Boreal fire records in Northern Hemisphere ice cores: A review

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Abstract. Here we review different attempts made since the early 1990s to reconstruct past forest fire activity using chemical signals recorded in ice cores extracted from the Greenland ice sheet and a few mid-northern latitude, high-elevation glaciers. We first examined the quality of various inorganic (ammonium, nitrate, potassium) and organic (black carbon, various organic carbon compounds including levoglucosan and numerous carboxylic acids) species proposed as fire proxies in ice, particularly in Greenland. We discuss limitations in their use during recent versus pre-industrial times, atmospheric lifetimes, and the relative importance of other non-biomass-burning sources. Different high-resolution records from several Greenland drill sites and covering various timescales, including the last century and Holocene, are discussed. We explore the extent to which atmospheric transport can modulate the record of boreal fires from Canada as recorded in Greenland ice. Ammonium, organic fractions (black and organic carbon), and specific organic compounds such as formate and vanillic acid are found to be good proxies for tracing past boreal fires in Greenland ice. We show that use of other species – potassium, nitrate, and carboxylates (except formate) – is complicated by either post-depositional effects or existence of large non-biomass-burning sources. The quality of levoglucosan with respect to other proxies is not addressed here because of a lack of high-resolution profiles for this species, preventing a fair comparison. Several Greenland ice records of ammonium consistently indicate changing fire activity in Canada in response to past climatic conditions that occurred during the last millennium and since the last large climatic transition. Based on this review, we make recommendations for further study to increase reliability of the reconstructed history of forest fires occurring in a given region.

1. Introduction

Biomass burning is a major source of gases and aerosols (Andreae and Merlet, 2001; Akagi et al., 2011) that strongly influence chemical composition of the atmosphere and the radiation balance. In turn, climate changes directly disturb the fire regime – for instance, through the frequency of lightning ignition following enhanced summer convective activity (Romps et al., 2014) – including the occurrence and duration of fire weather (Soja et al., 2007). Climate-induced changes in vegetation (e.g., changing vegetation type, species flammability, fuel

mass) also may influence the fire regime (Hély et al., 2001). In this context, the boreal forest – a key carbon reservoir – is of particular interest because natural fires dominate in this region where future warming likely will significantly modify summer weather conditions. Whereas the mean burned forest area is expected to increase in the future in boreal regions (Flannigan et al., 2005), the change will not be spatially uniform and may differ from

5   western to eastern North America and from North America to Siberia (Flannigan et al., 2001; Girardin et al., 2009). The availability of satellite data has strongly increased the accuracy of estimated burned areas (particularly for Siberian fires; Conard et al., 2002). Examination of present-day climate, fire conditions, and vegetation interactions, however, is complicated by the fact that, in addition to natural fires, many recent fires also are caused by human activities. Humans manage and extinguish fires, further complicating the spatial and

10   temporal record of fire activity. Thus, we need to examine climate, fire conditions, and vegetation interactions through time prior to the appearance of human-origin fires at high northern latitudes to understand both natural and human impacts on past and present burning and improve predictions of future fire activity.

Charcoal deposited in lake and peat sediments is a generally accepted proxy for reconstructing fire occurrence in the past (Clark et al., 1996). Fire signals derived from charcoal analysis is dependent on the applied technique

15   that either measures microscopic charcoal (<100 μm) in pollen slides or macroscopic charcoal (>200 μm) by sieving sediments (Carcaillet et al., 2002 and references therein). Whereas sieved macro-charcoal is representative of local-scale fire (typically a few hundred m from the sampling site), micro-charcoal from pollen slides is a proxy of regional burning history (up to 1 km^2 around the sampling site; Carcaillet et al., 2001). Because of this limited spatial representativeness of charcoal records, several individual records must be

20   assembled to derive a regional reconstruction of fire activity. In this way, paleo-fire records have been obtained at regional, continental, and global scales and can be compiled from the paleo-fire database for specific regions (Blarquez et al., 2014). Published North American paleo-fire compilations covering the Holocene, for example, already are available for four distinct regions (Northwestern boreal, St. Lawrence, western U.S., and central North America) (Marlon et al., 2013).

25   Studies of the chemical composition of snow and ice allow examination of natural variability of the chemical composition of the past atmosphere (see Legrand and Mayewski (1997) for a review). Numerous chemical species emitted or produced in combustion plumes are trapped in glacial archives. Thus, ice cores can be used to reconstruct past fire activity, providing a tool complementary to charcoal records but with unrivalled dating precision in examining the link between climate and fire activity. We also emphasize that in high northern

30   latitudes, charcoal records do not extend prior to 12 kyrs BP since most these regions were covered by ice. Potential fire proxies in ice are inorganic species (i.e., ammonium, nitrate, and potassium), as well as black carbon and numerous organic carbon species (or groups of species) that also are produced during combustion. These latter species include carbohydrates such as monosaccharide anhydrides (levoglucosan), aldehydes, short-chain (C1-C5) mono- and di-carboxylic acids, and acidic oligomers (humic-like substances). In addition, other

35   organic molecules are specifically emitted during combustion of certain types of fuel: dehydroabietic acid produced by pyrolysis of conifer resin (Simoneit et al., 1993) and phenolic acids produced during incomplete combustion of conifers (vanillic acid) and grass (p-hydroxybenzoic acid) (Simoneit et al., 2002).

Legrand et al. (1992) found that ice cores archive forest fire plumes by showing that the concentration of ammonium, formate, and oxalate (measured by ion chromatography (IC)) in some summer layers deposited at

40   Summit (central Greenland) greatly exceed their background levels. The authors attributed these

ammonium/carboxylate events – mainly constituted by ammonium formate salt (ammonium to formate mass ratio of 0.4) – to transport of forest fire plumes from North America to the Greenland ice cap. Although the mechanism leading to formation of ammonium formate in biomass-burning plumes was not elucidated at that time, the presence of micro-soot particles identified by electron microscopy in one of these events confirmed the

5   biomass-burning origin of these ammonium events (Legrand et al., 1995). Others confirmed the biomass-burning origin of ammonium formate events by atmospheric studies conducted at Summit showing a sudden increase in these chemical species in August 1994 and June 1993, when biomass-burning plumes were transported to the site from northern Canada (Dibb et al., 1996; Jaffrezo et al., 1998). Finally, Kehrwald et al. (2012) showed that Summit snow layers corresponding to August 1994 Canadian forest fires exhibited in addition to an oxalate peak

10   a large increase in levoglucosan, a carbohydrate specifically produced by cellulose burning.

Following these pioneering investigations, numerous studies have reported on past frequency of forest fires. Most of them were conducted in Greenland snow and ice, and often used different chemical proxies measured at different time resolution (sub-annual to multiple years). To date, using high-resolution (sub-annual) ammonium records obtained at central Greenland sites through the continuous flow analysis (CFA) technique, Fuhrer et al.

15   (1996) investigated biomass burning for part of the Holocene (from 7.9 to 11.6 kyrs BP and from 2.8 kyrs BP to present) at Summit and Fischer et al. (2015) during the last glacial cycle (from 10 to 110 kyrs BP) at North GRIP. Because ammonium (but not formate) can be measured with CFA, high-resolution records of both ammonium and formate are few in number and limited to the last millennium since IC measurements and sub-annual sampling are required (Legrand and De Angelis, 1996; Savarino and Legrand, 1998).

20   Development of continuous black carbon (BC) measurement methods in ice cores (McConnell et al., 2007) based on new BC analyzers (SP2 ; Droplet Measurement Technologies, Boulder, Colorado) enabled precise, high-resolution measurements of BC in ice cores for the first time, adding an important new ice-core indicator of biomass burning. The first high-resolution historical record of BC was developed from an ice core located at the western central Greenland site D4 and spanned the period 1788 to 2002. Complemented by high-resolution non-

25   sea-salt sulfur determinations and the first high-resolution measurements of vanillic acid in ice cores, this initial BC record permitted evaluation of the contribution of biomass burning and fossil fuel combustion in Greenland snow deposited during the two last centuries, as well as related impacts on radiative forcing (McConnell et al., 2007). Alternatively, a low-resolution (5- to 50-year average) profile of levoglucosan covering the last 15 kyrs at the NEEM site in northwestern Greenland was used by Zennaro et al. (2015) to investigate boreal fire activity

30   across millennial timescales. None of these studies, however, addressed three critical questions. First, how consistent are the fire records obtained at different Greenland sites (northern versus central)? Second, did atmospheric transport between the source regions and drill site influence the record? Third, how reliable are different fire proxies given that they have different emission factors depending on combustion conditions and fuel nature, different atmospheric lifetimes, and some proxies are not exclusively emitted by combustion.

35   Finally, biomass-burning ice records were obtained at sites located in mid-latitude northern regions but they remain sparse and limited to the recent centuries, see Eichler et al. (2011) for a Siberian Altai glacier (the last 750 yrs), Kawamura et al. (2012) for a Kamchatka glacier (the last 300 yrs), and Müller-Tautges et al. (2016) in the Swiss Alps (the last 40 yrs).

In this paper, we first review available ice core chemical records of biomass burning focusing mainly on

40   Greenland cores, exploring the quality of different proposed proxies, considering the intensity of their emission

factor during combustion and their atmospheric behavior (lifetimes and budgets). We then compare several high-resolution (sub-annual) records extracted at different sites and scrutinize recent decades (1950–1990) during which meteorological data are available for backward air mass trajectory calculations and burned boreal forest area more accurately known. This comparison permits exploration of boreal source regions influencing the Greenland ice core records of forest fires and evaluation of the extent to which atmospheric transport influences these records. Although not recorded in all Greenland ice cores, the origin of the 1908 event (the year of the Tunguska phenomenon) is discussed. Some conflicting conclusions on long-term trends in boreal forest fires, in particular for the last millennium and last glacial-interglacial change, are discussed. Based on this review, we make recommendations for further studies to strengthen the quality of ice core records required to examine the relation between climate, vegetation, and fires in the past.

2. Previously published and unpublished data

Ice core studies from different Greenland sites that investigated past boreal forest fires are summarized in Table 1. From North to South, the documented sites include NEEM (77°26'N, 51°03'W), North GRIP (75°N 42°W), Summit (72°36'N, 38°18'W), D4 (71°24'N, 43°54'W), and 20 D (65°N 44°52'W). In addition to these published data, we used several unpublished seasonally resolved CFA records obtained by the Desert Research Institute (DRI) on firn and ice cores from some of the sites shown in Table 1 (NEEM-2011-S1, SUMMIT-2010, SUMMIT-2015-Place, North GRIP2, and D4), and from the Humboldt site located in NW Greenland (78°31'N, 56°49' W; 1985 m asl; accumulation of 14.4 g cm^{-2} yr^{-1}). Other unpublished data used in this study were obtained in the field during the GRIP campaigns at Summit, including CFA measurements of ammonium and formaldehyde (Physics Institute and Oeschger Center for Climate Change Research at Bern), and IC investigations of short-chain mono and dicarboxylates (Laboratory of Glaciologie et Géophysique de l'Environnement at Grenoble). Finally, recent and new chemical investigations, including ammonium (not shown), document biomass-burning fallout in ice cores extracted at the NEGIS (Vallelonga et al., 2014) and Tunu-2013 sites (Sigl et al., 2015). Ongoing studies conducted on northeast Greenland ice cores will complement results discussed here.

Details on sampling and methods generally can be found in publications referenced in Table 1. Following the very first investigations made by Hagler et al. (2007) in snowpit samples collected at Summit, new investigations have recently addressed the amount of organic carbon (OC) present in Greenland ice. Quantification of the dissolved organic carbon (DOC) content of ice on discrete samples was developed at LGGE using an ultraviolet (UV) oxidation and infrared (IR) quantification of CO_2 with a commercial Phoenix 8000 system (Teledyne Tekmar Company, CA). To remove contamination present on the outer portion of ice samples, a glass device was designed in which ice samples are washed with ultrapure water and melted afterward (Preunkert et al., 2011). During sample melting, an inert gas atmosphere is maintained inside the glass device to prevent contact of the ice sample with ambient air in the laboratory. These working conditions allow analysis of small (5 mL) samples containing less than 10 ppb C (Preunkert et al., 2011). They are, however, tedious (15 min required for cleaning and analysis of one sample) and difficult to apply for high-resolution Greenland ice records. Recent improvements in sample handling and other techniques in the CFA system at DRI enable arguably the first reliable high-resolution measurements of total organic carbon (TOC). In this new method, a Sievers 900 TOC analyser is coupled to an ice core melter. The constantly flowing sample stream (isolated from any interaction

with laboratory air and after minimal contact with plastics and other sources of contamination in the flow lines) is analysed within a few minutes of initial melting. Total OC is determined in the Sievers 900 analyzer as the difference in total carbon and inorganic carbon. UV radiation and ammonium persulfate are used to oxidize organic compounds to CO_2, and the CO_2 is measured with a patented selective membrane-based conductometric detection method (details available in the Sievers 900 Series Total Organic Carbon Analyzers, Operation and Maintenance Manual, GE Analytical Instruments, 2011). We emphasize that for both DOC (Legrand et al., 2013) and TOC, measurements are most reliable in ice cores drilled without use of organic drilling fluids and in samples from below the pore close-off depth where potential contamination from circulating modern air through the core is eliminated.

3. Chemical species emitted by combustion and fingerprint of forest fires in ice

3.1. Chemical composition of biomass-burning plumes

For species identified in biomass-burning plumes, we summarize their origin in the plant biomass and their different chemical formation pathways (Fig. 1). Typically, the plant biomass contains C (45%), O (45%), H (6%), N (1.5%), K (1%), Ca (0.5%), S (0.1%), and Cl (0.01%) (Raven et al., 2007). At any time, a vegetation fire may proceed under both flaming and smoldering conditions. During flaming (around 1100°C) that dominates in the earlier phase of the fire, C, H, and N present in fuel are converted into highly oxidized simple molecules (H_2O, CO_2, N_2, and NO). Most BC also is produced at this stage. Later, smoldering conditions (below 230 to 430°C) tend to become dominant, leading to emission of most of the CO, non-methane hydrocarbons (NMHCs), and primary OC aerosol. Concerning the OC fraction, identification of individual species in many studies often is limited to short chain mono- and di-carboxylates that represent less than 10% of total OC mass (e.g., Ruellan et al., 1999). Following Simoneit et al. (1999) who identified levoglucosan as a tracer of cellulose in biomass burning, several studies conducted in combustion plumes extended OC speciation to this carbohydrate. To our knowledge, the most extended OC speciation was obtained for savannah fires (Gao et al., 2003) where, in addition to carbohydrates like levoglucosan and glucose, gluconic acid was tentatively identified as the most important carboxylate. At temperatures higher than 400°C, levoglucosan can be thermally destroyed into either smaller compounds producing various aldehydes and carboxylic acids or repolymerized into polysaccharides to then form high molecular organic-containing bonds and carbonyl groups (i.e., similar to humic-like substances; Fig. 1) (Kawamoto et al., 2003; Abella et al., 2007). Finally, in addition to these primary emissions, numerous non-methane hydrocarbons (NMHCs) and oxygenated volatile organic compounds (OVOCs) emitted during combustion will be oxidized into small carboxylic acids (Fig. 1). In contrast to combustion of fossil fuels, the relatively low temperature of biomass burning compared to fossil fuel combustion leads to emission of nitrogen (mostly NO and NH_3) mainly originating as nitrogen present in fuel (not as atmospheric N_2). Potassium, a major electrolyte in plant cytoplasm, is easily volatilized during combustion (boiling point of 760°C against 1484°C for calcium for instance).

As discussed, emission of many species often depends on combustion conditions, particularly for organic compounds. The content of burned matter is another important parameter for many inorganic compounds. Quantification of emission factors, defined as the mass of species emitted per kg of dry matter (DM) burned,

during combustion of different types of vegetation highlights some specific characteristics of boreal fires. For most species reported in Fig. 1, emission factors for savannah as well as tropical and extratropical forests (including boreal and temperate fires) can be found in Andreae and Merlet (2001). More recently, data have become available for some species distinguishing between temperate and boreal fires (Akagi et al., 2011). The case of nitrogen emissions is a good example of the need to get data distinguishing temperate from boreal fires. Indeed, whereas Andreae and Merlet (2001) reported an emission factor two-fold higher for NO than for NH_3 (3 g of NO against 1.4 g of NH_3 per kg of DM) for extratropical fires, Akagi et al. (2001) reported emission factors of 2.7 g for NH_3 against 0.9 g for NO per kg of DM for boreal fires (0.8 g of NH_3 against 2.5 g for NO per kg of DM for temperate fires). Thus, one of the most important emission features from boreal fires lies in nitrogen emissions dominated by ammonia but not NO_x emissions. For potassium, although no data are available for boreal fires, Andreae and Merlet (2001) reported emission factors ranging between 0.1 and 0.4 g of potassium per kg of DM for extratropical fires. Potassium emission factors are not expected to be strongly dependent on fire combustion (McMeeking et al., 2009) but more on potassium content of the fuel. For organic compounds (NMHCs, OVOCs, and OC primary aerosol), smoldering conditions that are predominant in boreal fires generally lead to higher emission factors than other vegetation fires. Only available for boreal fires are emission factors for NMHCs and OVOCs (a total of 59 g vs. 24 g kg^{-1} of DM for temperate fires; Akagi et al. (2011)). These emissions of NMHCs and OVOCs play a key role as precursors of short chain carboxylates, representing a large source of secondary OC aerosol (Fig. 1). For carbonaceous aerosol (BC and OC), laboratory experiments by McMeeking et al. (2009) show that, as expected, twice more BC is emitted under flaming conditions than under mixed conditions (flaming and smoldering) (1.0 g of BC per kg of DM for flaming and 0.5 g of BC per kg of DM for mixed conditions). Alternatively, far less OC is emitted under flaming conditions (1.6 g of OC per kg of DM for flaming and 16 g of OC per kg of DM for mixed conditions). Finally for levoglucosan, although less data are available, Andreae and Merlet (2001) reported emission factors of 0.75 g of levoglucosan per kg of DM for extratropical fires vs. 0.28 for savannah. The expected dependency of emission factors of levoglucosan with combustion conditions characterized by a quasi-zero emission during flaming, as observed by Gao et al. (2003) for savannah fires, was confirmed by laboratory experiments (Dhammapala et al., 2007; Kuo et al., 2008).

3.2. Fingerprint of forest fires in Greenland ice

With the goal to reconstruct past forest fire activity, ammonium has been used extensively to document fires in numerous Greenland ice cores at sub-annual resolution (Table 1). Many of these studies also documented nitrate and occasionally soluble potassium deposition. These high-resolution studies sometimes documented BC and some organic acids (particularly C1-C2 carboxylic and vanillic acid). Other Greenland records exist for levoglucosan but only at low resolution (Table 1). Since fires are episodic in nature, we first focus our discussion on ammonium, short chain carboxylates, BC, nitrate, and potassium for which several high-resolution Greenland profiles are available. The case of levoglucosan is discussed in Sects. 4.2 and 4.3.

High-resolution chemical profiles were obtained in Greenland ice cores by employing either IC analysis on discrete samples or CFA techniques (Table 1). The first records were achieved by subsampling pieces of firn and ice (several samples per year) with subsequent analysis by IC permitting investigations of potentially relevant species (e.g. , ammonium, potassium, nitrate, and several light carboxylates including formate, acetate, glycolate,

and oxalate). A second set of profiles was achieved using CFA – permitting investigation of high-resolution records of ammonium, nitrate, formaldehyde, BC, and sometimes vanillic acid.

Legrand and De Angelis (1996) found that the firn material is very sensitive to contamination for carboxylates during standard storage of cores in sealed plastic bags. To minimize this problem, a firn core (73 m depth) drilled at Summit in 1993 (Legrand and De Angelis, 1996) was processed in the field by shaving around 90% of the outer part of firn core sections within one or two hours after extraction. Note that this record still represents the only profile documenting carboxylates during recent decades in Greenland snow. In order to examine the chemical signature of ammonium events with respect to background levels, data from this firn core were used to examine the relationship between ammonium and nitrate as well as between ammonium and the different carboxylates (Fig. 2). Anthropogenic emissions impacting the budget of nitrate and carboxylates in Summit snow layers led us to restrict our examination to the pre-1940 time period (520 samples). Indeed, the level of nitrate between 1250 and 1940 AD (60 ± 17 ppb; Savarino and Legrand, 1998) was enhanced to 99 ± 37 ppb during recent decades as a result of growing NO_x emissions (Mayewski et al., 1990; Fischer et al., 1998). Furthermore, Legrand and De Angelis (1996) demonstrated that the levels of formate close to 9 ± 3 ppb between 1750 and 1940 have decreased to 6 ± 2 ppb as a result of acidification of the atmosphere following emission of SO_2 and NO_x. In Fig. 2, we used data obtained along pieces of ice (660 samples) from the deep GRIP ice core and corresponding to the Holocene period (Legrand and De Angelis, 1995, 1996).

In the following sections, we compare the different potential biomass-burning proxies to ammonium. In addition to the fact that many more high-resolution records are available for ammonium than for any other chemical species, the choice of ammonium as the reference species is legitimate since its non-biomass-burning background summer level in Greenland ice is relatively low (less than 18 ppb; Legrand et al., 1992). Estimates of the non-biomass-burning ammonium level were derived from simultaneous comparisons of formate and ammonium levels, exploiting the fact that forest fire debris reaching Greenland mainly consists of ammonium formate and that formate background levels in Greenland ice exhibit low temporal variability. These features are confirmed in Fig. 2a and b.

3.2.1. Ammonium and Carboxylates

As shown in Fig. 3, ammonium peaks are accompanied by a simultaneous increase in formate, oxalate, and sometimes nitrate and potassium. For glycolate and acetate, the snow or ice layers located in the vicinity of the ammonium peak also are disturbed. The presence of these wider peaks for glycolate and acetate than for ammonium likely are related to post-depositional processes acting on these two volatile species. A similar smoothing of formaldehyde (HCHO) fallout related to biomass-burning events also was reported by Fuhrer et al. (1993), as seen in Fig. 4. Therefore, in examining the relationship between ammonium and carboxylates in Fig. 2, we used glycolate and acetate concentrations in samples corresponding to the background and peak but discarded those in the neighboring layers of the ammonium peaks (i.e., 27 values of 524 during the 1773 to 1940 time period and 30 values of 630 during the Holocene). Fig. 2 shows that formate unambiguously increases well above its background level during ammonium events. The ammonium events also are accompanied by enhancement above background values for glycolate, and to a lesser extent oxalate, whereas for acetate the enhancement remains within the range of background variability (Fig. 2).

To compare deposition of carbon associated along ammonium events, we calculate enhancement of the different carboxylates above their respective background values for different ammonium events (Fig. 5). For species exhibiting broadening with respect to the ammonium peak (acetate and glycolate), we considered total deposition by calculating the total area of the perturbation. The same procedure was applied to formaldehyde data available along a few ammonium events, such those reported in Fig. 4. Using the slope of the linear regression between ammonium and carboxylates (expressed in carbon mass) plotted in Fig. 5 (formate: $[HCOO^-]$ = 0.65 $[NH_4^+]$ R^2 = 0.86, acetate: $[CH_3COO^-]$ = 0.07 $[NH_4^+]$ R^2 = 0.32, glycolate: $[CH_2OHCOO^-]$ = 0.105 $[NH_4^+]$ R^2 = 0.69, and oxalate: $[C_2O_4^{2-}]$ = 0.025 $[NH_4^+]$ R^2 = 0.45), and the one calculated for formaldehyde ($[HCHO]$ = 0.02 $[NH_4^+]$ R^2 = 0.86, not shown), we estimate that input of formate accounts alone for 74% of the total mass of identified OC species followed by glycolic acid (12%), and acetic acid (8%), HCHO and oxalate each accounting for 3%. This dominant presence of formate in ammonium-rich Greenland deposits contrasts with the relatively weak emission factors reported for boreal fires (0.16 gC for formic acid against 1.8 g C for acetic acid per kg of DM; Akagi et al. (2011)). This reflects the importance of secondary production of formic acid during aging of the plume (Lefer et al., 1994).

Fig. 5 includes a few data corresponding to ammonium events that occurred during the Younger Dryas (11,600–12,600 yrs BP); these are shown as triangles. Of the four events reported in the formate panel, we estimate enhancement above background levels for only one event because of lack of available ice samples adjacent to the event. This fully documented Younger Dryas event, with an ammonium peak reaching 145 ppb, indicates no enhancement of glycolate (Fig. 5). In fact, in the deep GRIP ice core, the background level of this carboxylate gradually decreases through time, from 1.3 ± 2.6 ppb during the last 5 kyrs to 0.3 ± 0.9 ppb between 5 and 10 kyrs BP and zero prior to 11 kyrs BP (not shown). This decreasing trend is not related to past climate changes since, even during the preceding warm period (the Eemian at around 120,000 yrs BP), glycolate was still not detected in ice whereas all other carboxylates are in the range of values seen during the Holocene. We therefore conclude that this species slowly degraded in the ice.

Although present at concentrations well below those of organic compounds (less than 1 ppb) discussed above, vanillic acid was investigated using CFA in Greenland snow layers (e.g, at D4; McConnell et al., 2007) with the aim of attributing the contributions of fossil fuel and biomass burning to the budget of BC during the two last centuries. We report annual levels of vanillic acid and ammonium in snow layers deposited at D4 between 1740 and 1870 (Fig. 6). Although formate was not measured in D4 snow, comparisons of temporal variability indicate that vanillic acid also can be used as a surrogate of ammonium (R^2 = 0.62 for vanillic acid versus ammonium, compared to R^2 = 0.87 for formate versus ammonium at Summit).

3.2.2. Ammonium versus Formate and Nitrate

Whitlow et al. (1994) and Savarino and Legrand (1998) found that some (but not all) NH_4^+ events in the Summit layers are accompanied by a moderate increase (a few tens of ppb) in nitrate. Fig. 3 illustrates this with the 1863 ammonium event showing an increase of nitrate (~40–50 ppb) but not the 1908 event. Fig. 2 suggests that, if it exists, an input of nitrate accompanying ammonium events remains in the range of variability of nitrate background levels. The variability of nitrate background level in Summit snow layers is mainly related to the seasonal change with values close to 50 ppb in winter and 90 ppb in summer. Although the budget of nitrate in pre-industrial Greenland ice has not been discussed yet, it is likely that the summer maximum is related to

natural NO sources like soil emissions from surrounding continents and possibly lightning, both being more active in summer than winter. Fig. 2 does not support use of nitrate in Greenland ice as a proxy of forest fires.

While Legrand and De Angelis (1996) reported a formate-to-ammonium molar ratio close to unity in NH_4^+ events recorded at Summit both during the last 200 years and the Holocene, Savarino and Legrand (1998) showed that from 1190 to 1770, more ammonium events were accompanied by a significant increase in nitrate. The input of nitrate plus formate equilibrates the ammonium input on a molar basis. The departure from unity of the ammonium to formate molar ratio in snow remains more an exception than an overall rule (Fig. 7). With an emission factor of 2.7 g of NH_3 against 0.9 g for NO per kg of DM in boreal fire emissions (see Sect. 3.1.), we would expect ammonium to dominate nitrate by a factor of five on a molar basis. The even larger observed dominance of ammonium in forest fire debris deposited in Greenland snow suggests that, in addition to emission factors of the two species, another parameter tends to minimize deposition of nitrate. Aircraft-based sampling completed during the NASA Arctic Boundary Layer Expedition (ABLE 3B) indicated an HNO_3 mixing ratio of 200–400 pptv against 1300–3000 pptv of formic acid and 1700–3000 pptv of acetic acid (Lefer et al., 1994). A detailed study of NO_y partitioning in boreal biomass-burning plumes was completed by Alvarado et al. (2010) in the framework of Artic Research of the Composition of the Troposphere from Aircraft and Satellite (ARCTAS-B), showing that PAN is the dominant NO_y species well above HNO_3. We also emphasize that the relative abundance of NO with respect to NH_3 would depend on the altitude of the plume. We expect that most NO emissions take place during flaming when release of energy is at its maximum, sometimes permitting plumes to reach the upper troposphere by pyro-convection. These events are rare, and boreal fire plumes are generally observed between 2 and 7 km (de Gouw et al., 2006).

Using the tropospheric emission spectrometer aboard the NASA Aura satellite, Alvarado et al. (2011) reported NH_3 mixing ratios of several ppbv (up to 7 ppbv) in fresh biomass-burning plumes in July 2008 over central Canada. Similarly, HCOOH mixing ratios ranging from 1 to 2.4 ppbv were observed. Given the dominant presence of these two gases in these boreal fire plumes, we may expect that – during transport toward Greenland – a neutralization of ammonia by formic acid would take place through in-cloud processes. Since satellite data indicate that ammonia is present in excess with respect to acidic species, it is likely that the neutralization process can continue until the secondary production of HCOOH from the oxidation of NMHCs and OVOCs stops. This may explain the quasi-invariant presence of ammonium formate in Greenland snow and ice layers impacted by boreal forest fire plumes.

3.2.3. Ammonium versus potassium

In the atmosphere, the fine fraction of soluble potassium is thought to be related to biomass combustion (Cachier et al., 1991). In the ice, this fraction can be estimated by subtracting both the contribution of sea salt by using sodium level ($[K]_{sea-salt}$ = 0.038 [Na]) and of dust by using calcium from the potassium present in ice (and measured with IC). For the latter contribution, Legrand and De Angelis (1996) derived a K^+/Ca^{2+} mass ratio of 0.04 based on the observed linear correlation in snow layers free of biomass-burning inputs along the GRIP 1993 firn core. In Fig. 3, the fine fraction calculated on this basis (i.e., $[K^+]_{bb} = [K^+] - 0.038 * [Na^+] - 0.04 * [Ca^{2+}]$) is reported for the ammonium events dated at Summit in 1908 and 1863. While for the 1863 event, an increase of potassium in the range of 2 ppb is detected, no significant change is detected for the 1908 event. Examination of the relationship between fine potassium and ammonium for ammonium events occurring between 1770 and 1890

confirms such a relatively poor relationship ($[K^+]_{bb}$ = 0.15 +0.03* $[NH_4^+]$ with R^2 = 0.3). Furthermore, even along the largest ammonium event of the Holocene (NH_4^+ concentrations reaching 410 ppb; Fig. 2), enhancement of potassium remained limited to 2 ppb (not shown) instead of 12 ppb if the preceding linear relationship is considered. Data from Summit therefore suggest that soluble potassium concentrations in snow and ice are enhanced by a few ppb along some (but not all) ammonium events. Given the high sensitivity of this species to contamination (Savarino and Legrand, 1998), it remains difficult to promote use of potassium as a proxy of boreal fires.

3.2.4. Ammonium versus BC and OC

The correlation between ammonium and BC remains relatively strong (R^2 = 0.69, Fig. 6), although slightly weaker than the one between ammonium and formate (R^2 = 0.87 at Summit). At least for the Greenland sites discussed here, the ammonium formate peaks always stay in summer snow layers without spreading to the rest of the year, in contrast to what is observed for formaldehyde and acetate (Sect. 3.2.1). We can, therefore, rule out that remobilization of ammonium formate after deposition (not foreseen for the irreversibly trapped BC species) renders the relationship between ammonium and BC weaker than the one between ammonium and formate. The most likely cause of the slightly weaker BC-NH_4^+ relationship compared to that of formate and ammonium is that flaming (the most important combustion phase for BC) is not the dominant phase in boreal fires, rendering the amount of BC reaching the Greenland ice cap variable from one event to another.

Apart from a snowpit study of recent snow layers deposited at Summit (Hagler et al., 2007), data on the OC content of Greenland ice are rare. A few investigations of the amount of OC present in Greenland ice were first accomplished using an UV oxidation and IR quantification of CO_2 (Preunkert et al., 2011). Deployed for the examination of an ammonium event in the NEEM-2011-S1 core, Legrand et al. (2013) showed that the OC background level close to 15-20 ppb C was enhanced by ~ 100 ppb C along the ammonium event. As seen in Fig. 8, a very similar picture was obtained at DRI using CFA coupled with a TOC analyser. Although limited, these data highlight three important points. First, the similar OC background levels observed in the dry-drilled Summit-2015-Place ice core and in the wet-drilled North GRIP2 and NEEM cores (Fig. 8), suggest that the use of drill fluid has not significantly contaminated the North GRIP2 and NEEM ice. Second, the carbon input related to biomass-burning is more than a factor of 10 higher as OC than as BC. Laboratory experiments by McMeeking et al. (2009) show that, under mixed conditions (flaming and smoldering), at the emission stage, the OC/BC ratio would exceed 10. Consistency between these two numbers, however, is likely coincidental since BC would have a longer atmospheric lifetime than OC but secondary OC production likely counteracts the larger sink of OC with respect to BC. Third, given that the ammonium fallout is mainly in the form of ammonium formate (Sect. 3.2.1), a large part of the OC enhancement in ice layers containing biomass-burning material can be attributed to formate. Therefore, the possibility of obtaining high-resolution TOC profiles using CFA offer an excellent complementary tool to ammonium CFA and BC measurements to extract relevant high-resolution biomass-burning records from Greenland ice.

3.2.5. Levoglucosan

Levoglucosan exclusively is produced by fuel combustion and formed in large quantities by combustion of cellulose (Simoneit et al., 1999) during smoldering. Therefore, levoglucosan has been widely used as tracer of biomass burning. This is even more interesting for boreal fires that are dominated by smoldering. Note, however, that as shown by Kuo et al. (2008), formation of levoglucosan is highly sensitive to the combustion temperature with a yield reaching a maximum around 250°C.

Furthermore, several recent laboratory studies have highlighted the existence of various degradation pathways that may be efficient under atmospheric conditions. They involve heterogeneous oxidation by gaseous oxidants (Lai et al., 2014; Henningan et al., 2010, Sang et al., 2016), gas phase oxidation of gaseous levoglucosan (May et al., 2012), and aqueous phase degradation (Holmes et al., 2006; Zhao et al., 2014). These laboratory studies suggest an atmospheric lifetime of levoglucosan against chemical degradation of approximately two days (Lai et al., 2014), or from two days to two weeks (Slade and Knopf, 1013). Given the lower range of estimated levoglucosan lifetime against chemical degradation we cannot rule out that chemical loss represent a significant loss for levoglucosan additional to the depositional loss that would apply to all biomass burning aerosol.

3.2.6 Quality of the different proxies

The importance of non-biomass-burning sources at a given site with respect to the perturbation associated with arrival of a biomass-burning plume influences the ability of a chemical species to represent a good proxy of fire in ice. The magnitude of the forest-fire perturbation depends on the strength of emission and atmospheric lifetime of the specific chemical species. As discussed for Greenland ice, ammonium, formate, OC (DOC or TOC), BC, as well as vanillic and glycolic acids were enhanced well above their background values during fire events. Levoglucosan would stay in this group of species (denoted as group 1) for which non-biomass-burning sources are relatively weak or do not exist. HCHO also would be in group 1 since biomass burning is expected to represent an important source in the free troposphere of remote regions where its main source is methane oxidation (Lowe and Schmidt, 1983). The use of HCHO as a fire proxy in ice, however, is strongly hampered by large post-depositional effects (see Fig. 4).

In contrast to the preceding species, other significant non-biogenic sources exist for soluble potassium (sea-salt and leachable potassium in dust), nitrate (NO soil emissions and/or lightning), and acetate (vegetation emissions and possibly marine biogenic emissions; Legrand and De Angelis, 1996).

Several other factors should be considered in ranking the different proxies. In group 1, most species can be used regardless of the studied time period, except BC for which, as discussed by McConnell et al. (2007), anthropogenic emissions have grown since 1850. Since glycolate slowly disappears from ice with time (Sect. 3.2.1), its use as fire proxy is restricted to recent times. Another important consideration when evaluating the ability of different chemical species to trace boreal fire in Greenland ice is the performance of available analytical methods to obtain high-resolution, contamination-free profiles. In group 1, only ammonium, BC, OC, and vanillic acid can be presently measured with CFA. We emphasize, however, that contamination-free measurement of OC in porous firn material (i.e., corresponding to the two last centuries in Greenland snow layers) is very difficult (Legrand et al., 2013). Although less significant than for OC, formic acid contamination as a result of firn core storage in sealed plastic bags also is a major concern.

3.3. Fingerprint of forest fires in mid-latitude, high-elevation glacier ice

A few attempts previously were made to reconstruct past biomass burning from ice cores extracted at cold glaciers located at mid-northern latitudes. One factor in addressing these mid-latitude records is proximity to the site of permanent large biogenic emissions making use of some proxies that were tested in Greenland difficult (impossible, in some cases). An exception is Mt. Logan (60° 35' N, 140° 35' W, 5346 m asl) located in Yukon (Canada) where ammonium background values are still as low as those observed in Greenland, suggesting a relatively weak contribution of non-biomass-burning sources in this region. On the basis of poor agreement in the occurrence of ammonium events recorded at Summit and at Mt. Logan during the last 250 years, Whitlow et al. (1994) suggested that this site is influenced by the Siberian fires in contrast to Summit which is more influenced by Canadian fires. Note that no analysis of air mass origin has been completed for Mt. Logan.

At lower latitudes, the impact of biogenic sources becomes more important than in Arctic regions. For instance, applying Principal Component Analysis (PCA) to major ions trapped in an ice core extracted from the Belukha glacier in the Siberian Altai mountains (49° 48'N, 86° 34'E, 4062 m asl) covering the last 750 years, Eichler et al. (2011) suggested that ammonium and formate mainly originate from biogenic emissions and that only soluble potassium and nitrate in ice seem to represent good proxies of biomass burning for this region. The importance of biogenic emissions at that site also is evidenced by background values of ammonium and formate being one order of magnitude higher than those in Greenland (140 ppb of ammonium and 200 ppb of formate; Olivier et al. (2006)). It also has to be emphasized that the PCA analysis by Eichler et al. (2011) indicates that, as expected, potassium and nitrate are influenced by large emissions of dust from the Central Asia desert.

Another site of interest to trace boreal fires from Siberia is located at Ushkovsky (56° 04' N, 160° 28' E, 3903 m asl) on the Kamchatka Peninsula, as shown by calculations of air mass back trajectories (Kawamura et al., 2012). At that site, data on major ions (ammonium, formate, and nitrate) are not available but we can suspect that their use as fire proxies is even more complicated than in Altai. The quasi-continuous volcanic emissions that occur in this region may strongly influence deposition of these ions at that site. Instead, more extended use of several organic fire proxies – levoglucosan, vanillic acid, p-hydroxybenzoic and dehydroabietic acids – was used on this ice core (Kawamura et al., 2012), showing some interesting differences both in the occurrence of peaks and the trend in background values. In particular, this work suggests that the levoglucosan signal is from biomass burning over a wider region (Siberia, Far East, Northeast Asia and Southeast Asia) than the one (Siberia) influencing other organics like dehydroabietic (a specific tracer of pyrolysis of conifer resin).

4. Comparison of high-resolution records of biomass burning proxies in Greenland ice

In this section we examine the consistency of different records of boreal fires archived in Greenland ice across different timescales, starting with the most recent times for which more observations are available.

4.1 Last two centuries

We compare five ammonium high-resolution records spanning the two last centuries; two from Summit, one from D4, and two from NEEM (Fig. 9). In general, the ammonium peaks tend to be better marked at NEEM than at Summit. The two sites have similar snow accumulation rates, but summer precipitation is more pronounced at NEEM than at Summit (Steen-Larsen et al., 2011). Accordingly, this difference suggests a higher likelihood of a

fire imprint in wet deposition at NEEM. Furthermore, as discussed in Sect. 4.1.1, there is more often direct atmospheric transport from the fire areas to NEEM than to Summit.

Whereas a peak-to-peak comparison is rarely perfect (matches are denoted with a dashed line in Fig. 9), in numerous cases the two sites reveal similar events within a departure of one or two years (i.e., within the dating errors of individual cores). It seems likely that many of these are actually in the same year and reflect a slight dating error. Note that, even for ice cores drilled in a distance of a few meters at the same site, glaciological noise by wind reworking is high and may lead to a differing imprint of the same event in the snowpack. Accordingly, based on a systematic shallow firn core study on aerosol deposition at the NEEM site, Gfeller et al. (2014) showed that for ammonium a single core archives only 70 to 80% of the interannual variability in the atmospheric aerosol load, while the rest is obliterated by wind reworking. This finding may explain the differences between the two NEEM records in 1921, 1973 and 1980 (Fig. 9).

During the two last centuries, the consistency is excellent between Summit and D4 whereas some differences appear between Summit and NEEM. The most striking are the absence of record of the 1908 event at NEEM, and the smaller magnitude of the 1863 and 1961 events at NEEM compared to Summit. Conversely, the 1980–1981 events are better detected at NEEM (at least in the 2011 S1 core) than at Summit. The large discrepancy between Summit and NEEM will be discussed in more detail in the following section, for the most recent 1961 event. The records for the year 1908 are discussed in Appendix A.

4.1.1. Source Regions and Atmospheric Transport

For the most recent years, we examined the extent to which air mass transport influences the record of fire events at a given Greenland site. The main boreal fire sources are Siberia and Alaska/Canada. Data on area burned in Canada are available since 1920 (Van Wagner, 1988) and became more accurate after 1959 with the Canadian national fire database (Canadian Forest Service, 2015, National Fire Database – Agency Fire Data. Natural Resources Canada, Canadian Forest Service, Northern Forestry Centre, Edmonton, Alberta. http://cwfis.cfs.nrcan.gc.ca/ha/nfdb) providing precise fire location, start date, and final size (Stocks et al., 2003). Far less precisely known is area burned in Siberia prior to 1997, when satellite data became available. Prior to 1997, only 1915 is known to have been a year of very large fires in Siberia. As discussed below, however, atmospheric transport greatly favors Canada as the main source for Greenland.

Area burned in summer (May to August) in Canada from 1959 to 1992 is reported in Fig. 10, distinguishing between western provinces located west of 96°W (British Columbia, Yukon, Alberta, Northwest Territories, Saskatchewan, Manitoba, and Wood Buffalo National Park) and East (Ontario, Quebec, Newfoundland and Labrador). For these 34 years, maximum area burned occurred in June and July except for 1968, 1977, 1986 (May), and 1981 (August). The increasing burned area during recent years concerned more western than eastern provinces (Stocks et al., 2003). As seen in Fig. 10, total area burned was high in 1961 (3.8 Mha), 1976 (2 Mha), 1980–1981, and 1989 (more than 4 Mha). Prior to 1959, total area burned (not shown) also was high in 1923 and 1929 (3 Mha), 1937 (2 Mha) and 1941 (2 Mha) (Van Wagner, 1998). Considering a possible dating error of one to two years, the Greenland ice records consistently indicate ammonium events in 1923, 1929, 1937, 1941, and 1961 (mainly at Summit and D4), and 1980–81. The relationship between ammonium deposition in Greenland ice and area burned in Canada is poor, however. For instance, an ammonium event was detected at all sites in

1950, a year during which only 1.2 Mha burned in Canada. In contrast, during 1981 in which a maximum of 5.6 Mha burned, only one ice core (NEEM-2011-S1; Fig. 9) reveals an outstanding ammonium peak.

Backward trajectories have been computed using the Hybrid Single-Particle Lagrangian Integrated Trajectory model (Stein et al. 2015; available at: http://ready.arl.noaa.gov/HYSPLIT.php) with meteorological data from NCEP/NCAR. Reanalysis data are available since 1948 (https://ready.arl.noaa.gov/archives.php). The model was run every 6 h in backward mode for three different altitudes (0, 250, and 500 m above ground level) for May/June/July/August when, as discussed above, the fire activity in Canada (Siberia as well; van der Werf et al. (2006)) reached its maximum. Backward air mass trajectory calculations documented the time that air masses reaching Greenland sites were over the forested area of Canada, distinguishing between western and eastern provinces, and north of 45°N in Eurasia, distinguishing between western Europe (from 7 to 45°E) and Siberia (from 45 to 164°E). Comparison of trajectories – arriving at each site at 0, 250 m, and 500 m above ground level – revealed no significant difference. In the following, we report results obtained at 500 m above ground level. Typical backward trajectories calculated for five and ten days for the Summit and NEEM sites (500 m agl) are reported for 1978 in Fig. 11, indicating transport that tends to be slower at NEEM than at Summit. As a consequence, considering ten-day backward trajectories, on average in June-July 1978, the time spent over Canada by air masses reaching Greenland was limited to 5.4% at NEEM compared to 10.8% at Summit (not shown). This compared to 4.2% at NEEM and 8.2% at Summit across 25 years (Table 2). Fig. 11 also indicates a larger fraction of time spent over eastern than western Canada at both sites, consistent with the 25-yr averaged values reported in Table 2. For instance, on average the ten-day backward trajectories arriving at NEEM spent 2.6% of time over eastern Canada against 1.6% over western Canada (4.6% over eastern Canada against 3.0% over western Canada at Summit). Given the fact that on average in June and July, only in a quarter of cases air mass arriving at Summit (40% at NEEM) had travelled over North America, over June-July during a total of 4.3 days the five-day backward trajectories arriving at Summit had spent at least one day over forested areas of Canada (1.4 days at NEEM). For ten-day backward trajectories, the number of days during which the air masses spent more than one day reaches 15 days at Summit and 9 days at NEEM. At both sites, when air masses are not coming from North America, they mainly have travelled over the Atlantic Ocean and only rarely (3% to 10% of cases) had travelled over Eurasia. This summer dominance of air masses coming from North America instead of Eurasia reaching Summit is consistent with other studies (Kahl et al., 1997; Gfeller, 2015). As a result, even for ten-day backward trajectories, the time spent over the fire region of Siberia is 1% at Summit and 0.4% at NEEM (Table 2). Interestingly, as shown in Table 2, there is no significant change of air mass origin for summers during which large fires took place in Canada. From this multiple summer analysis of air masses reaching NEEM and Summit sites, we conclude that for species having atmospheric lifetime of a few days boreal regions of Canada (in particular Eastern provinces) are the main source regions for fire signals archived in Greenland ice.

We now focus on the 1961 event that is well recorded in central Greenland but missed in North Greenland snow layers. With a total area burned of 2.8 Mha (maximum in June with contributions from both western and eastern provinces), 1961 is clearly a particularly high fire activity year of the 1960s and 1970s. In Fig. 12, we reported the starting date of large fires (>200,000 ha) having occurred in June and July 1961 together with the fraction of time spent by air masses over western and eastern provinces of Canada reaching the two Greenland sites. Most of the area burned and fire emissions took place during the first four to eight days after the start of the fire (Mike

Flannigan, personal communication 2016), Fig. 12 obviously shows that air masses reaching NEEM had far less sampled 1961 biomass-burning plumes than those arriving at Summit. This example suggests that, in addition to the occurrence of snowfall, atmospheric transport also can modulate the magnitude of deposition of fire debris from site to site in Greenland ice.

4.2. The last millennium

The NEEM and Summit ammonium records (annual means) spanning 1190–1990 are compared in Fig. 13. As already seen for the two last centuries, the ammonium peaks tend to be more pronounced at NEEM than at Summit. Again, whereas a peak-to-peak comparison is rarely perfect, the two sites reveal similar events within a departure of one or two years in numerous cases. Between 1790 and 1490, the agreement generally is good with only a few missed events: 1719 and 1683 events recorded at NEEM but not at Summit (Fig. 13). Between 1490 and ~1300, agreement is lower and a few peaks are not recorded in one of the two cores (e.g. 1369 and 1465 recorded at NEEM but not at Summit, Fig. 13). Agreement is higher around 1200–1300 perhaps because of the presence of the large sulphate peak attributed to the 1257 Samalas volcanic eruption (Lavigne et al., 2013) which resulted in precise synchronization of the two core records.

To investigate the change in fire frequency during the last 1000 years we deployed a similar peak detection technique as in Fischer et al. (2015) based on a robust outlier detection method (Fischer et al., 1998). The only difference was that, using singular spectrum analysis, we subtracted small background variations (on the order of 2–5 ppb) from the annual mean NH_4^+ data sets before peak detection (Fischer et al., 1998). For peak detection, all peaks that exceeded the median of a 200 yr window by 3.5 times the median of the absolute deviation from the median (MAD) were identified as fire peaks. In a second step the number of peaks in the 200 yr window was counted, where adjacent years identified as peaks were only counted as one. The resulting reduced peak count is shown in Fig. 14 for the three cores.

Despite some decadal variability in each of the three records and some differences between the sites in the overall peak count level, both the two NEEM and Summit ammonium records indicate high fire activity from 1200 to 1500 and after 1850, whereas low fire activity occurred particularly from 1600 to 1800 (Fig. 14). Based on the three records, this finding strengthens the previous conclusion drawn by Savarino and Legrand (1998) on the basis of the 1190–1990 Summit record and suggesting that temporal changes coincide fairly well with the occurrence of the warm and dry climate of the Warm Medieval Period (MWP; 1200–1350) and the cold climate of the little ice age (LIA; 1600–1830). Note that the peak count for each 200-yr window in each core should at first order follow a Poisson distribution. Hence, a peak count of about five peaks per 200 yr during the 18th and 17th centuries in the NEEM main core is significantly lower than its counterpart of about 12 peaks/200 yr prior to 1400. Recently, composite series of charcoal records related to Northeast boreal fires in North America were obtained (Power et al., 2012), confirming the high fire activity at the transition from the 19th to 20th century and to a lesser extent during MWP, and the very low fire activity at the end of the LIA.

As discussed previously, comparisons of high-resolution ammonium records with low-resolution levoglucosan records are difficult. To date, the NEEM record (5-yr averaged) of levoglucosan (Zennaro et al., 2014) suggests a different picture for past changes with an outstanding maximum around 1600 (not revealed by the BC and ammonium profiles). The authors suggested that this high fire activity revealed by the levoglucosan NEEM record was caused by extensively dry conditions in Asia despite the long transport pathway to Greenland. Note

that this conclusion conflicts with the hypothesis of a significant chemical degradation of levoglucosan suggested by laboratory studies (Sect. 3.2.5). More work is needed to elucidate why (1) levoglucosan might reflect Siberian fire activity in Greenland ice but not BC or ammonium, and (2) the finding that the levoglucosan record seems to mirror changes of fire activity at a larger spatial scales (Eurasia plus Canada) than ammonium records.

4.3. Younger Dryas/Holocene fires

Several ammonium events were detected during the cold Younger Dryas (YD) climate (11.6–12.8 kyrs BP) at Summit (Fuhrer et al., 1996) and NGRIP (Fischer et al., 2015). In their study of the origin of ammonium in Greenland, Melott et al. (2010) suggested that the Haber-like production of ammonium (Appendix A) may have been the cause of the large ammonium peak detected at the onset of the Younger Dryas (YD) in the Summit GISP deep ice core. In their discontinuous study of the deep GRIP Summit ice core, Legrand and De Angelis (1995) measured carboxylates along four events that occurred during the YD period, including the largest one dated at 12,610 yrs BP and detected by CFA continuous sampling. As seen in Fig. 5, these four ammonium events (open triangles on the formate panel) do not differ from other events with a large increase of formate, the 12,610 yrs BP event corresponding to the highest ammonium value of 210 ppb. Therefore, we rule out the hypothesis of a Haber-like production of ammonium induced by a comet for the ammonium event that occurred at the onset of the YD.

In a recent study, on the basis of a low-resolution levoglucosan record obtained in the deep NEEM ice core (Table 1), Zennaro et al. (2015) reported low fire activity during the YD and the preceding period of Bolling-Allerod (BA; 12.8–15 kyrs BP) followed by a steady increase during most of the Holocene (until 2.5 yrs BP) that they attributed to changes in fire emissions at the scale of the entire Northern Hemisphere. Although again it is not easy to compare this low-resolution Greenland levoglucosan record with high-resolution ammonium Greenland records, we note that the Greenland ammonium records indicate a different picture. Fischer et al. (2015) on the basis of the high-resolution (10–110 kyrs BP) ammonium record obtained from the North GRIP deep ice core indicated an increase of fire activity at the onset of BA, followed by a weak decrease during the YD, and a second increase toward the beginning of the Holocene. For the Holocene, on the basis of the ammonium record at Summit, Fuhrer et al. (1996) reported strong fire activity at 10 kyrs BP and an overall decreasing trend throughout the Holocene (Fuhrer et al., 1996). Such a change in trend during the Holocene is consistent with charcoal records from the Eastern part of North America (Carcaillet et al., 2002; Marlon et al., 2013). More work is needed to elucidate why levoglucosan and ammonium suggest such different temporal trends. At this stage, we can only emphasize again that the levoglucosan records appear to mirror changes of fire activity at a larger scales (Eurasia plus Canada as discussed in Sect. 4.2 for the last millennium, or even larger as discussed above for the last 15 krs) than ammonium and BC records.

5. What we have learned: Recommendations for further investigations.

This comparison of various chemical Greenland ice core records permitted evaluation of the quality of different proxies to trace boreal fires. Ammonium, organic fractions (BC as well as OC), and organic compounds like formate and vanillic acid are found to be good proxies whereas the use of potassium, nitrate, and carboxylates (except formate) is complicated by either post-depositional effects or the existence of large non-biomass-burning

sources. This comparison also highlighted important factors that may modulate records of such sporadic events including the occurrence of snowfall, wind erosion of snow surface, and atmospheric transport processes and pathways between the source regions of Canada and the different Greenland drill sites. Ammonium ice records consistently indicate Canada as the main source for fire plumes reaching Greenland (in agreement with charcoal

5   records) and suggest past changes in fire activity in response to climatic fluctuations.

From that, we recommend replicate high-resolution CFA measurements – particularly ammonium, TOC, and BC – along ice cores extracted from different sites to provide a composite Greenland ice record.

Further work dedicated to high-resolution measurements of levoglucosan also would be welcome. Such measurements would enable improved understanding of the cause of the observed difference in past fire activity

10   changes derived from levoglucosan and ammonium records. A large amount of ice would be needed to achieve high-resolution levoglucosan ice core profiles, but sampling Greenland snow in snow-pits would be a useful alternative. For instance, a 5 m depth pit at Summit would span the last 10 years during which numerous fire events have occurred in North America and Siberia that are well documented by satellite observations.

Finally field and ice core studies of post-depositional effects for several organic species (or groups of species)

15   are strongly recommended to enable more quantitative interpretation of the ice core archive and implications for past changes in atmospheric chemistry, aerosol and gas phase radiative forcing, and climate.

Appendix A: The particular 1908 Event

Whereas the different high-resolution ammonium profiles obtained in various Greenland ice cores covering the last century (Sect. 4.1) are generally in reasonably good agreement, there are some exceptions, including the

20   1908 summer. 1908 is unique in that on the 30th of June 1908, anomalous optical phenomena were observed in the sky over Eurasia. These observations were attributed to the explosion of a cosmic body above the region of the Tunguska River basin in central Siberia (60°55'N, 101°57'E). A review of this event can be found in Hugues (1976). This event has been the subject of debate regarding several aspects, including the nature of the bolide – a low-density cometary body or stony meteorite. In the first case, accompanying the progressive ablation of the

25   body during its entrance into the atmosphere, thermal decomposition of N_2 and O_2 would have efficiently produced NO through the mesosphere and stratosphere (Turco et al., 1982). Estimation of the production reached 30 Tg of NO and would be detected as enhanced nitrate levels in snow deposited in both Greenland and Antarctica during at least one year. Neither from Greenland (Camp Century and Dye 3; Rasmussen et al., 1984) nor from various Antarctic sites (Dome C; Legrand and Delmas, 1986; South Pole; Legrand and Kirchner, 1990)

30   was such a nitrate increase in ice detected. Based on a more accurate aerodynamic model of the bolide, Chyba et al. (1993) suggested that Tunguska was a stony body, which exploded at an altitude of 9 km with all the energy deposited between 12 and 5 km altitude. On this basis, Curci et al. (2004) calculated that 0.4 Tg of NO were produced within this elevation range and that nitric acid was mainly deposited downwind within the first month.

Another debate concerned the possibility that a fragment of the Tunguska asteroid survived strong heating within

35   the atmosphere and collided with the ground. For instance, Gasperini et al. (2007) suggested that Lake Cheko, a 300 m wide lake located a few km from the epicenter of the 1908 Tunguska event, is an impact crater. Based on observational evidence that contradicts this hypothesis (no evidence of an uplifted rim as seen at many fresh impact craters and the presence of unaffected mature trees close to the lake), Collins et al. (2008) concluded that Lake Cheko is highly unlikely to be an impact crater. This debate is of importance with respect to the possibility

raised by Melott et al. (2010) that the Tunguska event also may have significantly produced ammonia from nitrogen and hydrogen (the so-called "Haber-like process") under high pressure in the shock front of the bolide. Indeed, such ammonia production needs a sufficient amount of water to proceed and therefore requires the event to have been accompanied by a ground impact. There is a consensus that the shock wave of the Tunguska

5 explosion devastated trees across an area 0.215 Mha (Fast et al., 1967), and the flash burned vegetation covered an area of about 0.01 Mha. Abramov et al. (2003) estimated that following this event, a total of 0.09 Mha were burned. This burned area remains one or two orders of magnitude lower than the annual area burned in North America, however (2 Mha on average, up to 7 Mha during some years; Stocks et al., 2003) and in Eurasia (12 Mha on average; Conard et al. 2002).

10 Fig. A1 summarizes sub-annual-resolution NH_4^+ records from several Greenland ice cores spanning 1905 to 1916. It appears that, for ammonium, 1908 stands out at Summit and D4 but not at NEEM and Humboldt. As discussed in Sect. 3.2.2, an increase of nitrate is sometimes detected along with the ammonium peaks at Summit, but when present, they rarely exceeded a few tens of ppb. As seen in Fig. A1, the ammonium event neither at D4 nor at Summit was accompanied by a significant enhancement of nitrate. In contrast to the absence of nitrate

15 peak at Camp Century and Dye 3, two other studies conducted at Summit reported a large nitrate peak in the 1908 layer. McCracken et al. (2001) reported the presence of two narrow sharp spikes (one of them reaching 180 ppb above the usual background in summer) in the nitrate record during 1908, no other relevant species being reported in their study. Melott et al. (2010) reported unpublished data from Summit showing an ammonium peak (200 ppb above the usual background winter level) together with a nitrate peak (around 150 ppb above the usual

20 background winter level) during winter 1908/1909. Both of these studies assigned this ammonium to the Tunguska event. Since the 1908 ammonium event detected in Greenland has a very similar organic signature (an input of ammonium formate at Summit (Fig. 5), and the presence of vanillic acid at D4 (Fig. 6)) compared to other events, we can rule out the hypothesis that an event like Tunguska was able to produce ammonium following the Haber reaction as proposed by Melott et al. (2010). We, therefore, do not agree with the conclusion

25 from Zennaro et al. (2014) who explained that the absence of levoglucosan and ammonium spikes in the 1908 NEEM ice core suggest that ammonium peaks in other Greenland ice cores may not be caused by forest fires during the 1908 summer but by a Haber-like process as invoked by Melott et al. (2010). Instead, as discussed in Sect. 4.1, the lack of a pronounced 1908 peak at NEEM is likely due to the local character of fire plume transport and/or deposition onto the Greenland ice sheet.

30 Another point concerning the 1908 event may come from studies conducted in Eurasia. Kawamura et al. (2012) measured biomass-burning organic tracers in an ice core spanning 300 years extracted from Ushkovsky ice cap. Although discontinuous, the levoglucosan record showed sporadic peaks in 1705, 1759, 1883, 1915, 1949, and 1972, with the largest peak in 1949. Similarly, vanillic and p-hydroxybenzoic acids exhibited peaks in 1705, 1759, and 1949. Although estimates of burned area in Siberia are likely greatly underestimated, the 1915 year

35 was well recognized as a dry year during which a total of 140,000 km^2 were estimated to have burned in Siberia (Shostakovitch, 1925). Since the high levels of levoglucosan in the 1915 layer of the Ushkovsky ice core coincides very well with the year of large fires in Siberia and none of the measured biomass-burning organic tracers reveal a peak in the 1908 layer of the Ushkovsky ice core, the occurrence of large fires in Siberia in 1908 is unlikely and suggests that the 1908 event seen in some of the Greenland ice record of ammonium originated

40 from North America (as clearly supported by backward trajectory calculations in Sect. 4.1.1).

6. Data availability

Data from NEEM-2011-S1, SUMMIT-2010, North GRIP2, D4, and Humboldt can be made available for scientific purposes upon request to J. McConnell at DRI. CFA analyses of ammonium and formaldehyde at GRIP as well as CFA ammonium on the NEEM deep ice core can be made available for scientific purposes upon request to H. Fischer at the Physics Institute and Oeschger Center for Climate Change Research at Bern. IC data from GRIP, GRIP 1993, and Eurocore can be made available upon request to M. Legrand at the Laboratory of Glaciologie et Géophysique de l'Environnement at Grenoble. Canadian fire data are made available by the Canadian Forest Service under http://cwfis.cfs.nrcan.gc.ca/datamart.

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Table 1. Various Greenland ice records that were used to investigate past forest fire changes. Bold species were chosen by the authors of these previous studies as good fire proxies in ice (others were found to be influenced by fires but not enough to be considered as good proxies; Sect. 3.2).

Sites (snow accumulation)	Locations (elevation)	Time-period	Resolution	Proxies	References
Summit (GISP2) ($\sim$ 22 g cm^{-2} yr^{-1})	Central Greenland (3240 m asl)	1750-1980	Mostly biannual (Subsampling)	**NH_4^+** K^+, NO_3^-	Whitlow et al. (1994)
Summit (GRIP 93) ($\sim$ 22 g cm^{-2} yr^{-1})	Central Greenland (3240 m asl)	1767-1993	Seasonally resolved (Subsampling)	**NH_4^+ and $HCOO^-$** K^+, CH_3COO^-, $C_2O_4^{2-}$	Legrand and De Angelis (1996)
Summit (Eurocore) ($\sim$ 22 g cm^{-2} yr^{-1})	Central Greenland (3240 m asl)	1193-1767	Seasonally resolved (Subsampling)	**NH_4^+ and $HCOO^-$** $C_2O_4^{2-}$, NO_3^-	Savarino and Legrand (1998)
Summit (GRIP) ($\sim$ 22 g cm^{-2} yr^{-1})	Central Greenland (3240 m asl)	0-3 kyr BP, 8-12 kyr BP	Seasonally resolved (CFA)	**NH_4^+**	Fuhrer et al. (1996)
North GRIP ($\sim$ 19 g cm^{-2} yr^{-1})	Central Greenland (2917 m asl)	10-110 kyr BP	Yearly averaged CFA values	**NH_4^+**	Fischer et al. (2015)
D20 ($\sim$ 41 g cm^{-2} yr^{-1})	SE Greenland (2625 m asl)	1750-1980	Seasonally resolved (Subsampling)	**NH_4^+** K^+, NO_3^-	Whitlow et al. (1994)
D4 ($\sim$ 41 g cm^{-2} yr^{-1})	W central Greenland (1985 m asl)	1788-2002	Monthly (BC) (CFA) Annual (VA) (CFA)	**Black carbon (BC) and vanillic acid (VA)**	McConnell et al. (2007)
NEEM (deep core, 2011-S1) ($\sim$ 20 g cm^{-2} yr^{-1})	NW Greenland (2454 m asl)	0-2 kyr BP	5 years Monthly (BC) (CFA)	**Levoglucosan**, NH_4^+ BC	Zennaro et al. (2014)
NEEM (deep core) ($\sim$ 20 g cm^{-2} yr^{-1})	NW Greenland (2454 m asl)	0-15 kyr BP	5-50 years	**Levoglucosan**	Zennaro et al. (2015)

Table 2. Averaged fraction of time spent by air masses over different forested areas as calculated for June and July backward trajectories (five and ten days) arriving 500 m above Summit and NEEM sites. Calculations were made for 25 years between 1948 and 1991 (1948–1953, 1959–1965, 1978–1983, and 1986–1991) and during a few years characterised by large fires in Canada (1961, 1979–1981, and 1989: Fig. 10).

Site (Years)	Western Canada	Eastern Canada	Canada	Western Europe	Siberia
Summit (25 years)	0.6% (5 days) 3.0% (10 days)	2.6% (5 days) 4.6% (10 days)	3.2% (5 days) 7.6% (10 days)	0.3% (5 days) 1% (10 days)	- 0.6% (10 days)
NEEM (25 years)	0.3% (5 days) 1.6% (10 days)	1.0% (5 days) 2.6% (10 days)	1.2% (5 days) 4.2% (10 days)	- 0.4% (10 days)	- 0.8% (10 days)
Summit (Fires)	0.6% (5 days) 3.2% (10 days)	2.6% (5 days) 4.9% (10 days)	3.3% (5 days) 8.2% (10 days)	0.1% (5 days) 1% (10 days)	- 0.6% (10 days)
NEEM (Fires)	0.1% (5 days) 1.5% (10 days)	1.2% (5 days) 2.5% (10 days)	1.3% (5 days) 4.0% (10 days)	- 0.4% (10 days)	- 0.5% (10 days)
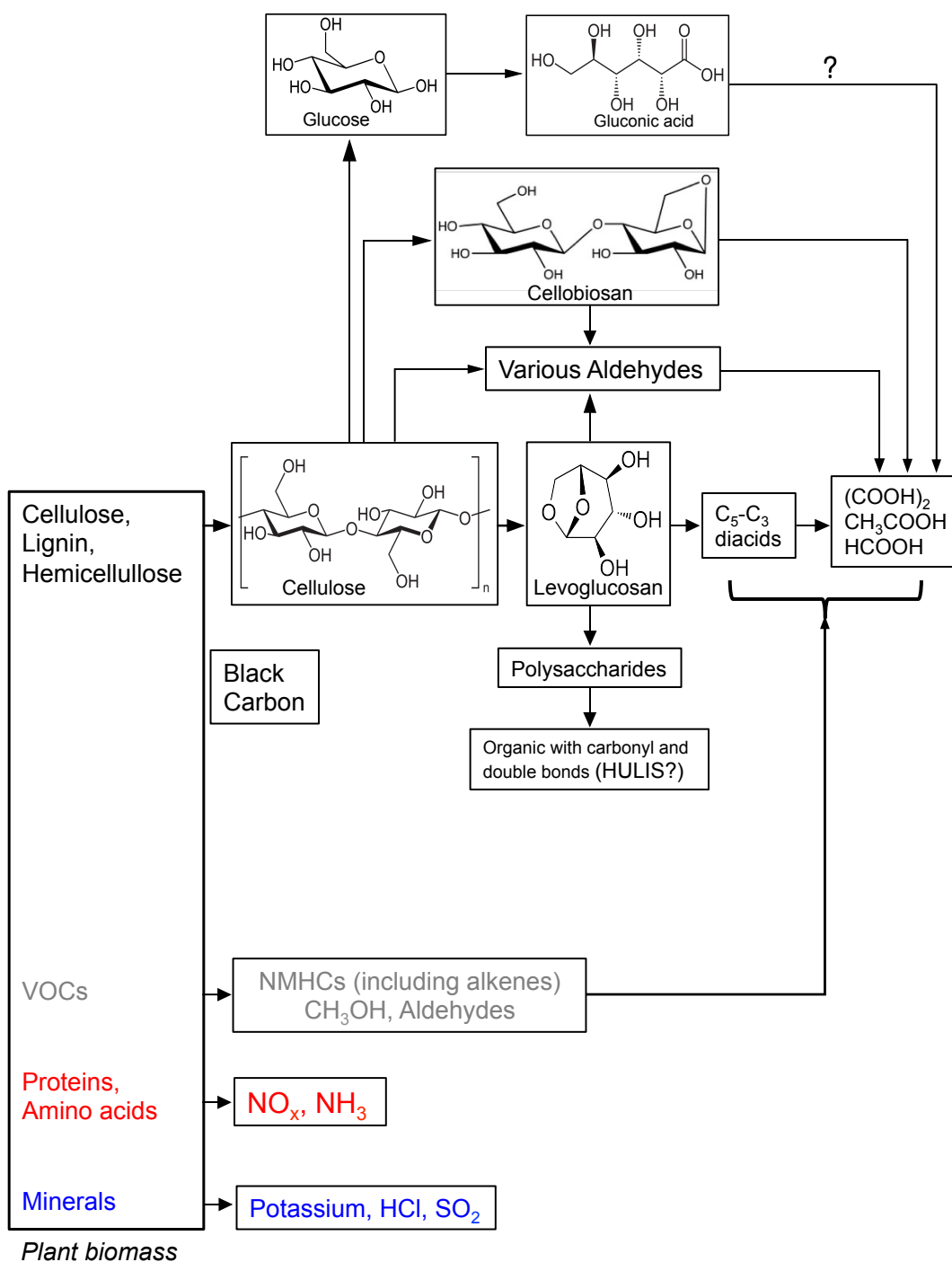
Figure 1: Proposed chemical pathways for formation of various chemical species identified in smoke aerosols. Adapted from Gao et al. (2003) and references therein, Kawamoto et al. (2003), and Abella et al. (2007).
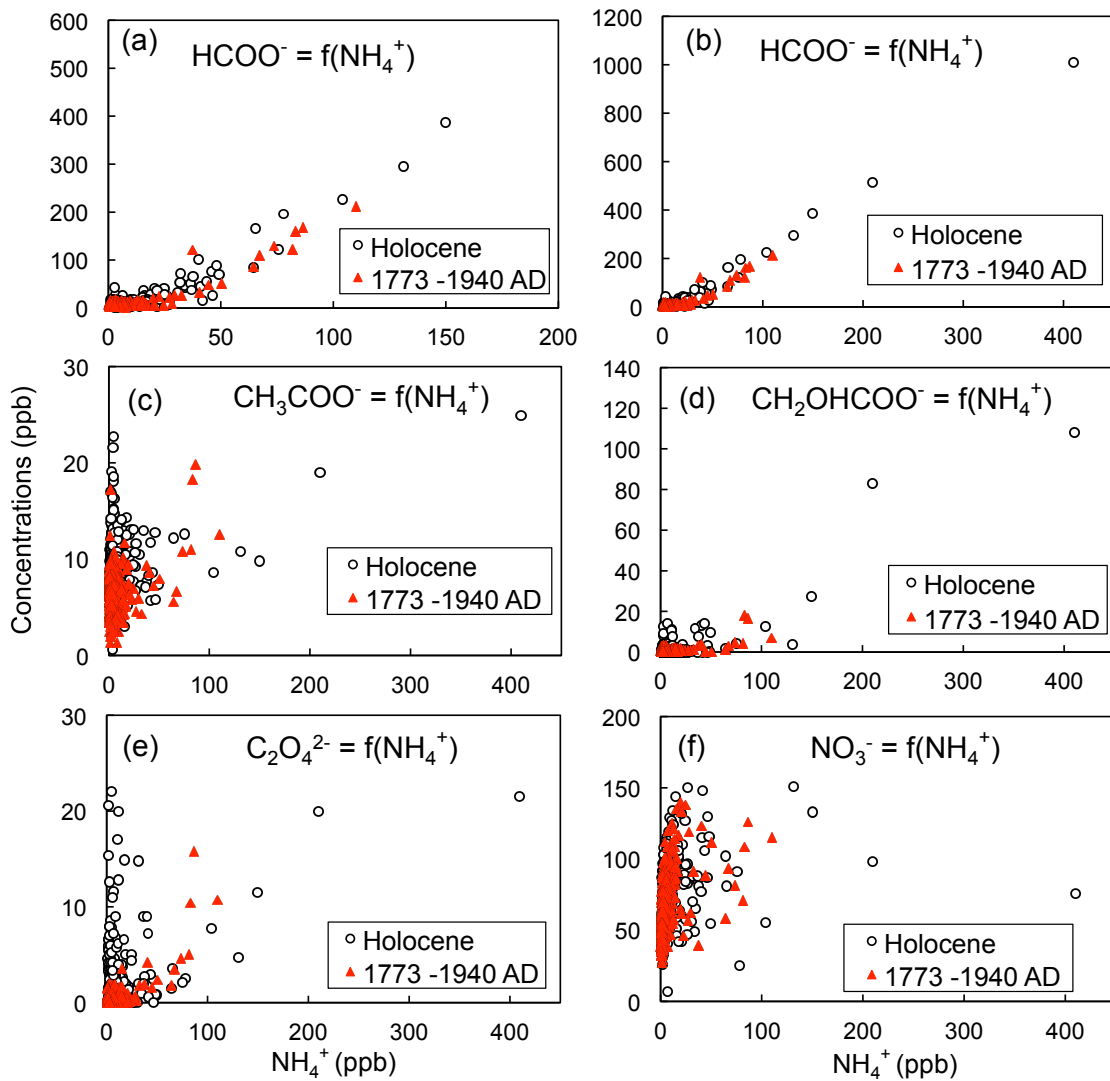
Figure 2: Concentrations of various carboxylates (a to e) and nitrate (NO_3^-, f) as a function of ammonium (NH_4^+) in Summit snow and ice layers. $HCOO^-$ is formate, CH_3COO^- is acetate, CH_2OHCOO^- is glycolate, and $C_2O_4^{2-}$ is oxalate. For formate, two panels (a and b) are shown to detail the relationship at ammonium concentrations lower than 200 ppb (panel a). The red triangles correspond to the layers deposited between 1773 and 1940 AD (520 values along the GRIP 93 firn core: Table 1); the black circles correspond to the Holocene period along the GRIP deep ice core (660 values between and 355 and 11,600 years BP).
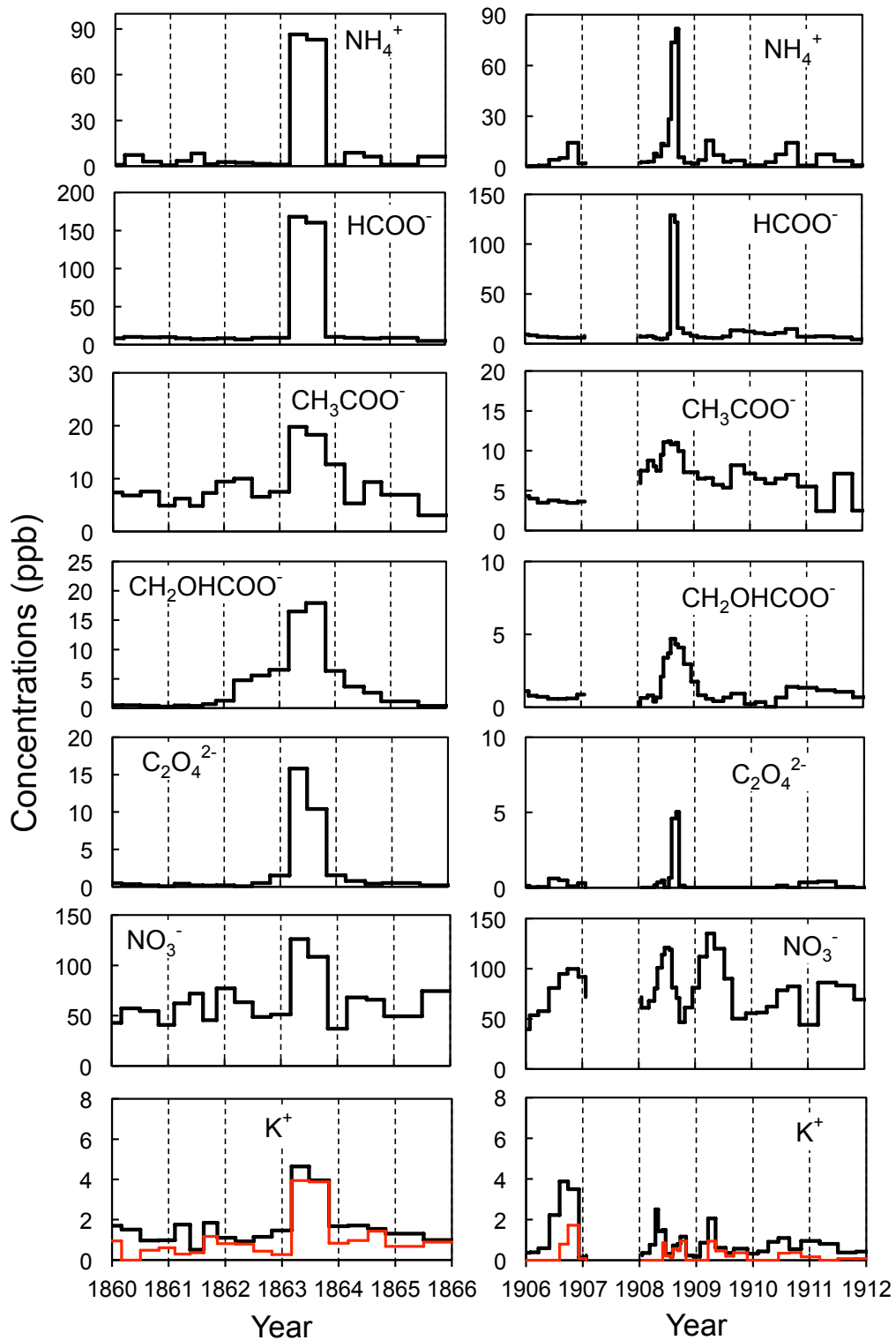
Figure 3: Chemical fingerprint of two ammonium events dated in the GRIP 93 firn core at 1863 AD (left) and 1908 AD (right). NH_4^+ is ammonium, $HCOO^-$ is formate, CH_3COO^- is acetate, CH_2OHCOO^- is glycolate, $C_2O_4^{2-}$ is oxalate, NO_3^- is nitrate, and K^+ is soluble potassium. For soluble potassium, the black and red curves refer to total and fine fraction, respectively (Sect. 3.2.3)
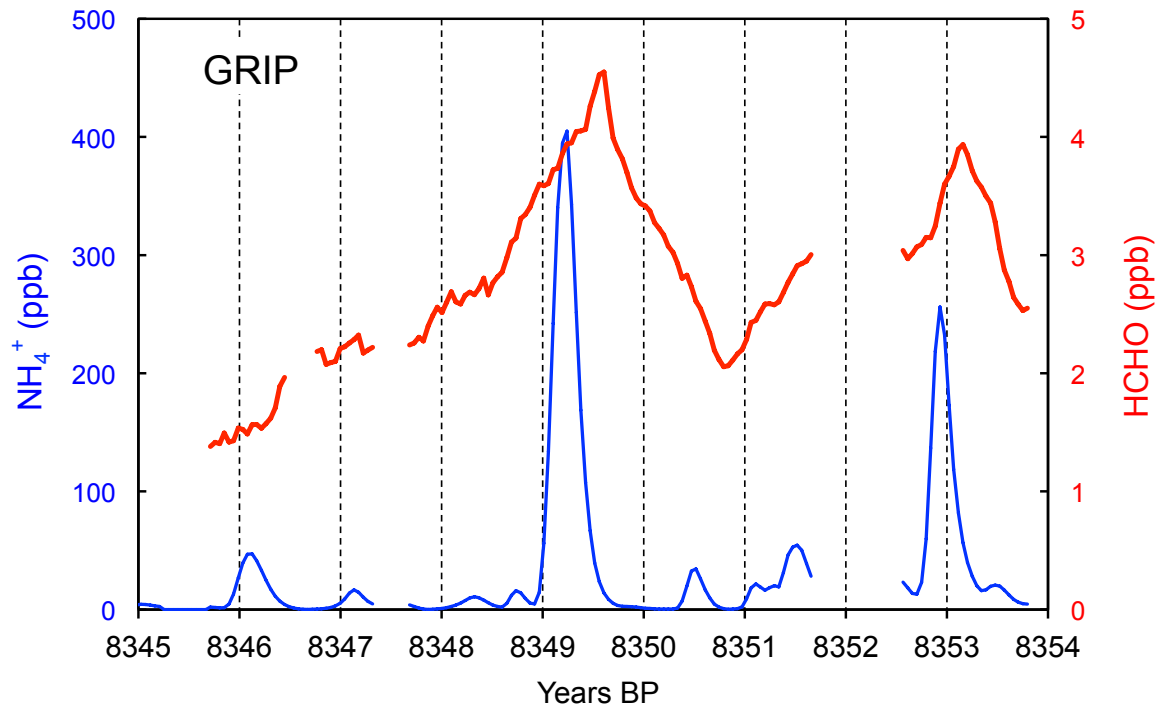
Figure 4: An example of formaldehyde (HCHO) perturbations detected at Summit (GRIP deep ice core) along two ammonium events.
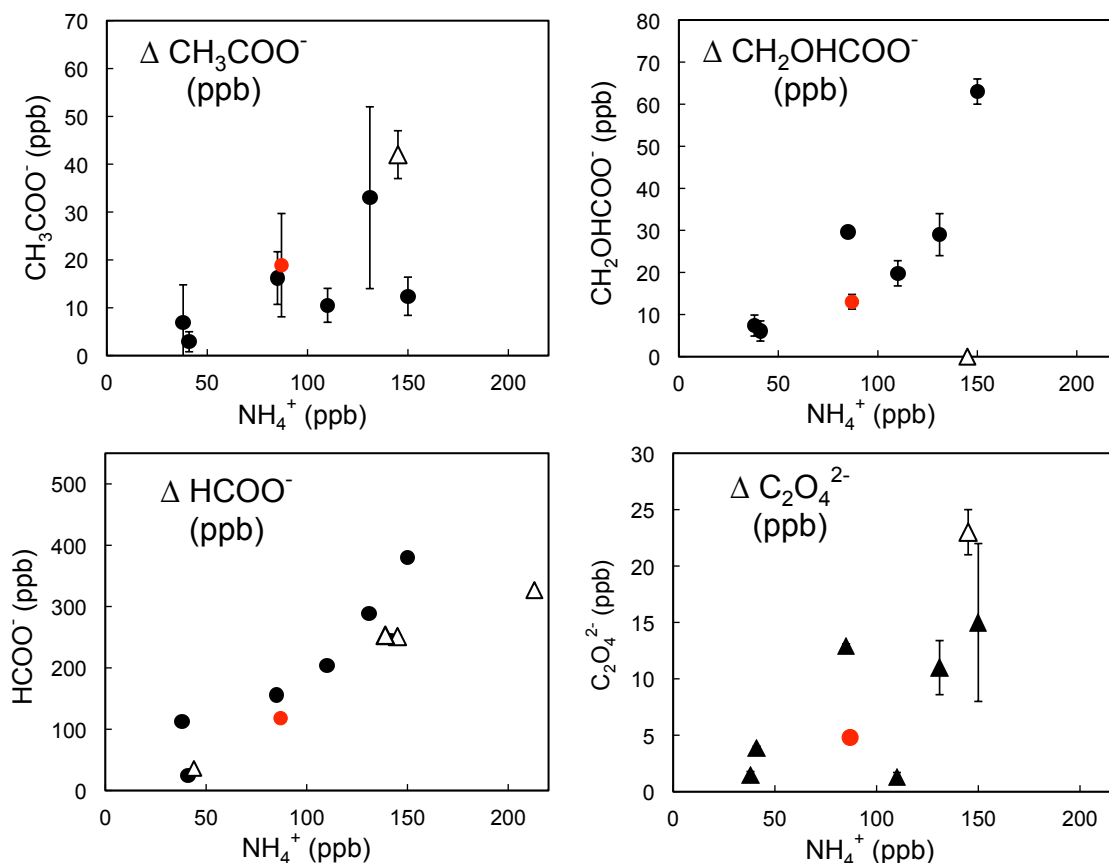
Figure 5: Enhancement of carboxylates above their background levels as a function of ammonium along several fire events detected in snow and ice layers deposited at Summit (GRIP 93 firn core and the deep GRIP ice core). HCOO⁻ is formate, CH₃COO⁻ is acetate, CH₂OHCOO⁻ is glycolate, and C₂O₄²⁻ is oxalate. The black circles refer to events that occurred during the Holocene (0 to 11,400 yrs BP); the red dots refer to the 1908 AD event shown in Fig. 3. Open triangles correspond to four ammonium events that occurred during the Younger Dryas (11,600 to 12,600 yrs BP). For acetate and glycolate, calculation of enhancements considered the smoothing of the perturbation around the ammonium perturbation. Vertical bars are uncertainties in calculating the enhancements above background values.
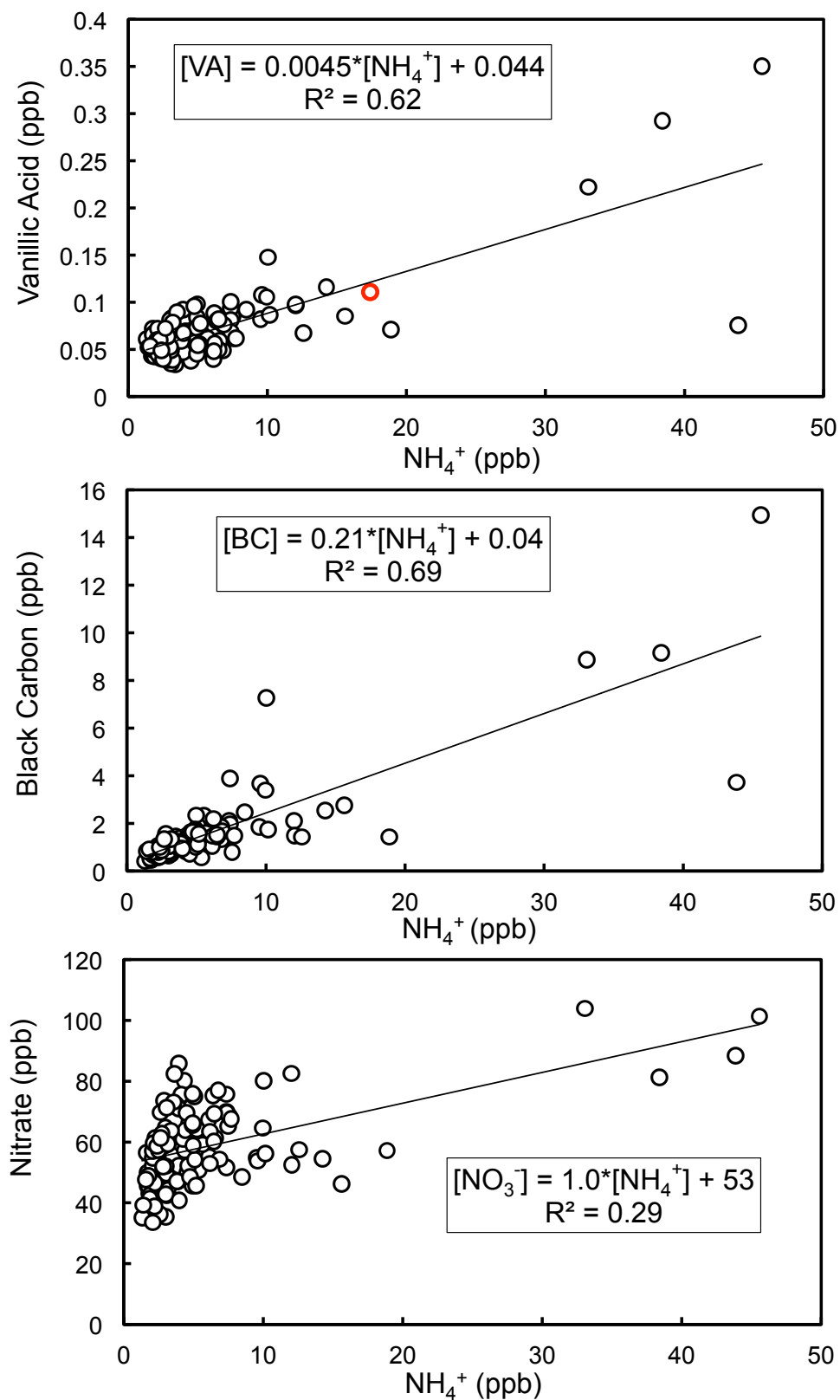
Figure 6: Annual mean concentrations of vanillic acid, BC, and nitrate versus ammonium in snow layers deposited at D4 during pre-industrial times (from 1740 to 1870). For vanillic acid, we also report the point corresponding to the 1908 event (red circle).
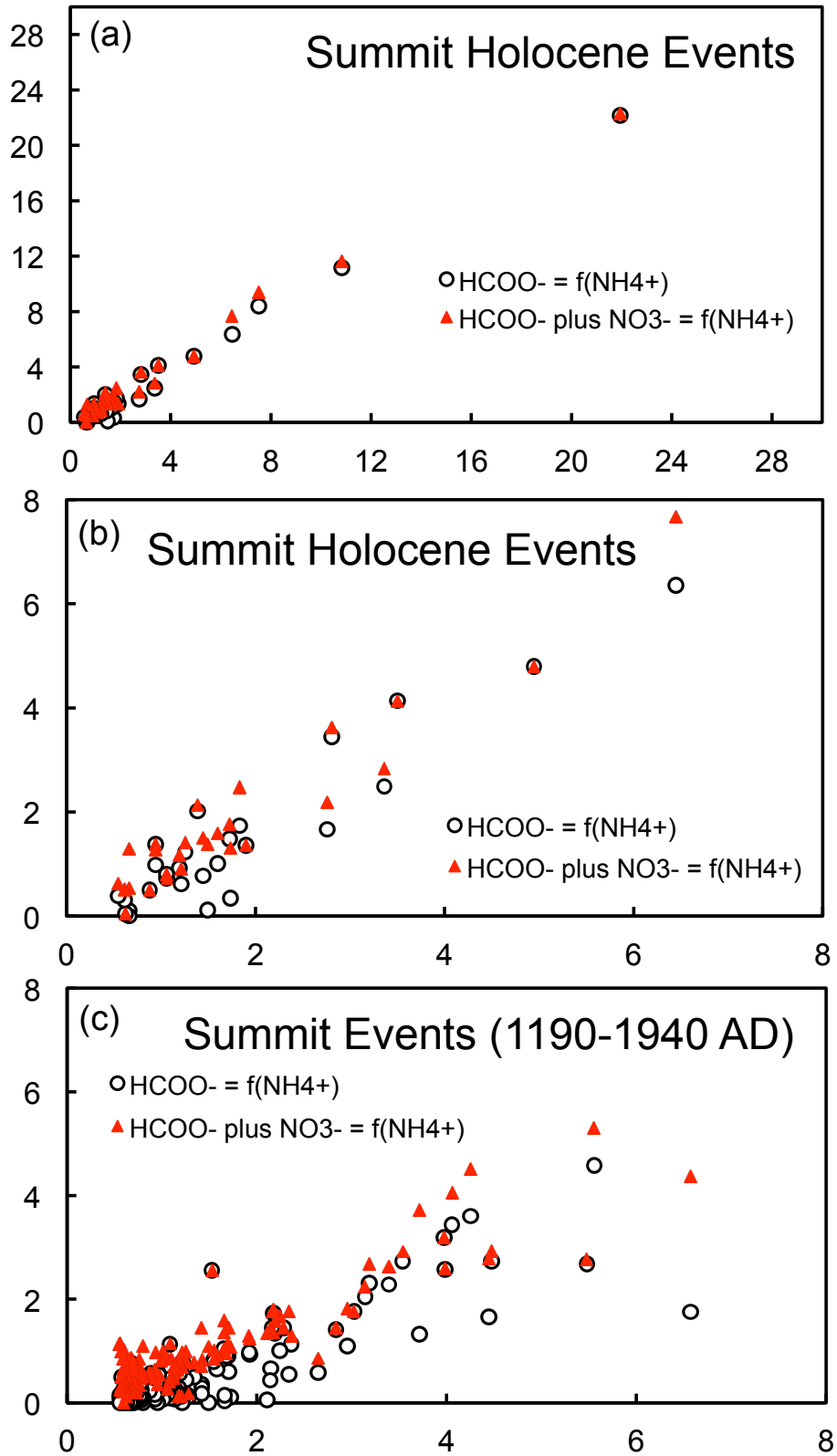
Figure 7: Ammonium versus formate (formate plus nitrate) along NH_4^+ events at Summit. All concentrations are expressed in $\mu Eq\ L^{-1}$.
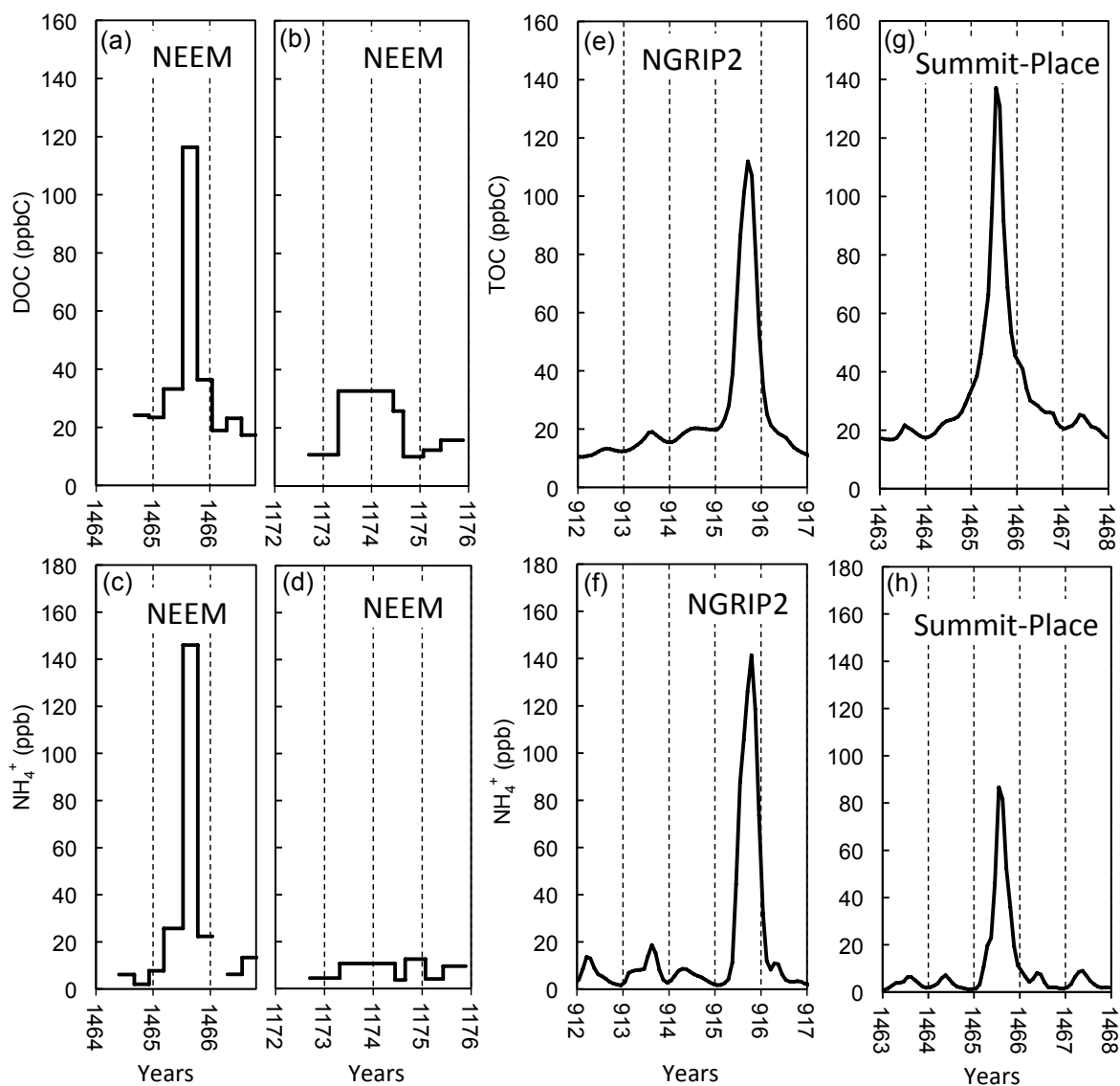
Figure 8: Example of OC changes along fire events in Greenland ice. (a) to (d) are from the NEEM-2011-S1 ice core for which OC was measured with a UV oxidation method (Sect. 2) and ammonium on discrete samples analysed with ion chromatography. (e) to (h) are from North GRIP2 and Summit-Place (collected in 2015) ice for which ammonium was measured with a CFA system and OC was investigated with a CFA coupled to a total organic carbon analyser (Sect. 2). The NEEM-2011-S1 and North GRIP2 cores were drilled with organic drilling fluid and the Summit-2015-Place core without.
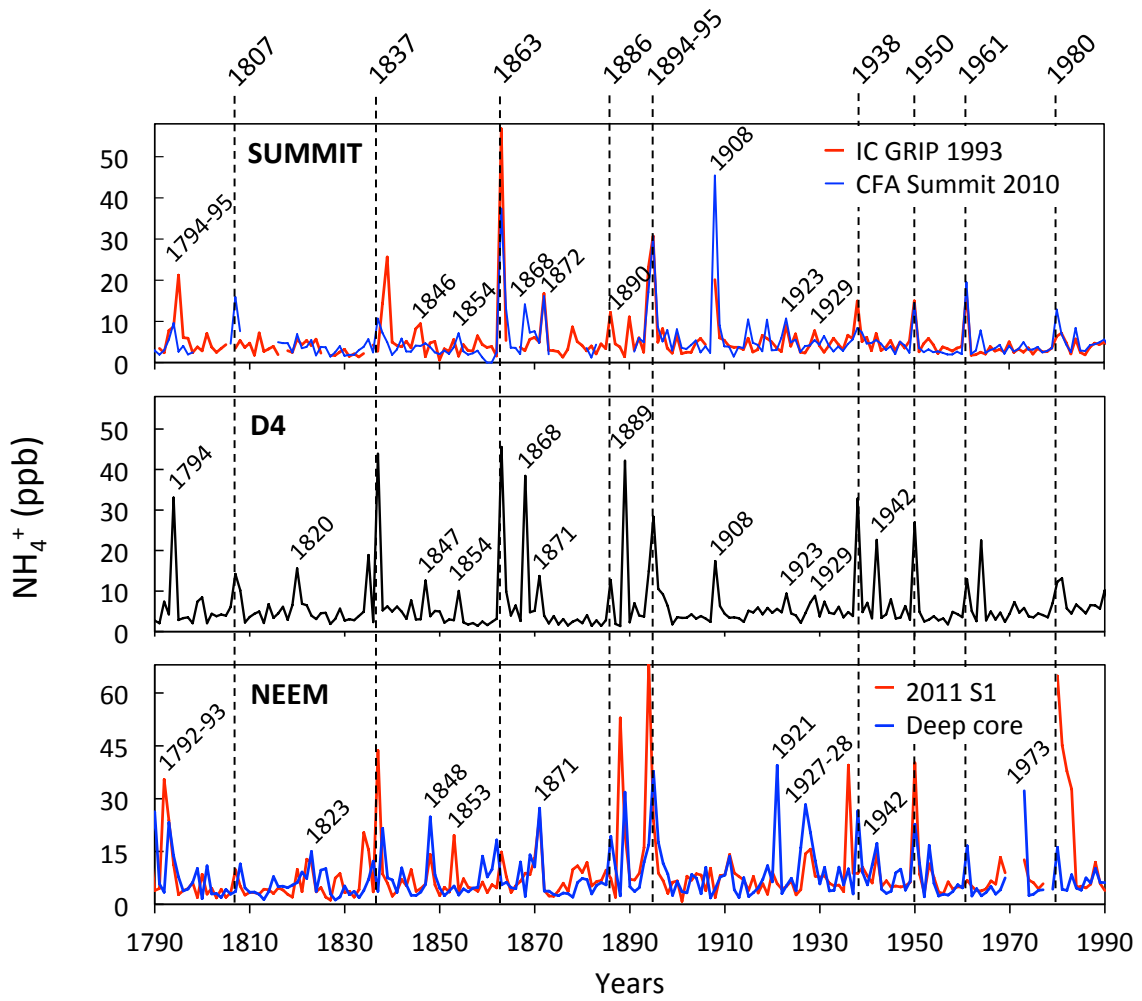
Figure 9: Comparison of several ammonium records obtained at Summit (IC for GRIP 1993, CFA for Summit 2010), D4 (CFA), and NEEM (CFA). All records are seasonally resolved, but data are presented here as annual means. Dashed lines denote the years for which a peak is identified at all sites. The IC GRIP 93 ammonium data are from Legrand and De Angelis (1996).
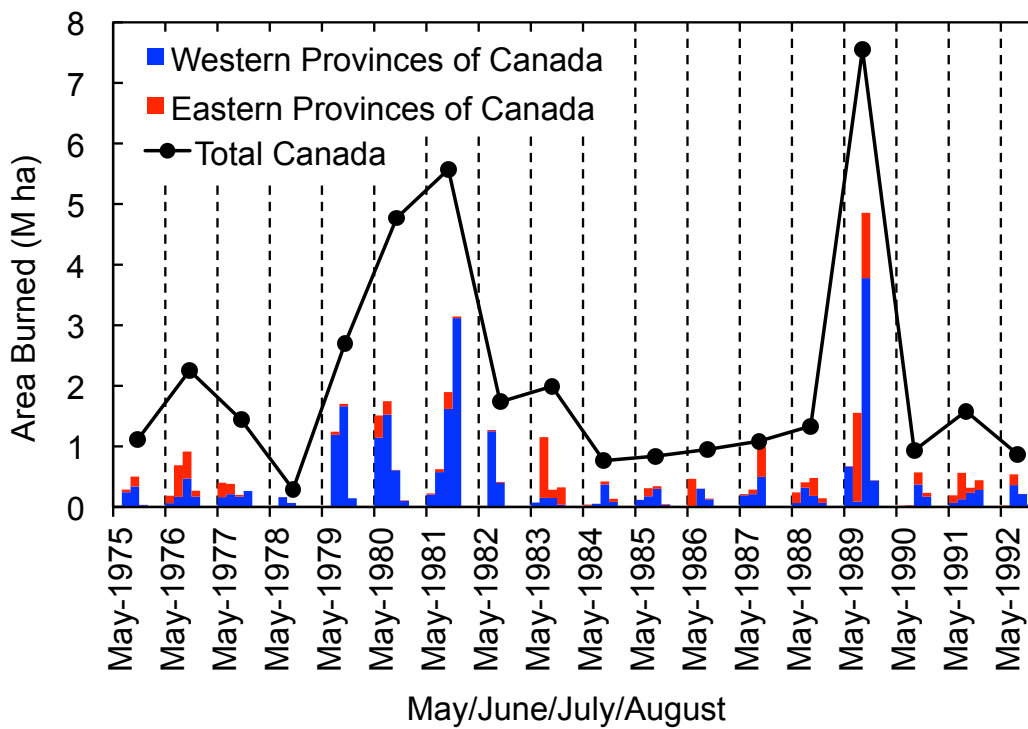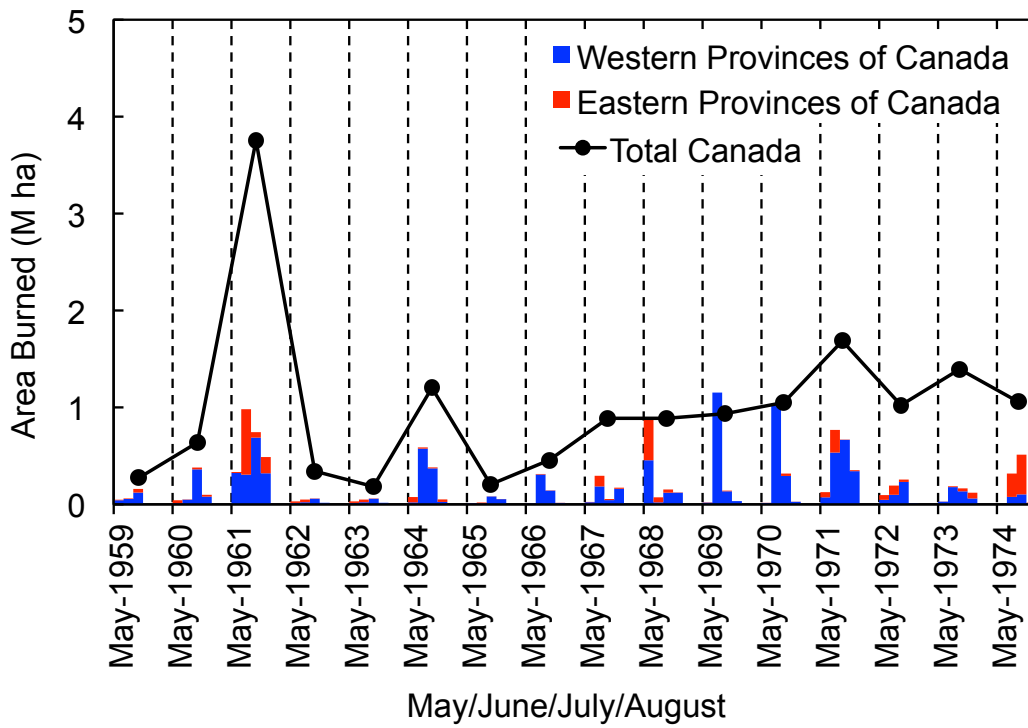
Figure 10: Area burned in Canada from 1959 to 1992 in summer (from May to August), distinguishing western (in red) and eastern (in blue) provinces (data from CNFD: Sect. 4.1.1). The black curves refer to total area burned in Canada (adapted from Van Wagner, 1988).

Summer 1978, Backward trajectories
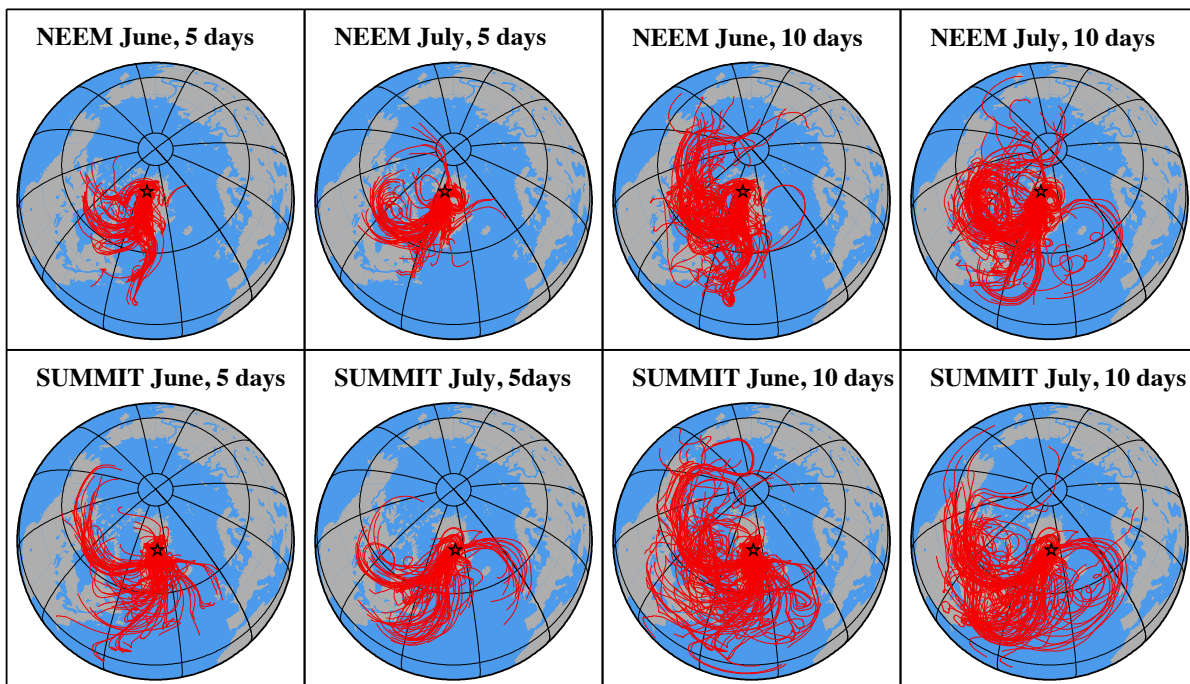
Figure 11: Five- and ten-day backward air mass trajectories arriving at the NEEM and Summit sites in June and July 1978 (site arrival at 500 m above ground level).
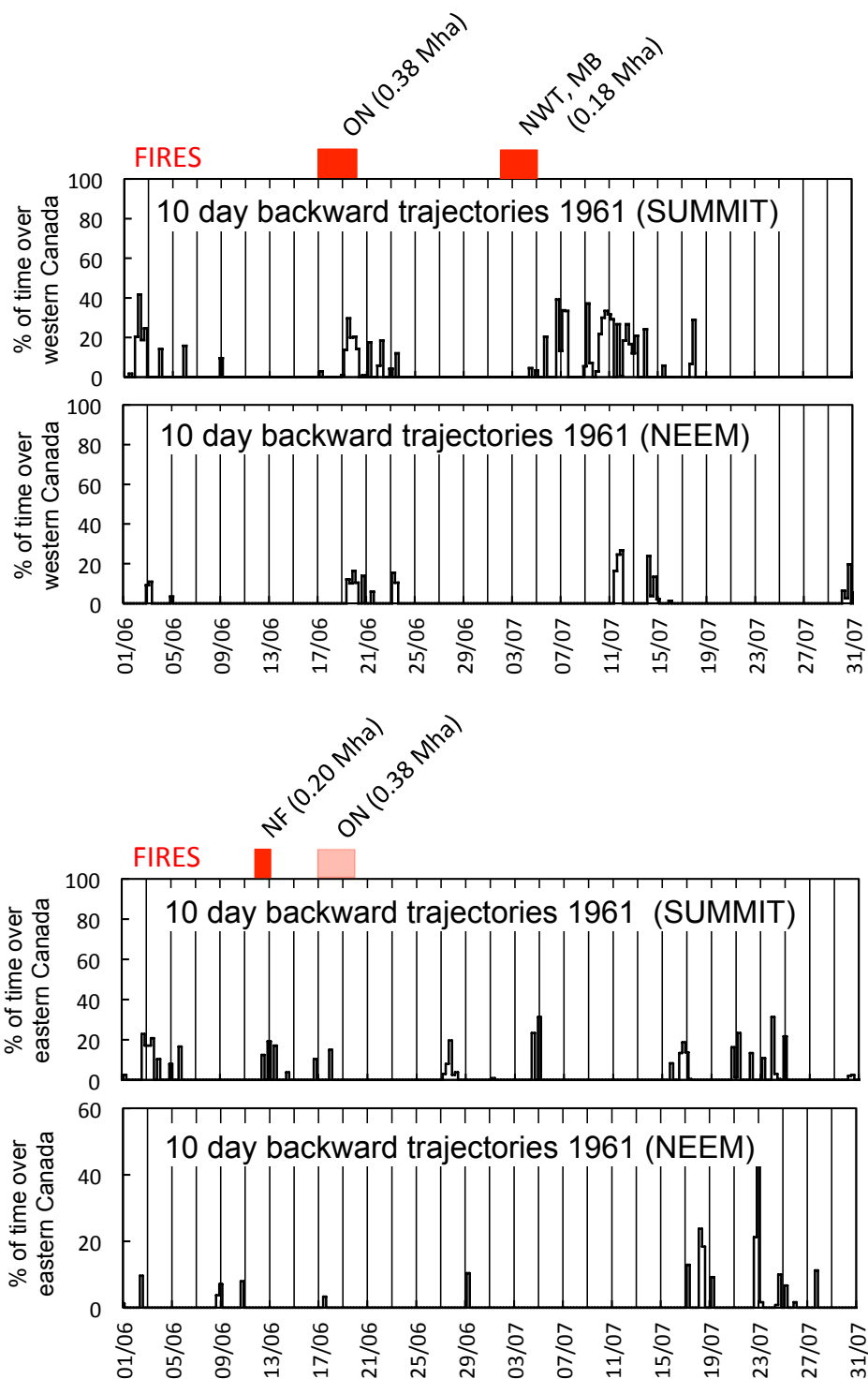
Figure 12: Fraction of time spent by air masses arriving at Summit and NEEM (ten-day backward trajectories) at 500 m agl and having traveled over a forested area of western (top) and eastern (bottom) provinces of Canada during the severe fire conditions of June/July 1961 (Fig. 10). Some of the largest fires are indicated on top of the panels (red symbols) with corresponding burned area: Ontario and Northwest Territories in the West, Newfoundland and Labrador in the East. The Ontario fire was located in the western portion of the province and we report the red symbol on both panels. Area burned data are from the Canadian National fire database (Sect. 4.1.1).
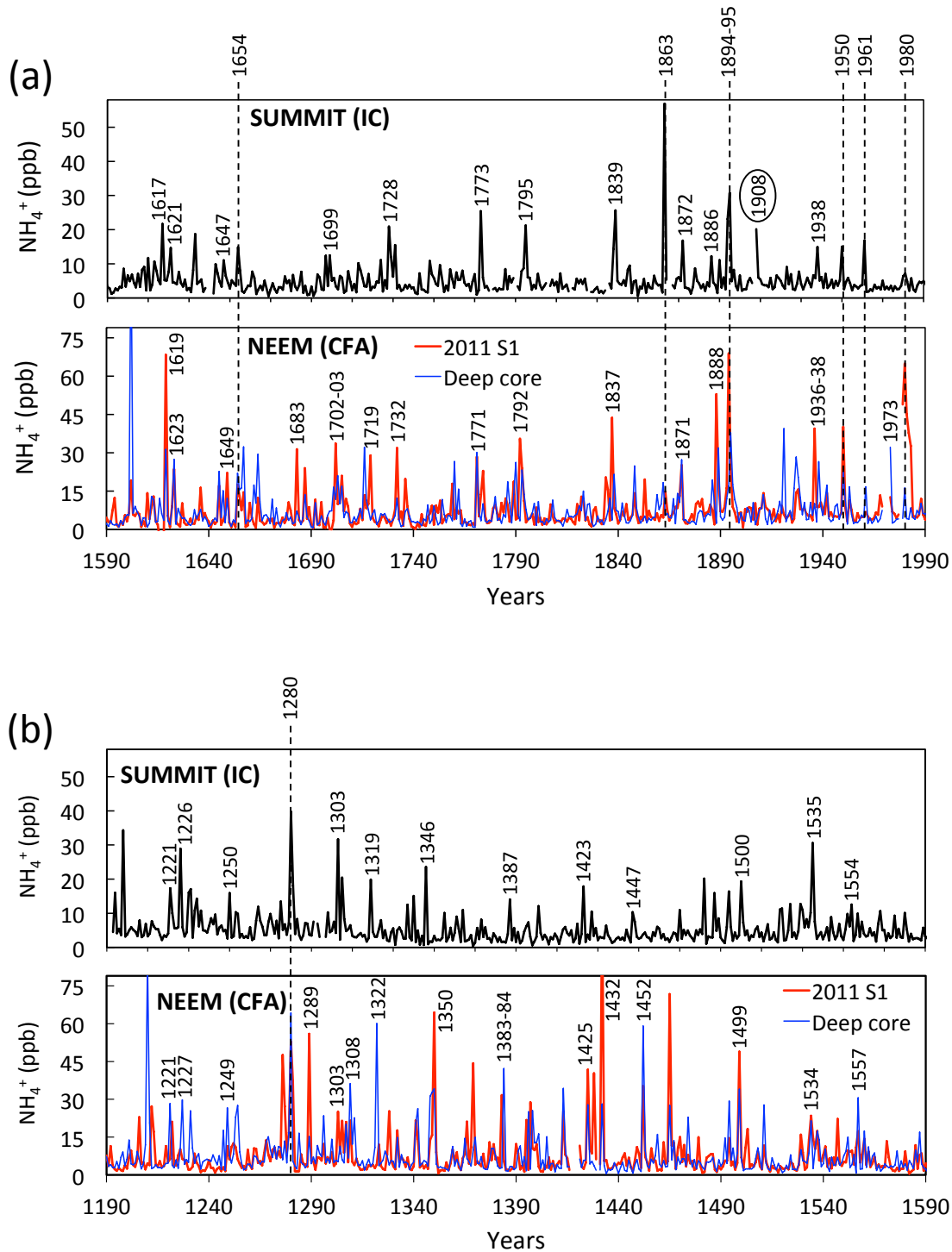
Figure 13: Comparison of ammonium records obtained at Summit and NEEM (NEEM-2011-S1 and the deep core) from 1590 to 1990 (a) and from 1190 to 1590 (b). All records are seasonally resolved, but data are presented here as annual means. Dashed lines denote the years for which a peak is identified in both cores. The Summit data are from Legrand and De Angelis (1996) and Savarino and Legrand (1998).
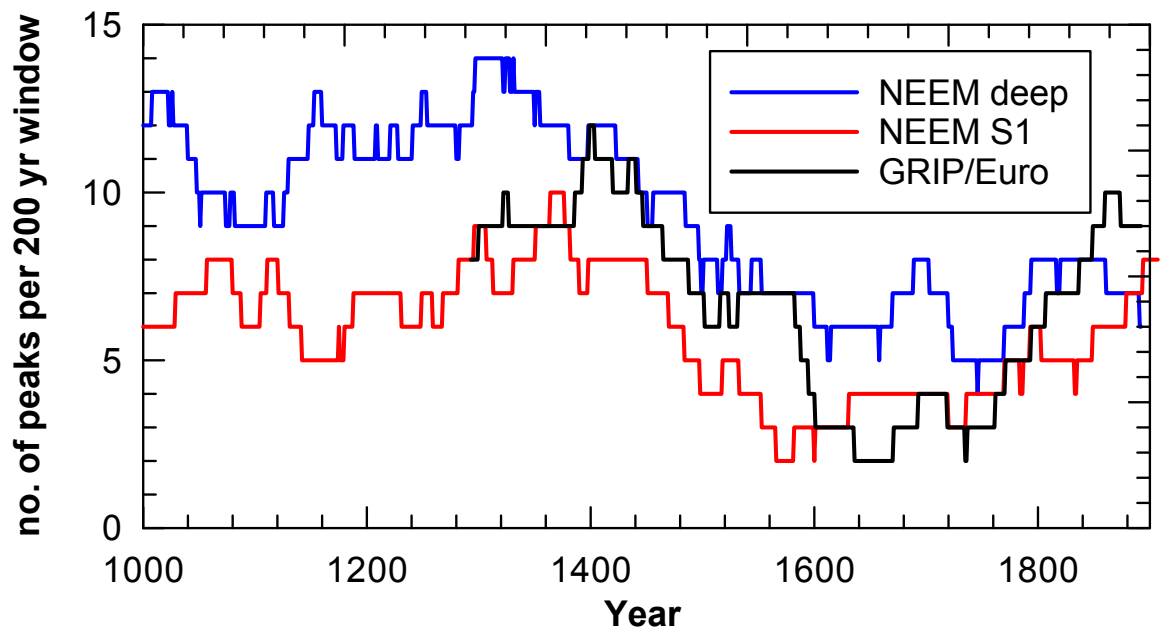
Figure 14: Fire peak frequency in a running 200-yr window for the Eurocore at Summit (black), the NEEM deep core (blue), and the NEEM 2011 S1 core (red). Peaks detected in adjacent years were only counted as one.
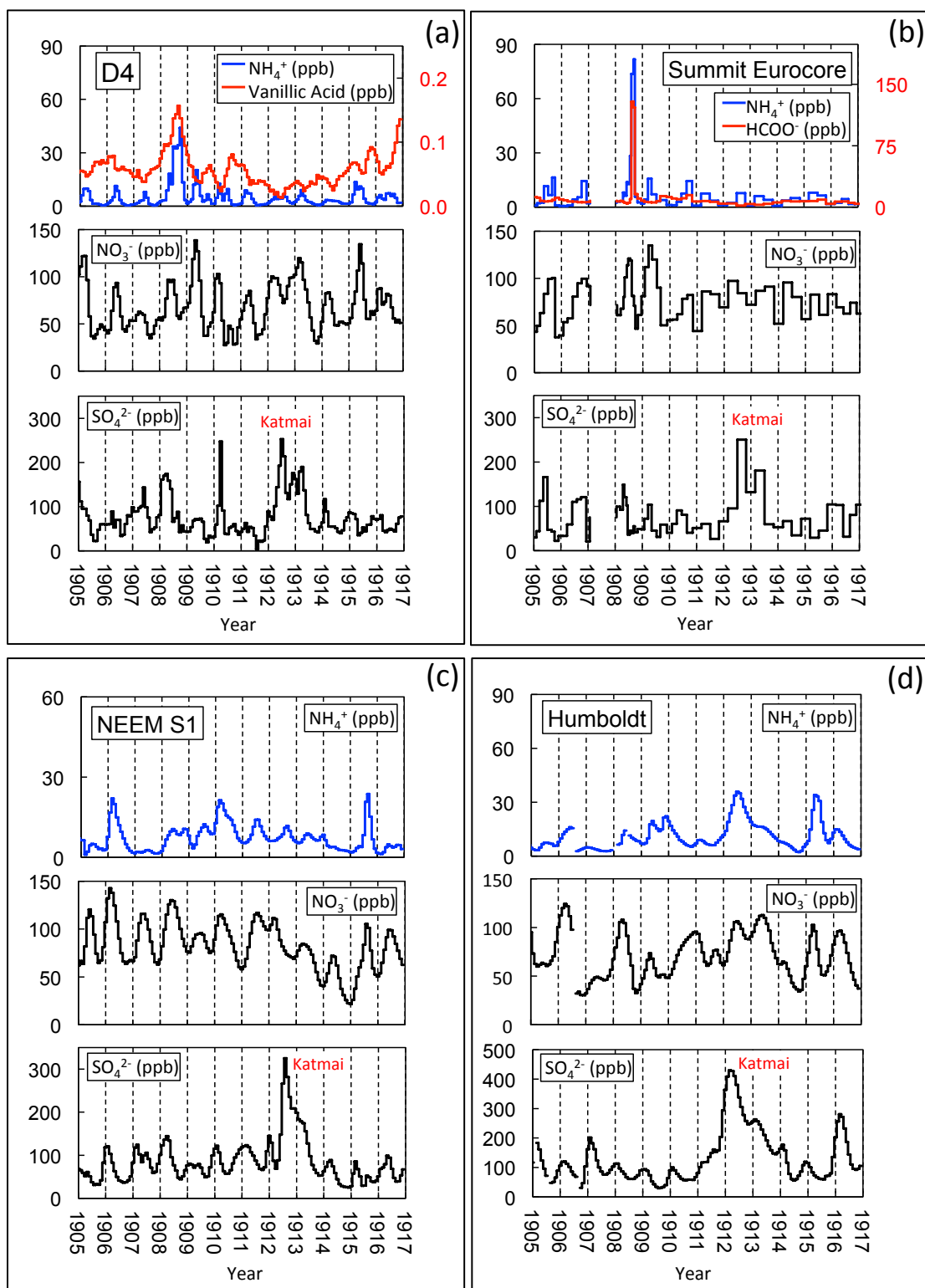
Figure A1: High-resolution 1905–1916 records of ammonium, nitrate, and sulfate at D4 (a), Summit (GRIP 93) (b), NEEM 2011 S1 (c), and Humbold (d). At Summit and D4, data on carboxylic acids also were available, formate at Summit (Legrand and De Angelis, 1998), and vanillic acid at D4 (McConnell et al., 2007). Note the presence of the Katmai volcanic layer (1912) in the sulfate records, permitting accuracy of the dating to be <1 yr during this sequence of years.