Atmos. Chem. Phys. Discuss., 9, C9815–C9842, 2010
www.atmos-chem-phys-discuss.net/9/C9815/2010/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Characterization of aerosol chemical composition by aerosol mass spectrometry in Central Europe: an overview" *by* V. A. Lanz et al.

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Received and published: 19 January 2010

We thank anonymous referee ♯1 for the useful comments and suggestions. The comments by the referee appear in *italics* below directly followed by our response.

The authors described results from 14 field campaigns using a commercial Aerodyne Aerosol Mass Spectrometer (AMS) at 10 sites in Switzerland, Austria, Liechtenstein, Germany, and France. Non-refractory aerosol species, including organics, sulfate, nitrate, ammonium, and chloride, were measured using AMS instruments; in addition, complementary black carbon measurements were made during most studies. For

most studies, factor analysis was utilized to separate the following organic components: low-volatility oxygenated, semi-volatile oxygenated, hydrocarbon-like, primary biomass burning, and local organic aerosol.

My major concern is that this "overview" reads as an archival data report, rather than a scientific discussion. While a worthwhile study, the context and overall findings of this overview are not clear. Who is the intended audience? What is the result of comparing all of the studies? What new was gained from the overview? These points are not clear and must be made so in a revised manuscript. In addition, care should be taken to making sure the manuscript flows and is organized well such that the main take-home points of each paragraph and section are clear. Much of the results and discussion section, for example, is difficult to read and does not flow well. In addition, the overview requires an added section discussing each of the sites and what aerosol sources and processes they are impacted by. Much of the manuscript only states the results of the data analysis, but it does not discuss the science. Overall, the manuscript requires a discussion of results and their implications. Major revisions are suggested with particular attention to data interpretation and discussion. For an overview manuscript, overall trends and patterns should be discussed in detail. If the authors do not believe that trends and assumptions may be discerned from this study and presented to the scientific audience for future research, then the authors should wait until additional field campaigns are completed to present this data.

We will consider the comments provided by the referee above and will discuss her/his explicit suggestions in the following. We trust that these suggestions were overall very helpful for putting our results into context and will improve both quality and impact of our paper. We agree that all mentioned trends and patterns need to be discussed in detail. This was done here extensively with respect to i) inorganic aerosol composition, ii) OA composition, iii) organic tracers vs. OA components, etc. Additional analyses based on the referee comments will be presented in the revised paper. Trends and patterns should be carefully examined and interpreted as some sites have to some extent their unique surroundings. It goes without saying that such intensive field campaigns are always limited in time and space and not all eventualities can be covered. This applies to all similar studies. Although we critically stated that “More field campaigns will still be necessary […]” (P. 25006, L5-12), we are convinced that the 13 datasets are representative for a variety of different sites (urban, rural, remote etc.) and seasons, valid for Central Europe. We consider it very interesting to provide more details on the variability between 10 sites in a relatively small region. It becomes obvious that seasonal differences and the location (Alpine vs. Alpine valley vs. Swiss Plateau) are important; for data sets with both the same season and location type, similar relative compositions were found.

Major and minor comments are noted below.

Major comments:

Abstract: Provide context for this work; why is it needed? What unique was gained from this overview?

In the revised abstract, we will i) stress the relevance of the study region, ii) pronounce the importance of biomass burning in this region even more, and iii) mention the fact that the variability in aerosol chemical composition can be reduced when the campaigns are sorted by season of the year and location of the sampling site (Alpine valleys, elevated sites in the Alps, or Plateau sites). More reasons for this work and its context will be provided in the (revised) introduction. 1) We will add on P. 24987, L4: “This region represents one of the most important economic and recreational spaces in Europe.” 2) On P. 24987, L12 we will insert: “The variability in aerosol chemical composition in this region could be largely explained when the measurement campaigns were sorted by time of the year and location of the sites (Alpine valleys, elevated sites in the Alps, or Plateau sites)”. 3) We will add on P. 24987, L19: “[…], particularly in

narrow Alpine valleys P-BBOA was often the most abundant OA component”

1 Introduction: Currently, the introduction is lacking in background motivation for this overview; over half of the introduction concentrates on introducing the locations and methods of analysis, rather than providing scientific motivation for the study. In addition, no background is provided for previous measurements of aerosol chemical composition in the “greater Alpine region”; this should be discussed and provide motivation for why an overview of AMS measurements is needed/useful. While it is noted that previous AMS studies for this region have been published, no information is provided regarding their results. I suggest moving the discussion of factor analytical approaches to the methods section. Further, while it is noted that the Zhang et al. 2007 overview did not include most of the sites within this overview, it is not discussed why this overview is needed in particular; what does this overview provide beyond Zhang et al. 2007?

In the revised introduction, we will stress further differences between this study and Putaud et al. (2004)/ Hueglin et al. (2005): i) online/real-time AMS measurements vs. offline filter-measurements, ii) focus on last decade 2002-2009 vs. measurements in the 1990ies, iii) size cut $PM_{1.0}$ vs. $PM_{2.5}$ and PM_{10} iv) non-refractory vs. refractory material v) greater Alpine area vs. Europe/Switzerland. We will furthermore highlight the different foci of the Zhang et al. and this study and largely re-organized the introductory section. The most important results of precedent OA studies will be mentioned in the discussion section. The new introduction will read:

“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 and eutrophication; Matson et al., 2002), as well as visibility (Watson, 2002). Particulate matter (PM) in the air represents 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). 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 PM_1 (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. This meta-analysis here extensively investigates the organic material (OM), its underlying components as well as the inorganic aerosol fractions (ammonium, nitrate, sulfate, and chloride) and their ion balance for all the 13 campaigns at the 10 measuring sites. The results obtained in this study will furthermore be compared to previous similar studies. Putaud et al. (2004) and Hueglin et al. (2005) examined the chemical composition of $PM_{2.5}$ and PM_{10} in Europe and Switzerland, respectively, for the years 1991-2001 determined by offline filter analyses. This study here represents an overview on aerosol chemical composition in the greater Alpine area during 2002-2009 determined via online mass spectrometry at high time-resolution. Furthermore, this paper is about submicron particles (AMS-PM_1 and black carbon): there are some indications that the smallest particles are even more detrimental to human health than larger ones (e.g., with respect to respiratory diseases; Ramgolam et al., 2009). However, the AMS can determine neither several trace elements such as potassium (K) or sodium (Na) (only the non-refractory portion of the aerosol is measured), nor water (due to interferences with other aerosol and background air ions) quantitatively. Water was estimated to be a main constituent of airborne PM (Hueglin et al., 2005).

Zhang et al. (2007) provided an overview on AMS data (NR-PM_1) for the Northern Hemisphere with a main focus on summer campaigns and the dichotomy of oxygenated and hydrocarbon-like OA (OOA vs. HOA). The pre-alpine site Hohenpeissenberg and the high-alpine site Jungfraujoch (but represented by different campaigns) are part of

Zhang et al. (2007) and this study. However, as we will show these remote background locations are not representative of other regions of the greater Alpine area/Central Europe: more different types of measuring sites need to be considered. In this study, additionally analyzed datasets comprise aerosol mass spectrometric measurements from an alpine village (Roveredo), a rural-agricultural (Payerne) and a rural-industrial (Massongex) site, two stations each at urban backgrounds (Zürich, Grenoble) and rural-kerbsides (Reiden, Härkingen) as well as on-road mobile measurements in the Alpine Rhine Valley (Table 1). Alfarra et al. (2007), Lanz et al. (2007, 2008), and Favez et al. (2010) have already described the OA composition and origin for three sampling locations (Roveredo, Zürich, and Grenoble, respectively). The presentation of results of in-depth OA analyses for the other sites is in preparation, e.g. by Weimer et al. for the Rhine Valley or by Perron et al. for Massongex. The AMS campaign at Hohenpeissenberg (Germany) was detailed by Hock et al. (2008). In this work, we further discuss both the organic as well as the inorganic fraction in detail. We applied factor analytical approaches to organic aerosol mass spectra (FA-AMS) that allowed identification and quantification of the main organic subfractions, such as OOA (oxygenated organic aerosol), HOA (hydrocarbon-like organic aerosol), but also distinct primary OA components, such as 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 was described in detail earlier (Lanz et al., 2007, 2008, Ulbrich et al., 2009). Most importantly, we show that primary wood burning OA, P-BBOA, makes up for a substantial fraction of OA and must no longer be ignored, at least in Central Europe.“

2 Methods: Is Section 2.5 needed, or could it be shortened and combined with Section 2.2 or provided as supplemental material? It appears that the factor analysis used is not new, and the discussion of it is tedious to read.

The reviewer is correct: the factor analytical tools used here for an in-depth analysis of the OA are not novel. Their application on mass spectrometric AMS data however has been introduced relatively recently by Lanz et al. and Ulbrich et al., and many readers are not familiar with these methods yet. We understand that a reader with a strong background in factor analysis might wish to skip reading these methods and, therefore, we organized it in a separate subsection.

3 Results and discussion:

-Expand the discussion of NR-PM$_1$ mass concentrations on page 24994 (lines 24-28). Provide values associated with "high" and "lower" concentrations in the text. Put these studies in the context of previous work and what would be expected. Provide more comparisons between studies.

The discussion on NR-PM$_1$ mass will be extended and read as follows:

"Absolute mass concentrations of NR-PM$_1$ typically ranged between 10 and 30 μg m^{-3} (Table 2). Relatively high concentrations can be associated with campaigns that overlapped with periods of strong thermal inversions: the winter campaigns in Reiden (56.6 μg m^{-3}) and Payerne (16.2-32.3 μg m^{-3}). Lower concentrations were observed at the two remote and elevated sites (Hohenpeissenberg, 6.7 μg m^{-3}, and Jungfraujoch, 1.6 μg m^{-3}). The typical values for NR-PM$_1$ reported by Zhang et al. (2007) were somewhat lower (3-16 μg m^{-3}). In this latter overview on the Northern Hemisphere, more campaigns were performed at remote sites, but less winter data were included. For the Central European campaigns, the the average for the summer data was lower (8-14 μg m^{-3}) than the average for winter data (22-26 μg m^{-3}). As an appreciable exception only 4.0-7.9 μg m^{-3} NR-PM$_1$ was observed in Massongex (located in a Central Alpine valley), during the winter 2006: the comparatively low concentrations could be attributed to strong Foehn influences (Southern winds, comparatively high temperatures, low relative humidity), which caused precipitation and deposition of air pollutants South of the Alps (additionally, snowfall was observed during the campaign in November/December 2006). The total PM$_{2.5}$ values found in the overview for Europe (Putaud et al., 2004, Hueglin et al., 2005) were somewhat higher than the NR-PM$_1$

values reported here but the former aerosol measurements also included supermicron (PM$_{2.5-1.0}$) and refractory material."

Section 3.1: - Currently, the first paragraph is difficult to read and easily glean the important points. In addition, it should be expanded with greater discussion of each of the chemical components, suggesting possible sources for sites other than Roveredo. In addition, a discussion of absolute species concentrations (similar to that done for sulfate) would likely be of interest. The following paragraphs provide a nice discussion of the data; this type of discussion, describing the sites and data in detail, should be emulated throughout the manuscript.

First, Section 3.1 will be re-organized and the following subtitles introduced: "3.1.1 Main NR-PM$_1$ constituents (OM, SO$_4^{2-}$, NO$_3^-$, NH$_4^+$)", "3.1.2 Other constituents", and "3.1.3 ion balance".

Second, the discussion on absolute sulfate loadings (P. 24996, L7) will be extended: "[...]. Also Putaud et al. (2004) found increasing non-sea salt sulfate contributions in PM$_{2.5}$ with increasing distances from large pollution sources. However, the sulfate concentrations reported in Putaud et al. (2004) and Hueglin et al. (2005) were consistently higher (typically 2-5 μg m^{-3}) than the values reported here ($\sim$2 μg m^{-3}). This difference can be explained by three reasons: i) a substantial fraction of sulfate mass was found at around 1 μm aerodynamic diameter (Putaud et al., 2004), a region with sub-optimum lens efficiency of the AMS (Liu et al., 2007). ii) Decreasing trends in sulfate mass were observed for Europe (decrease by 50-75% between 1980 and 2000 according to Lövblad et al., 2004). Assuming a lag period of about one decade between this study and the referenced earlier overviews might thus explain a decrease of the sulfate mass by about one third. iii) The potential refractiveness of sulfates (e.g., K$_2$SO$_4$, not measured by the AMS) might also cause a minor difference in the observed sulfate mass loadings. The same value for the average sulfate mass loading as calculated here ($\sim$2 μg m^{-3}) can be derived for North-America and Europe from the worldwide overview by Zhang et al. (2007; Table SI-2), while markedly higher values are found for Asian sites."

Third, an evaluation of absolute OM, NO_3^-, and NH_4^+ mass loadings in the context of precedent overviews (Putaud et al., 2005, Hueglin et al., 2004, Zhang et al., 2007) will be added: "In contrast, OM (on average 10.0 ± 1.8 μg m^{-3}), NH_4^+ (2.2 ± 0.6 μg m^{-3}), and NO_3^- (4.6 ± 1.5 μg m^{-3}) mass concentrations were comparable in this study and Putaud et al. (2005). It is possible that the loss of supermicron mass ($PM_{2.5-1.0}$), which can not be measured by the AMS instruments, was compensated by additional mass coverage of semi-volatile organics and ammonium nitrate, which are potentially lost by filter-techniques. These two opposing artifacts might have led to comparable mass loadings in that case. The average OM, NH_4^+, and NO_3^- values derived from Zhang et al. (2007) were clearly lower at about 5.0 μg m^{-3}, 1.5 μg m^{-3}, and 1.3 μg m^{-3}, respectively. The discrepancy can be explained by the fact that fewer winter campaigns (mostly linked to higher aerosol concentrations in Central Europe; see above) and more remote/coastal sites (often associated with lower aerosol burdens) were considered in this latter study. In fact, if we average our OM, NH_4^+, and NO_3^- concentrations for summer campaigns only (resulting in mass concentrations of 7.0 ± 2.2 μg m^{-3}, 1.1 ± 0.3 μg m^{-3}, 1.3 ± 0.3 μg m^{-3} respectively) the concentration ranges in the two studies are more similar."

Lastly, we prefer to discuss the results by constituents rather than by sites. Many results from different sites are similar, e.g. because the sites show similar characteristics (see Table 1), and can be discussed together. A wealth of site-specific information is condensed in Tables 1 and 2. By sorting the results by aerosol constituents rather than by site, repetitive discussions can be avoided. Where it is of particular interest, site-specific information that goes beyond the general characteristics already provided in Tables 1 and 2 was added. We note that on P. 24996, L. 26, the industrial vicinity of Massongex was mentioned, the specific situation for Zurich-Kaserne with respect to primary organic aerosol (POA) sources was discussed on P. 25000, L23-L27 (charbroiling, food cooking), etc.

- The paragraph spanning pages 24997-24998 seems to contradict that of the discussion spanning pages 24995-24996, where it seemed to state that the more aged, higher altitude aerosol was acidic. Please clarify these discussions so that they agree and are clearer.

The referee is correct that the discussion on P. 24997-24998 was somewhat confusing. We implicitly stated on P. 24995-24996 that there is generally a trend of a lower degree of aerosol neutralization with increasing distance from the main pollution sources, whereas on P. 24997-24998 we reported that the ion balance for the different sites in Central Europe was overall neutral. This can on average also be calculated for the remote site of the Jungfraujoch. However, it should be noted that the ammonium as measured by the AMS has a relatively high detection limit (as a result of interferences with high water- and air-related background signals) in the order of tens to hundreds of ng m^{-3} (Drewnick et al., 2009). The NH_4^+ values at the Jungfraujoch (on average ~0.2 μg m^{-3}) were often close to detection limit. Therefore, the ion balance (which explicitly includes ammonium concentrations, see Eq. 1) might not be conclusive here (as we stated on P. 24998, L1-L3). It is therefore possible that the aerosol at the Jungfraujoch were in fact acidic. Interestingly, the aerosol concentrations at the Jungfraujoch were anti-correlated with aerosol acidity (calculated according to Eq. 1) – in other words, very low aerosol concentrations (potentially indicative of free tropospheric and long-range transported aerosol) were acidic according to Eq. 1. On P. 24998, L3 we will thus delete "In contrast" as the trend observed by Cozic et al. does not really contrast our findings for the Jungfraujoch. The revised passage (P. 24998, L1) will read: "[...] As an exception, low aerosol loadings at the Jungfraujoch (which can be indicative of free tropospheric and long-range transported aerosol) coincided with an NH_4^+-deficiency according to Eq. 1 and thus potentially represent acidic aerosols. However, the NH_4^+-concentrations at the Jungfraujoch were often close to the detection limit such that this latter trend can not be fully confirmed from this AMS data set. Cozic et al. found [. . .]"

Section 3.2: - The first paragraph provides a nice discussion and comparison with Zhang et al. 2007, particularly with respect to outlier situations.

We will introduce further comparisons to the Zhang et al. study (see above).

- When separation of LV-OOA and SV-OOA is not possible, for the winter campaigns, do the organic mass spectra more resemble the SV-OOA mass spectral signature as one might expect, given the discussion on lines 16-20 on page 24999?

The referee is correct, OOA typically did not separate into SV-OOA and LV-OOA for the winter campaigns. We would explain this behaviour as follows: the semi-volatile OOA fraction that readily condenses and re-evaporates in summer is more likely to stay in the condensed phase in winter (due to lower temperatures, smaller temperature ranges, and higher OA concentrations). In the cold season its temporal variability is therefore similar to LV-OOA and the two OOA components can not be resolved by PMF. That is not to say that LV-OOA was not present in winter - rather it is not possible to distinguish it from the more volatile material by PMF and the all the OOAs are represented by one single PMF factor.

OOA that did not separate into a semi-volatile and a low-volatility fraction did typically resemble more LV-OOA than SV-OOA. As an example, the fraction of organic *m/z* 44, f_{44}, in OOA was on average f_{44}=14%. For the LV-OOA this value was f_{44}=17%, but only f_{44}=4% for SV-OOA. In this sense OOA was in between SV-OOA and LV-OOA, but closer to LV-OOA than to SV-OOA.

On the one hand, we agree that in winter, due to the lower temperature, also less oxidized (more volatile) compounds can partition to the aerosol in winter compared to summer. Following this reasoning, one would also expect that OOA in winter resembles more SV-OOA than LV-OOA.

On the other hand, even if more material with a lower oxidation state partitioned into the aerosol in winter, there could still be a highly stable and highly aged OOA fraction (considering the long periods without wet deposition that may occur in winter, yielding sufficient reaction time to form an LV-type OOA). The high f_{44} in this background OOA (showing the LV-OOA signature) will compensate the less oxidized, low f_{44}-material in the single OOA-factors calculated for the winter campaigns. We furthermore hypothesize that SVOCs from wood burning emissions (with a relatively high O/C ratio) need a shorter time than other primary SVOCs (with lower O/C ratios) to be aged and evolve towards an LV-OOA type aerosol. In fact, the only SV-OOA resolved for winter campaign (Payerne, January 2007) showed the highest f_{44} of all SV-OOAs.

More generally, one can say that the precursors are different in summer and winter and the oxidation time needed in summer and winter to form LV-OOA type organics is an open issue and a matter of future research. Also the different pathways and oxidation agents might be important: OOA may be mainly formed via O_3 / NO_3 in winter, but more prominently via OH in summer.

-What is the suggested reason for the "high" HOA contributions in Hohenpeissenberg? What is the suggested reason for the "low" P-BBOA fractions for the winter Swiss Plateau studies?

There is a multitude of potential reasons to explain the relatively high HOA fraction at Hohenpeissenberg, Germany (compared to Swiss remote-rural sites): i) a nearby railway with trains powered by diesel locomotives, ii) its vicinity to a large city (München), iii) electricity production by fossil-fuels has a prominent role in Germany/Eastern Europe, whereas in Switzerland it is solely produced by hydro and nuclear power (IEA, 2008), iv) higher share of diesel cars in Germany (due to lower diesel taxes and prices). These reasons will be added to the manuscript. Concerning the very high P-BBOA fractions in the Alpine valleys and comparatively lower fraction in the Swiss Plateau we hypothesize the following: "Stable thermal inversions, smog, low temperatures, and reduced sunlight inhibit local SOA formation and favor the accumulation of locally emitted POA. OOA is a partly regional pollutant and the thermal inversions may trap the air in narrow Alpine Valleys even more than at the sites belonging to the Swiss Plateau. P-BBOA in contrast is assumed to be more locally emitted and less diluted in the shallow PBL of Alpine Valleys".

4 Conclusions:

The first paragraph is a good start for a summary of overall findings. However, on page 25005 line 11, it is stated that "nearly homogeneous chemical composition. . .resulted from 13 campaigns. . ."; does this mean that the conclusion of the paper was that aerosol chemistry was similar/constant for all sites and seasons? Discuss this further as it is an important implication of the overview. Also, be careful with the word "homogeneous"; does this mean the aerosol is similar, or homogeneously mixed, or what? Further, on page 25006 line 1, it is stated that "large variation was observed" for the different inorganic aerosol fractions; this seems to contradict the above statement.

For clarification "nearly homogeneous chemical composition" will be replaced at this instance by "rather similar aerosol chemical composition" on P. 25005, L11. On P. 25006, L4 we will explain: "This large variability, again, could be markedly reduced when the campaigns were grouped by season of the year and location of the site. As an example, the variability in sulfate contributions (overall ranging from 3-26% of NR-PM$_1$) only varied between 10-16% for the Swiss Plateau site in summer, 11-17% for the Swiss Plateau sites in winter, 19-26% for the elevated Alpine sites (in spring), and 3-9% for the Alpine sites at low altitude (in winter) (see Figure 2)."

Another main result of the overview appears to be the importance of biomass burning in the region; however, hasn't this already been concluded from AMS work presented in other manuscripts?

The referee is correct. We will insert on P. 25005, L19: "First but exemplary evidence

for an appreciable amount of P-BBOA in ambient OA was provided for the alpine-village of Roveredo and an urban background site in Zürich by Alfarra et al. (2007) and Lanz et al. (2008), respectively. In this study, P-BBOA was identified and quantified by factor analysis at several more sites: at a rural-agricultural (Payerne), a rural-kerbside (Reiden), a rural-industrial (Massongex), and an urban background site in France (Grenoble): [. . .]".

At the end of the conclusions section, it is stated that additional field campaigns are necessary to validate trends and patterns. Little discussion in the conclusions is provided for any observed trends/patterns. However, the point of an overview should be to describe trends and resulting assumptions that can made for future work.

The outlook on P. 25006, L5-12 will be discussed in more detail and replaced by:

"More field campaigns will still be necessary to verify certain trends and patterns, e.g.

- As a main conclusion, time of the year (summer vs. winter) and location of the site (Alpine valleys, elevated sites in the Alps, or Plateau sites) were more helpful in explaining the variability in NR-PM$_1$ composition in Central Europe than e.g. type of the site (urban background, rural, remote etc.). Detailed analyses for other regions of the world will be necessary to validate this finding. Ideally, aerosol mass spectrometric measurements covering a full year should be available to get more representative PM$_1$ chemical composition data.

- Overall, we found lower sulfate loadings (at about 2 μg m^{-3}) for 2002-2009 than previous studies (Putaud et al., 2004, and Hueglin et al., 2005), which however focused on offline filter measurements. Future AMS studies are necessary to unambiguously attribute this trend to changes in policy (SO$_2$ emission reductions) rather than different instrumentations (online AMS measurements of submicron non-refractory aerosol vs. offline PM$_{2.5}$ or PM$_{10}$ filter analyses).

- It was found that OOA (mostly representing SOA) could be separated into a semi-volatile and a low-volatility fraction for all summer campaigns at Swiss Plateau sites (due to the large variability in photochemistry, temperature ranges, and OOA chemical signatures). To get a complete picture, further AMS campaigns should take place, e.g. in Alpine valleys during the summer season.

• By means of factor analytical modeling of AMS spectral data primary wood burning OA has been identified as a main OA source in Central Europe. The approach could be tested for other types of P-BBOA in other regions of the world, e.g. wild fires in the tropics.

• In this study, we observed that the HOA/OA ratios were lower in Switzerland and Grenoble, France (typically around 10% of OA) than in Germany and Austria. Future studies should also elucidate what influences most likely the differences in HOA levels: local traffic sources (e.g. share of diesel vehicles), regional energy use (fossil-fuel vs. nuclear/hydro power plants) etc."

Minor comments:

Page 24987, line 18 – Clarify what is meant by "low sites". Does this refer to altitude?

"low sites" will be replaced by "low altitude sites".

Page 24989, line 17 – "C" does not appear to be defined.

The standard ToF-AMS spectrometer is sometimes referred to as the "C-ToF" due to the C-like shape of the ion path in the instrument. "C-ToF" will be replaced by "standard ToF-AMS" at this instance and below on P. 24990, L27.

Figure 1 – Swiss border line not clear. I assume darker shades are higher altitude? This is not clear. I would suggest labeling the different countries on the map for individuals not as familiar with Europe. Label x and y as longitude and latitude. Show approximate

locations of mobile studies.

Will be revised.

Page 24989, line 26 – Provide altitude range for the elevated sites here as well.

Will be done.

Page 24990, lines 1-3 – The Swiss Plateau is discussed here; however, it would be helpful if these locations were also noted for reference in Figure 1.

Will be done.

Page 24990, line 14 – "on" should be "into"

Will be done.

Page 24990, lines 20-21 – Metals would also not be detected.

Will be added.

Page 24991, line 19 – Should say ". . .concentrations were. . .".

Will be changed.

Page 24991, lines 19-23 – Can you comment on any uncertainties/differences introduced from using these different techniques?

Hitzenberger et al. (2006) conducted an inter-comparison of several BC/EC methods with respect to differences in average mass concentrations. As can be derived from Fig. 3 therein, all methods resulted in comparable BC/EC mass concentrations not significantly differing from each other on average. It is however possible that, specifically, for the low concentrations at Hohenpeissenberg thermochemical methods under-estimate the mass concentrations compared to usually performed aethalometry. With respect to the mobile campaigns: given the high concentrations, the MAAP possibly only very slightly underestimates BC mass compared to an aethalometer. Using the default settings of the two instruments (absorption measurements at 880 nm for the Aethalometer and at 670 nm for the MAAP) the BC concentrations resulted in negligible differences (Christoph Hueglin, pers. comm.). These notes will be added to the revised manuscript on P. 24995, L6 sqq.: "In all campaigns BC was determined by online aethalometry with the exception of Hohenpeissenberg (EC measurements) and the Rhine Valley (MAAP). The lowest BC fraction was found at Hohenpeissenberg (4%), but it should be noted that thermochemical techniques as used for that latter site potentially underestimate BC mass compared to aethalometry (Hitzenberger et al., 2006). Contrarily, according to the latter intercomparison MAAP measurements were in relatively good agreement with aethalometry, at least at such high concentrations as found during the mobile campaigns (7 μg m^{-3})." It is necessary to refer to these results by Hitzenberger et al. carefully, as they were derived from urban aerosol.

Page 24991, lines 24-27 – Can you comment on uncertainties introduced from the different size cut-points?

Please see our response to specific comment on "Page 24994, lines 7-10" below.

Page 24992, line 14 – As worded, this is confusing since the AMS measures only positive ions. I believe the authors are trying to say that they assume ammonium is the only cation in the aerosol balancing sulfate, nitrate, and chloride. The passage was clarified accordingly: "…represents the main cation in the aerosol balancing …"

Page 24992, line 15 – "neq" is not defined.

We will add neq(NH$_4^{1+}$)=1*[NH$_4^+$]/M$_{NH_4^+}$

Page 24992, lines 21-22 – Should this say ". . .dimensions as samples. . ."?

Will be corrected.

Table 2 – Is it not clear why the mean mass concentrations are given as ranges for certain studies. Also, the label "BC (%NR-PM1)" is misleading since BC is not NR. The equation in the caption helps to clarify this; however, the phrase "fractions of NRPM1" is still misleading. Also, I assume "STP-conversion" in the table actually lists the "conversion factor" rather than the converted data(?). I assume that the mean mass concentrations shown take the listed CE and conversion factors into account(?); make sure this is clear in the caption.

In cases where no appropriate ancillary data for a CE determination was available, CE ranges (and PM concentration ranges correspondingly) were estimated as explained in Sects. 2.3 and 3. In the revised paper, these latter sections will be cross-referenced in the caption of Tab. 2. BC is in fact refractory and therefore we will change the label "% NR-PM$_1$" to "% NR-PM$_1$+BC" in Table 2 and its caption.

The referee is right: the column label "STP-conversion" refers to the STP conversion factors. This issue will be clarified in the revised manuscript. The listed concentration values will be provided for ambient conditions (rather than at STP) as noted in the first sentence of the Table caption.

Page 24994, line 2 – Note NR-PM1 here.

The term "mass" will be replaced by "NR-PM$_1$" on P. 24994, L2.

Page 24994, lines 7-10 – Does this refer to species other than sulfate, and thus, CE was based off of the sulfate comparisons alone? Make this statement clearer. Also, *can you add a comment about the impact of different size cut measurements?*

The comparisons were based on sulfate filter-measurements or via SMPS, nephelometer, and OPC data if available. We will change the sentence on P. 24994, L7-10: “Comparisons with other data were considered less robust [. . .] and were not used in this context.” While the NR-PM$_1$ as well as the OA composition in Zürich, January 2006, and Reiden, February 2006, was very similar (Figs. 2 and 3), the average collection efficiencies were different: CE=1.0 in Zurich and CE=0.5 in Reiden. In Zurich PM$_1$-SO$_4^{2-}$ was available, but only the larger size cut PM$_{10}$-SO$_4^{2-}$ in Reiden. There are some indications from aerosol mass size distribution that a considerable aerosols mass fraction was in the supermicron mode (representing a size range where the lens transmission efficiency of the AMS instrument is suboptimal; Liu et al., 2007) during this winter episode. Thus, it is possible that the different size cuts for the ancillary sulfate filter-measurements have had an influence on the estimated CE in this case. This comment will be added to the manuscript.

Page 24994, lines 13-17 – Add a short discussion about possible reasons for the changing CEs from study to study. Can this tell you something about the particles? Otherwise, lines 4-23 should be moved to the methods section presumably.

The collection efficiency of the AMS instrument is indeed closely related to particle characteristics. Explicitly, aerosol phase, shape etc. were found to prominently affect the CE in laboratory studies (Matthew et al., 2008). The CE (estimated based on comparisons with ancillary field data) can however not be used to unambiguously identify additional characteristics of ambient particles, as several reasons can cause, say, a high CE: aerosol size mass distribution showing a minor fraction of super-micron mass, spherical/liquid/liquid-coated particles due to high relative humidity in the sampling line, high nitrate/water content of the aerosol etc. In this sense, we agree that the paragraph could be part of the methods section. Lines 4-23 on P. 24994 will be moved to and merged with the second paragraph of subsection 2.3 (“Ancillary measurements”) and also the comment from above (on the effect of different size cuts) will be added. The subsection will be re-labeled (“Ancillary measurements and AMS collection efficiency”) and two subchapters will be introduced (“2.3.1 Determination of AMS collection efficiency” and “2.3.1 Black carbon measurements”).

Page 24995, lines 1-8 – Move the BC discussion to Section 3.1 as it a discussion of chemical composition.

Will be done.

Page 24995, line 3 – Missing parentheses after “PM1”.

Will be corrected.

Page 24995, line 3 – Perhaps list maximum BC fraction here as well?

Will be added.

Page 24995, line 5 – Provide actual values here in the text for the “low” BC fractions so that the reader can compare with the >15% value reported on line 3.

Will be added.

Page 24995, lines 6-8 – Without fractions listed in the above sentences it is difficult to use this discussion as a comparison.

Will be done.

Figure 2 – Mention that these are AMS measurements in the caption. Also, the division of the sites between the “Swiss Plateau” and “Alpine region” seems useful. Could this be done in the Tables and Figure 1 as well to make things clearer? It would also be useful to have a definition of these two areas (and what sites fall into them) somewhere

before the introduction of this figure in the text.

We will add to the caption of Figure 2: “[. . .] measured by aerosol mass spectrometers (AMS)”. The information concerning the location of the sites (Alpine region vs. Swiss Plateau) will be added to Table 1 of the revised paper and in Figure 1 the distinction between “Alpine region” and “Swiss Plateau” will be highlighted. We note that the discrimination was explicitly made on P. 24989, L20-23 (Section 2.1), a definition of “Swiss Plateau” was given (P. 24990, L1-3), and the caption of Figure 1 contained this distinction in the ACPD manuscript already.

Page 24996, lines 19-21 – Have other studies in this region, and/or others, observed this seasonal difference in chloride as well?

This seasonal difference in non-refractory submicron chloride fractions (enhanced in winter) has been reported from other continents as well (Japan: Takegawa et al., 2006; New York City: Drewnick et al., 2004, Weimer et al., 2006). These results will be added on P. 24996, L21 in the manuscript.

Page 24997, line 8 – By “homogeneous”, do you mean “similar”? “Homogeneous aerosol composition” can have different meanings, so I would suggest making this clearer.

We will replace “homogeneous” by “similar”.

Page 24997, line 21 – Reference for faster photochemical degradation of PAHs? Is the degradation itself actually faster, or is there just more photochemical reactions occurring?

Aceves and Grimalt (1993) concluded that photochemical decay was the main cause for PAH decrease in the atmosphere. Specifically degradation by OH, NO_2, and O_3 may be relevant as competing processes (Perraudin et al., 2007). The concentrations

of OH and O_3 are strongly linked to solar radiation and, therefore, we hypothesize that both faster reactions and more relevant pathways of degradation can be observed in summer. The citations above will be added to the revised paper.

Page 25000, line 8 – “. . .due the. . .” should say “. . .due to the. . .”.

Will be corrected.

Page 25000, line 22 – Clarify what is meant by “almost as uniform”.

The sentence will be re-written: “The relative abundance of the different organic components (OOA, HOA, P-BBOA) was similar at the different Swiss plateau sites (Payerne, Zürich, Härkingen, and Reiden) when the campaigns were grouped by season of the year (Figure 3) (as was observed for the total AMS-aerosol composition; Figure 2).”

Page 25000, line 25 – “. . .as relevant. . .” should say “. . .as a relevant. . .”.

Will be corrected.

Page 25000, last paragraph – This discussion seems misplaced within this section and doesn’t allow the section to flow properly; consider reorganizing.

Section 3.2 (“Organic components and OA sources”) will be reorganized as follows: first, we discuss the relative OA components in a general way, then we detail the more abundant OOA component and OOA subtypes, and lastly the POA components are assessed.

Page 25001 – Would it be possible to reorganize and combine these last two paragraphs with the earlier discussions of OOA and P-BBOA in this section? It may help the section flow better.

Section 3.2 ("Organic components and OA sources") will be reorganized as follows: first, we discuss the relative OA components in a general way, then we detail the more abundant OOA component and OOA subtypes, and lastly the POA components are assessed.

Figure 4 – Does "modeled" mean the result of factor analysis? This is not clear.

"Modeled" will be replaced by "retrieved by FA-AMS".

Page 25002, lines 18-21 – Is this saying that stronger correlations are observed for winter campaigns when high P-BBOA periods were excluded? This is not clear. Why should the relationship between m/z *44 and OOA fractions depend on OOA loading?*

The point here is that the correlations of total organic fragment *m/z* (org44) (which can be from SOA but from primary wood burning emissions as well) with OOA were higher for data sets that showed small amounts of P-BBOA. We stated that if "campaigns" (rather than certain periods within campaigns) with high P-BBOA fractions were excluded, the correlation org44 vs. OOA was higher (as for the remaining cases org44 mostly resulted from SOA components). The relationship between organic *m/z* 44 and OOA fractions does not depend on absolute OOA loadings but on the OOA abundance. We will revise the passage (P. 25002, L18-21) as follows to make this clear: "An even stronger correlation (R^2=0.83, n=11, not shown) resulted when winter campaigns with relatively low OOA fractions (OOA/OA $\leq$ 40%) but high P-BBOA fractions were excluded from these calculations, because a certain but not exactly known amount of organic *m/z* 44 needs to be attributed to primary wood combustion in these cases (Weimer et al., 2008)." We further added "... for all 13 campaigns" to P. 25002, L13, and "n=13" on L17.

"Figure 5 – What does "pre-Alpine" mean? I don't think this term had been used or defined yet."

The term pre-alpine (adj.) or Prealps (noun) is jargon referring to the transition zone between Alps and plains/lowlands/plateaus (foothills of the Alps). Similar terms exist in latin languages: Préalpes (French), Prealpi (Italian). We agree that it is not very frequently found in the English literature (e.g., the ISI Web of Knowledge accessed in December 2009 only filed 355 articles that included "pre-alpine"). Therefore the figure caption will be modified accordingly "pre-alpine/at the foothills of the Alps" (Figure 5) (and also P. 25003, L28).

Page 25003, line 29 – "is" should be "are"

Will be corrected ("[...] daily cycles [...] are [...]").

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