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Historic records of organic aerosols from a high Alpine glacier: implications 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 conducted using ultra-high performance liquid chromatography (UHPLC) coupled to electrospray ionization high resolution mass spectrometry (ESI-HRMS). For the first time, long-term records of the carboxylic acids and dicarbonyls as well as their source apportionment are reported for Western Europe. 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 and C8 dicarboxylic 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 C6, C10, and C12 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, 2004; Mayewski et al., 1986; Fischer et al., 1998a, 1998b; Döscher et al., 1996; Legrand et al., 2002; Eichler et al., 2000a; van de Velde et al., 2000; Barbante 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. 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 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.

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 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 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 formate and oxalate, as well calcium 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).

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 Zwischbergen-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, and PHT), two monocarboxylic acids (VAN and PHB), two α-dicarbonyls (G and MG) and major ions (calcium (CAL), 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 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 with an average concentration of 64 ng g^{-1}, followed by OXA, C6, G, and PIN with 15.9, 0.52, 0.38, and 0.22 ng g^{-1}, 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 determined in this work is in the same range as reported in glaciers from Siberian Altai (period 1250–2001 AD, mean concentration 89 $\mathrm{ng\,g^{-1}}$, Eichler et al., 2009), Col du Dôme (CDD, 1925–1995, 80 $\mathrm{ng\,g^{-1}}$, Legrand et al., 2003), and Tianshan (1981–1998, 102.8 $\mathrm{ng\,g^{-1}}$, Li et al., 2001), yet about two times lower than measured in an ice core from the Tibetan plateau (1983–1999, 186.6 $\mathrm{ng\,g^{-1}}$, Wang, 2004). The concentration of OXA in the Grenzgletscher ice core ranges from 1.5 to 49 $\mathrm{ng\,g^{-1}}$, with an average concentration of 15.9 $\mathrm{ng\,g^{-1}}$. These values are about two times higher than the concentration of OXA 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. Concentrations of C9 determined in this work (BDL–0.45 $\mathrm{ng\,g^{-1}}$, average 0.12 $\mathrm{ng\,g^{-1}}$) were about five times lower than in the Greenland ice core (< 0.06–2.38 $\mathrm{ng\,g^{-1}}$, average 0.64 $\mathrm{ng\,g^{-1}}$). PHT concentrations in the Grenzgletscher ranged between BDL and 0.47 $\mathrm{ng\,g^{-1}}$ with an average value of 0.099 $\mathrm{ng\,g^{-1}}$, which is also about five times lower than measured in the Greenland ice core. C12 and MPH have not been reported in ice cores yet. Their concentrations in the Grenzgletscher ice core were found to be comparable to that of C10, with an average value of 0.022 and 0.029 $\mathrm{ng\,g^{-1}}$, for C12 and MPH, respectively.

PIN has not yet been reported in ice cores either. Its concentration in the Grenzgletscher core is 0.22 $\mathrm{ng\,g^{-1}}$ on average, ranging from BDL to 0.92 $\mathrm{ng\,g^{-1}}$. These values are comparable to those detected for C7. Average concentrations of G and MG were 0.38 $\mathrm{ng\,g^{-1}}$ (ranging from BDL to 1.76 $\mathrm{ng\,g^{-1}}$) and 0.046 $\mathrm{ng\,g^{-1}}$ (BDL–0.27 $\mathrm{ng\,g^{-1}}$), respectively. The mean concentration of MG is about eight times lower than that of G. Concentration records of G and MG 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 are comparable to the concentrations found by Kawamura et al., 2001 (0.023–1.14 ng g^{-1}, average 0.26 ng g^{-1}), whereas MG concentrations determined in this work are much lower than reported in the Greenland ice core (0.031–1.36 ng g^{-1}, average 0.21 ng g^{-1}).

Concentrations of VAN ranged from below detection limit (BDL), which is 0.021, to 0.36 ng g^{-1} with an average value of 0.067 ng g^{-1}. These concentrations are in the same range as reported in an ice core from Greenland (0.01–0.125 ng g^{-1}, McConnell et al., 2007) and Ushkovsky ice cap in Northeast Asia (BDL – 0.13 ng g^{-1}, Kawamura et al., 2012). The concentration of PHB ranged from BDL (0.0087 ng g^{-1}) to 0.151 ng g^{-1} with an average concentration of 0.021 ng g^{-1}. Compared to the study by Kawamura et al. (2012) from the Ushkovsky ice cap, which is the only study reporting PHB in ice cores, our results are about ten times lower. Furthermore, the average concentration of PHB is about three times lower than that of VAN, whereas Kawamura et al. (2012) reported PHB concentrations in the Ushkovsky ice core to be 16 times higher than that of VAN. 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 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 and OXA 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), 1960 (e.g., VAN), between 1965 and 1970 (e.g., PIN), during the late 1970s (e.g., C6, PHB) or at the beginning of the 1990s (e.g., MG). During the period from 1984 to 1989 the concentrations of all compounds (except for MG) 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 1984–1989 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. The ratio MG/G 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 and MG 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.

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, and MPH are observed in PC1, which explains 31.5 % of the data variability. PC1 is correlated with the area burned by forest fires in 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, indicating a link between these species. Indeed, the five compounds are significantly correlated (Fig. S1). As C6 and PHT 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, and CAL. As mineral dust originating mainly from the Sahara is the major source of CAL 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 and C9, which are well correlated ($r = 0.601$, $p = 0.018$). VAN is reported to be a conifer biomass burning marker, while C9 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

Switzerland (FSS, see Fig. 5a). The main part of the burned species is hardwood forest, followed by grassland (Fig. 6b). 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.

PHB 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 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 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, both indicating biomass burning to be a major source for PIN deposited at the glacier. This was not expected so far, since PIN 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 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 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 is often used as a marker for biogenic emissions. 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, compared to natural biogenic emissions not influenced by fire events.

C7, C8, and MPH have not been described in the literature in connection to biomass burning so far. C8 is reported to be formed by photo-oxidation of unsaturated fatty acids (Stephanou and Stratigakis, 1993). The strong correlation observed for C8 and C7 ($r = 0.831$, $p < 0.001$) suggests C7 to be produced either by the same source as C8, or by further oxidation of C8, 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 is a secondary oxidation product formed from biogenic as well as anthropogenic precursors but has also been reported as a primary emission product by biomass burning, as indicated by the high loadings within PC1 and PC2. G is significantly correlated with the burned area in southern Switzerland and 22 % of the data variability in the G 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 is also loading partly on PC1. VAN 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 record exhibits a significant correlation to PHB ($r = 0.694$, $p = 0.004$), FSS, and C9 ($r = 0.524$ and 0.601, $p = 0.045$ and 0.018, respectively). Although 27 % of the data variability of VAN 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 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.

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 Switzerland reached a century maximum of about 7300 ha, which is ten times the mean annual area burned between 1942 and 1993 (see Fig. 6a).

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 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). Both dicarboxylic acids C10 and C12 are correlated to PHT ($r = 0.545$, $p = 0.036$ and $r = 0.519$, $p = 0.047$, respectively), indicating similar anthropogenic sources. C6 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. 5b). 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 are found to occur only in the late 1970s to early 1980s and the concentrations are still high in the early 1990s.

3.3.3 Mineral dust

The observed high correlations between OXA, FOR, and CAL are suggested to be caused by common transport with mineral dust to the glacier. 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, which serves as a marker for mineral dust (see Fig. 5c). OXA and FOR 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. This could be explained by the relatively high acidity and volatility of the small acids OXA and FOR compared to their larger homologues. The known Saharan dustfall of 1949 is visible in both the records of CAL and OXA, but not in the record of FOR. Therefore, sources of OXA and FOR might be similar but not identical over the whole time period covered by the ice core. An alternative explanation for the link of OXA 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).

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 and C9 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 has also a high loading in PC4, this component may additionally be influenced by biogenic emissions, as C9 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, and MPH 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. PHB 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 can be used as a fire marker in the observed region. A connection of elevated concentrations of C7, C8, MPH, and PIN to increased biomass burning was shown for the first time. PIN 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 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 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 and FOR. A strong correlation of the most abundant organic compounds OXA and FOR with CAL was observed, indicating the uptake of small acids by alkaline, calcareous aerosol and a common transport to the glacier. The concentration records of OXA and FOR are thus 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 analyzed in the Grenzgletscher ice core (below detection limit = BDL).

	Abbreviation (Cn)	LOD ($\mathrm{ng\,g^{-1}}$)	Concentration ($\mathrm{ng\,g^{-1}}$) 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					
Vanillic acid	VAN	0.021	0.067	BDL	0.36
p-Hydroxybenzoic acid	PHB	0.009	0.021	BDL	0.15
α-Dicabonyl compounds					
Glyoxal	G	0.003	0.38	BDL	1.8
Methylglyoxal	MG	0.003	0.046	BDL	0.27
Ions					
Calcium	CAL	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^{-1}.

	this work	Kawamura, 2001	Kawamura 2012	McConnell, 2007	Legrand, 2003	Eichler 2009	Li 2001	Wang 2004
	Switzerland	Greenland	Ushkovsky ice cap, Russia	Greenland	Alps, France	Siberian Altai, Russia	China	China
	1942–1993	1540–1989	1693–1997	1788–2002	1925–1995	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	186.6
Oxalate	15.9	2.1					6.9	

[a] summer snow layers

[b] converted from µeq L^{-1}

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. High factor loadings (> 0.56) are displayed in bold.

Variable	Components 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			**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 (coefficients 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

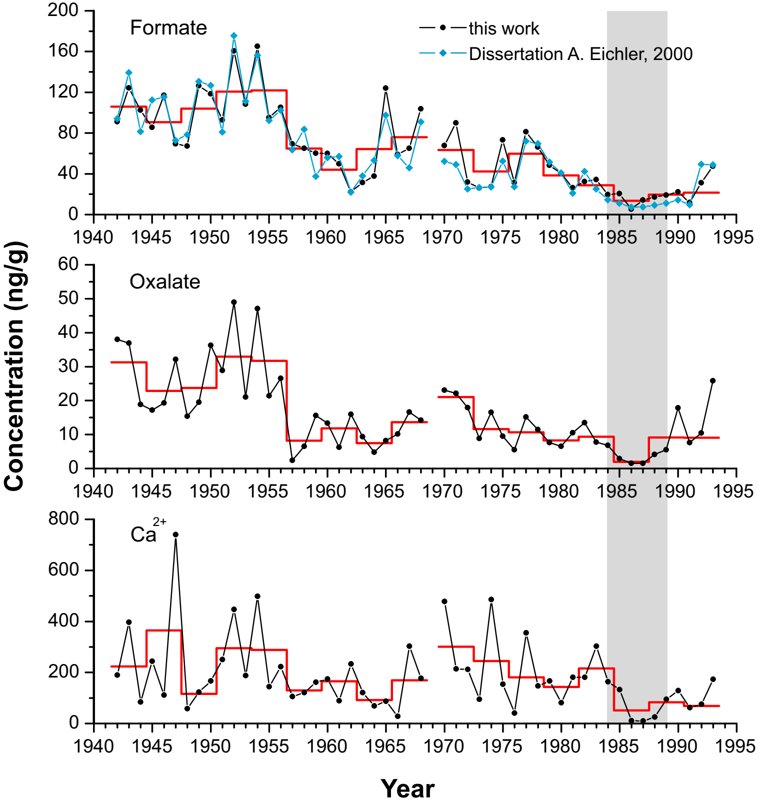

Figure 1. Ice core records of oxalate, formate, and calcium (black dots: annual averages, red line: three-year averages). The period influenced by meltwater (1984–1989) is marked in gray. The ice core record of formate obtained from previous high-resolution measurements (blue diamonds, annual averages based on 2148 measurements, Eichler, 2000) fits well with the record determined using the 1 year sampling strategy.

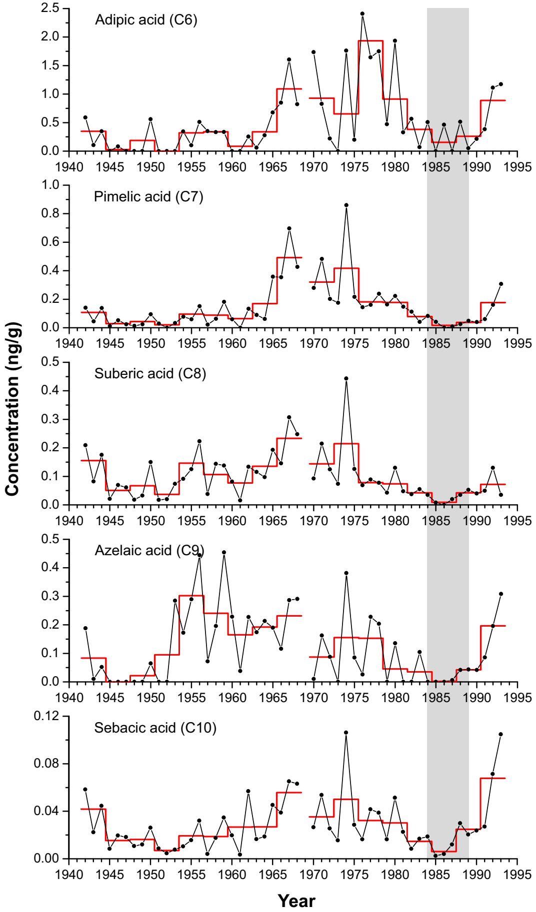

Figure 2. Ice core records of dicarboxylic acids C6–C10 in the Alpine ice core from upper Grenzgletscher (black dots: annual averages, red line: three-year averages). The period influenced by meltwater (1984–1989) is marked in gray.

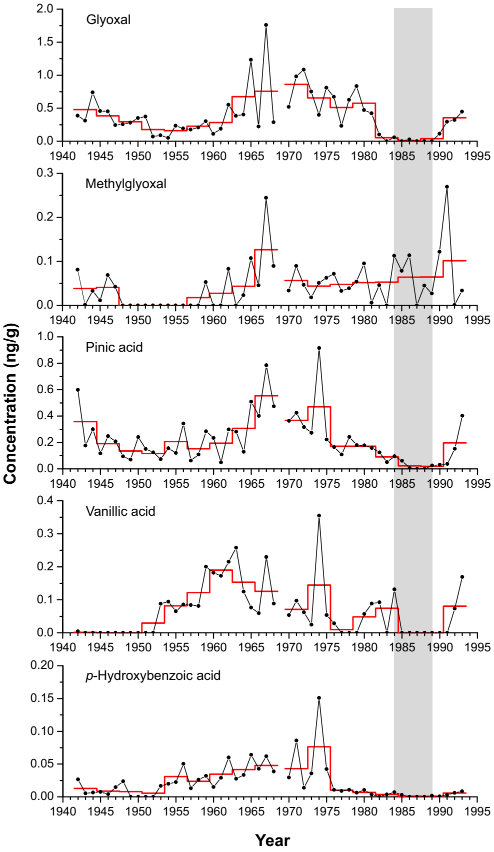

Figure 3. Ice core records of α-dicarbonyls (glyoxal and methylglyoxal), pinic acid, and monocarboxylic acids (vanillic and *p*-hydroxybenzoic acid) in the Alpine ice core from upper Grenzgletscher (black dots: annual averages, red line: three-year averages). The period influenced by meltwater (1984–1989) is marked in gray.

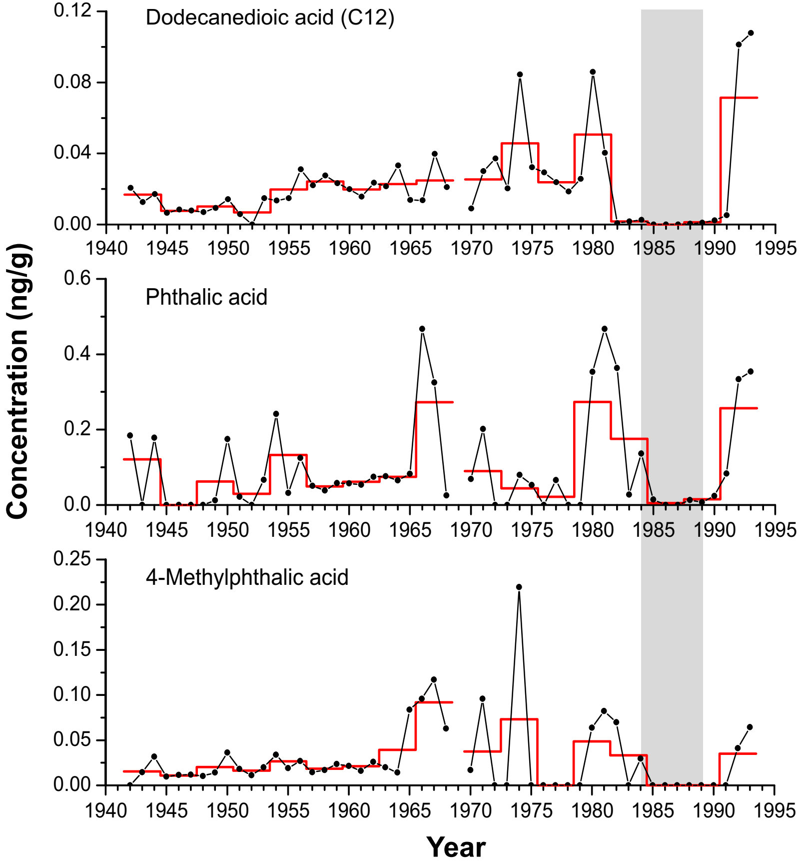

Figure 4. Ice core records of dicarboxylic acids (C12, phthalic acid, and methylphthalic acid) in the Alpine ice core from upper Grenzgletscher (black dots: annual averages, red line: three-year averages). The period influenced by meltwater (1984–1989) is marked in gray.

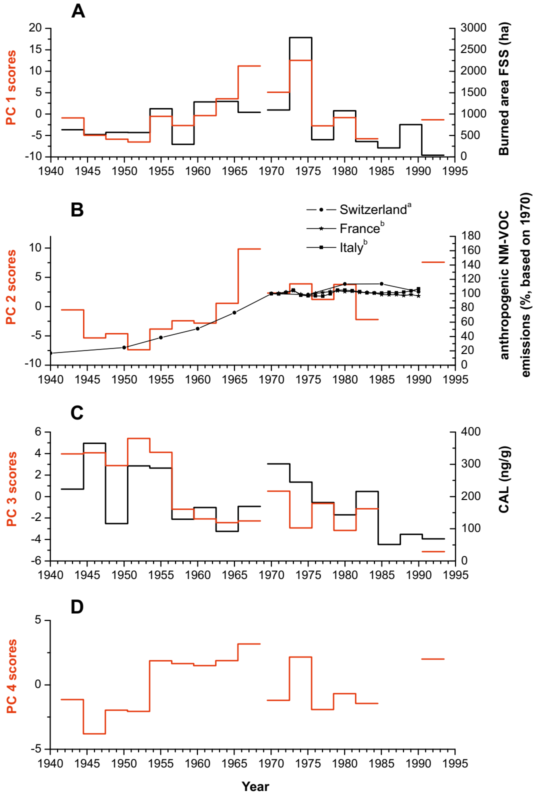

Figure 5. Records of PC1 and FSS (burned area by fires in southern Switzerland) **(a)**, PC2 and anthropogenic emissions of non-methane volatile organic compounds (NM-VOC) in Switzerland, France, and Italy from 1940 to 1990 (based on 1970) **(b)**, PC3 and historic record of CAL **(c)**, and PC4 **(d)**. Data in graph **(b)** were extracted from **(a)** (BUWAL, 1995) and **(b)** (EDGAR, 2010) (black symbols: annual averages, red/black line: three-year averages).

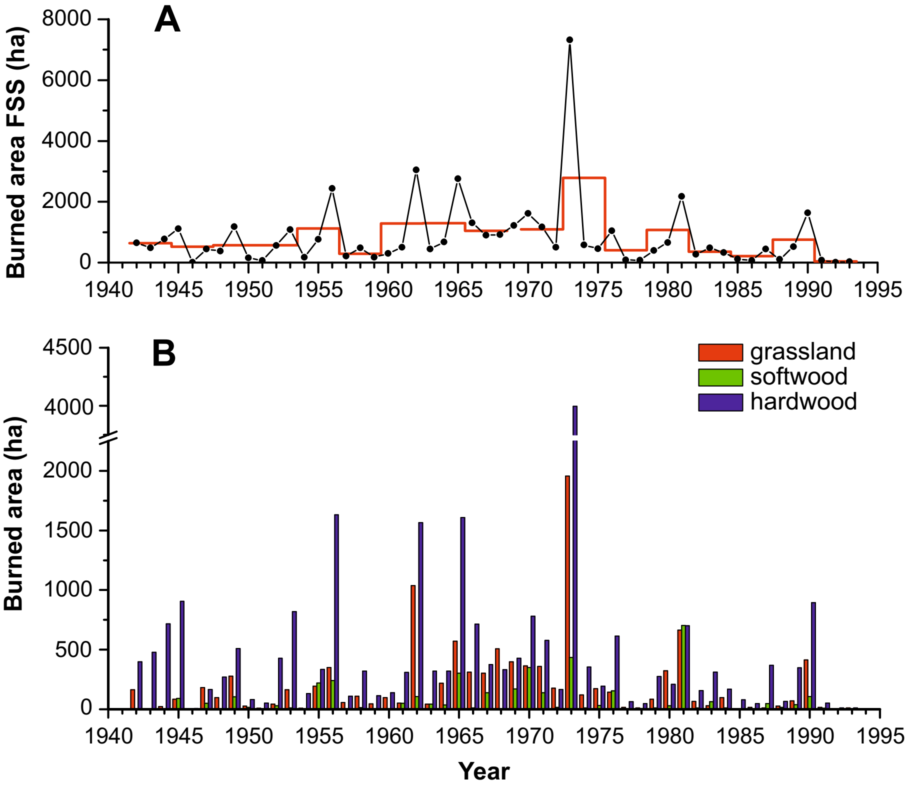

Figure 6. Record of the burned area by fires in southern Switzerland (FSS, black dots: annual averages, red line: three-year averages) **(a)** and annual burned area of grassland, softwood, and hardwood in southern Switzerland from 1942 to 1993 **(b)**.