Prospects for reconstructing paleoenvironmental conditions from organic compounds in polar snow and ice

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Abstract

Polar ice cores provide information about past climate and environmental changes over periods ranging from a few years up to 800,000 years. The majority of chemical studies have focused on determining inorganic components, such as major ions and trace elements as well as on their isotopic fingerprint. In this paper, we review the different classes of organic compounds that might yield environmental information, discussing existing research and what is needed to improve knowledge. We also discuss the problems of sampling, analysis and interpretation of organic molecules in ice. This review highlights the great potential for organic compounds to be used as proxies for anthropogenic activities, past fire events from different types of biomass, terrestrial biogenic emissions and marine biological activity, along with the possibility of inferring past temperature fluctuations and even large-scale climate variability. In parallel, comprehensive research needs to be done to assess the atmospheric stability of these compounds, their ability to be transported long distances in the atmosphere, and their stability in the archive in order to better interpret their fluxes in ice cores. In addition, specific decontamination procedures, analytical methods with low detection limits (ng/L or lower), fast analysis time and low sample requests need to be developed in order to ensure a good time resolution in the archive.

1 Introduction

Over the last half century, ice cores have provided a wealth of information about past climate and environmental changes (Jouzel, 2013) over periods ranging from a few years up to 800,000 years. For example, ice core results demonstrate the pattern of glacial-interglacial cycles (Epica community members, 2004), the existence of abrupt climate changes (Johnsen et al., 1992), and quantify how greenhouse gas concentrations increased above their pre-industrial values over the last two centuries (MacFarling Meure et al., 2006). The findings are based on three types of information recorded in ice cores: the isotopic content of the water molecules themselves, the gaseous content of air bubbles trapped in the ice (e.g. CH_4, CO_2), and the impurities that are trapped in or on snowflakes. This last component consists both of aerosol particles and of gaseous compounds that are absorbed onto snow surfaces. Multiple studies quantify many different analytes, and discuss, for example, atmospheric transport of dust, past variations of sea ice, and changes in concentrations of pollutants. The overwhelming majority of studies concentrate on the inorganic impurity – major cations and anions, trace elements, and simple components such as hydrogen peroxide. However, a very large proportion, often half or more, of atmospheric aerosols are organic (Jimenez et al., 2009), and such material is certainly present in polar ice.

Very few studies investigate the organic component in polar ice, either as a whole (Legrand et al., 2013), or for individual compounds. There are probably a number of reasons for this shortage: analytical issues, a lack of expertise in the ice core community, and difficulties in interpreting changing concentrations of reactive chemicals which may have relatively short lifetimes and limited stability in the atmosphere. Many of the studies that do exist concern: (a) very small molecules such as formaldehyde and low molecular weight organic acids (e.g. Legrand and De Angelis, 1995), (b) methanesulfonic acid (MSA) as a specific marker for marine biological activity and/or therefore sea ice extent (e.g. Curran et al., 2003), and (c) organic markers for biomass burning (Gambaro et al., 2008; Rubino et al., 2016). Studies in ice and snow of persistent organic pollutants (POPs) (Fuoco et al., 2012; Hermanson et al., 2005; Ruggirello et al., 2010) and of other molecules such as long chain fatty acids that are potential terrestrial biomarkers as they are produced by land-dwelling plants (Hopmans et al., 2004 and references therein; Kawamura et al., 1996; Pokhrel, 2015; Pokhrel et al., 2015) have been carried out but are not well developed in ice from the polar ice sheets.

Recent advances in analytical capability and in atmospheric chemistry modelling make it the right time to survey the field of organic geochemistry in ice cores and to discuss potential fields of study. Here, we consider only material in the solid ice phase. Air bubbles in ice do contain trace organic gases (such as methane), but these gases pose a different set of issues and are not discussed here. We also do not consider the use of the ^{14}C content of water-insoluble organic compounds to date glacier ice, which was recently reviewed by Uglietti et al. (2016). In this paper, we first review the problems of sampling, quantifying and interpreting the environmental relevance of organic molecules in ice. We then undertake a broad discussion of the different classes of organic compounds that might yield environmental information. Finally, we consider each class in more detail, discussing what has already been done, and what is needed to advance the study of each class.

2 Challenges with sampling and analysis of organic molecules

2.1 General issues during sampling, storage and analysis of organics in ice and snow

The issues that determine our ability to accurately estimate the concentrations of organic molecules in ice and snow differ with each class of compounds but some general considerations are worth

86   discussing. Challenges result from three main issues: (1) individual compounds are expected to be
87   present at low concentrations (typically ng/L or lower), posing problems for analytical detection and
88   interferences caused by contamination; (2) the range of physical-chemical properties of organic
89   compounds, especially their polarity, requires a variety of extraction and analytical techniques to
90   quantify the range of organic compounds with optimal sensitivity; (3) some of the compounds may
91   not be stable against chemical reactivity, biodegradation, and volatile loss back to the atmosphere.
92   Concentrations of inorganic compounds also occur at very low levels, and ice core scientists are no
93   strangers to the need to adopt contamination-free protocols (e.g. Boutron and Batifol, 1985).
94   Nonetheless, organic compounds require different protocols, not least because the procedures
95   adopted to avoid contamination for inorganics (e.g. involving clean rooms constructed from clean
96   plastic materials, and the use of plastic sample containers) may be unsuitable for organics.

97   Field sampling of solid ice cores is challenged by the ubiquitous presence of a host of organic
98   contaminants from both the sampling process and the environment. The most obvious of these
99   impurities is the drilling fluid which keeps the borehole open during deeper ice core drilling
100 projects, and which typically consists of a poorly characterised and variable hydrocarbon mixture
101 but some compounds present in drilling fluid might also be of interest for paleo-environmental
102 markers. The main examples used in recent years are dearomatised kerosenes (D30, D40, D60, with
103 or without added densifier) (Talalay and Gundestrup, 2002), butyl acetate, and the aliphatic ester
104 Estisol series, with or without Coasol (Sheldon et al., 2014). Any such fluid freely coats the outside
105 of all deep cores and remains on the surface throughout transport and storage. However, the
106 advantage of solid ice is that it is impermeable if no cracks penetrate from the outside to the inner
107 core. Therefore, it is possible to shave the outer layer of ice that was coated in fluid, or that has been
108 in contact with plastic bags or organic materials, to obtain clean inner material. A faster way to
109 obtain uncontaminated ice samples for analysis of organic impurity contents is to melt the ice in a
110 way so only the clean inner part is used for the analysis. In this case only the inner section which
111 was never in contact with ambient air and drilling fluid is used and is pumped into a warm lab
112 where it is aliquoted, whereas the possibly contaminated water from the outer part is rejected.

113 Firn (permeable material that has not yet consolidated into ice, mostly found in the upper 60-100 m
114 of a core depending on the site) and near-surface snow are often more challenging to sample in the
115 field than the deeper, solid ice. Although drilling fluid is not present in the borehole when firn cores
116 are drilled, the cores are vulnerable to contamination from a wide range of other sources: lubricants
117 that may have been used on drill components, spilled liquid and organic vapours in the air (e.g.
118 from fuel used in generators and vehicles and in the laboratories), plastics (bags and bottles) used to
119 contain the ice, and contamination from gloves and other materials used by drillers and core
120 processors. Because of the permeable nature of firn, these materials can penetrate deep into the core
121 (including the entire ~5 cm radius) through liquid ingress and vapour diffusion. The same issues
122 arise with sampling of surface snow, though collecting large blocks from which more material can
123 be discarded may mitigate the problem. Some molecules may be partly volatile (a process that has
124 been suggested to cause loss from surface snow *in situ* (Gregor, 1991)) and so sample preservation
125 should include preventing exposure to temperature gradients (i.e. warmer temperatures during
126 transport and storage compared to sampling conditions).

127 It is difficult to determine what precautions are necessary when sampling snow and firn for
128 individual organic compounds, without first testing to discover whether those individual target
129 molecules, or related interferences, are present in possibly contaminating media such as plastic bags
130 or the atmosphere. However, general studies of organic material in firn and snow argue for the
131 necessity of storing snow samples in airtight and recently pre-cleaned glass bottles (Legrand et al.,

132 2013) or stainless-steel containers (Domine et al., 2007; Giannarelli et al., 2017; Gustafsson et al.,
133 2005) and avoiding plastics, except perhaps for a low permeability grade of Teflon such as PFAs
134 (i.e. perfluoroalkoxy alkanes). Wrapping firn cores in aluminium foil instead of, or as well as,
135 plastic is also a precautionary measure, which also limits the possibilities for photochemical
136 degradation of some molecules. Maintaining samples in the solid phase rather than as melted
137 samples is preferable for long term storage. However, melted samples can be spiked with $HgCl_2$ to
138 prevent microbial degradation (Kawamura et al., 2012). For some organic molecules, such as MSA
139 it has been shown that diffusional loss through solid ice can be prevented if samples are refrozen as
140 discrete samples (Abram et al., 2008).

141 In the laboratory, similar precautions are necessary in order to avoid additional contamination from
142 ambient air and possible loss of the analytes. Traditional clean laboratories used by ice core analysts
143 are designed to be low in metal contaminants, but as a result often include numerous plastics, and
144 have particle filters that do nothing to exclude organic vapours. Although it will not always be
145 practical, metal surfaces, ceramic knives, glass and perhaps PFA containers are desirable for trace
146 organic work.

147 For solid ice, removing the contaminated outer layers of a sample is necessary not only to minimise
148 possible interferences related to coelution in chromatography, matrix effects and competitive
149 ionisation (e.g. if mass spectrometry is used) with analytes of interest likely to be at much lower
150 concentrations than that of the contaminants. Shaving 1 cm from the outside of cores using a
151 ceramic knife is a commonly used technique (Seki et al., 2015). In following such a procedure, it is
152 critical to avoid transferring contamination from the outside of the core towards the inside on the
153 surface of the knife. Researchers should always scrape in the same direction and should remove ice
154 in a sequence of layers, using a succession of clean knives as used for trace elements analyses
155 (Candelone et al., 1994). Alternative methods involving rinsing the ice with ultrapure water to
156 remove contaminated outer layers are also a common practice (e.g Zennaro et al., 2015). It is not
157 clear whether removal of 1 cm of ice is sufficient for cracked ice or firn and will depend on the
158 extent and length of the cracks. Due to this uncertainty, sampling radially across an ice core to
159 determine how far external contaminants have penetrated (Boutron and Batifol, 1985) is a necessity.

160 In recent years, the most popular method for sub-sampling ice cores for inorganic analysis is to melt
161 them on a hot plate, directing only the inner portion of melt to analytical systems in continuous flow
162 analysis (CFA). A similar system for organics might be achievable, but will require many tests to
163 see whether the hotplate and tubing materials are suitable or whether the melter temperatures alter
164 the organic content either due to evaporation, thermal degradation or chemical reaction.

165 Once a clean subsample has been obtained, the issues of contamination control are similar to those
166 encountered in any organic geochemistry laboratory that analyses samples with low concentrations
167 (Section 2.2). In this respect, one way to minimise contamination is to carry out extraction *in situ* as
168 soon as possible after sampling and storage of organic extracts either in liquid-phase (Fuoco et al.,
169 2012; Kang et al., 2012; Giannarelli et al., 2017; Vecchiato et al., 2015) or solid-phase extraction
170 materials (Dickhut et al., 2005; Lacorte et al., 2009). A final comment is that the issues discussed
171 above apply to organics as a whole. There may be specific molecules of interest that are not found
172 in significant quantities in drilling fluids, coatings on plastic and in the laboratory environment.
173 However, determining molecules that are not affected by plastic or drilling fluid contamination can
174 only be ascertained by quality control testing for each molecule and in each laboratory. Analytical
175 procedures that are highly selective for a particular molecule of interest (excluding background
176 contamination from interferents) will be advantageous from this viewpoint.

2.2 Analytical methods

Here we discuss methods for sample preparation and analysis of organics in polar ice and snow. The discussion focuses on specific markers and does not describe analytical methods for non-specific compounds that are routinely measured such as greenhouse gases in air bubbles. A more detailed list of methods for each discussed compound/compound class and method performance are available in Section 3 and in Table 1. In cases where many studies exist (e.g. MSA) we only cite a few studies describing the analytical method and its performances. This compilation includes prospective compounds that have not yet been measured in polar ice and snow but have been measured in mountain glaciers.

2.2.1 Glassware, solvent and reagent decontamination

A common practice for trace organic analysis is to use high purity solvents (or distilled solvents) and prebaked or prewashed inorganic reagents (Sankelo et al., 2013; Xie et al., 2000). For specific compounds, like fatty acids, solvents may be a large source of contamination that can be reduced by redistillation (Bosle et al., 2014). Common procedures for decontamination of plastic and glassware for inorganic analysis include soaking in ultrapure water, sonication for a typical time of 10-15 mins and additional rinsing (generally three times) with ultrapure water (Jauhiainen et al., 1999). This procedure has proven to be effective for removing inorganic contamination but other procedures are preferable for organics. Müller-Tautges et al. (2014) cleaned all glass containers by baking them at 450°C for 8 h. Similarly, Gowda et al. (2016) prebaked all glassware at 450°C overnight, followed by rinsing with ultrapure water, methanol and dichloromethane. Rinsing with *n*-hexane (after water and dichloromethane) is also recommended (Piazza et al., 2013) when measuring hydrophobic compounds.

2.2.2 Sample preparation and analysis

Organic compounds are present in polar ice and snow samples at trace levels that may challenge many state-of-the-art analytical methods and techniques. For this reason, the vast majority of studies so far have included a pre-concentration step (e.g. Garmash et al., 2013; Grieman et al., 2015; Legrand et al., 1997; McConnell et al., 2007; Pokhrel et al., 2015) with the exception of levoglucosan and vanillic acid which are most commonly analysed without pre-concentration (e.g. Gambaro et al., 2008; Zennaro et al., 2015). The most widely used pre-concentration method is solid phase extraction (SPE) which is applied to non-polar anthropogenic compounds, like polycyclic aromatic hydrocarbons (PAHs), pesticides, polychlorinated biphenyls (PCBs) and per- and polyfluoroalkyl substances (PFASs). For non-volatile compounds, another common pre-concentration method is solvent evaporation, often using a rotary evaporator (Fu et al., 2016; Kawamura, 1993; Pokhrel et al., 2015; Pokhrel et al., 2016). For some compounds stir bar sorptive extraction has shown potential (Müller-Tautges et al., 2014), however SPE via cartridge and disc materials are currently more versatile due to the availability of a wider range of sorbents, which allows more targeted method optimisations. For volatile compounds, such as volatile halogenated hydrocarbons, purge-and-trap injections, followed by GC-MS analysis, has been used as a preconcentration method for the analysis of Antarctic snow (Zoccolillo et al., 2005).

For PAHs, SPE leads to recoveries of >80% in Antarctic snow, with a starting sample volume of 10 L and limits of detection (LODs) of 0.1 ng/L using GC-MS analysis (Na et al., 2011). For the same compounds, Gabrieli et al. (2010b) used online SPE on a CFA system and obtained a recovery of 71-93% and LODs ranging between 0.007 and 0.466 ng/L using HPLC with fluorescence detection using an initial sample of 250-500 g of melted ice. Kukučka et al. (2010) achieved both

lower sample volume and lower LODs using solid phase micro-extraction (SPME) followed by thermal desorption and GC-MS analysis. This method gave good recoveries for small PAHs but it did not give satisfactory recoveries for PAHs with 4-6 rings (Table 1). Liquid-liquid extraction (LLE) for PAHs followed by GC-MS has also been used, reaching similar LODs to those of Gabrieli et al. (2010b) but starting with a much larger sample volume of 7 L (Fuoco et al., 2012). SPE has also been used for a range of different pesticides (e.g. aldrin, DDT), PCBs and PFASs reaching recoveries of >80% and LODs in the order of a few pg/L (Table 1).

For MSA analysis, a pre-concentration method similar to SPE using a Trace Anion Concentrator (TAC) with an anion exchange sorbent installed on-line in the ion chromatograph has achieved LODs of 20 ng/L with a 5 mL starting volume (Curran et al., 2003; Saltzman et al., 1997). Conversely, Jauhiainen et al. (1999) used a large loop injection (0.8 mL) reaching LODs of 300 ng/L. Saltzman et al. (2006) reached LODs of 100 ng/L using direct injection with an electrospray ionisation source – triple quadrupole mass spectrometer (ESI-MS/MS) upon sample dilution with methanol (50:50), however direct infusion in an ESI source without prior chromatographic separation has been often criticised for being non-quantitative due to competitive ionisation from non-separated matrix components (Kourtchev et al., 2014).

SPE was used also for pre-concentration of both natural and anthropogenic *n*-alkanes, *n*-alkan-2-ones and *n*-alkanoic acids prior to analysis with gas chromatography flame ionisation detection (GC-FID) and GC-MS however recoveries and LODs are not reported (Xie 2000). Fatty acids have also been pre-concentrated by LLE and solvent evaporation using a rotary evaporator (rotavap). Seki et al. (2015) effectively concentrated fatty acids in LLE, followed by saponification with KOH in methanol and derivatisation with N,O-Bis(trimethylsilyl)fluoroacetamide (BSTFA) before analysis by GC-MS, showing recoveries of 75-82%. Pokhrel et al. (2015) concentrated the samples with a rotavap (100 mL evaporated to dryness) with recoveries >70% and LODs of 1 ng/L with derivatisation with BF_3/butanol followed by GC-MS. A similar method was used for analysing monoterpene and isoprene secondary organic aerosol (SOA) products showing analogous performances (Pokhrel et al., 2016). Pokhrel et al. (2016) used a rotavap and 150 mL of melted ice after addition of KOH to convert organic acids into potassium salts making them less volatile, followed by derivatisation with BSFTA and analysis in GC-MS. Similarly, Kawamura et al. (2012) quantified dehydroabietic acid, p-hydroxybenzoic acid, levoglucosan, mannosan and galactosan (all biomass burning markers) by using GC-MS after LLE (80-250 mL of sample) and derivatisation with BSTFA reaching LODs of 3-5 ng/L with recoveries of 67-78%. You et al. (2014) obtained similar performances for levoglucosan, mannosan and galactosan with a smaller ice volume of 5 mL (Table 1).

Levoglucosan is one of the most widely used biomass burning markers. Gambaro et al. (2008) developed an analytical method for levoglucosan analysis based on direct analysis of melted ice with HPLC-ESI(-)-MS/MS and LOD of 3 ng/L. This analytical method is sensitive for ultratrace determination of levoglucosan in Arctic and Antarctic matrices but it is not able to distinguish levoglucosan from its isomers, galactosan and mannosan. In addition, when this method is applied to continental ice cores, where the matrix generally contains many more impurities, it appears to be less robust (i.e. higher LOD and lower accuracy and repeatability) due to strong matrix effects that reduce the analytical performance (Yao et al., 2013). Yao et al. (2013) developed a new HPLC/ESI-MS method that separates levoglucosan from other coeluting water-soluble organic compounds with small sample volumes of a few mL. This method allows the simultaneous quantification of all three isomers, however LODs are more than 1000 times higher than for the method proposed by Gambaro et al. (2008) (10,000 ng/L in Yao et al. (2013) and 3 ng/L in Gambaro et al. (2008)).

267   Grieman et al. (2015) developed an analytical method for the analysis of vanillic acid, another
268   biomass burning marker, based on HPLC-ESI-MS/MS which allows fast detection (4 minutes) with
269   a low sample requirement (injection volume of 100 μL) resulting in a LOD of 77 ng/L. Vanillic
270   acid was measured also in ESI(-)-MS/MS upon dilution (50:50) with methanol online in a CFA
271   system (McConnell et al., 2007). Although being able to detect organics online on a CFA system in
272   parallel with the quantification of inorganic compounds would be ideal, analysis by direct infusion
273   is likely to suffer more matrix effects than offline chromatographic methods. Future research is
274   needed to push forward fast chromatographic methods with low detection limits and requiring low
275   sample volume.

2.3   General issues about interpreting organics in terms of environmental variables

277   Interpreting proxies in terms of useful environmental variables is always complex, usually
278   involving issues of production, provenance, transport, lifetime and preservation in the archive.

279   In the case of polar ice caps, the distance from source to archive is considerable. The Arctic is a
280   "Mediterranean"-style sea, surrounded by boreal forests and by land masses that contain most of the
281   world's population and hence anthropogenic sources. Greenland, in particular, is relatively close to
282   North America, but long-range transport from Asia and Europe can also occur (Kahl et al., 1997). In
283   contrast, Antarctica is entirely surrounded by ocean. Terrestrial and anthropogenic emissions have
284   to be transported in the atmosphere across the Southern Ocean from South America, Africa and
285   Australia. Despite the barrier of distance and circumpolar winds, anthropogenic molecules do reach
286   Antarctica (Kallenborn et al., 2013).

287   The concentration of a compound archived in an ice core results (sequentially) from (a) its rate of
288   emission from the source (often the variable that really interests us), (b) the location of that source,
289   whose position may change with climate, (c) the proportion of emitted material that arrives over the
290   ice core site (which in turn depends on the transport speed and lifetime), (d) deposition processes,
291   and (e) subsequent loss processes. An additional factor is that many biological emissions are
292   seasonal, so it may be seasonal rather than annual parameters that determine the role of each
293   process mentioned here.

294   In particular, many aerosol species suffer from the fact that their lifetime before deposition is of a
295   similar magnitude to their transport time from source regions (on other continents, or the
296   surrounding ocean) to Greenland or Antarctica, so that changes in meteorological factors causing
297   changes in transport time or lifetime (often controlled by precipitation) compete with changes due
298   to varying source strength. Simple models have been used to correct for these changes across major
299   climatic changes (such as glacial-interglacial transitions) in the case of inorganics such as terrestrial
300   dust and ammonium (Fischer et al., 2015; Fischer et al., 2007). Some of these issues are avoided
301   when the source is quite close to the ice core site, but this proximity is rarely the case for
302   measurements on polar ice sheets. During relatively short time periods, it may be possible to
303   interpret changes in time while ignoring these considerations. One example of such a situation are
304   persistent organic pollutants (POPs) whose sources increased strongly through the last century.
305   However, natural biogenic emissions are likely to partly change in response to climate variability
306   and therefore separating out climatic influences on the source from other influence factors is tricky.

307   Most inorganic compounds are chemically stable, and so their lifetime is mainly determined by
308   depositional processes. However, the atmospheric lifetime of many organics is also influenced by
309   photo- and thermo-chemical transformations in the atmosphere that may degrade them, or in some
310   cases form them *en route* to the polar regions (Kawamura and Bikkina, 2016). Some organic

molecules may also be re-volatilised or chemically degraded after deposition which may change the proportional loss of the molecule (Kawamura et al., 2001). For example, changing snowfall rates alter the period of time in which chemicals are exposed to sunlight in the snowpack or when changes in snowpack temperature occur (Wolff, 2012). In the best cases, it may be possible to interpret time series of organics in ice with simple analytical methodologies and a straightforward interpretation. However, for more complex molecules an atmospheric modelling approach (using either a transport model, or a chemistry and transport model) may be needed in order to determine what part of the variability can be attributed to changes in source strength (Levine et al, 2011a; Levine et al., 2011b; McConnell et al., 2007; Vecchiato et al., 2015).

The complexities discussed here are applicable to analysis of time series of individual molecules. Comparing multiple organics in the same ice core can help determine the impacts of these complexities. For example, ratios of chemicals with similar source regions and transport, such as ratios of different long chain hydrocarbons, or isotopologues of the same chemical can help resolve the impacts of atmospheric transport on the investigated molecule.

3   Organic molecules as environmental proxies

Goldstein and Galbally (2007), estimate that 10^4-10^5 separate organic compounds are in the atmosphere. How do we then prioritise which molecules are interesting to investigate in ice cores? The answer must come from a confluence of our ability to measure these compounds in ice and the environmental questions that we would like to answer. Examples of organic markers that have already been detected in ice cores and yielded environmental information are reported in Figure 1. In this section, we outline important environmental aspects and discuss the organic molecules in ice cores that can address these aspects.

3.1   Terrestrial biogenic markers

The terrestrial biosphere is the largest emitter of both primary organic aerosols and volatile organic compounds (VOCs) where a fraction of the VOCs is oxidised in the atmosphere forming SOA. VOCs and SOA in ice cores may elucidate how the terrestrial biosphere has changed in recent decades due to anthropogenic land use changes, as well as across rapid climate changes or glacial-interglacial transitions. Measurements of compounds associated with primary emissions (such as leaf waxes) reflect the size of the biosphere while the relative proportions of these compounds may provide information on the composition of the relevant part of the biosphere. Clearly, given the distance of Greenland and especially Antarctica from source regions, interpretation in terms of which source is being sampled and how other factors have influenced the concentrations recorded will be critical for these molecules.

Biogenic VOCs, particularly isoprene and terpenes, are crucial in the atmosphere for many reasons. Emission rates are again expected to scale with the size and composition of the biosphere, modulated by emission factors related to climate. These molecules also play two crucial roles in the atmosphere. They are also a major control on the hydroxyl radical ($\cdot$OH) concentration in the atmosphere; constraining $\cdot$OH concentrations over time would be of interest for many reasons, not least in limiting the causes of methane change over time (Levine et al., 2011b). In addition, biogenic VOCs are on a global level the most important source of SOA, which is increasingly implicated as an important factor in the growth of cloud condensation nuclei (Trostl et al., 2016). It would therefore be very valuable to have proxies for VOC emissions, which will be complicated not only by transport effects but also by lifetime limitations caused by chemical degradation.

354   The recent identification of a multitude of biogenic organic markers in snow and ice samples
355   situated both near and far from source regions raises the exciting potential of new environmental
356   proxies that are present in the ice core record. Such compounds have, for example, been found in
357   Alaska (Pokhrel et al., 2015; Sankelo et al., 2013; Yamamoto et al., 2011), the Chinese Himalayas
358   (Xie et al., 2000), Greenland (Grannas et al., 2004; von Schneidemesser et al., 2008), Franz Josef
359   Land, Russia (Grannas et al., 2006), the Tibetan Plateau (Shen et al., 2015) and the Canadian Arctic
360   (Grannas et al., 2004), as well as in oceanic aerosol samples in the Canadian high Arctic (Fu et al.,
361   2013) and over ocean latitudes ranging from the Arctic to Antarctica (Hu et al., 2013). Here we
362   discuss the terrestrial organic compounds so far identified in snow or ice samples, or high latitude
363   atmospheric aerosols, that are most promising as biomarkers in ice.

364   *3.1.1   Primary emissions*

365   A number of lipid-based compounds with terrestrial sources have been shown to have long-range
366   transport potential in atmospheric aerosols, and to subsequently be preserved within ice layers. *N*-
367   alkanes, *n*-alkenes, *n*-alkanols, and *n*-alkanoic acids are sourced from terrestrial leaf epicuticular
368   waxes, soil dust, microbial processes or marine phytoplankton (Pokhrel, 2015). Specifically, lipid
369   compounds in epicuticular waxes are plucked from the leaf surface in high winds and entrained in
370   the atmosphere as primary aerosols (Yamamoto et al., 2011), and their concentrations may be
371   expected to demonstrate a record of biogeochemical cycles such as the relative amount of deciduous
372   vegetation and associated carbon storage (Kawamura et al., 1996). Relatively resistant to
373   degradation (Pancost and Boot, 2004), these lipid-based compounds persist in the atmosphere at
374   time scales of days to weeks which allow long-range transportation.

375   The process of emission, long range transport, deposition and entrainment of lipid-based
376   compounds within snow and ice has been demonstrated in previous work, from both shallow snow
377   pit studies and now extending back to ice layers on the order of several hundred years in age.
378   Identification within shallow snow pits in Japan (Sankelo et al., 2013; Yamamoto et al., 2011) and
379   China (Xie et al., 2000) demonstrate the potential of terrestrial organic compounds to be preserved
380   in snow layers, with the major source of the lipid compounds being large forested regions found
381   more proximally to the deposition sites. Extending to more far-reaching deposition sites, De
382   Angelis et al. (2012) observed terrestrial vegetation and biomass burning emissions dominating the
383   carboxylic acid budget within surface snow layers at Summit, Greenland, concluding that aerosols
384   generated by Northern Hemisphere terrestrial biomass are an important contributor to aerosol
385   deposits in the ice record at this high latitude location. Lipid compounds have further been detected
386   in snow layers dating back to 450 years at Site J in Greenland (Kawamura et al., 1996). Although
387   air masses that pass over Greenland contain a more complex mixture of both marine and terrestrial
388   organic aerosols, Kawamura et al. (1996) were able to identify compounds of specific terrestrial
389   origin using a number of distinguishing molecular characteristics (see below), which have been
390   used and expanded on in subsequent studies (Bendle et al., 2007; Pokhrel, 2015; Yamamoto et al.,
391   2011).

392   Lipid compounds from terrestrial sources may be identified as high molecular weight fatty acids
393   (HFA) (>C24), as opposed to low molecular weight fatty acids (LFA) (<C24) which are indicative
394   of marine and microbial sources (Pokhrel, 2015; Yamamoto et al., 2011). Terrestrial particles may
395   further be distinguished from those of anthropogenic sources using the Carbon Preference Index
396   (CPI), determined as the ratio of compounds with odd to even carbon numbers. CPI values >5
397   signify an absence of anthropogenic input, whilst values decreasing down to 1 imply an increasing
398   anthropogenic contribution. Furthermore, the average chain length (ACL) within the different

399   compound groups has been utilised as evidence of specific source regions. Within the *n*-alkane
400   group, for example, greater abundance of longer chain HFAs may indicate warm, tropical source
401   regions, whereas a greater abundance of shorter chain HFAs would suggest more temperate source
402   regions (Bendle et al., 2007). Calculating HFA to total organic carbon (TOC) ratios was further
403   used to identify a tentative link between this ratio and warmer or cooler periods of global
404   temperatures. There were, however, a number of possible explanations of higher ratio values
405   (higher plant emissions, enhanced atmospheric transport, increased area of arid environments, and
406   altering atmospheric transport pathways), and the idea needs refining (Bendle et al., 2007).

407   To date, these lipid compounds have been studied in a limited manner in snow and ice from Alaska,
408   Greenland and lower latitude glaciers (Table 1). It will be far more challenging to detect them in
409   Antarctica, which is further from any terrestrial sources.

410   *3.1.2   Secondary oxidation products*

411   Isoprene and terpenes are emitted from all plants including algal sources in ocean regions (Bonsang
412   et al., 1992; Yassaa et al., 2008) and form a significant contribution to the hydrocarbon budget of
413   the atmosphere (Sharkey et al., 2008). In particular, isoprene and monoterpenes have been
414   measured as significant terrestrial emissions, with isoprene dominating in flux studies above
415   Amazonian forest canopies (Kesselmeier et al., 2000; Rinne et al., 2002) and on a global level.
416   Sesquiterpenes also contribute to terrestrial emissions, although flux and oxidation pathways of
417   emissions are difficult to study because of their very high reactivity and lower concentrations (Fu et
418   al., 2013). The emission of isoprene and terpenes is conditional on both heat and light, and is
419   therefore proposed as a 'thermo-tolerance mechanism' of plants (Sharkey et al., 2008). The reactive
420   nature of isoprene and terpenes in the atmosphere presents a limitation to the potential for long
421   range transport from the emission site; isoprene, monoterpenes and sesquiterpenes have short
422   chemical lifespans from a few minutes up to a few hours (Kesselmeier et al., 2000), and have not
423   been directly observed in ice. However, the oxidation products of these compounds in both gas and
424   aerosol phase demonstrate a greater potential for longevity in the atmosphere, and possible
425   subsequent deposition into snow and ice further from the source region.

426   Isoprene and terpenes emitted by vegetation are subject to several possible degradation processes in
427   the atmosphere, each of which may or may not result in the formation of SOA (Hallquist et al.,
428   2009) with a multitude of secondary products forming from each primary compound. Table 2 lists a
429   compilation of isoprene and terpene-sourced SOA compounds identified over a range of forested
430   canopy locations and in snow samples from more remote locations. Despite this complexity, and
431   with both degradation pathways and atmospheric concentrations still needing further study (Kroll et
432   al., 2011), a transition in detection of some key SOA components from laboratory-confined
433   experiments to detection in natural atmospheric samples, as well as in some surface snow and ice
434   core studies, provides promising results for use of SOA constituents as climate markers (Fu et al.,
435   2009; Fu et al., 2016; Pokhrel et al., 2016).

436   Isoprene has been identified as the largest non-methane VOC emission globally, at ~600 Gt/yr
437   (Guenther et al., 2006). Thus, even a very small percentage of VOC to SOA transformation rates
438   could be significant in the total particulate organic matter budget of the atmosphere (e.g. 6 Gt/yr at
439   only 1% yield) (Carlton et al., 2009). Claeys et al. (2004a) first recognised two isoprene oxidation
440   products, 2-methylthreitol and 2-methylerythritol, in Amazonian air samples, bolstered by the
441   association of two gas-phase products of the oxidation process, methacrylic acid and methacrolein,
442   providing a reaction-pathway linking isoprene and the identified SOA composition (Claeys et al.,
443   2004b). It was later shown by Xia and Hopke (2006) that these compounds demonstrate the same

seasonal cycle (peak concentrations during summer) as isoprene in forests in the north-eastern United States. The compounds have now been identified in a number of forest-canopy aerosol samples (e.g. Finland (Kourtchev et al., 2005) and Hungary (Ion et al., 2005), and demonstrate the important contribution of isoprene oxidation products to total atmospheric SOA concentrations. However, highly variable lifetimes for these secondary compounds have been suggested (Noziere et al., 2015), which may limit the number of compounds available for consideration.

Methylthreitol (an isoprene SOA marker), pinic acid and pinonic acid (monoterpene SOA markers) were estimated to have short lifetimes of only 0.2 days by Noziere et al. (2015), clearly limiting transportation to high latitudes where transport to polar regions may require days. Others, such as MBTCA (3-methyl-1,2,3-butanetricarboxylic acid as a monoterpene SOA marker), nocaryophyllonic acid, caryophyllinic acid and nocaryophyllinic acid (sesquiterpene SOA markers), were estimated to have lifetimes up to 10 days. These values are highly uncertain but in general agree with SOA lifetimes as modelled using global chemistry transport models and general circulation models; with a review of 31 such models by Tsigaridis et al. (2014) finding an average range of SOA atmospheric lifetimes of 2.4-15 days. To further add to this uncertainty, Hu et al. (2013) identified both pinic acid and MBTCA in high latitude samples of atmospheric aerosol, of which a significant contribution to the total concentrations were identified as terrestrially sourced compounds based on atmospheric transport pathway reconstruction for the supplying air masses. More substantially, isoprene and monoterpene oxidation products, including many of those products with proposed short lifetimes of less than 0.2 days, have also been identified in an Alaskan ice core dating back 350 years. For example, Pokhrel et al. (2016) identified a number of terrestrial and marine sourced SOA compounds within the ice samples (Figure 1a), using atmospheric transport pathway reconstruction to determine the compounds' source region. Thus, these compounds demonstrate not only the atmospheric transport and deposition of SOA with terrestrial sources, but also the persistence of these compounds to older ice layers. Many of the observed concentration changes were correlated with Northern Hemisphere temperature fluctuations using a combination of compound groups as well as individual compounds for comparisons (Pokhrel et al., 2016). This observation suggests also that lifetime of these compounds in the particle phase may be longer than estimated, perhaps because SOA particles may have low viscosities limiting uptake and diffusion of oxidants (Virtanen et al., 2010). If the study of these compounds is extended to Antarctica, it will be necessary to distinguish compounds with mainly terrestrial sources from those with mainly marine origins. One method is to test for a temporal correlation between the organic markers of interest and uniquely terrestrial molecules, such as the biomass burning marker levoglucosan, or to compare the results against uniquely marine emissions such as MSA, an approach used by Fu et al. (2013).

While there is still much to be investigated regarding SOA compound characteristics, their detection in natural samples in high latitude regions seems to suggest the potential for using these compounds as biomarkers in ice. Furthermore, the ever-expanding number of identified monoterpene oxidation products, e.g. at least 24 monoterpene-derived organic compounds identified above a boreal forest in Hyytiala, Finland (Kourtchev et al., 2013) provides an ever-increasing scope of promising marker compounds, of which any number may have sufficient lifetimes allowing transport and deposition to polar snow.

The groups of compounds discussed here offer excellent potential as biomarkers in ice cores. In the northern hemisphere (Greenland), multi-compound studies could, in conjunction with broad determination of their source regions (for example, terrestrial versus marine), allow investigation of past changes in the extent and climate of boreal forests. The same application has yet to be

489 thoroughly tested for the southern hemisphere, where the compounds may be expected in even
490 lower concentrations.

3.2   Indicators of Biomass Burning

492 Biomass burning is a special case of terrestrial emissions that has received considerable attention.
493 Again, there is interest in quantifying shifts in biomass burning due both to climatic variations and
494 anthropogenic activity. Much of the literature about biomass burning records in ice cores is based
495 on inorganic or small organic molecules that have multiple sources but whose spikes are considered
496 to be indicative of biomass burning. Legrand et al. (2016) and Rubino et al. (2016) recently
497 reviewed these indicators and therefore we will not discuss them here. Black carbon, emitted during
498 incomplete combustion of fossil fuel and biomass in both natural and anthropogenic fires, is not
499 discussed in this review as it is not an organic chemical. Organic molecules can provide more
500 specific markers for burning, and in some cases for the type of material being burnt. However, the
501 episodic nature of burning events poses a challenge when examining changes in biomass burning
502 through time.

503 Methane and carbon dioxide are important greenhouse gases emitted from a wide range of natural
504 and anthropogenic sources. The isotopic ratio of atmospheric gases, such as methane and carbon
505 monoxide, in Antarctic (Ferretti et al., 2005; Wang et al., 2010) and Arctic (Sapart et al., 2012;
506 Wang et al., 2012) ice cores can be used as a fire proxy. These are also not discussed in this review,
507 which focusses on organic material found in the snow/ice phase.

508 Many potential proxies of past fire activity are found in polar snow. The majority of these tracers
509 are directly produced and volatilised during vegetation combustion (e.g. polycyclic aromatic
510 hydrocarbons, black carbon) or as partially combusted biological material (e.g. resin acids, anhydro
511 sugars) (Conedera et al., 2009). Biomass is a biopolymer mainly formed by cellulose,
512 hemicellulose, lignin and fillers (Simoneit, 2002). Cellulose is the main constituent (~30 %) of
513 woody tissue, where its structure of long linear chains of D-glucose monomers is responsible for the
514 structural strength of wood. Hemicellulose is a more complex mixture of polysaccharides derived
515 from glucose, mannose, galactose, xylose and arabinose and is less abundant than cellulose in the
516 woody tissue. Lignin is derived from the polymerisation of *p*-cumaryl, conyferyl and sinapyl
517 alcohols. Thus, the structure of this biopolymer mainly contains anisyl (phenols), guaiacyl
518 (methoxy-phenols) and syringyl (dimethoxy-phenols) nuclei, which are released during lignin
519 pyrolysis (Simoneit, 2002).

520 Fire products are first released into the atmosphere and may then be transported to polar regions.
521 Deep convection, generated by sensible heat released during fires, rapidly lifts the smoke plumes
522 and injects pyroproducts into the atmosphere. Biomass burning plumes from forest fires can reach
523 the upper troposphere and lower stratosphere, where the atmospheric lifetimes and the transport
524 efficiency of aerosols are greater than near the surface (Damoah et al., 2004; Dentener et al., 2006;
525 Hodzic et al., 2007; Trentmann et al., 2006). Nonetheless biomass burning plumes are often
526 relatively short lived. This timing creates the complication that individual fires may be recorded at
527 one location (for example in Greenland), but may not be recorded at others, either because the
528 plume did not pass over both sites, or because there was no snowfall during the passage of the
529 plume. Biomass burning signatures in ice are therefore best treated as a statistical sampling of
530 burning rather than a faithful one to one record.

531 Some biomass burning proxies are specific as they are produced solely from biomass burning, e.g.
532 monosaccharide anhydrides, but other proxies have multiple potential sources other than vegetation

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533 fires (e.g. coal burning or biogenic emissions). Here we focus on specific organic markers and how
534 combinations of markers can give additional information.

535 *3.2.1   Monosaccharide Anhydrides*

536 The most abundant monosaccharide anhydrides are levoglucosan and its isomers mannosan and
537 galactosan which are specific proxies for vegetation combustion products (Gambaro et al., 2008;
538 Simoneit, 2002; Zennaro et al., 2014). Levoglucosan (1,6-anhydro-β-D-glucopyranose) is a
539 monosaccharide anhydride which is released only during the pyrolysis of cellulose at temperatures
540 >300°C (Gambaro et al., 2008; Simoneit, 2002). Galactosan and mannosan are released into the
541 atmosphere during the pyrolysis of hemicellulose (Simoneit, 2002). The ratio between levoglucosan
542 and its isomers may help to differentiate contribution of different fuel loads (i.e. lignite,
543 angiosperms, gymnosperms) to the biomass burning signature detected in environmental samples
544 (Engling et al., 2006; Fabbri et al., 2009). These ratios were utilised by Kirchgeorg et al. (2014) in
545 sediment samples and in ice samples from the Ushkovsky, Kamchatka Peninsula, ice core
546 (Kawamura et al., 2012), but no attempts exist in polar ice core samples.

547 Levoglucosan may be oxidised by ·OH in the gas phase (Hennigan et al., 2010) and in atmospheric
548 water droplets (Hoffmann et al., 2010), resulting in an atmospheric lifetime on the order of days to a
549 few weeks (Fraser and Lakshmanan, 2000; Hennigan et al., 2010; Ramanathan and Carmichael,
550 2008). Levoglucosan, therefore, is a suitable tracer for the quantification of fire activity even to
551 remote locations due to its high concentration in vegetation fire plumes (Fraser and Lakshmanan,
552 2000; Holmes and Petrucci, 2006, 2007; Kehrwald et al., 2012; Zennaro et al., 2014). Kehrwald et
553 al. (2012) demonstrated the applicability of the levoglucosan analyses to reconstruct past fire
554 activity in Greenland snow pits with a known fire signature in August 1994 caused by biomass
555 burning plumes originating in Canada and transported eastward to Greenland within a matter of
556 days.

557 Zennaro et al. (2014) reconstructed fire activity during the past 2 millennia from analyses of
558 levoglucosan, black carbon and ammonium in the North Greenland Eemian Ice Drilling (NEEM)
559 ice core (Figure 1b). All three markers simultaneously recorded some fire events over the past 2,000
560 years, thus demonstrating the applicability of these markers in recording intense vegetation fires.
561 Combining specific biomass burning tracers (i.e. levoglucosan and vanillic acid (see next section))
562 and black carbon analyses helps distinguish between anthropogenic activities such as fossil fuel
563 combustion and biomass burning (McConnell et al., 2007; Zennaro et al., 2014). However, the lack
564 of strong correlations between levoglucosan and black carbon in the NEEM ice core over the
565 preindustrial era suggests that differences in emission, atmospheric stability and transport must be
566 carefully evaluated when comparing different biomass burning proxies (Zennaro et al., 2014).

567 *3.2.2   Lignin and conifer resin pyroproducts*

568 Lignin is an important constituent of vegetation, and consists of a more variable and complicated
569 structure than cellulose. Burning lignin releases a wide variety of compounds (Simoneit, 2002), and
570 in particular methoxy- and dimethoxy-phenols which can be detected in Antarctic aerosols
571 (Zangrando et al., 2013). Vanillic acid is a methoxy phenolic acid and it is one of the most abundant
572 products of conifer lignin combustion, and thus is a specific marker for conifer combustion
573 (Simoneit, 2002). McConnell et al. (2007) used black carbon and vanillic acid measurements along
574 the D4, Greenland, ice core to discriminate natural and anthropogenic origins of black carbon
575 reaching Greenland over the past two centuries. McConnell et al. (2007) concluded that the major
576 source of preindustrial black carbon to Greenland was conifer combustion.

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577 Specific tracers for biomass burning, including phenolic compounds such as vanillic acid (pyrolysis
578 product of conifers), p-hydroxybenzoic (specific marker of grass combustion), dehydroabietic acid
579 (specific marker of conifer resin combustion) and levoglucosan were quantified in high and mid-
580 latitude ice cores from the Kamchatka Peninsula in northeast Siberia (Kawamura et al., 2012).
581 However, determination of the type of burned biomass based on the presence of dehydroabietic acid
582 and levoglucosan gave different results from those suggested by ratios between levoglucosan and its
583 isomers (Kawamura et al., 2012), possibly due to different atmospheric lifetimes and natural
584 abundance of the tracers. The largest peaks of *p*-hydroxybenzoic and vanillic acid are coeval with
585 those of levoglucosan, suggesting that similar geographic sources, as well as similar long-range
586 transport paths apply to each.

587 *3.2.3   Polycyclic Aromatic Hydrocarbons (PAHs)*

588 PAHs are produced by both biomass burning and fossil fuel burning (Macdonald et al., 2000 and
589 references therein) (see also 3.4.3). The ratio of specific PAHs released during vegetation
590 combustion may help identify samples containing forest fire signatures (Li et al., 2011; Masclet et
591 al., 2000; Slater et al., 2002). In addition, burning vegetation produces carbon particles and gases
592 containing "modern" levels of ^{14}C, while compounds from fossil fuel combustion do not contain the
593 heavy carbon isotope (Slater et al., 2002). Combining PAH ratios with black carbon concentrations
594 and isotopic ratios of greenhouse gases can help differentiate biomass sources from anthropogenic
595 sources.

596 One of the most specific PAHs is retene, a PAH released during boreal forest fires. Fluoranthene
597 and pyrene, the two most abundant PAHs in superficial Greenland snow, are generally associated
598 with vehicular, industrial and biomass combustion including from household heating resulting in
599 seasonally-varying polar concentrations (Masclet et al., 2000; Slater et al., 2002). Other PAHs (i.e.
600 benzo[ghi]-perylene, benzo[e]pyrene) are mainly released by traffic sources (Li et al., 2011;
601 Masclet et al., 2000; Nielsen, 1996). Therefore, correlations between pyrene + fluoranthene and
602 sulfate indicate a common anthropogenic origin. The simultaneous deposition of retene and
603 ammonium indicate common boreal conifer fire sources, thus confirming these PAHs as good
604 tracers for biomass burning events (Masclet et al., 2000).

605 The difference in ^{14}C isotopic composition between woody and fossil fuel combustion identified
606 sources of combustion aerosols transported to Greenland in 1994 and 1995 (Currie et al., 1998).
607 Slater et al. (2002) combined radiocarbon measurements in elemental carbon and PAHs at Summit,
608 Greenland to differentiate between fossil fuel and biomass combustion contributions in the same
609 Greenland ice sample used by Currie et al. (1998). However, high errors (23%) and large sample
610 sizes (1 kg) for the radiocarbon measurements make this approach for biomass burning detection
611 difficult to apply routinely to ice core samples.

612 *3.2.4   Sources of biomass burning plumes reaching polar ice cores*

613 Generally, all of the fire reconstructions based on the chemical analyses of Greenland ice refer to
614 boreal North America as the most important geographical origin source of the biomass burning
615 plumes (Taylor et al., 1996). Zennaro et al. (2014) suggested that Central Asian forest fires may
616 also be an important contributor to fire products reaching northwest Greenland due to the
617 observations of peak fire proxy concentrations in the NEEM ice core during the most severe Central
618 Asian droughts of the last millennium. Source regions for biomass burning material reaching
619 Greenland most likely moved between the glacial and interglacial period (Zennaro et al., 2015). For
620 example, Siberian and Canadian boreal forests are likely the main sources in the Northern

621 Hemisphere of biomass burning products reaching Greenland (Zennaro et al., 2014), and ice cover
622 will have removed much of this source in the last glacial period.

623 During the glacial-interglacial transition, source regions for biomass burning in the Southern
624 Hemisphere probably remained the same as modern sources (De Angelis et al., 2012). The closest
625 possible biomass burning source regions to Antarctica are South America, Australia and Southern
626 Africa. Very little is known regarding the origin of biomass burning plumes reaching Antarctica
627 over centennial or longer timescales, especially as these timescales are dependent upon changing
628 fuel loads, circulation patterns and the atmospheric lifetime of pyrotracers. However, radiogenic
629 isotope analyses (Sr, Nd and Pb isotopes) demonstrate that the majority of dust in Antarctica comes
630 from South America over glacial-interglacial timescales, and particularly from Southern South
631 America regions such as Patagonia (Delmonte et al., 2008; Marino et al., 2008; Vallelonga et al.,
632 2010). Australia is also a possible aerosol source, especially during warm periods (Bory et al., 2010;
633 Marino et al., 2008; Siggaard-Andersen et al., 2007; Vallelonga et al., 2010). For these distant
634 sources in South America, Africa and Australia, it is necessary to consider both changes in biomass
635 burning locations, and possible increases in transport efficiency and lifetime (due to reduced
636 precipitation) when discussing glacial-interglacial record of past fire activity in Antarctic ice cores.

637 **3.3 Indicators of Marine Biogenic Activity**

638 The marine biosphere is also a source of organic emissions (Table 1). Many of the molecules
639 produced in the ocean are recorded, for example, in marine sediments, but are unlikely to be emitted
640 to the atmosphere in any significant quantity. However, a number of gases are emitted and
641 subsequently oxidised to form SOA, and organic particles are also mobilised from the sea surface.
642 Sea spray –derived aerosol particles are composed of sea salt, which is enriched with organic matter
643 when the sea surface is characterised by high concentrations of biogenic organic matter (O'Dowd et
644 al., 2004).

645 Primary organic aerosol particles are generated via wind driven bubble bursting processes, related
646 to breaking wave and near-surface wind properties in the sea surface microlayer (SML). The SML,
647 defined as the top 1000 μm of the ocean, is the boundary between the atmosphere and the ocean and
648 has distinct physiochemical and biological properties that differ from the underlying waters (Wurl
649 et al., 2017). Formed by a complex mixture of carbohydrates, proteins and lipids the enriched
650 biofilm is a potential site for enrichment of hydrophobic organic compounds (Stortini et al., 2009),
651 such as pesticides and marine pollutants which accumulate in the SML (Wurl and Obbard, 2004).

652 Marine aerosols contribute significantly to the global aerosol budget. Given that Antarctica and, to a
653 lesser extent Greenland, are surrounded by ocean, even relatively small emissions can be a
654 dominant source of some organic molecules to the ice sheet due to the proximity of the source
655 region. Ice core measurements of selected organics have the potential to reveal the impact of
656 climate on marine biogenic productivity, to assess sea ice extent, and to describe the strength of
657 winds that might mobilise material from the sea surface. Despite considerable advances in our
658 understanding of marine organic aerosols in recent years, the formation and sources remain poorly
659 constrained. Here we discuss the marine organic compounds identified in snow or ice samples and
660 the most promising marine aerosol markers not yet investigated in ice.

661 *3.3.1 Primary emissions*

662 The primary organic aerosols produced from bubble bursting typically contain homologous series of
663 oxohydroxy- or methoxy- branched fatty acids and mono-, di- and tricarboxylic acids,
664 monoterpenes and sugars (Schmitt-Kopplin et al., 2012) together with bacteria, fragments of marine

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organisms and secretions of algae (Leck and Bigg, 2005). Unsaturated fatty acids such as oleic acid ($C_{18:1}$), a major constituent of cell membranes in marine phytoplankton (especially diatoms), are abundant in the marine environment and dominate the sea surface micro layer (Hardy, 1982; Mochida et al., 2002).

Field and laboratory studies in the North Atlantic region have demonstrated that the fraction of organic matter in the submicrometer marine aerosol is higher during periods of high biological activity, such as phytoplankton blooms (O'Dowd et al., 2004). During the winter period, when biological activity is at its lowest, the organic fraction is greatly reduced. The seasonal surface-layer enrichment of organic matter, expected to be of biogenic origin such as lipids, proteinaceous material and humic substances, can also be observed by SeaWiFS remote sensing as increased chlorophyll concentrations.

In general, unsaturated fatty acids are easily decomposed during long-range transport or may be photochemically depleted (Mochida et al., 2002; Rontani et al., 2012). However, fatty acids in polar ice have been used as proxies for past changes in marine and terrestrial emission on multidecadal to centennial time scales. Oleic acid, and other unsaturated lower molecular weight fatty acids, have been detected as major species in ice cores from Greenland (Kawamura et al., 1996) and Alaska (Pokhrel et al., 2015) confirming that marine organic matter can be transported considerable distances in contrast to assumptions that the lifetime of these species is too short. The presence of fatty acids is largely unexplored in Antarctica but could potentially provide valuable indicators of Southern Ocean marine biogenic activity or atmospheric circulation, providing we understand both the biogenic activity at the source (marine boundary layer) and the physical processes responsible for their transport such as wind strength and transport pathways.

3.3.2 Secondary oxidation products

The best understood SOA component of marine aerosol is methanesulfonate or methanesulfonic acid (MSA), the oxidation product of dimethylsulfide (DMS), and the precursor compound dimethylsulfoniopropionate (DMSP) produced by phytoplankton. MSA was also one of the first organic aerosol components detected in polar ice cores (Legrand et al., 1997; Saltzman et al., 1997; Wolff et al., 2006). DMS and DMSP production in the Southern Ocean is highest within the sea ice zone, produced primarily by phytoplankton species associated with sea ice, or perhaps with sea ice retreat (Curran and Jones, 2000). When DMS oxidises in the atmosphere it creates sulfate and MSA. Sulfate has multiple possible sources including sea salts and volcanic activity while marine biological activity is the only known source of MSA in the Antarctic region. Thus, it was hypothesised that MSA preserved in ice cores could be used to reconstruct past marine productivity and sea ice coverage.

Statistically significant correlations between MSA and sea ice extent (Figure 1c) have been observed at a number of coastal sites around Antarctica (Abram et al., 2010; Curran et al., 2003; Foster et al., 2006; Thomas and Abram, 2016; Welch et al., 1993), where high MSA represents extensive winter sea ice extent. A greater sea ice extent leads to a larger area of sea ice breakup during the spring and summer, allowing for greater biological activity and DMS production. However, a converse relationship has also been observed with MSA from sites in West Antarctica, where elevated MSA represents summer productivity within the sea ice zone and the presence of open water polynyas (Criscitiello et al., 2013; Rhodes et al., 2009; Sinclair et al., 2014). MSA is less studied in the Arctic although MSA from coastal Svalbard has been related to summer sea ice extent (O'Dwyer et al., 2000). Satellite-derived connections between Arctic ice edge and algal blooms (Perrette et al., 2011) and atmospheric measurements of DMS (Sharma et al., 2012) show

710 promise for MSA as a proxy of past sea ice conditions. The amount of MSA preserved in an ice
711 core reflects not only changes in the amount of DMS produced within the sea ice zone but also the
712 transport, deposition and preservation of MSA on the ice sheet (Abram et al., 2007; Becagli et al.,
713 2009; Fundel et al., 2006; Preunkert et al., 2008) and thus careful site examination and calibration
714 of MSA with satellite sea ice data is essential.

715 Isoprene SOA tracers are believed to be derived from dual (marine and terrestrial) biogenic sources
716 (see also Section 3.1.2). However, the annual global marine SOA from isoprene and monoterpene
717 oxidation is considerably less than the oxidation products of DMS and marine amines (Vignati et
718 al., 2010 and references therein). Globally, terrestrial vegetation is a major source of isoprene
719 emissions, while marine vegetation is only a minor source of isoprene emissions (Hallquist et al.,
720 2009). However, the air masses reaching the Antarctic have a strong oceanic influence while
721 terrestrial sources have less of an influence due to their distance from the continent.

722 A number of other SOA tracers have been quantified in the marine environment, which have
723 potential as marine indicators for biogenic change. Dimethyl and diethylammonium salts (DMA^+
724 and DEA^+), believed to be of biogenic origin, and produced through the reaction of gaseous amines
725 with sulfuric acid or acidic sulfates (Facchini et al., 2008). They were identified over the North
726 Atlantic (Facchini et al., 2008) and over the Pacific Ocean (Sorooshian et al., 2009) and are found
727 to be the most abundant organic species, second only to MSA, detected in fine marine particles.
728 Like MSA, DMA^+ and DEA^+ have no anthropogenic origin and exhibit a clear seasonality, making
729 them potentially a viable indicator of marine biogenic activity, but as yet they have not been
730 measured in polar ice.

731 Azelaic acid, a product from the photochemical transformation of unsaturated fatty acids, has been
732 proposed as a proxy of marine biogenic activity. Equally, low molecular weight dicarboxylic acids,
733 such as succinic, malonic and oxalic acids, have been related to photochemical oxidation of marine
734 biogenic compounds and especially oxidation of unsaturated fatty acids, which are enriched in the
735 SML (Kawamura et al., 2001). Concerning oxalate, biomass burning and fossil fuel combustion are
736 additional sources (Kawamura et al., 2001; Legrand and De Angelis, 1996; Müller-Tautges et al.,
737 2016). Diagnostic ratios of dicarboxylic acids can be used to gather more information on the
738 possible emission sources and atmospheric processing (Kawamura and Bikkina, 2016). Higher
739 C_2/C_4 were observed in tropical aerosol compared with high latitude aerosol. High C_3/C_4 were
740 documented for marine aerosol as opposed to vehicular emissions, and linked to atmospheric aging
741 of the air masses, as malonic acid is less stable than succinic acid. Conversely, higher C_6/C_9 were
742 observed for anthropogenically influenced continental aerosol compared with oceanic air masses.
743 Measurements in an ice core from Site-J, Greenland, showed correlation between dicarboxylic acids
744 and sea ice advance/retreat. Their concentrations are additionally influenced by the oxidation
745 capacity of the atmosphere potentially providing information on atmospheric changes due to either
746 natural variability or anthropogenic activities (Kawamura et al., 1999). Fluctuations in oxalate
747 concentrations showed an association with sea-to-air emission of biogenic compounds as well as
748 Northern Hemisphere solar irradiance (Kawamura et al., 2001).

749 Organosulfates (sulfate esters of C_9–C_{13} hydroxyl carboxylic acids) can also be considered as
750 marine SOA tracers. They arise from the oxidation of unsaturated fatty acids derived from marine
751 algae (Claeys et al., 2010). Organosulfates have been observed at low concentrations in the Indian
752 Ocean and may be detectable at coastal polar locations close to sea ice algae (Grannas et al., 2006).
753 However, organosulfates have been observed in terrestrial SOA studies from reaction of organics

754 with anthropogenic H_2SO4 (Surratt et al., 2007) so specificity to marine sources needs to be tested
755 for each individual sulfate ester compound.

3.4 Anthropogenic Emissions

757 Human activity has influenced the emissions of many natural organic compounds into the
758 atmosphere, for example through altering biomass burning rates or changing forest into cropland (or
759 other land use changes). However, perhaps more obvious, is the introduction of new molecules into
760 the atmosphere that were not present (or present in much smaller quantities) until human industrial
761 manufacturing occurred. This class of new compounds includes PCBs and pesticides.
762 Measurements in ice cores can verify the timing of increased emissions and the effectiveness of
763 mitigation measures. These results can also serve as essential background determinations for
764 assessing any ecological effects observed in the polar regions themselves. The choice of chemicals
765 to be measured is therefore based on the strength of concern over ecological and human health
766 risks. The nature of this issue means that such molecules are of interest only in the last few decades
767 up to about two centuries in extreme cases, and will therefore be measured only in relatively
768 shallow cores, and often mainly in firn rather than ice.

769 The poles remain in the popular imagination as the final frontier of purely natural locations that are
770 far removed from effects of human activity. In fact, the poles are regions of "minimum
771 anthropogenic presence" (Kallenborn et al., 2013) but are not absent of human influence (Bossi et
772 al., 2013; Chen et al., 2015; Fuoco et al., 2012; Hermanson et al., 2005; Ma et al., 2011). Transport
773 of anthropogenically-emitted compounds from lower latitudes to the Arctic (and to a lesser extent
774 the Antarctic) has been recognised for many decades, and is commonly referred to as Arctic Haze
775 (e.g. Barrie et al., 1992). In addition, human presence in the polar regions is increasing with a
776 warming climate. Declining Arctic sea ice is opening up a September Northwest Passage for
777 shipping traffic (Laliberté et al., 2016), and mineral exploration in the Arctic has the potential to
778 substantially alter the regional concentrations of anthropogenic aerosols (e.g. Bedini, 2011). In
779 Antarctica, isolated research stations provide interesting case studies of the areal extent of
780 contamination from point sources. Here we discuss the most important classes of anthropogenic
781 organic compounds detected in polar regions and potential implications of their presence in the ice
782 caps. One common aspect of many of these compounds is that they may be re-volatilised to the
783 atmosphere as ice recedes in a warming climate, and therefore the potential to reintroduce phased-
784 out compounds to the atmosphere has to be recognised.

3.4.1 Persistent Organic Pollutants (POPs)

786 POPs are primarily anthropogenic compounds that are recalcitrant to biological and chemical
787 degradation under most environmental conditions. The persistence of these pollutants and their
788 resistance to degradation in the environment results in their accumulation in ice, sediments, and
789 within animal and human tissues (e.g. Andersen et al., 2015; Chen et al., 2015; Gustafsson et al.,
790 2005). Many POPs were first synthetically produced in the mid-twentieth century as pesticides,
791 industrial chemicals, and solvents. Due to the detrimental and far-reaching effects of POPs on
792 human health, the Stockholm Convention on Persistent Organic Pollutants, which entered into force
793 in 2004, restricts or bans the production and continued use of POPs (chm.pops.int; UNEP, 2004).
794 The Stockholm Convention identified an initial "dirty dozen" of POPs (Table 3) that required an
795 immediate cessation due to their toxicity, persistence, and noted bioaccumulation (chm.pops.int;
796 UNEP, 2004; Table 3). The majority of the "dirty dozen" are pesticides; as pesticides are primarily
797 used in areas with substantial agriculture, any pesticides present in polar regions arrived via long-
798 range transport.

799 As shown in Table 3, POPs, and pesticides in particular, have been detected in different Svalbard
800 ice cores (Figure 1d) (Hermanson et al., 2005; Ruggirello et al., 2010), Antarctic glacier ice,
801 penguins (Geisz et al., 2008), and Arctic foxes (Andersen et al., 2015) demonstrating their
802 widespread presence reaching the most pristine areas on the planet. Organochlorine pesticides have
803 also been reported in surface snow of East Antarctica (Kang et al., 2012; Peel, 1975) and in the
804 Devon Island ice cap in Canada (Zhang et al., 2013). Organophosphorus pesticides have been
805 detected in Svalbard ice, together with methyl parathion and Dieldrin (Barbante et al., 2017;
806 Isaksson et al., 2003). POPs are among the compounds with the possibility to re-volatilise from
807 Arctic ice back into the atmosphere (Ma et al., 2011; Wohrnschimmel et al., 2013). Adding to the
808 importance of studying POPs, recent models demonstrate that the northward extension of arable
809 land and the associated increase in the use of agrochemicals would double POPs concentrations in
810 Arctic air and quadruple their concentrations in Arctic water (Wohrnschimmel et al., 2013).

811 *3.4.2   Polychlorinated biphenyls (PCBs)*

812 PCBs are anthropogenic organic substances produced and used in the 1960s and 1970s. Increasing
813 awareness of their harmful environmental properties led to their diminished use in the 1970s and
814 eventually their worldwide ban as part of the Stockholm Convention on POPs in 2004
815 (chm.pops.int; UNEP, 2004).

816 PCBs can arrive to the poles through long-range atmospheric transport due to their high vapour
817 pressure, and a relatively long atmospheric lifetime of up to 30 days in the gas phase (Anderson and
818 Hites, 1996). PCBs have also been observed in the SML in coastal Antarctic waters (Fuoco et al.,
819 2005), where they are enriched relative to bulk sea water concentrations. PCBs are primarily
820 removed from the atmosphere by reacting with ·OH; oxidation is slower in polar areas due to low
821 temperatures, low humidity, and low tropospheric ozone concentrations (Ruggirello et al., 2010).
822 The lack of UV-B radiation during the polar night means that ·OH are not produced during the
823 corresponding winter months, resulting in a longer lifetime of PCBs in polar areas than in other
824 regions (Brönnimann et al., 2000).

825 PCBs are deposited on the surface by partitioning into aerosol particles and incorporation into
826 snowfall (Garmash et al., 2013; Wania et al., 1998). Lower-chlorinated PCB congeners tend to
827 return to the surface by dry deposition, while higher-chlorinated PCB congeners are mainly
828 deposited by wet deposition (Steinlin et al., 2014). This difference in deposition means that the
829 lower-chlorinated PCBs may re-volatise after deposition, and therefore may not be incorporated
830 into the deeper glacier ice. The surface snowpack acts as a filter for the compounds where heavy
831 PCBs may bind to fine suspended particles resulting in an enrichment of PCBs in particle layers
832 (Pavlova et al., 2015). The higher-chlorinated PCB congeners may then be more prevalent in glacier
833 ice (Steinlin et al., 2014). Once PCBs are incorporated into the glacier ice, they undergo a variety of
834 processes (e.g. volatilisation and chemical transformation) before they are permanently archived, as
835 discussed in general terms in section 2.3. In particular, they may be subject to vertical and
836 horizontal transport within the glacier, leading to a subsequent release into meltwater (Blais et al.,
837 2001; Schmid et al., 2011), or to surface meltwater containing dissolved PCBs that percolate
838 through the firn where they may then refreeze at a deeper level in the glacier ice (Pavlova et al.,
839 2015).

840 Similar to the other POPs polar ice caps are also increasingly becoming a source of PCBs through
841 re-volatilisation into the atmosphere (Ma et al., 2011). Concentrations of PCBs in the Arctic
842 steadily declined in atmospheric samples collected at Alert, Canada from 1992 to 2000 due to the
843 restrictions on the current and future production of PCBs (Hung et al., 2005). This declining trend

844 in PCB concentrations was also observed until approximately 2000 is also present in a 37 m ice
845 core from Lomonosovfonna, Svalbard (Garmash et al., 2013). However, the ΣPCB concentrations
846 increased in the Lomonsovfonna ice core and remain elevated from 1998 until 2009 (Garmash et
847 al., 2013). Back trajectories demonstrate that air masses influencing Lomonosovfonna originate in
848 Europe and western Russia where relic PCBs from urban areas and/or incineration of older
849 materials that contain PCBs may influence the high PCB concentrations in Svalbard over the last
850 decade. These high PCB concentrations are consistent with model simulations and high Arctic
851 atmospheric concentrations resulting from the revolatilisation of POPs from ice into the atmosphere
852 due to warming temperatures (Garmash et al., 2013; Ma et al., 2011). Due to their persistence and
853 previous entrapment in sinks such as snow and ice, atmospheric concentrations of PCBs and other
854 POPs may continue to increase in a warming climate, where these concentrations may be especially
855 high in polar regions.

3.4.3 *Polycyclic aromatic hydrocarbons or pseudo-POPs*

857 PAHs can be produced by both biomass and fossil fuel burning (see section 3.2.3). The incomplete
858 combustion of both oil and coal release PAHs, where PAHs produced by burning crude and refined
859 oil can be highly alkylated (Yunker and Macdonald, 1995). These alkylated PAHs may be more
860 harmful to life than the PAHs without alkyl substitutions (Barron and Holder, 2003). While PAHs
861 are toxic, they are only accepted as POPs under the Aarhus Protocol instead of under the Stockholm
862 Convention, and therefore are subject to less regulation (Aarhus-Protocol, 1998).

863 PAHs primarily arrive to polar regions through atmospheric transport. Heavier, less-volatile PAHs
864 travel with particles in the atmosphere, where they arrive along the same trajectories that transfer
865 chemicals from the mid-latitudes (Barrie et al., 1992). As heavier PAHs are associated with
866 particles, they are removed from the atmosphere by precipitation. During the Arctic winter months,
867 PAHs may remain in the atmosphere for up to ~30 days, while the more frequent summer Arctic
868 precipitation results in atmospheric residence times of less than a week (Macdonald et al., 2000).
869 PAHs may re-enter the atmosphere even after they are deposited through the resuspension by
870 winds, by the removal of sediments or snow that had covered the PAHs and associated particles, or
871 by re-volatilising due to increased temperatures (Macdonald et al., 2000; Wania and Mackay,
872 1996).

873 Less-volatile PAHs travel with particles in the atmosphere, where they arrive along the same
874 trajectories that transfer chemicals from the mid-latitudes (Barrie et al., 1992). As heavier PAHs are
875 associated with particles, they are removed from the atmosphere by precipitation. During the Arctic
876 winter months, PAHs may remain in the atmosphere for up to ~30 days, while the more frequent
877 summer Arctic precipitation results in atmospheric residence times of less than a week (Macdonald
878 et al., 2000). PAHs may re-enter the atmosphere even after they are deposited through the
879 resuspension of dust or snow by winds, by the removal of sediments or snow that had covered the
880 PAHs and associated particles, or by revolatilizing due to increased temperatures (Macdonald et al.,
881 2000; Wania and Mackay, 1996).

882 PAHs from human activities are pervasive in the Arctic and Antarctic including in the seawater and
883 air (Lohmann et al., 2009), as well as snow and ice (Masclet et al., 2000; Vecchiato et al., 2015).
884 Innovative work examining PAHs in Arctic snow and ice cores over the past few centuries
885 demonstrate an exponential increase in PAHs beginning in the 1930s associated with the major
886 increase in fossil fuel burning (Jaffrezo et al., 1993; Jaffrezo et al., 1994; Kawamura et al., 1994;
887 Masclet et al., 1995; Masclet et al., 2000). This increase in PAH concentrations is consistent across
888 the Arctic, yet the concentrations vary by region where the Agassiz Ice Cap, Canada has the highest

21

889 concentrations (mean of ~60 ng/L with a peak concentration of 640 ng/L), while Lomonosovfonna,
890 Svalbard contains mid-range concentrations of 5-53 ng/kg, and Greenland ice core concentrations
891 tend to have the lowest PAH values with a maximum of only 0.5 ng/L (Vehvilainen et al., 2002 and
892 references therein). PAH concentrations in the Lomonosovfonna ice core are characterised by a
893 clear seasonality, with higher concentrations associated with the buildup of the wintertime Arctic
894 Haze due to transports of chemicals/aerosols from the mid-latitudes (Macdonald et al., 2000;
895 Vehvilainen et al., 2002 and references therein). Less is known about PAH concentrations in the
896 Antarctic compared to the Arctic. However, the Talos Dome, Antarctica ice core demonstrates
897 similar trends in PAH concentrations as the Arctic ice cores, where ΣPAHs markedly increase
898 beginning in the 1930s due to fossil fuel burning (Fuoco et al., 2012). This increase is less than in
899 the comparable Arctic ice cores, as the Talos Dome PAH concentrations rise by 50% instead of an
900 exponential increase observed in the Arctic (Fuoco et al., 2012). Future studies regarding the
901 seasonality and spatial distribution of PAHs in Antarctic ice can help better compare these two
902 locations.

903 *3.4.4 Emerging pollutants*

904 Emerging pollutants, i.e. substances that are not commonly monitored but have the potential to
905 enter into the environment and cause ecological and/or public health effects (Geissen et al., 2015),
906 are worth investigating in shallow cores and surface snow in polar regions to understand the extent
907 of pollution. These can include new classes of pesticides, pharmaceuticals, disinfection by-products,
908 wood preservation and industrial chemicals (Geissen et al., 2015) that could potentially enter into
909 global atmospheric or marine transport. For example, little is known about Arctic concentrations of
910 the most recent replacement pesticides, like the widely-used neonicotinoids that have dominated the
911 insecticide market since the early 1990s and are only very recently partially being banned
912 (Bonmatin et al., 2015; Giorio et al., 2017; Simon-Delso et al., 2015). In addition, brominated
913 flame-retardants (BFRs), compounds that are used to slow the spread of flames in residential and
914 commercial indoor fabrics, foams, and electronics, have been found in Arctic wildlife, lake
915 sediments, ice and air samples (Barbante et al., 2017 and references therein).

916 Perfluorinated chemicals (PFCs), also known as per- and polyfluoroalkyl substances (PFASs),
917 contain many of the same concerns as previous POPs in the fact that they are present throughout the
918 globe, bioaccumulate, do not degrade in the environment, and can be toxic to both animals and
919 humans (Ahrens et al., 2011; Wang et al., 2014 and references therein). Increasing evidence
920 demonstrates that long-chain PFASs (LC PFASs) with 6 and more perfluoroalkyl carbons, and
921 long-chain perfluoroalkyl carboxylic acids (LC PFCAs) with 7 and more perfluoroalkyl carbons are
922 more toxic and more prone to bioaccumulate than their shorter-chained variations (Buck et al.,
923 2011; OECD, 2013). Due to their persistence in the environment, bioaccumulation, and toxic
924 effects, both industry and government regulators are attempting to reduce the production and release
925 of LC PFCAs. Although these substances have been phased-out in much of Western Europe, Japan,
926 and the United States, these chemicals are still produced in continental Asia (Wang et al., 2014).

927 Although PFASs and PFCAs are ubiquitous in the environment, their transport mechanisms still
928 require further study (Armitage et al., 2009; Wang et al., 2014). PFCAs do not attach to particulate
929 matter settling into the deep ocean, and therefore remain dissolved in water (Armitage et al., 2009;
930 Scheringer et al., 2004). Modelling and observational studies show that PFCAs primarily arrive to
931 the Arctic and Antarctic Oceans via marine transport (Armitage et al., 2009; Prevedouros et al.,
932 2006; Yamashita et al., 2005). PFCAs can volatise from the ocean in more temperate locations, but

933 the polar low temperatures and sea ice cover inhibit their volatilization once PFCAs reach the poles
934 (Wania, 2006).

935 If the continued production of PFCAs and PFASs in Asia directly emits these substances into the
936 atmosphere, where they can then also be subject to atmospheric transport to the poles (Benskin et
937 al., 2012). The presence of PFASs in Arctic ice cap samples suggests that atmospheric oxidation of
938 volatile precursors is another source of PFASs to inland Arctic regions (Young et al., 2007).
939 Consistently high atmospheric PFAS concentrations near the Antarctic Peninsula (mean 23.5
940 pg/m^3) are due to the supply of PFASs from new air masses, combined with decreased degradation
941 in the polar atmosphere, and the air-snow exchange (Wang et al., 2015). The re-volatilisation of
942 PFASs from polar snow is a source of PFASs to the atmosphere, where this source may become
943 increasingly important under warming conditions (Wang et al., 2015). Currently, very limited
944 studies exist that examine PFASs in Antarctic (Wang et al., 2015) and Arctic (Young et al., 2007)
945 snow. Examining spatial transects and temporal profiles of PFASs in snow and ice would help to
946 determine the atmospheric spread and fate in snow of these persistent toxic chemicals.

947 **4   Conclusions**

948 There is a great potential for organic aerosol compounds to be used as proxies for terrestrial
949 biogenic emissions, past fire events of different types of biomasses, marine biogenic activity and
950 anthropogenic activities, all further leading to the possibility of inferring temperature fluctuations,
951 changes in sea ice and even large-scale climate variability. However, their measurement in polar ice
952 has proved to be challenging. More research is needed to advance our understanding of compound-
953 specific behaviour and stability related to atmospheric and ice archive lifetimes and characterization
954 of sources of sample contamination that may arise during drilling, and subsequent storage and
955 transport. Specific decontamination and clean handling procedures suited for organic analysis still
956 needs development and validation. This aspect may include installing clean rooms specifically
957 designed for handling samples for organic analysis, avoiding plastic materials and installing
958 appropriate filters to eliminate organic vapours.

959 A wide range of analytical methods have been developed to analyse specific organic compounds or
960 important compound classes in ice cores. The majority of these methods use GC-MS and LC-MS
961 and in general researchers can choose the method that best fits their research objectives and
962 availability of different lab facilities and instrumentations. More research is needed in order to
963 lower detection limits, especially for the cleaner Antarctic samples, as well as decreasing the
964 amount of sample needed to ensure a good time resolution in the archive. Fast analytical methods
965 and small sample volume may open up the possibility of coupling organic analysis to the
966 continuous flow analysis systems routinely used for analysis of inorganic compounds in the ice
967 cores.

968 Concerning terrestrial emissions, fatty acids, together with isoprene, monoterpene, and
969 sesquiterpene SOA products, offer excellent potential as terrestrial biomarkers in ice cores. While
970 detection of all individual compounds may prove challenging due to their variable reactivities, long-
971 distance transport and long-term preservation of many of the compounds of interest was shown in
972 snow layers well within the perimeters of the polar regions. Biomass burning is by far the most
973 studied area in terms of available measurements of organic markers in the Arctic. Yet in this area,
974 more studies are needed to assess atmospheric lifetimes of biomass burning markers, improve the
975 predictability of past transport dynamics in air masses around the globe and improve analytical
976 capabilities towards the measurement of multiple proxies with the same method and in high
977 temporal resolution (i.e. low sample volume). Lignin pyrolysis products and resin acids show the

978 potential, if coupled with measurements of levoglucosan and its isomers, to differentiate between
979 different types of biomass being burned. Furthermore, it would be interesting to assess the
980 possibility to use mega fire events (i.e. recorded as levoglucosan or black carbon spikes) as
981 temporal horizons for precise ice core chronologies.

982 The use of marine organic aerosols in polar ice is a relatively new area of research and one that
983 requires considerable investigation. The main problems are that marine organic aerosols are
984 influenced not only by oceanic emissions of primary aerosols and SOA precursors, but also by
985 continental emissions through long-range atmospheric transport. This should have less of an
986 influence in the Antarctic, especially at coastal locations. However, careful site assessment and
987 calibration with observational records such as satellite measurements of sea ice extent is required
988 and may also be hindered by a lack of field measurements of marine aerosols, especially in the polar
989 regions, limiting our understanding of the abundances of biogenic SOA in the marine boundary
990 layer. Dimethyl and diethylammonium salts can be potentially viable indicators of marine biogenic
991 activity, but as yet they have not been measured in polar ice. Low molecular weight dicarboxylic
992 acids, from the oxidation of unsaturated fatty acids from primary marine emissions, have been
993 proposed as proxies for the reconstruction of past oxidative capacity of the atmosphere (Kawamura
994 et al., 2001).

995 Despite the poles, and especially Antarctica, being the most pristine regions on Earth, human
996 influence has been recorded on both surface snow and shallow ice cores. A plethora of
997 anthropogenic compounds have been measured in ice samples, including many pesticides, POPs,
998 PCBs, PAHs, and PFASs, and in the local fauna. Ice cores can document the input of compounds
999 with harmful environmental properties, bioaccumulation, and toxic effects to the polar regions, as
1000 well as the beneficial effects of mitigation measures. Additional complexity occurs since some of
1001 these compounds may be released from the archives in a warming climate by re-evaporation in the
1002 air-snow interface or re-dissolution in the ocean. Finally, research is needed to establish baseline ice
1003 core measurement and to develop robust analytical techniques to better understand the
1004 environmental spread of replacement pesticides and other emerging pollutants introduced in the
1005 environment by human activities.

1006 ## Acknowledgments

1011
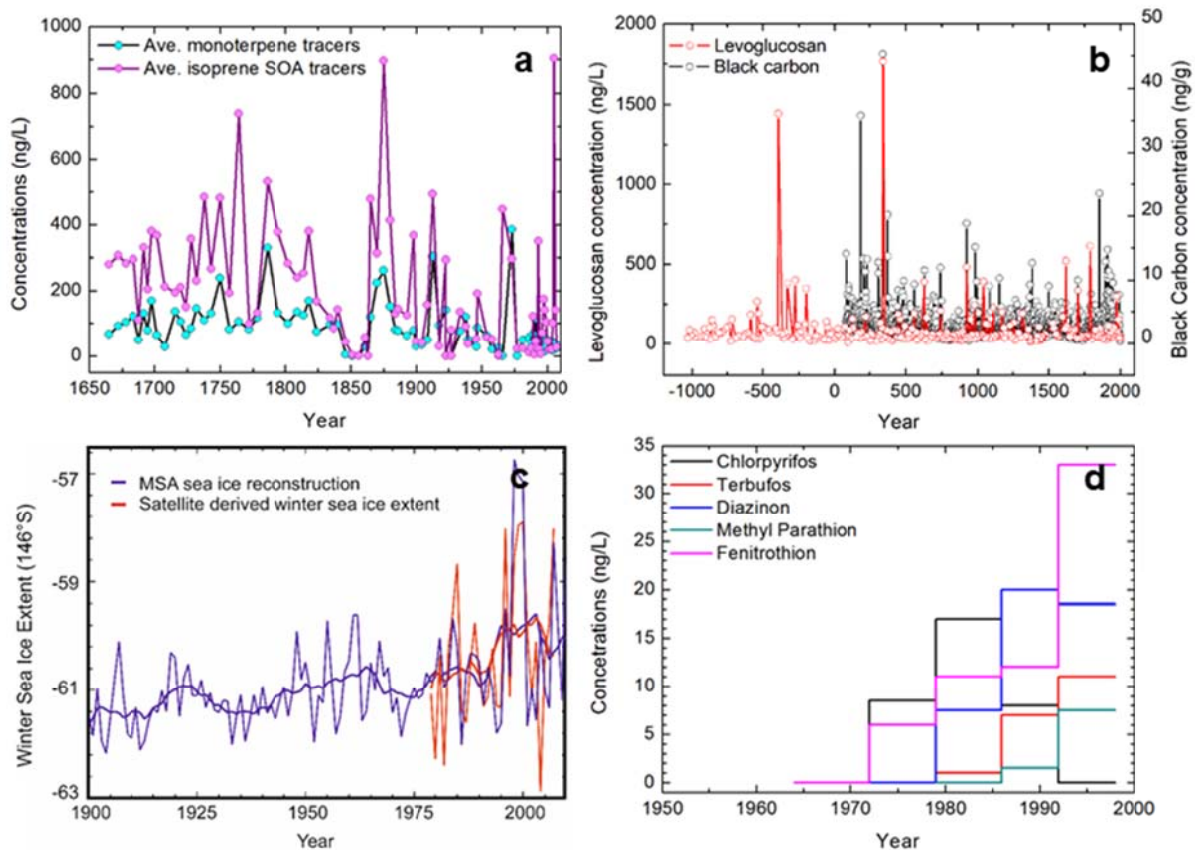
Figure 1. (a) Average concentration changes of monoterpene tracers and total annual average concentrations of isoprene SOA tracers in the Alaska ice core records collected from Aurora peak (Pokhrel et al., 2016); (b) levoglucosan concentration profile measured in the deep NEEM core and black carbon concentration profile measured in the NEEM-2011-S1 ice core (Zennaro et al., 2014); (c) winter sea ice reconstruction derived from MSA and satellite derived winter sea ice extent for the Amundsen-Ross sea (adapted from Thomas and Abram (2016)); (d) concentration trends of five organophosphorus compounds at Austfonna, Svalbard (reproduced from Hermanson et al. (2005)).

Table 1. Analytical methods used and method performances for the measurement of terrestrial, marine, biomass burning and anthropogenic markers in polar ice and snow.

Compounds	Sample preparation	Technique	Amount used for analysis	Recovery	Method LOD[a]	Concentration range	Archive/Sample[b]	Age/depth	References[c]
				Anthropogenic markers					
Pesticides	SPE	GC-MS	11 L	80%	1-84 pg/L	1.1-87.0 ng/L	Austfonna ice core, Svalbard	70 m 1906-1998AD	(Muir et al., 2004) (Hermanson et al., 2005)
Pesticides	SPE	GC-MS	11-15 L	80%	1-84 pg/L	0.08-77.6 ng/L	Holtedahlfonna ice core, Svalbard	1953-2005AD	(Muir et al., 2004) (Ruggirello et al., 2010)
Pesticides	SPE	GC-MS	~4.5 L		0.04-2.5 pg/L	up to 8.91 pg/L	Sea ice and snow, Antarctica	Sept-Oct 2001	(Dickhut et al., 2005)
Pesticides	LLE Fractionation	GC-FID and GC-ECD	9 L	>70%	10-30 pg/L	0-870 pg/L	pack ice, Terra Nova Bay, Antarctica	1988/1989 AD	(Desideri et al., 1991)
Pesticides and PCBs	LLE	GC-ECNI-MS	1 L	64-310%	1-10 ng/L	0-80 ng/L	arctic snow/sea ice, Alaska	1995-1996 annual snowfall	(Garbarino et al., 2002)
PCBs	LLE in GLVE[d] Solvent Evaporation Fractionation	GC-ECD	14.8-20 L	46-125%		100-4000 pg/L	ice cap, Canada	1963-1993AD	(Gregor et al., 1995)
PCBs	LLE Evaporation to 1mL	GC-MS	7 L	59-85%	2-6 pg/L	< 0.2 ng/L as ΣPCBs	firn/snow cores, Talos Dome, Antarctica	1600-2000AD	(Fuoco et al., 2012)
PCBs	SPE	GC-MS	15-20 L	59-130%	pg/samples (blank=LOD)		snow and ice core, Lomonosovfonna Glacier (Svalbard)	37m 1957-2009AD	(Garmash et al., 2013)

Analyte	Extraction	Instrument	Volume	Recovery	LOD	Concentration	Location	Date	Reference
PCDD/Fs, PCBs, PBDEs	LLE Clean-up in silica column	GC-HRMS	10 L	95±11%	0.1-0.5 pg/L	0-0.48 pg/L PCDD/Fs 0-180 pg/L PCBs 0-170 pg/L PBDEs	Surface snow, Antarctica	Austral summer 2011-2012AD	(Vecchiato et al., 2015)
PCBs	Sorption in capillary PDMS solvent elution	GC-EI-HRMS	>=0.5 L	21-88%	10-20 pg/L	0.5 – 5 ng/L	Alpine ice core (Switzerland)	107m 1940-2002AD	(Pavlova et al., 2014) (Pavlova et al., 2015)
PFASs	SPE	GC-PCI-MS	5-8 L		0.1-5.9 pg/L	125-303 pg/L	Surface snow, Antarctica	January 2011	(Wang et al., 2015)
PFASs	SPE	LC-MS/MS	0.5-1 L	83-110%	5-13 pg/L LOQ (S/N 10)	2.6-246 pg/L	Melville Ice cap, Canada	Spring 2005-Spring 2006	(Young et al., 2007)
PFASs	SPE	GC-PCI-MS	5-8 L	84-95%	0.1-5.9 pg/L	330-690 pg/L	Fresh snow Ny-Ålesund, Svalbard, Norway	January-May 2012	(Xie et al., 2013) (Xie et al., 2015)
Volatile halogenated hydrocarbons	On-line purge and trap	GC-MS	10 mL	30-90%	1 ng/L	0-236 ng/L	Fresh snow, Antarctica		Zoccolillo et al., 2005)

Markers of both anthropogenic fossil fuel combustion sources and biomass burning

Analyte	Extraction	Instrument	Volume	Recovery	LOD	Concentration	Location	Date	Reference
PAHs	LLE Clean-up in silica column	GC-HRMS	10 L	95±11%	0.1-0.5 pg/L	0-125 ng/L	Surface snow, Antarctica	Austral summer 2011-2012 AD	(Vecchiato et al., 2015)
PAHs	SPE	GC/MS	7.6-17.9 L			mean of 16 PAHs 20.45-60.57 ng/L	Qiyi glacier, Yuzhufeng glacier, Xiaodongkemadi glacier and Gurenhekou glacier, Tibetan Plateau glacier	surface, present time 2008 AD	(Li et al., 2011)

PAHs	filtration, solvent extraction, filtration, evaporation	HPLC-fluorescence	5-12 L		20 ng/L (lower calibr. standard)	∑14-PAHs 100 – 10,630 ng/L	ATM station, Summit, Greenland	5 m 1989-1993 AD	(Masclet et al., 2000)
PAHs	filtration, essication	SFE-GC/MS[e]	100-200 mL			∑10 PAHs 3130 – 21,083 ng/L	GISP2, Greenland	3 m snowpit 1994-1995 AD	(Slater et al., 2002)
PAHs	filtration, essication	SFE-GC/MS[e]	120 mL			8-18 pg	GISP2, Greenland	August 1994	(Currie et al., 1998)
PAHs	Filtration, soxhlet, evaporation for insoluble material; SPE (after filtration) for soluble PAH	HPLC-fluorescence	~16 L		pg/L	ΣPAH 598-2367 pg/L (insoluble); < LOD (soluble)	Insoluble PM Greenland ice Summit, Greenland	1988-1991 AD	(Jaffrezo et al., 1994)
PAHs	SPME Thermal desorption in GC	GC-MS	30 mL	65–>80%, <20% for 4–6 ring PAHs	0.13-5.14 ng/L	<35 ng/L (ΣPAH)	Firn, Ekström Shelf Ice in the Weddell Sea, Antarctica	2002-2005 AD	(Kukučka et al., 2010)
PAHs	SPE, elution, evaporation	GC-MS	10 L	82±8%	0.1 ng/L	52-272 ng/L (ΣPAH)	Antarctic snow, Fildes Peninsula	December 2009	(Na et al., 2011)
PAHs	LLE in GLVE[d] Solvent Evaporation Fractionation	GC-MS	15 L		0.01-0.4 ng/L	35-660 ng/L (ΣPAH)	ice cap, Canada	8.3 m 1963-1993 AD	(Peters et al., 1995)
PAHs	On-line SPE on CFA, elution, solvent evaporation	HPLC-fluorescence	250-500 mL	71-93%	7-466 pg/L	0-12 ng/L	ice/firn cores, Colle Gnifetti, Monte Rosa (Swiss/Italian Alps)	~58 m 1700-2003 AD	(Gabrieli et al., 2010a)
PAHs	LLE Evaporation to 1mL	GC-MS	7 L	67-91%	2-6 pg/L	< 4 ng/L (ΣPAH)	firn/snow cores, Talos Dome, Antarctica	1600-2000 AD	(Fuoco et al., 2012)

Terrestrial biomarkers									
$C_{12:0}$-$C_{30:0}$ monocarboxylic acids	Preconc. in rotavap Extraction Derivatisation (BF$_3$/n-butanol)	GC-MS	100 mL	>70%	0.001 µg/L	average 0.09-20.3 µg/L, range 0-189 µg/L	Ice core, Aurora Peak, Alaska	180m 1734AD-2008AD	(Kawamura, 1993) (Ho et al., 2010) (Pokhrel et al., 2015)
Monoterpene and isoprene SOA tracers	Preconc. in rotavap Extraction Derivatisation (BSTFA)	GC-MS	150 mL	>70%	0.001 µg/L	average 7-692 µg/L, range 0-3509 µg/L average 2890 ng/L, range 50.2-18400 ng/L	Ice core, Aurora Peak, Alaska Kamchatka Ushkovsky ice core	180 m 1665AD-2008AD 1.32-152.5 m 1693-1997AD	(Kawamura, 1993) (Ho et al., 2010) (Pokhrel et al., 2016) (Fu et al., 2016)
$C_{26:0}$-$C_{30:0}$ monocarboxylic acids	LLE Saponification Derivatisation (BSTFA)	GC-MS	350 mL	75-82%		average 20 µg/L-ice, range 1.9-105 µg/L	Ice core, Site J, Greenland Kamchatka Ushkovsky ice core	1550-2000AD	(Kawamura et al., 1996) (Seki et al., 2015)
C_{15-33} n-alkanes, C_{24-31} n-alkan-2-ones, C_{6-18} n-alkanoic acids	SPE	GC-FID and GC-MS	21.1-24.92 L			0.86-1.57 µg/L n-alkanes 2.12-3.07 µg/L n-alkan-2-ones 0.54-0.68 µg/L n-alkanoic acids	Snowpit, Xixiabangma Ice cores, Dasuopu glacier, Tibetan Plateau	240cm-900m Summer 1996-Summer 1997	(Xie et al., 2000)
Marine biomarkers									
MSA/MS-	Online preconc. with TAC	IC-conductimetry	5 mL		0.02 µg/L	0.04 – 11.82 µg/L	Ice core, Summit, Greenland	3040m ~110kyr BP (BP=1950)	(Saltzman et al., 1997)
MSA/MS-	Online preconc. with TAC	IC-conductimetry	5 mL		0.25 µg/L	mean background 1.2-	Ice cores GRIP 93a and GRIP 93b,	GRIP 93a: 73m	(Legrand et al., 1993)

Compound	Pretreatment	Detection	Volume	Recovery	LOD	Concentration	Location	Depth/Period	Reference
						2.9 µg/L	Summit, Greenland	1767-1993AD / GRIP 93b 67m, 1790-1993AD	(Legrand et al., 1997)
MSA/MS-	dil 50:50 with MeOH / direct injection	ESI-MS/MS	20 µL	-	0.1 µg/L	range 1.7-73.2 µg/L, mean 14.5 µg/L	Ice core, Siple Dome, Antarctica	~110kyr	(Saltzman et al., 2006)
MSA/MS-	direct injection	IC-conductimetry	0.8 mL	-	0.3 µg/L	mean 5.6 µg/L, range 0-51.1 µg/L	Ice core Lomonosovfonna, Svalbard	121m / 1800-1997AD	(Jauhiainen et al., 1999) (Isaksson et al., 2005)
MSA/MS-	Online preconc. with TAC	IC-conductimetry	5 mL		~0.1 µg/L	~2.88-13.45 µg/L	Ice core, Law Dome, Antarctica	1841-1995AD	(Curran and Palmer, 2001) (Curran et al., 2003)
MSA/MS-	Online preconc. with TAC	IC-conductimetry	3 mL		0.15 µg/L	mean 3.30 µg/L, range 0.16-38.12 µg/L	Ice core 20D, Greenland	116m / 1767-1984AD	(Whung et al., 1994)
Oleic acid ($C_{18:1}$)	Preconc. in rotavap / Extraction / Derivatisation (BF3/n-butanol)	GC-MS	100 mL		0.001 µg/L	mean 0.09-20.3 µg/L, range 0-189 µg/L	Ice core, Aurora Peak, Alaska	180m / 274y BP (i.e. 1734AD-2008AD)	(Pokhrel et al., 2015)
Oleic acid ($C_{18:1}$)	LLE / Saponification / Derivatisation (BSTFA)	GC-MS	350 mL	75-82%		mean 20 µg/L, range 1.9-105 µg/L	Ice core, Greenland	1550-2000AD	(Kawamura et al., 1996) (Seki et al., 2015)
Azelaic acid, low molecular weight dicarboxylic	Preconc. in rotavap / Extraction	GC-FID / GC-MS	150 mL	70->90%		Total dicarboxylic acids (C_2-C_{10})	Ice core, Site-J, Greenland	0-205 m / 1546-1989 AD	(Kawamura et al., 1999) (Kawamura et al.,

						range 3.11-32.5 µg/L			2001)
acids	Derivatisation (BF3/n-butanol)								

<div align="center">Biomass burning markers</div>

								2396.8 m (274.1 kyr BP)	
Levoglucosan	direct injection	HPLC-ESI(-)-MS/MS	100 µL	-	3 ng/L	4 – 30 ng/L	Dome C, Antarctica	2721.4 m (401.6 kyr BP)	(Gambaro et al., 2008)
Levoglucosan	direct injection	HPLC-ESI(-)-MS/MS	100 µL	-	3 ng/L	up to ~ 600 µg/L	Summit, Greenland	3 m snowpit	(Gambaro et al., 2008) (Kehrwald et al., 2012)
Levoglucosan	direct injection	HPLC-ESI(-)-MS/MS	100 µL	-	3 ng/L	9 – 1767 ng/L	NEEM, Greenland	4.95 – 602.25 m 1999 CE – 1036 BCE	(Gambaro et al., 2008) (Zennaro et al., 2014) (Zennaro et al., 2015)
Levoglucosan	direct injection	HPLC-ESI(+)-MS/MS	1 mL	-	10 µg/L	10 – 718 µg/L, mean 33 µg/L (Muztagh Ata) 10 – 93 µg/L, mean 39 µg/L (Longxiazailongba)	Muztagh Ata and Longxiazailongba glaciers, Tibetan Plateau	Muztagh Ata 71 m Longxiazailongba 190 m	(Yao et al., 2013)
Levoglucosan	dil. 50:50 with AcN direct injection	UHPLC-ESI(-)-MS/MS	5 µL (dil 50:50)	-	0.11 µg/L	mean 0.28-1.14 µg/L (snow) LOD-7.56 µg/L (ice core)	Snow and ice core Zangsegangri, Tibetan Plateau		(You et al., 2016)
Levoglucosan, mannosan,	Freeze-drying	GC/MS	5 mL	65-81%	0.070 µg/L (levoglucosan	up to 1.93 µg/L	Muztagh Ata and Kuokuosele		(You et al., 2014)

Compound	Preparation	Analysis	Volume	Recovery	LOD	Concentration	Location	Depth / Age	Reference
galactosan	Extraction Derivatization (MSTFA)				) 0.058 µg/L (mannosan) 0.046 µg/L (galactosan)	mean 0.44 µg/L	glaciers, Tibetan Plateau		
Levoglucosan, mannosan, galactosan	Preconc. in rotavap Extraction Derivatization (BSTFA)	CG/MS	80-250 mL	73±10%	0.005 µg/L	up to 19 µg/L mean 0.75 µg/L	Ushkovsky ice cap, Kamchatka	1.32 – 152.6 m 1997 - 1963 yr AD	(Kawamura et al., 2012)
Vanillic acid	dil. 50:50 with MeOH CFA	ESI(-)-MS/MS		-		7.6–368.2 ng/L	D4, Greenland	144 m 1788 – 2002 AD	(McConnell et al., 2007)
Vanillic acid	Preconc. in rotavap Extraction Derivatization (BSTFA)	CG/MS	80-250 mL	78±15%	0.005 µg/L	up to 0.13 µg/L mean 0.015 µg/L	Ushkovsky ice cap, Kamchatka	1.32 – 152.6 m 1997 - 1963 AD	(Kawamura et al., 2012)
Vanillic acid	direct injection	HPLC-ESI(-)-MS/MS	100 µL	-	77 ng/L	59 – 698 ng/L mean 226±189 ng/L	Akademii Nauk, Eurasian Arctic	200 – 350 AD	(Grieman et al., 2015)
Methyl dehydroabietate	filtration, essication	SFE-GC/MS[e]	100-200 mL				GISP2, Greenland	3 m snowpit 1994-1995 AD	(Slater et al., 2002)
Dehydroabietic acid	Preconc. in rotavap Extraction Derivatization (BSTFA)	CG/MS	80-250 mL	67±40%	0.003 µg/L	up to 0.47 µg/L mean 0.054 µg/L	Ushkovsky ice cap, Kamchatka	1.32 – 152.6 m 1997 - 1963 AD	(Kawamura et al., 2012)
p-hydroxybenzoic	Preconc. in rotavap	CG/MS	80-250 mL	78±18%	0.005 µg/L	up to 1.74 µg/L	Ushkovsky ice cap,	1.32 – 152.6 m	(Kawamura et al.,

acid	Extraction					mean 0.24 µg/L	Kamchatka	1997 - 1963 AD	2012)
	Derivatization (BSTFA)								
Oxalate	Preconc. in rotavap Extraction Derivatisation (BF3/n-butanol)	GC-FID GC-MS	150 mL	70->90%		mean 2.10 µg/L range 0.36-10.7 µg/L	Ice core, Site-J, Greenland	0-205 m 1546-1989AD	(Kawamura et al., 1999) (Kawamura et al., 2001)
Oxalate		IC-conductimetry			0.5 µg/L	background 0.1-0.8 µg/L mean 0.4 µg/L non-bb 0.3 µg/L	Summit, Greenland	1767–1993 AD	(Legrand et al., 1993) (Legrand and De Angelis, 1996)
Oxalate		IC-conductimetry				0.1 – 9.5 µg/L	Summit, Greenland	3 m snowpit	(Kehrwald et al., 2012)

[a] LODs refer to concentration in initial sample (i.e. melted ice or snow). [b] Arctic and Antarctic ice cores samples were considered whenever available. When not available, literature search has been extended to fresh snow and ice-cores from mountain glaciers. [c] References refer to measurements of snow and ice samples, and description of analytical methods and their performances. [d] GLVE=Goulden large-volume extractor. [e] SFE=Supercritical Fluid Extraction

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1024 **Table 2**. Isoprene, Monoterpene and Sesquiterpene SOA compounds identified in natural atmospheric aerosol
1025 samples from forest locations and in snow samples from remote locations.

Isoprene SOA	Location

2-methyltetrols:
    2-methylthreitol
    2-methylerythritol
	Canadian High Arctic (Fu et al., 2009), Boreal Forest Finland (Kourtchev et al., 2013; Kourtchev et al., 2005), Forested areas China (Wang et al., 2008), Amazonian Forest Brazil (Claeys et al., 2004a), Tibetan Plateau (Shen et al., 2015), Alaskan ice core (Pokhrel et al., 2016), Kamchatka ice core (Fu et al., 2016)

2-methylglyceric acid	Canadian High Arctic (Fu et al., 2009), Boreal Forest Finland (Kourtchev et al., 2013; Kourtchev et al., 2005), Forested areas China (Wang et al., 2008), Tibetan Plateau (Shen et al., 2015), Alaskan ice core (Pokhrel et al., 2016), Kamchatka ice core (Fu et al., 2016)

C_5-alkene triols:
    cis-2-methyl-1,3,4,trihydroxy-1-butene
    trans-2-methyl-1,3,4-trihydroxy-1-butene
    3-methyl-2,3,4-trihydroxy-1-butene
	Canadian High Arctic (Fu et al., 2009), Boreal Forest Finland (Kourtchev et al., 2005), Forested areas China (Wang et al., 2008), Tibetan Plateau (Shen et al., 2015), Alaskan ice core (Pokhrel et al., 2016)

Monoterpene SOA	Location
3-hydroxyglutaric acid	Canadian High Arctic (Fu et al., 2009), Forested areas China (Wang et al., 2008), Alaskan ice core (Pokhrel et al., 2016), Kamchatka ice core (Fu et al., 2016)
pinic acid, pinonic acid	Canadian High Arctic (Fu et al., 2009), Boreal Forest Finland (Kourtchev et al., 2013), Tibetan Plateau (Shen et al., 2015), Alaskan ice core (Pokhrel et al., 2016), Kamchatka ice core (Fu et al., 2016)
pinanoldehyde; pinanediol mononitrate; norpinonic acid; terebic acid; ketolimononic acid; limonic acid; homoterpenylic acid; deterpenylic acid acetate; caric acid; caronic acid; 2-hydroxyterpenylic acid; HHDCA (1-hydroxy-3-(hydroxymethyl)- 2,2 dimethylcyclobutane-carboxylic acid); DHHMDMCP (2,3-dihydroxy-2-(hydroxymethyl)-7,7-dimethylbicycloheptan6-one); HODSA (3-(2-hydroxy-3-oxobutyl)-2,2-dimethylsuccinaldehyde); 2,6,6-trimethylbicycloheptane-2,3,-diol	Boreal Forest Finland (Kourtchev et al., 2013)
norpinic acid	Canadian High Arctic (Fu et al., 2009), Boreal Forest Finland (Kourtchev et al., 2013), Forested areas China (Wang et al., 2008)
3-hydroxyglutaric acid, 3-hydroxy-4,4-dimethylglutaric acid	Tibetan Plateau (Shen et al., 2015)
MBTCA (3-methyl-1,2,3-butanetricarboxylic acid)	Canadian High Arctic (Fu et al., 2009), Boreal Forest Finland (Kourtchev et al., 2013), Forested areas China (Wang et al., 2008), Tibetan Plateau (Shen et al., 2015), Kamchatka ice core (Fu et al., 2016)

Sesquiterpene SOA	Location
β-caryophyllinic acid	Canadian High Arctic (Fu et al., 2009), North Carolina, USA (Jaoui et al., 2007), Boreal Forest Finland (van Eijck et al., 2013), Tibetan Plateau (Shen et al., 2015)

DCCA (3,3-dimethyl-2-(3oxobutyl)cyclobutanecarboxylic acid)	Boreal Forest Finland (Kourtchev et al., 2013; van Eijck et al., 2013)
β-nocaryophyllonic acid; 2-(2-carboxyethyl)-3,3-dimethylcyclobutanecarboxylic acid	Boreal Forest Finland (van Eijck et al., 2013)

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1027 **Table 3**. The "Dirty Dozen" of Persistent Organic Pollutants (POPs) as identified by the Stockholm Convention
1028 determined in polar regions.

POP	Global Historical Use/Source	Presence in polar regions
Aldrin and Dieldrin	Insecticide; Also used for termite control.	Austfonna, Svalbard, ice core (Hermanson et al., 2005); Seawater and pack ice, Terra Nova Bay, Antarctica (Desideri et al., 1991)
Chlordane	Insecticide; Used on home lawn and garden pests. Also used extensively to control termites.	Holtedahlfonna, Svalbard ice core (Ruggirello et al., 2010); Alaskan sea ice (Garbarino et al., 2002)
DDT	Insecticide for insects that carry diseases such as malaria and typhus.	Antarctic glacier ice as inferred from Adelie penguin DDT concentrations (Geisz et al., 2008)
Endrin	Insecticide; Also used to control rodents.	Holtedahlfonna, Svalbard ice core (Ruggirello et al., 2010)
Mirex	Insecticide; Also used as a fire retardant in plastics, rubber, and electrical products.	Arctic foxes (Andersen et al., 2015)
Heptachlor	Insecticide used primarily against soil insects and termites. Also used against some crop pests and to combat malaria.	Atmospheric samples from north-east Greenland (Bossi et al., 2013); Air, seawater, sea ice, and snow in the western Antarctic Peninsula (Dickhut et al., 2005)
Hexachlorobenzene	Fungicide used for seed treatment. Also an industrial chemical used to make fireworks, ammunition, synthetic rubber, and other substances. Also unintentionally produced during combustion.	Arctic Ocean sea water and boundary layer air (Cai et al., 2012); North-east Greenland air (Bossi et al., 2013); Antarctic peninsula snow (Dickhut et al., 2005)
PCBs	Used for a variety of industrial processes and purposes, including in electrical transformers and capacitors, as heat exchange fluids, as paint additives, in carbonless copy paper, and in plastics. Also unintentionally produced during combustion.	Talos Dome, Antarctica snow/ice cores (Fuoco et al., 2012); Northern Victoria Land, Antarctica surface snow (Vecchiato et al., 2015)
Toxaphene	Insecticide; also used and to kill unwanted fish in lakes.	Arctic Ocean seawater (Macdonald et al., 2000 and references therein)
Dioxins and Furans	Unintentionally produced during most forms of combustion, including burning of municipal and medical wastes	Canadian Arctic ringed seals and polar bears (Muir et al., 1992)
The "POPs" and "Global Historical Use/Source" columns are modified from the U.S. Environmental Protection Agency (US EPA): https://www.epa.gov/international-cooperation/persistent-organic-pollutants-global-issue-global-response The compiled literature gives precedence first to polar snow and ice studies, then seawater and atmospheric studies, and if such research was not available, then biological studies are included in the summary.		

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