Composition and sources of particulate matter in an industrialised Alpine valley

N. Perron\textsuperscript{1}, J. Sandradewi\textsuperscript{1}, M. R. Alfarra\textsuperscript{1,*}, P. Lienemann\textsuperscript{2,**}, R. Gehrig\textsuperscript{2}, A. Kasper-Giebl\textsuperscript{3}, V. A. Lanz\textsuperscript{1}, S. Szidat\textsuperscript{4,5}, M. Ruff\textsuperscript{4}, S. Fahrni\textsuperscript{4,5}, L. Wacker\textsuperscript{6}, U. Baltensperger\textsuperscript{1}, and A. S. H. Prévôt\textsuperscript{1}

\textsuperscript{1}Laboratory of Atmospheric Chemistry, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland
\textsuperscript{2}Swiss Federal Laboratories for Materials Testing and Research (Empa), 8600 Duebendorf, Switzerland
\textsuperscript{3}Institute of Chemical Technologies and Analytics, Vienna University of Technology, Getreidemarkt 9/164-UPA, 1060 Vienna, Austria
\textsuperscript{4}Department of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, 3012 Bern, Switzerland
\textsuperscript{5}Oeschger Centre for Climate Change Research, University of Bern, 3012 Bern, Switzerland
\textsuperscript{6}Institute for Particle Physics, ETH Hönggerberg, 8093 Zürich, Switzerland
Abstract

A three-week long field campaign was carried out under autumnal meteorological conditions at four valley floor sites in the industrialised Swiss Rhone Valley. For one week of stable meteorological conditions, particulate matter with an aerodynamic diameter below 10 µm (PM$_{10}$) was analysed from daily filters using ion chromatography, X-ray fluorescence, anhydrosugars and radiocarbon analysis of the organic and elemental matter (OM and EM, respectively). Furthermore, PM$_1$ composition along the whole campaign was monitored in Massongex (a site near industries) by a seven-wavelength aethalometer and a quadrupole aerosol mass spectrometer (Q-AMS). At all sites, PM$_{10}$ secondary inorganics and non-fossil EM and OM exhibited relatively stable concentrations over the selected days. On the contrary, PM$_{10}$ fossil carbonaceous fractions, mineral dust components and several trace elements showed a significant decrease on Sunday, compared to the analysed working days. Their concentrations were also highly correlated. This evidenced the role of exhaust and resuspension emissions by heavy-duty vehicle traffic to the PM$_{10}$ concentrations along the valley.

In Massongex, organic matter and black carbon (BC) were the main contributors to PM$_1$ over the campaign (accounting for 45% and 18% of PM$_1$, respectively). An optical discrimination of BC highlighted the prevalence of fossil over wood-burning sources. Three types of PM$_1$ organics could be identified by factor analysis: primary wood-burning organic aerosol (P-WBOA) dominated the PM$_1$ carbonaceous fraction, followed by oxygenated organics (OOA) mostly representing secondary organics, and by traffic or possibly industry-related hydrocarbon-like organics (HOA) as the smallest carbonaceous contribution.

Furthermore, unusually high contributions of fine chloride were detected at all sites. They were attributed to ammonium chloride (NH$_4$Cl) in Massongex and represented the only significant component exclusively attributable to industrial emissions.
1 Introduction

Particulate matter with an aerodynamic diameter below 10 µm (PM$_{10}$) corresponds to the size range of particles that can readily penetrate and deposit in the respiratory system, thus being potentially detrimental to human health. Indeed, several studies have evidenced a link between PM$_{10}$ increase and enhanced adverse health effects such as hospitalisation for myocardial infarction (e.g. Miller et al., 2007) or premature mortality (Mokdad et al., 2004). High PM$_{10}$ concentrations can also enhance the sensitivity for other pathologies, foster chronic respiratory diseases and contribute to hinder the development of new-born children’s pulmonary capacity (Latzin et al., 2009). In Switzerland, about 3700 premature deaths per year are imputed to PM$_{10}$, which corresponds to a loss of more than 40 000 years of life (Röösli et al., 2005), or to 6 months of the population life expectancy. Guidelines issued by the WHO recommend maximum PM$_{10}$ concentrations of 50 µg m$^{-3}$ as daily average and 20 µg m$^{-3}$ as yearly average (WHO, 2006). These thresholds have also been adopted by the Swiss legislation since 1998, but are still regularly exceeded in winter time (Barmpadimos et al., 2010). This is particularly true in Alpine valleys, where the topography, the local meteorology and the presence of significant emitters such as traffic and residential wood combustion create potential conditions for intense particulate pollution episodes. In the case of the industrialised Swiss Rhone valley, this is particularly critical, as 60% of the population of the Swiss canton of Valais are exposed to this excessive pollution (Résival, 2006). Therefore, needs for targeted abatement policies are important and require a better knowledge of PM composition and sources. Such source apportionment studies have already been performed in Alpine valleys and have mainly focused on the contribution of the carbonaceous aerosol to particulate pollution, investigating its sources by studying the seasonal variations of organic and elemental carbon (respectively OC and EC) (Aymoz et al., 2007), their respective radiocarbon ($^{14}$C) compositions (Szidat et al., 2007), sometimes combined with on-line aerosol mass spectrometer (AMS) measurements (Alfarra et al., 2007). Aerosol light absorption at different wavelengths...
(Sandradewi et al., 2008a) was also exploited and compared to results of chemical mass balance and factorial analysis of AMS organics (Favez et al., 2010). In this study, the combination of different analytical techniques such as ion chromatography, X-ray fluorescence, liquid chromatography for the determination of anhydrosugars and radiocarbon analyses of OC and EC enabled a detailed characterisation of PM$_{10}$ at four different floor sites along the Swiss Rhone valley. In addition, AMS and aethalometer PM$_1$ measurements at one site allowed an enhanced characterisation of the fine fraction of the PM$_{10}$.

2 Observation area and meteorology

2.1 Measurement area

The campaign was conducted from 22 November to 17 December 2006 in the Swiss Rhone valley. This 1.8 to 3.6-km broad, U-shaped valley stretches over about 80 km and broadens downwards, opening to the Rhone plain between Massongex and Lake Geneva (Fig. 1). Due to its particular topography, this deep valley surrounded by high mountain chains constitutes a specific ventilation and meteorological system, similar to the Mesolcina valley (Prévôt et al., 2000). However, the Rhone valley is more secluded in the Central Alps and the rather frequent foehn conditions lead to a warmer and dryer climate than in the neighbouring regions.

The valley floor hosts most of the population of the Swiss Rhone valley and exhibits also the highest PM$_{10}$ concentrations (Résival, 2006). Therefore, four valley floor stations of the air quality monitoring network of Valais Canton (Résival, 2006) were selected as PM$_{10}$ sampling locations (Table 1). Among them, Massongex is a rural site located a few kilometres away from chemical and petrochemical industries and from the motorway. The station of Saxon is a rural site downwind from industries, between the motorway located 400 m away in the northwest and the cantonal road in the southeast. The station in Sion, the largest city in the valley with 28 000 inhabitants, is installed on
a parking lot in the town centre, close to the big roadways of the city. Last, Brigerbad is a rural site located at a higher altitude and surrounded by industries situated a few kilometres away in the west and the east.

2.2 Meteorological conditions during the campaign

Average temperatures during the campaign ranged from 2.1°C in Brigerbad to 6.4°C in Massongex, where temperatures below 0°C were seldom observed.

At all stations, the campaign divides into two kinds of meteorological periods (Fig. 2): the first and third complete weeks were characterised by stable meteorological conditions including rather low temperatures, higher PM$_{10}$ concentrations as well as weak winds (typically less than 2 m s$^{-1}$ wind speed at 2 m above ground level) showing no consistent direction. The second week experienced higher wind speeds and temperatures, as well as lower PM$_{10}$ concentrations.

Due to the stable meteorological conditions characterising the week of 27 November to 3 December 2006 at all sites, the high PM$_{10}$ concentrations can be regarded as resulting mainly from locally produced aerosols. Consequently, five days of this week (further related to as “week 1”) were selected for PM$_{10}$ analyses: Tuesday, Wednesday and Friday to Sunday (28 and 29 December, 1–3 December 2006). Additional filters, corresponding to 26 and 27 November and 5 December 2006 were analysed for Massongex.

3 Instrumentation

3.1 Sampling methodology

PM$_{10}$ aerosols were collected at the four stations on a 24 h-basis (from midnight to midnight) on pre-heated (8 h at 900°C) quartz-fibre filters (Pall 2500 QAT-UP; Pallflex Products Co., USA, 150 mm diameter) with high-volume samplers (DHA-80, Digitel...
Elekronik AG, Hegnau, Switzerland – about 30 m³/h flow rate). After sampling, the filters were wrapped in aluminium foils, packed into air-tight polyethylene bags and stored at -20 °C for later off-line analyses (Table 2).

To characterise the PM₁₀ fraction, additional instruments were set up in Massongex (Table 2): a Rupprecht and Patashnick TEOM Series 1400a real-time monitor heated at 30 °C, an Aerodyne quadrupole aerosol mass spectrometer (Q-AMS, Canagaratna et al., 2007) and a seven-wavelength aethalometer (AE31, Magee Scientific). They were operated in a temperature-controlled measurement container located by the monitoring station on the fringe of the village.

Additional meteorological parameters such as ambient temperature, ambient pressure, ambient relative humidity, wind speed and directions, as well as air quality data including CO, NO, NO₂, O₃, SO₂ and PM₁₀ concentrations were also continuously monitored and recorded by the Environmental Protection Agency of the Canton Valais at the four measuring sites. A list of the corresponding analytical methods can be found in their annual report (Résival, 2006).

3.2 PM₁₀ analyses

3.2.1 PM₁₀ concentrations

At all stations, the PM₁₀ total mass was measured using a beta-meter (Thermo Electron FHT 62-IR). This instrument contains a small ¹⁴C beta source coupled to a sensitive detector that counts the emitted beta particles. The beta ray transmission across a filter tape is measured before and after particulate matter collection on this filter section and the difference converted to a particulate concentration by calibration with PM₁₀ weighted filters.
3.2.2 Radiocarbon analyses ($^{14}$C) of organic and elemental matter

Carbonaceous species are traditionally divided into two fractions: organic carbon (OC) and elemental carbon (EC) or black carbon (BC). The two different names given to the latter fraction depends on whether its analysis relies on its thermal refractivity (EC) or on its strong light absorption properties (BC), thus leading to possible discrepancies.

The radiocarbon signatures of OC and EC for the selected PM$_{10}$ filters were investigated, according to the method described in Szidat et al. (2006). For each sample OC was removed from one filter punch by oxidation in pure O$_2$ at 340°C, and EC was combusted at 650°C from two additional filter punches after removal of the OC by water extraction and oxidation in air at 375°C during 4 h (Szidat et al., 2004). For each type of sample, the resulting CO$_2$ was trapped cryogenically and stored in sealed glass ampoules for later off-line analysis, using the gas ion source of the accelerator mass spectrometer MICADAS (Ruff et al., 2007). Average recoveries for OC and EC amounted to 80% and 60%, respectively, of the masses measured by the OC/EC analyser. The recovered material was assumed to be representative of the whole fraction and therefore to present a similar radiocarbon signature. Results of the $^{14}$C measurements were expressed in fractions of modern carbon (fM), which corresponds to the $^{14}$C/$^{12}$C ratios of the samples normalised to that of the reference year 1950 (Stuiver and Polach, 1977). The carbonaceous aerosol was considered as stemming either from fossil (f), or from biogenic (bio) and wood-burning (wb) sources, associated to the following fM values: fM$_f$=0, fM$_{bio}$=1.055 and fM$_{wb}$=1.16±0.05 (Szidat et al., 2009).

Using the measured fM's, the EC and OC concentrations deduced from EC/OC off-line analyses with a Sunset EC/OC analyser (Bae et al., 2004) and a modified NIOSH thermal program (Birch and Cary, 1996) were apportioned to their respective fossil and non-fossil parts EC$_f$, EC$_{wb}$, OC$_f$ and OC$_{nf}$. The latter was regarded as a 50%/50% mix of biogenic and biomass-burning sources, furthering the absence of more detailed information. If all non-fossil carbon were assumed to stem from wood burning, this would lower down the determined OC$_{nf}$ concentrations by 5%.
The above mentioned carbon fractions were then converted to their respective total aerosol mass by using conversion ratios. \((\text{OM/OC})_{nf}=1.7\) and \((\text{OM/OC})_f=1.5\) were estimated from Aiken et al. (2008), considering that non-fossil OM consists of a mix of primary wood-burning emission and secondary non-fossil organic aerosol, but less aged than in Mexico, whereas fossil OM contains primary and secondary fossil organics. Furthermore, \((\text{EM/EC})=1.1\) was used for both fossil and non-fossil sources.

### 3.2.3 Anhydrosugars (levoglucosan, mannosan)

Biomass burning induces high emissions of anhydrosugars resulting from the thermal degradation of structural biomass polysaccharides. Resulting from the pyrolysis of cellulose, levoglucosan is the most abundantly emitted anhydrosugar and has been widely used as a tracer of biomass burning (Simoneit et al, 1999; Fraser et al., 2000). Its emissions are followed in importance by those of mannosan (Caseiro et al., 2009; Schmidl et al., 2008), produced by the pyrolysis of hemicellulose.

In this study, anhydrosugar analysis was performed by sonicating in Milli-Q water 21-mm diameter punches of the selected PM$_{10}$ HiVol filters and by analysing the aqueous extract with a high-pressure liquid chromatography (HPLC) column for carbohydrate separation (Puxbaum et al., 2007; Caseiro et al., 2007).

### 3.2.4 Major ions and trace metals

To analyse major ions \((\text{Cl}^-, \text{NO}_3^-, \text{SO}_4^{2-}, \text{Na}^+, \text{NH}_4^+, \text{K}^+, \text{Mg}^{2+} \text{and Ca}^{2+})\), 25-mm diameter punches of the selected PM$_{10}$ filter were placed in 50 mL milli-Q water, agitated and then left overnight (about 12 h) before being agitated once again. The resulting extract was then filtered and analysed with ion chromatography (IC).

The selected filters also provided 40 mm-diameter punches used to analyse the following elements: Pb, Zn, Cu, Ni, Fe, Mn, Cr, Ca, K, S, P, Al, Mg, and Na by wavelength dispersive X-ray fluorescence spectrometry (WD-XRF) (Gehrig et al., 2007). The XRF technique measures the total amount of each element, whereas IC deter-
mines water-soluble species. For most of the elements measured by both analytical techniques, such as S (measured as sulphate by IC), K, Na, and Ca, high correlations with slopes between 0.78 and 1.30 were found between both methods (Fig. S1 in the supplementary material, see http://www.atmos-chem-phys-discuss.net/10/9391/2010/acpd-10-9391-2010-supplement.pdf), indicating a reasonable agreement between the two techniques, and that these species were mainly in a water-soluble form. On the contrary, the Mg concentrations for XRF were twice as high as for IC and the correlation was lower, due probably to a lower water-soluble fraction. Further evaluation of the total PM\textsubscript{10} composition was performed by using XRF-deduced concentrations.

Due to the use of quartz-fibre filters as a collection medium, Si could not be detected in the SiO\textsubscript{2} matrix, therefore a ratio Si/Al of 3.41 was applied to estimate the Si concentrations from those of Al, as already done by Hueglin et al. (2005) for other sites in Switzerland.

Elements Al, Mg, Ca, Fe, Si and K were assumed to stem mainly from mineral dust, the mass concentration of which was estimated by considering these metals as oxides (Chow et al., 2002; Hueglin et al., 2005; Marenco et al., 2006). Therefore, the metal mass concentrations were scaled to those of the associated oxides using the equation:

\[
[\text{Mineral dust}]=1.89[\text{Al}]_{\text{tot}}+1.66[\text{Mg}]_{\text{tot}}+1.40[\text{Ca}]_{\text{tot}}+1.43[\text{Fe}]_{\text{tot}}+2.14[\text{Si}]_{\text{tot}}+1.21[\text{K}]_{\text{tot}}.
\]

### 3.3 PM\textsubscript{1} analyses

#### 3.3.1 Aethalometer-based source apportionment of BC

The multi-wavelength aethalometer equipped with a PM\textsubscript{1} inlet delivered PM\textsubscript{1}-BC concentrations measured at 880 nm as well as attenuation coefficient \(b_{\text{ATN}}\) of the sampled aerosol at 370, 470, 550, 520, 590, 660, 880 and 950 nm. Since the raw \(b_{\text{ATN}}\) values correspond to filter-deposited particles, they are biased by multiple scattering of the light within the filter fibres and by the “shadowing” effect occurring at high filter loads. These artefacts were corrected according to the procedure described by Weingartner...
et al. (2003) to yield the absorption coefficients, \( b_{\text{abs}} \), corresponding to airborne particles.

In winter, the ambient fine light-absorbing aerosol fraction present in Switzerland (where no combustion of coal is performed) can be regarded as resulting from two main contributions: the brown-carbon-rich (Andreae and Gelencsér, 2006; Lukács et al., 2007; Alexander et al., 2008) aerosol emitted by biomass burning (Reid et al., 2005) on the one hand and the fossil fuel combustion aerosol (including mostly traffic, but also industry and heating oil) on the other hand. Mineral dust, which can also absorb light (Moosmüller et al., 2009), was neglected because it is mostly absent from the submicron mode and likely negligible in absolute light absorption coefficient concentrations values.

Relying on the work by Sandradewi et al. (2008b), we calculated the absorption coefficients for both sources at 470 and 950 nm, using the following Ångström absorption exponents: \( \alpha_{\text{wb}}=1.86 \), empirically determined by Sandradewi et al. (2008b) for wood burning during winter campaigns in a Swiss Alpine valley, and \( \alpha_{\text{t}}=1 \) for the traffic source.

BC measurements were performed at 880 nm, where it is considered to be the only light absorber, by converting the retrieved \( b_{\text{abs}}(950) \) to \( b_{\text{abs}}(880) \) with the following equation:

\[
\frac{b_{\text{abs}}(880)_t}{b_{\text{abs}}(950)_t} = \left(\frac{880}{950}\right)^{-\alpha_{\text{t}}} \tag{1}
\]

This allowed to calculate the contribution of both sources to BC by considering:

\[
\text{BC}_t = \frac{b_{\text{abs}}(880)_t}{b_{\text{abs}}(880)} \ast \text{BC} \tag{2}
\]

and:

\[
\text{BC}_{\text{wb}} = \text{BC} - \text{BC}_t \tag{3}
\]
3.3.2 AMS and aethalometer source apportionment of PM$_1$ organics

The non-refractory fraction of the sub-micrometer aerosol includes OM, NO$_3^-$, SO$_4^{2-}$, NH$_4^+$ and Cl$^-$, which were analysed with on-line aerosol mass spectrometry (Q-AMS). Because part of the mass of the sampled aerosol bounces off the AMS heater and is therefore not measured (Alfarra et al., 2004), a collection efficiency (CE) is applied to the AMS measurements to yield the absolute concentrations. In our case, the CE was determined by comparing the sum of the AMS and aethalometer measurements (OM + NO$_3^-$ + SO$_4^{2-}$ + NH$_4^+$ + Cl$^-$ + BC) with the total PM$_1$ concentrations provided by the TEOM. A good agreement between the two datasets was found when applying a CE of 0.5 (see Sect. 4.2.1).

The different sources or components of AMS organics were investigated by applying factor analytical modelling – more specifically, positive matrix factorisation (Paatero and Tapper, 1994) and the multilinear engine (Paatero, 1999) – to the organic aerosol mass spectra (Lanz et al., 2007, 2008).

4 Results and discussion

4.1 PM$_{10}$ composition

4.1.1 Total mass

From 27 November to 3 December 2006, Brigerbad exhibited the highest average PM$_{10}$ concentrations (~60 µg m$^{-3}$) whereas the other three stations exhibited equivalent amounts (~40 µg m$^{-3}$). The PM$_{10}$ compositions for the corresponding three working days (Tuesday, Wednesday and Friday) and Sunday are presented in Fig. 3. PM$_{10}$ on Saturday exhibited an intermediate composition between the working days and Sunday and is not shown here. Compositions of PM$_{10}$ at all stations showed rather similar patterns. In all cases, the carbonaceous aerosol and especially the non-fossil OM were
dominant, the latter representing 19 to 31% of the total PM$_{10}$ on the working days and 35 to 42% on the Sunday. As expected, the city centre site of Sion exhibited the highest fossil contributions to OM and EM, and was followed by Brigerbad, whereas Saxon and Massongex showed lower fossil contributions to OM and EM. A significant part of the PM$_{10}$ mass was also constituted by the secondary inorganics, which represented 11 to 20% of the PM$_{10}$ on the working days and 27 to 37% on Sunday. Additionally, chloride contributed also noticeably to PM$_{10}$ (up to 12%).

At all sites, a significant fraction ranging from 11 to 29% remained unaccounted on the working days, and was lower on Sunday (Table 3). Several studies (e.g. Putaud et al., 2004; Hueglin et al., 2005) stated that the remaining unaccounted mass fraction typically represents 30% of the total PM$_{10}$, when considering an OM/OC of 1.4. This remainder is thought to result from aerosol-bound water and from random and possibly systematic errors, including too low OM/OC ratios.

### 4.1.2 Traffic-related emissions

The lower concentrations measured on the Sunday concern notably OM$_{f}$ and EM$_{f}$, which were approximately cut by half between the considered working days and Sunday at all stations, whereas no such trend was observed for the non-fossil OM and EM (Table 3).

The stable meteorological conditions recorded during week 1 as well as the constancy of the biomass-burning EM concentrations at all sites suggests that meteorology played a negligible role for the PM$_{10}$ fluctuations during this period. Therefore, variations in PM$_{10}$ observed on the different days result mainly from the variations of the intensities in emissions or secondary formation processes.

In this case, the reduction of the carbonaceous PM by up to 26% on Sunday 3 December 2006 compared to the working days can be attributed to a reduction of the fossil source emissions. The ban on dominical truck circulation imposed by the Swiss legislation is more likely to cause such a drop than the variations of emissions from oil refineries, which keep some activity also on Sundays. This indicates a significant
influence of traffic on PM$_{10}$ emissions all along the valley during working days and highlights the importance of heavy-duty traffic in the fossil emissions.

The elements Cu, Zn and Mn stem to some extent from brake abrasion, tyre wear (Thorpe and Harrison, 2008 and references therein) and fossil fuel combustion (Pacyna and Pacyna, 2001), respectively. This explains why they are highly correlated with EM$_f$ (Table 4). High correlations with EM$_f$ were also observed for the crustal elements (such as Ca, Mg, Fe, and Al) associated with mineral dust, and for Na, possibly coming from the salt sprinkled on the roads for deicing or from natural sources (Fig. 4). Similarly to EM$_f$, all these species showed also a dominical decrease in concentrations, compared to the working days.

The interpretation that working day traffic is the main reason for the enhanced concentrations of Ca, Mg, Fe, Al, and Na is also supported by the low correlations between these elements and EM$_{wb}$ on the one hand, and between EM$_f$ and the mainly secondary species NH$_4^+$, NO$_3^-$ and SO$_4^{2-}$ on the other hand. This is consistent with the findings of Gehrig et al. (2004) that road traffic represents a significant source of abrasion and resuspension-induced PM$_{10}$. Moreover, Bukowiecki et al. (2010) showed that resuspension due to trucks is much more important than for gasoline cars, providing an explanation for this pattern. We expect the traffic dependence in this Alpine valley to be especially important during low-wind conditions like in week 1, because higher wind speed could cause considerable resuspension of crustal particles in the air, masking the effect due to traffic.

### 4.1.3 Wood-burning emissions

At all stations, non-fossil OC concentrations remained relatively constant over the whole week (Table 3). To assess the primary wood-burning contribution OC$_{nf}$, the anhydrosugar (levoglucosan and mannmosan) concentrations were compared to OC$_{nf}$ concentrations (Fig. 5). Slope values of the scatterplots amount to 3.5 for levoglucosan and 29.1 for mannmosan (Fig. 5). The slope for the former plot is lower than most OC/levoglucosan emission ratios compiled by Puxbaum et al. (2007), who recommend...
a value of 7.35 for the Alpine region. The lower value found in our case suggests other origins of non-fossil OC than primary wood-burning. It could be partly due to the fact that wood-burning exhaust can produce significant additional secondary organic mass within a few hours of aging (Grieshop et al., 2009). However, the intercepts of \( \sim 3.4 \mu g \text{cm}^3 \) OC\(_{nf}\) found in Fig. 5 in the absence of anhydrosugars supports the contribution of other OC\(_{nf}\) sources, such as secondary production from biogenic gaseous precursors, but also resuspension of primary biological particles. In our case, applying a OC/levoglucosan ratio of 7.35 led to wood-burning OC concentrations exceeding those of OC\(_{nf}\). Considering a lower range value of 6 as proposed by Gelencsér et al. (2007) was more realistic and yielded wood-burning contributions to OC of 63–100% for Massongex, 80–100% for Saxon, 39–50% for Sion and 70–75% for Brigerbad.

### 4.1.4 Other sources and summary for PM\(_{10}\) contributions

As pointed out earlier, industry-related Zn was observed in Saxon. Particulate Cl\(^-\) concentrations exceeding by far those of Na\(^+\) and therefore originating from other sources of chloride than NaCl suggested additional emissions of industrial origin. In Fig. 6, the PM\(_{10}\) source apportionment averaged for the four stations is presented for the working days and the Sunday. It highlights the strong reduction of traffic-related aerosol sources such as dust resuspension and carbonaceous fossil emissions on the one hand, and the stability of the concentrations of non-fossil carbonaceous aerosol, which includes wood burning. Although this picture has been drawn using only one week of data, it has been found to be consistent at the four sites along the Swiss Rhone Valley.

### 4.2 PM\(_1\) chemical composition

#### 4.2.1 Validation of the AMS collection efficiency (CE)

The right-hand panel of Fig. 7 shows a scatterplot of the PM\(_1\) total mass concentration measured by the TEOM and from the sum of BC and AMS total mass concentrations
using a CE value of 0.5. A good agreement between both methods is noted, thus validating the choice of CE=0.5. The lower agreement observed for the days with lowest PM$_1$ loadings stems probably from the lack of accuracy and precision of the TEOM at low concentrations. Since NH$_4^+$ belongs exclusively to PM$_1$, the consistency between NH$_4^+$ concentrations from PM$_{10}$ filters and from 24-h-averaged AMS values (slope=0.9, $r^2=0.97$, 9 samples) provided an additional support to the choice of the CE value.

4.2.2 PM$_1$ general composition during the week 1

The PM$_1$ average mass amounted to 11.4 µg m$^{-3}$ over the whole campaign and to 16.9 µg m$^{-3}$ during the identified week 1. This lies in the lower range of concentrations measured in Switzerland during winter (Lanz et al., 2009). Indeed, the relatively high temperatures (−2 to 22°C) observed during this campaign prevented the formation of strong inversions and the subsequent accumulation of high aerosol concentrations. In Fig. 8, the average PM$_1$ compositions for the working days and the Sunday of week 1 confirm the dominical increase in the relative contribution of BC and secondary inorganics already noticed in PM$_{10}$. Note that the working days included only the 27 and 28 November 2006 and 1 December 2006 here, due to the lack of AMS data during part of the 29 November 2006. However, the composition for the working days was close to the average composition for the whole campaign. Sunday 3 December 2006, on the contrary, differed from the average composition on the three Sundays, which did not show much difference compared to the average composition on the working days. The difference between working days and Sunday on week 1 was probably due to the enhanced presence of locally emitted PM$_1$.

4.2.3 Fine carbonaceous aerosol source apportionment

Sources of organics in Massongex were investigated by factor analysis of the AMS organics mass spectra (FA-AMS) (Lanz et al., 2007; Ulbrich et al., 2009). Up to
three factors could be related to meaningful organic aerosol (OA) sources, namely hydrocarbon-like OA (HOA), primary OA from wood burning (P-WBOA), and oxygenated (mostly secondary) OA (OOA) (see the discussion and Table S2 in the supplementary material, see http://www.atmos-chem-phys-discuss.net/10/9391/2010/acpd-10-9391-2010-supplement.pdf). The most satisfying solution was obtained using the multilinear engine (ME-2: Paatero, 1999) with a degree of variability $a=0.4$ (see Lanz et al. (2008) for a discussion of $a$). This solution led to average OA contributions of 14% (9–18%) for HOA, 49% (45–54%) for P-WBOA and 36% (36–37%) for OOA, with the uncertainty ranges encompassing the different ME-2 solutions between $a=0.2$ and $a=0.8$ (see supplementary material). Combining the $a=0.4$ solution with the $^{14}$C results suggested that 40% of the OOA was fossil. This is comparable to the 31% found by Lanz et al. (2008) during a winter campaign at an urban background site in Zurich.

Times series of the identified OA factors, together with BC$_{wb}$ and BC$_{t}$, and their relative contributions to the PM$_{1}$ carbonaceous aerosol on the selected working days and on the Sunday are presented in Fig. 9. PM$_{1}$ carbonaceous concentrations are very similar for both the working days and the Sunday, due to the fact that the enhanced wood-burning emissions of BC and primary organics as well as the OOA production compensate the reduction in fossil emissions, especially of BC$_{t}$.

Average diurnal cycles of the retrieved organic components are presented in Fig. 10, along with the diurnal cycles of gaseous and particulate species. Two main concentration enhancements, one in the morning (around 06:00 a.m.–11:00 a.m. LT) and in the evening (03:00 p.m.–09:00 p.m. LT) characterise the daily cycles of HOA, NO$_{x}$ and BC$_{t}$ and likely correspond to the traffic rush hours with low vertical dilution. An additional contribution of domestic fuel heaters in the evening might be speculated. In contrast, P-WBOA, AMS-potassium and BC$_{wb}$ show only one main increase between 04:00 p.m. and 03:00 a.m. LT. Similarly to what observed in other wood-burning-dominated locations, this probably corresponds to the increased use of domestic wood heaters in the evening (Alfarra et al., 2007; Sandradewi et al., 2008a; b; Krecl et al., 2008). The fact that, despite being determined independently, the daily patterns of HOA and BC$_{t}$
are similar, the same being true for P-WBOA and BC\textsubscript{wb}, validates the FA-AMS and aethalometer-based methods as source apportionment tools to discriminate between the fossil and biomass-burning sources of fine organics and BC, respectively. Further comparison of these results with those from the \textsuperscript{14}C analyses will be discussed in another paper (Perron et al., 2010).

The OOA diurnal cycles correlate well with those of AMS nitrate and sulphate, displaying two peaks. The first one in the beginning of the afternoon probably corresponds to the maximal light intensity, which is around 01:00 p.m. LT in winter, and to a correspondingly enhanced photochemistry. The second one might be linked to the night-time oxidation (e.g. by the NO\textsubscript{3} radical) of the organics emitted in the evening. However, the enhanced OOA concentrations in the evening may also partially stem from primary wood-burning emissions, which during the smouldering phase in the later evening can exhibit organic mass spectra that are similar to OOA (Weimer et al., 2008).

### 4.2.4 Chloride

In Fig. 11, the chloride concentrations deduced from IC on PM\textsubscript{10} filters and from AMS measurements of the PM\textsubscript{1} aerosol show a good agreement, indicating that the high amount of chloride mentioned in Sect. 4.1.4 is overwhelmingly coming from the fine mode. AMS NH\textsubscript{4}\textsuperscript{+} concentrations and the total anion concentrations – i.e. Cl\textsuperscript{-} + NO\textsubscript{3}\textsuperscript{-} + SO\textsubscript{4}\textsuperscript{2-} – display very similar time series, the Cl\textsuperscript{-} excess peaks following exactly those of ammonium. Consequently, the presence of submicron chloride is likely to result from the neutralisation of HCl by gaseous ammonia (NH\textsubscript{3}). No PM\textsubscript{1} measurements were performed at the other stations; nevertheless it might be possible that the high PM\textsubscript{10} chloride measured in Saxon, Sion and Brigerbad result from similar processes. Chloride may stem from incineration of domestic and industrial waste (Kaneyasu et al., 1999), or from other industrial sources, which needs further investigation.
5 Conclusions

PM$_{10}$ composition investigated at four valley-floor stations along the Swiss Rhone valley during a week of stable meteorological conditions appeared to be very similar at all sites. On working days, PM$_{10}$ concentrations ranged between 25 and 82 µg m$^{-3}$ and were dominated by carbonaceous matter (28–38% OM and 6–9% EM of the PM$_{10}$), followed by secondary inorganics (10 to 18%) and mineral dust in about equal proportions (13 to 18%). During these days, PM$_{10}$ was mainly influenced by wood burning on the one hand and by heavy-duty traffic on the other hand. The latter source included direct exhaust emissions as well as resuspension of non-exhaust particles, and was reduced by about two thirds on the following Sunday. In Massongex, at the entrance of the valley, the PM$_{1}$ aerosol as measured by an AMS and a seven-wavelength aethalometer during this week and the following two weeks consisted of organics (45%), secondary inorganics (33%), and black carbon (18%). The latter stemmed mainly from traffic sources, whereas the submicron OM was composed of primary wood-burning organic aerosol (P-WBOA, 45–54%), followed by oxygenated organics (OOA, 36–37%), and by traffic or industry-related hydrocarbon-like organics (HOA, 9–18%) as the smallest contribution. A significant contribution of chloride (up to 12% of PM$_{10}$) was also detected at all sites and appeared in Massongex to most probably result from so far unidentified HCl emissions neutralised by NH$_3$. Public health protection would require further investigation of this source and should moreover focus on curtailing the heavy-duty traffic and biomass burning emissions.

Acknowledgements. This work was financially supported by the Canton of Valais, by the Swiss Federal Office for the Environment and by the EU project EUCAARI. We thank Pierre-Alain Moulin and François Coquoz from the Environmental Office of the Valais Canton for providing us with the continuous monitoring data and with some general information about the Swiss Rhone Valley. Gratitude is also expressed to René Richter and Markus Furger for their help during the campaign.
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Table 1. Description of the four sampling sites: coordinates, altitudes (meter above sea level, m a.s.l.), site characteristics and traffic intensity.

<table>
<thead>
<tr>
<th>Coordinates</th>
<th>Massongex (MAS)</th>
<th>Saxon (SAX)</th>
<th>Sion (SIO)</th>
<th>Brigerbad (BRI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Massonege</td>
<td>46°14′35″ N, 6°08′06″ E</td>
<td>46°08′24″ N, 7°08′57″ E</td>
<td>46°13′57″ N, 7°21′24″ E</td>
<td>46°17′58″ N, 7°55′02″ E</td>
</tr>
<tr>
<td>Altitude</td>
<td>400 m a.s.l.</td>
<td>460 m a.s.l.</td>
<td>505 m a.s.l.</td>
<td>650 m a.s.l.</td>
</tr>
<tr>
<td>Rural zone</td>
<td>Rural zone</td>
<td>Rural zone</td>
<td>Town centre</td>
<td>Rural zone</td>
</tr>
<tr>
<td>Industrial proximity</td>
<td>Industrial proximity</td>
<td>Exposed to traffic</td>
<td>Exposed to traffic</td>
<td>Exposed to traffic</td>
</tr>
<tr>
<td>Traffic</td>
<td>Medium</td>
<td>Intense</td>
<td>Medium</td>
<td>Medium</td>
</tr>
</tbody>
</table>

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Table 2. Instruments and analytical techniques used during the campaign.

<table>
<thead>
<tr>
<th>Instrument/Method</th>
<th>Instrument/Method characteristics</th>
<th>Parameters</th>
<th>Time resolution</th>
<th>Inlet</th>
<th>Stations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerosol mass spectrometer (AMS)</td>
<td>Aerodyne Research Inc., Massachusetts, USA Described in Canagartha et al., 2007.</td>
<td>Cl(^+), NO(_3)^{2-}, SO(_4)^{2-}, NH(_4)^+, organic mass in PM(_1).</td>
<td>5 min</td>
<td>PM(_1)</td>
<td>Massongex</td>
</tr>
<tr>
<td>Aethalometer</td>
<td>Magee Scientific, USA, type AE31 Described in Hansen et al., 1984.</td>
<td>BC, aerosol light absorption coefficients at 370, 470, 520, 590, 660, 880, and 950 nm.</td>
<td>2 min</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TEOM</td>
<td>Rupprecht &amp; Pataschnick Co., Inc., USA, Series 1400a.</td>
<td>Particle mass.</td>
<td>30 min</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hi-Vol filters</td>
<td>DIGITEIL Elektronik AG, Switzerland, type DHA-80, 30 m(^3)/h.</td>
<td></td>
<td>24 h</td>
<td>PM(_{10})</td>
<td>Massongex, Saxon, Sion, Brigerbad</td>
</tr>
<tr>
<td>Off-line thermo-optical OC/EC</td>
<td>Sunset Laboratory, Inc., USA, type RT-3080/NIOSH-like protocol.</td>
<td>OC/EC.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(^{14})C analysis</td>
<td>Described in Szidat et al., 2004, 2006.</td>
<td>Fossil/non-fossil OC and EC.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ion chromatography</td>
<td>Described in the EMEP manual for sampling and chemical analysis: <a href="http://tarantula.nilu.no/projects/ccc/manual">http://tarantula.nilu.no/projects/ccc/manual</a>.</td>
<td>Ions: Cl(^+), NO(_3)^{2-}, SO(_4)^{2-}, Na(^+), NH(_4)^+, K(^+), Mg(^{2+}), Ca(^{2+}).</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>X-ray fluorescence</td>
<td>Described in Gehrig et al., 2007.</td>
<td>Elements: Pb, Zn, Cu, Ni, Fe, Mn, Cr, Ca, K, S, P, Al, Mg, Na.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HPLC/ICs 3000</td>
<td>Described in Caseiro et al., 2007.</td>
<td>Anhydrosugars.</td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>
Table 3. Absolute concentrations (right) and relative contributions normalised to the total PM$_{10}$ mass concentrations (left) for the analysed PM$_{10}$ components at Massongex, Saxon, Sion and Brigerbad. “Working days” correspond to the average for the days 27 and 28 November and 1 December 2006, and “Sunday” represents the 3 December 2006. The rest was calculated as the difference between the PM$_{10}$ concentrations given by the beta-meter and the sum of the identified components. b.d.l. stands for “below detection limit”.

<table>
<thead>
<tr>
<th>PM$_{10}$ concentrations (µg m$^{-3}$)</th>
<th>Contributions to PM$_{10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Massongex Working days</td>
<td>Sunday Working days</td>
</tr>
<tr>
<td>PM$_{10}$</td>
<td>40.23</td>
</tr>
<tr>
<td>EM$_{tot}$</td>
<td>7.0%</td>
</tr>
<tr>
<td>OM$_{tot}$</td>
<td>12.26</td>
</tr>
<tr>
<td>EM</td>
<td>30.5%</td>
</tr>
<tr>
<td>EM$_{wb}$</td>
<td>5.3%</td>
</tr>
<tr>
<td>OM</td>
<td>2.89</td>
</tr>
<tr>
<td>OM$_{wb}$</td>
<td>23.3%</td>
</tr>
<tr>
<td>CL</td>
<td>23.9%</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>0.10</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>1.89</td>
</tr>
<tr>
<td>NH$_4$</td>
<td>1.01</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>2.5%</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>2.6%</td>
</tr>
<tr>
<td>MgO</td>
<td>4.5%</td>
</tr>
<tr>
<td>CaO</td>
<td>1.6%</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>1.6%</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>1.6%</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>1.6%</td>
</tr>
<tr>
<td>Pb</td>
<td>6.5%</td>
</tr>
<tr>
<td>Zn</td>
<td>0.06%</td>
</tr>
<tr>
<td>Cu</td>
<td>0.01%</td>
</tr>
<tr>
<td>Ni</td>
<td>0.00%</td>
</tr>
<tr>
<td>Cr</td>
<td>0.13%</td>
</tr>
<tr>
<td>Mn</td>
<td>0.00%</td>
</tr>
<tr>
<td>P</td>
<td>0.00%</td>
</tr>
<tr>
<td>Rest</td>
<td>23.7%</td>
</tr>
</tbody>
</table>
Table 4. Pearson correlation coefficients ($r$) between the respectively fossil and non-fossil fractions of EM (EM$_f$ and EM$_{wb}$) and the other identified PM$_{10}$ components for the four stations taken together ($n=23$ samples). Significant correlations are indicated in bold with the following levels of confidence $\alpha$: 99%<$\alpha$<99.9%$^a$, $\alpha$>99.9%$^b$. * The station of Saxon was dismissed owing to local emissions of Zn from a galvanization plant 5 km upwind from the station ($n=18$ remaining samples). ** The station of Massongex was dismissed ($n=15$ remaining samples). Correlation coefficients including Massongex amount to $r=0.63$ between EM$_f$ and Mg and to $r=0.58$ between EM$_f$ and Al, respectively (95%<$\alpha$<99% for both). However, no industrial sources of Al and Mg could be clearly identified around Massongex.

<table>
<thead>
<tr>
<th></th>
<th>OM$_f$</th>
<th>OM$_{wb}$</th>
<th>Cl$^-$</th>
<th>NO$_2$</th>
<th>SO$_4^{2-}$</th>
<th>NH$_4^+$</th>
<th>Ca</th>
<th>Al$^{**}$</th>
<th>Mg$^{**}$</th>
<th>Fe</th>
<th>Na</th>
<th>K</th>
<th>Cu</th>
<th>Zn$^{*}$</th>
<th>Mn</th>
<th>Cr</th>
<th>Ni</th>
<th>P</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>EM$_f$</td>
<td>0.92$^b$</td>
<td>0.39</td>
<td>0.23</td>
<td>–0.02</td>
<td>0.42</td>
<td>0.03</td>
<td><strong>0.90</strong>$^b$</td>
<td><strong>0.88</strong>$^b$</td>
<td><strong>0.86</strong>$^b$</td>
<td><strong>0.72</strong>$^b$</td>
<td>0.53$^a$</td>
<td>0.88$^b$</td>
<td><strong>0.86</strong>$^b$</td>
<td><strong>0.82</strong>$^b$</td>
<td>0.68$^b$</td>
<td>0.64$^b$</td>
<td>0.58$^b$</td>
<td>0.43</td>
<td></td>
</tr>
<tr>
<td>EM$_{wb}$</td>
<td>0.38</td>
<td><strong>0.91</strong>$^b$</td>
<td>0.24</td>
<td>0.48</td>
<td>0.49</td>
<td>0.35</td>
<td>0.31</td>
<td>0.07</td>
<td>0.15</td>
<td>0.41</td>
<td>0.25</td>
<td>0.48</td>
<td>0.45</td>
<td>0.44</td>
<td>0.37</td>
<td>0.23</td>
<td>–0.08</td>
<td>0.38</td>
<td>0.07</td>
</tr>
</tbody>
</table>
Fig. 1. Geographical situation within Switzerland (left) and within the Canton Valais (right) of the four PM$_{10}$ sampling sites on the floor of the Swiss Rhone valley: Massongex (MAS), Saxon (SAX), Sion (SIO) and Brigerbad (BRI). ©2009 Swisstopo (JD082777).
Fig. 2. 24 h-averaged temperatures (top panel) and PM$_{10}$ concentrations (bottom panel) at the four valley floor stations (Massongex, Saxon, Sion and Brigerbad) during the campaign.
**Fig. 3.** PM$_{10}$ compositions at the four stations, averaged for the working days 27 and 28 November and 1 December 2006 (left), and on Sunday 3 December 2006 (right). The metals likely to belong to mineral dust were considered as oxides. The following carbon-to-total mass ratios were considered: $(OM/OC)=1.5$ and $1.7$ for fossil and non-fossil organics, respectively, and $EM/EC=1.1$ for both fossil and non-fossil EC.
Fig. 4. Comparison of fossil EM (EM_f) with Ca (left) and Na (right) concentrations measured by XRF at the four stations.
Fig. 5. Comparison of anhydrosugars and $^{14}$C-deduced non-fossil OC concentrations at the four stations: levoglucosan and $\text{OC}_{\text{nf}}$ (top), and mannosan and $\text{OC}_{\text{nf}}$ (bottom).
Fig. 6. PM$_{10}$ source apportionment averaged for the four stations and for the working days 27 and 28 November and 1 December 2006 and the Sunday 3 December 2006. Traffic-induced resuspension includes mineral dust as well as Na, Mn, Cu and Zn; traffic carbonaceous: EM$_{f}$ and OM$_{f}$; secondary organics: nitrate, sulphate and ammonium; non-fossil carbonaceous: EC$_{wb}$ and OM$_{nf}$; and others: chloride, and trace elements others than Mn, Cu and Zn.
Fig. 7. (a) 30-min-time-resolved PM$_1$ composition, deduced from AMS and Aethalometer measurements at Massongex. The collection efficiency used was CE=0.5. (b) Comparison between AMS+BC and TEOM 24 h-averaged concentrations. The dashed line represents the 1:1 line.
Fig. 8. Working days (left) and Sunday (right) PM$_1$ composition at Massongex during the week 1, deduced from AMS and Aethalometer measurements. The working days correspond to 27 and 28 November and 1 December 2006, whereas Sunday refers to the 3 December 2006.
Fig. 9. Left: time series of the different contributors to the PM$_1$ carbonaceous aerosol (OOA, HOA, BC$_t$, P-WBOA and BC$_{wb}$) in Massongex during the whole campaign. Right: average composition of the PM$_1$ carbonaceous aerosol for the following working days of week 1: 27 and 28 November and 1 December 2006, and for the Sunday 3 December 2006. OOA, HOA and P-WBOA are deduced from ME-2-AMS, BC$_t$ and BC$_{wb}$ from the aethalometer model.
Fig. 10. Diurnal cycles in Massongex for HOA, P-WBOA, OOA, NO$_x$, CO, BC$_t$, BC$_{wb}$, K, NO$_3^-$, NH$_4^+$ and SO$_4^{2-}$, averaged over the whole campaign.
**Fig. 11.** Time series of the ammonium (a) and summed chloride, nitrate and sulphate (b) AMS equivalent concentrations during the whole campaign, and comparison of chloride concentrations measured by AMS and IC (c).