Authors' response letter

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

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 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 relatively 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 (pKs = 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 at 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 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 at 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 Ca^{2+}, 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:

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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, last access: 08-30-2015.

Referee #2

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 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 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 therehein 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 chromatography (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 Ca2+. 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 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 Ca^{2+} 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 know 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 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 at 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 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, 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 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 NOx emissions. (+ Comment on Table 3: "transport with mineral dust")

(2) We agree with the referee that the effect of the pH on the format 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 SO_2 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 Ca^{2+} ($r=0.46$ 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)."

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Historic records of organic ~~aerosols~~compounds from a high Alpine glacier: ~~Implications~~Influences of biomass burning, anthropogenic emissions, and dust transport

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Abstract

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 with annual resolution in an ice core from Grenzgletscher in the southern Swiss Alps, covering the time period from 1942 to 1993. ~~Measurements were~~Chemical analysis of the organic compounds was conducted using ultra-high performance liquid chromatography (UHPLC) coupled to electrospray~~-~~-ionization high resolution mass spectrometry (ESI-HRMS~~). For the first time,~~) for dicarbonyls and long-chain carboxylic acids and ion chromatography for short-chain carboxylates. Long-term records of the carboxylic acids and dicarbonyls as well as their source apportionment are reported for Western Europe. This is the first study comprising long-term trends of dicarbonyls and long-chain dicarboxylic acids (C6-C12) in Alpine precipitation. Source

assignment of the organic species present in the ice core was performed using principal component analysis. Our results suggest biomass burning, anthropogenic emissions, and transport of mineral dust to be the main parameters influencing the concentration of organic compounds. Ice core records of several highly correlated compounds (e.g. *p*-hydroxybenzoic acid, pinic acid, ~~C7~~pimelic and ~~C8 dicarboxylic~~suberic acids) can be related to the forest fire history in ~~southern~~Southern Switzerland. *P*-hydroxybenzoic acid was found to be the best organic fire tracer in the study area, revealing the highest correlation with the burned area from fires. Historical records of methylglyoxal, phthalic acid, and dicarboxylic acids ~~C6, C10~~adipic acid, sebacic acid, and ~~C12~~dodecanedioic acid are comparable with that of anthropogenic emissions of volatile organic compounds (VOCs). The small organic acids oxalic acid and formic acid are both highly correlated with calcium, suggesting their records to be affected by changing mineral dust transport to the drilling site.

1 Introduction

To place recent environmental and climatic changes in a longer-term context, and disentangle anthropogenic and natural sources of air pollution, information on past atmospheric conditions is necessary. Glaciers are valuable environmental archives, as they preserve past atmospheric aerosol deposited with snowfall. Hence, the analysis of aerosol-related chemical compounds in ice core samples can give information on past environmental and climatic conditions. Most studies have focused on inorganic aerosol related parameters such as NH_4^+, NO_3^-, SO_4^{2-}, as well as black carbon and heavy metals, for which a significant increase was observed in snow during the twentieth century (Preunkert et al., 2001, 2003; Schwikowski et al., 1999; Mayewski et al., 1986; Fischer et al., 1998a; Fischer et al., 1998b; Döscher et al., 1996; Legrand et al., 2002; Eichler et al., 2000a; van de Velde et al., 2000; Barbante et al., 2004; Schwikowski et al., 2004; Gabrielli et al., 2005). This was mainly assigned to enhanced anthropogenic emissions of the respective precursors, e.g. enhanced anthropogenic SO_2 emissions resulting in high sulphate concentrations archived in ice.

In contrast to the well-established analysis of inorganic species, organic compounds have been analyzed in ice cores to a much smaller extent (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. 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, mainly formic acid and acetic acid have been determined in ice cores from the Alps (Legrand et al., 2003), Greenland (Legrand et al., 1992; Legrand and Angelis, 1996) and Antarctica (Angelis et al., 2012). These compounds can be attributed to vegetation emission, boreal forest fires or anthropogenic (vehicle) emissions. Short dicarboxylates (C2-C5) were analyzed in distinct sections of Alpine firn and ice cores from Col du Dôme and Colle Gnifetti. They were attributed to secondary formation from vegetation emissions (Legrand et al., 2007). Historic records of dicarboxylic acids (C2-C10), oxocarboxylic acids (C2-C9), and α-dicarbonyls (C2-C3) were reported in an ice core from Greenland (Kawamura et al., 2001), suggesting dicarboxylic acids in ice cores to serve as proxies for the oxidative capacity of the atmosphere in the past. Long-chain carboxylic acids (fatty acids, C14-C22) were also detected in an ice core from Greenland and attributed to marine and terrestrial biological sources (Kawamura et al., 1996). Formaldehyde was analyzed in a firn core from Lys glacier (Largiuni, 2003) and ice cores from Greenland (Staffelbach et al., 1991), but there are indications that it is not well preserved under most conditions (Hutterli et al., 2002). Some studies focus on persistent organic pollutants (POPs) (Pavlova et al., 2014; Wang et al., 2008; Lacorte et al., 2009; Villa et al., 2006) and polycyclic aromatic hydrocarbons (PAHs) in ice cores (Gabrieli et al., 2010). Humic-like-substances (HULIS) were also analyzed in an Alpine ice cores (Guilhermet et al., 2013; Legrand et al., 2007). The concentration of organic carbon in the Alpine region was reported to have doubled since the middle of the twentieth century, which was assigned to an enhanced oxidative capacity of the atmosphere, resulting in increased production of secondary organic aerosol (Legrand et al., 2007). Only recently, a study comprising the analysis of organic compounds formaldehyde, short chain (C1-C5) mono- and dicarboxylates, HULIS, dissolved organic carbon (DOC), and water-insoluble organic carbon (WinOC) revealed a rather unexpected increase in water-soluble organic aerosol by a factor of 3 since the 1950s, which was attributed mainly to an increase in biogenic emissions (Preunkert and Legrand, 2013). ~~Therefore, biogenic sources for the highly abundant organic matter in atmospheric aerosols have to be brought into focus and investigated in more detail using ice cores~~Legrand et al. (2013) also reported the trend of water-soluble organic carbon (WOC) including C2-C5 dicarboxylic acids in an Alpine ice core to be influenced to a greater extend by natural than by anthropogenic sources. The two smallest alpha-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.

Cold glaciers from mid-latitude mountain areas, such as the Alps, serve as an excellent archive of regional short-lived air pollution, covering a time span of decades to centuries. In this work, an array of organic compounds reported to be important constituents of SOA were analyzed in a well characterized ice core from Grenzgletscher (Monte Rosa Massif) in the southern Swiss Alps. Here we present the first long-term records of α-dicarbonyls (glyoxal, methylglyoxal) and carboxylic acids (C6-C10 and C12 dicarboxylic acids, pinic acid, *p*-hydroxybenzoic acid, phthalic acid, 4-methylphthalic acid, and vanillic acid) in the Alpine region, covering the period 1942-1993. Source apportionment of the investigated organic species was performed to evaluate the influence of biogenic emissions, forest fires, as well as anthropogenic emissions on past aerosol composition in Western Europe.

2 Experimental / Material and methods

2.1 Field site and sampling

The samples analyzed in this work originate from a 125 m long ice core recovered in 1994 from the Grenzgletscher located in the Monte Rosa massif in the southern Swiss Alps near the Italian border (4200 m a.s.l., 45°55' N, 7°52' E) (Eichler et al., 2000b). The drilling site is characterized by a high annual net accumulation rate of 2.7 m w.e. Using radar sounding the glacier thickness at the drilling site was estimated to be approximately 190 m with a relatively flat glacier geometry (slope of about 10°) revealing the suitability of the upper Grenzgletscher to serve as an environmental archive. The drilling was performed using an electromechanical drill with an inner diameter of 7.8 cm. Two hundred and forty ice core sections were recovered, each 50-80 cm long. The ice core sections were packed in polyethylene bags in the field and kept at -25 °C during transport and storage. The ice core covers the period 1937-1994 (see Eichler et al., 2000b for details on the ice core dating). Dating accuracy is ±2 years for the time before 1970 and ±1 year for the period of 1970 to 1993.

Samples were cut out from the ice core sections at -20 °C in a cold room at the PSI in Villigen, Switzerland, using a modified band saw (stainless steel blades, tabletop and saw guides covered with PTFE). All surfaces of the cutting devices the ice came into contact with were cleaned with ethanol before and after cutting each ice core section to prevent cross

contamination. To reduce potential contaminations from drilling, transport, or storage, the outer layer (about 0.5 cm) of each ice core section was removed with the band saw. To obtain annual averages, equal aliquots of the ice sections belonging to a certain year (2 to 9 sections per year) were combined in a pre-cleaned glass jar, resulting in a final sample mass of 215 - 410 g. The jars were closed tightly using screw caps with PTFE-coated septa and kept frozen until analysis. Fifty-one samples were prepared, covering the years 1942 to 1993 (with the exception of 1969, due to poor ice quality). Ultrapure water was frozen to obtain procedural blank samples, which were treated like real ice core samples to correct for possible contamination from sample preparation and analysis.

2.2 Chemical analysis

The analysis of α-dicarbonyls glyoxal (G) and methylglyoxal (MG) was performed based on a method by Müller-Tautges et al. (2014) using a sample weight of 75-85 g. Measurements were conducted using ultra high performance liquid chromatography (UHPLC) coupled to electrospray ionization high resolution mass spectrometry (ESI-HRMS). The adapted method is described in the supporting material section. Monocarboxylic acids (vanillic acid (VAN), *p*-hydroxybenzoic acid (PHB)) and dicarboxylic acids (adipic acid (C6), pimelic acid (C7), suberic acid (C8), azelaic acid (C9), sebacic acid (C10), ~~dodecanoic~~dodecanedioic acid (C12), methylphthalic acid (MPH), pinic acid (PIN), phthalic acid (PHT)) were analyzed using solid phase extraction (SPE) with strong anion exchange, followed by derivatization (esterification) and UHPLC-ESI-HRMS. The measurements were conducted using the same UHPLC-HRMS system as described above. A detailed description of the SPE process as well as derivatization and LC-MS is given in the supporting material section.

Concentrations of ~~water soluble organic ions~~the small carboxylates formate (FOR) and oxalate~~,~~ (OXA), as well the concentration of calcium (Ca^{2+}) in the 51 annual samples were determined using ion chromatography (Metrohm 850 Professional IC combined with a 872 Extension Module and a 858 Professional Sample Processor autosampler). The pH was determined using an 8103 Orion Electrode coupled to a Metrohm pH meter 605.

2.3 Calculations of the burned area from historical forest fires in Southern Switzerland

Forest fire data for Southern Switzerland (hereafter FSS) were gathered from the Swissfire database (Pezzatti et al., 2010) by extracting the fire events which occurred during the study period in the southern Swiss Alps. This region comprises the area of Zwischenberg-Gondo in the Canton of Valais, the whole Canton Ticino, and the valleys Misox, Bergell, and Puschlav in the Canton of Grisons. For each recorded event, the burned area was grouped in vegetation cover types (grassland, softwood, and hardwood) relevant for the resulting emissions of organic components. When details on the forest composition were missing (ca. 2% of the fire events), the softwood to hardwood proportion of the burned forest area was calculated by overlaying the burned area perimeter with forest stand maps (events occurred from 1969 onwards) or estimated based on the available information, namely location and altitude of the ignition point and main tree species hit by the event.

3 Results and discussion

Ice core records covering the period from 1942 to 1993 were obtained for nine dicarboxylic acids (C6-C10, C12, ~~MPH, PIN~~methylphthalic acid, pinic acid, and ~~PHT~~phthalic acid), two monocarboxylic acids (~~VAN~~vanillic and ~~PHB~~*p*-hydroxybenzoic acids), two α-dicarbonyls (~~G~~glyoxal and ~~MG~~methylglyoxal) and ~~major~~ ions (calcium (~~CAL),~~Ca^{2+}), formate ~~(FOR),~~ and oxalate ~~(OXA)).~~).

To evaluate if the applied annual sampling strategy was representative for the assigned years, the new established annual ~~FOR~~ record of formate was compared to an already existing high-resolution record (comprising 2148 distinct samples, (Eichler, 2000) see Fig. 1). The records obtained by 1-year sampling and 1-year averaging of the high-resolution data show excellent agreement (correlation coefficient $r = 0.954$, $p < 0.001$), revealing that the sampling was representative for the distinct years.

3.1 Concentrations of the organic compounds

The concentration range and average concentrations of the compounds detected in the ice core are presented in Table 1. The most abundant organic compound detected in the ice core was

~~FOR~~formate with an average concentration of 64 ng/g, followed by ~~OXA, C6, G~~oxalate, adipic acid, glyoxal, and ~~PIN~~pinic acid with 15.9, 0.52, 0.38, and 0.22 ng/g, respectively. There are only few studies reporting concentration records of mono- and dicarboxylic acids as well as α-dicarbonyls in ice cores (see Table 2). The average concentration of ~~FOR~~formate determined in this work is in the same range as reported in glaciers from Siberian Altai (period 1250-2001 AD, mean concentration 89 ng/g, Eichler et al., 2009), Col du Dôme (CDD, 1925-1995, 80 ng/g, Legrand et al., 2003), and Tianshan (1981-1998, 102.8 ng/g, Li et al., 2001), yet about two times lower than measured in an ice core from the Tibetan plateau (1983-1999, 186.6 ng/g, Wang, 2004). The concentration of ~~OXA~~oxalate in the Grenzgletscher ice core ranges from 1.5 to 49 ng/g, with an average concentration of 15.9 ng/g. These values are about two times higher than the concentration of ~~OXA~~oxalate in the glacier from Tianshan, China (Li et al., 2001) and about seven times higher than those reported in a study from Greenland (Kawamura et al., 2001), the latter comprising the analysis of dicarboxylic acids and α-dicarbonyls between 1540 and 1989. The observed concentration ranges of C6-C10 dicarboxylic acids in the Grenzgletscher ice core are comparable to those reported in the Greenland ice core by Kawamura et al., 2001, with the exception of ~~C9~~azelaic acid. Concentrations of ~~C9~~azelaic acid determined in this work (BDL–0.45 ng/g, average 0.12 ng/g) were about five times lower than in the Greenland ice core (<0.06–2.38 ng/g, average 0.64 ng/g). ~~PHT~~Phthalic acid concentrations in the Grenzgletscher ranged between BDL and 0.47 ng/g with an average value of 0.099 ng/g, which is also about five times lower than measured in the Greenland ice core. ~~C12 and MPH~~Dodecanedioic acid and methylphthalic acid have not been reported in ice cores yet. Their concentrations in the Grenzgletscher ice core were found to be comparable to that of ~~C10~~sebacic acid, with an average value of 0.022 ng/g and 0.029 ng/g, for ~~C12~~dodecanedioic acid and ~~MPH~~methylphthalic acid, respectively.

~~PIN~~Pinic acid has not yet been reported in ice cores either. Its concentration in the Grenzgletscher core is 0.22 ng/g on average, ranging from BDL to 0.92 ng/g. These values are comparable to those detected for ~~C7~~pimelic acid. Average concentrations of ~~G~~glyoxal and ~~MG~~methylglyoxal were 0.38 ng/g (ranging from BDL to 1.76 ng/g) and 0.046 ng/g (BDL–0.27 ng/g), respectively. The mean concentration of ~~MG~~methylglyoxal is about eight times lower than that of G. Concentration records of ~~G~~glyoxal and ~~MG~~methylglyoxal in ice cores have only been reported for Greenland (Kawamura et al., 2001), although they are ubiquitous

compounds in atmospheric aerosols and precipitation. The results obtained for ~~G~~glyoxal are comparable to the concentrations found by Kawamura et al. (2001) (0.023–1.14 ng/g, average 0.26 ng/g), whereas ~~MG~~methylglyoxal concentrations determined in this work are much lower than reported in the Greenland ice core (0.031–1.36 ng/g, average 0.21 ng/g).

Concentrations of ~~VAN~~vanillic acid ranged from below detection limit (BDL), which is 0.021 ng/g, to 0.36 ng/g with an average value of 0.067 ng/g. These concentrations are in the same range as reported in an ice core from Greenland (0.01-0.125 ng/g, McConnell et al., 2007) and Ushkovsky ice cap in Northeast Asia (BDL-0.13 ng/g, Kawamura et al., 2012). The concentration of ~~PHB~~*p*-hydroxybenzoic acid ranged from BDL (0.0087 ng/g) to 0.151 ng/g with an average concentration of 0.021 ng/g. Compared to the study by Kawamura et al. (2012) from the Ushkovsky ice cap, which is the only study reporting ~~PHB~~*p*-hydroxybenzoic acid in ice cores, our results are about ten times lower. Furthermore, the average concentration of ~~PHB~~*p*-hydroxybenzoic acid is about three times lower than that of ~~VAN~~vanillic acid, whereas Kawamura et al. (2012) reported ~~PHB~~ concentrations of *p*-hydroxybenzoic acid in the Ushkovsky ice core to be 16 times higher than that of ~~VAN~~vanillic acid. Such differences are likely to result from distinctions in sources and atmospheric transport of organic aerosol to the respective glacier site.

3.2 Historic records

The historic records obtained for the (di)carboxylic acids and α-dicarbonyls are shown in Fig. 1-4. Three-year averages were calculated to compensate for year-to-year fluctuations of the aerosol transport to the glacier site (analogous to Schwikowski et al., 2004). All the obtained records, based on three-year averages, exhibit fluctuations of about one order of magnitude in concentration during the investigated time period. Concentration maxima of ~~FOR~~formate and ~~OXA~~oxalate are during the 1940s and beginning of the 1950s. This is different for all other organic compounds, revealing minimum concentration before the 1950s, followed by an increase in concentration starting in about 1950-1955. Depending on the individual compound, the maximum concentrations are reached around 1955 (e.g., ~~C9~~azelaic acid), 1960 (e.g., ~~VAN~~vanillic acid), between 1965 and 1970 (e.g., ~~PIN~~pinic acid), during the late 1970s (e.g., ~~C6, PHB~~adipic acid, *p*-hydroxybenzoic acid) or at the beginning of the 1990s (e.g., ~~MG~~methylglyoxal). During the period from 1984 to 1989 the concentrations of all

compounds (except for ~~MG~~methylglyoxal) dropped to levels close to the detection limit, before they increased again in the early 1990s. This sudden drop in concentration was also observed by Eichler et al. (2001) for certain ionic species detected in the same ice core and was attributed to the relocation of ions with meltwater in the firn section of the glacier. While the normal seasonal pattern of ions like Cl^-, F^-, NO_3^-, and NH_4^+ was preserved, the concentrations of K^+, Mg^{2+}, or Ca^{2+}, for example, were significantly decreased. Eichler et al. (2001) suggested rearrangement processes during snow metamorphism in the ice to be the main reason for the fractionation of the ions. Depending on the solubility of an ionic compound in ice, it is located either inside the grain or at its surface. In the latter case, the ion is prone to be relocated by percolating water. As the possibility of being incorporated into the ice lattice is rather unlikely for the organic compounds detected in the ice core because of the molecule size, they are assumed to be located at the grain surfaces. The observed decrease in concentration during the period 1984-89 can thus not be interpreted as an atmospheric signal, but is due to a post-depositional leaching of the organic species.

Interestingly, no significant decrease in concentration was detected for ~~MG.~~methylglyoxal. The ratio ~~MG/G~~methylglyoxal/glyoxal is about 0.13 on average during the time not influenced by meltwater influx, yet rises up to 7 during the percolation period. This indicates a fractionation of ~~G~~glyoxal and ~~MG~~methylglyoxal possibly caused by the leaching process. ~~Further investigation of the post-depositional behavior of organic compound in the ice is necessary, as for example solubility data of organic species in ice are lacking so far.~~

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 at 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.

3.3 Source assignment

To investigate the main sources of the organic trace species, a principal component analysis (PCA) with Varimax rotation was performed. Three-year average values of the obtained records were used and the years affected by the meltwater influx removed from the record. Four PCs were found to account for 82% of the data variance in total (see Table 3). High loadings (>0.65) of ~~PHB, PIN, C7, C8, G~~*p*-hydroxybenzoic acid, pinic acid, pimelic acid, suberic acid, glyoxal, and ~~MPH~~methylphthalic acid are observed in PC1, which explains 31.5% of the data variability. PC1 is correlated with the area burned by forest fires in ~~southern~~Southern Switzerland (FSS) and a major part (57%) of the variance of PC1 is explained by the changes in FSS (Table 4). PC1 is therefore suggested to be linked to biomass burning.

The highest loadings within PC2 are observed for ~~MG, C6, C10, C12, and~~ ~~PHT~~methylglyoxal, adipic acid, sebacic acid, dodecanedioic acid, and phthalic acid, indicating a link between these species. Indeed, the five compounds are significantly correlated (Fig. S1). As ~~C6~~adipic acid and ~~PHT~~phthalic acid are reported to be mainly of anthropogenic origin (Hatakeyama et al., 1987; Koch et al., 2000; Zhang et al., 2010), this group may be influenced by anthropogenic emissions, explaining 24.4% of the data variability.

PC3 accounts for 16.3 % of the data variability. It is dominated by high positive loadings of ~~OXA, FOR~~oxalate, formate, and ~~CAL.~~Ca^{2+}. As mineral dust originating mainly from the Sahara is the major source of ~~CAL~~Ca^{2+} being transported to the glacier, PC3 is a dust-related component.

PC4 explains 10.0% of the data variance and is dominated by high loadings of ~~VAN~~vanillic acid and ~~C9~~azelaic acid, which are well correlated (r=0.601, p=0.018). ~~VAN~~Vanillic acid is reported to be a conifer biomass burning marker, while ~~C9~~azelaic acid is formed by photo-oxidation of oleic acid, for example. Therefore, PC4 may have a mixed biomass burning and/or biogenic origin.

The records of all PCs are shown in Fig. 5. In addition, the underlying correlations of the PCA are visualized in a correlation matrix in the supplementary material section (Fig. S1).

The performed PCA suggests that the major sources influencing the organic composition of the ice core were (in order of decreasing importance) i) biomass burning, ii) anthropogenic emissions, iii) mineral dust, and iv) biomass burning/biogenic emission. In the following, these source assignments of organic species deposited at the Grenzgletscher are discussed in more detail.

3.3.1 Biomass burning

The main factor influencing the composition of organic species in the ice core from upper Grenzgletscher is suggested to be biomass burning. The record of the PC1 scores resulting from the PCA is in good agreement with the total burned area in ~~southern~~Southern Switzerland (FSS, see Fig. 5 A). The main part of the burned species is hardwood forest, followed by grassland (Fig. 6 B). Due to the fire selectivity in terms of burned forest types (Pezzatti et al., 2009; Bajocco et al., 2011), softwood only accounts for a small part of the total burned area in ~~southern~~Southern Switzerland.

~~PHB~~*P*-hydroxybenzoic acid is a pyrolysis product of lignin, and was used as a biomass burning marker compound especially resulting from incomplete combustion of grasses (Kawamura et al., 2012; Simoneit, 2002). The applicability as a fire marker is supported by our results, as 75% of the variance of ~~PHB~~*p*-hydroxybenzoic acid is explained by the changes in FSS in general. Furthermore, 73% and 69% of the variance is explained by the changes in burned grassland and hardwood area, respectively (Table 4). However, as the burned grassland and hardwood areas are correlated, a discrimination between these two sources is not possible.

~~PIN~~Pinic acid is found to exhibit a good correlation ($r=0.609$, $p=0.016$) to FSS and a strong correlation ($r=0.864$, $p<0.01$) to the biomass burning marker compound ~~PHB~~*p*-hydroxybenzoic acid, both indicating biomass burning to be a major source for ~~PIN~~pinic acid deposited at the glacier. This was not expected so far, since ~~PIN~~pinic acid is unlikely to be emitted directly through biomass burning, as it is formed in the atmosphere as an oxidation product of biogenic VOCs. However, its precursors, α- and β-pinene, are formed and emitted by a wide range of plant species, especially monoterpene storing conifers, like Scots pine (*pinus sylvestris* L.) (Bäck et al., 2012), and to a minor extend also deciduous trees (e.g., European beech (*fagus sylvatica* L.) (Dindorf et al., 2006) or English oak (*quercus robur* L.)

(Pérez-Rial et al., 2009)), which are both *Fagaceae* similar to the deciduous oaks and chestnut trees that dominate ~~southern~~Southern Switzerland. Indeed, several studies report enhanced emissions of α- and β-pinene through biomass burning (Kahnt et al., 2013; Simpson et al., 2011; Cheng et al., 2011; Lee et al., 2005). Pinenes are emitted from the burning trees, provided that not all of the emitted terpenes are oxidized in the flames. Emissions from smoldering are generally found to be higher than from flaming (Lee et al., 2005). As the emission rate of α-pinene increases exponentially with temperature (Janson, 1993; Martin et al., 1999; Komenda, 2002), one could also assume that the heat wave associated with forest fires may cause enhanced emission of terpenes from the surrounding trees. The formation of pinonic acid associated with wood burning was reported by Cheng et al. ~~(Cheng et al., (~~2011); hence, the formation of pinic acid in wood burning plumes is also likely, as both pinonic acid and pinic acid are major products of pinene oxidation (Hoffmann et al., 1998; O'Dowd et al., 2002; Yu et al., 1999). In addition to the described enhanced emission of precursors, a second factor leading to high concentrations of ~~PIN~~pinic acid in connection with biomass burning might generally be the presence of a higher aerosol concentration. As biomass burning is a source of primary particles, the increase in particle matter might lead to enhanced partitioning of the newly formed pinic acid into the particle phase, preventing its further degradation. ~~PIN~~Pinic acid is often used as a marker for biogenic emissions. However, the results of this study indicate that the concentration of ~~PIN~~pinic acid detected in the ice core from Grenzgletscher is dominated by biomass burning origin~~, compared to natural~~ 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 ~~not influenced by fire events.~~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, but lowest during the periods with the highest pinic acid concentrations (1960s and 70s) (MeteoSwiss, 2015).

~~C7, C8~~Pimelic acid, suberic acid, and ~~MPH~~methylphthalic acid have not been described in the literature in connection to biomass burning so far. ~~C8~~Suberic acid is reported to be formed by photo-oxidation of unsaturated fatty acids (Stephanou and Stratigakis, 1993). The strong correlation observed for ~~C8~~suberic acid and ~~C7~~pimelic acid ($r=0.831$, $p<0.001$) suggests ~~C7~~pimelic acid to be produced either by the same source as ~~C8~~suberic acid, or by further oxidation of ~~C8~~suberic acid, yielding dicarboxylic acids with lower carbon number. As much

as 31% - 41% of the variance of these compounds is explained by the changes in FSS (Table 4).

~~G~~Glyoxal 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. ~~G~~Glyoxal is significantly correlated with the burned area in ~~southern~~Southern Switzerland and 22% of the data variability in the ~~G~~glyoxal record is explained by fire induced changes, increasing to 29% considering only grassland fires (Table 4).

In addition to the six species described above, ~~VAN~~vanillic acid is also loading partly on PC1. ~~VAN~~Vanillic acid is used as a marker for biomass burning as it is predominantly emitted by biomass burning processes. It is a pyrolysis product of lignin and is primarily associated with conifer species (Kawamura et al., 2012; McConnell et al., 2007). The ~~VAN~~vanillic acid record exhibits a significant correlation to ~~PHB~~*p*-hydroxybenzoic acid (r=0.694, p=0.004), FSS, and ~~C9~~azelaic acid (r=0.524 and 0.601, p=0.045 and 0.018, respectively). Although 27% of the data variability of ~~VAN~~vanillic acid is explained by changes in the burned area (FSS), the variability explained by changes in burned softwood area is negligible. Therefore, the applicability of ~~VAN~~vanillic acid as a fire marker especially for softwood (conifers) cannot be confirmed in the region of ~~southern~~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).

A strong concentration maximum of many organic compounds is observed in the year 1974. Within the limits of dating accuracy (±1 year in the period 1970-1993), the observed concentration maximum might be assigned to biomass burning aerosol from the historic fire season in 1973. In this particular year, the burned area in ~~southern~~Southern Switzerland reached a century maximum of about 7300 ha, which is ten times the mean annual area burned between 1942 and 1993 (see Fig. 6 A).

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.

3.3.2 Anthropogenic emissions

The second PC reveals the emission of anthropogenic VOCs to be an important source of organic species detected in the ice core, which is consistent with the sampling site being located in proximity to several highly industrialized countries in Central Europe. The compounds exhibiting high loadings in PC2 are ~~MG, PHT, C6, C10, and C12.~~ ~~PHT~~methylglyoxal, phthalic acid, adipic acid, sebacic acid, and dodecanedioic acid. Phthalic acid has been reported to be mainly formed by photo-oxidation of anthropogenic emissions, such as polycyclic aromatic hydrocarbons and phthalates (Kautzman et al., 2010), whereas a minor part can also be attributed to primary emissions by biomass burning and vehicle exhaust (Zhang et al., 2010). One major source for methylglyoxal 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 ~~C10~~sebacic acid and ~~C12~~dodecanedioic acid are correlated to ~~PHT~~phthalic acid (r=0.545, p=0.036 and r=0.519, p=0.047, respectively), indicating similar anthropogenic sources. ~~C6~~Adipic acid has also been reported to be of anthropogenic origin (Grosjean et al., 1978). The PC2 score is in good agreement with the emission record of non-methane(NM)-VOCs in Switzerland from 1940 to 1990 (Fig. 5 B). Both PC2 scores and VOC emissions in Switzerland show an increase from the 1940s to 1970, afterwards they remain on an almost constant level. For France and Italy, data are only available starting from 1970. Like for Switzerland, the emissions from both countries do not change significantly from 1970 to 1990. Actually, this trend is also indicated in the ice core records, as the maximum concentration levels of major VOC oxidation products ~~PHT, C6, and C12~~phthalic acid, adipic acid, and dodecanedioic acid are found to

occur only in the late 1970s to early 1980s and the concentrations are still high in the early 1990s.

As already mentioned in chapter 3.3.1, glyoxal is loading both in PC1 and PC2, indicating mixed sources. Glyoxal (and methylglyoxal) are formed by the oxidation of VOCs emitted by cars (e.g. toluene). Glyoxal concentrations in the glacier show an increase starting in the 1950s and reach their maximum in the 1970s. This trend is consistent with enhanced road traffic emissions in the second half of the 20th century.

3.3.3 Mineral dust

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 ~~OXA, FOR~~oxalate, formate, and ~~CAL~~Ca^{2+} suggest that their records are ~~suggested to be caused~~mainly determined by the common transport with mineral dust to the glacier, but not by the source. The historic records observed for these compounds are shown in Fig. 1. The scores of PC3 are in good agreement with the record of ~~CAL,~~Ca^{2+}, which serves as a marker for mineral dust (see Fig. 5 C). ~~OXA~~Oxalate and ~~FOR~~formate are taken up by the alkaline mineral dust during transport mainly from the Sahara to the glacier by acid-base reaction. Larger (di)carboxylic acids are not found to be correlated to ~~CAL,~~Ca^{2+}. This could be explained by the relatively high acidity and volatility of the small acids ~~OXA~~oxalate and ~~FOR~~format compared to their larger homologues. The known Saharan dustfall of 1949 is visible in both the records of ~~CAL~~Ca^{2+} and ~~OXA~~oxalate, but not in the record of ~~FOR~~formate. Therefore, sources of ~~OXA~~oxalate and ~~FOR~~formate might be similar but not identical over the whole time period covered by the ice core. An alternative explanation for the link of ~~OXA~~oxalate to mineral dust containing Ca^{2+} is the stabilization of oxalate due to the formation of calcium oxalate, thus preventing photo-induced decomposition of oxalate ions (which is reported to occur in the presence of iron oxides Rodríguez et al., 2009; Kim et al., 2010).

The strong relation between Ca^{2+} and oxalate was also observed from another Alpine ice core (Col du Dôme, Mt. Blanc). At this 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 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 SO_2 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 Ca^{2+} ($r=0.46$ 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.

3.3.4 Biomass burning / biogenic emissions

We interpret PC4 (see Fig. 5D) as a component of mixed sources. This component with high loadings of ~~VAN~~vanillic acid and ~~C9~~azelaic acid is partly explained by changes in the burned grassland area (22%, see Table 4). The record of PC4 shows an early maximum around 1960, so does the burned area of grassland. However, since ~~C9~~azelaic acid has also a high loading in PC4, this component may additionally be influenced by biogenic emissions, as ~~C9~~azelaic acid is reported to be formed mainly by photo-oxidation of unsaturated fatty acids (Stephanou and Stratigakis, 1993).

4 Summary and Conclusions

For the first time, long-term measurements of organic trace components such as mono- and dicarboxylic acids and α-dicarbonyls have been reported in an Alpine ice core from upper Grenzgletscher, Switzerland, covering the period 1942-1993. The characterization of aerosol in the ice concerning sources of organic compounds using PCA revealed four PCs to be responsible for 82% of the data variance in total, of which PC1-3 enabled source assignment of organic compounds detected in the ice core at trace levels.

Obtained concentration records of ~~PHB, PIN, C7, C8, G~~*p*-hydroxybenzoic acid, pinic acid, pimelic acid, suberic acid, glyoxal, and ~~MPH~~methylphthalic acid were shown to represent changes in the area affected by forest fires in ~~southern~~Southern Switzerland. Thus, biomass

burning was found to be the main parameter influencing the composition of these organic compounds present in the ice. ~~PHB~~*P*-hydroxybenzoic acid showed the strongest correlation of all organic trace species with the total area burned by forest fires and correlated well with the burned area of grassland and hardwood. Thus, ~~PHB~~*p*-hydroxybenzoic acid can be used as a fire marker in the observed region. A connection of elevated concentrations of ~~C7, C8, MPH~~pimelic acid, suberic acid, methylphthalic acid, and ~~PIN~~pinic acid to increased biomass burning was shown for the first time. ~~PIN~~Pinic acid quantified in the ice core is suggested to be formed as a secondary oxidation product as a result of the enhanced emission of monoterpenes at elevated temperature during biomass burning. Although ~~VAN~~vanillic acid has been used as a typical marker for (softwood) burning before, no such correlation was observed in this study. This is explained by the high selectivity of hardwood and grass vegetation by forest fires in Southern Switzerland.

Concentration trends of the organic compounds ~~MG, PHT, C6, C10, and C12~~methylglyoxal, phthalic acid, adipic acid, sebacic acid, and dodecanedioic acid were found to represent changes in anthropogenic emissions. The anthropogenic emission of VOCs, leading to polar oxidation products being deposited at the glacier site, is therefore considered to be a second parameter influencing the composition of organic species in the ice.

These observations are in contrast to the results obtained for the small carboxylic acids ~~OXA~~oxalate and ~~FOR~~formate. A strong correlation of the most abundant organic compounds ~~OXA~~oxalate and ~~FOR~~formate with ~~CAL~~Ca^{2+} was observed, indicating the uptake of small acids by alkaline, calcareous aerosol and a common transport to the glacier. The concentration records of ~~OXA~~oxalate and ~~FOR~~formate are thus not determined by their source, but mainly affected by changing dust transport to the drilling site. No such connection was detected for larger dicarboxylic acids.

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Table 1. Limits of detection (LOD) and obtained concentrations of dicarboxylic acids, monocarboxylic acids, α-dicarbonyls, and ~~major ions~~Ca^{2+} analyzed in the Grenzgletscher ice core (below detection limit = BDL).

	Abbreviation (Cn)	LOD (ng/g)	Concentration (ng/g) Average	Minimum	Maximum
Dicarboxylic acids					
Adipic acid	C6	0.001	0.52	BDL	2.4
Pimelic acid	C7	0.0007	0.15	BDL	0.86
Suberic acid	C8	0.0002	0.099	BDL	0.44
Azelaic acid	C9	0.0002	0.12	BDL	0.45
Sebacic acid	C10	0.0002	0.029	0.002	0.11
Dodecanedioic acid	C12	0.005	0.022	BDL	0.11
Pinic acid	PIN	0.0003	0.22	BDL	0.92
Phthalic acid	PHT	0.004	0.099	BDL	0.47
4-Methylphthalic acid	MPH	0.0003	0.029	BDL	0.22
Monocarboxylic acids / carboxylates					
Vanillic acid	VAN	0.021	0.067	BDL	0.36
p-Hydroxybenzoic acid	PHB	0.009	0.021	BDL	0.15
Formate	FOR	0.8	64	5	165
Oxalate	OXA	0.8	15.9	1.5	49
α-Dicabonyl compounds					
Glyoxal	G	0.003	0.38	BDL	1.8
Methylglyoxal	MG	0.003	0.046	BDL	0.27
Ions					
Calcium	~~CAL~~Ca^{2+}	0.9	186	10	740
~~Formate~~	~~FOR~~	~~0.8~~	~~64~~	~~5~~	~~165~~
~~Oxalate~~	~~OXA~~	~~0.8~~	~~15.9~~	~~1.5~~	~~49~~

Table 2. Comparison to other ice core data. All concentration values are given in ng/g.

	this work	Kawamura 2001	Kawamura 2012	McConnell 2007	Legrand 2003	Legrand 2007	Eichler 2009	Li 2001	W
	Switzerland	Greenland	Ushkovsky ice cap, Russia	Greenland	Alps, France	Alps, France	Siberian Altai, Russia	China	China
	1942-1993	1540-1989	1693-1997	1788-2002	1925-1995	1568-1910	1250-2001	1981-1998	1983-1999
Adipic acid	0.52	0.42							
Pimelic acid	0.15	0.18							
Suberic acid	0.099	0.18							
Azelaic acid	0.12	0.64							
Sebacic acid	0.029	0.069							
Dodecanedioic acid	0.022								
Pinic acid	0.22								
Phthalic acid	0.099	0.56							
4-Methylphthalic acid	0.029								
Vanillic acid	0.067		0.015	~0.08					
p-Hydroxybenzoic acid	0.021		0.24						
Glyoxal	0.38	0.26							
Methylglyoxal	0.046	0.21							
Formate	64				80[a]		89[b]	102.8	18
Oxalate	15.9	2.1				~15-35[a]		6.9	

[a]summer snow layers; [b]converted from µeq/l

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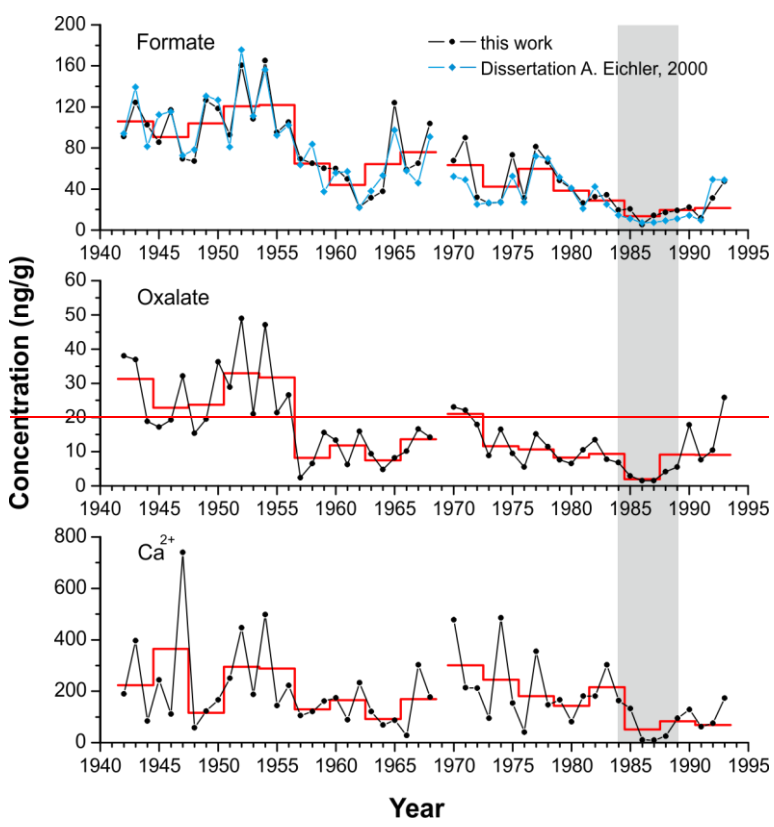
Table 3 Loadings of the PCA with Varimax rotation performed on the normalized 3-year means and the variance explained by each component for the time period 1942-1993. Factor loadings >|0.4| are shown.

	Components			
Variable	**PC1**	**PC2**	**PC3**	**PC4**
PHB	**0.95**			
PIN	**0.87**	0.41		
C7	**0.79**	0.56		
C8	**0.85**			
G	**0.70**	0.46		
MPH	**0.69**	0.44		
FSS	**0.88**			
MG		**0.84**		
C6		**0.69**		
C10		**0.80**		
C12		**0.61**	-0.43	
PHT		**0.77**		
OXA			**0.92**	
FOR			**0.90**	
~~CAL~~Ca^{2+}			**0.57**	
VAN	0.51		-0.56	**0.58**
C9				**0.85**
Variance explained (%)	31.5	24.4	16.3	10.0
	Biomass burning	Anthropogenic emissions	Transport with mineral dust	Biogenic/burning ?

Table 4 Coefficients of determination (r^2) for compounds and components linked to biomass burning (r^2, significant at the 0.05 level marked in bold).

r^2	FSS (area all fires)	grassland	softwood	hardwood
PHB	**0.75**	**0.73**	0.17	**0.69**
PIN	**0.37**	**0.40**	0.06	**0.34**
C7	**0.31**	**0.44**	0.14	**0.20**
C8	**0.41**	**0.39**	0.08	**0.39**
MPH	**0.34**	**0.51**	0.16	**0.21**
G	**0.22**	**0.29**	**0.24**	0.13
VAN	**0.27**	**0.36**	0.04	**0.21**
PC1	**0.57**	**0.65**	0.19	**0.47**
PC4	0.17	**0.22**	0.02	0.13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Concentration (ng/g)
Year

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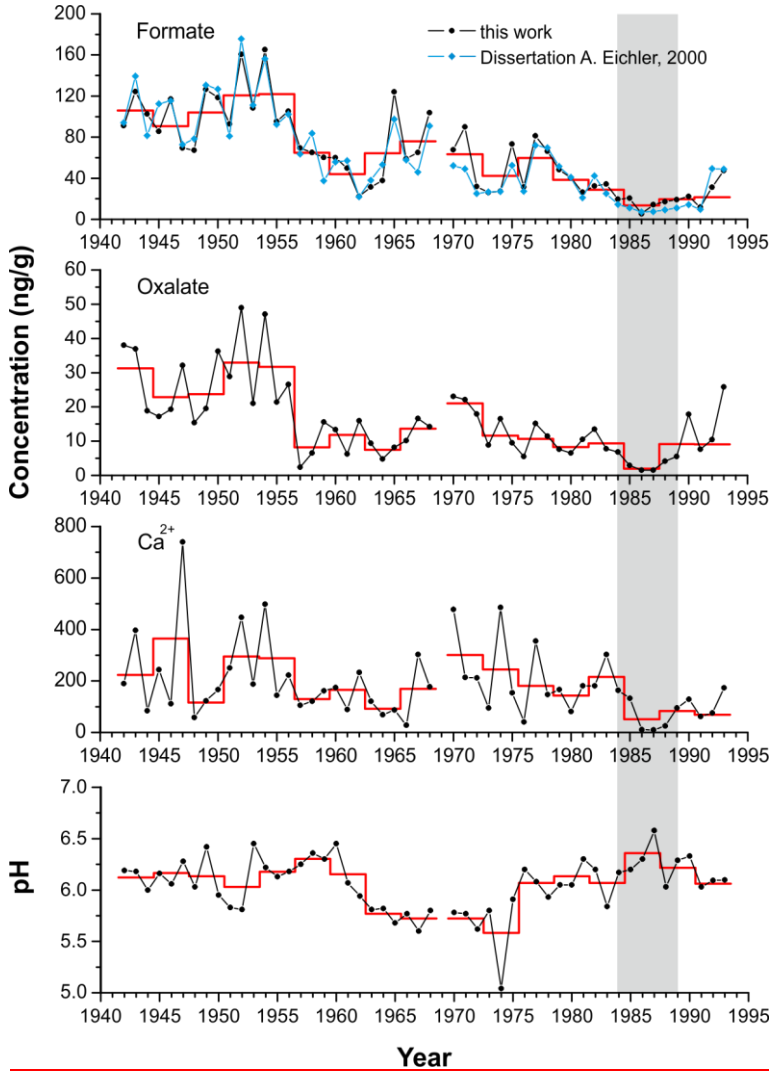


Fig. 1 Ice core records of oxalate, formate, ~~and~~ calcium, and pH (black dots: annual averages, red line: three-year averages). The period influenced by meltwater (1984-89) is marked in gray. The ice core record of formate obtained from previous high-resolution measurements (blue diamonds, annual averages based on 2148 measurements, Eichler, 2000) fits well with the record determined using the 1-year sampling strategy.

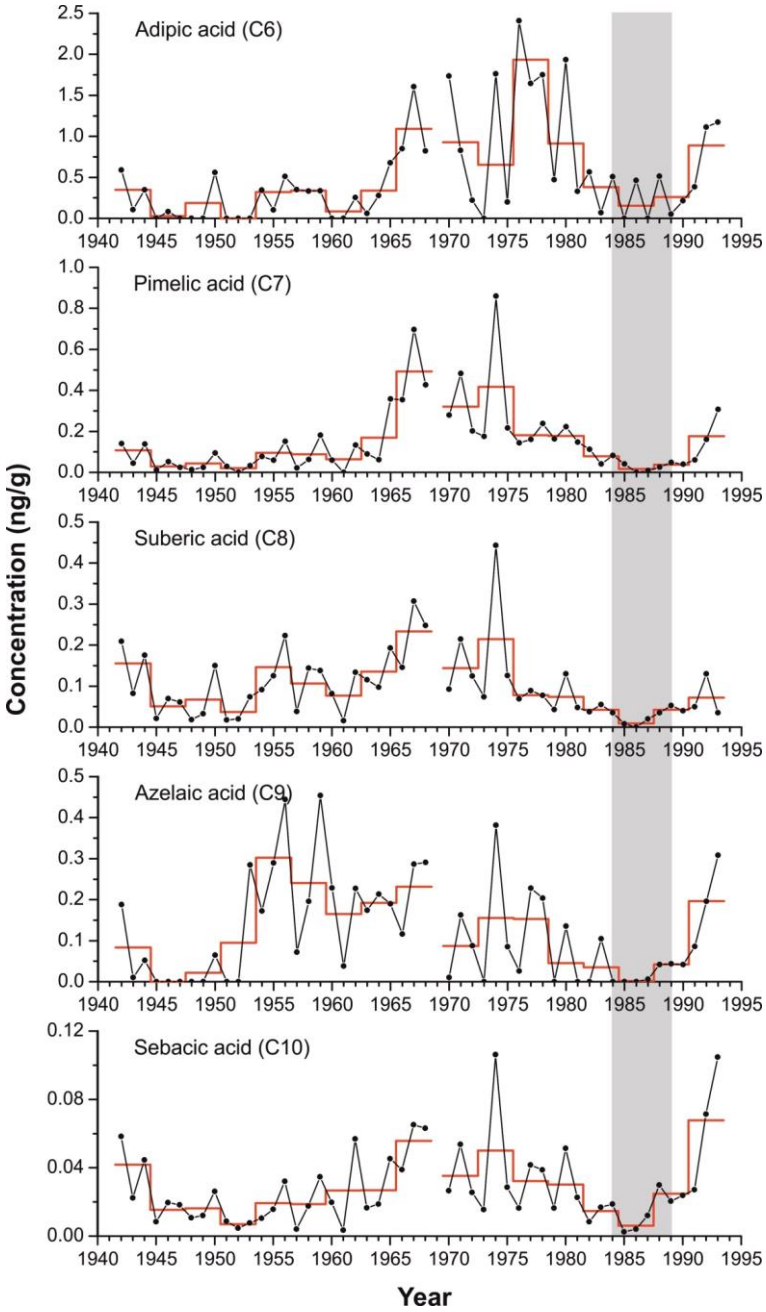


Fig. 2 Ice core records of dicarboxylic acids C6-C10 in the Alpine ice core from upper Grenzgletscher (black dots: annual averages, red line: three-year averages). The period influenced by meltwater (1984-89) is marked in gray.

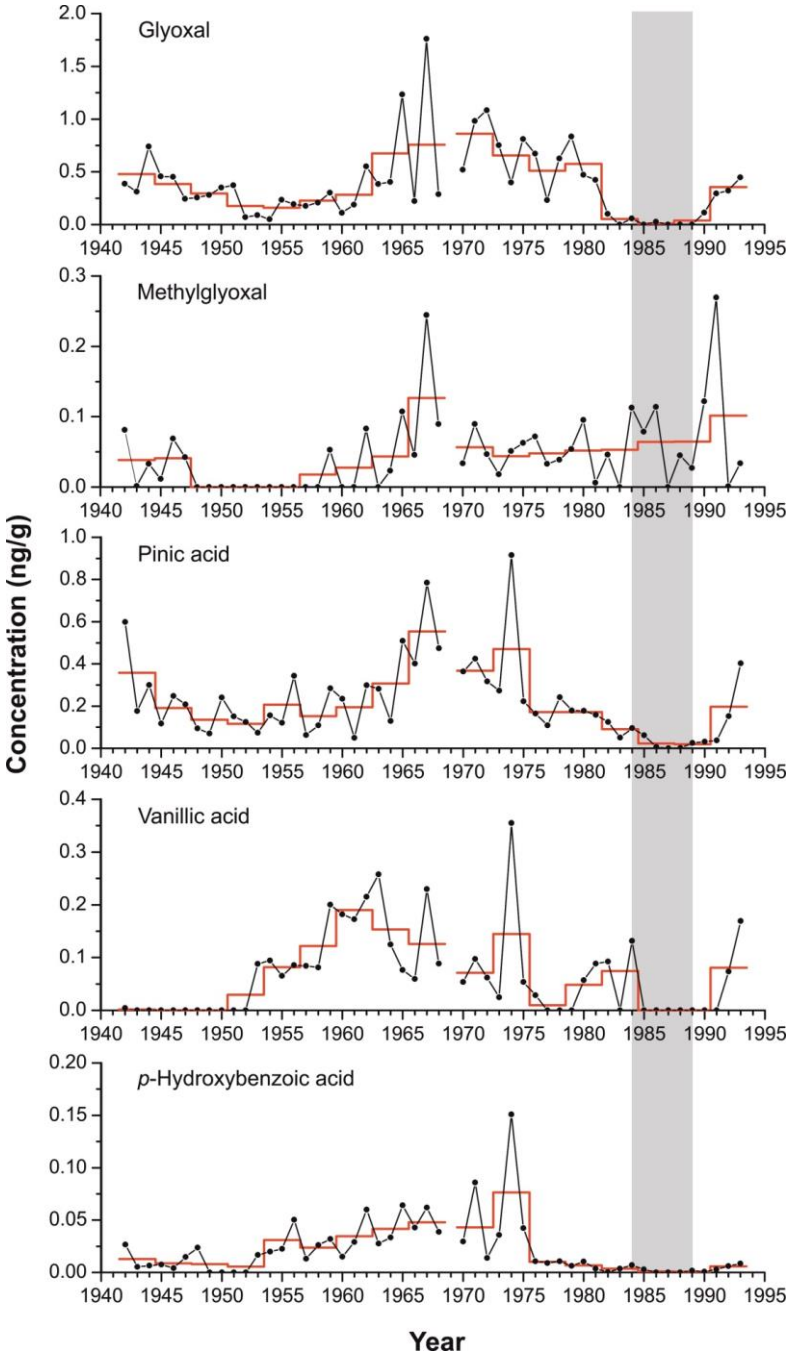


Fig. 3 Ice core records of α-dicarbonyls (glyoxal and methylglyoxal), pinic acid, and monocarboxylic acids (vanillic and *p*-hydroxybenzoic acid) in the Alpine ice core from upper

Grenzgletscher (black dots: annual averages, red line: three-year averages). The period influenced by meltwater (1984-89) is marked in gray.

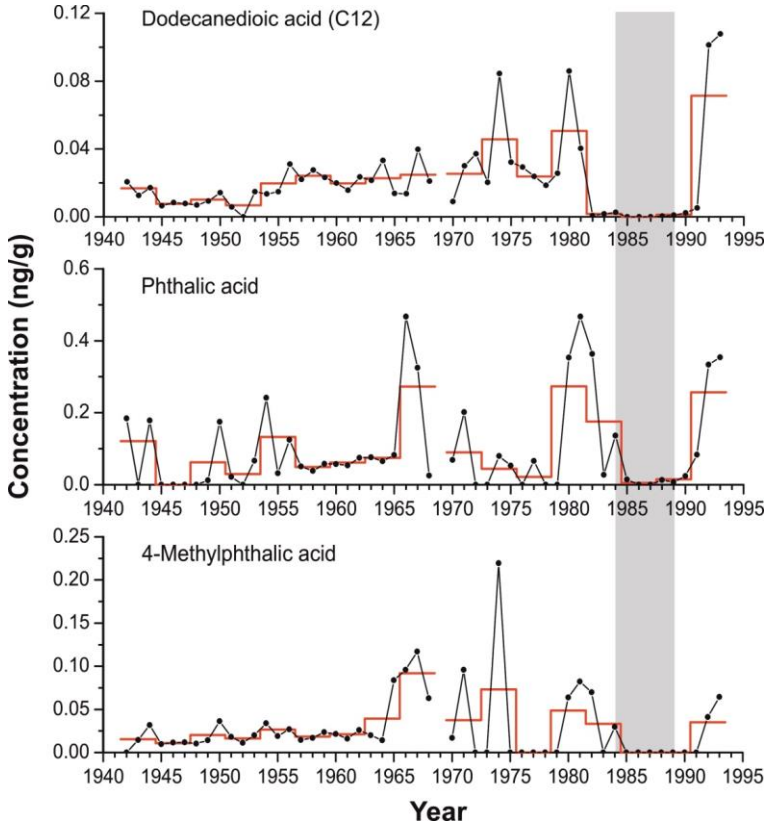
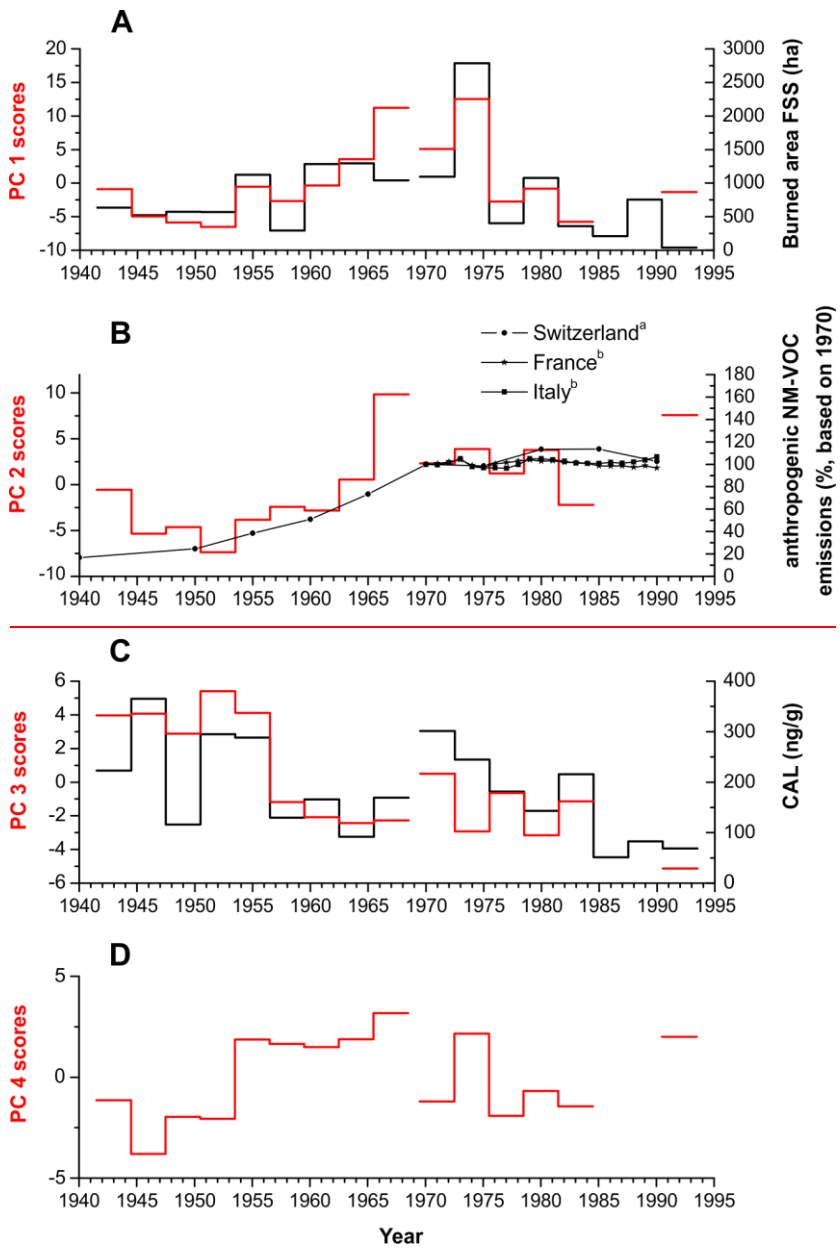


Fig. 4 Ice core records of dicarboxylic acids (~~C12~~dodecanedioic acid, phthalic acid, and methylphthalic acid) in the Alpine ice core from upper Grenzgletscher (black dots: annual averages, red line: three-year averages). The period influenced by meltwater (1984-89) is marked in gray.


A
PC 1 scores
Burned area FSS (ha)
B
Switzerland[a]
France[b]
Italy[b]
PC 2 scores
anthropogenic NM-VOC emissions (%, based on 1970)
C
PC 3 scores
CAL (ng/g)
D
PC 4 scores
Year

1

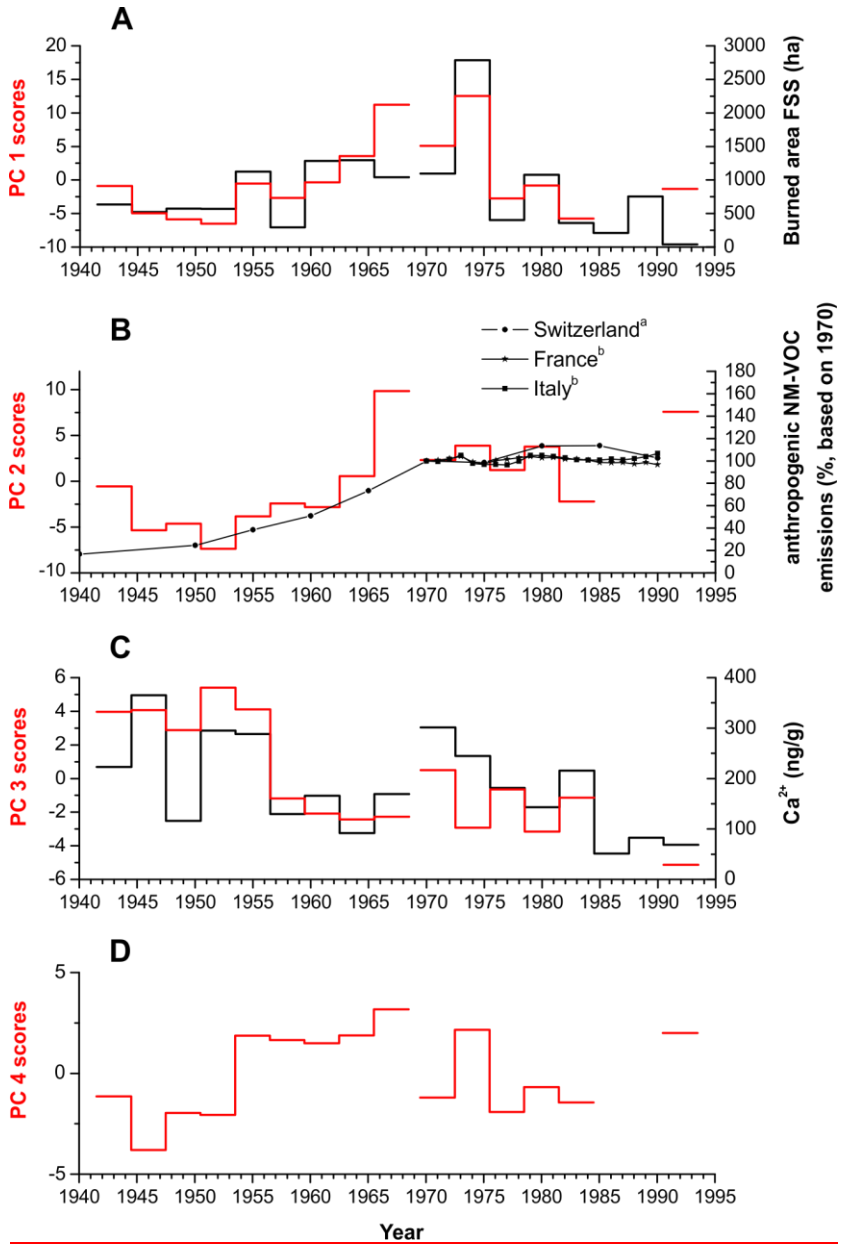


Fig.Figure 5. A) Records of PC1 and FSS (burned area by fires in southernSouthern Switzerland) (A),), B) PC2 and anthropogenic emissions of non-methane volatile organic compounds (NM-VOC) in Switzerland, France, and Italy from 1940 to 1990 (based on 1970) (B),, C) PC3 and historic record of CAL (C), andCa^{2+}, D) PC4 (D).. Data in graph B were extracted from (a) (BUWAL, 1995) and (b) (EDGAR, 2010) (black symbols: annual averages, red/black line: three- year-averages).

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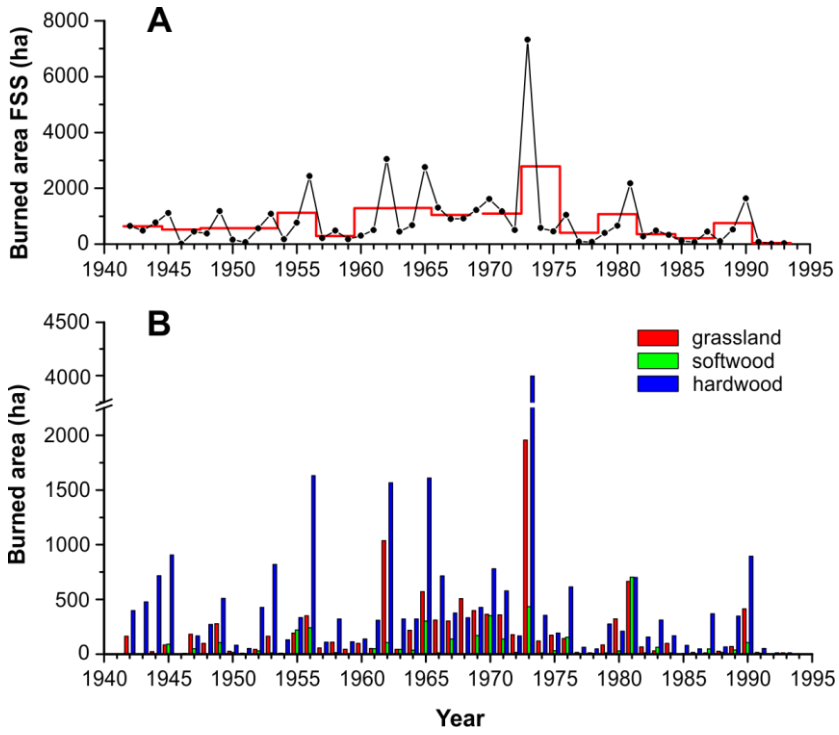

~~Fig.~~Figure 6. A) Record of the burned area by fires in ~~southern~~Southern Switzerland (FSS, black dots: annual averages, red line: three-year averages~~) (A) and~~), B) annual burned area of grassland, softwood, and hardwood in ~~southern~~Southern Switzerland from 1942 to 1993 ~~(B).~~.