 81.5		0.00; 11.6		0.00; 6.9
Switzerland							
The Netherlands	2.4; 19.9		0.1; 3.4		2.3; 95.7		
Germany							
France							
		Summer mean					
	Germany [μg/m^3; % of PM mass]	Traffic [μg/m^3; % of Ind]	Urban [μg/m^3; % of Ind]	Regional [μg/m^3; % of Ind]		Continental [μg/m^3; % of Ind]	
		Anthr.	Anthr.	Natural	Anthr.	Natural	Anthr.
Coal_Local	0.01; 0.03	0.00; 73.7	0.00; 0.0		0.00; 24.1		
Coal	0.03; 0.2	0.02; 67.1	0.0; 0.0		0.01; 33.3		
Cooking	1.5; 8.2	1.0; 65.1	0.5; 31.0		0.0; 4.0		
Photochemistry	2.7; 14.6	0.2; 7.4	0.3; 10.1		2.2; 83.0		
SS/RS	0.5; 2.4	0.0; 8.0	0.5; 91.0		0.0, 0.0		
Fungal spores	0.4; 2.0			0.0; 0.0			
		Summer mean					
	France [μg/m^3; % of PM mass]	Traffic [μg/m^3; %]	Urban [μg/m^3;%]	Regional [μg/m^3; %]		Continental [μg/m^3; %]	
		Anthr.	Anthr.	Natural	Anthr.	Natural	Anthr.
Marine bio	3.8; 18.4			3.8; 100			
Land bio	2.4; 12.0			2.4; 100			

[(A)] Source contributions calculated for Barcelona (BCN; Spain), Zurich (ZUE; Switzerland), Schiedam (SCH; The Netherlands), Leipzig-Mitte (LMI; Germany) and Lens (LENS; France).