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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.

Keywords	organic compounds; molecular markers; ice core; polar; environmental proxies
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To the Editor-in-chief of *Quaternary Science Reviews*

Dear Editor,

I would like to submit a review paper entitled “Prospects for reconstructing paleoenvironmental conditions from organic compounds in polar snow and ice” for consideration for publication in “*Quaternary Science Reviews*”.

Polar ice cores have provided information about past climate and environmental changes over periods ranging from a few years up to 800,000 years. The majority of studies focus on determining the inorganic component, such as major ions, and trace elements as well as on their isotopic fingerprint. In contrast, 10^4 - 10^5 individual organic compounds were identified in the atmosphere, and a large proportion of atmospheric aerosols that are transported globally and may be embedded in ice are organic. However, 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 scarce stability in the atmosphere have so far translated into a shortage of studies determining organic compounds in polar ice cores. 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.

In this paper, we review the different classes of organic compounds that might yield environmental information, discussing what has been done and what is needed to improve knowledge. We first review the problems of sampling, quantifying and interpreting the environmental relevance of organic molecules in ice. We then take a broad look at the different classes of organic compounds that might yield environmental information. Finally, we consider each class in more detail, discussing what has been done, and what is needed to progress study of each class.

We believe that this review paper is appropriate for publication in *Quaternary Science Reviews*, and will serve as the basis for future studies on measurements of organic markers in polar ice and snow.

Best regards,
Chiara Giorio

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.

40 **Keywords**

41 organic compounds, molecular markers, ice core, polar, environmental proxies

42 **1 Introduction**

43 Over the last half century, ice cores have provided a wealth of information about past climate and
44 environmental changes (Jouzel, 2013) over periods ranging from a few years up to 800,000 years.
45 For example, ice core results demonstrate the pattern of glacial-interglacial cycles (Epica
46 community members, 2004), the existence of abrupt climate changes (Johnsen et al., 1992), and
47 quantify how greenhouse gas concentrations increased above their pre-industrial values over the last
48 two centuries (MacFarling Meure et al., 2006). The findings are based on three types of information
49 recorded in ice cores: the isotopic content of the water molecules themselves, the gaseous content of
50 air bubbles trapped in the ice (e.g. CH₄, CO₂), and the impurities that are trapped in or on
51 snowflakes. This last component consists both of aerosol particles and of gaseous compounds that
52 are absorbed onto snow surfaces. Multiple studies quantify many different analytes, and discuss, for
53 example, atmospheric transport of dust, past variations of sea ice, and changes in concentrations of
54 pollutants. The overwhelming majority of studies concentrate on the inorganic impurity – major
55 cations and anions, trace elements, and simple components such as hydrogen peroxide. However, a
56 very large proportion, often half or more, of atmospheric aerosols are organic (Jimenez et al., 2009),
57 and such material is certainly present in polar ice.

58 Very few studies investigate the organic component in polar ice, either as a whole (Legrand et al.,
59 2013), or for individual compounds. There are probably a number of reasons for this shortage:
60 analytical issues, a lack of expertise in the ice core community, and difficulties in interpreting
61 changing concentrations of reactive chemicals which may have relatively short lifetimes and limited
62 stability in the atmosphere. Many of the studies that do exist concern: (a) very small molecules such
63 as formaldehyde and low molecular weight organic acids (e.g. Legrand and De Angelis, 1995), (b)
64 methanesulfonic acid (MSA) as a specific marker for marine biological activity and/or therefore sea
65 ice extent (e.g. Curran et al., 2003), and (c) organic markers for biomass burning (Gambaro et al.,
66 2008; Rubino et al., 2016). Studies in ice and snow of persistent organic pollutants (POPs) (Fuoco
67 et al., 2012; Hermanson et al., 2005; Ruggirello et al., 2010) and of other molecules such as long
68 chain fatty acids that are potential terrestrial biomarkers as they are produced by land-dwelling
69 plants (Hopmans et al., 2004 and references therein; Kawamura et al., 1996; Pokhrel, 2015; Pokhrel
70 et al., 2015) have been carried out but are not well developed in ice from the polar ice sheets.

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

82 **2 Challenges with sampling and analysis of organic molecules**

83 **2.1 General issues during sampling, storage and analysis of organics in ice and snow**

84 The issues that determine our ability to accurately estimate the concentrations of organic molecules
85 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) and avoiding plastics, except perhaps for a low permeability grade of Teflon such as PFAs
133 (i.e. perfluoroalkoxy alkanes). Wrapping firn cores in aluminium foil instead of, or as well as,
134 plastic is also a precautionary measure, which also limits the possibilities for photochemical
135 degradation of some molecules. Maintaining samples in the solid phase rather than as melted
136 samples is preferable for long term storage. However, melted samples can be spiked with HgCl₂ to
137 prevent microbial degradation (Kawamura et al., 2012). For some organic molecules, such as MSA
138 it has been shown that diffusional loss through solid ice can be prevented if samples are refrozen as
139 discrete samples (Abram et al., 2008).

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

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

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

164 Once a clean subsample has been obtained, the issues of contamination control are similar to those
165 encountered in any organic geochemistry laboratory that analyse samples with low concentrations
166 (Section 2.2). A final comment is that the issues discussed above apply to organics as a whole.
167 There may be specific molecules of interest that are not found in significant quantities in drilling
168 fluids, coatings on plastic and in the laboratory environment. However, determining molecules that
169 are not affected by plastic or drilling fluid contamination can only be ascertained by quality control
170 testing for each molecule and in each laboratory. Analytical procedures that are highly selective for
171 a particular molecule of interest (excluding background contamination from interferences) will be
172 advantageous from this viewpoint.

173 **2.2 Analytical methods**

174 Here we discuss methods for sample preparation and analysis of organics in polar ice and snow.
175 The discussion focuses on specific markers and does not describe analytical methods for non-

176 specific compounds that are routinely measured such as greenhouse gases in air bubbles. A more
177 detailed list of methods for each discussed compound/compound class and method performance are
178 available in Section 3 and in Table 1. In cases where many studies exist (e.g. MSA) we only cite a
179 few studies describing the analytical method and its performances. This compilation includes
180 prospective compounds that have not yet been measured in polar ice and snow but have been
181 measured in mountain glaciers.

182 2.2.1 *Glassware, solvent and reagent decontamination*

183 A common practice for trace organic analysis is to use high purity solvents (or distilled solvents)
184 and prebaked or prewashed inorganic reagents (Sankelo et al., 2013; Xie et al., 2000). For specific
185 compounds, like fatty acids, solvents may be a large source of contamination that can be reduced by
186 redistillation (Bosle et al., 2014). Common procedures for decontamination of plastic and glassware
187 for inorganic analysis include soaking in ultrapure water, sonication for a typical time of 10-15 mins
188 and additional rinsing (generally three times) with ultrapure water (Jauhiainen et al., 1999). This
189 procedure has proven to be effective for removing inorganic contamination but other procedures are
190 preferable for organics. Müller-Tautges et al. (2014) cleaned all glass containers by baking them at
191 450°C for 8 h. Similarly, Gowda et al. (2016) prebaked all glassware at 450°C overnight, followed
192 by rinsing with ultrapure water, methanol and dichloromethane. Rinsing with *n*-hexane (after water
193 and dichloromethane) is also recommended (Piazza et al., 2013) when measuring hydrophobic
194 compounds.

195 2.2.2 *Sample preparation and analysis*

196 Organic compounds are present in polar ice and snow samples at trace levels that may challenge
197 many state-of-the-art analytical methods and techniques. For this reason, the vast majority of
198 studies so far have included a pre-concentration step (e.g. Garmash et al., 2013; Grieman et al.,
199 2015; Legrand et al., 1997; McConnell et al., 2007; Pokhrel et al., 2015) with the exception of
200 levoglucosan and vanillic acid which are most commonly analysed without pre-concentration (e.g.
201 Gambaro et al., 2008; Zennaro et al., 2015). The most widely used pre-concentration method is
202 solid phase extraction (SPE) which is applied to non-polar anthropogenic compounds, like
203 polycyclic aromatic hydrocarbons (PAHs), pesticides, polychlorinated biphenyls (PCBs) and per-
204 and polyfluoroalkyl substances (PFASs). For some compounds stir bar sorptive extraction has
205 shown potential (Müller-Tautges et al., 2014), however SPE via cartridge and disc materials are
206 currently more versatile due to the availability of a wider range of sorbents, which allows more
207 targeted method optimisations.

208 For PAHs, SPE leads to recoveries of >80% in Antarctic snow, with a starting sample volume of
209 10 L and limits of detection (LODs) of 0.1 ng/L using GC-MS analysis (Na et al., 2011). For the
210 same compounds, Gabrieli et al. (2010b) used online SPE on a CFA system and obtained a recovery
211 of 71-93% and LODs ranging between 0.007 and 0.466 ng/L using HPLC with fluorescence
212 detection using an initial sample of 250-500 g of melted ice. Kukučka et al. (2010) achieved both
213 lower sample volume and lower LODs using solid phase micro-extraction (SPME) followed by
214 thermal desorption and GC-MS analysis. This method gave good recoveries for small PAHs but it
215 did not give satisfactory recoveries for PAHs with 4-6 rings (Table 1). Liquid-liquid extraction
216 (LLE) for PAHs followed by GC-MS has also been used, reaching similar LODs to those of
217 Gabrieli et al. (2010b) but starting with a much larger sample volume of 7 L (Fuoco et al., 2012).
218 SPE has also been used for a range of different pesticides (e.g. aldrin, DDT), PCBs and PFASs
219 reaching recoveries of >80% and LODs in the order of a few pg/L (Table 1).

220 For MSA analysis, a pre-concentration method similar to SPE using a Trace Anion Concentrator
221 (TAC) with an anion exchange sorbent installed on-line in the ion chromatograph has achieved
222 LODs of 20 ng/L with a 5 mL starting volume (Curran et al., 2003; Saltzman et al., 1997).
223 Conversely, Jauhiainen et al. (1999) used a large loop injection (0.8 mL) reaching LODs of
224 300 ng/L. Saltzman et al. (2006) reached LODs of 100 ng/L using direct injection with an
225 electrospray ionisation source – triple quadrupole mass spectrometer (ESI-MS/MS) upon sample
226 dilution with methanol (50:50), however direct infusion in an ESI source without prior
227 chromatographic separation has been often criticised for being non-quantitative due to competitive
228 ionisation from non-separated matrix components (Kourtchev et al., 2014).

229 SPE was used also for pre-concentration of both natural and anthropogenic *n*-alkanes, *n*-alkan-2-
230 ones and *n*-alkanoic acids prior to analysis with gas chromatography flame ionisation detection
231 (GC-FID) and GC-MS however recoveries and LODs are not reported (Xie 2000). Fatty acids have
232 also been pre-concentrated by LLE and solvent evaporation using a rotary evaporator (rotavap).
233 Seki et al. (2015) effectively concentrated fatty acids in LLE, followed by saponification with KOH
234 in methanol and derivatisation with N,O-Bis(trimethylsilyl)fluoroacetamide (BSTFA) before
235 analysis by GC-MS, showing recoveries of 75-82%. Pokhrel et al. (2015) concentrated the samples
236 with a rotavap (100 mL evaporated to dryness) with recoveries >70% and LODs of 1 ng/L with
237 derivatisation with BF₃/butanol followed by GC-MS. A similar method was used for analysing
238 monoterpene and isoprene secondary organic aerosol (SOA) products showing analogous
239 performances (Pokhrel et al., 2016). Pokhrel et al. (2016) used a rotavap and 150 mL of melted ice
240 after addition of KOH to convert organic acids into potassium salts making them less volatile,
241 followed by derivatisation with BSFTA and analysis in GC-MS. Similarly, Kawamura et al. (2012)
242 quantified dehydroabietic acid, p-hydroxybenzoic acid, levoglucosan, mannosan and galactosan (all
243 biomass burning markers) by using GC-MS after LLE (80-250 mL of sample) and derivatisation
244 with BSTFA reaching LODs of 3-5 ng/L with recoveries of 67-78%. You et al. (2014) obtained
245 similar performances for levoglucosan, mannosan and galactosan with a smaller ice volume of 5
246 mL (Table 1).

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

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

266 needed to push forward fast chromatographic methods with low detection limits and requiring low
267 sample volume.

268 **2.3 General issues about interpreting organics in terms of environmental variables**

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

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

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

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

299 Most inorganic compounds are chemically stable, and so their lifetime is mainly determined by
300 depositional processes. However, the atmospheric lifetime of many organics is also influenced by
301 photo- and thermo-chemical transformations in the atmosphere that may degrade them, or in some
302 cases form them *en route* to the polar regions. Some organic molecules may also be re-volatilised or
303 chemically degraded after deposition which may change the proportional loss of the molecule. For
304 example, changing snowfall rates alter the period of time in which chemicals are exposed to
305 sunlight in the snowpack or when changes in snowpack temperature occur. In the best cases, it may
306 be possible to interpret time series of organics in ice with simple analytical methodologies and a
307 straightforward interpretation. However, for more complex molecules an atmospheric modelling
308 approach (using either a transport model, or a chemistry and transport model) may be needed in
309 order to determine what part of the variability can be attributed to changes in source strength.

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

315 **2.4 Environmental issues and organic molecules**

316 Goldstein and Galbally, (2007), estimate that 10^4 - 10^5 separate organic compounds are in the
317 atmosphere. How do we then prioritise which molecules are interesting to investigate in ice cores?
318 The answer must come from a confluence of our ability to measure these compounds in ice and the
319 environmental questions that we would like to answer. Examples of organic markers that have
320 already been detected in ice cores and yielded environmental information are reported in Figure 1.
321 In this section, we briefly outline important environmental aspects which then lead into Section 3
322 which discusses the organic molecules in ice cores that can address these aspects.

323 *2.4.1 Terrestrial biogenic emissions*

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

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

344 *2.4.2 Biomass burning emissions*

345 Biomass burning is a special case of terrestrial emissions that has received considerable attention.
346 Again, there is interest in quantifying shifts in biomass burning due both to climatic variations and
347 anthropogenic activity. Much of the literature about biomass burning records in ice cores is based
348 on inorganic or small organic molecules that have multiple sources but whose spikes are considered
349 to be indicative of biomass burning. Legrand et al. (2016) and Rubino et al. (2016) recently
350 reviewed these indicators and therefore we will not discuss them here. Black carbon, emitted during
351 incomplete combustion of fossil fuel and biomass in both natural and anthropogenic fires, is not
352 discussed in this review as it is not an organic chemical. Organic molecules can provide more
353 specific markers for burning, and in some cases for the type of material being burnt. However, the

354 episodic nature of burning events poses a challenge when examining changes in biomass burning
355 through time.

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

361 2.4.3 *Marine biogenic emissions*

362 The marine biosphere is also a source of organic emissions (Table 1). Many of the molecules
363 produced in the ocean are recorded, for example, in marine sediments, but are unlikely to be emitted
364 to the atmosphere in any significant quantity. However, a number of gases are emitted and
365 subsequently oxidised to form SOA, and organic particles are also mobilised from the sea surface
366 microlayer. Given that Antarctica and, to a lesser extent Greenland, are surrounded by ocean, even
367 relatively small emissions can be a dominant source of some organic molecules to the ice sheet due
368 to the proximity of the source region. Ice core measurements of selected organics have the potential
369 to reveal the impact of climate on marine biogenic productivity, to assess sea ice extent, and to
370 describe the strength of winds that might mobilise material from the sea surface.

371 2.4.4 *Anthropogenic emissions*

372 The poles remain in the popular imagination as the final frontier of purely natural locations that are
373 far removed from effects of human activity. In fact, the poles are regions of “minimum
374 anthropogenic presence” (Kallenborn et al., 2013) but are not absent of human influence (Bossi et
375 al., 2013; Chen et al., 2015; Fuoco et al., 2012; Hermanson et al., 2005; Ma et al., 2011).

376 Human activity has influenced the emissions of many natural organic compounds into the
377 atmosphere, for example through altering biomass burning rates or changing forest into cropland (or
378 other land use changes). However, perhaps more obvious, is the introduction of new molecules into
379 the atmosphere that were not present (or present in much smaller quantities) until human industrial
380 manufacturing occurred. This class of new compounds includes PCBs and pesticides.

381 Measurements in ice cores can verify the timing of increased emissions and the effectiveness of
382 mitigation measures. These results can also serve as essential background determinations for
383 assessing any ecological effects observed in the polar regions themselves. The choice of chemicals
384 to be measured is therefore based on the strength of concern over ecological and human health
385 risks. The nature of this issue means that such molecules are of interest only in the last few decades
386 up to about two centuries in extreme cases, and will therefore be measured only in relatively
387 shallow cores, and often mainly in firn rather than ice.

388 **3 Organic molecules as environmental proxies**

389 **3.1 Terrestrial biogenic markers**

390 The recent identification of a multitude of biogenic organic markers in snow and ice samples
391 situated both near and far from source regions raises the exciting potential of new environmental
392 proxies that are present in the ice core record. Such compounds have, for example, been found in
393 Alaska (Pokhrel et al., 2015; Sankelo et al., 2013; Yamamoto et al., 2011), the Chinese Himalayas
394 (Xie et al., 2000), Greenland (Grannas et al., 2004; von Schneidmesser et al., 2008), Franz Josef
395 Land, Russia (Grannas et al., 2006), the Tibetan Plateau (Shen et al., 2015) and the Canadian Arctic

396 (Grannas et al., 2004), as well as in oceanic aerosol samples in the Canadian high Arctic (Fu et al.,
397 2013) and over ocean latitudes ranging from the Arctic to Antarctica (Hu et al., 2013). Here we
398 discuss the terrestrial organic compounds so far identified in snow or ice samples, or high latitude
399 atmospheric aerosols, that are most promising as biomarkers in ice.

400 3.1.1 Primary emissions

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

411 The process of emission, long range transport, deposition and entrainment of lipid-based
412 compounds within snow and ice has been demonstrated in previous work, from both shallow snow
413 pit studies and now extending back to ice layers on the order of several hundred years in age.
414 Identification within shallow snow pits in Japan (Sankelo et al., 2013; Yamamoto et al., 2011) and
415 China (Xie et al., 2000) demonstrate the potential of terrestrial organic compounds to be preserved
416 in snow layers, with the major source of the lipid compounds being large forested regions found
417 more proximally to the deposition sites. Extending to more far-reaching deposition sites, De
418 Angelis et al. (2012) observed terrestrial vegetation and biomass burning emissions dominating the
419 carboxylic acid budget within surface snow layers at Summit, Greenland, concluding that aerosols
420 generated by Northern Hemisphere terrestrial biomass are an important contributor to aerosol
421 deposits in the ice record at this high latitude location. Lipid compounds have further been detected
422 in snow layers dating back to 450 years at Site J in Greenland (Kawamura et al., 1996). Although
423 air masses that pass over Greenland contain a more complex mixture of both marine and terrestrial
424 organic aerosols, Kawamura et al. (1996) were able to identify compounds of specific terrestrial
425 origin using a number of distinguishing molecular characteristics (see below), which have been
426 used and expanded on in subsequent studies (Bendle et al., 2007; Pokhrel, 2015; Yamamoto et al.,
427 2011).

428 Lipid compounds from terrestrial sources may be identified as high molecular weight fatty acids
429 (HFA) (>C₂₄), as opposed to low molecular weight fatty acids (LFA) (<C₂₄) which are indicative
430 of marine and microbial sources (Pokhrel, 2015; Yamamoto et al., 2011). Terrestrial particles may
431 further be distinguished from those of anthropogenic sources using the Carbon Preference Index
432 (CPI), determined as the ratio of compounds with odd to even carbon numbers. CPI values >5
433 signify an absence of anthropogenic input, whilst values decreasing down to 1 imply an increasing
434 anthropogenic contribution. Furthermore, the average chain length (ACL) within the different
435 compound groups has been utilised as evidence of specific source regions. Within the *n*-alkane
436 group, for example, greater abundance of longer chain HFAs may indicate warm, tropical source
437 regions, whereas a greater abundance of shorter chain HFAs would suggest more temperate source
438 regions (Bendle et al., 2007). Calculating HFA to total organic carbon (TOC) ratios was further
439 used to identify a tentative link between this ratio and warmer or cooler periods of global
440 temperatures. There were, however, a number of possible explanations of higher ratio values

441 (higher plant emissions, enhanced atmospheric transport, increased area of arid environments, and
442 altering atmospheric transport pathways), and the idea needs refining (Bendle et al., 2007).

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

446 3.1.2 *Secondary oxidation products*

447 Isoprene and terpenes are emitted from all plants including algal sources in ocean regions (Bonsang
448 et al., 1992; Yassaa et al., 2008) and form a significant contribution to the hydrocarbon budget of
449 the atmosphere (Sharkey et al., 2008). In particular, isoprene and monoterpenes have been
450 measured as significant terrestrial emissions, with isoprene dominating in flux studies above
451 Amazonian forest canopies (Kesselmeier et al., 2000; Rinne et al., 2002) and on a global level.
452 Sesquiterpenes also contribute to terrestrial emissions, although flux and oxidation pathways of
453 emissions are difficult to study because of their very high reactivity and lower concentrations (Fu et
454 al., 2013). The emission of isoprene and terpenes is conditional on both heat and light, and is
455 therefore proposed as a ‘thermo-tolerance mechanism’ of plants (Sharkey et al., 2008). The reactive
456 nature of isoprene and terpenes in the atmosphere presents a limitation to the potential for long
457 range transport from the emission site; isoprene, monoterpenes and sesquiterpenes have short
458 chemical lifespans from a few minutes up to a few hours (Kesselmeier et al., 2000), and have not
459 been directly observed in ice. However, the oxidation products of these compounds in both gas and
460 aerosol phase demonstrate a greater potential for longevity in the atmosphere, and possible
461 subsequent deposition into snow and ice further from the source region.

462 Isoprene and terpenes emitted by vegetation are subject to several possible degradation processes in
463 the atmosphere, each of which may or may not result in the formation of SOA (Hallquist et al.,
464 2009) with a multitude of secondary products forming from each primary compound. Table 2 lists a
465 compilation of isoprene and terpene-sourced SOA compounds identified over a range of forested
466 canopy locations and in snow samples from more remote locations. Despite this complexity, and
467 with both degradation pathways and atmospheric concentrations still needing further study (Kroll et
468 al., 2011), a transition in detection of some key SOA components from laboratory-confined
469 experiments to detection in natural atmospheric samples, as well as in some surface snow studies,
470 provides promising results for use of SOA constituents as climate markers (Fu et al., 2009; Pokhrel
471 et al., 2016).

472 Isoprene has been identified as the largest non-methane VOC emission globally, at ~600 Gt/yr
473 (Guenther et al., 2006). Thus, even a very small percentage of VOC to SOA transformation rates
474 could be significant in the total particulate organic matter budget of the atmosphere (e.g. 6 Gt/yr at
475 only 1% yield) (Carlton et al., 2009). Claeys et al. (2004a) first recognised two isoprene oxidation
476 products, 2-methylthreitol and 2-methylerythritol, in Amazonian air samples, bolstered by the
477 association of two gas-phase products of the oxidation process, methacrylic acid and methacrolein,
478 providing a reaction-pathway linking isoprene and the identified SOA composition (Claeys et al.,
479 2004b). It was later shown by Xia and Hopke (2006) that these compounds demonstrate the same
480 seasonal cycle (peak concentrations during summer) as isoprene in forests in the north-eastern
481 United States. The compounds have now been identified in a number of forest-canopy aerosol
482 samples (e.g. Finland (Kourtchev et al., 2005) and Hungary (Ion et al., 2005), and demonstrate the
483 important contribution of isoprene oxidation products to total atmospheric SOA concentrations.
484 However, highly variable lifetimes for these secondary compounds have been suggested (Noziere et
485 al., 2015), which may limit the number of compounds available for consideration.

486 Methylthreitol (an isoprene SOA marker), pinic acid and pinonic acid (monoterpene SOA markers)
487 were estimated to have short lifetimes of only 0.2 days by Noziere et al. (2015), clearly limiting
488 transportation to high latitudes where transport to polar regions may require days. Others, such as
489 MBTCA (3-methyl-1,2,3-butanetricarboxylic acid as a monoterpene SOA marker),
490 nocaryophyllonic acid, caryophyllinic acid and nocaryophyllinic acid (sesquiterpene SOA markers),
491 were estimated to have lifetimes up to 10 days. These values are highly uncertain but in general
492 agree with SOA lifetimes as modelled using global chemistry transport models and general
493 circulation models; with a review of 31 such models by Tsigaridis et al. (2014) finding an average
494 range of SOA atmospheric lifetimes of 2.4-15 days. To further add to this uncertainty, Hu et al.
495 (2013) identified both pinic acid and MBTCA in high latitude samples of atmospheric aerosol, of
496 which a significant contribution to the total concentrations were identified as terrestrially sourced
497 compounds based on atmospheric transport pathway reconstruction for the supplying air masses.
498 More substantially, isoprene and monoterpene oxidation products, including many of those products
499 with proposed short lifetimes of less than 0.2 days, have also been identified in an Alaskan ice core
500 dating back 350 years. For example, Pokhrel et al. (2016) identified a number of terrestrial and
501 marine sourced SOA compounds within the ice samples (Figure 1a), using atmospheric transport
502 pathway reconstruction to determine the compounds' source region. Thus, these compounds
503 demonstrate not only the atmospheric transport and deposition of SOA with terrestrial sources, but
504 also the persistence of these compounds to older ice layers. Many of the observed concentration
505 changes were correlated with Northern Hemisphere temperature fluctuations using a combination of
506 compound groups as well as individual compounds for comparisons (Pokhrel et al., 2016). This
507 observation suggests also that lifetime of these compounds in the particle phase may be longer than
508 estimated, perhaps because SOA particles may have low viscosities limiting uptake and diffusion of
509 oxidants (Virtanen et al., 2010). If the study of these compounds is extended to Antarctica, it will be
510 necessary to distinguish compounds with mainly terrestrial sources from those with mainly marine
511 origins. One method is to test for a temporal correlation between the organic markers of interest and
512 uniquely terrestrial molecules, such as the biomass burning marker levoglucosan, or to compare the
513 results against uniquely marine emissions such as MSA, an approach used by Fu et al. (2013).

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

521 The groups of compounds discussed here offer excellent potential as biomarkers in ice cores. In the
522 northern hemisphere (Greenland), multi-compound studies could, in conjunction with broad
523 determination of their source regions (for example, terrestrial versus marine), allow investigation of
524 past changes in the extent and climate of boreal forests. The same application has yet to be
525 thoroughly tested for the southern hemisphere, where the compounds may be expected in even
526 lower concentrations.

527 **3.2 Indicators of Biomass Burning**

528 Many potential proxies of past fire activity are found in polar snow. The majority of these tracers
529 are directly produced and volatilised during vegetation combustion (e.g. polycyclic aromatic
530 hydrocarbons, black carbon) or as partially combusted biological material (e.g. resin acids, anhydro

531 sugars) (Conedera et al., 2009). Biomass is a biopolymer mainly formed by cellulose,
532 hemicellulose, lignin and fillers (Simoneit, 2002). Cellulose is the main constituent (~30 %) of
533 woody tissue, where its structure of long linear chains of D-glucose monomers is responsible for the
534 structural strength of wood. Hemicellulose is a more complex mixture of polysaccharides derived
535 from glucose, mannose, galactose, xylose and arabinose and is less abundant than cellulose in the
536 woody tissue. Lignin is derived from the polymerisation of *p*-cumaryl, conyferyl and sinapyl
537 alcohols. Thus, the structure of this biopolymer mainly contains anisyl (phenols), guaiacyl
538 (methoxy-phenols) and syringyl (dimethoxy-phenols) nuclei, which are released during lignin
539 pyrolysis (Simoneit, 2002).

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

551 Some biomass burning proxies are specific as they are produced solely from biomass burning, e.g.
552 monosaccharide anhydrides, but other proxies have multiple potential sources other than vegetation
553 fires (e.g. coal burning or biogenic emissions). Here we focus on specific organic markers and how
554 combinations of markers can give additional information.

555 3.2.1 *Monosaccharide Anhydrides*

556 The most abundant monosaccharide anhydrides are levoglucosan and its isomers mannosan and
557 galactosan which are specific proxies for vegetation combustion products (Gambaro et al., 2008;
558 Simoneit, 2002; Zennaro et al., 2014). Levoglucosan (1,6-anhydro- β -D-glucofuranose) is a
559 monosaccharide anhydride which is released only during the pyrolysis of cellulose at temperatures
560 $>300^{\circ}\text{C}$ (Gambaro et al., 2008; Simoneit, 2002). Galactosan and mannosan are released into the
561 atmosphere during the pyrolysis of hemicellulose (Simoneit, 2002). The ratio between levoglucosan
562 and its isomers may help to differentiate contribution of different fuel loads (i.e. lignite,
563 angiosperms, gymnosperms) to the biomass burning signature detected in environmental samples
564 (Engling et al., 2006; Fabbri et al., 2009). These ratios were utilised by Kirchgeorg et al. (2014) in
565 sediment samples and in ice samples from the Ushkovsky, Kamchatka Peninsula, ice core
566 (Kawamura et al., 2012), but no attempts exist in polar ice core samples.

567 Levoglucosan may be oxidised by $\cdot\text{OH}$ in the gas phase (Hennigan et al., 2010) and in atmospheric
568 water droplets (Hoffmann et al., 2010), resulting in an atmospheric lifetime on the order of days to a
569 few weeks (Fraser and Lakshmanan, 2000; Hennigan et al., 2010; Ramanathan and Carmichael,
570 2008). Levoglucosan, therefore, is a suitable tracer for the quantification of fire activity even to
571 remote locations due to its high concentration in vegetation fire plumes (Fraser and Lakshmanan,
572 2000; Holmes and Petrucci, 2006, 2007; Kehrwald et al., 2012; Zennaro et al., 2014). Kehrwald et
573 al. (2012) demonstrated the applicability of the levoglucosan analyses to reconstruct past fire
574 activity in Greenland snow pits with a known fire signature in August 1994 caused by biomass

575 burning plumes originating in Canada and transported eastward to Greenland within a matter of
576 days.

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

587 3.2.2 *Lignin and conifer resin pyroproducts*

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

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

607 3.2.3 *Polycyclic Aromatic Hydrocarbons (PAHs)*

608 PAHs are produced by both biomass burning and fossil fuel burning (Macdonald et al., 2000 and
609 references therein) (see also 3.4.3). The ratio of specific PAHs released during vegetation
610 combustion may help identify samples containing forest fire signatures (Li et al., 2011; Masclet et
611 al., 2000; Slater et al., 2002). In addition, burning vegetation produces carbon particles and gases
612 containing “modern” levels of ¹⁴C, while compounds from fossil fuel combustion do not contain the
613 heavy carbon isotope (Slater et al., 2002). Combining PAH ratios with black carbon concentrations
614 and isotopic ratios of greenhouse gases can help differentiate biomass sources from anthropogenic
615 sources.

616 One of the most specific PAHs is retene, a PAH released during boreal forest fires. Fluoranthene
617 and pyrene, the two most abundant PAHs in superficial Greenland snow, are generally associated

618 with vehicular, industrial and biomass combustion including from household heating resulting in
619 seasonally-varying polar concentrations (Masclat et al., 2000; Slater et al., 2002). Other PAHs (i.e.
620 benzo[ghi]-perylene, benzo[e]pyrene) are mainly released by traffic sources (Li et al., 2011;
621 Masclat et al., 2000; Nielsen, 1996). Therefore, correlations between pyrene + fluoranthene and
622 sulfate indicate a common anthropogenic origin. The simultaneous deposition of retene and
623 ammonium indicate common boreal conifer fire sources, thus confirming these PAHs as good
624 tracers for biomass burning events (Masclat et al., 2000).

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

632 *3.2.4 Sources of biomass burning plumes reaching polar ice cores*

633 Generally, all of the fire reconstructions based on the chemical analyses of Greenland ice refer to
634 boreal North America as the most important geographical origin source of the biomass burning
635 plumes (Taylor et al., 1996). Zennaro et al. (2014) suggested that Central Asian forest fires may
636 also be an important contributor to fire products reaching northwest Greenland due to the
637 observations of peak fire proxy concentrations in the NEEM ice core during the most severe Central
638 Asian droughts of the last millennium. Source regions for biomass burning material reaching
639 Greenland most likely moved between the glacial and interglacial period (Zennaro et al., 2015). For
640 example, Siberian and Canadian boreal forests are likely the main sources in the Northern
641 Hemisphere of biomass burning products reaching Greenland (Zennaro et al., 2014), and ice cover
642 will have removed much of this source in the last glacial period.

643 During the glacial-interglacial transition, source regions for biomass burning in the Southern
644 Hemisphere probably remained the same as modern sources (De Angelis et al., 2012). The closest
645 possible biomass burning source regions to Antarctica are South America, Australia and Southern
646 Africa. Very little is known regarding the origin of biomass burning plumes reaching Antarctica
647 over centennial or longer timescales, especially as these timescales are dependent upon changing
648 fuel loads, circulation patterns and the atmospheric lifetime of pyrotracers. However, radiogenic
649 isotope analyses (Sr, Nd and Pb isotopes) demonstrate that the majority of dust in Antarctica comes
650 from South America over glacial-interglacial timescales, and particularly from Southern South
651 America regions such as Patagonia (Delmonte et al., 2008; Marino et al., 2008; Vallelonga et al.,
652 2010). Australia is also a possible aerosol source, especially during warm periods (Bory et al., 2010;
653 Marino et al., 2008; Siggaard-Andersen et al., 2007; Vallelonga et al., 2010). For these distant
654 sources in South America, Africa and Australia, it is necessary to consider both changes in biomass
655 burning locations, and possible increases in transport efficiency and lifetime (due to reduced
656 precipitation) when discussing glacial-interglacial record of past fire activity in Antarctic ice cores.

657 **3.3 Indicators of Marine Biogenic Activity**

658 Marine aerosols contribute significantly to the global aerosol budget and comprise both organic and
659 inorganic components. The organic component of marine aerosols arises from either primary or
660 secondary organic aerosols. Primary organic aerosol particles are generated via wind driven bubble
661 bursting processes at the ocean surface resulting in sea spray. Sea spray –derived aerosol particles

662 are composed of sea salt, which is enriched with organic matter when the sea surface is
663 characterised by high concentrations of biogenic organic matter (O'Dowd et al., 2004). SOA can
664 form in the marine boundary layer from biogenic volatile organic compounds emitted by the sea
665 surface. Despite considerable advances in our understanding of marine organic aerosols in recent
666 years, the formation and sources remain poorly constrained. Here we discuss the marine organic
667 compounds identified in snow or ice samples and the most promising marine aerosol markers not
668 yet investigated in ice.

669 *3.3.1 Primary emissions*

670 The primary organic aerosols produced from bubble bursting typically contain homologous series of
671 oxohydroxy- or methoxy- branched fatty acids and mono-, di- and tricarboxylic acids,
672 monoterpenes and sugars (Schmitt-Kopplin et al., 2012) together with bacteria, fragments of marine
673 organisms and secretions of algae (Leck and Bigg, 2005). Unsaturated fatty acids such as oleic acid
674 (C_{18:1}), a major constituent of cell membranes in marine phytoplankton (especially diatoms), are
675 abundant in the marine environment and dominate the sea surface micro layer (Hardy, 1982;
676 Mochida et al., 2002).

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

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

695 *3.3.2 Secondary oxidation products*

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

705 hypothesised that MSA preserved in ice cores could be used to reconstruct past marine productivity
706 and sea ice coverage.

707 Statistically significant correlations between MSA and sea ice extent (Figure 1c) have been
708 observed at a number of coastal sites around Antarctica (Abram et al., 2010; Curran et al., 2003;
709 Foster et al., 2006; Thomas and Abram, 2016; Welch et al., 1993), where high MSA represents
710 extensive winter sea ice extent. A greater sea ice extent leads to a larger area of sea ice breakup
711 during the spring and summer, allowing for greater biological activity and DMS production.
712 However, a converse relationship has also been observed with MSA from sites in West Antarctica,
713 where elevated MSA represents summer productivity within the sea ice zone and the presence of
714 open water polynyas (Criscitiello et al., 2013; Rhodes et al., 2009; Sinclair et al., 2014). MSA is
715 less studied in the Arctic although MSA from coastal Svalbard has been related to summer sea ice
716 extent (O'Dwyer et al., 2000). Satellite-derived connections between Arctic ice edge and algal
717 blooms (Perrette et al., 2011) and atmospheric measurements of DMS (Sharma et al., 2012) show
718 promise for MSA as a proxy of past sea ice conditions. The amount of MSA preserved in an ice
719 core reflects not only changes in the amount of DMS produced within the sea ice zone but also the
720 transport, deposition and preservation of MSA on the ice sheet (Abram et al., 2007; Becagli et al.,
721 2009; Fundel et al., 2006; Preunkert et al., 2008) and thus careful site examination and calibration
722 of MSA with satellite sea ice data is essential.

723 Isoprene SOA tracers are believed to be derived from dual (marine and terrestrial) biogenic sources
724 (see also Section 3.1.2). However, the annual global marine SOA from isoprene and monoterpene
725 oxidation is considerably less than the oxidation products of DMS and marine amines (Vignati et
726 al., 2010 and references therein). Globally, terrestrial vegetation is a major source of isoprene
727 emissions, while marine vegetation is only a minor source of isoprene emissions (Hallquist et al.,
728 2009). However, the air masses reaching the Antarctic have a strong oceanic influence while
729 terrestrial sources have less of an influence due to their distance from the continent.

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

739 Organosulfates (sulfate esters of C₉–C₁₃ hydroxyl carboxylic acids) can also be considered as
740 marine SOA tracers. They arise from the oxidation of unsaturated fatty acids derived from marine
741 algae (Claeys et al., 2010). Organosulfates have been observed at low concentrations in the Indian
742 Ocean and may be detectable at coastal polar locations close to sea ice algae (Grannas et al., 2006).
743 However, organosulfates have been observed in terrestrial SOA studies from reaction of organics
744 with anthropogenic H₂SO₄ (Surratt et al., 2007) so specificity to marine sources needs to be tested
745 for each individual sulfate ester compound.

746 **3.4 Anthropogenic Emissions**

747 Transport of anthropogenically-emitted compounds from lower latitudes to the Arctic (and to a
748 lesser extent the Antarctic) has been recognised for many decades, and is commonly referred to as

749 Arctic Haze (e.g. Barrie et al., 1992). In addition, human presence in the polar regions is increasing
750 with a warming climate. Declining Arctic sea ice is opening up a September Northwest Passage for
751 shipping traffic (Laliberté et al., 2016), and mineral exploration in the Arctic has the potential to
752 substantially alter the regional concentrations of anthropogenic aerosols (e.g. Bedini, 2011). In
753 Antarctica, isolated research stations provide interesting case studies of the areal extent of
754 contamination from point sources. Here we discuss the most important classes of anthropogenic
755 organic compounds detected in polar regions and potential implications of their presence in the ice
756 caps. One common aspect of many of these compounds is that they may be re-volatilised to the
757 atmosphere as ice recedes in a warming climate, and therefore the potential to reintroduce phased-
758 out compounds to the atmosphere has to be recognised.

759 3.4.1 *Persistent Organic Pollutants (POPs)*

760 POPs are primarily anthropogenic compounds that are recalcitrant to biological and chemical
761 degradation under most environmental conditions. The persistence of these pollutants and their
762 resistance to degradation in the environment results in their accumulation in ice, sediments, and
763 within animal and human tissues (e.g. Andersen et al., 2015; Chen et al., 2015; Gustafsson et al.,
764 2005). Many POPs were first synthetically produced in the mid-twentieth century as pesticides,
765 industrial chemicals, and solvents. Due to the detrimental and far-reaching effects of POPs on
766 human health, the Stockholm Convention on Persistent Organic Pollutants, which entered into force
767 in 2004, restricts or bans the production and continued use of POPs (chm.pops.int; UNEP, 2004).
768 The Stockholm Convention identified an initial “dirty dozen” of POPs (Table 3) that required an
769 immediate cessation due to their toxicity, persistence, and noted bioaccumulation (chm.pops.int;
770 UNEP, 2004; Table 3). The majority of the “dirty dozen” are pesticides; as pesticides are primarily
771 used in areas with substantial agriculture, any pesticides present in polar regions arrived via long-
772 range transport.

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

785 3.4.2 *Polychlorinated biphenyls (PCBs)*

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

790 PCBs can arrive to the poles through long-range atmospheric transport due to their high vapour
791 pressure, and a relatively long atmospheric lifetime of up to 30 days in the gas phase (Anderson and
792 Hites, 1996). PCBs are primarily removed from the atmosphere by reacting with ·OH; oxidation is

793 slower in polar areas due to low temperatures, low humidity, and low tropospheric ozone
794 concentrations (Ruggirello et al., 2010). The lack of UV-B radiation during the polar night means
795 that ·OH are not produced during the corresponding winter months, resulting in a longer lifetime of
796 PCBs in polar areas than in other regions (Brönnimann et al., 2000).

797 PCBs are deposited on the surface by partitioning into aerosol particles and incorporation into
798 snowfall (Garmash et al., 2013; Wania et al., 1998). Lower-chlorinated PCB congeners tend to
799 return to the surface by dry deposition, while higher-chlorinated PCB congeners are mainly
800 deposited by wet deposition (Steinlin et al., 2014). This difference in deposition means that the
801 lower-chlorinated PCBs may re-volatise after deposition, and therefore may not be incorporated
802 into the deeper glacier ice. The surface snowpack acts as a filter for the compounds where heavy
803 PCBs may bind to fine suspended particles resulting in an enrichment of PCBs in particle layers
804 (Pavlova et al., 2015). The higher-chlorinated PCB congeners may then be more prevalent in glacier
805 ice (Steinlin et al., 2014). Once PCBs are incorporated into the glacier ice, they undergo a variety of
806 processes (e.g. volatilisation and chemical transformation) before they are permanently archived, as
807 discussed in general terms in section 2.3. In particular, they may be subject to vertical and
808 horizontal transport within the glacier, leading to a subsequent release into meltwater (Blais et al.,
809 2001; Schmid et al., 2011), or to surface meltwater containing dissolved PCBs that percolate
810 through the firn where they may then refreeze at a deeper level in the glacier ice (Pavlova et al.,
811 2015).

812 Similar to the other POPs polar ice caps are also increasingly becoming a source of PCBs through
813 re-volatilisation into the atmosphere (Ma et al., 2011). Concentrations of PCBs in the Arctic
814 steadily declined in atmospheric samples collected at Alert, Canada from 1992 to 2000 due to the
815 restrictions on the current and future production of PCBs (Hung et al., 2005). This declining trend
816 in PCB concentrations was also observed until approximately 2000 is also present in a 37 m ice
817 core from Lomonosovfonna, Svalbard (Garmash et al., 2013). However, the Σ PCB concentrations
818 increased in the Lomonosovfonna ice core and remain elevated from 1998 until 2009 (Garmash et
819 al., 2013). Back trajectories demonstrate that air masses influencing Lomonosovfonna originate in
820 Europe and western Russia where relic PCBs from urban areas and/or incineration of older
821 materials that contain PCBs may influence the high PCB concentrations in Svalbard over the last
822 decade. These high PCB concentrations are consistent with model simulations and high Arctic
823 atmospheric concentrations resulting from the revolatilisation of POPs from ice into the atmosphere
824 due to warming temperatures (Garmash et al., 2013; Ma et al., 2011). Due to their persistence and
825 previous entrapment in sinks such as snow and ice, atmospheric concentrations of PCBs and other
826 POPs may continue to increase in a warming climate, where these concentrations may be especially
827 high in polar regions.

828 3.4.3 Polycyclic aromatic hydrocarbons or pseudo-POPs

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

835 PAHs primarily arrive to polar regions through atmospheric transport. Heavier, less-volatile PAHs
836 travel with particles in the atmosphere, where they arrive along the same trajectories that transfer
837 chemicals from the mid-latitudes (Barrie et al., 1992). As heavier PAHs are associated with

838 particles, they are removed from the atmosphere by precipitation. During the Arctic winter months,
839 PAHs may remain in the atmosphere for up to ~30 days, while the more frequent summer Arctic
840 precipitation results in atmospheric residence times of less than a week (Macdonald et al., 2000).
841 PAHs may re-enter the atmosphere even after they are deposited through the resuspension by
842 winds, by the removal of sediments or snow that had covered the PAHs and associated particles, or
843 by re-volatilising due to increased temperatures (Macdonald et al., 2000; Wania and Mackay,
844 1996).

845 Less-volatile PAHs travel with particles in the atmosphere, where they arrive along the same
846 trajectories that transfer chemicals from the mid-latitudes (Barrie et al., 1992). As heavier PAHs are
847 associated with particles, they are removed from the atmosphere by precipitation. During the Arctic
848 winter months, PAHs may remain in the atmosphere for up to ~30 days, while the more frequent
849 summer Arctic precipitation results in atmospheric residence times of less than a week (Macdonald
850 et al., 2000). PAHs may re-enter the atmosphere even after they are deposited through the
851 resuspension of dust or snow by winds, by the removal of sediments or snow that had covered the
852 PAHs and associated particles, or by revolatilizing due to increased temperatures (Macdonald et al.,
853 2000; Wania and Mackay, 1996).

854 PAHs from human activities are pervasive in the Arctic and Antarctic including in the seawater and
855 air (Lohmann et al., 2009), as well as snow and ice (Masclat et al., 2000; Vecchiato et al., 2015).
856 Innovative work examining PAHs in Arctic snow and ice cores over the past few centuries
857 demonstrate an exponential increase in PAHs beginning in the 1930s associated with the major
858 increase in fossil fuel burning (Jaffrezo et al., 1993; Jaffrezo et al., 1994; Kawamura et al., 1994;
859 Masclat et al., 1995; Masclat et al., 2000). This increase in PAH concentrations is consistent across
860 the Arctic, yet the concentrations vary by region where the Agassiz Ice Cap, Canada has the highest
861 concentrations (mean of ~60 ng/L with a peak concentration of 640 ng/L), while Lomonosovfonna,
862 Svalbard contains mid-range concentrations of 5-53 ng/kg, and Greenland ice core concentrations
863 tend to have the lowest PAH values with a maximum of only 0.5 ng/L (Vehvilainen et al., 2002 and
864 references therein). PAH concentrations in the Lomonosovfonna ice core are characterised by a
865 clear seasonality, with higher concentrations associated with the buildup of the wintertime Arctic
866 Haze due to transports of chemicals/aerosols from the mid-latitudes (Macdonald et al., 2000;
867 Vehvilainen et al., 2002 and references therein). Less is known about PAH concentrations in the
868 Antarctic compared to the Arctic. However, the Talos Dome, Antarctica ice core demonstrates
869 similar trends in PAH concentrations as the Arctic ice cores, where ΣPAHs markedly increase
870 beginning in the 1930s due to fossil fuel burning (Fuoco et al., 2012). This increase is less than in
871 the comparable Arctic ice cores, as the Talos Dome PAH concentrations rise by 50% instead of an
872 exponential increase observed in the Arctic (Fuoco et al., 2012). Future studies regarding the
873 seasonality and spatial distribution of PAHs in Antarctic ice can help better compare these two
874 locations.

875 3.4.4 *Emerging pollutants*

876 Emerging pollutants, i.e. substances that are not commonly monitored but have the potential to
877 enter into the environment and cause ecological and/or public health effects (Geissen et al., 2015),
878 are worth investigating in shallow cores and surface snow in polar regions to understand the extent
879 of pollution. These can include new classes of pesticides, pharmaceuticals, disinfection by-products,
880 wood preservation and industrial chemicals (Geissen et al., 2015) that could potentially enter into
881 global atmospheric or marine transport. For example, little is known about Arctic concentrations of
882 the most recent replacement pesticides, like the widely-used neonicotinoids that have dominated the

883 insecticide market since the early 1990s and are only very recently partially being banned
884 (Bonmatin et al., 2015; Simon-Delso et al., 2015). In addition, brominated flame-retardants (BFRs),
885 compounds that are used to slow the spread of flames in residential and commercial indoor fabrics,
886 foams, and electronics, have been found in Arctic wildlife, lake sediments, ice and air samples
887 (Barbante et al., 2017 and references therein).

888 Perfluorinated chemicals (PFCs), also known as per- and polyfluoroalkyl substances (PFASs),
889 contain many of the same concerns as previous POPs in the fact that they are present throughout the
890 globe, bioaccumulate, do not degrade in the environment, and can be toxic to both animals and
891 humans (Ahrens et al., 2011; Wang et al., 2014 and references therein). Increasing evidence
892 demonstrates that long-chain PFASs (LC PFASs) with 6 and more perfluoroalkyl carbons, and
893 long-chain perfluoroalkyl carboxylic acids (LC PFCAs) with 7 and more perfluoroalkyl carbons are
894 more toxic and more prone to bioaccumulate than their shorter-chained variations (Buck et al.,
895 2011; OECD, 2013). Due to their persistence in the environment, bioaccumulation, and toxic
896 effects, both industry and government regulators are attempting to reduce the production and release
897 of LC PFCAs. Although these substances have been phased-out in much of Western Europe, Japan,
898 and the United States, these chemicals are still produced in continental Asia (Wang et al., 2014).

899 Although PFASs and PFCAs are ubiquitous in the environment, their transport mechanisms still
900 require further study (Armitage et al., 2009; Wang et al., 2014). PFCAs do not attach to particulate
901 matter settling into the deep ocean, and therefore remain dissolved in water (Armitage et al., 2009;
902 Scheringer et al., 2004). Modelling and observational studies show that PFCAs primarily arrive to
903 the Arctic and Antarctic Oceans via marine transport (Armitage et al., 2009; Prevedouros et al.,
904 2006; Yamashita et al., 2005). PFCAs can volatilise from the ocean in more temperate locations, but
905 the polar low temperatures and sea ice cover inhibit their volatilization once PFCAs reach the poles
906 (Wania, 2006).

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

919 **4 Conclusions**

920 There is a great potential for organic aerosol compounds to be used as proxies for terrestrial
921 biogenic emissions, past fire events of different types of biomasses, marine biogenic activity and
922 anthropogenic activities, all further leading to the possibility of inferring temperature fluctuations,
923 changes in sea ice and even large-scale climate variability. However, their measurement in polar ice
924 has proved to be challenging. More research is needed to advance our understanding of compound-
925 specific behaviour and stability related to atmospheric and ice archive lifetimes and characterization
926 of sources of sample contamination that may arise during drilling, and subsequent storage and
927 transport. Specific decontamination and clean handling procedures suited for organic analysis still

928 needs development and validation. This aspect may include installing clean rooms specifically
929 designed for handling samples for organic analysis, avoiding plastic materials and installing
930 appropriate filters to eliminate organic vapours.

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

940 Concerning terrestrial emissions, fatty acids, together with isoprene, monoterpene, and
941 sesquiterpene SOA products, offer excellent potential as terrestrial biomarkers in ice cores. While
942 detection of all individual compounds may prove challenging due to their variable reactivities, long-
943 distance transport and long-term preservation of many of the compounds of interest was shown in
944 snow layers well within the perimeters of the polar regions. Biomass burning is by far the most
945 studied area in terms of available measurements of organic markers in the Arctic. Yet in this area,
946 more studies are needed to assess atmospheric lifetimes of biomass burning markers, improve the
947 predictability of past transport dynamics in air masses around the globe and improve analytical
948 capabilities towards the measurement of multiple proxies with the same method and in high
949 temporal resolution (i.e. low sample volume). Lignin pyrolysis products and resin acids show the
950 potential, if coupled with measurements of levoglucosan and its isomers, to differentiate between
951 different types of biomass being burned. Furthermore, it would be interesting to assess the
952 possibility to use mega fire events (i.e. recorded as levoglucosan or black carbon spikes) as
953 temporal horizons for precise ice core chronologies.

954 The use of marine organic aerosols in polar ice is a relatively new area of research and one that
955 requires considerable investigation. The main problems are that marine organic aerosols are
956 influenced not only by oceanic emissions of primary aerosols and SOA precursors, but also by
957 continental emissions through long-range atmospheric transport. This should have less of an
958 influence in the Antarctic, especially at coastal locations. However, careful site assessment and
959 calibration with observational records such as satellite measurements of sea ice extent is required
960 and may also be hindered by a lack of field measurements of marine aerosols, especially in the polar
961 regions, limiting our understanding of the abundances of biogenic SOA in the marine boundary
962 layer. Dimethyl and diethylammonium salts can be potentially viable indicators of marine biogenic
963 activity, but as yet they have not been measured in polar ice.

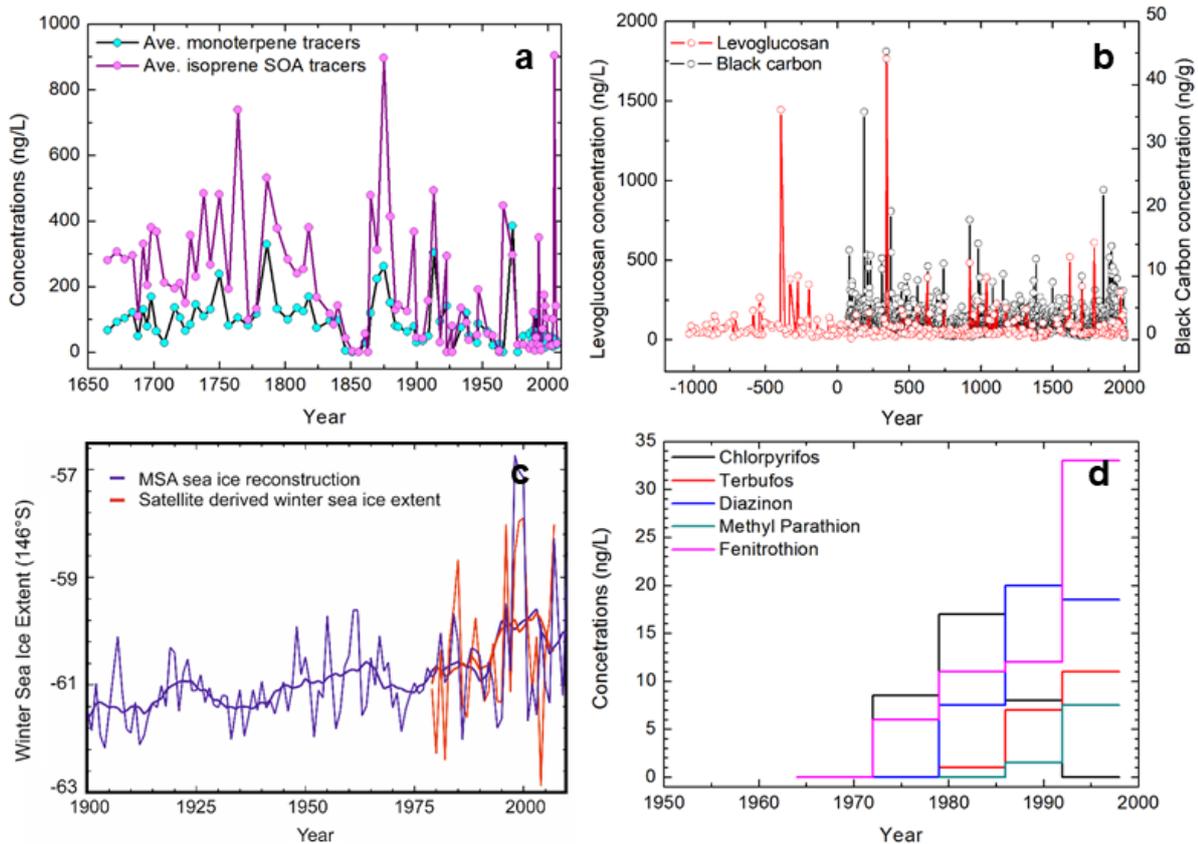
964 Despite the poles, and especially Antarctica, being the most pristine regions on Earth, human
965 influence has been recorded on both surface snow and shallow ice cores. A plethora of
966 anthropogenic compounds have been measured in ice samples, including many pesticides, POPs,
967 PCBs, PAHs, and PFASs, and in the local fauna. Ice cores can document the input of compounds
968 with harmful environmental properties, bioaccumulation, and toxic effects to the polar regions, as
969 well as the beneficial effects of mitigation measures. Additional complexity occurs since some of
970 these compounds may be released from the archives in a warming climate by re-evaporation in the
971 air-snow interface or re-dissolution in the ocean. Finally, research is needed to establish baseline ice
972 core measurement and to develop robust analytical techniques to better understand the

973 environmental spread of replacement pesticides and other emerging pollutants introduced in the
974 environment by human activities.

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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)

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)

Markers of both anthropogenic fossil fuel combustion sources and biomass burning

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	(Mascllet et al., 2000)

PAHs	filtration, essication	SFE-GC/MS ^e	100-200 mL			Σ 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	Σ PAH 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 (Σ PAH)	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 (Σ PAH)	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 (Σ PAH)	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 (Σ PAH)	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				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)
	Extraction	GC-MS	100 mL	>70%					(Ho et al., 2010)
Monoterpene and isoprene SOA tracers	Preconc. in rotavap				0.001 µg/L	average 7-692 µg/L, range 0-3509 µg/L	Ice core, Aurora Peak, Alaska	180 m 1665AD-2008AD	(Kawamura, 1993)
	Derivatisation (BF ₃ / <i>n</i> -butanol)	GC-MS	150 mL	>70%					(Ho et al., 2010)
C _{26:0} -C _{30:0} monocarboxylic acids	LLE	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)
	Saponification								(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	Snowpit, Xixiabangma Ice cores, Dasuopu glacier, Tibetan Plateau	240cm-900m Summer 1996-Summer 1997		(Xie et al., 2000)
					2.12-3.07 µg/L n-alkan-2-ones				
Marine biomarkers									
MSA/MS-	Online precon. 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 precon. with TAC	IC-conductimetry	5 mL		0.25 µg/L	mean background 1.2-2.9 µg/L	Ice cores GRIP 93a and GRIP 93b, Summit, Greenland	GRIP 93a: 73m	(Legrand et al., 1993)
								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 precon. 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 precon. 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)
	Precon. in rotavap							180m	
Oleic acid (C _{18:1})	Extraction Derivatisation (BF ₃ /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	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)
Biomass burning markers									
Levoglucosan	direct injection	HPLC-ESI(-)-MS/MS	100 µL	-	3 ng/L	4 – 30 ng/L	Dome C, Antarctica	2396.8 m (274.1 kyr BP) 2721.4 m (401.6 kyr BP)	(Gambaro et al., 2008)

Levoglucozan	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)
Levoglucozan	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)
Levoglucozan	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)
Levoglucozan	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)
Levoglucozan, mannosan, galactosan	Freeze-drying Extraction Derivatization (MSTFA)	GC/MS	5 mL	65-81%	0.070 µg/L (levoglucozan) 0.058 µg/L (mannosan) 0.046 µg/L (galactosan)	up to 1.93 µg/L mean 0.44 µg/L	Muztagh Ata and Kuokuosele glaciers, Tibetan Plateau		(You et al., 2014)

Levoglucosan, mannosan, galactosan	Preconc. in rotavap								
	Extraction	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	Derivatization (BSTFA)								
	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	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	Derivatization (BSTFA)								
	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	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)
<i>p</i> - hydroxybenzoic acid	Derivatization (BSTFA)								
	Preconc. in rotavap								
	Extraction	CG/MS	80-250 mL	78±18%	0.005 µg/L	up to 1.74 µg/L mean 0.24 µg/L	Ushkovsky ice cap, Kamchatka	1.32 – 152.6 m 1997 - 1963 AD	(Kawamura et al., 2012)
	Derivatization (BSTFA)								

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

Isoprene SOA	Location
2-methyltetrols:	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)
2-methylthreitol	
2-methylerythritol	
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)
C ₅ -alkene triols:	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)
<i>cis</i> -2-methyl-1,3,4-trihydroxy-1-butene	
<i>trans</i> -2-methyl-1,3,4-trihydroxy-1-butene	
3-methyl-2,3,4-trihydroxy-1-butene	
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)
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)
pinanaldehyde; pinanediol mononitrate; norpinonic acid; terebic acid; ketolimononic acid; limonic acid; homoterpenylic acid; diterpenylic 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-dimethylbicycloheptan-6-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)

Sesquiterpene SOA	Location
<i>β</i> -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)
<i>β</i> -nocaryophyllonic acid; 2-(2-carboxyethyl)-3,3-dimethylcyclobutanecarboxylic acid	Boreal Forest Finland (van Eijck et al., 2013)

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Table 3. The "Dirty Dozen" of Persistent Organic Pollutants (POPs) as identified by the Stockholm Convention 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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