

Interactive
Comment

Interactive comment on “Historic records of organic aerosols from a high Alpine glacier: implications of biomass burning, anthropogenic emissions, and dust transport” by C. Müller-Tautges et al.

C. Müller-Tautges et al.

hoffmant@uni-mainz.de

Received and published: 27 September 2015

The authors thank the referees for their effort in reviewing the manuscript and improving it by helpful comments. In the following, Referee’s comments, author’s responses and changes in the manuscript are indicated as follows:

(1) comments from Referees (2) authors’ response (3) authors’ changes in manuscript

Referee #1

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



The paper by Müller-Tautges et al describes the concentrations of various organic compounds (α -dicarbonyls, acids) and ions (calcium, oxalate, formate) analyzed from ice core samples drilled in Grenzgletscher, in the southern Swiss Alps. The ice core covers the period 1937-1994 and the dating accuracy is ± 2 years for the time before 1970 and ± 1 year after that. Source apportionment was then applied for the results in order to detect the influence of anthropogenic and biogenic emissions and forest fires to the aerosol composition in the past years. The information received is valuable since usually the chemical data from ice cores is from polar areas and not from populated areas. The paper is well written and clear and I think it is suitable for publication in ACP after minor corrections. The analytical details as well as sampling procedure are described in detail.

(1) What raises questions is on what basis where exactly these compounds chosen for analysis? (2) In contrast to the well-established analysis of inorganic species, organic compounds have been analyzed in ice cores to a much smaller extent (e.g. Legrand et al., 2013). These compounds, however, play an important role as constituents of secondary organic aerosol (SOA), which is a major part of atmospheric aerosol. Thus, the original idea of this study was to characterize the organic compounds in the Grenzgletscher ice core in order to obtain information about SOA composition in the Alpine region (see Introduction). Carboxylic acids were chosen since they are one of the most abundant groups of water-soluble organics in this region (see e.g. Legrand et al., 2007) emerging from atmospheric oxidation processes of different precursors. The target acids were selected as major tracers for anthropogenic activity (e.g. phthalic acid), biogenic emissions (e.g. pinic acid), or biomass burning (e.g. p-hydroxybenzoic acid) and based on the accessibility with the applied UHPLC-ESI-HRMS method. Two of the most abundant organic acids, formic and oxalic acid, could not be analyzed with this method due to their small size and were thus quantified using ion chromatography. In addition, calcium was analyzed as mineral dust tracer that is known to influence the uptake of carboxylic acids. The two smallest α -dicarbonyls glyoxal and methylglyoxal (also derived from atmospheric oxidation) have received increasing scientific interest

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

in recent years due to their important role in the formation and growth of SOA. However, no data on the long-term trend of these compounds are available for the Alpine area so far. (3) Page 13750, line 14: “These compounds, however, play an important role as constituents of secondary organic aerosol (SOA), which is a major part of atmospheric aerosol. Generally, carboxylic acids are one of the most abundant groups of water-soluble organics in the atmosphere (e.g. Legrand et al., 2007). Concentrations of monocarboxylic acids, . . .” Page 13751, line 14: “. . . .by a factor of 3 since the 1950s, which was attributed mainly to an increase in biogenic emissions (Preunkert and Legrand, 2013). The two smallest α -dicarbonyls glyoxal and methylglyoxal are final products of the oxidation chain of many VOCs. They have received increasing scientific interest in recent years due to their important role in the formation and growth of SOA (Fu et al., 2008). However, no data on the long-term trend of these compounds are available for the Alpine area so far.”

(1) When one goal was to evaluate the contribution of forest fires to the aerosol load, alternatives would be levoglucosan or potassium, which are known tracers for biomass burning. Why were they not chosen? (2) Potassium was already analyzed in the ice core and has been shown to have several sources including anthropogenic ones in the second half of the 20th century (Eichler, 2000). Thus, during the industrial period in Europe it cannot unambiguously be related to forest fires. Levoglucosan could not be analyzed with the methods used in this study. Unfortunately, a separate analysis using a different method was not possible in the frame of this study. As levoglucosan is a pyrolysis product of carbohydrates often used as a biomass burning marker compound, it would definitely be beneficial to include it in future studies.

(1) Another issue is the stability of the compounds in the snowpack. The organic compounds are known to undergo photochemical reactions in the snowpack. Is there any information concerning possible losses of the compounds after deposition? (2) This is an important point, as of course postdepositional effects cannot be excluded. Possible processes are 1) Evaporation due to high vapor pressure: Organic compounds with rel-

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

atively high vapor pressure (e.g. formic acid and acetic acid) can be remobilized after deposition and during firnification (Legrand et al. 2003). Since the underlying diffusion processes are active on the cm-scale, losses by evaporation are particularly important at sites featuring low annual snow accumulation rates in the cm range, whereas the sampling site on the Grenzgletscher is a high accumulation site (2.7 m weq/y) with regular precipitation throughout the year. 2) Influence of acidic layers: Concerning formic acid, Legrand et al. (2003) reported postdepositional migration to be additionally influenced by the acidity of the snowpack. As formic acid is a weak acid ($pK_s = 3.77$) with significant vapor pressure over ice, high acidity of a snow layer may result in a shift in the equilibrium (formate/formic acid) towards the protonated form. Due to its high vapor pressure, formic acid is subsequently released into open pore space of firn followed by migration into adjacent less acidic snow layers. Regarding years with low snow accumulation, the migration has a stronger impact compared to years with high accumulation, where the distance of layers is large enough. In order to minimize the impact of migrated compounds into adjacent layers (and thus into younger or older precipitation layers) data analysis was performed using three-year averages. 3) Aqueous phase reactions: A further postdepositional effect is aqueous phase oxidation as reported for methylglyoxal by Ervens et al. (2004). Although there is only a limited aqueous phase present at the grain boundaries under the conditions at this site (ice temperature between -1 and -9°C), oxidation of methylglyoxal cannot be excluded as a possible reason for the generally low concentration of methylglyoxal in the glacier. 4) Photochemical reactions: Photochemical reactions may happen in the snowpack after deposition, as the fresh precipitation layers are exposed to solar radiation. It is not known to what extent the compounds analyzed are degraded by photochemistry. However, this effect is considered to be also less distinct at high accumulation sites, where the exposure time is shorter. (3) End of chapter 3.2., page 13757 line 18: "This indicates a fractionation of G and MG possibly caused by the leaching process. Further postdepositional processes that may influence records of the organic species in the snowpack are aqueous phase oxidation, photochemistry, and remobilization after

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

deposition and during firnification (Ervens et al., 2004, Grannas et al., 2007, Legrand et al., 2003). Aqueous phase oxidation was reported for methylglyoxal by Ervens et al. (2004). Although there is only a limited aqueous phase present at the grain boundaries under the conditions at this site (ice temperature between -1 and -9°C), oxidation of methylglyoxal cannot be excluded as a possible reason for the generally low concentration of methylglyoxal in the glacier. Processes involving photochemistry or migration/evaporation of compounds are particularly important at sites with very low accumulation rates. Since the mean annual accumulation rate at the Grenzgletscher site is high (2.7 m weq), the latter processes are assumed to have a minor effect on the concentration record presented here.”

(1) The source apportionment was applied for the results and it showed that biomass burning was the main factor influencing the composition of organic species in the ice core. Biomass burning factor also follows nicely the curve describing the burned area in Switzerland. Is the amount of forest fires so large that domestic wood burning is totally negligible in producing organic aerosols? (2) Indeed, organic biomass burning aerosols are also emitted from domestic wood burning. We however think that the discussed signal mostly derives from forest fires. We add a comment accordingly. (3) Page 13761, end of paragraph 3.3.1.: “Besides biomass burning, organic species having a high loading in PC1 are known to be also emitted during domestic wood burning (see e.g. Gaeggeler et al., 2008). However, residential heating strongly peaks in winter and is restricted to urban areas at low altitudes. In winter, due to the stability of the atmosphere, pollution is trapped in the boundary layer close to the surface and does not affect the high-altitude Grenzgletscher site within the free troposphere. Forest fires in Southern Switzerland peak in spring, especially during days with warm Foehn-wind that causes a drop in both fuel moisture and air humidity (de Angelis et al. 2015). In such weather and atmospheric conditions, thermally-driven convection enables the transport of the organic aerosols from forest fires to the glacier. Furthermore, energy consumption by wood burning in Switzerland peaked during the 1940s and from the 1980s on (Schweizerische Gesamtenergiestatistik 2012). This is in contrast to the

records of fire tracers (e.g., p-hydroxybenzoic acid) showing a maximum in the 1970s. In conclusion, we assume that the record of PC1 and thus the organic biomass burning tracers at the Grenzgletscher site are dominated by emissions from forest fires, but not from domestic wood burning.”

(1) Technical aspects: It would be clearer if the letter describing the Figures in figure captions would be in front of a sentence and not at the end as it is now. (2) We agree with the reviewer. (3) The figure caption of Figure 5 was changed into: “Figure 5. A) Records of PC1 and FSS (burned area by fires in Southern Switzerland), B) PC2 and anthropogenic emissions of non-methane volatile organic compounds (NM-VOC) in Switzerland, France, and Italy from 1940 to 1990, C) PC3 and historic record of Ca²⁺, D) PC4. Data in graph B were extracted from (a) (BUWAL, 1995) and (b) (EDGAR, 2010) (black symbols: annual averages, red/black line: three year-averages).” The figure caption of Figure 6 was changed into: “Figure 6. A) Record of the burned area by fires in Southern Switzerland (FSS, black dots: annual averages, red line: three-year averages), B) annual burned area of grassland, softwood, and hardwood in Southern Switzerland from 1942 to 1993.”

References:

Angelis, A. de, Ricotta, C., Conedera, M., and Pezzatti, G.B.: Modelling the meteorological forest fire niche in heterogeneous pyrologic conditions. PLoS ONE 10, 2: e0116875, 17 p., doi: 10.1371/journal.pone.0116875, 2015.

Eichler, A., Dissertation, University of Bern, Bern, 2000.

Ervens, B., Feingold, G., Frost, G. J., and Kreidenweis, S. M.: A modeling study of aqueous phase production of dicarboxylic acids: 1. Chemical pathways and speciated organic mass production, J. Geophys. Res., 109, D15205, doi:10.1029/2003JD004387, 2004.

Fu, T., Jacob, D., Wittrock, F., Burrows, J., Vrekoussis, M., and Henze, D.: Global

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

budgets of atmospheric glyoxal and methylglyoxal, and implications for formation of secondary organic aerosols, *J. Geophys. Res.*, 113, (D15), D15303, doi:10.1029/2007JD009505, 2008.

Gaeggeler, K., Prevot, A. S. H., Dommen, J., Legreid, G., Reimann, S., and Baltensperger, U.: Residential wood burning in an Alpine valley as a source for oxygenated volatile organic compounds, hydrocarbons and organic acids, *Atmos. Environ.*, 42, 8278-8287, doi:10.1016/j.atmosenv.2008.07.038, 2008.

Grannas, A. M. et al.: An overview of snow photochemistry: evidence, mechanisms and impacts, *Atmos. Chem. Phys.*, 7, 4329-4373, doi:10.5194/acp-7-4329-2007, 2007.

Legrand, M., Preunkert, S., Wagenbach, D., Cachier, H., and Puxbaum, H.: A historical record of formate and acetate from a high-elevation Alpine glacier: Implications for their natural versus anthropogenic budgets at the European scale, *J. Geophys. Res. Atmos.*, 108, D24, doi:10.1029/2003JD003594, 2003.

Legrand, M., Preunkert, S., Schock, M., Cerqueira, M., Kasper-Giebl, A., Afonso, J., Pio, C., Gelencsér, A., and Dombrowski-Etchevers, I.: Major 20th century changes of carbonaceous aerosol components (EC, WinOC, DOC, HULIS, carboxylic acids, and cellulose) derived from Alpine ice cores, *J. Geophys. Res.*, 112, doi:10.1029/2006JD008080, 2007.

Legrand, M., Preunkert, S., Jourdain, B., Guilhermet, J., Faïn, X., Alekhina, I., and Petit, J. R.: Water-soluble organic carbon in snow and ice deposited at Alpine, Greenland, and Antarctic sites: a critical review of available data and their atmospheric relevance, *Clim. Past*, 9, 2195–2211, doi:10.5194/cp-9-2195-2013, 2013.

Schweizerische Gesamtenergiestatistik 2012, Schweizerische Eidgenossenschaft, Bundesamt für Energiewirtschaft, http://www.bfe.admin.ch/themen/00526/00541/00542/00631/index.html?dossier_id=00763&lang=en, Discussion Paper last access: 08-30-2015.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

en, Discussion Paper



The paper reports on the concentrations of various organic compounds (α -dicarbonyls, carboxylic acids or carboxylates) and calcium analysed along an ice core drilled in the Grenzgletscher (Swiss Alps) and covering the period 1937-1994. Results are discussed in terms of anthropogenic and biogenic emissions as well as burned vegetation area over the last 60 years. Whereas such a large array of organic species is rarely documented in ice cores and from this point of view merits to be published, there are many weaknesses in the paper as it stands. In addition to miss a few previous works and important conclusions (minor criticism), there are several misleading wordings and the text contains too many uncomfortable abbreviates rendering the understanding of the text sometimes difficult. Furthermore, the discussion of data is not enough argued. Therefore, given the interest of these kinds of organic data in ice, I would recommend to authors to work further their data discussion in view to reach a sufficient level of usefulness to be published in the ACP journal.

Missed previous works and conclusions: (1) Your statement “For the first time, long-term records of the carboxylic acids and dicarbonyls as well as their source apportionment are reported for Western Europe” is not correct for carboxylic acids since Legrand et al. (2003) already extensively discussed the budget of formic acid in the Alps concluding that vegetation emissions largely dominate anthropogenic emissions (vehicular emissions of alkenes). The trend of C2-C5 dicarboxylic acids was also discussed in terms of anthropogenic versus natural sources over Western Europe (one third and two thirds, respectively) by Legrand et al. (2013). Finally the long-term trend of polyacids (HUmic Like Substances, HULIS) was discussed by Guilhermet et al. (2013) in the study of an ice core extracted from the Mt Blanc. (2) The authors agree with the reviewer. (3) The sentence “For the first time, long-term records of the carboxylic acids and dicarbonyls as well as their source apportionment are reported for Western Europe” in the abstract (p. 13749, line 8) was changed as follows: “Long-term records of the carboxylic acids and dicarbonyls as well as their source apportionment are reported

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



for Western Europe. This is the first study comprising long-term trends of dicarbonyls and long-chain dicarboxylic acids (C6-C12) in Alpine precipitation". In the introduction chapter (p. 13751, line 14), the reference Legrand et al. (2013) was added: "Legrand et al. (2013) also reported the long-term trend of water-soluble organic carbon (WOC) including C2-C5 dicarboxylic acids in an Alpine ice core and the dominance of natural compared to anthropogenic sources."

(1) More generally concerning previous works, I think that the idea of your Table 2 was (and it is legitimate) to summarize organics measured in ice (including those in this work and the previous ones) related to at least aldehydes and acids. If so, you missed species discussed in the following paper that includes HCHO (the dominant aldehyde in ice), short-chain monocarboxylates other than formate (lactate, acetate, glycolate, and glyoxylate), short chain dicarboxylates other than oxalate (malate, malonate, succinate, and glutarate) as well as polyacids (HUMic Like Substances, HULIS). Legrand, M., S. Preunkert, B. May, J. Guilhermet, H. Hoffmann, and D. Wagenbach, Major 20th century changes of the content and chemical speciation of organic carbon archived in Alpine ice cores: implications for the long-term change of organic aerosol over Europe, *J. Geophys. Res. Atmos.*, 118, doi :10.1002/jgrd.50202, 2013. (2) The idea of Table 2 was indeed to compare the concentration results of the species measured in our study to other studies targeting the same species. We think this is justified, but agree with the referee that we missed to include the oxalate levels from the Legrand et al. 2007 study. (3) A column was added to Table 2 containing the oxalate levels according to Legrand et al. (2007).

(1) All your discussion in section 3.3.3 missed to introduce a key point related to the effect of pH (not only the effect of calcium) on deposition of formate as already detailed for the case of Alpine ice cores by Legrand et al. (2003). (2) We agree with the referee that we did not discuss the effect of pH adequately. See below.

Misleading wording: (1) The title of the paper is misleading since species like formate (in fact formic acid) is a gaseous atmospheric species not an aerosol species: see the

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

paper from Preunkert et al. 2007 who examined the gas/particulate phase of formic acid nearby the Mt Blanc summit (French Alps) (see also references therein on previous works done at Sonnblick by Kasper and Puxbaum). Preunkert, S., M. Legrand, B. Jourdain, and I. Dombrowski-Etchevers, Acidic gases (HCOOH, CH₃COOH, HNO₃, HCl, and SO₂) and related aerosol species at a high mountain Alpine site (4360 m elevation) in Europe, J. Geophys. Res., 112, D23S12, doi:10.1029/2006JD008225, 2007. (2) As we measured organic compounds in the melted ice sample, it is not possible to distinguish between species transported to the glacier in aerosol particles and species incorporated in snow during or after deposition from the gas phase. (3) The first part of the title was changed into: “Historic records of organic compounds from a high Alpine glacier”

(1) The rest of the title is also misleading what means “implications” you mean “influence on their budget” ? (2) We agree that the term implication (“a possible effect or result”) is usually used when referring to the future, so in the case of interpreting historic records it might be misleading. (3) That’s why the second part of the title was changed into “influences of biomass burning, anthropogenic emissions, and dust transport”

(1) The first sentence of the abstract and at other places in the text: Historic records of α -dicarbonyls (glyoxal, methylglyoxal), carboxylic acids (C₆–C₁₂ dicarboxylic acids, pinic acid, p-hydroxybenzoic acid, phthalic acid, 4-methylphthalic acid), and major ions (oxalate, formate, calcium) were determined...: The wording is confusing since formate (or formic acid) is a carboxylate (or carboxylic acid) and oxalate (or oxalic acid) is a C₂ dicarboxylic acid (see also my comment on Table 1). (2) The division into dicarbonyls, carboxylic acids and major ions was due to the different analytical methods used for the analysis of the ice samples. Indeed, this might be confusing for the reader. (3) Page 13749, line 6, abstract: The sentence “Measurements were conducted using ultra-high performance liquid chromatography (UHPLC) coupled to electrospray-ionization high resolution mass spectrometry (ESI-HRMS)” was changed into “Chemical analysis of the organic compounds was conducted using ultra-high performance liquid chromatog-

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

raphy (UHPLC) coupled to electrospray-ionization high resolution mass spectrometry (ESI-HRMS) for dicarbonyls and long-chain carboxylic acids and ion chromatography for short-chain carboxylates”.

(1) Also for me, calcium, ammonium, nitrate and sulfate are major ions in Alpine ice cores, not oxalate. (2) The referee is right as the most abundant ions in aerosol (sulphate, ammonium, nitrate) are not included in the study. (3) The word “major ions” was changed into “ions”.

(1) The use of abbreviates throughout the text like VAN for vanillic acid or G for glyoxal renders the lecture of the manuscript very difficult. The reader needs to know that G is an aldehyde and that VAN is an acid, please use the chemical name everywhere in the text. The abbreviate used for calcium (CAL) is very confusing and totally un-useful compared to the common notation “Ca” or Ca^{2+} . When reading a sentence with the abbreviate “C6” I think about benzene or cyclohexane etc. So as many chemists are expected to read your paper, please use the normal wording using complete chemical name of compounds. (2) This is a good point. Although we intended to enhance readability of the manuscript using abbreviates, we agree that the mix of capital letter abbreviates (e. g. G or VAN) and chain length (C6-C12, common in organic chemistry) might be confusing. In the case of calcium we agree that CAL is not common. (3) Chemical names were used in the text instead of abbreviates except when addressing a group of species (e.g. “C6-C10 dicarboxylic acids”). “CAL” was changed into “ Ca^{2+} ”.

(1) In Table 1 you separate formate and oxalate from other carboxylate like phthalate etc: I cannot see at all why ? (2) The separation of acids and ions is made due to different analytical techniques used for analysis. Oxalate and formate were measured using ion chromatography. We agree with the referee that it is more consistent to put together the carboxylates and carboxylic acids. (3) In Table 1, formate and oxalate were moved to “Monocarboxylic acids”.

(1) In Table 3: while I understand that PC4 that includes mainly formate and oxalate

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



merges from the correlation with calcium, I think the wording transport with mineral dust is very misleading. Referring to the paper from Legrand et al. (JGR, 2013) you can say that these two carboxylates mainly originate from vegetation emissions with an effect of the pH of cloud (partly and only partly driven by its calcium level) on their scavenging in snow? See more comments later on your section 3.3.3. (2) The reference by Legrand et al. 2013 as discussed by the referee was added to section 3.3.3. For a more detailed discussion on the effect of pH see below. (3) Page 13762, Line 9: “Major sources of the low-chain carboxylates formate and oxalate in the Alps are biogenic emissions (see e.g. Legrand et al. 2013). The observed high correlations between oxalate, formate, and Ca²⁺ suggest that their concentrations are mainly determined by the common transport with mineral dust to the glacier, but not by the source. The historic record. . .

Data Discussion: Your discussion in terms of sources is only based on PCs and leads to strange (conflicting or unexpected) conclusions. This part has to be reworked. I just list below the most critical points that need to be addressed.

(1) Since you stated “To obtain annual averages, equal aliquots of the ice sections belonging to a certain year (2 to 9 sections per year) were combined” you can therefore report on the seasonality of your organic species. Such information certainly will strengthen the discussions in terms of sources (biogenic and wild fires are restricted to the summer season whereas most of anthropogenic emissions, except domestic wood burning, are similar in winter and summer). Also this will serve to demonstrate that the trends seen in your core are not biased by change of the winter to summer partitioning over the past. That may also permit to address partly the possible post depositional effect. For instance when discussing aldehydes I think you cannot discard the possibility that changes seen with depth for methyl glyoxal is due to destruction of this species in the glacier (aqueous phase oxidation of methyl glyoxal are known to be quite efficient, see Ervens et al., JGR 2004). (2) Due to the required sample mass of ~100 g for the organic analyses, seasonal resolution is restricted to two years only (1992-93). Unfortunately, this reduced high-resolution data set was not sufficient to draw significant

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

conclusions about seasonal changes of the investigated organic species and further studies are required. As discussed above, postdepositional processes are particularly important at sites with very low accumulation rates. For the Grenzgletscher site with a high mean annual accumulation rate of 2.7 m weq, postdepositional effects are assumed to have a minor influence. However, the authors agree that postdepositional decay of methylglyoxal cannot be excluded completely. Information on possible postdepositional processes including aqueous phase oxidation was added accordingly. (3) End of chapter 3.2., page 13757 line 18: “This indicates a fractionation of glyoxal and methylglyoxal possibly caused by the leaching process. Further postdepositional processes that may influence records of the organic species in the snowpack are aqueous phase oxidation, photochemistry, and remobilization after deposition and during firnification (Ervens et al., 2004, Grannas et al., 2007, Legrand et al., 2003). Aqueous phase oxidation was reported for methylglyoxal by Ervens et al. (2004). Although there is only a limited aqueous phase present at the grain boundaries under the conditions at this site (ice temperature between -1 and -9°C), oxidation of methylglyoxal cannot be excluded as a possible reason for the generally low concentration of methylglyoxal in the glacier. Processes involving photochemistry or migration/evaporation of compounds are particularly important at sites with very low accumulation rates. Since the mean annual accumulation rate at the Grenzgletscher site is high (2.7 m weq), the latter processes are assumed to have a minor effect on the concentration record presented here.”

(1) The discussion of data using PCs seems to me too strong. Some existing correlations may be driven by something else than the sources. (2) Principal component analyses is a well-established and common technique in ice core science to reduce the data set combining (grouping) those species that share variance due to a common source or transport pattern. In our study we received 4 groups for the investigated species (Table 3). The species within the respective groups reveal similar long-term trends (Figs. 1-5). P-hydroxybenzoic acid has a unique source – pyrolysis of lignin and is a pure fire tracer (see chapter 3.3.1.). Furthermore it is well correlated with the

fire area in Southern Switzerland. We think this justifies claiming “biomass burning” as one of the major source for species having a high loading in PC1. Similarly, phthalic acid and adipic acid are reported to be mainly of anthropogenic origin and the record of PC2 is in agreement with that of anthropogenic VOC emissions. Thus, we do not agree that the discussion of the data is too strong. It is not only based on the PCA, but also corroborated by findings from previous studies. The only exceptions with somehow unexpected results are vanillic acid and pinic acid (see below).

(1) The correlation with burned area is not obvious at all. I am surprised that you attributed pinic acid to biomass burning: if so that means that the precursors (pinenes emitted by conifers) have been produced and here I am surprised that vanillic acid is not there ? (2) We do not agree with the referee. The good correspondence between PC1 (and biomass burning related species) and burned area is shown in Figure 5 and Table 4. We do not state in the manuscript that forest fires are the exclusive source of the species having a high loading in PC1. Indeed, the calculated values of r^2 (Table 4) indicate that between 22% and 75% of the variance of these organic compounds is explained by the changes in burned area (FSS) (Paragraph 3.3.1). Whereas the good correlation of the p-hydroxybenzoic acid with the FSS was expected from other ice core studies discussed in the manuscript (Chapter 3.3.1.), the deviation between the vanillic acid record and the FSS was indeed somehow surprising. The fact that vanillic acid does not appear in the PC1 is probably site-specific and was already given in the manuscript: “the applicability of vanillic acid as a fire marker especially for softwood (conifers) cannot be confirmed in the region of Southern Switzerland, where hardwood forest and grasses are the dominant vegetation types hit by forest fires, especially in the main spring fire season (Pezzatti et al. 2009).” Pinic acid is expected to originate from the atmospheric oxidation of naturally emitted biogenic precursor species pinenes as mentioned by the referee. However, several studies report enhanced emissions of pinenes from biomass burning (see Chapter 3.3.1.). A further argument that the trend of pinic acid in the Grenzgletscher is influenced by biomass burning instead of direct biogenic emissions is the missing link to temperature. Direct biogenic emissions from

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

forests have been shown to follow temperatures (Eichler et al., 2009, Kellerhals et al., 2010). Temperatures in Southern Switzerland in the period 1940-1993 are high during the 1940s, 80s, and 90s (meteo Swiss), but lowest during the periods with the highest pinic acid concentrations (1960s and 70s). We added a discussion accordingly. (3) The possible reason that vanillic acid does not appear in the PC1 is probably site-specific and was already given in the manuscript (page 13761, lines 6-9). Page 13760, lines 11-14: “However, the results of this study indicate that the concentration of PIN detected in the ice core from Grenzgletscher is dominated by biomass burning origin and not by direct biogenic emission of the respective precursors. A further argument that the trend of pinic acid in the Grenzgletscher is influenced by biomass burning instead of direct biogenic emissions is the missing link to temperature. Direct biogenic emissions from forests have been shown to follow temperatures (Eichler et al., 2009, Kellerhals et al., 2010). Temperatures in Southern Switzerland in the period 1940-1993 are high during the 1940s, 80s, and 90s (meteo Swiss), but lowest during the periods with the highest pinic acid concentrations (1960s and 70s).”

(1) In addition to the fact that I don't believe that your signal is restricted to sources located in Switzerland, many organic that you have investigated are also produced during domestic wood burning (a common practice in mountain alpine area) not only wild fires. Also the presence of azelaic acid suggests me a source emitting precursors like unsaturated fatty acids like oleic acid: so what about cooking in summer during which you emit both wood burning and cooking derived products like fatty acids ? (2) Indeed, the organic biomass burning aerosols are also emitted from domestic wood burning. We add a discussion accordingly. (3) Page 13761, end of paragraph 3.3.1.: “Besides biomass burning, organic species having a high loading in PC1 are known to be also emitted during domestic wood burning (see e.g. Gaeggeler et al., 2008). However, residential heating strongly peaks in winter and is restricted to urban areas at low altitudes. In winter, due to the stability of the atmosphere, pollution is trapped in the boundary layer close to the surface and does not affect the high-altitude Grenzgletscher site within the free troposphere. Forest fires in Southern Switzerland peak in spring,

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

especially during days with warm Foehn-wind that causes a drop in both fuel moisture and air humidity (de Angelis et al. 2015). In such weather and atmospheric conditions, thermally-driven convection enables the transport of the organic aerosols from forest fires to the glacier.. Furthermore, energy consumption by wood burning in Switzerland peaked during the 1940s and from the 1980s on (Schweizerische Gesamtenergiestatistik 2012). This is in contrast to the records of fire tracers (e.g., p-hydroxybenzoic acid) showing a maximum in the 1970s. In conclusion, we assume that the record of PC1 and thus the organic biomass burning tracers at the Grenzgletscher site are dominated by emissions from forest fires, but not from domestic wood burning.”

(1) Methyl glyoxal and glyoxal are produced by oxidation of toluene emitted by cars: any comment in discussing their trends ? (2) As very small oxidized organic molecules, methylglyoxal and glyoxal are final products of the oxidation chain of many VOCs, for example toluene. As discussed by the referee, one source of methylglyoxal and glyoxal is emission of toluene from cars (Nishino et al., 2010). Toluene dominates VOC concentrations of car exhaust at many sites in Switzerland (Stemmler et al., 2005). Direct measurements of toluene in Switzerland started only in the 1990s and showed a decreasing trend between 1993 and 1998 (Heeb et al., 2000). Similar to the trend in the total VOC concentrations in Switzerland (Fig. 5), toluene concentrations are assumed to increase until the end of the 1980s and decrease after the introduction of the catalysts. (3) Page 13760: “G is a secondary oxidation product formed from biogenic as well as anthropogenic precursors (e.g., toluene emitted from car exhaust), but has also been reported as a primary emission product by biomass burning, as indicated by the high loadings within PC1 and PC2.” Page 13761: “. . . vehicle exhaust (Zhang et al., 2010). One major source for MG is toluene emission from cars (Nishino et al., 2010), dominating VOC emissions from traffic exhaust at many sites in Switzerland (Stemmler et al., 2005). Both dicarboxylic acids sebacic acid and dodecanedioic acid. . .”

(1) Discussing of formate in section 3.3.3 missed a key point: formate in ice has been incorporated from the gaseous weak acid (formic acid). The dependency of the henry

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

law constant to the pH of cloud has to be considered for past change. Not only the input of calcium from alkaline dust material controls the pH but also the huge acidification of precipitation in Europe after 1940. So at first the decreasing trend of formate is also relative to acidification over the recent decades by growing SO₂ and NO_x emissions. (+ Comment on Table 3: “transport with mineral dust”) (2) We agree with the referee that the effect of the pH on the formate concentrations was not addressed properly and we add a discussion into the manuscript accordingly (end of paragraph 3.3.3) and the record of the pH into Fig. 1. (3) Page 13762, end of paragraph 3.3.3: “A further factor that might influence formate (and to a lesser extent oxalate) concentrations in the atmosphere is the acidity (pH). Generally, a stronger acidification of the cloud water leads to a less efficient scavenging of the weak acid HCOOH. Periods of enhanced SO₂ and NO_x emissions have caused a decrease in ice core formate concentrations (see e.g., Legrand et al., 2003, Eichler et al., 2009, Legrand and de Angelis, 1996). Although at the Grenzgletscher site the formate and oxalate concentrations drop in the 1950s parallel with the acidification of the atmosphere, the increase of the pH after the 1970s did not lead to a rise in the concentrations of the weak short-chain acids (Fig. 1). While formate and oxalate are significantly correlated with Ca²⁺ ($r=0.46$ and 0.63 , $p<0.05$, respectively), there is no significant correlation between formate/oxalate and pH ($r=0.2$ and 0.17 , $p<0.05$, respectively). We conclude that the dust concentration of the air masses transported to the Grenzgletscher site is the dominating factor determining the uptake of formic and oxalic acid.” The figure caption of Figure 1 was changed into: “Fig. 1 Ice core records of oxalate, formate, calcium, and pH (black dots. . .”

(1) By the way not that your trend of oxalate is opposite to the ones found at the Mt Blanc glacier ? This oxalate trend is quite unexpected: Are you sure that you have not lost a part of oxalate because of bacterial activity acting during your sampling (many researchers have experienced such a problem). (2) We are aware of possible bacterial decay and tried to reduce it by filtrating the melted samples using syringe filters. Unfortunately, this led to high blanks, especially concerning phthalic acid and glyoxal, so analysis was performed without filtration. However, all ice core sections were handled

at -25°C during sampling and were kept frozen until the day of analysis to prevent decay as far as possible. We do not agree that our findings from the oxalate record are different from those at the Mt Blanc glacier. We postulate that oxalate is taken up by the alkaline mineral dust air masses during transport mainly from the Sahara to the glacier by acid-base reaction. Both records, Ca^{2+} and oxalate peak at the Grenzgletscher site during the 1940s and 1950s. At the Mt. Blanc site, Ca^{2+} (dust) maxima were found between 1950 and 1960 (Preunkert and Legrand, 2013). Similarly, oxalate peaked in the 1950s (Legrand et al., 2007). A comment was added in the manuscript accordingly. (3) Page 13762, end of paragraph 3.3.3: “The strong relation between Ca^{2+} and oxalate was also observed from another Alpine ice core (Col du Dôme, Mt. Blanc). At that site, Ca^{2+} (dust) maxima were found between 1950 and 1960 (Preunkert and Legrand, 2013). Similarly, oxalate peaked in the 1950s (Legrand et al., 2007).”

References:

Angelis, A. de; Ricotta, C.; Conedera, M.; Pezzatti, G.B.: Modelling the meteorological forest fire niche in heterogeneous pyrologic conditions. *PLoS ONE* 10, 2: e0116875, 17 p., doi: 10.1371/journal.pone.0116875, 2015.

Eichler, A., Brüttsch, S., Olivier, S., Papina, T., and Schwikowski, M.: A 750 year ice core record of past biogenic emissions from Siberian boreal forests, *Geophys. Res. Lett.*, 36, doi:10.1029/2009GL038807, 2009.

Ervens, B., Feingold, G., Frost, G. J., and Kreidenweis, S. M.: A modeling study of aqueous phase production of dicarboxylic acids: 1. Chemical pathways and speciated organic mass production, *J. Geophys. Res.*, 109, D15205, doi:10.1029/2003JD004387, 2004.

Gaeggeler, K., Prevot, A. S. H., Dommen, J., Legreid, G., Reimann, S., Baltensperger, U.: Residential wood burning in an Alpine valley as a source for oxygenated volatile organic compounds, hydrocarbons and organic acids, *Atmos. Environ.*, 42, 8278-8287, doi:10.1016/j.atmosenv.2008.07.038, 2008.

Grannas, A. M. et al.: An overview of snow photochemistry: evidence, mechanisms and impacts, *Atmos. Chem. Phys.*, 7, 4329–4373, doi:10.5194/acp-7-4329-2007, 2007.

Heeb, N. V., Forss, A. M., Bach, C., Reimann, S., Herzog, A., and Jaekle, H. W.: A comparison of benzene, toluene and C2-benzenes mixing ratios in automotive exhaust and in the suburban atmosphere during the introduction of catalytic converter technology to the Swiss Car Fleet, *Atmos. Environ.*, 34, 3103–3116, doi:10.1016/S1352-2310(99)00446-X, 2000.

Kellerhals, T., Brütsch, S., Sigl, M., Knüsel, S., Gäggeler, H.W., and Schwikowski, M.: Ammonium concentration in ice cores – a new proxy for regional temperature reconstruction? *J. Geophys. Res. Atmospheres* 115, D16123, doi:10.1029/2009JD012603, 2010.

Legrand, M. and Angelis, M. de: Light carboxylic acids in Greenland ice: A record of past forest fires and vegetation emissions from the boreal zone, *J. Geophys. Res. Atmos.*, 101, 4129–4145, doi:10.1029/95JD03296, 1996.

Legrand, M., Preunkert, S., Wagenbach, D., Cachier, H., and Puxbaum, H.: A historical record of formate and acetate from a high-elevation Alpine glacier: Implications for their natural versus anthropogenic budgets at the European scale, *J. Geophys. Res. Atmos.*, 108, D24, doi:10.1029/2003JD003594, 2003.

Legrand, M., Preunkert, S., Schock, M., Cerqueira, M., Kasper-Giebl, A., Afonso, J., Pio, C., Gelencsér, A., and Dombrowski-Etchevers, I.: Major 20th century changes of carbonaceous aerosol components (EC, WinOC, DOC, HULIS, carboxylic acids, and cellulose) derived from Alpine ice cores, *J. Geophys. Res.*, 112, doi:10.1029/2006JD008080, 2007.

Legrand, M., Preunkert, S., Jourdain, B., Guilhermet, J., Faïn, X., Alekhina, I., and Petit, J. R.: Water-soluble organic carbon in snow and ice deposited at Alpine, Greenland, and Antarctic sites: a critical review of available data and their atmospheric relevance,

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

Clim. Past, 9, 2195–2211, doi:10.5194/cp-9-2195-2013, 2013.

MeteoSwiss, Federal Office of Meteorology and Climatology, Climate trends in Switzerland, <http://www.meteoswiss.admin.ch/home/climate/present-day/climate-trends.html#ths200m0;south;year;1864-smoother>, last access: 08-30-2015.

Nishino, N., Arey, J., and Atkinson, R.: Formation Yields of Glyoxal and Methylglyoxal from the Gas-Phase OH Radical-Initiated Reactions of Toluene, Xylenes, and Trimethylbenzenes as a Function of NO₂ Concentration, *J. Phys Chem. A*, 114, 10140–10147, doi:10.1021/jp105112h, 2010.

Pezzatti, G. B., Bajocco, S., Torriani, D., and Conedera, M.: Selective burning of forest vegetation in Canton Ticino (Southern Switzerland), *Plant Biosyst.*, 143, 609–620, doi:10.1080/11263500903233292, 2009.

Preunkert, S. and Legrand, M.: Towards a quasi-complete reconstruction of past atmospheric aerosol load and composition (organic and inorganic) over Europe since 1920 inferred from Alpine ice cores, *Clim. Past*, 9, 1403–1416, doi:10.5194/cp-9-1403-2013, 2013.

Schweizerische Gesamtenergiestatistik 2012, Schweizerische Eidgenossenschaft, Bundesamt für Energiewirtschaft, http://www.bfe.admin.ch/themen/00526/00541/00542/00631/index.html?dossier_id=00763&lang=en, last access: 08-30-2015.

Stemmler, K., Bugmann, S., Buchmann, B., Reimann, S., and Staehelin, J.: Large decrease of VOC emissions of Switzerland's car fleet during the past decade: results from a highway tunnel study, *Atmos. Environ.*, 39, 1009–1018, doi:10.1016/j.atmosenv.2004.10.010, 2005.

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 15, 13747, 2015.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

