<u>Supplemental material for:</u>

Composition And sources of Particulate matter in an industrialised Alpine valley

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S1 Comparison of XRF and IC measurements

See Fig. S1.

S2 Factorial analysis of the AMS organics

AMS organics measured in Massongex were first analysed with positive matrix factorisation (PMF) (Lanz et al. 2007; Ulbrich et al., 2009). Up to three factors could be related to previously described organic aerosol (OA) components, namely hydrocarbon-like OA (HOA), primary wood-burning OA (P-WBOA) and oxygenated OA (OOA) (Table S2). Several rotations (induced by varying *fpeaks* from -0.5, -0.4, …, 0.4, 0.5) of the PMF solution were investigated. The resulting spectra were compared with reference profiles from the literature (HOA and OOA Winter Zurich, Lanz et al. 2008; P-WBOA Winter Roveredo, Alfarra et al. 2007) and their corresponding time series with ancillary data (such as particulate sulphate or CO – not included in the PMF input) (Table S2). The most realistic factor profiles was found for a central rotation at *fpeak*=0.0.

Nevertheless, this PMF2-based solution was not supported by ^{14}C measurements. According to Lanz et al. (2007, 2008, 2009) HOA can mostly be interpreted as primarily emitted fossil OA from combustion sources, whereas P-WBOA represents primary wood combustion and consists of non-fossil carbon. In contrast, OOA is expected to originate from both fossil and non-fossil precursor gases. At Massongex, the PM_{10} fossil OM (OM_f) contributions averaged from the analysed filters amounted to 25% of the PM_{10} OM. This corresponds to about 29% of the PM_1 OM, considering that the fossil OM in the PM_{10} was fully belonging to the PM_1. HOA making up 26% of the PM_1 fossil OM would result in a remaining fossil contribution to OOA representing 3% of the PM_1 OM and 1% of the total OOA, which was regarded as too low.

Therefore, the 3-factor solution was further investigated using ME-2 (Lanz et al., 2008). The HOA profile in ME-2 was a priori constrained to values close to measured HOA-profiles provided in the literature (Schneider et al., 2006), while the HOA contributions over time were unconstrained, as well as the P-WBOA and OOA profiles. For different parameterisation (i.e., different degrees of relaxation, *a*, for the HOA-profile, ranging from *a*=0.2 to *a*=0.8), coefficients of determination r^2 between the factor profiles and reference profiles were higher than 0.9 for HOA and OOA, and ranged between 0.79 and 0.90 for P-WBOA. Furthermore, Table S2 presents the r^2 values between the factor time series and those of auxiliary data. Relatively similar r^2 values were found for all the different investigated ME-2

parameterisations using 3 factors. However, the degree of relaxation influenced the relative contributions of HOA and P-WBOA, the former varying between 9 and 18% of the total OM mass, whereas the OOA contributions remained at 36-37%. OOA as well as ancillary inorganics (nitrate, ammonium, sulphate in Table S2), representing all particulate species, were all retrieved with the same AMS instrument and all mostly secondarily formed. Therefore, their correlation should be given more weight for the evaluation of the statistical model output than those of ancillary data measured by other instruments. The ME-2 solution at a=0.0 (HOA profile fixed), where OOA showed somewhat weaker correlations with AMS inorganics than the other solutions (a = 0.2, 0.4, 0.6, 0.8), was consequently not considered further. The correlation of NO_x with the HOA series at a=0.2 was comparatively low, whilst relaxing the HOA profile in ME-2 above a=0.4 (to a=0.6, 0.8 or higher) yielded profiles increasingly dissimilar to HOA spectra from the literature. The ME-2 solution at a=0.4 was therefore regarded as the most satisfying solution and used in this work.
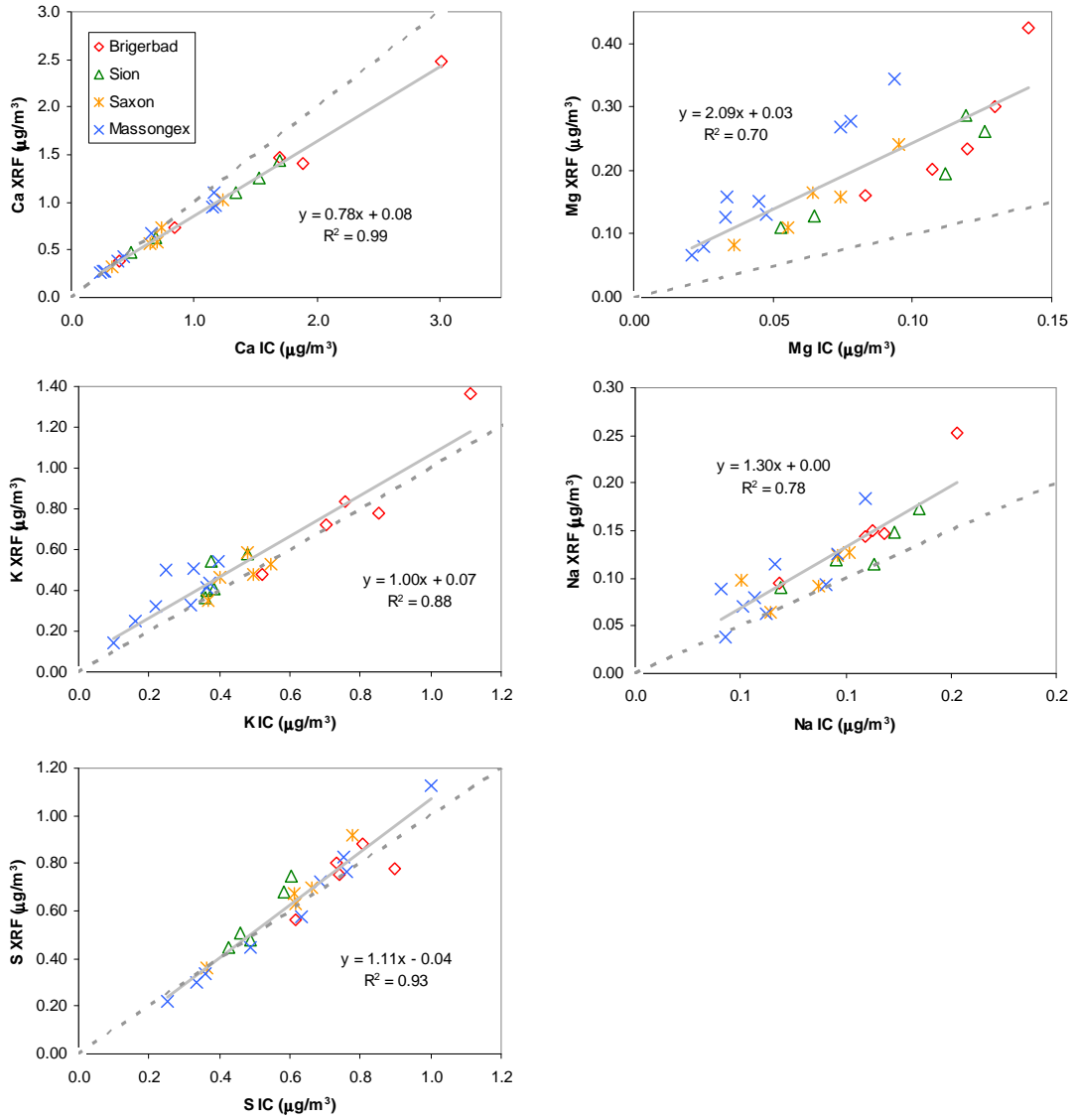
Supplemental material: figure and table

Figure S1

PMF2		NO$_x$	CO	K$^+$	NO$_3^-$	SO$_4^{2-}$	NH$_4^+$	BC$_t$	BC$_{wb}$	%OM
f$_{peak}$=0	**HOA**	**0.62**	**0.65**	0.57	0.43	0.45	0.42	**0.61**	0.61	26%
	P-WBOA	0.36	0.59	**0.67**	0.48	0.43	0.41	0.38	**0.80**	37%
	OOA	0.42	0.52	0.58	**0.58**	**0.60**	**0.53**	0.45	0.55	36%
ME-2										
a=0	**HOA**	**0.62**	0.60	0.48	0.35	0.39	0.35	**0.61**	0.51	12%
	P-WBOA	0.44	**0.64**	**0.69**	0.51	0.47	0.45	0.46	**0.81**	56%
	OOA	0.39	0.48	0.54	**0.56**	**0.59**	**0.52**	0.43	0.50	32%
a=0.2	**HOA**	**0.55**	0.45	0.31	0.23	0.27	0.24	**0.52**	0.31	9%
	P-WBOA	0.43	**0.63**	**0.69**	0.50	0.46	0.44	0.44	**0.81**	54%
	OOA	0.41	0.52	0.58	**0.58**	**0.60**	**0.53**	0.45	0.55	36%
a=0.4	**HOA**	**0.60**	0.54	0.42	0.32	0.36	0.31	**0.58**	0.44	14%
	P-WBOA	0.41	**0.62**	**0.69**	0.50	0.47	0.43	0.43	**0.80**	49%
	OOA	0.45	0.57	0.63	**0.61**	**0.65**	**0.57**	0.48	0.62	36%
a=0.6	**HOA**	**0.62**	0.60	0.49	0.38	0.41	0.37	**0.60**	0.52	18%
	P-WBOA	0.40	**0.61**	**0.68**	0.49	0.45	0.42	0.42	**0.80**	45%
	OOA	0.42	0.52	0.58	**0.58**	**0.60**	**0.53**	0.45	0.55	36%
a=0.8	**HOA**	**0.60**	0.52	0.38	0.31	0.35	0.31	**0.57**	0.39	16%
	P-WBOA	0.38	**0.60**	**0.68**	0.48	0.44	0.42	0.40	**0.80**	47%
	OOA	0.42	0.52	0.58	**0.58**	**0.60**	**0.53**	0.45	0.55	37%

Table S2

Supplemental material: figure and table captions

Fig. S1: Comparison of IC and XRF concentrations for the following elements: Ca, Mg, K, S and Na measured from PM_{10} filters collected at the four stations of Massongex, Saxon, Sion and Brigerbad. The dashed line represents the 1:1 line.

Table S2. For different PMF and ME-2 three-factorial solutions, coefficients of determination (r^2) between the time series of the retrieved factors and those of different chemicals. The last column indicates the source apportionment of PM_1 organic matter (OM) for each solution