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**NR-PM₁ chemical
composition in
Central Europe**

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Characterization of aerosol chemical composition by aerosol mass spectrometry in Central Europe: an overview

V. A. Lanz¹, A. S. H. Prévôt¹, M. R. Alfarra^{1,2}, C. Mohr¹, P. F. DeCarlo¹, S. Weimer³, M. F. D. Gianini⁴, C. Hueglin⁴, J. Schneider⁵, O. Favez⁶, B. D'Anna⁶, C. George⁶, and U. Baltensperger¹

¹Paul Scherrer Institut, Laboratory of Atmospheric Chemistry, 5232 Villigen PSI, Switzerland

²National Centre for Atmospheric Science (NCAS), School of Earth, Atmospheric and Environmental Sciences, University of Manchester, Manchester, M60 1QD, UK

³Empa, Swiss Federal Laboratories for Materials Testing and Research, Laboratory for Internal Combustion Engines, 8600 Duebendorf, Switzerland

⁴Empa, Swiss Federal Laboratories for Materials Testing and Research, Laboratory for Air Pollution and Environmental Technology, 8600 Duebendorf, Switzerland

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⁵ Particle Chemistry Dept., Max Planck Institute for Chemistry, Mainz, Germany

⁶ Université Lyon 1, Lyon, 69626, France; CNRS, UMR5256, IRCELYON, Institut de recherches sur la catalyse et l'environnement de Lyon, Villeurbanne, 69626, France

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Correspondence to: V. A. Lanz (valentin.lanz@psi.ch)

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Abstract

Real-time measurements of non-refractory submicron aerosols (NR-PM₁) were conducted within the greater Alpine region (Switzerland, Germany, Austria, France and Liechtenstein) during several week-long field campaigns in 2002–2009. A large variety of sites was covered including urban backgrounds, motorways, rural, remote, and high-Alpine stations, and also mobile on-road measurements were performed. Inorganic and organic aerosol (OA) fractions were determined by means of aerosol mass spectrometry (AMS). The average mass concentration of NR-PM₁ for the different campaigns typically ranged between 10 and 30 $\mu\text{g m}^{-3}$. Overall, the organic portion was most abundant, ranging from 36% to 81% of NR-PM₁. Other main constituents comprised ammonium (5–15%), nitrate (8–36%), sulfate (3–26%), and chloride (0–5%). These latter anions were, on average, fully neutralized by ammonium. The OA was further divided (based on factor analysis, FA) into its underlying components, such as oxygenated (mostly secondary) organic aerosol (OOA), hydrocarbon-like and freshly emitted organic aerosol (HOA), as well as primary OA from biomass burning (P-BBOA). OOA was ubiquitous, ranged between 36% and 94% of OA, and could be separated into a low-volatility and a semi-volatile fraction (LV-OOA and SV-OOA) for all summer campaigns at low sites. Primary wood combustion (P-BBOA) accounted for a considerable fraction during wintertime (17–49% OA). HOA/OA ratios were comparatively low for all campaigns (6–16%) with the exception of on-road, mobile measurements (23%).

1 Introduction

Atmospheric aerosols are currently a subject of high scientific and political interest, which is due to their important effects on climate (Forster et al., 2007), human health (Peng et al., 2005), ecosystems and agricultural yields (acidification; Matson et al., 2002), as well as visibility (Watson, 2002). Particulate matter (PM) in the air represents

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a complex mixture of organic matter, inorganic salts, trace elements, mineral dust, elemental carbon and water suspended in the air. Detailed analyses of physicochemical properties and spatiotemporal variability are crucial to understand the mechanisms of aerosol toxicity (Peng et al., 2005) and their role in climate change (IPCC, 2007).

5 The identification and quantification of processes and sources that govern global and regional aerosol abundances are the indispensable basis for efficient abatement strategies. In this paper the chemical composition of non-refractory PM₁ (particulate matter with an aerodynamic diameter of 1 μm or less) is investigated for various sites in the greater Alpine region (Switzerland, Germany, Austria, France and Liechtenstein), representing one of the most important economic and leisure areas in Europe. The analyzed datasets comprise aerosol mass spectrometric measurements from a high-Alpine (Jungfrauoch) and a pre-Alpine background location (Hohenpeissenberg), an Alpine village (Roveredo), rural-agricultural (Payerne), rural-kerbside (Reiden, Härkingen) and rural-industrial (Massongex) sites, two urban background sites (Zürich and Grenoble) as well as on-road mobile measurements in the Alpine Rhine Valley (Table 1). Summer campaigns and winter campaigns were analyzed.

Factor analytical approaches were applied to organic aerosol mass spectra (FA-AMS) in order to identify and quantify the main organic subfractions, such as OOA (oxygenated organic aerosol), HOA (hydrocarbon-like organic aerosol), and P-BBOA (primary biomass burning organic aerosol). The used methods are based on positive matrix factorization (PMF, Paatero and Tapper, 1993, 1994) and the multilinear engine (ME; Paatero, 1999). Their application to AMS organic data data was described in detail earlier (Lanz et al., 2007, 2008; Ulbrich et al., 2009). Alfarrá et al. (2007), Lanz et al. (2007, 2008), and Weimer et al. (2009) have already described the OA composition and origin for three sampling locations (Roveredo, Zürich, and Rhine Valley, respectively). The presentation of results of in-depth PMF analyses for the other sites is in preparation, e.g. by Favez et al. (2009) for Grenoble or by Perron et al. (2009) for Massongex. The AMS campaign in Hohenpeissenberg (Germany) was detailed by Hock et al. (2008).

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This meta-analysis here extensively compares the organic components (retrieved from FA-AMS) as well as the inorganic fractions (ammonium, nitrate, sulfate, and chloride) for all the 13 campaigns at the 10 measuring sites. The results obtained in this study will furthermore be compared to Putaud et al. (2004), Hueglin et al. (2005), and Zhang et al. (2007). The two former studies investigated the chemical composition of PM_{2.5} and PM₁₀ in Europe and Switzerland, respectively, whereas this paper is about the non-refractory portion in submicron particles (NR-PM₁); there are some indications that the smallest particles (PM₁) are even more detrimental to human health than larger ones, e.g., with respect to respiratory diseases (Ramgolam et al., 2009). Zhang et al. (2007) provided an overview on AMS data (NR-PM₁) for the Northern Hemisphere with a main focus on summer campaigns and the dichotomy of oxygenated and hydrocarbon-like OA (OOA vs. HOA). Only the pre-alpine site Hohenpeissenberg and high-alpine Jungfrauoch (but represented by different campaigns) are part of both the Zhang et al. (2007) and this study.

2 Methods

2.1 Measurement sites and campaigns

Aerodyne aerosol mass spectrometers (quadrupole based Q-AMS, time-of-flight C-ToF-AMS, and high-resolution time-of-flight HR-ToF-AMS) were deployed at various sites in Central Europe (Fig. 1). Usually, an AMS was deployed during 2- to 3-week campaigns in the years 2002 and 2005–2009 (for details see Table 1). Six sampling sites were located in the Alps or Pre-Alps (Massongex, Jungfrauoch, Roveredo, Rhine Valley, Grenoble and Hohenpeissenberg) and four sampling sites in the Swiss Plateau (Payerne, Härkingen, Reiden and Zürich). The Alpine measurement locations can be separated into low and elevated sites. Low sites (between 200 and 500 m a.s.l.) comprise Massongex, Roveredo, the Rhine Valley and Grenoble, which are – in contrast to the elevated sites Jungfrauoch and Hohenpeissenberg – all situated in relatively nar-

row valleys. The Swiss Plateau is a hilly basin (300–700 m a.s.l.) confined by the Jura mountains in the Northwest, by the Alps in the Southeast and by Lakes Geneva and Constance (Rhine river). The Swiss plateau climate is in between humid oceanic (the predominant wind comes from the West/Atlantic ocean) and continental temperate.

5 The individual sites are characterized in Table 1 and references therein. Jungfraujoch, Härkingen, Zürich and Payerne are part of NABEL, the Swiss National Air Pollution Monitoring Network (www.empa.ch/nabel).

2.2 Aerosol mass spectrometry

10 Aerosol mass spectra were obtained using three types of aerosol mass spectrometers (AMS, Aerodyne Research Inc.) at 2–15 min resolution for the fixed measurement locations and 1 min averages for the mobile campaigns in the Rhine Valley. A detailed description of the AMS instruments can be found in Canagaratna et al. (2007), and references therein. In principle, aerosols are introduced through a critical orifice, separated from gaseous species by a series of aerodynamic lenses, focused on a particle beam and directed onto a vaporizer. After vaporization (at about 600°C) and electron ionization at 70 eV, the chemical composition is determined by the analysis of the resulting mass spectrum measured by a quadrupole (Q-AMS) or a Time-of-Flight mass spectrometer (ToF-AMS). The AMS measures the non-refractory fraction of submicron aerosol particles, which include components that evaporate at the standard vaporizer temperature of approximately 600°C and excludes elemental carbon, sea-salt, and crustal material.

15 The use of the HR-ToF-AMS (DeCarlo et al., 2006) allows for the unit mass peaks to be separated into their contributing ion fragments and for the determination of their elemental composition (e.g., the separation of $C_4H_9^+$ and $C_3H_5O^+$ at m/z 57). The HR-ToF-AMS instrument was deployed in only one (Jungfraujoch) out of 13 campaigns and the corresponding data were analyzed at unit mass resolution (UMR, as for the Q-AMS). A C-ToF-AMS as characterized in Drewnick et al. (2005) was used in Grenoble.

25 The measured particles approximately cover the size range of $PM_{1.0}$ for all AMS instru-

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ments. A vacuum aerodynamic diameter can be calculated from particle time-of-flight (PTOF) measurements (DeCarlo et al., 2004). However, this study focuses solely on the chemical composition data obtained from the entire particle population sampled by the AMS.

5 The UMR Q-AMS data were analyzed using the Igor-based software package described by Allan et al. (2003, 2004): in summary, the measured ion current is converted into the mass concentration using the measured ionization efficiency (IE) of nitrate, with which the instrument was calibrated (using pure ammonium nitrate particles; Jayne et al., 2000). For the other species, an IE relative to nitrate (RIE) is used (calibrated in laboratory studies; Jimenez et al., 2003; Allan et al., 2004; Alfarra, 10 2004). Organics were defined as the difference between signals from the total and inorganic aerosol (ammonium, sulfate, nitrate and chloride) for peaks with known organic contributions; organics determined by this method include the elements carbon (C), oxygen (O), hydrogen (H), and nitrogen (N) (i.e. they represent organic matter, OM). The principles of PAH quantification using the Q-AMS were provided by Dzepina et al. (2007). ToF-AMS data was analyzed with the ToF-AMS toolkit available from <http://cires.colorado.edu/jimenez-group/ToFAMSResources/ToFSoftware/index.html>.

2.3 Ancillary measurements

Black carbon (BC) mass concentration was determined by an Aethalometer (Magee Scientific, USA, type AE31; also see Sandradewi et al., 2008a) except for Hohenpeissenberg, where EC_{2.5} measurements were used (see Hock et al., 2008), and for the campaign in the Rhine Valley, where a MAAP (Multi Angle Absorption Photometer 5012, Thermo) was deployed (Weimer et al., 2009).

Offline filter analyses (PM₁ inlet in Zurich and Roveredo, PM_{2.5} in Grenoble, and 25 PM₁₀ in Reiden) were performed to compare ambient sulfate concentrations measured by the AMS and ion chromatography, and where available derive an AMS collection efficiency (CE).

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2.4 Aerosol neutralization

In order to characterize the neutralization state (ion balance) of an aerosol, the measured NH_4^+ -concentration, $[\text{NH}_4^+]_i$, and a predicted value, $[\text{NH}_4^+]_{\text{eq},i}$, are often compared (e.g., Takegawa et al., 2006):

$$[\text{NH}_4^+]_i = a[\text{NH}_4^+]_{\text{eq},i} + b, \quad (1)$$

where $[\text{NH}_4^+]_{\text{eq},i}$ represents the concentration of NH_4^+ -cations theoretically needed to balance the anions SO_4^{2-} , NO_3^- , and Cl^- in each sample i . On a molar basis

$$m(\text{NH}_4^+) = M(\text{NH}_4^+)(2n(\text{SO}_4^{2-}) + n(\text{NO}_3^-) + n(\text{Cl}^-)), \quad (2)$$

where n is the number of moles (1), m is the mass (g), and M is the molar mass (g/mol). Explicitly,

$$[\text{NH}_4^+]_{\text{eq},i} = 18.04(([\text{SO}_4^{2-}]_i \cdot 2/96.06) + ([\text{NO}_3^-]_i/62.00) + ([\text{Cl}^-]_i/35.45)). \quad (3)$$

In an ideally balanced case $[\text{NH}_4^+]_i = [\text{NH}_4^+]_{\text{eq},i}$ and the regression coefficients $a=1$ and $b=0$ in Eq. (1). For the studied submicron non-refractory aerosols we implicitly assumed that NH_4^+ represents a main contributor to positive ions (determined as *neq*). Indeed, it can be calculated from Hueglin et al. (2005) that even in $\text{PM}_{2.5}$ – including refractory species – the positive ions mainly were represented by $n(\text{NH}_4^+)$, making up for about 90% of the sum of the measured positive ions, i.e. $n(\text{NH}_4^+) + n(\text{Na}^+) + 2n(\text{Mg}^{2+}) + 2n(\text{Ca}^{2+}) + n(\text{K}^+)$.

2.5 Factor analysis

Factor analysis as used for air quality source apportionment starts with ambient concentrations of pollutants (gases or aerosols) arranged as a matrix, \mathbf{X} , with the dimensions samples in time (rows) and chemical properties (columns). In the case of AMS

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data, samples in time are represented by single AMS spectra and chemical properties are mass fragments (e.g., organic mass-to-charge ratios m/z 's 12–300 in this case here). The measurement matrix, \mathbf{X} ($\mu\text{g m}^{-3}$), is factorized into two matrices, \mathbf{G} and \mathbf{F} :

$$\mathbf{X} = \mathbf{G}\mathbf{F} + \mathbf{E} = \widehat{\mathbf{X}} + \mathbf{E}, \quad (4)$$

where matrix \mathbf{F} [dimensionless] represents p factor profiles (or “factor loadings”, “calculated mass spectra”), while \mathbf{G} ($\mu\text{g m}^{-3}$) contains the p time series of the corresponding factor contributions. The values in \mathbf{G} and \mathbf{F} are estimated based on an uncertainty-weighted least-square algorithm implemented in PMF2, a factor analytical tool by P. Paatero (see Paatero and Tapper, 1993, 1994). In this approach all measured mass spectra (\mathbf{X}) are approximated ($\widehat{\mathbf{X}} = \mathbf{G}\mathbf{F}$) by linear combinations of these factor profiles (\mathbf{F}) times their corresponding time series (\mathbf{G}) up to some errors, \mathbf{E} (see Eq. 4). The factor profiles, \mathbf{F} , can be interpreted as (combinations of) source profiles (e.g., P-BBOA) or characteristic mass spectra that cannot be directly linked to specific physical emission sources (e.g., OOA, which mostly results from the oxidation and condensation of various gaseous precursors rather than from direct particulate emissions). These factor interpretations were validated by independent studies or data (e.g. by comparing the time series of OOA or SOA retrieved by FA-AMS with the time series of measured secondary inorganics; see Sect. 3 and supplementary information, SI, see <http://www.atmos-chem-phys-discuss.net/9/24985/2009/acpd-9-24985-2009-supplement.pdf>). In PMF modeling, typically no further information about the sources/components other than the usual non-negativity of \mathbf{G} and \mathbf{F} are assumed. In contrast, in the ME-2 (Paatero, 1999) based approach used here, \mathbf{F} is partially known and constrained (for details see Lanz et al., 2008). This latter approach has proven to be useful when a factor with a rather well-defined profile or chemical fingerprint (e.g., HOA) is temporally correlated with other factors (showing more spatio-temporal variability in their profiles) and their time series (\mathbf{G}) cannot be separated by PMF2. The program PMF2 as applied to AMS organics data has been detailed by Lanz et al. (2007) and Ulbrich et al. (2009).

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3 Results and discussion

Average AMS-aerosol concentrations for the 13 campaigns in Central Europe are shown in Table 2. These mass concentrations ($\mu\text{g m}^{-3}$) also depend on the assumed collection efficiency (CE) of the AMS instrument. Ambient sulfate concentrations from offline filter measurements were compared to online AMS-sulfate and campaign-specific CEs were derived, assuming for example that refractory sulfates such as K_2SO_4 only negligibly contributed to PM_{10} . Comparisons with other ancillary data were considered less robust (e.g., gravimetric reference methods may not represent the true total PM_{10} due to losses of volatile aerosol components such as NH_4NO_3 and semi-volatile OM). A CE of unity for Jungfraujoch and CE=0.5 for Hohenpeissenberg (see Hock et al., 2008) was validated by SMPS and nephelometer/OPC data. In Table 2, mass concentration ranges for CE=0.5–1.0 are reported for the other cases. CE=0.5 represents the default value which is in agreement with the parameterized treatments of Crosier et al. (2007) and Matthew et al. (2008). However, CEs up to 1.0 have been reported in the literature for ambient particles (Takegawa et al., 2009) and there are some indications that this was the case during some of campaigns listed here as well. Thus, the average aerosol concentrations for certain campaigns included in Table 2 may be smaller by a factor of 0.5 compared to the mass concentration at default CE. Due to incomplete or inappropriate ancillary data we are not in the position to give unambiguous proof of such high CEs in those cases and thus the concentration at CE=1 given in Table 2 represents a lowest estimate. Howsoever, we exclusively discuss the relative values hereafter (e.g., sulfate vs. total AMS-aerosol in Sect. 3.2), which are independent of CEs under the assumption of internally mixed aerosols.

Absolute mass concentrations of NR-PM_{10} typically ranged between 10 and $30 \mu\text{g m}^{-3}$ (Table 2). Relatively high concentrations can be associated with campaigns that overlapped with periods of strong thermal inversions (winter campaigns in Reiden, Roveredo, and Payerne). Clearly lower concentrations were observed at the two remote and elevated sites (Hohenpeissenberg and Jungfraujoch).

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Black carbon, BC (or elemental carbon, EC) typically varied between 6–15% of NR-PM₁+BC (or EC) (i.e., PM₁ if one assumes that BC/EC makes up for most of the refractory PM₁). High BC fractions (>15% of NR-PM₁+BC) were found for the industrial site of Massongex and the on-road mobile measurements in the Alpine Rhine Valley, and relatively low values at the (remote) sites in Payerne, Hohenpeissenberg, and Jungfrauoch. Note that Hueglin et al. (2005) reported EC mass contributions of about 5%, 10% and up to 20% for rural/elevated sites, urban background/near-city sites, and kerbsides, respectively, for PM_{2.5}.

3.1 Chemical composition of NR-PM₁

On the basis of campaign averages, the organic material made up about 33% to 66% in NR-PM₁ for the 13 campaigns in Central Europe (Fig. 2). As an exception, more than 80% OM was found in Roveredo (December 2005), which can be explained by a considerable impact of local wood combustion (Alfarra et al., 2007) as confirmed by radiocarbon (¹⁴C) and multi-wavelength particulate light absorption measurements (Szidat, 2007; Sandradewi et al., 2008b). The smallest relative sulfate contribution (3%) was found at the same site, highlighting a regime of stagnant air with limited influences of regional and aged background air. In contrast, sulfate was most abundant (26%) in aerosols from the high-alpine background site Jungfrauoch, and aerosols from Hohenpeissenberg showed relatively high sulfate contributions (19%) as well. Note that the absolute sulfate values (about $1.8 \pm 0.4 \mu\text{g m}^{-3}$) were comparable across Central Europe, indicating that it represents a regional pollutant (in the absence of local wood burning; Weimer et al., 2009). It is plausible that sulfate showed relatively high contributions (in % of NR-PM₁) at Jungfrauoch and Hohenpeissenberg, because other main aerosol constituents (OM, nitrate, ammonium) were low due to missing emission sources (e.g., no local biomass burning and little traffic) and are depleted more efficiently during the transport of the air masses from source to receptor. More precisely, ammonium is depleted by wet deposition during transport, without being replenished. Furthermore, NO_x shows a faster oxidation rate than SO₂, resulting in an initially in-

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creasing nitrate-to-sulfate ratio close to the sources, which then decreases on further transport (Colbeck, 1998). Thus, sticking to the reasoning by Henning et al. (2003) the equivalent ratio of ammonium to the sum of sulfate and nitrate will decrease during the chemical aging of air masses as soon as there is not enough ammonia left to neutralize the aerosol. This in turn results in a continuous decrease of the nitrate-to-sulfate ratio, since $\text{HNO}_3(\text{g})$ is outgassed under low ammonium conditions (Wexler and Seinfeld, 1990).

The average chemical composition of NR-PM₁ was very similar for the different sites in the Swiss plateau when the campaigns were classified according to the season of the year (Fig. 2). It is important to note that the campaigns in the Swiss Plateau were carried out at sites with rather different characteristics: urban background (Zürich), rural/motorway (Härkingen and Reiden), and rural/agricultural (Payerne). In summer, roughly 66% of NR-PM₁ was organic and only 33% inorganic (with comparable contributions from SO_4^{2-} , NH_4^+ , and NO_3^-). The most volatile compound, chloride (Cl^-), accounted for <1% NR-PM₁. In winter, only about 33% of NR-PM₁ was organic and NH_4^+ plus NO_3^- was most abundant (about 50% of NR-PM₁). Low temperatures strongly favor the formation of particulate ammonium nitrate ($\text{NH}_4\text{NO}_3(\text{aer})$) from its gaseous precursors ammonia ($\text{NH}_3(\text{g})$) and nitric acid ($\text{HNO}_3(\text{g})$) (Seinfeld and Pandis, 1998). The same applies for the equilibrium between $\text{NH}_3(\text{g})$, hydrochloric acid ($\text{HCl}(\text{g})$), and $\text{NH}_4\text{Cl}(\text{aer})$ and probably explains (in analogy to NO_3^-) the slightly higher contributions of Cl^- in the winter season (about 1%). Chloride is unlikely due to de-icing salts because most mass of these particles is found in the super-micron mode and because they are mostly refractory (however, heterogeneous reactions involving $\text{NaCl}(\text{s})$ also need to be considered: $\text{NaCl}(\text{s}) + \text{HNO}_3(\text{g}) \rightarrow \text{NaNO}_3(\text{s}) + \text{HCl}(\text{g})$; see Leu et al., 1995). The most abundant chloride fraction (~5% NR-PM₁) was observed in Massongex, which might be explained by the industrial vicinity ($\text{HCl}(\text{g})$ emissions with availability of $\text{NH}_3(\text{g})$). A comparable chloride fraction (~4%) was reported for Tokyo, winter 2004 (Takegawa et al., 2006).

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As for the seasonally grouped campaigns in the Swiss Plateau, relatively similar chemical compositions are obtained for the Alpine sites, when sorted by type of site (and season of the year) (Fig. 2). The two elevated and remote sites of Jungfraujoch and Hohenpeissenberg (May campaigns) showed similar compositions: OM was highest (43% and 50%) and SO_4^{2-} (26% and 19%) was more abundant than NO_3^- (18% and 19%) and NH_4^+ (13% and 11%), which has to be attributed to transformation processes occurring during transport of the air masses to Jungfraujoch and Hohenpeissenberg as discussed above. Also a rather homogeneous aerosol composition can be observed for the different Alpine locations at low altitude in winter (showing about 50–60% OM, 5–10% SO_4^{2-} , 10–12% NH_4^+ , and 20–27% NO_3^-) with the above mentioned exception of Roveredo (November 2005) where the relative OM contribution exceeded the typical OM fraction at the other sites and was probably mostly due to strong local emissions (residential wood combustion) in combination with stable air masses (thermal inversions) and lack of precipitation.

The PAH (polycyclic aromatic hydrocarbons) contributions were typically rather low (at about 0.1% of OM or less) compared with the other aerosol components discussed above (SO_4^{2-} , NO_3^- , Cl^- , NH_4^+ , OM), but higher in winter (Zürich: 0.10% of OM; Payerne 0.08% of OM) than in summer (Zürich: 0.03% of OM; Payerne 0.00% of OM), indicating that PAH levels are possibly related to the amount of wood burning emissions which are increased in winter (see Sect. 3.2.). In addition, enhanced photochemistry in summer leads to faster photochemical degradation of PAHs. Even higher PAH/OM ratios (0.1–0.2%) were observed for winter campaigns at Alpine locations (e.g. Massongex, Roveredo, and Grenoble). In summer, the highest ratio (0.12%) was found for Härkingen, a site near a motorway. Overall, on-road mobile measurements in winter (strong influence of both traffic and wood burning) showed the highest average ratios PAH/OM (namely 0.3%).

Despite the large variability in the inorganic components the ion balance was overall neutral ($a=0.99\pm 0.03$ in Eq. (1) including all the $n=13$ campaigns), leading to the hypothesis that there is usually enough ammonia (NH_3 ,g) available to neutralize the

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5 SO_4^{2-} , NO_3^- , and Cl^- anions in Central Europe. The NH_4^+ -concentrations on Jungfraujoch are close to the detection limit, such that the fact of neutralization cannot be confirmed from this AMS data set. In contrast, Cozic et al. (2008) have shown based on a 6-year data set of filter measurements that with decreasing aerosol concentration a lower degree of neutralization is generally achieved (which is in line with the above discussion on transformation processes during aging). Thus, we can not rule out that there are no episodes of acidic aerosol over Central Europe. A general aerosol neutralization can also be derived from Hueglin et al. (2005; Tables 3 and 4 therein) for $\text{PM}_{2.5}$ (yearly averages) in Swiss cities (Basel, Bern, and Zürich) and one site in the Jura mountains (Chaumont). This is different for coastal/marine sites, where the amount of NH_4^+ often cannot balance the negative ions (as can be derived from Putaud et al., 2004, and Zhang et al., 2007) and suggests that at such sites the tropospheric aerosol as well can be acidic.

3.2 Organic components and OA sources

15 The organic subfractions discussed here were identified and quantified as described in Sect. 2.5 and references therein. OOA (oxygenated organic aerosol, mostly interpreted as secondary OA, SOA) was typically the most abundant organic component, ranging from 36% of OM (in an industrialized Alpine valley in winter; Massongex) up to >80% of OM at rural and remote sites (Jungfraujoch, Hohenpeissenberg, Härkingen and Payerne in summer) (Fig. 3). Generally, the ubiquity and dominance of OOA found here are in good agreement with the findings by Zhang et al. (2007). However, in Alpine Valleys in wintertime, OOA contributions to OA can be relatively low (<50%) due to strong local influences of wood burning (P-BBOA) and traffic (HOA): e.g., also in Roveredo (December 2005-campaign with large primary wood burning emissions), OOA was comparatively low (<43%). Concerning maximum OOA/OA ratios, note that the Jungfraujoch represents a site intermittently advected from the free tropospheric air as well as air from the polluted boundary layer (PBL) (Lugauer et al., 2000). For

periods with exclusively free tropospheric air (or highly processed PBL air), the m/z 57 fragment can be completely depleted (accordingly, HOA can not be retrieved) at the Jungfraujoch and OOA then accounts for nearly 100% of OM in such situations (which was actually the case for the Jungfraujoch campaign in 2002 analyzed by Zhang et al., 2007; see Fig. 2 therein).

It is interesting to note that the separation of OOA into low-volatility OOA, LV-OOA, and semivolatile OOA, SV-OOA (formerly called OOA1 and OOA2, respectively), could be observed for all summer campaigns (Fig. 3). A literature survey of PMF applications on organic AMS data suggests that this observation is also valid for North-America (Cotrell et al., 2007, Nemitz et al., 2008, Docherty et al., 2008, Aiken et al., 2008, Ulbrich et al., 2009, DeCarlo et al., 2009). PMF-AMS studies for other parts of the world (see above) typically focused on summer campaigns. As an exception, Slowik et al. (2009) studied an AMS winter campaign in Toronto and Allan et al. (2009) three winter campaigns in Manchester and London, UK; no separation of OOA into a low-volatility and a semi-volatile fraction was observed for these data based on the PMF-AMS analysis. It was described in detail that LV-OOA follows the time trends of sulfate and oxidant gases (odd oxygen, O_3+NO_2) (regional build-up in the afternoon; Lanz et al., 2007; Herndorn et al., 2008) and SV-OOA may trace the nitrate series (condensation during the night, showing more diurnal variation than LV-OOA) (Lanz et al., 2007; Ulbrich et al., 2009). In winter, the colder temperature and the smaller temperature ranges might explain the lower OOA variability (and the same reasoning would explain the fact that OOA did not separate into different OOA at the Jungfraujoch). Note that during the Payerne campaign in winter, for which LV- and SV-OOA could be differentiated, a temperature range of $\Delta T (T_{\max} - T_{\min}) = 26^\circ C$ was observed, which is similar to the one observed for the Zürich summer campaign ($\Delta T = 25^\circ C$).

HOA was typically between 6–16% of OA, but enhanced contributions were found for on-road mobile measurements in the Alpine Rhine Valley (23% on average). HOA contributed to OA in all campaigns, but in about half of the cases (see SI section) a measured HOA-profile from the literature (Canagaratna et al., 2004, Schneider et

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al., 2006) had to be imposed on the data to separate its contribution from temporally correlated P-BBOA or OOA series (details see Lanz et al., 2008). Compared to the Swiss (remote) sites Jungfrauoch and Payerne, relatively high HOA contributions were observed in Hohenpeissenberg, Germany (~15% OA), and a similar HOA fraction (~20% OA) was identified by the multiple component analysis (MCA) for this latter campaign (Zhang et al., 2007, Hock et al., 2008). Also note that Weimer et al. (2009) found lower HOA/OA ratios on Swiss roads compared to Austrian roads and hypothesized that this could be due the smaller number of heavy-duty diesel vehicles and to the comparatively low share of diesel powered passenger cars in Switzerland (~10%; HBEFA, 2004) compared to Austria (60%; Umweltbundesamt, 2007). About 26–49% of OA was attributed to P-BBOA for lower Alpine sites (all of them can be classified as winter campaigns). For the winter campaigns conducted in the Swiss Plateau, this fraction was typically lower (17–38%). P-BBOA could not be resolved for the high- and pre-alpine background stations (Hohenpeissenberg and Jungfrauoch), which might be explained by the season (limited residential wood burning and only a few open fires can be expected in spring). Furthermore, P-BBOA is semi-volatile (Lipsky and Robinson, 2006) and might have evaporated and/or oxidized (Capes et al., 2008) during transport to these remote sites – but also for the campaigns in the Swiss plateau in summer, only a small P-BBOA fraction (~10% OA) could be observed in Zürich exclusively, potentially emitted from local open fires.

The relative abundance of organic components (OOA, HOA, P-BBOA) in the Swiss plateau is almost as uniform (when grouped seasonally; Fig. 3) as compared to the total NR-PM₁ composition (i.e. SO₄²⁻, NO₃⁻, Cl⁻, NH₄⁺, and OM). However, in Zürich (summer 2005) local POA sources could be identified (wood burning, charbroiling, and potentially food cooking, which was identified as relevant POA source in London and Manchester as well, Allan et al., 2009) but not in the summer campaigns in Härkingen (rural-motorway) and Payerne (rural-agricultural). The OA components at these latter two stations (Härkingen and Payerne) were similar: 65% and 60% LV-OOA, 33% and 34% SV-OOA, and 12% and 6% HOA, respectively. In winter, primary organics (i.e.

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P-BBOA+HOA) were somewhat lower (27% OA) at the remote site Payerne (due to its distance to major combustive aerosol sources) than for Zürich (urban site) and Reiden (near motorway), showing primary OA fractions of 45% and 41%, respectively. The relative contribution of OA components for the two latter stations (Zürich and Reiden) was comparable (55% and 59% OOA, 7% and 8% HOA, and 38% and 33% P-BBOA, respectively). Further note that also Zürich (located in the Swiss Plateau) and Grenoble (Alpine site) (both represent urban background sites) showed similar OA compositions in wintertime (Fig. 3), in particular, high P-BBOA contributions were observed (~40% OA).

OOA had a strong temporal correlation with ammonium, ranging between $R^2=0.51$ (coefficient of determination) for Massongex and $R^2=0.85$ for Reiden/Rhine Valley (see SI section) and similarly correlated with the sum $\text{SO}_4^{2-} + \text{NO}_3^-$. The latter behavior is to be expected as the concentration of NH_4^+ is highly correlated with the sum of SO_4^{2-} and NO_3^- (R^2 is typically 0.8–0.9). The time series of LV-OOA were typically correlated with sulfate ($R^2=0.41$ –0.54), while SV-OOA could be related to nitrate showing episodically linear correlations: e.g., for four fifths of the Zürich, summer campaign ($R^2=0.55$), or for the last third of the Payerne, summer-campaign ($R^2=0.67$). The strong correlation with secondary inorganics found here further supports previous evidence that OOA is mainly secondary in its origin (Zhang et al., 2005, 2007; Lanz et al., 2007, 2008; Ulbrich et al., 2009). However, also primary OA from wood fire emissions may be characterized by an OOA-like signature, depending on burning conditions (Weimer et al., 2008), representing one reason why no perfect correlation between OOA and secondary inorganics can be expected and a portion of OOA may represent fresh wood combustion OA.

The primary wood burning component identified by FA-AMS (P-BBOA) had a consistently higher correlation with CO ($R^2=0.38$ –0.78) than with NO_x ($R^2=0.11$ –0.72) for all campaigns. On the other hand, primary HOA had stronger correlation with NO_x compared to P-BBOA. These latter findings support the results from previous publications (Lanz et al., 2007, 2008; Allan et al., 2009) that HOA is most strongly connected with

primary traffic emissions, while the correlation of P-BBOA with CO supports its origin from wood burning emissions. However, non-linearities (e.g., as found in the relation SV-OOA vs. nitrate) suggest that these R^2 's can only serve as an approximate measure of similarity between the time series and, furthermore, variable emission ratios, removal processes, and reactivity of CO, NO_x and OA need to be considered: at the remote sites of Jungfraujoch and Hohenpeissenberg, e.g., HOA was very weakly correlated with reactive NO_x ($R^2 < 0.10$), but better with the more stable CO ($R^2 = 0.15$ and $R^2 = 0.31$, respectively).

3.2.1 Organic components and spectral tracers

In the past, several papers have made use of specific mass fragments as tracers for different aerosol sources. Figure 4 shows the relation between organic mass spectral tracers (measured m/z 's 44, 57, and 60) and OOA, HOA, and P-BBOA as estimated by FA-AMS. Mass fragment m/z 44 is a proxy for oxygenated/secondary OA (Alfarra, 2004; Zhang et al., 2005), m/z 57 traces freshly emitted anthropogenic OA (Alfarra, 2004; Zhang et al., 2005), and m/z 60 more specifically indicates time trends of primary biomass burning OA (Schneider et al., 2006; Alfarra et al., 2007). The strongest correlation ($R^2 = 0.68$) was found for organic m/z 44 and OOA (or Σ "LV-OOA" + "SV-OOA") normalized to total OA (Fig. 4). An even stronger correlation ($R^2 = 0.83$, not shown) resulted when campaigns in winter with relatively low OOA (i.e. OOA/OA $\leq 60\%$) but high P-BBOA were excluded, because a certain (but not exactly known) amount of m/z 44 needs to be attributed to wood combustion in these cases. Organic m/z 60 mostly represents fragments from the ionization of levoglucosan (Alfarra et al., 2007) and similar molecules found in smoke from incomplete wood pyrolysis. Organic m/z 60 correlates well ($R^2 = 0.41$) with P-BBOA (normalized by OA). However, mass fragment m/z 60 is not completely unique to fire emissions (DeCarlo et al., 2008) and mass fragment m/z 60 (C₂H₄O₂⁺) might also represent organic acids, which can be emitted primarily as well as formed through secondary processes. In the absence of biomass burning DeCarlo et al. (2008) found m/z 60 to be about 0.3% of OA – a similar value

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can be derived here (0.26–0.68%), representing the intercept (at P-BBOA=0) in the plot m/z 60/OA vs. P-BBOA/OA (Fig. 4). Lastly, HOA/OA versus organic m/z 57/OA shows the weakest correlation ($R^2=0.23$), and this is plausible due to the following circumstances: the two main fragments at m/z 57 ($C_4H_9^+$, $C_3H_5O^+$) represent different sources and processes and the relative proportion of these two ions change with processing (Chirico et al., 2009). Organic m/z 57 is part of wood burning emissions as well and the HOA/OA-range covered by Central European data sets is rather small (usually 6–16%), whereas in other parts of the Northern Hemisphere, HOA accounts for ~37% in urban OA (Zhang et al., 2007). Furthermore, the fraction of these mass spectral tracers (m/z 's 44, 57, 60) within the OA components (HOA, OOA, P-BBOA) as retrieved by FA-AMS was investigated. The PMF2/ME-2 profiles for the presented data sets were usually relatively similar, e.g. m/z 60 as the key fragment for wood burning accounted for 2–3% in P-BBOA (with the exception of 1% in Zürich, winter, and 4% in Roveredo, winter), and m/z 57 accounted for 6–9% in HOA at all locations (but 10% and 18% in Zürich winter and summer, respectively). However, there was also a considerable variability in the m/z 44 as a part of OOA (9–21%) – and LV- and SV-OOA even represent two separate populations with respect to their m/z 44-content, which was 13–20% (LV-OOA) and $\leq 8\%$ (SV-OOA), respectively. Photochemical aging of the air masses increases the organic m/z 44-to-OA ratio (Alfarra et al., 2006; Duplissy et al., 2008). A high m/z 44-to-organics ratio could be linked to high oxygen content (O/C atomic ratio, Aiken et al., 2008) and low volatility (Huffman et al., 2009). It therefore can be expected that LV-OOA is enriched with m/z 44, whereas SV-OOA consequently should be depleted in m/z 44. Typical (SV-/LV-) OOA, P-BBOA, and HOA spectra can be found in Lanz et al. (2007, 2008) as well as on the AMS Spectral Database at <http://cires.colorado.edu/jimenez-group/AMSSd/>.

3.2.2 Diurnal variability of organic components (OOA, HOA, P-BBOA)

The daily cycles for the FA-AMS retrieved organic components is shown in Fig. 5 for Zürich, summer (urban), Hohenpeissenberg (pre-Alpine) and Jungfrauoch (high-

Alpine). The HOA/OA cycle at the urban site (represented by Zürich, summer) shows a bimodal pattern with increases at 06:00–09:00 a.m. (local time) and at 08:00–10:00 p.m. again.

By contrast in the urban winter (see Lanz et al., 2008; Zürich), the first HOA/OA peak was observed later (09–12:00 a.m.) and the second peak earlier (05:00–08:00 p.m.): planetary boundary layer height (delayed down-mixing of aged OOA) and changed emissions patterns (daylight depending activities start later and stop earlier) can account for these shifts. Similar diurnal patterns were observed in Grenoble during the winter season. HOA/OA behavior as found at the urban background site can be observed for sites near motorways as well (Härkingen, Reiden, and Roveredo). This HOA/OA cycle however was less pronounced at remote sites (represented here in Fig. 5 by Hohenpeissenberg; a comparable pattern was found e.g. for Payerne) and was almost constant for the high-alpine site Jungfrauoch. In Zürich (summer campaign) the OOA/OA cycle is approximately inverse to HOA/OA (i.e. including dips in the morning at 06:00–09:00 a.m. and in the evening at 08:00–10:00 p.m., and an increase during the after-noon due to photochemical production of secondary OOA). These typical daily patterns for the urban HOA (traffic-related) and OOA (photochemically produced) have also been reported for several other cities, e.g. in New York (Drewnick et al., 2004). As for HOA/OA, the daily cycles of the OOA/OA ratios level off for stations more distant to emission sources, as shown in Fig. 5 for Hohenpeissenberg and Jungfrauoch. P-BBOA/OA cycles in winter (not shown here) were generally similar to HOA/OA, but the evening peaks were found to be typically higher than the corresponding P-BBOA peaks in the morning and later than the HOA evening-peaks (Lanz et al., 2008; also see Sandradewi et al., 2008). Food cooking aerosols showed peaks at mealtimes (at noon and in the evening; Lanz et al., 2007; Allan et al., 2009).

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Ambient aerosols (NR-PM₁) were analyzed at ten locations with widely different characteristics: urban to rural sites, background and kerbside locations, low (~200 m a.s.l.) to elevated sites (~3600 m a.s.l.). Summer as well as winter campaigns were investigated in balanced numbers. Regarding the averages from 13 campaigns, typical NR-PM₁ concentrations ranged between 10 and 30 $\mu\text{g m}^{-3}$. Campaigns that included periods of persistent thermal inversions in wintertime represent the upper concentration range (up to ~60 $\mu\text{g m}^{-3}$ at the kerbside in Reiden), whereas relatively low values were found for elevated sites in spring (~2 $\mu\text{g m}^{-3}$ at the high-alpine site Jungfrauoch).

Overall consistent and – when grouped by season of the year and type of site – nearly homogeneous chemical composition and OA fractions resulted from 13 campaigns performed by different groups and by using different types of AMS instruments. The organic fraction was most abundant in NR-PM₁ – and within the organics the OOA prevailed (determined by factor analysis of aerosol mass spectral data, FA-AMS). This main result is in good agreement with Zhang et al. (2007). In Alpine valleys in winter, however, organic concentrations were strongly influenced by primary wood burning emissions (26–49% of OA); and most of the OOA component could be attributed to non-fossil sources (as resulted from combinations of FA-AMS and radiocarbon analysis, Prévôt et al., 2009). We conclude here from AMS measurements and factor analytical modeling that biomass burning (or more specifically wood combustion) is a seasonally important PM source in Central Europe (Alpine region) as well, along with urban areas in Scandinavia (Glasius et al., 2006; Hedberg et al., 2006; Yttri et al., 2009), Ghent, Belgium (Zdrhal et al., 2002) or Paris, France (Favez et al., 2009). The strong influence of wood burning on ambient aerosol mass in the Alpine region found here is in line with analyses based on molecular markers (e.g., levoglucosan; Caseiro et al., 2009), multi-wavelength light absorption measurement analysis (Sandradewi et al., 2008a) or radiocarbon analysis (Szidat et al., 2007).

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With respect to the inorganic aerosol fractions, large variation was observed for SO_4^{2-} (3–26% NR-PM₁), NO_3^- (8–36%), and Cl^- (0–5%), and somewhat less variability for NH_4^+ (5–15%), which on average fully neutralized the former anions for all studied campaigns in Central Europe.

More field campaigns will still be necessary in order to verify certain trends and patterns (e.g. the relatively similar aerosol composition within the Swiss Plateau, Alpine valleys, or for elevated sites, respectively), or validate the observation that HOA/OA ratios are lower in Switzerland and Grenoble, France (typically around 10% OA) than in Germany and Austria. To get a complete picture, further AMS campaigns should take place, e.g. in Alpine valleys during the summer season. In general, longer periods (half a year or a full year) of aerosol mass spectrometric measurements should ideally be available to get more representative PM₁ chemical composition data.

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Table 1. Sampling sites, altitude (meters above sea level, m.a.s.l.), type of site, duration of the AMS field campaigns, abbreviation, and ambient temperature (in °C), as well as related publications. Quadrupole aerosol mass spectrometers (Q-AMS) were deployed in all campaigns with the exceptions of Jungfraujoch and Grenoble, where time-of-flight mass spectrometers (ToF-AMS) were used. (Country codes: CH=Switzerland, AT=Austria, LI=Liechtenstein, DE=Germany, FR=France).

measuring site (country, altitude)	type	date	abbrev.	$T_{\text{avg}}(T_{\text{min}}, T_{\text{max}})$	publication
Rhine Valley (CH/AT/LI, 400 m.a.s.l.)	mobile/ on-road	16–22 Feb 2007/ 8–13 Feb 2008	RHI FEB_2007	+04 (−03, +14)	Weimer et al., 2009
Zürich (CH, 410 m.a.s.l.)	urban/ background	14 Jul–4 Aug 2005 6–25 Jan 2006	ZUE JUL_2005 ZUE JAN_2006	+23 (+15, +35) +00 (−07, +07)	Lanz et al., 2007 Lanz et al., 2008
Grenoble (FR, 220 m.a.s.l.)	urban/ background	14–30 Jan 2009	GRE JAN_2009	+04 (−07, +14)	Favez et al., 2009
Massongex (CH, 310 m.a.s.l.)	rural/ industrial	23 Nov–17 Dec 2006	MAS DEC_2006	+08 (−02, +22)	Perron et al., 2009
Härkingen (CH, 430 m.a.s.l.)	rural/ motorway	12–30 May 2005	HAE MAY_2005	+14 (+04, +32)	
Reiden (CH, 460 m.a.s.l.)	rural/ motorway	27 Jan–13 Feb 2006	REI FEB_2006	+00 (−08, +09)	
Roveredo (CH, 300 m.a.s.l.)	residential/ motorway	1–15 Mar 2005 25 Nov–15 Dec 2005	ROV MAR_2005 ROV DEC_2005	+03 (−07, +15) −01 (−06, +04)	Alfarra et al., 2007 Alfarra et al., 2007
Payerne (CH, 490 m.a.s.l.)	rural/ agricultural	31 May–3 Jul 2006 12 Jan–17 Feb 2007	PAY JUN_2006 PAY JAN_2007	+18 (+03, +31) +03 (−11, +14)	
Hohenpeissenberg (DE, 985 m.a.s.l.)	remote	19–31 May 2002	MOHp MAY_2002	+13 (+04, +32)	Hock et al., 2008
Jungfraujoch (CH, 3580 m.a.s.l.)	remote	30 Apr–29 May 2008	JFJ MAY_2008	−04 (−09, +02)	

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Table 2. Average ambient concentrations (arithmetic mean, μ , and geometric mean, μ_{geom} , in $\mu\text{g m}^{-3}$) for the non-refractory aerosol as measured by the AMS instruments (NR-PM₁) for all campaigns (abbreviations see Table 1). The geometric mean was calculated by omitting non-positive values and the standard deviation of this mean was typically about $1 \mu\text{g m}^{-3}$. The standard deviation of the arithmetic mean is 0.5–2% of the absolute concentrations, $\mu(\text{NR-PM}_1)$. Larger uncertainties are associated with the choice of the collection efficiency (CE) of the AMS instrument (see text). Conversion factors to STP (standard temperature, $T_0=273.15 \text{ K}$, and pressure, $p_0=101325 \text{ Pa}$) were calculated as the ratio $(p_0T)/(pT_0)$. BC (EC) averages are given in $(\mu\text{g m}^{-3})$ and their relative fractions in (%) of NR-PM₁ were calculated as $\text{BC}/(\text{BC}+\text{NR-PM}_1)$.

campaign (abbrev.)	$\mu(\text{NR-PM}_1)$	rel. std. dev.	$\mu_{\text{geom}}(\text{NR-PM}_1)$	CE	STP-conversion	BC (%NR-PM ₁)
RHI FEB_2007	13.5–26.9	1.00%	10.0–20.0	1.0–0.5	1.13	7.1 (21–35%)
ZUE JUL_2005	9.6–19.2	0.52%	8.1–16.3	1.0–0.5	1.13	1.5 (7–14%)
ZUE JAN_2006	12.8	0.70%	9.4	1.0	1.12	2.2 (15%)
GRE JAN_2009	14.8	0.74%	10.2	0.5	1.10	2.2 (13%)
MAS DEC_2006	4.0–7.9	1.53%	2.6–5.1	1.0–0.5	1.13	1.7 (18–30%)
HAE MAY_2005	12.5–25.0	0.48%	10.8–21.6	1.0–0.5	1.13	BC not measured
REI FEB_2006	56.6	0.85%	45.1	0.5	1.13	4.4 (7%)
ROV MAR_2005	26.3	0.75%	18.8	0.33	1.12	1.6 (6%)
ROV DEC_2005	28.6	1.00%	21.1	0.67	1.12	2.9 (9%)
PAY JUN_2006	9.7–19.4	0.72%	8.7–17.4	1.0–0.5	1.14	BC not measured
PAY JAN_2007	16.2–32.3	1.05%	11.7–23.4	1.0–0.5	1.14	1.1 (3–6%)
MOHp MAY_2002	6.7	1.65%	4.6	0.5	1.22	0.3 (4%)
JFJ MAY_2008	1.6	1.89%	0.8	1.0	1.67	0.1 (7%)

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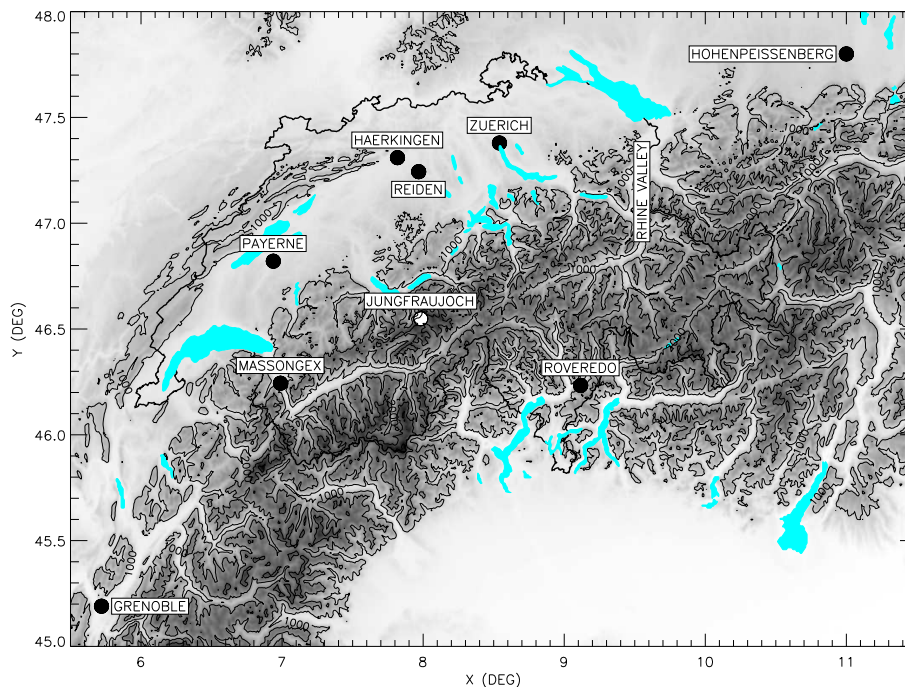


Fig. 1. AMS-campaigns in Central Europe conducted in the years 2002 and 2005–2009. Four sampling sites (Payerne, Härkingen, Reiden, and Zürich) are located in the Swiss Plateau (between Alps and Jura), the others in the greater Alpine region. Ten campaigns took place in Switzerland (Swiss border indicated by black solid line) (Härkingen, Payerne 2x, Reiden, Zürich 2x, Massongex, Jungfrauoch, Roveredo 2x), and one in Germany (Hohenpeissenberg) and France (Grenoble) each. The mobile measurements in the (Alpine) Rhine Valley covered Austria, Liechtenstein and Switzerland.

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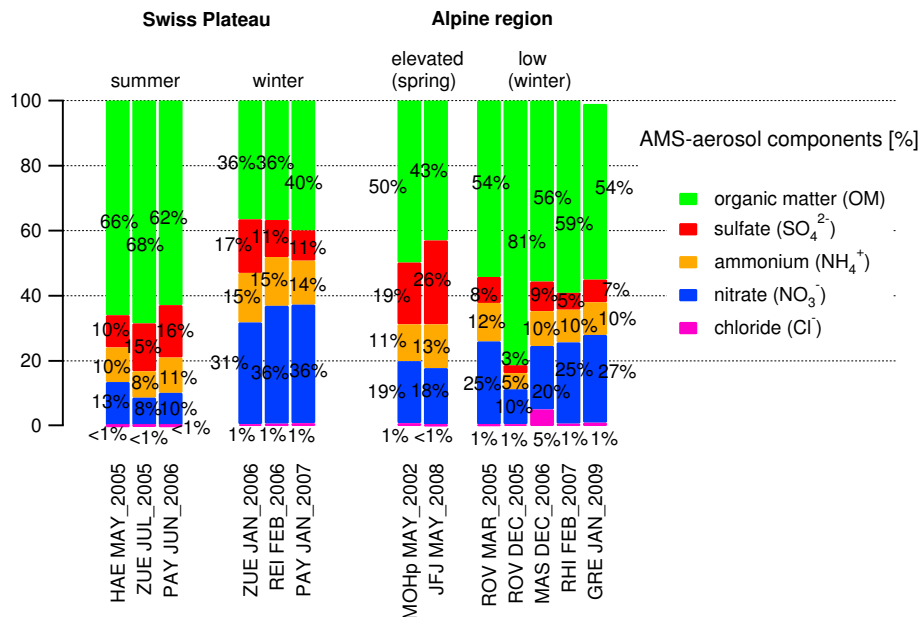


Fig. 2. Relative composition of non-refractory submicron aerosols (NR-PM₁) in Central Europe: Organic matter (OM), sulfate (SO₄²⁻), ammonium (NH₄⁺), nitrate (NO₃⁻) and chloride (Cl⁻). The standard deviation of the relative means (%) reported here is typically about 1% or less.

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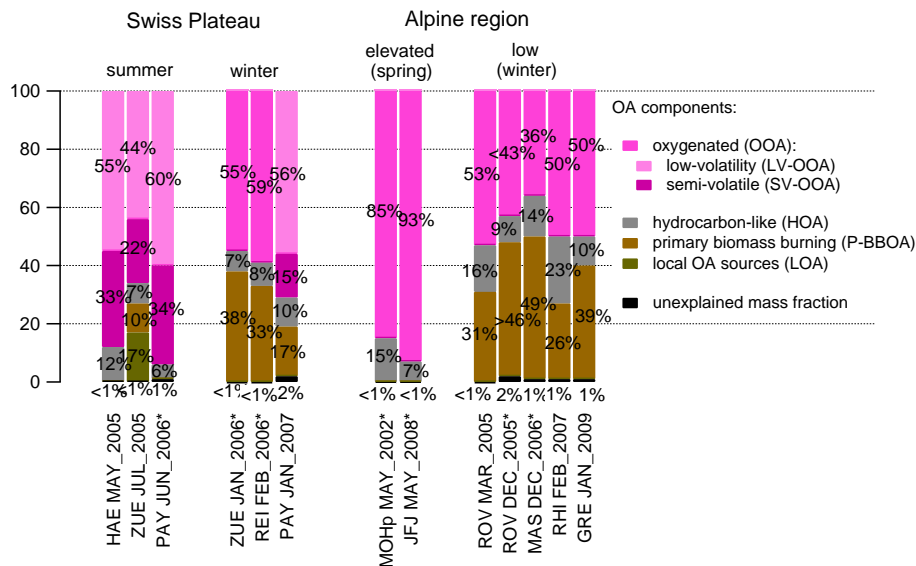


Fig. 3. Relative composition of the organic matter (OM, determined by the AMS instrument). The components OOA (oxygenated and mostly secondary OA), HOA (hydrocarbon-like and mostly primary fossil OA), P-BBOA (primary biomass and wood burning OA), and local OA sources (LOA) were determined by applying factor analysis (PMF2 and ME-2) to ~270 organic mass fragments (m/z 's) (FA-AMS). The low-volatility (LV-OOA) and semi-volatile (SV-OOA) fractions of OOA had previously been called OOA1 and OOA2, and were now changed into more descriptive terms (Jimenez et al., 2009). LOA in ZUE 2005 represents charbroiling and potentially food cooking (Lanz et al., 2007). The standard deviation of the relative means (%) reported here is typically about 1% or less, but due to the sensitivity of the PMF2-(ME-2)-results to several program settings (e.g. number of factors) an uncertainty of about $\pm 5\%$ needs to be assumed (Lanz et al., 2007, 2008). Additional but unknown uncertainty is due to factor interpretation. In Roveredo, November 2005, a primary wood burning contribution is possibly present in the OOA-factor (m/z 60 is at about 1% in this latter factor) and, therefore, total P-BBOA is expected to be higher (>46%) and SOA (OOA) lower (<43%) than the averages of the corresponding factors. (*) FA results based on a ME-2 analysis (for details see SI section).

NR-PM₁ chemical composition in Central Europe

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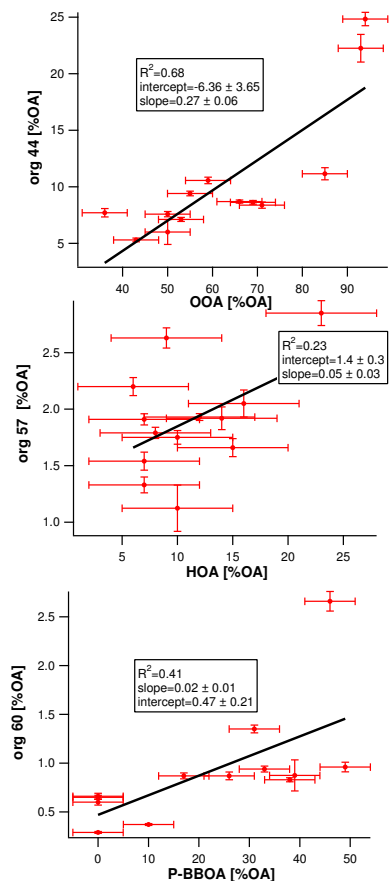


Fig. 4. Relation between m/z 44 (measured) and OOA (modeled), m/z 57 (measured) and HOA (modeled), as well as m/z 60 (measured) and P-BBOA (modeled). Results normalized by OA (measured). Slope and intercept calculated with an orthogonal distance regression are represented by solid black lines. An uncertainty estimate for the FA-AMS method ($\pm 5\%$) is indicated by horizontal red lines, whereas vertical red lines equal the uncertainty associated with the mean ratio (m/z_i)/OA ($i=44, 57, 60$). OOA represents SV-OOA plus LV-OOA. P-BBOA was set to 0% in data sets where it could not be identified by means of FA-AMS.

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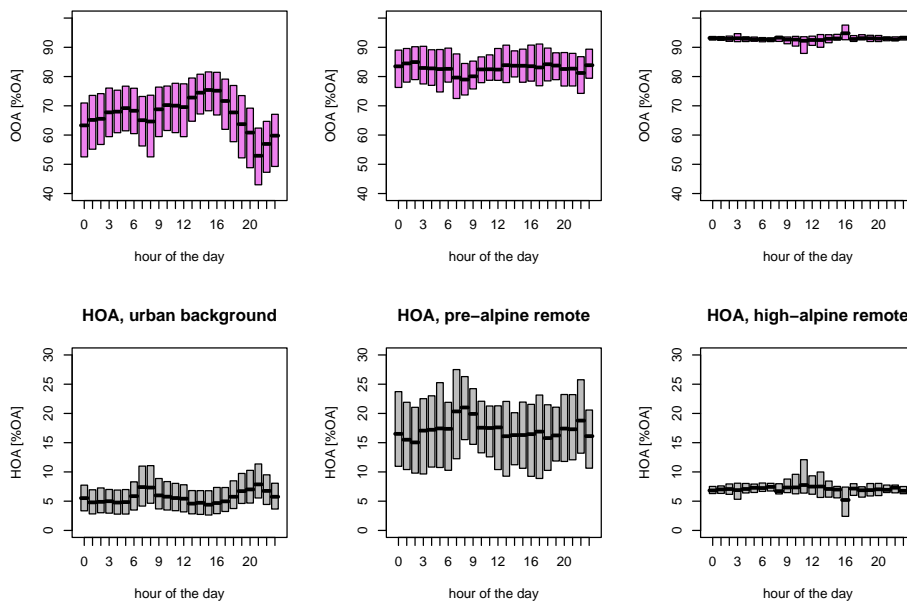


Fig. 5. Daily cycles for OOA/OA (top) and HOA/OA (bottom) (the median values per hour are represented by bold horizontal bars, the 1st and 3rd quartile of the observations by the boxes) for a site close to anthropogenic OM emissions (left; urban background in Zürich, summer), a remote pre-Alpine site (Hohenpeissenberg; middle) and the remote high-Alpine station Jungfrauoch (right).

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