

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

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## Abstract

Historic records of  $\alpha$ -dicarbonyls (glyoxal, methylglyoxal), carboxylic acids (C6-C12 dicarboxylic acids, pinic acid, *p*-hydroxybenzoic acid, phthalic acid, 4-methylphthalic acid), and 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. 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. 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, pimelic and suberic acids) can be related to the forest fire history in 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 adipic acid, sebacic acid, and 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  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , 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  $\text{SO}_2$  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

1 cores from the Alps (Legrand et al., 2003), Greenland (Legrand et al., 1992; Legrand and  
2 Angelis, 1996) and Antarctica (Angelis et al., 2012). These compounds can be attributed to  
3 vegetation emission, boreal forest fires or anthropogenic (vehicle) emissions. Short  
4 dicarboxylates (C2-C5) were analyzed in distinct sections of Alpine firn and ice cores from  
5 Col du Dôme and Colle Gnifetti. They were attributed to secondary formation from  
6 vegetation emissions (Legrand et al., 2007). Historic records of dicarboxylic acids (C2-C10),  
7 oxocarboxylic acids (C2-C9), and  $\alpha$ -dicarbonyls (C2-C3) were reported in an ice core from  
8 Greenland (Kawamura et al., 2001), suggesting dicarboxylic acids in ice cores to serve as  
9 proxies for the oxidative capacity of the atmosphere in the past. Long-chain carboxylic acids  
10 (fatty acids, C14-C22) were also detected in an ice core from Greenland and attributed to  
11 marine and terrestrial biological sources (Kawamura et al., 1996). Formaldehyde was  
12 analyzed in a firn core from Lys glacier (Largiuni, 2003) and ice cores from Greenland  
13 (Staffelbach et al., 1991), but there are indications that it is not well preserved under most  
14 conditions (Hutterli et al., 2002). Some studies focus on persistent organic pollutants (POPs)  
15 (Pavlova et al., 2014; Wang et al., 2008; Lacorte et al., 2009; Villa et al., 2006) and  
16 polycyclic aromatic hydrocarbons (PAHs) in ice cores (Gabrieli et al., 2010). Humic-like-  
17 substances (HULIS) were also analyzed in an Alpine ice cores (Guilhermet et al., 2013;  
18 Legrand et al., 2007). The concentration of organic carbon in the Alpine region was reported  
19 to have doubled since the middle of the twentieth century, which was assigned to an enhanced  
20 oxidative capacity of the atmosphere, resulting in increased production of secondary organic  
21 aerosol (Legrand et al., 2007). Only recently, a study comprising the analysis of organic  
22 compounds formaldehyde, short chain (C1-C5) mono- and dicarboxylates, HULIS, dissolved  
23 organic carbon (DOC), and water-insoluble organic carbon (WinOC) revealed a rather  
24 unexpected increase in water-soluble organic aerosol by a factor of 3 since the 1950s, which  
25 was attributed mainly to an increase in biogenic emissions (Preunkert and Legrand, 2013).  
26 Legrand et al. (2013) also reported the trend of water-soluble organic carbon (WOC)  
27 including C2-C5 dicarboxylic acids in an Alpine ice core to be influenced to a greater extend  
28 by natural than by anthropogenic sources. The two smallest alpha-dicarbonyls glyoxal and  
29 methylglyoxal are final products of the oxidation chain of many VOCs. They have received  
30 increasing scientific interest in recent years due to their important role in the formation and  
31 growth of SOA (Fu et al., 2008). However, no data on the long-term trend of these  
32 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  $\alpha$ -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, see Fig. 1) (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  $\pm 2$  years for the time before 1970 and  $\pm 1$  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  $\alpha$ -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), 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 the small carboxylates formate (FOR) and oxalate (OXA), as well the concentration of calcium ( $\text{Ca}^{2+}$ ) 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 (see Fig. 1). 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, methylphthalic acid, pinic acid, and phthalic acid), two monocarboxylic acids (vanillic and *p*-hydroxybenzoic acids), two  $\alpha$ -dicarbonyls (glyoxal and methylglyoxal) and ions (calcium ( $\text{Ca}^{2+}$ ), formate, and oxalate).

To evaluate if the applied annual sampling strategy was representative for the assigned years, the new established annual record of formate was compared to an already existing high-resolution record (comprising 2148 distinct samples, (Eichler, 2000) see Fig. 2). 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 formate with an average concentration of 64 ng/g, followed by oxalate, adipic acid, glyoxal, and 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  $\alpha$ -dicarbonyls in ice cores (see Table 2). The average concentration of formate determined in this work is in the same range as reported in glaciers from Siberian Altai (period 1250-2001 AD, mean

1 concentration 89 ng/g, Eichler et al., 2009), Col du Dôme (CDD, 1925-1995, 80 ng/g,  
2 Legrand et al., 2003), and Tianshan (1981-1998, 102.8 ng/g, Li et al., 2001), yet about two  
3 times lower than measured in an ice core from the Tibetan plateau (1983-1999, 186.6 ng/g,  
4 Wang, 2004). The concentration of oxalate in the Grenzgletscher ice core ranges from 1.5 to  
5 49 ng/g, with an average concentration of 15.9 ng/g. These values are about two times higher  
6 than the concentration of oxalate in the glacier from Tianshan, China (Li et al., 2001) and  
7 about seven times higher than those reported in a study from Greenland (Kawamura et al.,  
8 2001), the latter comprising the analysis of dicarboxylic acids and  $\alpha$ -dicarbonyls between  
9 1540 and 1989. The observed concentration ranges of C6-C10 dicarboxylic acids in the  
10 Grenzgletscher ice core are comparable to those reported in the Greenland ice core by  
11 Kawamura et al., 2001, with the exception of azelaic acid. Concentrations of azelaic acid  
12 determined in this work (BDL–0.45 ng/g, average 0.12 ng/g) were about five times lower than  
13 in the Greenland ice core (<0.06–2.38 ng/g, average 0.64 ng/g). Phthalic acid concentrations  
14 in the Grenzgletscher ranged between BDL and 0.47 ng/g with an average value of 0.099  
15 ng/g, which is also about five times lower than measured in the Greenland ice core.  
16 Dodecanedioic acid and methylphthalic acid have not been reported in ice cores yet. Their  
17 concentrations in the Grenzgletscher ice core were found to be comparable to that of sebacic  
18 acid, with an average value of 0.022 ng/g and 0.029 ng/g, for dodecanedioic acid and  
19 methylphthalic acid, respectively.

21 Pinic acid has not yet been reported in ice cores either. Its concentration in the Grenzgletscher  
22 core is 0.22 ng/g on average, ranging from BDL to 0.92 ng/g. These values are comparable to  
23 those detected for pimelic acid. Average concentrations of glyoxal and methylglyoxal were  
24 0.38 ng/g (ranging from BDL to 1.76 ng/g) and 0.046 ng/g (BDL–0.27 ng/g), respectively.  
25 The mean concentration of methylglyoxal is about eight times lower than that of G.  
26 Concentration records of glyoxal and methylglyoxal in ice cores have only been reported for  
27 Greenland (Kawamura et al., 2001), although they are ubiquitous compounds in atmospheric  
28 aerosols and precipitation. The results obtained for glyoxal are comparable to the  
29 concentrations found by Kawamura et al. (2001) (0.023–1.14 ng/g, average 0.26 ng/g),  
30 whereas methylglyoxal concentrations determined in this work are much lower than reported  
31 in the Greenland ice core (0.031–1.36 ng/g, average 0.21 ng/g).

Concentrations of 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 *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 *p*-hydroxybenzoic acid in ice cores, our results are about ten times lower. Furthermore, the average concentration of *p*-hydroxybenzoic acid is about three times lower than that of vanillic acid, whereas Kawamura et al. (2012) reported concentrations of *p*-hydroxybenzoic acid in the Ushkovsky ice core to be 16 times higher than that of 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  $\alpha$ -dicarbonyls are shown in Fig. 2-5. 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 formate and 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., azelaic acid), 1960 (e.g., vanillic acid), between 1965 and 1970 (e.g., pinic acid), during the late 1970s (e.g., adipic acid, *p*-hydroxybenzoic acid) or at the beginning of the 1990s (e.g., methylglyoxal). During the period from 1984 to 1989 the concentrations of all compounds (except for 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  $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{NO}_3^-$ , and  $\text{NH}_4^+$  was preserved, the concentrations of  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , or  $\text{Ca}^{2+}$ , 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 methylglyoxal. The ratio 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 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.

### 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 *p*-hydroxybenzoic acid, pinic acid, pimelic acid, suberic acid, glyoxal, and methylphthalic acid are observed in PC1, which explains 31.5% of the data variability. PC1 is

1 correlated with the area burned by forest fires in Southern Switzerland (FSS) and a major part  
2 (57%) of the variance of PC1 is explained by the changes in FSS (Table 4). PC1 is therefore  
3 suggested to be linked to biomass burning.

4  
5 The highest loadings within PC2 are observed for methylglyoxal, adipic acid, sebacic acid,  
6 dodecanedioic acid, and phthalic acid, indicating a link between these species. Indeed, the five  
7 compounds are significantly correlated (Fig. S1). As adipic acid and phthalic acid are reported  
8 to be mainly of anthropogenic origin (Hatakeyama et al., 1987; Koch et al., 2000; Zhang et  
9 al., 2010), this group may be influenced by anthropogenic emissions, explaining 24.4% of the  
10 data variability.

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

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

18 The records of all PCs are shown in Fig. 6. In addition, the underlying correlations of the PCA  
19 are visualized in a correlation matrix in the supplementary material section (Fig. S1).

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

### 25 *3.3.1 Biomass burning*

26 The main factor influencing the composition of organic species in the ice core from upper  
27 Grenzgletscher is suggested to be biomass burning. The record of the PC1 scores resulting  
28 from the PCA is in good agreement with the total burned area in Southern Switzerland (FSS,  
29 see Fig. 6 A). The main part of the burned species is hardwood forest, followed by grassland  
30 (Fig. 7 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 Switzerland.

*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 *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.

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 *p*-hydroxybenzoic acid, both indicating biomass burning to be a major source for pinic acid deposited at the glacier. This was not expected so far, since 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,  $\alpha$ - and  $\beta$ -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 Switzerland. Indeed, several studies report enhanced emissions of  $\alpha$ - and  $\beta$ -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  $\alpha$ -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. (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

1 of pinic acid in connection with biomass burning might generally be the presence of a higher  
2 aerosol concentration. As biomass burning is a source of primary particles, the increase in  
3 particle matter might lead to enhanced partitioning of the newly formed pinic acid into the  
4 particle phase, preventing its further degradation. Pinic acid is often used as a marker for  
5 biogenic emissions. However, the results of this study indicate that the concentration of pinic  
6 acid detected in the ice core from Grenzgletscher is dominated by biomass burning origin and  
7 not by direct biogenic emission of the respective precursors. A further argument that the trend  
8 of pinic acid in the Grenzgletscher is influenced by biomass burning instead of direct biogenic  
9 emissions is the missing link to temperature. Direct biogenic emissions from forests have  
10 been shown to follow temperatures (Eichler et al., 2009, Kellerhals et al., 2010).  
11 Temperatures in Southern Switzerland in the period 1940-1993 are high during the 1940s,  
12 80s, and 90s, but lowest during the periods with the highest pinic acid concentrations (1960s  
13 and 70s) (MeteoSwiss, 2015).

14 Pimelic acid, suberic acid, and methylphthalic acid have not been described in the literature in  
15 connection to biomass burning so far. Suberic acid is reported to be formed by photo-  
16 oxidation of unsaturated fatty acids (Stephanou and Stratigakis, 1993). The strong correlation  
17 observed for suberic acid and pimelic acid ( $r=0.831$ ,  $p<0.001$ ) suggests pimelic acid to be  
18 produced either by the same source as suberic acid, or by further oxidation of suberic acid,  
19 yielding dicarboxylic acids with lower carbon number. As much as 31% - 41% of the variance  
20 of these compounds is explained by the changes in FSS (Table 4).

21 Glyoxal is a secondary oxidation product formed from biogenic as well as anthropogenic  
22 precursors (e.g., toluene emitted from car exhaust) but has also been reported as a primary  
23 emission product by biomass burning, as indicated by the high loadings within PC1 and PC2.  
24 Glyoxal is significantly correlated with the burned area in Southern Switzerland and 22% of  
25 the data variability in the glyoxal record is explained by fire induced changes, increasing to  
26 29% considering only grassland fires (Table 4).

27 In addition to the six species described above, vanillic acid is also loading partly on PC1.  
28 Vanillic acid is used as a marker for biomass burning as it is predominantly emitted by  
29 biomass burning processes. It is a pyrolysis product of lignin and is primarily associated with  
30 conifer species (Kawamura et al., 2012; McConnell et al., 2007). The vanillic acid record  
31 exhibits a significant correlation to *p*-hydroxybenzoic acid ( $r=0.694$ ,  $p=0.004$ ), FSS, and  
32 azelaic acid ( $r=0.524$  and  $0.601$ ,  $p=0.045$  and  $0.018$ , respectively). Although 27% of the data

variability of 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 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).

A strong concentration maximum of many organic compounds is observed in the year 1974. Within the limits of dating accuracy ( $\pm 1$  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 Switzerland reached a century maximum of about 7300 ha, which is ten times the mean annual area burned between 1942 and 1993 (see Fig. 7 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 *Föhn*-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 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 sebacic acid and dodecanedioic acid are correlated to phthalic acid ( $r=0.545$ ,  $p=0.036$  and  $r=0.519$ ,  $p=0.047$ , respectively), indicating similar anthropogenic sources. 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. 6 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 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 20<sup>th</sup> 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 oxalate, formate, and  $\text{Ca}^{2+}$  suggest that their records are 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. 2. The scores of PC3 are in good agreement with the record of

Ca<sup>2+</sup>, which serves as a marker for mineral dust (see Fig. 6 C). Oxalate and 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 Ca<sup>2+</sup>. This could be explained by the relatively high acidity and volatility of the small acids oxalate and formate compared to their larger homologues. The known Saharan dustfall of 1949 is visible in both the records of Ca<sup>2+</sup> and oxalate, but not in the record of formate. Therefore, sources of oxalate and formate might be similar but not identical over the whole time period covered by the ice core. An alternative explanation for the link of oxalate to mineral dust containing Ca<sup>2+</sup> 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, see Rodríguez et al., 2009; Kim et al., 2010).

The strong relation between Ca<sup>2+</sup> and oxalate was also observed from another Alpine ice core (Col du Dôme, Mt. Blanc). At this site, Ca<sup>2+</sup> (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<sub>2</sub> and NO<sub>x</sub> 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. 2). While formate and oxalate are significantly correlated with Ca<sup>2+</sup> (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. 6 D) as a component of mixed sources. This component with high loadings of vanillic acid and 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 azelaic acid has also a high loading in PC4, this component may additionally be influenced by biogenic emissions, as 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  $\alpha$ -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 *p*-hydroxybenzoic acid, pinic acid, pimelic acid, suberic acid, glyoxal, and methylphthalic acid were shown to represent changes in the area affected by forest fires in Southern Switzerland. Thus, biomass burning was found to be the main parameter influencing the composition of these organic compounds present in the ice. *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, *p*-hydroxybenzoic acid can be used as a fire marker in the observed region. A connection of elevated concentrations of pimelic acid, suberic acid, methylphthalic acid, and pinic acid to increased biomass burning was shown for the first time. 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 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 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.



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

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1 acids and nitrophenols in fine and coarse air particulate matter, *Atmos. Chem. Phys.*, 10,  
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1 Table 1. Limits of detection (LOD) and obtained concentrations of dicarboxylic acids,  
2 monocarboxylic acids,  $\alpha$ -dicarbonyls, and  $\text{Ca}^{2+}$  analyzed in the Grenzgletscher ice core  
3 (below detection limit = BDL).

	Abbreviation (Cn)	LOD (ng/g)	Concentration (ng/g)		
			Average	Minimum	Maximum
<b><i>Dicarboxylic acids</i></b>					
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
<b><i>Monocarboxylic acids / carboxylates</i></b>					
Vanillic acid	VAN	0.021	0.067	BDL	0.36
<i>p</i> -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
<b><i>α-Dicabonyl compounds</i></b>					
Glyoxal	G	0.003	0.38	BDL	1.8
Methylglyoxal	MG	0.003	0.046	BDL	0.27
<b><i>Ions</i></b>					
Calcium	Ca <sup>2+</sup>	0.9	186	10	740

1 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	Wang 2004
	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	1983-1998
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					
<i>p</i> -Hydroxybenzoic acid	0.021		0.24						
Glyoxal	0.38	0.26							
Methylglyoxal	0.046	0.21							
Formate	64				80 <sup>a</sup>		89 <sup>b</sup>	102.8	186.6
Oxalate	15.9	2.1				~15-35 <sup>a</sup>		6.9	

2 <sup>a</sup>summer snow layers; <sup>b</sup>converted from µeq/l

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

Variable	Components			
	PC1	PC2	PC3	PC4
<i>p</i> -Hydroxybenzoic acid	<b>0.95</b>			
Pinic acid	<b>0.87</b>	0.41		
Pimelic acid	<b>0.79</b>	0.56		
Suberic acid	<b>0.85</b>			
Glyoxal	<b>0.70</b>	0.46		
4-Methylphthalic acid	<b>0.69</b>	0.44		
FSS	<b>0.88</b>			
Methylglyoxal		<b>0.84</b>		
Adipic acid		<b>0.69</b>		
Sebacic acid		<b>0.80</b>		
Dodecanedioic acid		<b>0.61</b>	-0.43	
Phthalic acid		<b>0.77</b>		
Oxalate			<b>0.92</b>	
Formate			<b>0.90</b>	
Ca <sup>2+</sup>			<b>0.57</b>	
Vanillic acid	0.51		-0.56	<b>0.58</b>
Azelaic acid				<b>0.85</b>
Variance explained (%)	31.5	24.4	16.3	10.0
	Biomass burning	Anthropogenic emissions	Transport with mineral dust	Biogenic/burning ?

4

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

$r^2$	FSS (area all fires)	grassland	softwood	hardwood
<i>p</i> -Hydroxybenzoic acid	<b>0.75</b>	<b>0.73</b>	0.17	<b>0.69</b>
Pinic acid	<b>0.37</b>	<b>0.40</b>	0.06	<b>0.34</b>
Pimelic acid	<b>0.31</b>	<b>0.44</b>	0.14	<b>0.20</b>
Suberic acid	<b>0.41</b>	<b>0.39</b>	0.08	<b>0.39</b>
4-Methylphthalic acid	<b>0.34</b>	<b>0.51</b>	0.16	<b>0.21</b>
Glyoxal	<b>0.22</b>	<b>0.29</b>	<b>0.24</b>	0.13
Vanillic acid	<b>0.27</b>	<b>0.36</b>	0.04	<b>0.21</b>
PC1	<b>0.57</b>	<b>0.65</b>	0.19	<b>0.47</b>
PC4	0.17	<b>0.22</b>	0.02	0.13

3

4



1

2 Figure 1. Map of Switzerland (geodata © swisstopo, 2015); the drilling site at the  
3 Grenzgletscher (red star) and the area of the southern Swiss Alps (green) used to extract fire  
4 events are indicated.

5

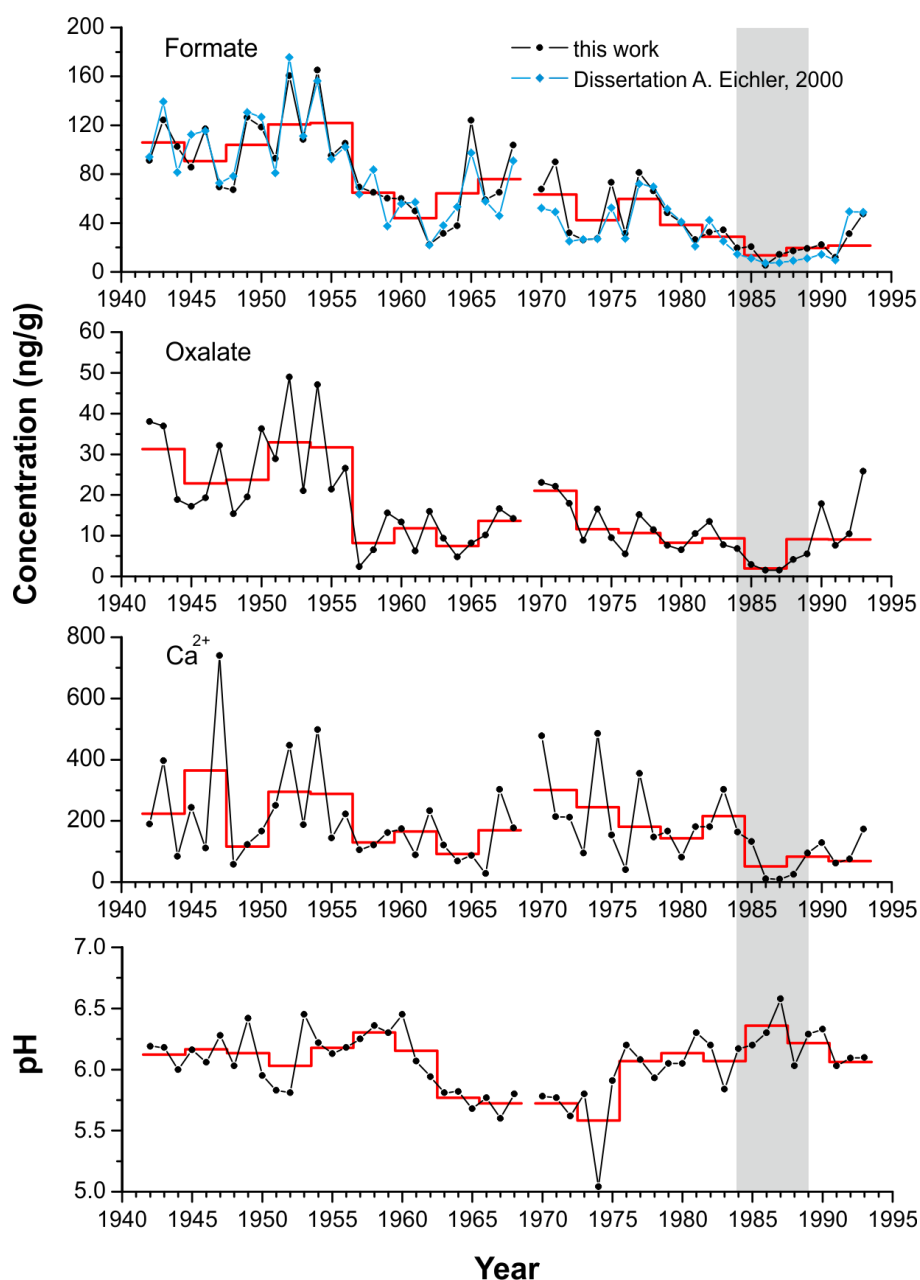


Figure 2. Ice core records of oxalate, formate, calcium, and pH (black dots: annual averages, red line: three-year averages). The period influenced by meltwater (1984-89) is marked in gray. The ice core record of formate obtained from previous high-resolution measurements (blue diamonds, annual averages based on 2148 measurements, Eichler, 2000) fits well with the record determined using the 1-year sampling strategy.

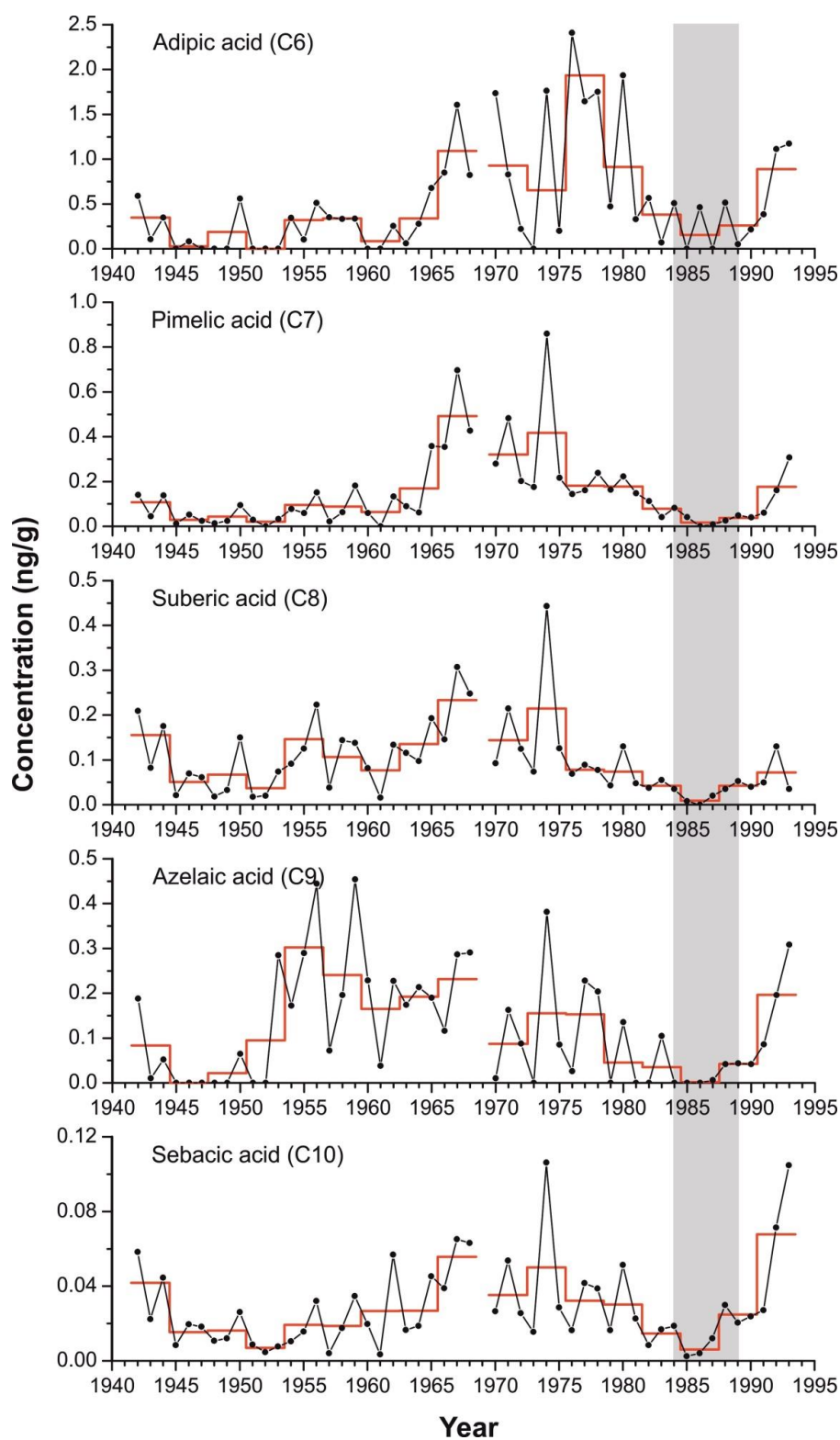
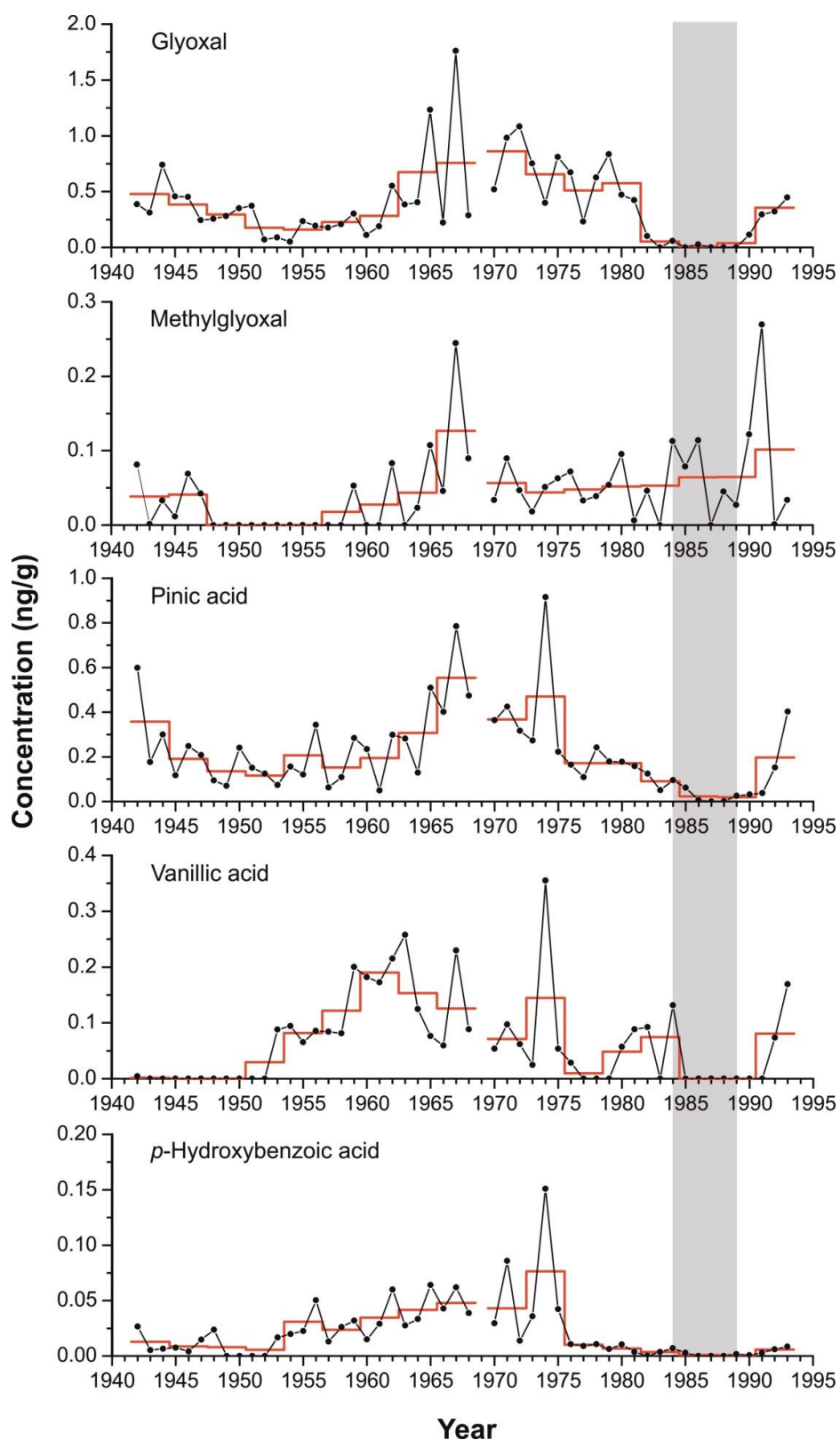


Figure 3. Ice core records of dicarboxylic acids C6-C10 in the Alpine ice core from upper Grenzgletscher (black dots: annual averages, red line: three-year averages). The period influenced by meltwater (1984-89) is marked in gray.





1  
2 Figure 4. Ice core records of  $\alpha$ -dicarbonyls (glyoxal and methylglyoxal), pinic acid, and  
3 monocarboxylic acids (vanillic and *p*-hydroxybenzoic acid) in the Alpine ice core from upper

1   Grenzgletscher (black dots: annual averages, red line: three-year averages). The period  
2   influenced by meltwater (1984-89) is marked in gray.  
3

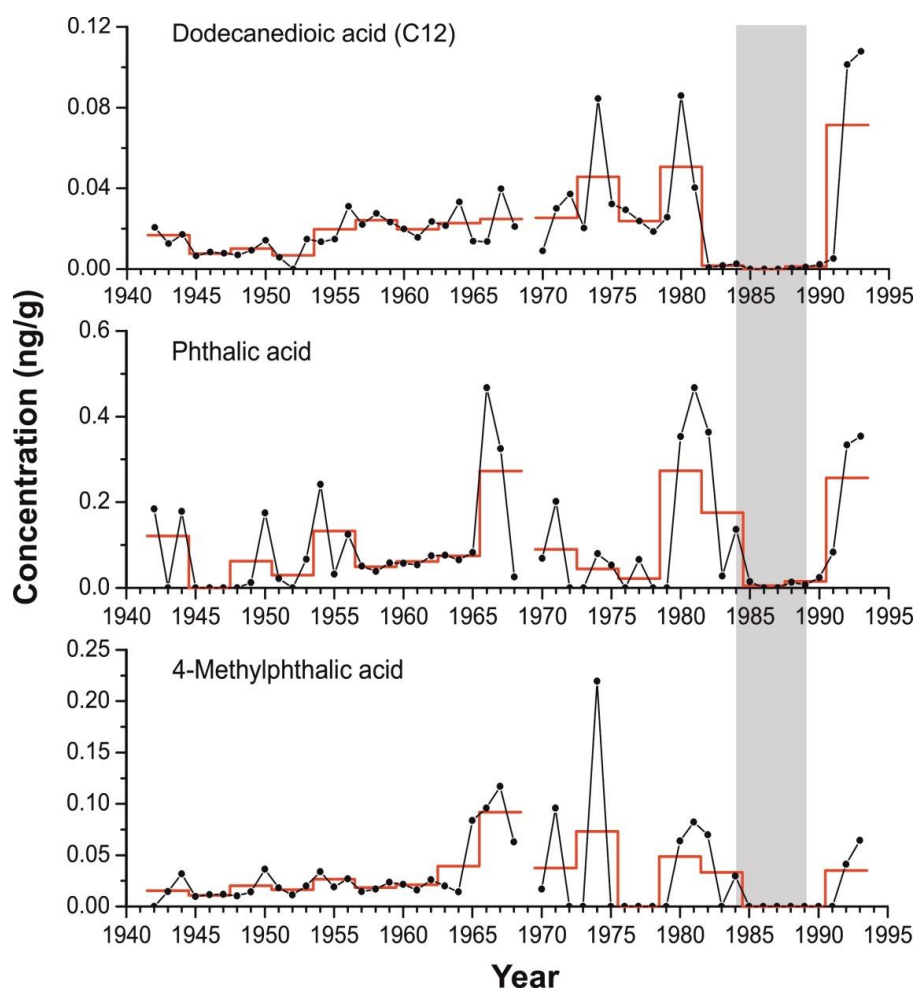
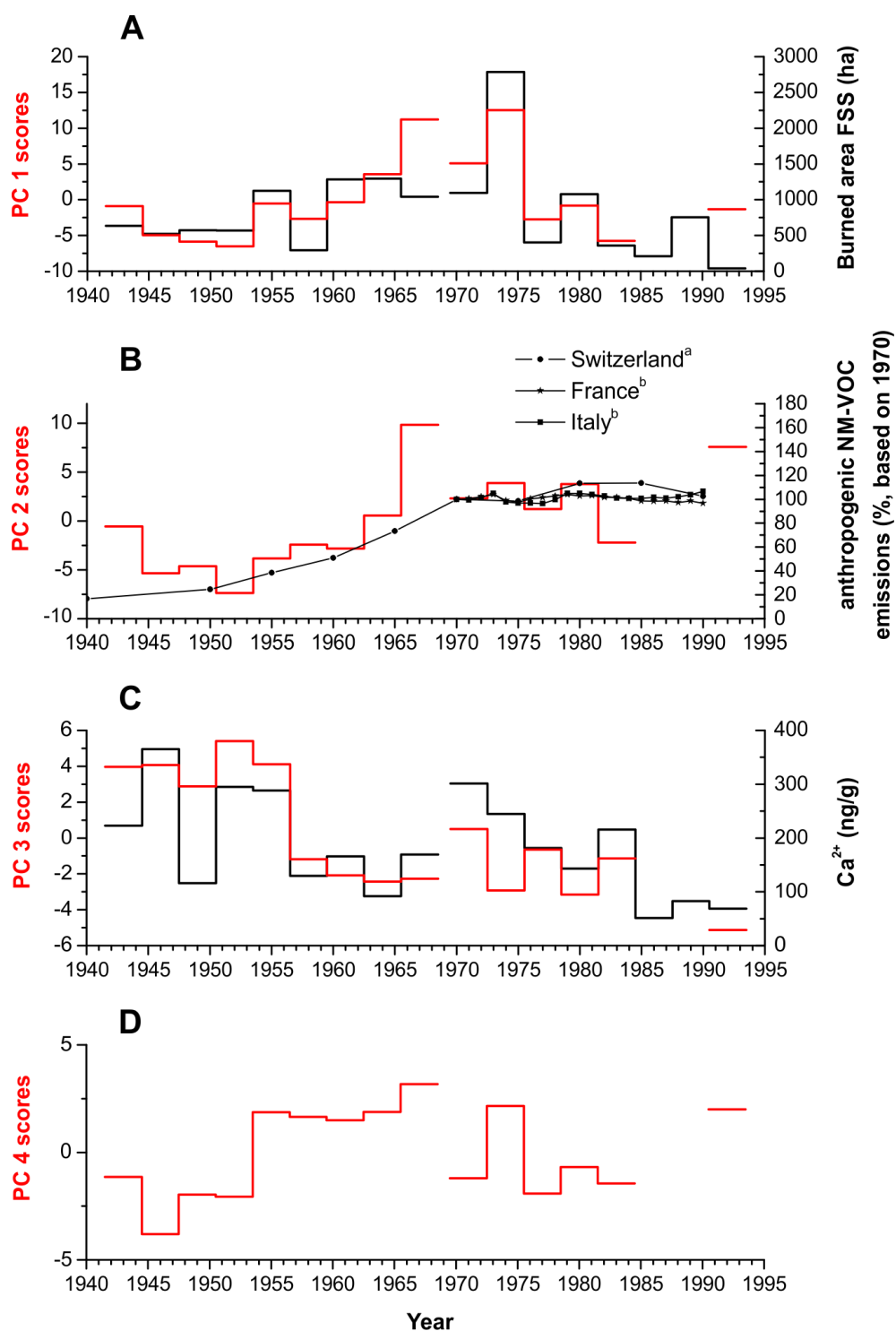


Figure 5. Ice core records of dicarboxylic acids (dodecanedioic acid, phthalic acid, and methylphthalic acid) in the Alpine ice core from upper Grenzgletscher (black dots: annual averages, red line: three-year averages). The period influenced by meltwater (1984-89) is marked in gray.



1

2 Figure 6. A) Records of PC1 and FSS (burned area by fires in Southern Switzerland), B) PC2

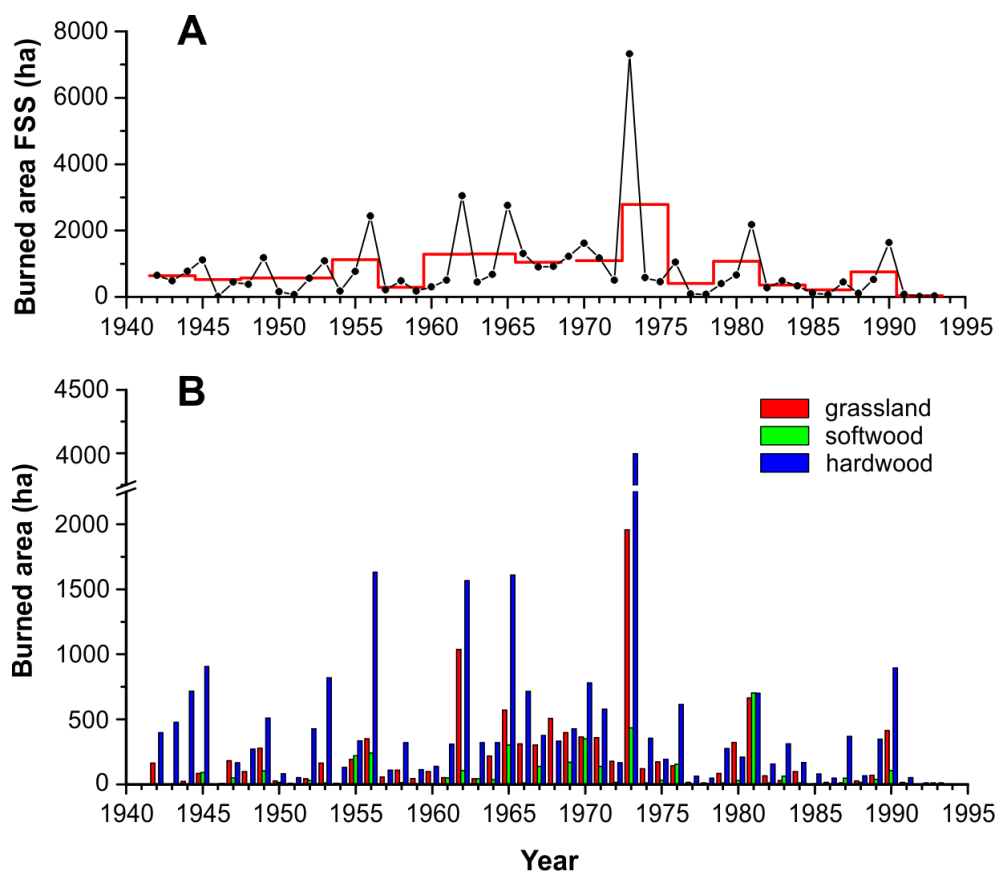
3 and anthropogenic emissions of non-methane volatile organic compounds (NM-VOC) in

4 Switzerland, France, and Italy from 1940 to 1990, C) PC3 and historic record of Ca<sup>2+</sup>, D)

5 PC4. Data in graph B were extracted from (a) (BUWAL, 1995) and (b) (EDGAR, 2010)

6 (black symbols: annual averages, red/black line: three year-averages). Records of the PC1-

1 PC4 are given as z-scores (records normalized and scaled to a mean of 0 and a standard  
2 deviation of 1).  
3



1

2 Figure 7. A) Record of the burned area by fires in Southern Switzerland (FSS, black dots:

3 annual averages, red line: three-year averages), B) annual burned area of grassland, softwood,

4 and hardwood in Southern Switzerland from 1942 to 1993.