

Ice-core records of biomass burning

The Anthropocene Review

1–23

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DOI: 10.1177/2053019615605117

anr.sagepub.com



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Abstract

We review the approaches for estimating biomass burning from ice-cores and consider the challenges and assumptions in their application. In particular, we consider the potential of biomarker proxies for biomass burning, hitherto not widely applied to glacial ice archives. We also review the available records of biomass burning in ice-cores and consider how variations in fire regimes have been related to atmospheric and land-use changes. Finally, we suggest that future developments in ice-core science should aim to combine multiple biomarkers with other records (black carbon, charcoal) and models to discern the types of material being burnt (C_3 versus C_4 plants, angiosperms, gymnosperms, peat fires, etc.) and to improve constraints on source areas of biomass burning. An ultimate goal is to compare the biomass burning record from ice-cores with hindcasts from models to project how future climate change will influence biomass burning and, inversely, how fire will affect climate.

Keywords

ammonium, carboxylic acids, dehydroabiatic acid, $\delta^{13}C$ - CH_4 , $\delta^{18}O$ - CO , formate, levoglucosan, nitrate, vanillic acid

Introduction

Biomass burning is a major driver of vegetation changes and of ecosystem dynamics (Bond et al., 2005). Fire emissions affect atmospheric chemistry and composition (Cofer et al., 1997; Harrison et al., 2010), and are an important factor influencing the carbon cycle, radiative balance and the climate (Clark, 1997; Prentice et al., 2011; Saleh et al., 2014). Understanding past fire dynamics can provide insights into the role of fire in past atmospheric composition and climate changes (Ferretti et al., 2005; Wang et al., 2010) and, vice versa, the influence of past climate on fire regimes (Zennaro et al., 2014). Also, it is a key step towards better preservation and management of present biodiversity and ecosystem functions (Heyerdahl and Card, 2000; Swetnam et al., 1999).

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Studies of sedimentary charcoal have shown how past fire regimes depend not only on climatic and biological factors, such as climate and vegetation properties (Marlon et al., 2013; Power et al., 2008), but also reflect the cultural background of how people manage ecosystems and fire (Marlon et al., 2008; Pechony and Shindell, 2010). Over the last 150 years, the influence of human activities on global fire regime has become extremely significant and is thought to occur primarily through land-use change and suppression (Marlon et al., 2008), while satellite data suggest that the widely assumed dependence of fire frequency on ignition rates is incorrect (Bistinas et al., 2014). Disentangling natural and anthropogenic causes of fire depends crucially on the ability to demonstrate synchronicity, which in turn is dependent on having fire records based on reliable proxies of biomass burning with sufficient sampling resolution and robust chronologies.

Ice-cores contain a wealth of information about past environmental and climatic changes. They can reveal aspects of Earth System change through the deposition of trace chemicals trapped in the snow and trace gases trapped in air bubbles. Such tracers include many potential indicators of past fire activity (Conedera et al., 2009), that can be used to reconstruct variations in the past history of biomass burning. Combined with complementary methodologies based on, e.g., charcoal (Marlon et al., 2013) and/or counting tree rings between fire scars (Holz et al., 2012), ice-core studies of past biomass burning provide an additional, powerful tool to document changes in past fire regime and to identify the causes of these changes.

This article reviews the types of evidence that have been used to reconstruct past fire activity from ice-cores, and examines the advantages and limitations of each (section: ‘Types of chemical species used to reconstruct past biomass burning’); analyses the inferred changes, with special focus on the transition between the Pre-industrial and the Industrial period (section: ‘Ice-core records of changes in biomass burning’); explores methodological developments and what additional information can potentially be extracted from ice-core records of past biomass burning (section ‘Future developments’).

Types of chemical species used to reconstruct past biomass burning

Numerous chemical species from ice-cores have been used as indicators of past fire, ranging from atoms and simple molecules (e.g. potassium, ammonium and formate) to more complex chemical species (e.g. levoglucosan and vanillic acid). In this review, they are grouped in two categories (Table 1) and described in different sections: ‘Chemical species with multiple potential sources’ and ‘Chemical species specific to biomass burning’. The isotopic composition of trace gases (e.g. the stable carbon isotopic composition of atmospheric methane, $\delta^{13}\text{C}-\text{CH}_4$, and the oxygen isotope ratio of carbon monoxide, $\delta^{18}\text{O}-\text{CO}$), used to infer changes of global biomass burning, will be discussed in the section ‘Trace gases and their isotopic composition’. Figure 1 and Table 2 show the location of ice cores used to study past biomass burning.

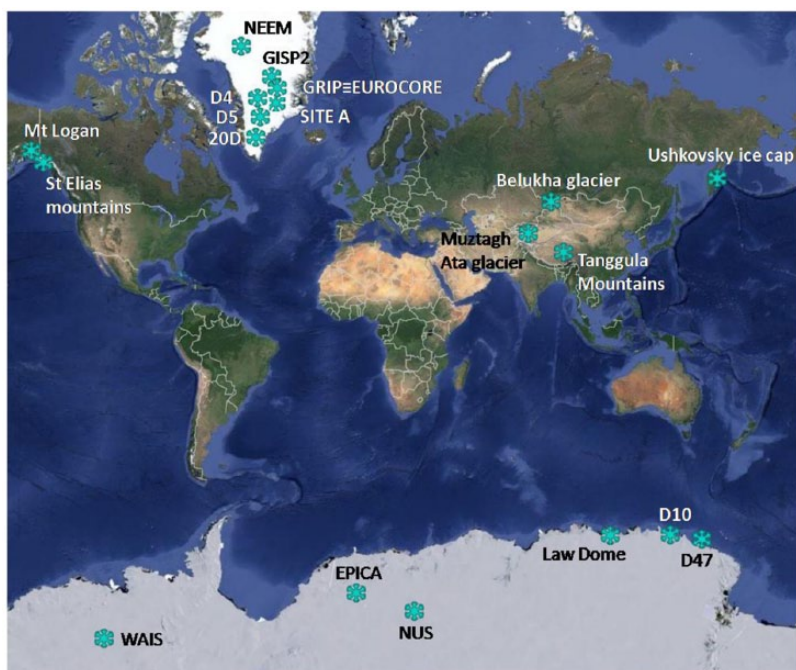
Chemical species with multiple potential sources

The detection of species such as light-molecular-weight carboxylic acids (formate: HCOO^- , acetate: CH_3COO^- , glycolate: CH_3O_3^- , oxalate: C_2O_4^-) and major ions (ammonium: NH_4^+ , nitrate: NO_3^- , potassium: K^+) in fire plumes (Andreae et al., 1988; Echalar et al., 1995; Lebel et al., 1991; Talbot et al., 1992) stimulated a number of studies linking their presence in polar and mid-latitude ice-cores to fire.

The first study to correlate biomass burning events with the concentration of ions measured by ion chromatography directly in the field at Summit (GRIP, central Greenland) was performed by

Table I. List of proxies used for past biomass burning reconstruction.

Species with multiple sources	Species specific to biomass burning	Isotopic composition of trace gases
ammonium (NH ₄ ⁺)	levoglucosan (C ₆ H ₁₀ O ₅)	δ ¹³ C-CH ₄
formate (HCOO ⁻)	dehydroabietic acid (C ₂₀ H ₂₈ O ₂)	δD-CH ₄
acetate (CH ₃ COO ⁻)	vanillin (C ₈ H ₈ O ₃)	δ ¹⁸ O-CO
glycolate (C ₂ H ₃ O ₃ ⁻)	syringic acid (C ₉ H ₁₀ O ₅)	δ ¹⁸ O-CO
oxalate (C ₂ O ₄ ²⁻)	vanillic acid (C ₈ H ₈ O ₄)	
formaldehyde (HCHO)	galactosan (C ₆ H ₁₂ O ₆)	
hydrogen peroxide (H ₂ O ₂)	mannosan (C ₆ H ₁₂ O ₆)	
potassium (K ⁺)		
nitrate (NO ₃ ⁻)		
nitrite (NO ₂ ⁻)		
Electrical conductivity measurements		
Black carbon		

**Figure I.** Geographical location of the ice-core sites used for past biomass burning reconstruction.

Legrand et al. (1992). The authors showed that large increases of ammonium concentrations (higher than 18 ng/g) in specific ice layers are associated with elevated levels of formate, acetate, oxalate and glycolate (Legrand et al., 1992: figure 2) with a NH₄⁺/HCOO⁻ molar ratio of 0.4. The spikes take place when minimum levels of Na⁺ are detected, suggesting that they occurred

Table 2. List of sites used for past biomass burning reconstruction, with coordinates of each site, reference that used the site and its source region. Most sites are located in the (high latitude) Northern Hemisphere, while there is not much coverage of the tropics or mid-latitudes.

Location	Coordinates	References	Source region
NEEM	77.49°N, 51.2°W	Zennaro et al. (2014), Sapart et al. (2012)	North America–Siberia
GISP	72.2°N, 37.80°W	Whitlow et al. (1994); Chýlek et al. (1995); Taylor et al. (1996)	North America
GRIP	72.34°N, 37.38°W	Legrand et al. (1992); Fuhrer et al. (1993); Legrand and De Angelis (1995); Fuhrer et al. (1996); Legrand and De Angelis (1996); Fuhrer and Legrand (1997); Savarino and Legrand (1998)	North America
D4	71.4°N, 44.0°W	McConnell et al. (2007)	North America
SITE A	71°N, 36°W	Laj et al. (1992)	North America
D5	68.5°N, 42.9°W	McConnell et al. (2007)	North America
20D	65.01°N, 44.87°W	Whitlow et al. (1994)	North America
Mt Logan	60.58°N, 140.58°W	Whitlow et al. (1994)	Siberia
St Elias Mountains	60.51°N, 139.47°W	Yalcin et al. (2006)	Alaska and Yukon
Ushkovky ice cap	56.04°N, 160.28°E	Kawamura et al. (2012)	Russia-Siberia
Belukha glacier	49.48.26°N, 86.34.43°E	Eichler et al. (2011)	Southern Siberian Altai region
Muztagh Ata glacier	38.17°N, 75.04°E	Yao et al. (2013)	Central Asia
Tanggula Mountains	33.6.6°N, 92.4.4°E	Yao et al. (2013)	North India
WAIS	79.27.7°S, 112.7.51°W	Mischler et al. (2009)	Gas – global
EPICA	75°S, 00.04°E	Fischer et al. (2008)	Gas – global
NUS	77.00°S, 26.03°E	Pasteris et al. (2014)	Southern Ocean
Law Dome	66.43°S, 113.12°E	Ferretti et al. (2005)	Gas – global
D10	66.40°S, 140.01°E	Legrand and De Angelis (1995)	Southern Ocean
D47	67.23°S, 154.03°E	Wang et al. (2010)	Gas – global
South Pole	90°S	Wang et al. (2010)	Gas – global

in summer (Na^+ is a proxy for sea salts which peak during winter because of the effect of severe winter storm systems that agitate the sea surface). Based on these considerations of the signal chemistry, intensity and chronology, the authors claimed that these chemical events are due to high-latitude biomass-burning inputs.

The observation that concentrations of ammonium are up to five times lower in Antarctica ice-cores compared with Greenland (Legrand and Delmas, 1988; Palais and Legrand, 1985; Silvente and Legrand, 1993) and that concentrations of carboxylic acids are also lower in Antarctica (Legrand and De Angelis, 1995) led to the conclusion that the ammonium and carboxylic acids deposited on the Greenland polar ice sheet are mainly of continental origin (given the closer proximity of Greenland to continents compared with Antarctica). Apart from sublimation of snow, post-depositional changes are thought to be negligible for background ammonium, since it is believed to be deposited irreversibly as NH_4HSO_4 and $(\text{NH}_4)_2\text{SO}_4$ as indicated by the well-preserved atmospheric

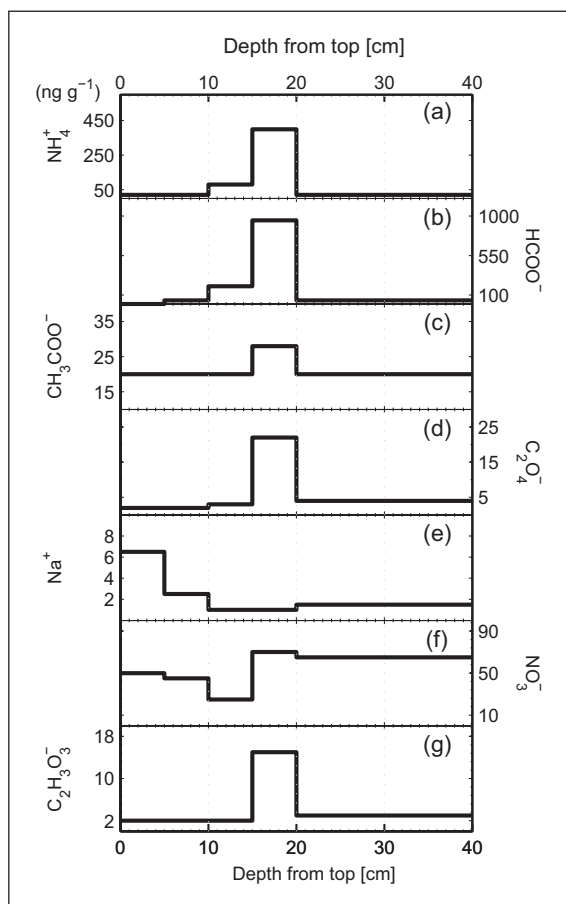


Figure 2. Chemical perturbations observed along a NH_4^+ event recorded in the Summit ice-core (GRIP) at 238 m depth corresponding to 930 years BP. (a) Ammonium; (b) formate; (c) acetate; (d) oxalate; (e) sodium; (f) nitrate; (g) glycolate.

Source: Modified from Legrand et al. (1992).

ratio of $\text{NH}_4^+/\text{SO}_4^{2-}$ in the snow (Silvente and Legrand, 1993). For carboxylic acids, ‘in cloud’ and post-depositional changes can be present (Legrand and De Angelis, 1995), but the intensity of these changes is not such to affect the biomass burning signal found in ice.

Other species have been attributed to biomass burning events in ice-cores because they co-occur with ammonium spikes. Enhanced formaldehyde (HCHO) and hydrogen peroxide (H_2O_2) content were observed in ammonium-rich snow layers from the GRIP ice-core (Fuhrer et al., 1993). In ice-cores from Greenland (20D and GISP2) and Yukon (Mt Logan), higher concentrations of K^+ and NO_3^- were measured in samples with high NH_4^+ concentration (Whitlow et al., 1994). Legrand and De Angelis (1995) suggested that a biomass-burning contribution, at around the 10 ng/g level, to the nitrate Greenland ice budget cannot be ruled out. Although nitrate is clearly enhanced in many biomass burning peaks in polar ice-cores (Whitlow et al., 1994), Legrand and De Angelis (1996) found that only some formate-rich layers along a 73 m Summit core showed a nitrate enrichment and that this was relatively small. Such a partitioning between nitrogen-derived species in favour

of ammonium relative to nitrate in biomass burning material reaching Greenland was interpreted as related to boreal forest fires being rich in NH_3 relative to NO , due to the dominance of smouldering fires (Lebel et al., 1991). A significant input of nitrite was identified in ammonium-rich layers during the Younger Dryas (11,550 to 12,700 years BP) suggesting that peroxyacetyl nitrate (PAN) present in the atmosphere was more effectively hydrolyzed by more alkaline cloud waters (Legrand and De Angelis, 1995).

Even though ammonium has often been considered the reference species for biomass burning, the presence of ammonium spikes alone is sometimes insufficient to identify biomass burning events. For example, ammonium values up to 40 ng/g were measured in Summit snow layers dating back to AD 1193 with no change of the formate level (Savarino and Legrand, 1998). Some authors have claimed that the likelihood that ammonium spikes originate from biomass burning increases when a concurrent decrease of Electrical Conductivity Measurements (ECM) is measured. Chýlek et al. (1995) found good correlation between peaks of black carbon, peaks of NH_4^+ and dips in ECM measured in GISP2 during the period AD 320–330. In the Holocene portion of the GISP2 core (Greenland), abrupt, short-duration reductions in the ECM were found to be closely associated with the alkaline ice caused by increased levels of ammonium that were attributed to biomass burning (Taylor et al., 1996). Extending the study of carboxyl acids in the GRIP ice-core to a full glacial–interglacial cycle, Legrand and De Angelis (1996) claimed that the main chemical feature of Greenland ice layers with biomass burning signals is the presence of oxalate in addition to ammonium and formate. They based their conclusions on the observation that the $\text{NH}_4^+/\text{HCOO}^-$ molar ratio of NH_4^+ spikes is close to 0.4 in the Summit ice-core. They excluded acetate, nitrate and non-sea-salt potassium as straightforward indicators of aged biomass burning plumes in Greenland ice.

It is not easy to make a clear distinction between the background NH_4^+ level (that may be partly due to biomass burning) and the spikes (mainly biomass burning). Recent studies have applied more sophisticated statistical techniques to distinguish between NH_4^+ spikes that originate from fire from those that do not have a biomass burning source. In an ice-core from the Eclipse Icefield in Yukon (Canada), forest fire signals were identified as NH_4^+ residuals above a robust spline and corroborated by an empirical orthogonal function analysis that found a chemical association in the NH_4^+ , $\text{C}_2\text{O}_4^{2-}$ and K^+ records similar to that observed in forest fire plumes (Yalcin et al., 2006). Principal component analysis of chemical species and charcoal concentration identified K^+ and NO_3^- as the most reliable indicators of biomass burning in an ice-core from the Belukha glacier in the Siberian Altai mountains (Eichler et al., 2011). However, the strong relationship of NH_4^+ and HCOO^- with air temperature suggests that the two species are released to the atmosphere also by direct biogenic emissions rather than biomass burning only (Eichler et al., 2009).

Continuous flow (CF) techniques are now available to derive high resolution records of multiple chemical species. High resolution-CF measurements of Black Carbon (BC), in association with vanillic acid and non-sea-salt sulphur (used as indicators of forest fires and industrial pollution), indicate that the sources and concentrations of BC in Greenland precipitation have varied greatly since 1788 (McConnell et al., 2007). Measurements of acidity in seven ice-cores across the Dronning Maud Land region from the East Antarctic Plateau (NUS) have shown reduced acidity between AD 1500 and 1900 (coincident with the ‘Little Ice Age’, LIA), linked to declines in ExCl^- (excess chloride) and HNO_3 (Pasteris et al., 2014). The nitrate decline was found to correlate well with published methane isotope ($\delta^{13}\text{C}_4$) data from Antarctica (Mischler et al., 2009: section 2.3), suggesting that it could be caused by a decrease in biomass burning. However, given the difference of atmospheric lifetime of CH_4 (several years) and NO_3^- (a few days), the cause of the correlation is unclear. Nonetheless, this example suggests that the coupling of high resolution-CF measurements of multiple species with gas

analysis of air trapped in ice-cores can provide a very powerful technique to study past biomass burning and its influence on the atmosphere.

The main limitation of chemical species with multiple potential sources as records of biomass burning is that they can also be derived from other sources. Atmospheric ammonium and ammonia, for example, are produced by lightning and soil processes (Legrand et al., 1998; Olivier et al., 2006) or agricultural activity (Hristov et al., 2011), atmospheric oxalate is formed through vehicle emissions (Kawamura and Kaplan, 1987), potassium is a product of biological activity (Rankin and Wolff, 2000), water-soluble potassium is transported with sea salts, while elemental potassium is transported with mineral aerosols (Laj et al., 1997). Assuming an ammonium to formate molar ratio of 0.4 in spikes corresponding to biomass burning event, Legrand and De Angelis (1996) claimed that high-latitude biomass burning contributed between 20% and 30% to the formate, oxalate, glycolate and ammonium inventories of central Greenland over the last 200 years, whereas Fuhrer et al. (1996) estimated that forest fires contributed between 10% and 40% of the total NH_4^+ deposited on the Greenland Ice Sheet during the Holocene. Therefore, chemical species with multiple potential sources can provide useful insights into past biomass burning, but, because of their inherent ambiguity, the interpretation of these records is difficult and needs to be supported by independent lines of evidence.

Chemical species specific to biomass burning

The observation that complex organic tracers, such as levoglucosan (1,6-anhydro- β -D-glucopyranose) and other compounds (e.g. amyrones, friedelin, dehydroabietic acid, and thermal derivatives from terpenoids and from lignin-syringaldehyde, vanillin, syringic acid, vanillic acid, etc.) are found in aerosols and are specific to types of biomass fuel has identified a new source of information about biomass burning (Simoneit et al., 1999). Levoglucosan is the most widely used biomarker because it is emitted in large quantities during biomass burning events, it is a molecular marker of cellulose burning at temperatures $>300^\circ\text{C}$ (Simoneit, 2002), and is stable in the atmosphere for at least 10 days (Fraser and Lakshmanan, 2000). Hence, this compound is long-range transported to remote regions, and is ubiquitous in the atmosphere from the Arctic to Antarctic (Fu et al., 2009; Hu et al., 2013). However, levoglucosan is known to degrade in the atmosphere with exposure to high concentrations of hydroxyl radicals (Hennigan et al., 2010; Hoffmann et al., 2010; Holmes and Petrucci, 2006, 2007; Mochida et al., 2010).

Gambaro et al. (2008) used high-performance liquid chromatography/Electrospray Ionization with triple quadrupole tandem mass spectrometric detection to be able to measure concentrations of levoglucosan down to 3 pg/ml in the EPICA Dome C (Antarctica) ice-core. Kehrwald et al. (2012) applied the technique developed by Gambaro et al. (2008) to a snow pit study in the region of Summit (Greenland) revealing that the levoglucosan profile replicates oxalate concentrations from a known forest fire event over Canada in August 1994.

Continental ice-cores show much higher levoglucosan concentrations than polar ice-cores. The average levoglucosan concentration of 39 ng/ml in the Tanggula ice-core (Yao et al., 2013) is 100 times higher than concentrations in samples from far east Russia (Kawamura et al., 2012), and 1000 times higher than concentrations in Greenland (Kehrwald et al., 2012).

The relative proportions of levoglucosan and other biomarkers have been used to identify sources of biomass burning, based on their different abundance in different types of biomass fuels. For example, the isomers of levoglucosan, galactosan and mannosan, are also emitted to the atmosphere by the combustion of hemicellulose (Simoneit, 2002). Although the combustion

of lignite that contains fossilized cellulose emits levoglucosan significantly, its isomers are not emitted or emitted at relatively low concentrations (Kuo et al., 2008). A levoglucosan/mannosan ratio ranging from 3.3 to 5.0 was obtained for the ice sections where high levels of levoglucosan were detected (Kawamura et al., 2012) in an ice-core from the Ushkovsky volcano (Kamchatka Peninsula, Russian Federation). This ratio is much lower than those (30–90) reported for lignite burning at 200°C (Kuo et al., 2008), and is typical of gymnosperm (conifer) burning. However, dehydroabietic acid (a gymnosperm biomarker) did not consistently show coeval peaks with levoglucosan. Kawamura et al. (2012) suggest that the apparent discrepancy between these two biomass burning tracers could be explained by dehydroabietic acid being derived from boreal forest fires in Siberia, with levoglucosan being transported from other regions further south including the mid-latitudes in East Asia where broadleaf trees are common. Alternatively, dehydroabietic acid may have been in part decomposed during long-range atmospheric transport because the aromatic structure of the compound has a higher sensitivity to photodegradation than levoglucosan, making it unstable compared with levoglucosan (Shakya et al., 2011; Simoneit, 2002; Simoneit and Elias, 2001). In the same ice-core, concentrations of vanillic acid and of p-hydroxybenzoic acid were consistent with those of levoglucosan (Kawamura et al., 2012). A lack of covariance between resin (dehydroabietic acid) and lignin/cellulose burning tracers (vanillic acid, levoglucosan) may imply that conifer tree barks and needles are more readily burnt than woody parts during biomass burning events, as observed in Siberia by Eichler et al. (2011).

In contrast to the importance of changing transport pathways identified by Kawamura et al. (2012), a recent study of variations in biomass burning over the past 2000 years using the NEEM (North Greenland Eemian) ice-core claimed that the observed levoglucosan variability is not dominated by changes in transport or in wind strength (Zennaro et al., 2014). The authors based their conclusion on the fact that no relationship was found between levoglucosan concentrations and dust and Ca²⁺ concentrations (used as tracers of crustal particulate). However, the source areas for dust and biomass burning are different so the lack of correlation does not rule out that transport changes dominate the changes in levoglucosan. In the same study, levoglucosan concentrations were found to correlate only slightly with ammonium (Zennaro et al., 2014; Figure 3), showing that using only ammonium to reconstruct biomass burning could potentially overestimate major fire events. The authors propose that matching levoglucosan concentrations above a threshold of ≥ 245 pg/ml with peaks in charcoal (from the Global Charcoal Database (GCD), Power et al., 2008) allows the identification of temporal trends that are not overly affected by the high peaks of anomalous fire events, providing a more confident identification of broad-scale patterns in paleofire activity.

Biomass-burning-specific tracers, such as levoglucosan, offer more reliable reconstructions of biomass burning events than chemical species with multiple potential sources. However, a common challenge to both specific and ambiguous chemical tracers is the difficulty of separating the influence of changing source location from that of variations in fire plume type on the glaciochemical properties measured in an ice-core.

Modelling of atmospheric transport

An advantage of ice-core records is that they typically represent a more integrated regional signal than lake or speleothem records. Some disadvantages of ice-core records are related to the distance between the source of biomass burning proxies and the ice sheet/mountain glacier. To observe a biomass burning spike, it is necessary both for there to be a fire and for there to be transport from the fire region to the ice-core site. This means that only some plumes can be recorded and that any

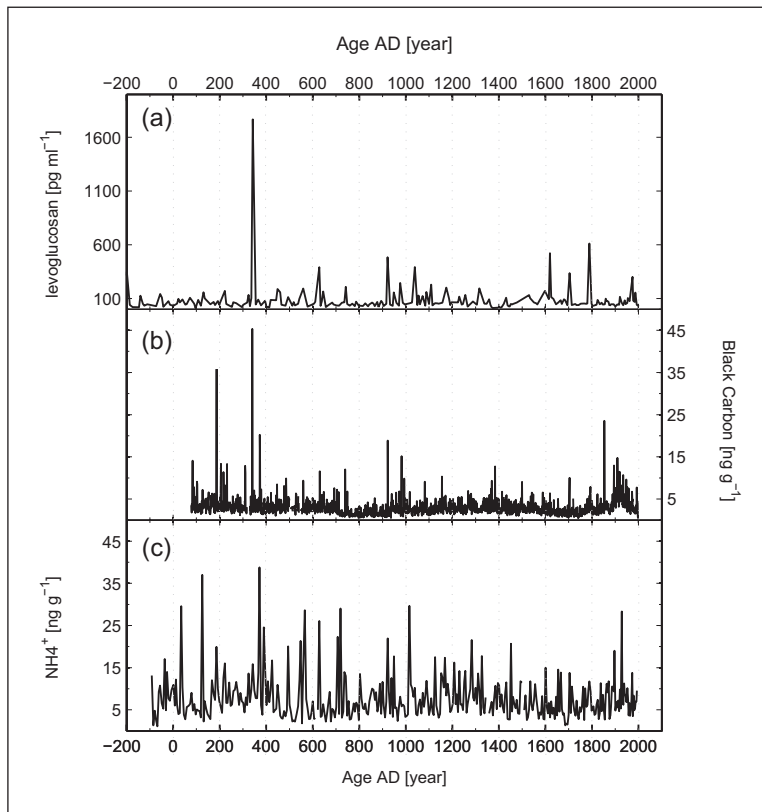


Figure 3. (a) Levoglucosan concentration profile measured in the deep NEEM core; (b) black carbon concentration profile measured in the NEEM-2011-SI ice-core; (c) ammonium concentration profile in the deep NEEM ice-core.

Source: Modified from Zennaro et al. (2014).

change in net transport will change the record fire frequency in the absence of changes at source. Since biomass-burning plumes are chemically heterogeneous and depositional processes and post-depositional alteration can produce considerable spatial variability in glaciochemical signals, there is not, nor should one expect, a one-to-one relationship between forest fires in the source region and detectable forest fire signals in ice-core. The amount of material reaching a site depends on, inter alia: (a) source strength; (b) transport distances; (c) atmospheric lifetime; (d) meteorological conditions (e.g. wet versus dry deposition); and (e) snow/ice accumulation rates within ice-core archives (affecting the dilution of the primary biomass burning record). All these are likely to change over climatically important boundaries (such as Glacial–Holocene) and must be considered when comparing fire frequencies on longer timescales. There are atmospheric transport models developed to allow back-trajectories reconstruction, e.g. NOAA ARL’s online HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory, <http://www.ready.noaa.gov/ready/open/hysplit4.html>) tool (Draxler and Rolph, 2015; Rolph, 2015). These modelling tools are useful to reconstruct the most likely transport path over recent days. The information derived is extended over previous, longer timescales (Pre-industrial or Holocene), assuming that the main atmospheric circulation mode has not changed significantly during those periods. This

consideration outline how critical the atmospheric modelling issue is in interpreting ice-core data of past biomass burning. Just recently, Fischer et al. (2015) have derived an estimate of the NH_4^+ concentration in the source region, by making first-order assumptions about past changes in lifetime/washout of NH_4^+ aerosols along its transport path. They have corrected the effect of local deposition using recent NH_4^+ observations in Greenland snow and atmospheric aerosol. Their analysis suffers from the considerable uncertainties associated with their simple approach. However, it results in the first attempt to deconvolve the NH_4^+ signal of changes in emissions, transport and aerosol deposition.

Trace gases and their isotopic composition

Records of trace gases provide a tool to study the influence of biomass burning on the past atmosphere. These records are smoothed because of the diffusion process occurring in firn (Buizert et al., 2012), and can be representative of regional- or global-scale signals, depending on the atmospheric lifetime of the analysed gas.

Changes of biomass burning at the global scale are reflected by variations of isotopic ratio of methane (CH_4) in the atmosphere. Methane has multiple sources with different Carbon isotopic composition ($\delta^{13}\text{C}-\text{CH}_4$). Natural sources of CH_4 include wetlands, wildfires, termites and ocean sediments, while rice paddies, ruminants, landfills, natural gas extraction and biomass burning are the major anthropogenic sources (Reeburgh, 2004). The sources of atmospheric methane can be roughly separated into three categories based on their $\delta^{13}\text{C}-\text{CH}_4$: biogenic (e.g. wetlands, $\delta^{13}\text{C}-\text{CH}_4$ near -60‰), fossil ($\delta^{13}\text{C}-\text{CH}_4$ near -40‰) and pyrogenic or biomass burning ($\delta^{13}\text{C}-\text{CH}_4$ near -25‰ for C3 vegetation or -12‰ for C4 vegetation). Changes in atmospheric $\delta^{13}\text{C}-\text{CH}_4$ allow the contributions from each of these source types to be deduced by applying an isotopic mass balance (Craig et al., 1988). However, the interpretation of gaseous and isotopic signals requires some type of box model to be applied, and is based on broad assumptions about the isotopic composition of sources of atmospheric gases and about isotopic fractionations of sinks.

Using an atmospheric box model (Lassey et al., 2000) to quantify the source evolution over the last 1000 years, Ferretti et al. (2005) attributed a drop of $\delta^{13}\text{C}-\text{CH}_4$ during the LIA in Law Dome (East Antarctica) to a decrease of pyrogenic sources of CH_4 . An alternative interpretation of the Ferretti et al. (2005) $\delta^{13}\text{C}-\text{CH}_4$ record ascribes the drop in $\delta^{13}\text{C}-\text{CH}_4$ to the effects of an increase in the agricultural source (rice farming and animal husbandry) scaled to world population, in tandem with reduced plant growth and wetland emissions caused by the cooling of the LIA (Houweling et al., 2008). The decline of $\delta^{13}\text{C}-\text{CH}_4$ during the LIA has been confirmed in Greenland ice-cores from NEEM and EUROCORE (Sapart et al., 2012). Using a two-box model, the authors claimed that centennial-scale variations in isotope ratios can be attributed to changes in pyrogenic and biogenic sources. Despite the differences in sources and their geographical distribution, the NEEM $\delta^{13}\text{C}-\text{CH}_4$ isotopic record contains similar features to the levoglucosan data (Zennaro et al., 2014), suggesting that high-latitude Northern Hemisphere biomass burning had a significant influence on the atmosphere at the global scale over the last 2000 years. Mischler et al. (2009) added an additional constraint to measurements of $\delta^{13}\text{C}-\text{CH}_4$ by measuring also the isotopic composition of hydrogen in CH_4 ($\delta\text{D}-\text{CH}_4$) in an ice-core from WAIS (West Antarctic Ice Sheet, Antarctica). Using a simple box model, they found that an increasing agricultural source and a decreasing biomass-burning source, with most of the change between the 1500s and the 1600s, best fit their data. With a sensitivity analysis, they demonstrated that their results were relatively insensitive to changes in source isotopic compositions or sink isotopic fractionation.

Records of carbon monoxide (CO) can indicate changes of past biomass burning. Reliable CO records can only be derived from Antarctic ice, given that, in Greenland, higher concentrations of impurities can produce CO in situ and contaminate the atmospheric record (Francey et al., 1997). Isotopologues of CO differ between CO sources (methane oxidation, fossil fuel and biomass burning), with $\delta^{18}\text{O-CO}$ being a particularly sensitive indicator of biomass burning. A reduction trend during the LIA of CO and its isotopes ($^{13}\text{C-CO}$ and $^{18}\text{O-CO}$) in ice-cores from a South Pole and the D47 (Antarctica), with an inversion performed through the three-dimensional chemical transport model MOZART-4 (Model for Ozone and Related chemical Tracers), suggested that large variations in the degree of biomass burning in the Southern Hemisphere occurred during the last 650 years (Wang et al., 2010). These variations are in line with the global charcoal record (Marlon et al., 2008) and the results from CH_4 and its isotopologues (Ferretti et al., 2005; Houweling et al., 2008; Mischler et al., 2009; Sapart et al., 2012)

Ice-core records of changes in biomass burning

Last glacial and deglaciation (110,000 to 12,000 years BP)

The biomass burning record for the last Glacial and deglaciation have been inferred through records of ammonium and formate from Greenland. Such very old records do not have the resolution to detect spikes, so the concentration of non-specific tracers reflects only partly biomass burning. The last Glacial period (110,000 to 19,000 years BP) is characterized by very low formate (1–3 ng/g) and ammonium (around 3 ng/g) levels during the ice age compared with the levels (4–20 ng/g) recorded during the current interglacial (Holocene: 11,700 years BP to Industrial) and the previous interglacial (Fuhrer et al., 1996; Legrand and De Angelis, 1996). Formate levels do not evolve parallel to the climate as indicated by the Greenland isotope profile, suggesting that vegetation emissions from North America represent a main source of HCOO^- (Legrand and De Angelis, 1995). Thus, low levels of formate during the Glacial suggest low emissions from vegetation and/or biomass burning activity (Figure 4). However, there were intervals during the Glacial with somewhat higher levels of ammonium and formate, for example between 80,000 and 100,000 years BP, which might indicate increased biomass burning (Legrand and De Angelis, 1996). Very recently, Fischer et al. (2015) have inferred North America wildfire activity with continuous, high resolution measurements of ammonium concentrations between 110,000 and 10,000 years ago from the NGRIP and GRIP ice cores. They conclude that sudden warming events result in a substantial increase in the frequency of North America wildfires.

During the deglaciation (19,000 to 12,000 years BP), the formate levels recorded in Greenland ice appears to be tightly related to the evolution of the Laurentide ice sheet (Legrand and De Angelis, 1995) as reconstructed from geologic and paleoecologic evidence (Mayewski et al., 1981). Formate levels started to increase at around 16,000 years BP, reaching a maximum at 12,000 years BP and declining thereafter (Legrand and De Angelis, 1996). The ammonium concentration increased slightly before 16,000 years BP and increased steadily throughout the Bølling-Allerød, reaching its highest concentrations during the cold event of the Younger Dryas (YD, Fuhrer et al., 1996). The overall evidence for the last Glacial–deglaciation period suggests that both the ammonium and the formate records parallel the build up of biomass with a warming climate toward the end of the last glaciation resulting from increased decomposition and possibly biomass burning.

Whilst ammonium and formate records suggest a variable Northern Hemisphere fire history (Legrand and De Angelis, 1996), the $\delta^{13}\text{C-CH}_4$ record from Antarctic ice (Fischer et al., 2008) over

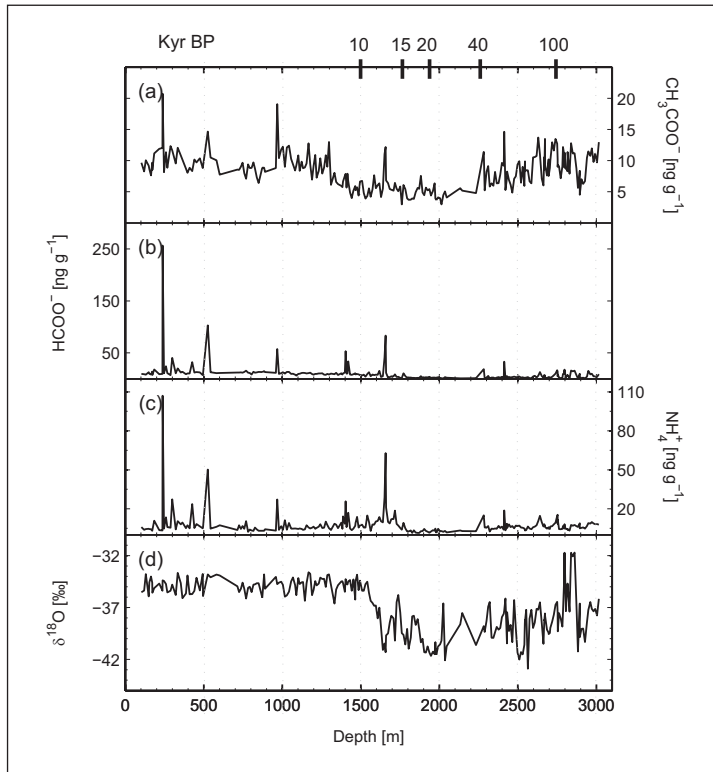


Figure 4. Depth profiles of acetate, formate, and ammonium concentrations of the Greenland Ice-Core Project (GRIP) core down to 3015 m depth along the $\delta^{18}\text{O}$ isotopic profile from Dansgaard et al. (1993). The timescale from Johnsen et al. (1992) is reported at the top in kiloyears. Source: Reproduced from Legrand and De Angelis (1996).

the last deglaciation suggests that global biomass burning was roughly stable (45 TgCH₄/yr) over a wide range of climatic conditions. The two results are not necessarily in contrast because it is possible that, while high-latitude biomass burning in North America varied in parallel to the expansion and retreat of the Laurentide ice sheet (Legrand and De Angelis, 1996; Fuhrer et al., 1996), global biomass burning remained approximately stable at the global scale. An increased glacial ¹³CH₄ signature of tropical floodplains and biomass burning emissions owing to isotopic changes in the plant precursor material would bring reconstructions of wildfire activity from charcoal records and ¹³CH₄ into closer agreement (Möeller et al., 2013). However, given that the global charcoal records support a globally increasing biomass burning over the last deglaciation (Power et al., 2008), and that the study of biomass burning through the $\delta^{13}\text{C}-\text{CH}_4$ is based on assumptions about the isotopic composition of sources and isotopic fractionation of sinks of CH₄, it is likely that the result of Fischer et al. (2008) is not precise enough to be compared with the charcoal and the ammonium/formate records.

Holocene (12,000 to 250 years BP)

Compared with the last Glacial period, the evidence available for the Holocene–Pre-industrial is more abundant. The most prominent feature in the Holocene ammonium record is the decreasing

trend of average concentrations of ammonium in the GRIP ice-core from more than 20 ppb in the YD, to less than 6 ppb in present time (Fuhrer et al., 1996). During the preboreal up to 8000 years BP and between 3000 years BP and present time the general decrease in average concentration is induced by a decrease of both biomass burning (ammonium spikes) and background ammonium. Assuming unchanged meteorological conditions over the Holocene and that northern North America is the main source area for ammonium deposited on the central Greenland Ice Sheet, Fuhrer et al. (1996) inferred that the ammonium ice-core record from Greenland reflects decreasing fire activity in northern North America during the Holocene. The authors proposed that the ammonium decrease is a consequence of the decreasing temperature in the source region. The ammonium-biomass burning decrease detected in ice-cores does not agree with the general increase of charcoal-biomass burning from North America during the Holocene (Marlon et al., 2013). Different regions in North America show different charcoal-biomass burning patterns (Marlon et al., 2013). However, a detailed comparison between ice-core and charcoal records is beyond the scope of this review. In contrast to the record from GRIP (Fuhrer et al., 1996), time periods of high biomass-burning activity were identified by Taylor et al. (1996) in 0–150 BP, 350–750 BP, and 5000 to >6000 BP by looking at concurrent reduction of electrical conductivity (ECM) and increased levels of ammonium from the GISP2 ice-core in central Greenland. These periods are associated with drier conditions and correspond with periods of high fire activity previously identified in eastern Canada by using charcoal records (Filion et al., 1991; Payette and Gagnon, 1985; Payette and Morneau, 1993; Wein et al., 1987). The authors also found that the period 1150–3250 BP is characterized by moderately elevated levels of biomass-burning activity. The difference between the GRIP (Fuhrer et al., 1996) and the GISP2 (Taylor et al., 1996) records are difficult to explain because the two sites are only 30 km apart and it is unlikely that the impurities in the two ice-cores come from different source regions.

Globally, the Late Pre-Industrial Holocene (the last 2000 years) was characterized by two major climatic events (Mann et al., 2008, 2009): a warmer ‘Medieval Climate Anomaly’ (MCA) period between AD 950 and 1250, and the colder ‘Little Ice Age’ (LIA) period between AD 1400 and 1850. Records of trace gases in ice-cores (Ferretti et al., 2005; Mischler et al., 2009; Wang et al., 2010) consistently show a remarkable decrease of biomass burning going from the MCA to the LIA, in agreement with the decreasing amount of ammonium deposited in the GRIP ice-core (Fuhrer et al., 1996), the levoglucosan record in the NEEM ice-core (Zennaro et al., 2014) and the GCD composite curve (Power et al., 2008). However, there are regional differences between ice-core records of biomass burning derived from chemical species. In the following, we discuss these differences by grouping the records regionally.

Belukha glacier. Based on nitrates, potassium and charcoal concentrations, Eichler et al. (2011) reported high forest fire activity between AD 1600 and 1680 in the Altai region of southern Siberia (Figure 5a). The cause of the strongly increased forest fire activity is most probably a preceding dry period AD 1540 and 1600 in Central Asia identified by a maximum in mineral dust (Eichler et al., 2011).

Ushkovsky ice-core (Kamchatka Peninsula). Kawamura et al. (2012) conducted 7 days backward air mass trajectory analyses at the Ushkovsky ice-core-sampling site for four seasons in 2001 using the HYSPLIT model of the National Oceanic and Atmospheric Administration suggesting that the emission source regions for the Ushkovsky ice-core were Siberia, Far East, North China and Eastern Europe as well as the western Northern North Pacific (Figure 5a). Sporadic peaks of levoglucosan, some of which having a corresponding peak of vanillic acid and p-hydroxybenzoic acid, suggest that large-scale forest fires may have occurred in those source regions in the past 300 years.

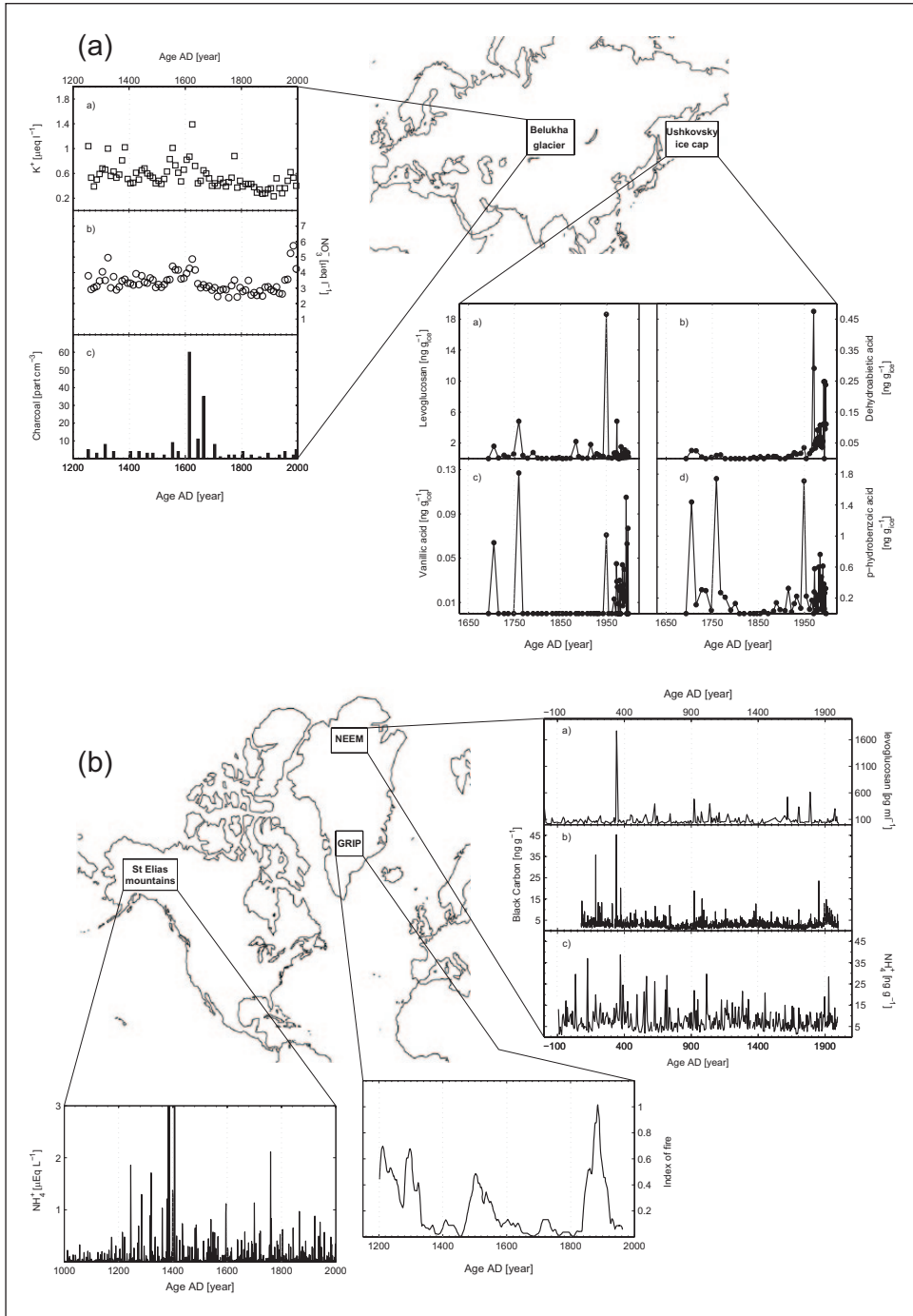


Figure 5. (a) Pre-industrial records of biomass burning from Ushkowsky ice cap (Kawamura et al., 2012) and Belukha glacier (Eichler et al., 2011). (b) Pre-industrial records of biomass burning from NEEEM (Zennaro et al., 2014), GRIP (Savarino and Legrand, 1998) and St Elias mountains (Yalcin et al., 2006).

GRIP. Savarino and Legrand (1998) identified three periods of enhanced biomass burning input over central Greenland: AD 1200–1350, AD 1830–1930, and to a lesser extent AD 1500–1600 (Figure 5b), all deduced from simultaneous spikes of ammonium and formate. The two oldest time periods (AD 1200–1350 and AD 1500–1600) correspond to a high frequency of fire events with a low flux of deposition compared with the AD 1830–1930 time period, which was characterized by less frequent events of high intensity (Savarino and Legrand, 1998). The authors found that their Index of Fire is in fairly good agreement with charcoal records obtained from three sites in Maine (Conroy Lake and Basin Pond) and New York (Clear Pond) by Gajewski (1985), suggesting that Eastern North America is the source of biomass burning material in central Greenland over the last millennium.

Eclipse ice-core (St Elias mountains). High fire activity, identified through spikes of ammonium, in association with oxalate and potassium, was found from 1240 to 1410 during the waning stages of the MCA (Figure 5b) and should correspond to warmer and drier conditions in Alaska and the Yukon (Yalcin et al., 2006).

NEEM. Several levoglucosan spikes were recorded between AD 920 and 1110 in the NEEM ice-core (Figures 3 and 5b). Zennaro et al. (2014) suggest that these peaks were caused by human activity because this period coincides with the foundation of Viking settlements in Greenland beginning in AD 982 in southwest Greenland, relatively close to the NEEM site. The highest levels of levoglucosan in the NEEM record occur between AD 1500 and 1700. This is also an interval of high fire activity inferred in the Belukha ice-core (Eichler et al., 2011) and, partly, in the GRIP ice-core (Savarino and Legrand, 1998), and corresponds to the LIA period of cold and dry climatic conditions in the Northern Hemisphere. However, the HLNH $> 55^\circ$ GCD and levoglucosan data differ near AD 1600, when the HLNH $> 55^\circ$ GCD demonstrates only a modest increase in fire activity, while the smoothed NEEM levoglucosan curve strongly peaks. Zennaro et al. (2014) infer that the AD 1500–1700 maximum in fire activity is due to increased Eurasian boreal forest fires, which are underrepresented in the GCD (Figures 3 and 5b). By looking at ice-core, tree ring proxy records and archival evidence, Zennaro et al. (2014) claim that Siberian fire activity during the last 2000 years is closely related to precipitation changes, where extreme biomass burning peaks are synchronous with precipitation anomalies. This inference is consistent with the modelling study of Pechony and Shindell (2010) that found global fire regimes to be strongly driven by precipitation rather than temperature during the Pre-industrial period.

The postindustrial period

GISP2 and 20D. Records of ammonium show increased fire activity in North America between 1790 and 1810 (Figure 6a) and again from 1830 to 1910 (Whitlow et al., 1994). The latter period is likely to reflect the large-scale burning of forests to clear land for agricultural use during the westward expansion of European settlers in North America (Holdsworth et al., 1996). The post-1910 decrease in forest fire activity mirrors the increasing importance of active fire suppression in eastern North America (Whitlow et al., 1994), but it might also have been due to landscape fragmentation which reduces fire spread (Marlon et al., 2008). The most recent NH $_4^+$ spikes at 20D (Whitlow et al., 1994) may reflect the increase in total number of acres burned in North America since the seventies (Fuller, 1991; Stocks, 1991; Van Wagner, 1988).

Site A. The low resolution NH $_4^+$ record by Laj et al. (1992) shows increased NH $_4^+$ concentration during the 19th century and decreased NH $_4^+$ during the 20th century.

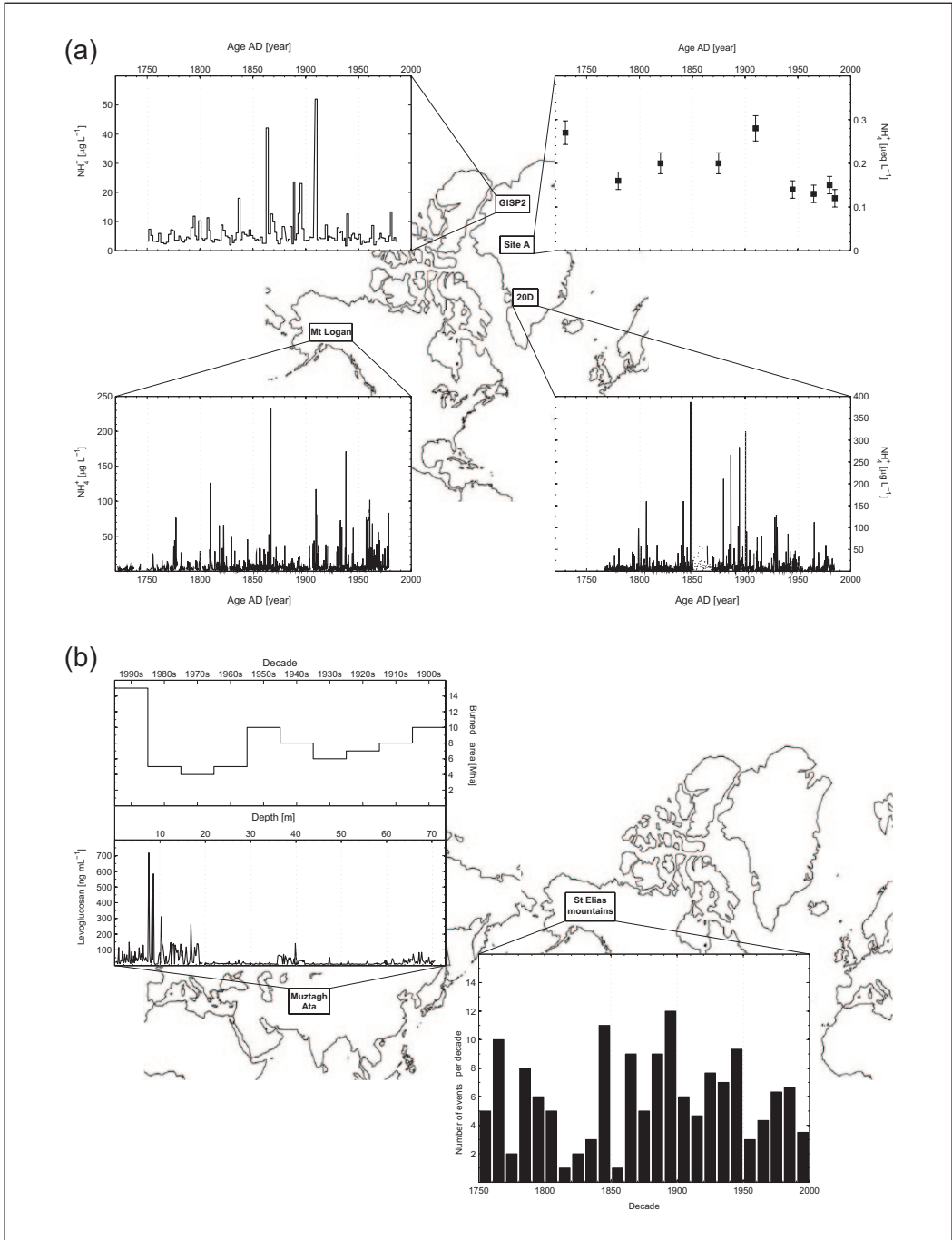


Figure 6. (a) Industrial records of biomass burning from: Mt Logan, 20D and GISP2 (Whitlow et al., 1994), Site A (Laj et al., 1992). (b) Industrial records of biomass burning from: St Elias mountains (Yalcin et al., 2006), Muztagh Ata (Yao et al., 2013).

GRIP. Savarino and Legrand (1998) found that the AD 1830–1930 time period was the most active period of fire events of the last 800 years (Figure 5b). This may result from the high amount of organic matter accumulated during the LIA, but the authors do not exclude anthropogenic ignition of fires during this period. Very little fire activity is recorded between AD 1930 and 1990. It is likely that the policy of fire suppression adopted by governments in 1910 contributed to this low fire activity despite the fact that climate has warmed since the LIA.

Mt Logan and Eclipse ice-core (St Elias mountains). The NH_4^+ records indicate that peak-fire activity (Figure 6a and b) occurred in the period 1870–1890 (Whitlow et al., 1994; Yalcin et al., 2006). This may reflect anthropogenic ignition sources associated with the large influx of people to the Yukon during the Klondike Gold Rush. A notable exception occurs during the 1830s and 1850s, when both the Eclipse and Mt Logan records indicate low fire activity, while the 20D record indicates high fire activity (Figure 6a and b). This breakdown in the correspondence of high fire activity in eastern and northwest North America might be the result of the expansion of settlement and agriculture and associated biomass burning in eastern and central North America in the early to mid 1800s, a major source region for forest fire plumes affecting Greenland. Meanwhile, northwest North America remained relatively free of anthropogenic ignition sources during this time. However, it may also indicate that Mt Logan and St Elias mountains have a completely different source region (e.g. Siberia) at times.

In synthesis, ice-core records of NH_4^+ , NO_3^- , COOH^- and K^+ suggest an increase in biomass burning during the 19th century (Savarino and Legrand, 1998; Whitlow et al., 1994), while hinting to a decline in biomass burning during the 20th century (Laj et al., 1992; Savarino and Legrand, 1998; Whitlow et al., 1994). The only exception to this pattern is Fuhrer et al. (1996).

Ice-core records of levoglucosan covering the Industrial period suggest a more variable biomass burning history, with important spatial and temporal differences.

Ushkovsky ice-core (Kamchatka Peninsula). Major peaks occurred in 1705, 1759, 1883, 1915, 1949 and 1972 (Kawamura et al., 2012). Terrestrial plant-derived biomarkers such as n-alkanes, n-alkanols and n-fatty acids show a similar trend in the Ushkovsky ice-core (Izawa, 2004). Kawamura et al. (2012) also found a gradual increase in the concentration of dehydroabietic acid, a specific tracer of coniferous tree burning, from the mid 1900s to the 1990s (Figure 5a).

Muztagh Ata (Tibetan plateau). The levoglucosan concentration record (Figure 6b) shows three periods of peak-fire events, with a strong maximum in the 1990s, and two lesser maxima in the 1950s and 1900s (Yao et al., 2013). This is similar to the fire history reconstructed by Mouillot and Field (2005) using historical and tree ring analyses. During the 1990–2000 period covered by the Tanggula ice-core section (1 to 3.5 m depth), levoglucosan concentrations showed a strong maximum in 1995 and smaller peak in 1997/1998 (Yao et al., 2013). The 1995 peak corresponds to forest fires in May–June 1995 in Uttarakhand and Himachal Pradesh, northern India, which resulted in 677,700 ha of forest burnt (Kimothi and Jadhav, 1998; Roy, 2004), while the 1997/1998 peak corresponds to a widespread drought triggered by an El Niño event.

NEEM. The levoglucosan profile contains low concentrations until the beginning of the 20th century, followed by a modest concentration increase (Zennaro et al., 2014).

Future developments

Ice-core records of biomass burning have already provided important contributions to the understanding of past changes in fire regimes and the relationship between climate and fire, as well as

the impact of anthropogenic activity on biomass burning. There are a number of points that could be exploited in the future, in order to increase the impact of the methodology.

1. *Extending the levoglucosan record back to through the glacial–interglacial:* Records of the last Glacial and Deglaciation are based on non-specific chemical tracers, such as ammonium and nitrates. Extending records of proxies specific to biomass burning, such as levoglucosan, back to periods of rapid change (Glacial–Interglacial transitions, Dansgaard–Oeschger events, etc.) would be especially important.
2. *Matching the information derived from different archives with ice-core records:* Different archives (charcoal, trees, ice-cores, etc.) sometimes provide histories of biomass burning which are not consistent. Being able to match records from sedimentary fire proxies and tree scars with those from ice-cores would increase the confidence of the conclusions one can derive. For recent periods, comparing records of different proxies from different regions (tropical versus high latitude, different continents) with the history of societies and colonisations, can help disentangle the role of natural versus anthropogenic fire on the history of biomass burning (Marlon et al., 2013).
3. *Pushing the sensitivity of measuring techniques:* There are many records of biomass burning from Greenland and sites on the Northern Hemisphere continents, but much less information from Antarctica. This is because the region is further from sources of biomass burning and therefore concentrations of the tracers are very low. Thus, being able to measure chemical species and biomarkers at very low concentration is a necessary step to increasing the number of Southern Hemisphere records. This requires increasing the sensitivity of current measuring techniques.
4. *Measurements of the isotopic composition of proxies:* Measuring the isotopic composition of biomass burning biomarkers, such as levoglucosan, in ice could provide new information about the source of biomass burning (e.g. C3 versus C4 plants). Several studies have already shown that it is possible to use isotopic measurements to determine the source of fire-derived organic matter (Ballentine et al., 1998; Liu et al., 2013; Sang et al., 2012). The stable carbon and hydrogen isotopic composition of organic molecules in snow has already been measured (Sankelo et al., 2012; Yamamoto et al., 2011). Measuring the isotopic composition of organics in polar ice is, however, a challenging task because of small quantities of organics, and will need highly sensitive techniques.

Conclusions

Ice-core records of biomass burning have provided important information about the history of fire in the past. While a number of chemical species, such as ammonium and formate, has been used as non-specific proxies of biomass burning, unambiguous evidence has more recently come from chemical species that only derive from biomass burning (e.g. levoglucosan, vanillic acid, dehydroabietic acid). Although they have great potential, records of these biomass-burning specific tracers are so far only available for short time periods and few regions (the last 2000 years in North Greenland and the last 300 years in the Kamchatka Peninsula). Associating these records with records of trace gases in ice-core could provide important information about the influence of fire on the atmosphere and the relationship with past climate change.

The story of past biomass burning that can be drawn suggests that biomass burning was low during the last Glacial period, tended to increase during the last termination and decreased during the Holocene, with a significant drop going from the MCA to the LIA. During the last three centuries, an increase in biomass burning is registered during the 17th–19th centuries, while decreasing

fire activity is recorded during the 20th century. Anthropogenic activities might have had a significant influence on biomass burning during the last centuries by increasing fire activity during the 19th century and suppressing fire in the 20th century.

Future developments in methodologies and applications, including extending records into unexplored periods, synthesizing the records in a global dataset for model benchmarking, and measuring very low concentration in e.g. Antarctic ice, as well as measuring the isotopic composition of biomass burning proxies, could provide new, more powerful results to better constrain the relationship between climate, anthropogenic activities and fire, in order to more reliably predict future changes.

Acknowledgements

We are grateful to the two reviewers (Eric Wolff and Jennifer Marlon) for the constructive comments they provided that have helped to improve the original manuscript. We thank MR Legrand, P Laj, P Mayewski, M Twickler, KC Taylor, K Yalcin, A Eichler, J Savarino, K Kawamura, P Yao, P Zennaro, J McConnell and S Schüpbach for sharing their data and allowing us to re-plot them.

Funding

This study has been supported by the Italian POLIGRID project (CUP B65B0900002007).

References

- Andreae MO, Brownell EV, Garstang M et al. (1988) Biomass-burning emissions and associated haze layers over Amazonia. *Journal of Geophysical Research* 93(D2): 1509–1527.
- Ballentine DC, Macko SA and Turekian VC (1998) Variability of stable carbon isotopic compositions in individual fatty acids from combustion of C4 and C3 plants: Implications for biomass burning. *Chemical Geology* 152: 151–161.
- Bistinas I, Harrison SP, Prentice IC et al. (2014) Causal relationships vs. emergent patterns in the global controls of fire frequency. *Biogeosciences* 11: 5087–5101.
- Bond WJ, Woodward FI and Midgley GF (2005) The global distribution of ecosystems in a world without fire. *New Phytologist* 165(2): 525–538.
- Buizert C, Martinerie P, Petrenko VV et al. (2012) Gas transport in firn: Multiple-tracer characterisation and model intercomparison for NEEM, Northern Greenland. *Atmospheric Chemistry Physics* 12(9): 4259–4277.
- Chýlek P, Johnson B, Damiano PA et al. (1995) Biomass burning record and black carbon in the GISP2 ice core. *Geophysical Research Letters* 22(2): 89–92.
- Clark JS (1997) An introduction to sediment records of biomass burning. In: Clark JS, Cachier H, Goldammer JG et al. (eds) *Sediment Records of Biomass Burning and Global Change*. Berlin, Heidelberg: Springer, pp. 1–8.
- Cofer WR, Koutzenogii KP, Kokorin A et al. (1997) Biomass burning emissions and the atmosphere. In: Clark JS, Cachier H, Goldammer JG et al. (eds) *Sediment Records of Biomass Burning and Global Change*. Berlin, Heidelberg: Springer, pp. 189–206.
- Conedera M, Tinner W, Neff C et al. (2009) Reconstructing past fire regimes: Methods, applications, and relevance to fire management and conservation. *Quaternary Science Reviews* 28: 435–456.
- Craig H, Chou CC, Welhan JA et al. (1988) The isotopic composition of methane in polar ice cores. *Science* 242(1535): 1714–1717.
- Dansgaard W, Johnsen SJ, Clausen HB et al. (1993) Evidence for general instability of past climate from a 250-kyr ice-core record. *Nature* 64: 118–120.
- Draxler RR and Rolph GD (2015) HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY. Available at: <http://ready.arl.noaa.gov/HYSPLIT.php>. Silver Spring, MD: NOAA Air Resources Laboratory.
- Echalar F, Gaudichet A, Cachier H et al. (1995) Aerosol emissions by tropical forest and savanna biomass burning: Characteristic trace elements and fluxes. *Geophysical Research Letters* 22(22): 3039–3042.

- Eichler A, Brüttsch S, Olivier S et al. (2009) A 750 year ice-core record of past biogenic emissions from Siberian boreal forests. *Geophysics Research Letters* 36: L18813.
- Eichler A, Tinner W, Brüttsch W et al. (2011) An ice-core based history of Siberian forest fires since AD 1250. *Quaternary Science Reviews* 30: 1027–1034.
- Ferretti DF, Miller JB, White JWC et al. (2005) Unexpected changes to the global methane budget over the past 2000 years. *Science* 309: 1714–1717.
- Filion L, Saint-Laurent D, Desonts M et al. (1991) The late Holocene record of aeolian and fire activity in northern Québec, Canada. *The Holocene* 3: 201–208.
- Fischer H, Behrens M and Bock M (2008) Changing boreal methane sources and constant biomass burning during the last termination. *Nature* 452(7189): 864–867.
- Fischer H, Schupbach S, Gfeller G et al. (2015) Millennial changes in North American wildfire and soil activity over the last glacial cycle. *Nature Geoscience* 8: 723–727.
- Francey RJ, Michel E, Etheridge D et al. (1997) The pre-industrial difference in CO₂ from Antarctica and Greenland ice. Extended abstract of the Fifth International Carbon Dioxide Conference, Cairns, Australia, pp. 211–212.
- Fraser MP and Lakshmanan K (2000) Using levoglucosan as a molecular marker for the long-range transport of biomass combustion aerosols. *Environmental Science Technology* 34: 4560–4564.
- Fu P, Kawamura K and Barrie LA (2009) Photochemical and other sources of organic compounds in the Canadian High Arctic Aerosol pollution during Winter-Spring. *Environmental Science & Technology* 43: 286–292.
- Fuhrer and Legrand (1997) Continental biogenic species in the Greenland Ice Core Project ice core: Tracing back the biomass history of the North American continent. *Journal of Geophysical Research* 102(C12): 26,735–26,745.
- Fuhrer K, Neftel A, Anklin M et al. (1993) Continuous measurements of hydrogen peroxide, formaldehyde, calcium and ammonium concentrations along the new grip ice-core from Summit, central Greenland. *Atmospheric Environment* 27A(12): 1873–1880.
- Fuhrer K, Neftel A, Anklin M et al. (1996) High-resolution ammonium ice-core record covering a complete glacial-interglacial cycle. *Journal of Geophysical Research* 101(D2): 4147–4164.
- Fuller M (1991) *Forest Fires: An Introduction to Wildland Fire Behavior, Management, Firefighting, and Prevention*. New York, NY: John Wiley and Sons, Inc.
- Gajewski K (1985) *Late-Holocene pollen data from lakes with varved sediments in northeastern and north central United States*. Study Report 124. Madison, WI: Institute for Environment, University of Wisconsin-Madison.
- Gambaro A, Zangrando R, Gabrielli P et al. (2008) Direct determination of levoglucosan at the picogram per milliliter level in Antarctic ice by high-performance liquid chromatography/electrospray ionization triple quadrupole mass spectrometry. *Analytical Chemistry* 80: 1649–1655.
- Harrison SP, Marlon JR and Bartlein PJ (2010) Fire in the Earth system. In: Dodson J (ed.) *Changing Climates, Earth Systems and Society*. Dordrecht: Springer, pp. 21–48.
- Hennigan CJ, Sullivan AP, Collett JL et al. (2010) Levoglucosan stability in biomass burning particles exposed to hydroxyl radicals. *Geophysical Research Letters* 37: L09806.
- Heyerdahl EK and Card V (2000) Implications of paleorecords for ecosystem management. *Trends in Ecology & Evolution* 15(2): 49–50.
- Hoffmann D, Tilgner A, Iinuma Y et al. (2010) Atmospheric stability of levoglucosan: A detailed laboratory and modeling study. *Environmental Science & Technology* 44: 694–699.
- Holdsworth G, Higuchi K, Zielinski GA et al. (1996) Historical biomass burning: late 19th century pioneer agriculture revolution in northern hemisphere ice-core data and its atmospheric interpretation. *Journal of Geophysical Research* 101: 23,317–23,334.
- Holmes BJ and Petrucci GA (2006) Water-soluble oligomer formation from acid-catalyzed reactions of levoglucosan in proxies of atmospheric aqueous aerosols. *Environmental Science & Technology* 40: 4983–4989.
- Holmes BJ and Petrucci GA (2007) Oligomerization of levoglucosan by Fenton chemistry in proxies of biomass burning aerosols. *Journal of Atmospheric Chemistry* 58: 151–166.

- Holz A, Haberle S, Veblen TT et al. (2012) Fire history in western Patagonia from paired tree-ring fire-scar and charcoal records. *Climate of the Past* 8(2): 451–466.
- Houweling S, van der Werf GR, Goldewijk KK et al. (2008) Early anthropogenic CH₄ emissions and the variation of δ¹³CH₄ over the last millennium. *Global Biogeochemical Cycles* 22: GB1002.
- Hristov AN, Hanigan M and Cole A (2011) Review: Ammonia emissions from dairy farms and beef feedlots. *Canadian Journal of Animal Science* 91: 1–35.
- Hu QH, Xie ZQ, Wang XM et al. (2013) Levoglucosan indicates high levels of biomass burning aerosols over oceans from the Arctic to Antarctic. *Scientific Reports* 3: 3119.
- Izawa Y (2004) *Changes in the atmospheric environments reconstructed from the Ushkovsky ice-core taken from the Kamchatka Peninsula for the last 300 years*. Master's thesis, Hokkaido University, 71 pp.
- Johnsen S, Clausen HB and Dansgaard W (1992) Irregular glacial interstadials recorded in a new Greenland ice-core. *Nature* 359: 311–313.
- Kawamura K and Kaplan IR (1987) Motor exhaust emissions as a primary source for dicarboxylic acids in Los Angeles air. *Environmental Science & Technology* 21: 105–110.
- Kawamura K, Izawa Y, Mochida M et al. (2012) Ice-core records of biomass burning tracers (levoglucosan and dehydroabietic, vanillic and p-hydroxybenzoic acids) and total organic carbon for past 300 years in the Kamchatka Peninsula, Northeast Asia. *Geochimica et Cosmochimica Acta* 99: 317–329.
- Kehrwald N, Zangrando R, Gabrielli P et al. (2012) Levoglucosan as a specific marker of fire events in Greenland snow. *Tellus B* 64: 18196.
- Kimothi MM and Jadhav RN (1998) Forest fire in the Central Himalaya: An extent, direction and spread using IRS LISS-I data. *International Journal Remote Sensing* 19(12): 2261–2274.
- Kuo LJ, Herbert BE and Louchouart P (2008) Can levoglucosan be used to characterize and quantify char/charcoal black carbon in environmental media? *Organic Geochemistry* 39: 1466–1478.
- Laj P, Ghermandi G, Cecchi R et al. (1997) Distribution of Ca, Fe, K, and S between soluble and insoluble material in the Greenland Ice-core Project ice-core. *Journal of Geophysical Research* 102: 26,615–26,623.
- Laj P, Palais JM and Sigurdsson H (1992) Changing sources of impurities to the Greenland Ice Sheet over the last 250 years. *Atmospheric Environment* 1: 2627–2640.
- Lassey KR, Lowe DC and Manning MR (2000) The trend in atmospheric methane δ¹³C and implications for isotopic constraints on the global methane budget. *Global Biogeochemical Cycles* 14: 41–49.
- Lebel PJ, Vay SA and Roberts PD (1991) Ammonia and nitric acid emissions from wetlands and boreal forest fires. In: Levine JS (ed.) *Global Biomass Burning*. Cambridge, MA: MIT Press, pp. 225–229.
- Legrand M and De Angelis M (1995) Origins and variations of light carboxylic acids in polar precipitation. *Journal of Geophysical Research* 100(D1): 1445–1462.
- Legrand M and De Angelis M (1996) Light carboxylic acids in Greenland ice: A record of past forest fires and vegetation emissions from the boreal zone. *Journal of Geophysical Research* 101(D2): 4129–4145.
- Legrand M, De Angelis M, Staffelbach T et al. (1992) Large perturbations of ammonium and organic acids content in Summit-Greenland ice-core. Fingerprint from forest fires? *Geophysical Research Letters* 19(5): 473–475.
- Legrand M, Ducroz F, Wagenbach D et al. (1998) Ammonium in coastal Antarctic aerosol and snow: Role of polar ocean and penguin emissions. *Journal of Geophysical Research* 103(D9): 11,043–11,056.
- Legrand MR and Delmas RJ (1988) Formation of HCl in the Antarctic atmosphere. *Journal of Geophysical Research* 93(D6): 7153–7168.
- Liu D, Li J, Zhang Y et al. (2013) The use of levoglucosan and radiocarbon for source apportionment of PM_{2.5} carbonaceous aerosols at a background site in east China. *Environmental Science & Technology* 47: 10,454–10,461.
- McConnell JR, Edwards R, Kok GL et al. (2007) 20th-century industrial black carbon emissions altered Arctic climate forcing. *Science* 317: 1381–1384.
- Mann ME, Zhang Z and Hughes MK (2008) Proxy-based reconstructions of hemispheric and global surface temperature variations over the past two millennia. *Proceedings of National Academic Science* 105: 13,252–13,257.

- Mann ME, Zhang Z, Rutherford S et al. (2009) Global signatures and dynamical origins of the Little Ice Age and Medieval Climate Anomaly. *Science* 326: 1256–1260.
- Marlon JR, Bartlein PJ, Carcaillet C et al. (2008) Climate and human influences on global biomass burning over the past two millennia. *Nature Geoscience* 1(10): 697–702.
- Marlon JR, Bartlein PJ, Daniau AL et al. (2013) Global biomass burning: A synthesis and review of Holocene paleofire records and their controls. *Quaternary Science Reviews* 65: 2–25.
- Mayewski PA, Denton GH and Hughes TJ (1981) Late Wisconsin ice sheets in North America. In: Denton GH and Hughes TJ (eds) *The Last Great Ice Sheets*. New York: John Wiley and Sons, pp 67–178.
- Mischler JA, Sowers TA, Alley RB et al. (2009) Carbon and hydrogen isotopic composition of methane over the last 1000 years. *Global Biogeochemical Cycles* 23(4): GB4024.
- Mochida M, Kawamura K, Fu P et al. (2010) Seasonal variations of levoglucosan in aerosols over the western North Pacific and its assessment as a biomass-burning tracer. *Atmospheric Environment* 33: 3511–3518.
- Möeller L, Sowers T, Bock M et al. (2013) Independent variations of CH₄ emissions and isotopic composition over the past 160,000 years. *Nature Geoscience* 6(10): 885–890.
- Mouillot F and Field CB (2005) Fire history and the global carbon budget: A 1°X1° fire history reconstruction for the 20th century. *Global Change Biology* 11(3): 398–420.
- Olivier S, Blaser C, Brütsch S et al. (2006) Temporal variations of mineral dust, biogenic tracers, and anthropogenic species during the past two centuries from Belukha ice-core, Siberian Altai. *Journal of Geophysical Research* 111: D05309.
- Palais JM and Legrand M (1985). Soluble impurities in the Byrd Station ice-core, Antarctica: Their origin and sources. *Journal of Geophysical Research* 90(C1): 1143–1154.
- Pasteris DR, McConnell JR and Edwards R (2014) Acidity decline in Antarctic ice-cores during the Little Ice Age linked to changes in atmospheric nitrate and sea salt concentrations. *Environmental Science and Technology* 46(3): 1659–1666.
- Payette S and Gagnon R (1985) Late Holocene deforestation and tree regeneration in the forest-tundra of Québec. *Nature* 313: 570–572.
- Payette S and Morneau C (1993) Holocene relict woodlands at the eastern Canadian treeline. *Quaternary Research* 39: 84–89.
- Pechony O and Shindell DT (2010) Driving forces of global wildfires over the past millennium and the forthcoming century. *PNAS* 107(45): 19,167–19,170.
- Power MJ, Marlon J, Ortiz N et al. (2008) Changes in fire regimes since the last glacial maximum: An assessment based on a global synthesis and analysis of charcoal data. *Climate Dynamics* 30(7–8): 887–907.
- Prentice IC, Kelley DI, Foster PN et al. (2011) Modeling fire and the terrestrial carbon balance. *Global Biogeochemical Cycles* 25(3): GB3005.
- Rankin AM and Wolff EW (2000) Ammonium and potassium in snow around an emperor penguin colony. *Antarctic Science* 12: 154–159.
- Reeburgh WS (2004) Global methane biogeochemistry. *Treatise on Geochemistry* 4: 65–89.
- Rolph GD (2015) Real-time Environmental Applications and Display sYstem (READY). Available at: <http://ready.arl.noaa.gov>. Silver Spring, MD: NOAA Air Resources Laboratory.
- Roy PS (2004) Forest fire and degradation assessment using satellite remote sensing and geographic information system. In: Sivakumar MVK, Roy PS, Harmsen K et al. (eds) *Satellite Remote Sensing and GIS Applications in Agricultural Meteorology*. Proceedings of the Training Workshop, 7–11 July 2003, Dehra Dun, India. Geneva: World Meteorological Organisation, pp. 361–400.
- Saleh R, Robinson ES, Tkacik DS et al. (2014) Brownness of organics in aerosols from biomass burning linked to their black carbon content. *Nature Geoscience* 7: 647–650.
- Sang XF, Gensch I, Laumer W et al. (2012) Stable carbon isotope ratio analysis of anhydrosugars in biomass burning aerosol particles from source samples. *Environmental Science Technology* 46: 3312–3318.
- Sankelo P, Kawamura K, Seki O et al. (2012) Compound specific $\delta^{13}\text{C}$ and δD compositions of n-alkanes in fresh snow: Implications for ice-core studies. *Antarctic, Arctic and Alpine Research* 45(1): 119–131.
- Sapart CJ, Monteil G, Prokopiou M et al. (2012) Natural and anthropogenic variations in methane sources during the past two millennia. *Nature* 490: 85–88.

- Savarino J and Legrand M (1998) High northern latitude forest fires and vegetation emissions over the last millennium inferred from the chemistry of a central Greenland ice-core. *Journal of Geophysical Research* 103(D7): 8267–8279.
- Shakya KM, Louchouart P and Griffin RJ (2011) Lignin derived phenols in Houston aerosols: Implications for natural background sources. *Environmental Science & Technology* 45: 8268–8275.
- Silvente E and Legrand M (1993). Ammonium to sulphate ratio in aerosol and snow of Greenland and Antarctic regions. *Geophysical Research Letters* 20(8): 687–690.
- Simoneit BRT (2002) Biomass burning – A review of organic tracers for smoke from incomplete combustion. *Applied Geochemistry* 17(3): 129–162.
- Simoneit BRT and Elias VO (2001) Detecting organic tracers from biomass burning in the atmosphere. *Marine Pollution Bulletin* 42: 805–810.
- Simoneit BRT, Schauer JJ, Nolte CG et al. (1999) Levoglucosan, a tracer for cellulose in biomass burning and atmospheric particles. *Atmospheric Environment* 33(2): 173–182.
- Stocks BJ (1991) The extent and impact of forest fires in northern circumpolar countries. In: Levine JS (ed.) *Global Biomass Burning*. Cambridge, MA: MIT Press, pp. 197–202.
- Swetnam TW, Allen CD and Betancourt JL (1999) Applied historical ecology: Using the past to manage for the future. *Ecological Applications* 9(4): 1189–1206.
- Talbot RW, Vijgen AS and Harriss RC (1992) Soluble species in the Arctic summer troposphere: Acidic gases, aerosols, and precipitation. *Journal of Geophysical Research* 97(D15): 16,531–16,543.
- Taylor KC, Mayewski PA, Twickler MS et al. (1996) Biomass burning recorded in the GISP2 ice-core: A record from eastern Canada? *The Holocene* 6(1): 1–6.
- Van Wagner CE (1988) The historical pattern of annual burned area in Canada. *The Forestry Chronicle* June: 182–185.
- Wang Z, Chappellaz J, Park K et al. (2010) Large variations in Southern Hemisphere biomass burning during the last 650 years. *Science* 330: 1663–1666.
- Wein RW, Burzyski MP and Sreenivasa BA (1987) Bog profile evidence of fire and vegetation dynamics since 3000 years BP in the Acadian Forest. *Canadian Journal of Botany* 65: 1180–1186.
- Whitlow S, Mayewski P, Dibb J et al. (1994) An ice-core-based record of biomass burning in the Arctic and subarctic, 1750–1980. *Tellus* 46B(3): 234–242.
- Yalcin K, Wake CP, Kreutz KJ et al. (2006) A 1000-yr record of forest fire activity from Eclipse Icefield, Yukon, Canada. *The Holocene* 16(2): 200–209.
- Yamamoto S, Kawamura K and Seki O (2011) Long-range transport of terrestrial biomarkers by the Asian winter monsoon: Evidence from fresh snow from Sapporo, northern Japan. *Atmospheric Environment* 45: 3353–3360.
- Yao P, Schwab VF and Roth VN (2013) Levoglucosan concentrations in ice-core samples from the Tibetan Plateau determined by reverse-phase high-performance liquid chromatography–mass spectrometry. *Journal of Glaciology* 59(216): 599–612.
- Zennaro P, Kehrwald N, McConnell JR et al. (2014) Fire in ice: Two millennia of Northern Hemisphere fire history from the Greenland NEEM ice-core. *Climate of the Past* 10: 1905–1924.