

Figure S1: Measurement results of hourly-mean values NO, NO<sub>x</sub>, O<sub>3</sub>, CO, PM<sub>2.5</sub> and PM<sub>10</sub> concentrations at the sites Bourgesplatz (LÜB), LfU (LÜB), HSA and AVA.

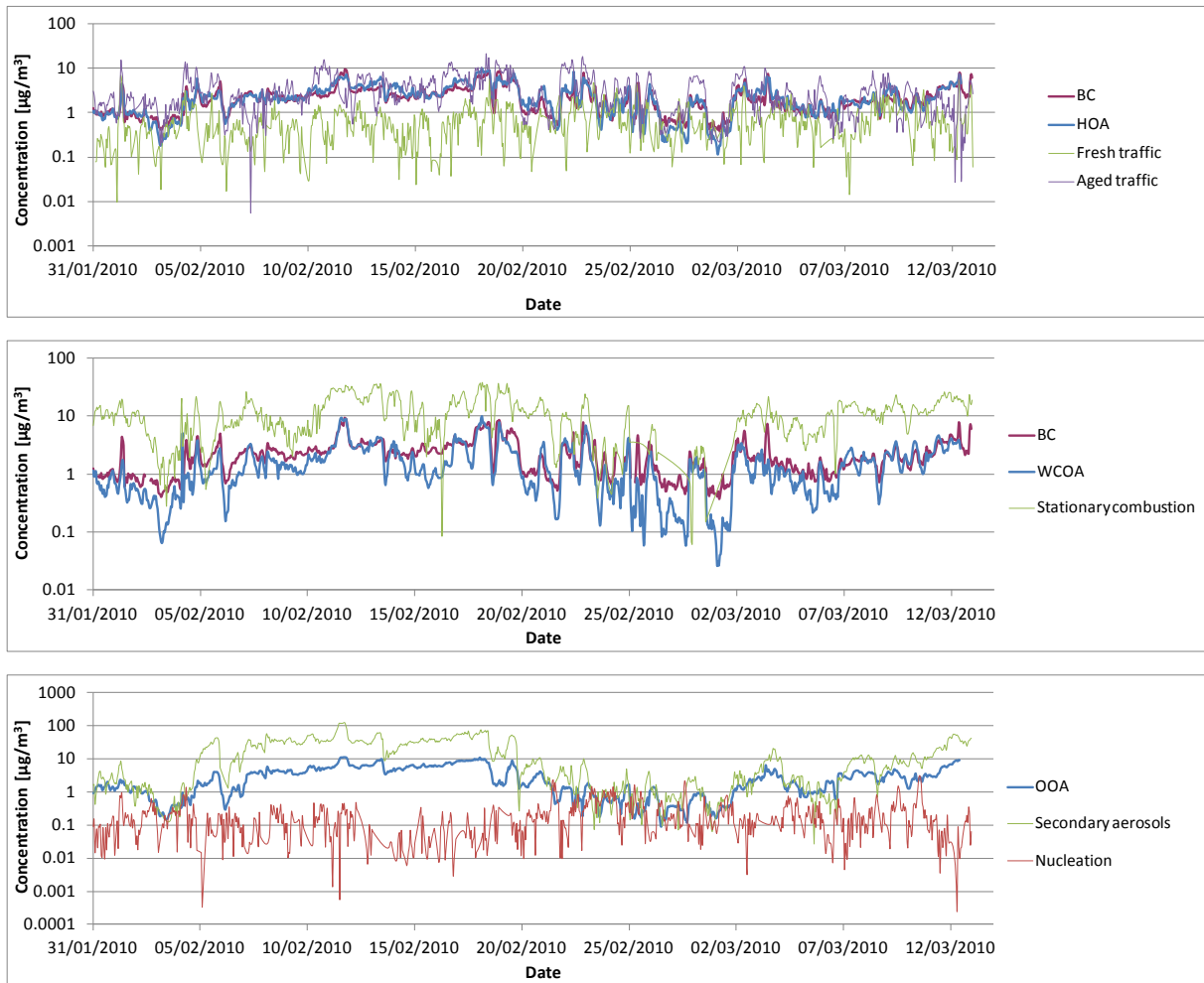


Figure S2: Comparison of the different factors from PMF analyses of PSD data with those from PMF analyses of  $\text{PM}_{10}$  composition on the basis of hourly-mean values: fresh traffic and aged traffic aerosol factors with black carbon (BC) and hydrocarbon-like organic aerosol (HOA, traffic factor or primary organic factor), stationary combustion aerosol factor with black carbon (BC) and wood combustion organic aerosol (WCOA, wood combustion factor) as well as secondary aerosol factor with oxygenated organic aerosol (OOA, secondary organic factor) together with nucleation aerosol factor.

Table S1: Quantitative characterization of the 10 temporal phases from 31 January, 00:00 CET to 12 March 2010, 24:00 CET of PM components soot (BC - black carbon), OOA - oxygenated organic aerosol (secondary organic factor), HOA - hydrocarbon-like organic aerosol (traffic factor or primary organic factor), WCOA - wood combustion organic aerosol (wood combustion factor), nitrate ( $\text{NO}_3^-$ ), sulphate ( $\text{SO}_4^{2-}$ ) and ammonium ( $\text{NH}_4^+$ ) (see text).

Phase	Description	mean [ $\mu\text{g}/\text{m}^3$ ]			relative	Starting date in CET
1	Constant phase with relatively low PMC and higher $\text{NO}_3^-$ content. Wind speeds from 1 to 9 m/s. Prevailing wind direction west-southwest. Temperatures from -9 to -3°C.	Organic	Total	3.21	0.30	31/01/2010 00:00
			OOA	1.32	0.12	
			HOA	1.10	0.10	
			WCOA	0.70	0.07	
		Nitrate		4.17	0.36	
		Sulphate		1.29	0.12	
		Ammonium		1.46	0.13	
		Soot		1.11	0.10	
2	Decrease to very low PMC. Soot and primary PMF factor HOA play the dominant role. Wind speeds from 6 to 14 m/s. Prevailing wind direction west-southwest. Temperatures from -3 to +3°C.	Organic	Total	1.15	0.36	02/02/2010 13:00
			OOA	0.37	0.11	
			HOA	0.48	0.16	
			WCOA	0.28	0.09	
		Nitrate			0.20	
		Sulphate		0.34	0.11	
		Ammonium		0.38	0.11	
		Soot		0.65	0.23	
3	Increase of PMC with mean composition, some less organic components. Wind speeds from 1 to 5 m/s. Varying wind directions from northwest to east. Temperatures from -8 to +7°C.	Organic	Total	6.72	0.31	04/02/2010 04:00
			OOA	3.00	0.13	
			HOA	2.26	0.11	
			WCOA	1.40	0.07	
		Nitrate			0.30	
		Sulphate		3.73	0.15	
		Ammonium		2.60	0.12	
		Soot		2.22	0.11	
4	Special event with strong PMC	Organic	Total	18.23	0.36	11/02/2010

	increase during "wet" snow fall. Higher $\text{SO}_4^{2-}$ and WCOA contents. High CO, NO and $\text{NO}_x$ concentrations. Wind speeds from 0.5 to 5 m/s. Wind directions west-northwest and north-northwest. Temperatures from -9 to -4°C.		<b>OOA</b>	7.99	0.15	00:00
			<b>HOA</b>	5.29	0.10	
			<b>WCOA</b>	5.53	0.10	
		<b>Nitrate</b>			0.24	
		<b>Sulphate</b>		10.05	0.20	
		<b>Ammonium</b>		5.08	0.10	
		<b>Soot</b>		5.35	0.10	
<b>5</b>	Steady high PMC with much $\text{SO}_4^{2-}$ and OOA (secondary). Daily variations. Wind speeds from 0.5 to 3 m/s. Prevailing wind direction southeast. Temperatures from -7 to -3°C.	<b>Organic</b>	<b>Total</b>	11.22	0.34	12/02/2010 00:00
			<b>OOA</b>	5.84	0.18	
			<b>HOA</b>	3.41	0.10	
			<b>WCOA</b>	2.11	0.06	
		<b>Nitrate</b>			0.26	
		<b>Sulphate</b>			0.20	
		<b>Ammonium</b>			0.11	
		<b>Soot</b>			0.09	
<b>6</b>	Further PMC increase with high $\text{NO}_3^-$ content. Highest CO, NO and $\text{NO}_x$ concentrations. HOA (primary) and OOA (secondary) contents similar. Wind speeds from 0.5 to 7 m/s. Varying wind directions from north-northeast via east and south to west. Temperatures from -8 to +7°C.	<b>Organic</b>	<b>Total</b>	12.91	0.34	16/02/2010 04:00
			<b>OOA</b>	5.51	0.14	
			<b>HOA</b>	4.51	0.13	
			<b>WCOA</b>	2.84	0.07	
		<b>Nitrate</b>			0.35	
		<b>Sulphate</b>			0.09	
		<b>Ammonium</b>			0.11	
		<b>Soot</b>			0.10	
<b>7</b>	Strong PMC decrease. Main content is organic origin with HOA. WCOA and soot (BC) contents high. Some peak CO, NO and $\text{NO}_x$ concentrations. Wind speeds from 1 to 13 m/s. Varying wind directions from south-southeast to west-southwest. Temperatures from -3 to	<b>Organic</b>	<b>Total</b>	3.48	0.46	21/02/2010 01:00
			<b>OOA</b>	0.72	0.12	
			<b>HOA</b>	1.62	0.22	
			<b>WCOA</b>	1.09	0.13	
		<b>Nitrate</b>			0.15	
		<b>Sulphate</b>			0.06	

	+13°C.	<b>Ammonium</b>		0.07		
		<b>Soot</b>		0.26		
<b>8</b>	Second special event with high PMC increase and high NO <sub>3</sub> <sup>-</sup> content during "wet" snow fall. Some peak CO, NO and NO <sub>x</sub> concentrations. Wind speeds from 0 to 6 m/s. Prevailing wind direction east-northeast. Temperatures from -3 to +4°C.	<b>Organic</b>	<b>Total</b>	7.85	0.29	02/03/2010 15:00
			<b>OOA</b>	3.23	0.12	
			<b>HOA</b>	3.14	0.12	
			<b>WCOA</b>	1.24	0.05	
		<b>Nitrate</b>			0.39	
		<b>Sulphate</b>			0.11	
		<b>Ammonium</b>			0.12	
		<b>Soot</b>			0.09	
<b>9</b>	Phase with low up to mean PMC. Mean composition with a little bit more WCOA. Wind speeds from 1 to 11 m/s. Wind directions northeast to east northeast and west-southwest. Temperatures from -12 to +4°C.	<b>Organic</b>	<b>Total</b>	5.48	0.36	04/03/2010 00:00
			<b>OOA</b>	2.41	0.15	
			<b>HOA</b>	1.65	0.11	
			<b>WCOA</b>	1.36	0.09	
		<b>Nitrate</b>			0.27	
		<b>Sulphate</b>			0.16	
		<b>Ammonium</b>			0.11	
		<b>Soot</b>			0.11	
<b>10</b>	PMC increase with more WCOA. Wind speeds from 0 to 4 m/s. Varying wind directions from west southwest to north northeast. Temperatures from -12 to +2°C.	<b>Organic</b>	<b>Total</b>	12.61	0.36	11/03/2010 01:00
			<b>OOA</b>	5.59	0.15	
			<b>HOA</b>	3.79	0.11	
			<b>WCOA</b>	3.23	0.10	
		<b>Nitrate</b>			0.30	
		<b>Sulphate</b>		4.96	0.13	
		<b>Ammonium</b>		4.27	0.11	
		<b>Soot</b>		3.76	0.11	

Table S2: Pearson correlation coefficients between all pollutants during the total measurement period (all temporal phases) on the basis of hourly-mean values. Correlation coefficients > 0.8 are in bold, and correlations < 0.1 in italics

Phase.Total	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2+</sup>	NH <sub>4</sub> <sup>+</sup>	OOA	HOA	WCOA	BC	O <sub>3</sub>	NO	NO <sub>2</sub>	NO <sub>x</sub>	Benzene	Toluene	o.Xylene	CO	PM <sub>2.5</sub>	PM <sub>10</sub>	NC3-10	NC10-30	NC30-50	NC50-100	NC100-500	Nucleation	Fresh traffic	Aged traffic	Stationary combustion	Secondary aerosols	
NO <sub>3</sub> <sup>-</sup>	1																											
SO <sub>4</sub> <sup>2+</sup>	0.681	1																										
NH <sub>4</sub> <sup>+</sup>	<b>0.969</b>	<b>0.836</b>	1																									
OOA	<b>0.824</b>	<b>0.903</b>	<b>0.912</b>	1																								
HOA	0.736	0.609	0.740	0.758	1																							
WCOA	0.556	0.568	0.594	0.658	<b>0.847</b>	1																						
BC	0.568	0.564	0.604	0.681	<b>0.897</b>	<b>0.847</b>	1																					
O <sub>3</sub>	-0.395	-0.202	-0.350	-0.259	-0.613	-0.490	-0.575	1																				
NO	0.173	0.044	0.143	0.121	0.442	0.270	0.519	-0.433	1																			
NO <sub>2</sub>	0.314	0.167	0.285	0.323	0.655	0.531	0.681	-0.665	0.695	1																		
Nox	0.247	0.100	0.214	0.216	0.567	0.401	0.629	-0.565	<b>0.953</b>	<b>0.880</b>	1																	
Benzene	0.572	0.638	0.630	0.729	<b>0.844</b>	<b>0.811</b>	<b>0.910</b>	-0.570	0.474	0.629	0.577	1																
Toluene	0.206	0.065	0.164	0.166	0.569	0.457	0.683	-0.587	0.653	0.664	0.710	0.670	1															
o-Xylene	<i>0.086</i>	<i>-0.075</i>	<i>0.030</i>	<i>0.017</i>	0.445	0.334	0.556	-0.505	0.623	0.634	0.678	0.527	<b>0.903</b>	1														
CO	0.491	0.422	0.497	0.560	0.787	0.698	<b>0.830</b>	-0.669	0.640	0.780	0.751	<b>0.893</b>	0.748	0.641	1													
PM <sub>2.5</sub>	0.794	<b>0.881</b>	<b>0.883</b>	<b>0.934</b>	<b>0.811</b>	0.772	0.786	-0.413	0.236	0.433	0.338	<b>0.823</b>	0.293	0.143	0.674	1												
PM <sub>10</sub>	0.766	<b>0.826</b>	<b>0.845</b>	<b>0.897</b>	<b>0.816</b>	0.764	<b>0.807</b>	-0.420	0.319	0.505	0.424	<b>0.821</b>	0.354	0.223	0.701	<b>0.970</b>	1											
NC3-10	-0.158	-0.158	-0.167	-0.153	-0.069	-0.068	-0.019	0.085	0.191	0.086	0.163	-0.087	0.133	0.168	-0.042	-0.142	-0.074	1										
NC10-30	0.097	<i>0.009</i>	<i>0.071</i>	<i>0.051</i>	0.244	0.108	0.281	-0.196	0.476	0.398	0.483	0.155	0.372	0.387	0.242	<i>0.075</i>	0.166	0.547	1									
NC30-50	0.268	0.160	0.244	0.238	0.473	0.336	0.470	-0.394	0.532	0.599	0.604	0.411	0.512	0.480	0.506	0.282	0.358	0.222	0.771	1								
NC50-100	0.388	0.293	0.376	0.399	0.671	0.526	0.639	-0.569	0.590	0.742	0.701	0.610	0.611	0.540	0.700	0.452	0.499	0.111	0.514	0.826	1							
NC100-500	0.664	0.655	0.703	0.740	<b>0.876</b>	<b>0.806</b>	<b>0.830</b>	-0.580	0.446	0.647	0.567	<b>0.847</b>	0.533	0.403	<b>0.801</b>	<b>0.815</b>	<b>0.808</b>	-0.055	0.244	0.527	0.789	1.000						
Nucleation	-0.279	-0.253	-0.289	-0.259	-0.230	-0.159	-0.173	0.203	-0.029	-0.063	-0.046	-0.202	0.006	0.059	-0.174	-0.256	-0.203	<b>0.900</b>	0.356	0.007	-0.110	-0.213	1.000					
Fresh traffic	<i>0.083</i>	-0.022	<i>0.052</i>	<i>0.034</i>	0.199	0.111	0.234	-0.190	0.366	0.408	0.413	0.161	0.383	0.421	0.260	<i>0.066</i>	0.151	0.430	<b>0.936</b>	0.694	0.431	0.193	0.223	1.000				
Aged traffic	0.254	0.132	0.223	0.238	0.531	0.373	0.508	-0.537	0.561	0.697	0.663	0.485	0.574	0.537	0.616	0.294	0.356	<i>0.012</i>	0.498	<b>0.821</b>	<b>0.942</b>	0.637	-0.110	0.351	1.000			
Stationary combustion	0.613	0.632	0.663	0.677	0.739	0.760	0.674	-0.372	0.240	0.387	0.322	0.704	0.323	0.192	0.597	0.717	0.672	-0.132	<i>0.057</i>	0.245	0.474	<b>0.851</b>	-0.217	<i>0.045</i>	0.225	1.000		
Secondary aerosols	0.729	<b>0.873</b>	<b>0.829</b>	<b>0.894</b>	0.707	0.670	0.705	-0.363	0.182	0.349	0.269	0.761	0.225	0.078	0.605	<b>0.955</b>	<b>0.923</b>	-0.164	<i>0.050</i>	0.245	0.363	0.712	-0.238	<i>0.021</i>	0.245	0.557	1.000	

Table S3: Pearson correlation coefficient of each pollutant with each meteorological parameter (T (temperature), RH (relative humidity), AH (absolute humidity), WS (wind speed), MLH (mixing layer height)) during the total measurement period on the basis of hourly-mean values. Bold values are values, which are not lower than 25 % of the maximum value, and italic values are those <0.1.

Phase.Total	T	RH	AH	WS	MLH
NO <sub>3</sub> <sup>-</sup>	<b>-0.493</b>	<b>0.433</b>	-0.274	-0.397	-0.218
SO <sub>4</sub> <sup>2-</sup>	<b>-0.654</b>	<b>0.396</b>	<b>-0.473</b>	-0.355	-0.106
NH <sub>4</sub> <sup>+</sup>	<b>-0.593</b>	<b>0.452</b>	<b>-0.371</b>	<b>-0.403</b>	-0.188
OOA	<b>-0.600</b>	<b>0.393</b>	<b>-0.409</b>	<b>-0.409</b>	-0.141
HOA	-0.390	<b>0.473</b>	-0.120	<b>-0.556</b>	<b>-0.372</b>
WCOA	-0.387	<b>0.376</b>	-0.183	-0.392	-0.268
BC	-0.299	<b>0.415</b>	<i>-0.051</i>	<b>-0.484</b>	-0.311
O <sub>3</sub>	0.182	-0.624	-0.218	0.643	0.546
NO	<i>-0.005</i>	0.166	<i>0.096</i>	-0.249	-0.169
NO <sub>2</sub>	-0.107	0.296	<i>0.086</i>	-0.532	<b>-0.370</b>
Nox	<i>-0.048</i>	0.233	<i>0.099</i>	-0.388	-0.260
Benzene	-0.400	<b>0.445</b>	-0.151	<b>-0.488</b>	-0.275
Toluene	<i>0.031</i>	0.267	0.219	-0.387	<b>-0.312</b>
o-Xylene	0.143	0.174	0.289	-0.301	-0.289
CO	-0.274	<b>0.429</b>	<i>-0.019</i>	<b>-0.515</b>	<b>-0.330</b>
PM <sub>2.5</sub>	<b>-0.552</b>	<b>0.478</b>	<b>-0.308</b>	<b>-0.446</b>	-0.189
PM <sub>10</sub>	<b>-0.481</b>	<b>0.397</b>	-0.286	<b>-0.437</b>	-0.167
NC3-10	0.200	-0.311	<i>-0.001</i>	0.140	0.162
NC10-30	<i>0.022</i>	<i>-0.082</i>	<i>-0.027</i>	-0.162	<i>-0.084</i>
NC30-50	-0.171	<i>0.082</i>	-0.123	-0.343	-0.233
NC50-100	-0.325	0.269	-0.164	<b>-0.502</b>	<b>-0.373</b>
NC100-500	<b>-0.510</b>	<b>0.460</b>	-0.260	<b>-0.527</b>	<b>-0.345</b>
Nucleation	0.306	<b>-0.410</b>	<i>0.043</i>	0.234	0.242
Fresh traffic	<i>0.032</i>	<i>-0.053</i>	<i>0.016</i>	-0.159	<i>-0.072</i>
Aged traffic	-0.186	0.184	<i>-0.068</i>	<b>-0.448</b>	<b>-0.360</b>
Stationary combustion	<b>-0.547</b>	<b>0.434</b>	<b>-0.319</b>	-0.352	-0.231
Secondary aerosols	<b>-0.489</b>	<b>0.433</b>	-0.276	<b>-0.405</b>	-0.145