

1 Prospects for reconstructing paleoenvironmental conditions from organic 2 compounds in polar snow and ice

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21 **Notes**

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24 **Abstract**

25 Polar ice cores provide information about past climate and environmental changes over periods
26 ranging from a few years up to 800,000 years. The majority of chemical studies have focused on
27 determining inorganic components, such as major ions and trace elements as well as on their
28 isotopic fingerprint. In this paper, we review the different classes of organic compounds that might
29 yield environmental information, discussing existing research and what is needed to improve
30 knowledge. We also discuss the problems of sampling, analysis and interpretation of organic
31 molecules in ice. This review highlights the great potential for organic compounds to be used as
32 proxies for anthropogenic activities, past fire events from different types of biomass, terrestrial
33 biogenic emissions and marine biological activity, along with the possibility of inferring past
34 temperature fluctuations and even large-scale climate variability. In parallel, comprehensive
35 research needs to be done to assess the atmospheric stability of these compounds, their ability to be
36 transported long distances in the atmosphere, and their stability in the archive in order to better
37 interpret their fluxes in ice cores. In addition, specific decontamination procedures, analytical
38 methods with low detection limits (ng/L or lower), fast analysis time and low sample requests need
39 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) or stainless-steel containers (Domine et al., 2007; Giannarelli et al., 2017; Gustafsson et al.,
133 2005) and avoiding plastics, except perhaps for a low permeability grade of Teflon such as PFAs
134 (i.e. perfluoroalkoxy alkanes). Wrapping firn cores in aluminium foil instead of, or as well as,
135 plastic is also a precautionary measure, which also limits the possibilities for photochemical
136 degradation of some molecules. Maintaining samples in the solid phase rather than as melted
137 samples is preferable for long term storage. However, melted samples can be spiked with HgCl₂ to
138 prevent microbial degradation (Kawamura et al., 2012). For some organic molecules, such as MSA
139 it has been shown that diffusional loss through solid ice can be prevented if samples are refrozen as
140 discrete samples (Abram et al., 2008).

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

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

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

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

177 **2.2 Analytical methods**

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

186 *2.2.1 Glassware, solvent and reagent decontamination*

187 A common practice for trace organic analysis is to use high purity solvents (or distilled solvents)
188 and prebaked or prewashed inorganic reagents (Sankelo et al., 2013; Xie et al., 2000). For specific
189 compounds, like fatty acids, solvents may be a large source of contamination that can be reduced by
190 redistillation (Bosle et al., 2014). Common procedures for decontamination of plastic and glassware
191 for inorganic analysis include soaking in ultrapure water, sonication for a typical time of 10-15 mins
192 and additional rinsing (generally three times) with ultrapure water (Jauhiainen et al., 1999). This
193 procedure has proven to be effective for removing inorganic contamination but other procedures are
194 preferable for organics. Müller-Tautges et al. (2014) cleaned all glass containers by baking them at
195 450°C for 8 h. Similarly, Gowda et al. (2016) prebaked all glassware at 450°C overnight, followed
196 by rinsing with ultrapure water, methanol and dichloromethane. Rinsing with *n*-hexane (after water
197 and dichloromethane) is also recommended (Piazza et al., 2013) when measuring hydrophobic
198 compounds.

199 *2.2.2 Sample preparation and analysis*

200 Organic compounds are present in polar ice and snow samples at trace levels that may challenge
201 many state-of-the-art analytical methods and techniques. For this reason, the vast majority of
202 studies so far have included a pre-concentration step (e.g. Garmash et al., 2013; Grieman et al.,
203 2015; Legrand et al., 1997; McConnell et al., 2007; Pokhrel et al., 2015) with the exception of
204 levoglucosan and vanillic acid which are most commonly analysed without pre-concentration (e.g.
205 Gambaro et al., 2008; Zennaro et al., 2015). The most widely used pre-concentration method is
206 solid phase extraction (SPE) which is applied to non-polar anthropogenic compounds, like
207 polycyclic aromatic hydrocarbons (PAHs), pesticides, polychlorinated biphenyls (PCBs) and per-
208 and polyfluoroalkyl substances (PFASs). For non-volatile compounds, another common pre-
209 concentration method is solvent evaporation, often using a rotary evaporator (Fu et al., 2016;
210 Kawamura, 1993; Pokhrel et al., 2015; Pokhrel et al., 2016). For some compounds stir bar sorptive
211 extraction has shown potential (Müller-Tautges et al., 2014), however SPE via cartridge and disc
212 materials are currently more versatile due to the availability of a wider range of sorbents, which
213 allows more targeted method optimisations. For volatile compounds, such as volatile halogenated
214 hydrocarbons, purge-and-trap injections, followed by GC-MS analysis, has been used as a
215 preconcentration method for the analysis of Antarctic snow (Zoccolillo et al., 2005).

216 For PAHs, SPE leads to recoveries of >80% in Antarctic snow, with a starting sample volume of
217 10 L and limits of detection (LODs) of 0.1 ng/L using GC-MS analysis (Na et al., 2011). For the
218 same compounds, Gabrieli et al. (2010b) used online SPE on a CFA system and obtained a recovery
219 of 71-93% and LODs ranging between 0.007 and 0.466 ng/L using HPLC with fluorescence
220 detection using an initial sample of 250-500 g of melted ice. Kukučka et al. (2010) achieved both

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

228 For MSA analysis, a pre-concentration method similar to SPE using a Trace Anion Concentrator
229 (TAC) with an anion exchange sorbent installed on-line in the ion chromatograph has achieved
230 LODs of 20 ng/L with a 5 mL starting volume (Curran et al., 2003; Saltzman et al., 1997).
231 Conversely, Jauhiainen et al. (1999) used a large loop injection (0.8 mL) reaching LODs of
232 300 ng/L. Saltzman et al. (2006) reached LODs of 100 ng/L using direct injection with an
233 electrospray ionisation source – triple quadrupole mass spectrometer (ESI-MS/MS) upon sample
234 dilution with methanol (50:50), however direct infusion in an ESI source without prior
235 chromatographic separation has been often criticised for being non-quantitative due to competitive
236 ionisation from non-separated matrix components (Kourtchev et al., 2014).

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

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

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

276 **2.3 General issues about interpreting organics in terms of environmental variables**

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

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

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

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

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

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

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

325 **3 Organic molecules as environmental proxies**

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

333 **3.1 Terrestrial biogenic markers**

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

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

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

364 3.1.1 Primary emissions

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

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

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

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

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

410 3.1.2 Secondary oxidation products

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

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

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

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

450 Methylthreitol (an isoprene SOA marker), pinic acid and pinonic acid (monoterpene SOA markers)
451 were estimated to have short lifetimes of only 0.2 days by Noziere et al. (2015), clearly limiting
452 transportation to high latitudes where transport to polar regions may require days. Others, such as
453 MBTCA (3-methyl-1,2,3-butanetricarboxylic acid as a monoterpene SOA marker),
454 nocyophyllonic acid, caryophyllinic acid and nocyophyllinic acid (sesquiterpene SOA markers),
455 were estimated to have lifetimes up to 10 days. These values are highly uncertain but in general
456 agree with SOA lifetimes as modelled using global chemistry transport models and general
457 circulation models; with a review of 31 such models by Tsigaridis et al. (2014) finding an average
458 range of SOA atmospheric lifetimes of 2.4-15 days. To further add to this uncertainty, Hu et al.
459 (2013) identified both pinic acid and MBTCA in high latitude samples of atmospheric aerosol, of
460 which a significant contribution to the total concentrations were identified as terrestrially sourced
461 compounds based on atmospheric transport pathway reconstruction for the supplying air masses.
462 More substantially, isoprene and monoterpene oxidation products, including many of those products
463 with proposed short lifetimes of less than 0.2 days, have also been identified in an Alaskan ice core
464 dating back 350 years. For example, Pokhrel et al. (2016) identified a number of terrestrial and
465 marine sourced SOA compounds within the ice samples (Figure 1a), using atmospheric transport
466 pathway reconstruction to determine the compounds' source region. Thus, these compounds
467 demonstrate not only the atmospheric transport and deposition of SOA with terrestrial sources, but
468 also the persistence of these compounds to older ice layers. Many of the observed concentration
469 changes were correlated with Northern Hemisphere temperature fluctuations using a combination of
470 compound groups as well as individual compounds for comparisons (Pokhrel et al., 2016). This
471 observation suggests also that lifetime of these compounds in the particle phase may be longer than
472 estimated, perhaps because SOA particles may have low viscosities limiting uptake and diffusion of
473 oxidants (Virtanen et al., 2010). If the study of these compounds is extended to Antarctica, it will be
474 necessary to distinguish compounds with mainly terrestrial sources from those with mainly marine
475 origins. One method is to test for a temporal correlation between the organic markers of interest and
476 uniquely terrestrial molecules, such as the biomass burning marker levoglucosan, or to compare the
477 results against uniquely marine emissions such as MSA, an approach used by Fu et al. (2013).

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

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

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

491 **3.2 Indicators of Biomass Burning**

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

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

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

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

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

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

535 3.2.1 *Monosaccharide Anhydrides*

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

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

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

567 3.2.2 *Lignin and conifer resin pyroproducts*

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

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

587 3.2.3 Polycyclic Aromatic Hydrocarbons (PAHs)

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

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

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

612 3.2.4 Sources of biomass burning plumes reaching polar ice cores

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

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

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

637 **3.3 Indicators of Marine Biogenic Activity**

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

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

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

661 *3.3.1 Primary emissions*

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

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

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

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

687 3.3.2 *Secondary oxidation products*

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

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

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

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

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

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

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

754 with anthropogenic H₂SO₄ (Surratt et al., 2007) so specificity to marine sources needs to be tested
755 for each individual sulfate ester compound.

756 **3.4 Anthropogenic Emissions**

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

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

785 *3.4.1 Persistent Organic Pollutants (POPs)*

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

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

811 3.4.2 Polychlorinated biphenyls (PCBs)

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

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

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

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

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

856 3.4.3 Polycyclic aromatic hydrocarbons or pseudo-POPs

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

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

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

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

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

903 3.4.4 *Emerging pollutants*

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

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

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

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

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

947 **4 Conclusions**

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

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

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

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

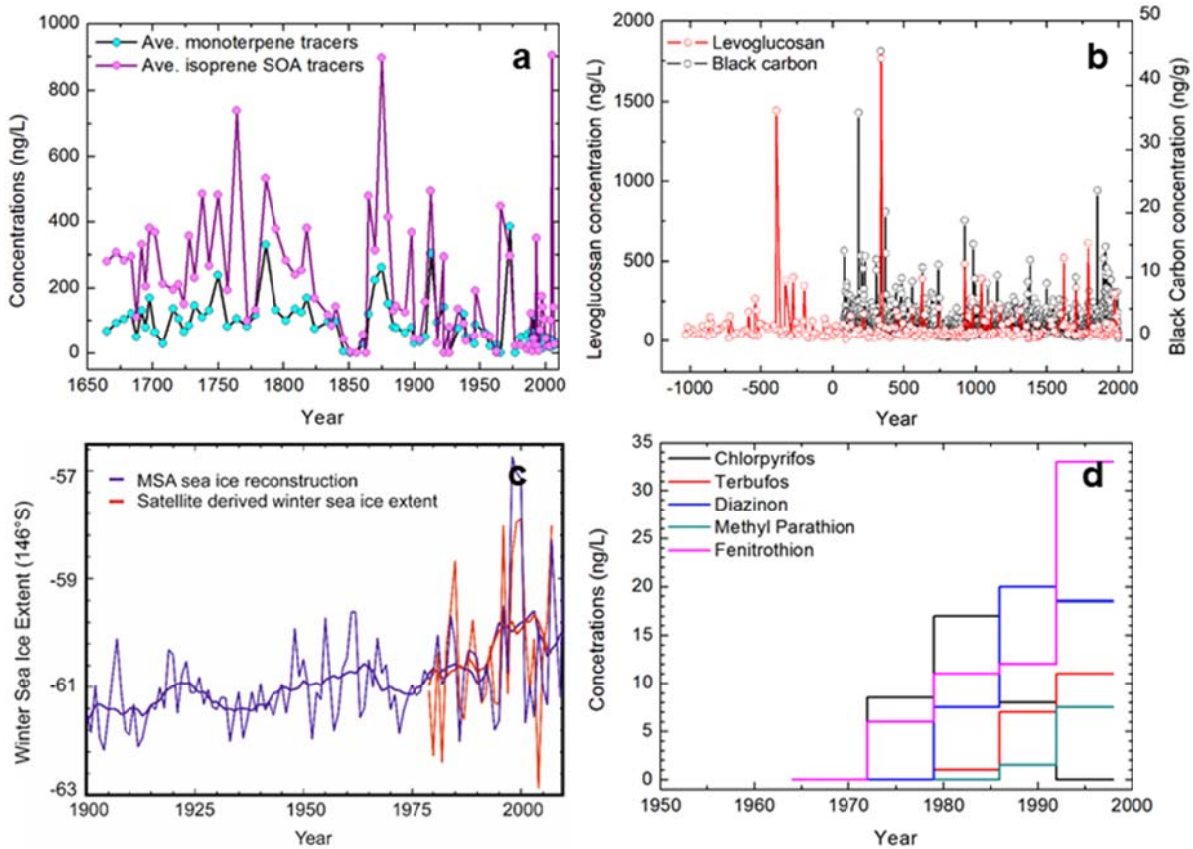
982 The use of marine organic aerosols in polar ice is a relatively new area of research and one that
983 requires considerable investigation. The main problems are that marine organic aerosols are
984 influenced not only by oceanic emissions of primary aerosols and SOA precursors, but also by
985 continental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

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

1006 **Acknowledgments**

1007 EW is supported by a Royal Society professorship. The research leading to these results has
1008 received funding from the European Union's Seventh Framework Programme (“Ideas” Specific
1009 Programme, ERC Advanced and Consolidator Grants) under grant agreement 267696
1010 “EARLYhumanIMPACT” and under grant agreement 279405 “CO_rANE”.

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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)
Volatile halogenated hydrocarbons	On-line purge and trap	GC-MS	10 mL	30-90%	1 ng/L	0-236 ng/L	Fresh snow, Antarctica		Zoccolillo et al., 2005)
Markers of both anthropogenic fossil fuel combustion sources and biomass burning									
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)	Σ 14-PAHs 100 – 10,630 ng/L	ATM station, Summit, Greenland	5 m 1989-1993 AD	(Masclet et al., 2000)
PAHs	filtration, essication	SFE-GC/MS ^e	100-200 mL			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		GC-MS	100 mL	>70%	0.001 µg/L	average 0.09-20.3 µg/L, range 0-189 µg/L	Ice core, Aurora Peak, Alaska	180m 1734AD-2008AD	(Kawamura, 1993)
	Extraction	Derivatisation (BF ₃ / <i>n</i> -butanol)								(Ho et al., 2010)
Monoterpene and isoprene SOA tracers	Preconc. in rotavap		GC-MS	150 mL	>70%	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)
	Extraction	Derivatisation (BSTFA)								(Ho et al., 2010)
C _{26:0} -C _{30:0} monocarboxylic acids	LLE		GC-MS	350 mL	75-82%	average 2890 ng/L, range 50.2-18400 ng/L	Kamchatka Ushkovsky ice core	1.32-152.5 m 1693-1997AD	1550-2000AD	(Fu et al., 2016)
	Saponification	Derivatisation (BSTFA)								(Kawamura et al., 1996)
C ₁₅₋₃₃ n-alkanes, C ₂₄₋₃₁ n-alkan-2-ones, C ₆₋₁₈ n-alkanoic acids	SPE	GC-FID and GC-MS	21.1-24.92 L			0.86-1.57 µg/L n-alkanes 2.12-3.07 µg/L n-alkan-2-ones 0.54-0.68 µg/L n-alkanoic acids	Snowpit, Xixiabangma Ice cores, Dasuopu glacier, Tibetan Plateau	240cm-900m Summer 1996-Summer 1997		(Xie et al., 2000)
Marine biomarkers										
MSA/MS-	Online preconc. with TAC	IC-conductimetry	5 mL			0.02 µg/L	0.04 – 11.82 µg/L	Ice core, Summit, Greenland	3040m ~110kyr BP (BP=1950)	(Saltzman et al., 1997)
MSA/MS-	Online preconc. with TAC	IC-conductimetry	5 mL			0.25 µg/L	mean background 1.2-	Ice cores GRIP 93a and GRIP 93b,	GRIP 93a: 73m	(Legrand et al., 1993)

						2.9 µg/L	Summit, Greenland	1767-1993AD GRIP 93b 67m, 1790-1993AD	(Legrand et al., 1997)
MSA/MS-	dil 50:50 with MeOH direct injection	ESI-MS/MS	20 µL	-	0.1 µg/L	range 1.7-73.2 µg/L, mean 14.5 µg/L	Ice core, Siple Dome, Antarctica	~110kyr	(Saltzman et al., 2006)
MSA/MS-	direct injection	IC- conductimetry	0.8 mL	-	0.3 µg/L	mean 5.6 µg/L, range 0-51.1 µg/L	Ice core Lomonosovfonna, Svalbard	121m 1800-1997AD	(Jauhiainen et al., 1999) (Isaksson et al., 2005)
MSA/MS-	Online 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)
	Preconc. 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)
	LLE								
Oleic acid (C _{18:1})	Saponification Derivatisation (BSTFA)	GC-MS	350 mL	75-82%		mean 20 µg/L, range 1.9-105 µg/L	Ice core, Greenland	1550-2000AD	(Kawamura et al., 1996) (Seki et al., 2015)
Azelaic acid, low molecular weight dicarboxylic	Preconc. in rotavap Extraction	GC-FID GC-MS	150 mL	70->90%		Total dicarboxylic acids (C ₂ -C ₁₀)	Ice core, Site-J, Greenland	0-205 m 1546-1989 AD	(Kawamura et al., 1999) (Kawamura et al.,

acids	Derivatisation (BF ₃ /n-butanol)					range 3.11-32.5 µg/L			2001)
Biomass burning markers									
Levogluconan	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)
Levogluconan	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)
Levogluconan	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)
Levogluconan	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 (Longxiazailong ba)	Muztagh Ata and Longxiazailongba glaciers, Tibetan Plateau	Muztagh Ata 71 m Longxiazailongba 190 m	(Yao et al., 2013)
Levogluconan	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)
Levogluconan, mannosan,	Freeze-drying	GC/MS	5 mL	65-81%	0.070 µg/L (levogluconan)	up to 1.93 µg/L	Muztagh Ata and Kuokuosele		(You et al., 2014)

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

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

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

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1025**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: 2-methylthreitol 2-methylerythritol	Canadian High Arctic (Fu et al., 2009), Boreal Forest Finland (Kourtchev et al., 2013; Kourtchev et al., 2005), Forested areas China (Wang et al., 2008), Amazonian Forest Brazil (Claeys et al., 2004a), Tibetan Plateau (Shen et al., 2015), Alaskan ice core (Pokhrel et al., 2016), Kamchatka ice core (Fu et al., 2016)
2-methylglyceric acid	Canadian High Arctic (Fu et al., 2009), Boreal Forest Finland (Kourtchev et al., 2013; Kourtchev et al., 2005), Forested areas China (Wang et al., 2008), Tibetan Plateau (Shen et al., 2015), Alaskan ice core (Pokhrel et al., 2016), Kamchatka ice core (Fu et al., 2016)
C ₅ -alkene triols: <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	Canadian High Arctic (Fu et al., 2009), Boreal Forest Finland (Kourtchev et al., 2005), Forested areas China (Wang et al., 2008), Tibetan Plateau (Shen et al., 2015), Alaskan ice core (Pokhrel et al., 2016)
Monoterpene SOA	Location
3-hydroxyglutaric acid	Canadian High Arctic (Fu et al., 2009), Forested areas China (Wang et al., 2008), Alaskan ice core (Pokhrel et al., 2016), Kamchatka ice core (Fu et al., 2016)
pinic acid, pinonic acid	Canadian High Arctic (Fu et al., 2009), Boreal Forest Finland (Kourtchev et al., 2013), Tibetan Plateau (Shen et al., 2015), Alaskan ice core (Pokhrel et al., 2016), Kamchatka ice core (Fu et al., 2016)
pinanaldehyde; pinanediol mononitrate; norpinonic acid; terebic acid; ketolimonic 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)
norpinonic 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)
3-hydroxyglutaric acid, 3-hydroxy-4,4-dimethylglutaric acid	
MBTCA (3-methyl-1,2,3-butanetricarboxylic acid)	Canadian High Arctic (Fu et al., 2009), Boreal Forest Finland (Kourtchev et al., 2013), Forested areas China (Wang et al., 2008), Tibetan Plateau (Shen et al., 2015), Kamchatka ice core (Fu et al., 2016)
Sesquiterpene SOA	Location
β -caryophyllinic acid	Canadian High Arctic (Fu et al., 2009), North Carolina, USA (Jaoui et al., 2007), Boreal Forest Finland (van Eijck et al., 2013), Tibetan Plateau (Shen et al., 2015)

DCCA (3,3-dimethyl-2-(3-oxobutyl)cyclobutanecarboxylic acid)	Boreal Forest Finland (Kourtchev et al., 2013; van Eijck et al., 2013)
β -nocyrophyllonic 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)
<p>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.</p>		

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1031 **References**

- 1032 Aarhus-Protocol, 1998. Protocol to the 1979 Convention on Long-Range Transboundary Air
1033 Pollution on Persistent Organic Pollutants; United Nations Economic Commission for
1034 Europe: Geneva.
- 1035 Abram, N.J., Curran, M.A.J., Mulvaney, R., Vance, T., 2008. The preservation of
1036 methanesulphonic acid in frozen ice-core samples. *J Glaciol* 54, 680-684.
- 1037 Abram, N.J., Mulvaney, R., Wolff, E.W., Mudelsee, M., 2007. Ice core records as sea ice
1038 proxies: An evaluation from the Weddell Sea region of Antarctica. *J. Geophys. Res.-Atmos.*
1039 112.
- 1040 Abram, N.J., Thomas, E.R., McConnell, J.R., Mulvaney, R., Bracegirdle, T.J., Sime, L.C.,
1041 Aristarain, A.J., 2010. Ice core evidence for a 20th century decline of sea ice in the
1042 Bellingshausen Sea, Antarctica. *J. Geophys. Res.-Atmos.* 115.
- 1043 Ahrens, L., Shoeib, M., Del Vento, S., Codling, G., Halsall, C., 2011. Polyfluoroalkyl
1044 compounds in the Canadian Arctic atmosphere. *Environ Chem* 8, 399-406.
- 1045 Andersen, M.S., Fuglei, E., Konig, M., Lipasti, I., Pedersen, A.O., Polder, A., Yoccoz, N.G.,
1046 Routti, H., 2015. Levels and temporal trends of persistent organic pollutants (POPs) in arctic
1047 foxes (*Vulpes lagopus*) from Svalbard in relation to dietary habits and food availability. *Sci*
1048 *Total Environ* 511, 112-122.
- 1049 Anderson, P.N., Hites, R.A., 1996. OH Radical Reactions: The Major Removal Pathway for
1050 Polychlorinated Biphenyls from the Atmosphere. *Environmental Science & Technology* 30,
1051 1756-1763.
- 1052 Armitage, J.M., MacLeod, M., Cousins, I.T., 2009. Modeling the Global Fate and Transport
1053 of Perfluorooctanoic Acid (PFOA) and Perfluorooctanoate (PFO) Emitted from Direct
1054 Sources Using a Multispecies Mass Balance Model. *Environmental Science & Technology*
1055 43, 1134-1140.
- 1056 Barbante, C., Spolaor, A., Cairns, W.R.L., Boutron, C., 2017. Man's footprint on the Arctic
1057 environment as revealed by analysis of ice and snow. *Earth-Science Reviews* 168, 218-231.
- 1058 Barrie, L.A., Gregor, D., Hargrave, B., Lake, R., Muir, D., Shearer, R., Tracey, B., Bidleman,
1059 T., 1992. Arctic contaminants: sources, occurrence and pathways. *Sci Total Environ* 122, 1-
1060 74.
- 1061 Barron, M.G., Holder, E., 2003. Are Exposure and Ecological Risks of PAHs Underestimated
1062 at Petroleum Contaminated Sites? *Human and Ecological Risk Assessment: An International*
1063 *Journal* 9, 1533-1545.
- 1064 Becagli, S., Castellano, E., Cerri, O., Curran, M., Frezzotti, M., Marino, F., Morganti, A.,
1065 Proposito, M., Severi, M., Traversi, R., Udisti, R., 2009. Methanesulphonic acid (MSA)
1066 stratigraphy from a Talos Dome ice core as a tool in depicting sea ice changes and southern
1067 atmospheric circulation over the previous 140 years. *Atmospheric Environment* 43, 1051-
1068 1058.

- 1069 Bedini, E., 2011. Mineral mapping in the Kap Simpson complex, central East Greenland,
1070 using HyMap and ASTER remote sensing data. *Advances in Space Research* 47, 60-73.
- 1071 Bendle, J., Kawamura, K., Yamazaki, K., Niwai, T., 2007. Latitudinal distribution of
1072 terrestrial lipid biomarkers and n-alkane compound-specific stable carbon isotope ratios in
1073 the atmosphere over the western Pacific and Southern Ocean. *Geochim Cosmochim Acta* 71,
1074 5934-5955.
- 1075 Benskin, J.P., Ahrens, L., Muir, D.C., Scott, B.F., Spencer, C., Rosenberg, B., Tomy, G.,
1076 Kylin, H., Lohmann, R., Martin, J.W., 2012. Manufacturing origin of perfluorooctanoate
1077 (PFOA) in Atlantic and Canadian Arctic seawater. *Environ Sci Technol* 46, 677-685.
- 1078 Blais, J.M., Schindler, D.W., Derek, C.G.M., Sharp, M., Donald, D., Lafreniere, M.,
1079 Braekevelt, E., Williams, M.J.S., 2001. Melting Glaciers: A Major Source of Persistent
1080 Organochlorines to Subalpine Bow Lake in Banff National Park, Canada. *Ambio* 30, 410-
1081 415.
- 1082 Bonmatin, J.-M., Giorio, C., Girolami, V., Goulson, D., Kreuzweiser, D.P., Krupke, C.,
1083 Liess, M., Long, E., Marzaro, M., Mitchell, E.A., Noome, D.A., Simon-Delso, N., Tapparo,
1084 A., 2015. Environmental fate and exposure; neonicotinoids and fipronil. *Environmental
1085 Science and Pollution Research* 22, 35-67.
- 1086 Bonsang, B., Polle, C., Lambert, G., 1992. Evidence for marine production of isoprene.
1087 *Geophysical Research Letters* 19, 1129-1132.
- 1088 Bory, A., Wolff, E., Mulvaney, R., Jagoutz, E., Wegner, A., Ruth, U., Elderfield, H., 2010.
1089 Multiple sources supply eolian mineral dust to the Atlantic sector of coastal Antarctica:
1090 Evidence from recent snow layers at the top of Berkner Island ice sheet. *Earth Planet. Sci.
1091 Lett.* 291, 138-148.
- 1092 Bosle, J.M., Mischel, S.A., Schulze, A.-L., Scholz, D., Hoffmann, T., 2014. Quantification of
1093 low molecular weight fatty acids in cave drip water and speleothems using HPLC-ESI-IT/MS
1094 - development and validation of a selective method. *Anal Bioanal Chem* 406, 3167-3177.
- 1095 Bossi, R., Skjoth, C.A., Skov, H., 2013. Three years (2008-2010) of measurements of
1096 atmospheric concentrations of organochlorine pesticides (OCPs) at Station Nord, North-East
1097 Greenland. *Environ Sci Process Impacts* 15, 2213-2219.
- 1098 Boutron, C.F., Batifol, F.M., 1985. Assessing Laboratory Procedures for the
1099 Decontamination of Polar Snow or Ice Samples for the Analysis of Toxic Metals and
1100 Metalloids. *Annals of Glaciology* 7, 7-11.
- 1101 Brönnimann, S., Voigt, S., Wanner, H., 2000. The influence of changing UVB radiation in
1102 near-surface ozone time series. *Journal of Geophysical Research: Atmospheres* 105, 8901-
1103 8913.
- 1104 Buck, R.C., Franklin, J., Berger, U., Conder, J.M., Cousins, I.T., de Voegt, P., Jensen, A.A.,
1105 Kannan, K., Mabury, S.A., van Leeuwen, S.P., 2011. Perfluoroalkyl and polyfluoroalkyl
1106 substances in the environment: terminology, classification, and origins. *Integr Environ Assess
1107 Manag* 7, 513-541.

- 1108 Cai, M., Ma, Y., Xie, Z., Zhong, G., Möller, A., Yang, H., Sturm, R., He, J., Ebinghaus, R.,
 1109 Meng, X.-Z., 2012. Distribution and air–sea exchange of organochlorine pesticides in the
 1110 North Pacific and the Arctic. *Journal of Geophysical Research: Atmospheres* 117, n/a-n/a.
- 1111 Candelone, J.-P., Hong, S., F. Boutron, C., 1994. An improved method for decontaminating
 1112 polar snow or ice cores for heavy metal analysis. *Anal Chim Acta* 299, 9-16.
- 1113 Carlton, A.G., Wiedinmyer, C., Kroll, J.H., 2009. A review of Secondary Organic Aerosol
 1114 (SOA) formation from isoprene. *Atmos Chem Phys* 9, 4987-5005.
- 1115 Chen, D., Hale, R.C., La Guardia, M.J., Luellen, D., Kim, S., Geisz, H.N., 2015.
 1116 Hexabromocyclododecane flame retardant in Antarctica: Research stations as sources.
 1117 *Environ Pollut* 206, 611-618.
- 1118 Claeys, M., Graham, B., Vas, G., Wang, W., Vermeylen, R., Pashynska, V., Cafmeyer, J.,
 1119 Guyon, P., Andreae, M.O., Artaxo, P., Maenhaut, W., 2004a. Formation of secondary organic
 1120 aerosols through photooxidation of isoprene. *Science* 303, 1173-1176.
- 1121 Claeys, M., Wang, W., Ion, A.C., Kourtchev, I., Gelencsér, A., Maenhaut, W., 2004b.
 1122 Formation of secondary organic aerosols from isoprene and its gas-phase oxidation products
 1123 through reaction with hydrogen peroxide. *Atmospheric Environment* 38, 4093-4098.
- 1124 Claeys, M., Wang, W., Vermeylen, R., Kourtchev, I., Chi, X., Farhat, Y., Surratt, J.D.,
 1125 Gómez-González, Y., Sciare, J., Maenhaut, W., 2010. Chemical characterisation of marine
 1126 aerosol at Amsterdam Island during the austral summer of 2006–2007. *Journal of Aerosol
 1127 Science* 41, 13-22.
- 1128 Conedera, M., Tinner, W., Neff, C., Meurer, M., Dickens, A.F., Krebs, P., 2009.
 1129 Reconstructing past fire regimes: methods, applications, and relevance to fire management
 1130 and conservation. *Quat. Sci. Rev.* 28, 555-576.
- 1131 Criscitiello, A.S., Das, S.B., Evans, M.J., Frey, K.E., Conway, H., Joughin, I., Medley, B.,
 1132 Steig, E.J., 2013. Ice sheet record of recent sea-ice behavior and polynya variability in the
 1133 Amundsen Sea, West Antarctica. *Journal of Geophysical Research: Oceans* 118, 118-130.
- 1134 Curran, M.A.J., Jones, G.B., 2000. Dimethyl sulfide in the Southern Ocean: Seasonality and
 1135 flux. *Journal of Geophysical Research: Atmospheres* 105, 20451-20459.
- 1136 Curran, M.A.J., Palmer, A.S., 2001. Suppressed ion chromatography methods for the routine
 1137 determination of ultra low level anions and cations in ice cores. *J Chromatogr A* 919, 107-
 1138 113.
- 1139 Curran, M.A.J., van Ommen, T.D., Morgan, V.I., Phillips, K.L., Palmer, A.S., 2003. Ice core
 1140 evidence for Antarctic sea ice decline since the 1950s. *Science* 302, 1203-1206.
- 1141 Currie, L.A., Dibb, J.E., Klouda, G.A., Benner, B.A., Conny, J.M., Biegalski, S.R.,
 1142 Klinedinst, D.B., Cahoon, D.R., Hsu, N.C., 1998. The pursuit of isotopic and molecular fire
 1143 tracers in the polar atmosphere and cryosphere. *Radiocarbon* 40, 381-390.
- 1144 Damoah, R., Spichtinger, N., Forster, C., James, P., Mattis, I., Wandinger, U., Beirle, S.,
 1145 Wagner, T., Stohl, A., 2004. Around the world in 17 days - hemispheric-scale transport of
 1146 forest fire smoke from Russia in May 2003. *Atmos Chem Phys* 4, 1311-1321.

- 1147 De Angelis, M., Traversi, R., Udisti, R., 2012. Long-term trends of mono-carboxylic acids in
1148 Antarctica: Comparison of changes in sources and transport processes at the two EPICA deep
1149 drilling sites. *Tellus, Series B: Chemical and Physical Meteorology* 64, 1-21.
- 1150 Delmonte, B., Andersson, P.S., Hansson, M., Schoberg, H., Petit, J.R., Basile-Doelsch, I.,
1151 Maggi, V., 2008. Aeolian dust in East Antarctica (EPICA-Dome C and Vostok): Provenance
1152 during glacial ages over the last 800 kyr. *Geophysical Research Letters* 35.
- 1153 Dentener, F., Kinne, S., Bond, T., Boucher, O., Cofala, J., Generoso, S., Ginoux, P., Gong,
1154 S., Hoelzemann, J.J., Ito, A., Marelli, L., Penner, J.E., Putaud, J.P., Textor, C., Schulz, M.,
1155 van der Werf, G.R., Wilson, J., 2006. Emissions of primary aerosol and precursor gases in the
1156 years 2000 and 1750 prescribed data-sets for AeroCom. *Atmos Chem Phys* 6, 4321-4344.
- 1157 Desideri, P., Lepri, L., Santianni, D., Checchini, L., 1991. Chlorinated pesticides in sea-water
1158 and pack ice in Terra-Nova Bay (Antarctica). *Annali di Chimica* 81, 533-540.
- 1159 Dickhut, R.M., Cincinelli, A., Cochran, M., Ducklow, H.W., 2005. Atmospheric
1160 Concentrations and Air–Water Flux of Organochlorine Pesticides along the Western
1161 Antarctic Peninsula. *Environmental Science & Technology* 39, 465-470.
- 1162 Domine, F., Cincinelli, A., Bonnaud, E., Martellini, T., Picaud, S., 2007. Adsorption of
1163 phenanthrene on natural snow. *Environ. Sci. Technol.* 41, 6033–6038.
1164 <https://doi.org/10.1021/es0706798>
- 1165 Engling, G., Carrico, C.M., Kredenweis, S.M., Collett, J.L., Day, D.E., Malm, W.C.,
1166 Lincoln, E., Hao, W.M., Iinuma, Y., Herrmann, H., 2006. Determination of levoglucosan in
1167 biomass combustion aerosol by high-performance anion-exchange chromatography with
1168 pulsed amperometric detection. *Atmospheric Environment* 40, S299-S311.
- 1169 Epica community members, 2004. Eight glacial cycles from an Antarctic ice core. *Nature*
1170 429, 623-628.
- 1171 Fabbri, D., Torri, C., Simonei, B.R.T., Marynowski, L., Rushdi, A.I., Fabianska, M.J., 2009.
1172 Levoglucosan and other cellulose and lignin markers in emissions from burning of Miocene
1173 lignites. *Atmospheric Environment* 43, 2286-2295.
- 1174 Facchini, M.C., Decesari, S., Rinaldi, M., Carbone, C., Finessi, E., Mircea, M., Fuzzi, S.,
1175 Moretti, F., Tagliavini, E., Ceburnis, D., O’Dowd, C.D., 2008. Important Source of Marine
1176 Secondary Organic Aerosol from Biogenic Amines. *Environmental Science & Technology*
1177 42, 9116-9121.
- 1178 Ferretti, D.F., Miller, J.B., White, J.W.C., Etheridge, D.M., Lassey, K.R., Lowe, D.C.,
1179 Meure, C.M.M., Dreier, M.F., Trudinger, C.M., van Ommen, T.D., Langenfelds, R.L., 2005.
1180 Unexpected changes to the global methane budget over the past 2000 years. *Science* 309,
1181 1714-1717.
- 1182 Fischer, H., Schüpbach, S., Gfeller, G., Bigler, M., Röthlisberger, R., Erhardt, T., Stocker,
1183 T.F., Mulvaney, R., Wolff, E.W., 2015. Millennial changes in North American wildfire and
1184 soil activity over the last glacial cycle. *Nat Geosci* 8, 723-728.

- 1185 Fischer, H., Siggaard-Andersen, M.-L., Ruth, U., Röhlisberger, R., Wolff, E., 2007.
1186 Glacial/interglacial changes in mineral dust and sea-salt records in polar ice cores: Sources,
1187 transport, and deposition. *Rev Geophys* 45.
- 1188 Foster, A.F.M., Curran, M.A.J., Smith, B.T., van Ommen, T.D., Morgan, V.I., 2006.
1189 Covariation of sea ice and methanesulphonic acid in Wilhelm II Land, East Antarctica.
1190 *Annals of Glaciology* 44, 429-432.
- 1191 Fraser, M.P., Lakshmanan, K., 2000. Using levoglucosan as a molecular marker for the long-
1192 range transport of biomass combustion aerosols. *Environmental Science & Technology* 34,
1193 4560-4564.
- 1194 Fu, P.Q., Kawamura, K., Chen, J., Barrie, L.A., 2009. Isoprene, Monoterpene, and
1195 Sesquiterpene Oxidation Products in the High Arctic Aerosols during Late Winter to Early
1196 Summer. *Environmental Science & Technology* 43, 4022-4028.
- 1197 Fu, P.Q., Kawamura, K., Chen, J., Charrière, B., Sempéré, R., 2013. Organic molecular
1198 composition of marine aerosols over the Arctic Ocean in summer: Contributions of primary
1199 emission and secondary aerosol formation. *Biogeosciences* 10, 653-667.
- 1200 Fu, P., Kawamura, K., Seki, O., Izawa, Y., Shiraiwa, T., Ashworth, K., 2016. Historical
1201 Trends of Biogenic SOA Tracers in an Ice Core from Kamchatka Peninsula. *Environ. Sci.*
1202 *Technol. Lett.* 3, 351–358. <https://doi.org/10.1021/acs.estlett.6b00275>
- 1203 Fundel, F., Fischer, H., Weller, R., Traufetter, F., Oerter, H., Miller, H., 2006. Influence of
1204 large-scale teleconnection patterns on methane sulfonate ice core records in Dronning Maud
1205 Land. *Journal of Geophysical Research* 111.
- 1206 Fuoco, R., Giannarelli, S., Onor, M., Ghimenti, S., Abete, C., Termine, M., Francesconi, S.,
1207 2012. A snow/firn four-century record of polycyclic aromatic hydrocarbons (PAHs) and
1208 polychlorobiphenyls (PCBs) at Talos Dome (Antarctica). *Microchem J* 105, 133-141.
- 1209 Fuoco, R., Giannarelli, S., Wei, Y., Abete, C., Francesconi, S., Termine, M., 2005.
1210 Polychlorobiphenyls and polycyclic aromatic hydrocarbons in the sea-surface micro-layer
1211 and the water column at Gerlache Inlet, Antarctica. *J. Environ. Monit.* 7, 1313.
1212 <https://doi.org/10.1039/b507329b>
- 1213 Gabrieli, J., Decet, F., Luchetta, A., Valt, M., Pastore, P., Barbante, C., 2010a. Occurrence of
1214 PAH in the seasonal snowpack of the Eastern Italian Alps. *Environ Pollut* 158, 3130-3137.
- 1215 Gabrieli, J., Vallelonga, P., Cozzi, G., Gabrielli, P., Gambaro, A., Sigl, M., Decet, F.,
1216 Schwikowski, M., Gäggeler, H., Boutron, C., Cescon, P., Barbante, C., 2010b. Post 17th-
1217 century changes of European PAH emissions recorded in high-altitude Alpine snow and ice.
1218 *Environmental science & technology* 44, 3260-3266.
- 1219 Gambaro, A., Zangrando, R., Gabrielli, P., Barbante, C., Cescon, P., 2008. Direct
1220 determination of levoglucosan at the picogram per milliliter level in Antarctic ice by high-
1221 performance liquid chromatography/electrospray ionization triple quadrupole mass
1222 spectrometry. *Analytical chemistry* 80, 1649-1655.

- 1223 Garbarino, J.R., Snyder-Conn, E., Leiker, T.J., Hoffman, G.L., 2002. Contaminants in arctic
1224 snow collected over northwest Alaskan sea ice. *Water, Air, and Soil Pollution* 139, 183-214.
- 1225 Garmash, O., Hermanson, M.H., Isaksson, E., Schwikowski, M., Divine, D., Teixeira, C.,
1226 Muir, D.C.G., 2013. Deposition History of Polychlorinated Biphenyls to the
1227 Lomonosovfonna Glacier, Svalbard: A 209 Congener Analysis. *Environmental Science &*
1228 *Technology* 47, 12064-12072.
- 1229 Geissen, V., Mol, H., Klumpp, E., Umlauf, G., Nadal, M., van der Ploeg, M., van de Zee,
1230 S.E.A.T.M., Ritsema, C.J., 2015. Emerging pollutants in the environment: A challenge for
1231 water resource management. *International Soil and Water Conservation Research* 3, 57-65.
- 1232 Geisz, H.N., Dickhut, R.M., Cochran, M.A., Fraser, W.R., Ducklow, H.W., 2008. Melting
1233 glaciers: A probable source of DDT to the Antarctic marine ecosystem. *Environmental*
1234 *Science and Technology* 42, 3958-3962.
- 1235 Giannarelli, S., Ceccarini, A., Tiribilli, C., Spreafico, R., Francesconi, S., Fuoco, R., 2017.
1236 Paleo-environmental record of polycyclic aromatic hydrocarbons and polychlorobiphenyls at
1237 the peripheral site GV7 in Victoria Land (East Antarctica). *Chemosphere* 174, 390–398.
1238 <https://doi.org/10.1016/j.chemosphere.2017.01.126>
- 1239 Giorio, C., Safer, A., Sánchez-Bayo, F., Tapparo, A., Lentola, A., Girolami, V., Bijleveld van
1240 Lexmond, M., Bonmatin, J.-M., 2017. An update of the Worldwide Integrated Assessment
1241 (WIA) on systemic insecticides. Part 1: new molecules, metabolism, fate, and transport.
1242 *Environ. Sci. Pollut. Res.* <https://doi.org/10.1007/s11356-017-0394-3>
- 1243 Goldstein, A.H., Galbally, I.E., 2007. Known and Unexplored Organic Constituents in the
1244 Earth's Atmosphere. *Environmental Science & Technology* 41, 1514-1521.
- 1245 Gowda, D., Kawamura, K., Tachibana, E., 2016. Identification of hydroxy- and keto-
1246 dicarboxylic acids in remote marine aerosols using gas chromatography/quadruple and time-
1247 of-flight mass spectrometry. *Rapid Communications in Mass Spectrometry* 30, 992-1000.
- 1248 Grannas, A.M., Hockaday, W.C., Hatcher, P.G., Thompson, L.G., Mosley-Thompson, E.,
1249 2006. New revelations on the nature of organic matter in ice cores. *Journal of Geophysical*
1250 *Research* 111, D04304.
- 1251 Grannas, A.M., Shepson, P.B., Filley, T.R., 2004. Photochemistry and nature of organic
1252 matter in Arctic and Antarctic snow. *Global Biogeochemical Cycles* 18, n/a-n/a.
- 1253 Gregor, D.J., 1991. Organic micropollutants in seasonal snowcover and firn, in: Davies, T.D.,
1254 Tranter, M., Jones, H.G. (Eds.), *Seasonal Snowpacks. Processes of Compositional Change.*
1255 Springer-Verlag.
- 1256 Gregor, D.J., Peters, A.J., Teixeira, C.F., Jones, N., Spencer, C., 1995. The historical residue
1257 trend of PCBs in the Agassiz Ice Cap, Ellesmere Island, Canada. *Sci Total Environ* 160-161,
1258 117-126.
- 1259 Grieman, M.M., Greaves, J., Saltzman, E.S., 2015. A method for analysis of vanillic acid in
1260 polar ice cores. *Clim. Past.* 11, 227-232.

- 1261 Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P.I., Geron, C., 2006. Estimates
1262 of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and
1263 Aerosols from Nature). *Atmos Chem Phys* 6, 3181-3210.
- 1264 Gustafsson, O., Andersson, P., Axelman, J., Bucheli, T.D., Komp, P., McLachlan, M.S.,
1265 Sobek, A., Thorngren, J.O., 2005. Observations of the PCB distribution within and in-
1266 between ice, snow, ice-rafted debris, ice-interstitial water, and seawater in the Barents Sea
1267 marginal ice zone and the North Pole area. *Sci Total Environ* 342, 261-279.
- 1268 Hallquist, M., Wenger, J.C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M.,
1269 Dommen, J., Donahue, N.M., George, C., Goldstein, A.H., Hamilton, J.F., Herrmann, H.,
1270 Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M.E., Jimenez, J.L., Kiendler-Scharr, A.,
1271 Maenhaut, W., McFiggans, G., Mentel, T.F., Monod, A., Prévôt, A.S.H., Seinfeld, J.H.,
1272 Surratt, J.D., Szmigielski, R., Wildt, J., 2009. The formation, properties and impact of
1273 secondary organic aerosol: current and emerging issues. *Atmos Chem Phys* 9, 5155-5236.
- 1274 Hardy, J.T., 1982. The sea surface microlayer: Biology, chemistry and anthropogenic
1275 enrichment. *Progress in Oceanography* 11, 307-328.
- 1276 Hennigan, C.J., Sullivan, A.P., Collett, J.L., Robinson, A.L., 2010. Levoglucosan stability in
1277 biomass burning particles exposed to hydroxyl radicals. *Geophysical Research Letters* 37.
- 1278 Hermanson, M.H., Isaksson, E., Teixeira, C., Muir, D.C.G., Compher, K.M., Li, Y.F.,
1279 Igarashi, M., Kamiyama, K., 2005. Current-use and legacy pesticide history in the Austfonna
1280 ice cap, Svalbard, Norway. *Environmental Science and Technology* 39, 8163-8169.
- 1281 Ho, K.F., Lee, S.C., Ho, S.S.H., Kawamura, K., Tachibana, E., Cheng, Y., Zhu, T., 2010.
1282 Dicarboxylic acids, ketocarboxylic acids, α -dicarbonyls, fatty acids, and benzoic acid in urban
1283 aerosols collected during the 2006 Campaign of Air Quality Research in Beijing
1284 (CAREBeijing-2006). *Journal of Geophysical Research* 115.
- 1285 Hodzic, A., Madronich, S., Bohn, B., Massie, S., Menut, L., Wiedinmyer, C., 2007. Wildfire
1286 particulate matter in Europe during summer 2003: meso-scale modeling of smoke emissions,
1287 transport and radiative effects. *Atmos Chem Phys* 7, 4043-4064.
- 1288 Hoffmann, D., Tilgner, A., Iinuma, Y., Herrmann, H., 2010. Atmospheric Stability of
1289 Levoglucosan: A Detailed Laboratory and Modeling Study. *Environmental Science &*
1290 *Technology* 44, 694-699.
- 1291 Holmes, B.J., Petrucci, G.A., 2006. Water-soluble oligomer formation from acid-catalyzed
1292 reactions of levoglucosan in proxies of atmospheric aqueous aerosols. *Environmental Science*
1293 *& Technology* 40, 4983-4989.
- 1294 Holmes, B.J., Petrucci, G.A., 2007. Oligomerization of levoglucosan by Fenton chemistry in
1295 proxies of biomass burning aerosols. *Journal of Atmospheric Chemistry* 58, 151-166.
- 1296 Hopmans, E.C., Weijers, J.W.H., Schefuß, E., Herfort, L., Sinninghe Damsté, J.S., Schouten,
1297 S., 2004. A novel proxy for terrestrial organic matter in sediments based on branched and
1298 isoprenoid tetraether lipids. *Earth Planet. Sci. Lett.* 224, 107-116.

- 1299 Hu, Q.H., Xie, Z.Q., Wang, X.M., Kang, H., He, Q.F., Zhang, P., 2013. Secondary organic
1300 aerosols over oceans via oxidation of isoprene and monoterpenes from Arctic to Antarctic.
1301 *Sci Rep* 3, 2280.
- 1302 Hung, H., Blanchard, P., Halsall, C.J., Bidleman, T.F., Stern, G.A., Fellin, P., Muir, D.C.,
1303 Barrie, L.A., Jantunen, L.M., Helm, P.A., Ma, J., Konoplev, A., 2005. Temporal and spatial
1304 variabilities of atmospheric polychlorinated biphenyls (PCBs), organochlorine (OC)
1305 pesticides and polycyclic aromatic hydrocarbons (PAHs) in the Canadian Arctic: results from
1306 a decade of monitoring. *Sci Total Environ* 342, 119-144.
- 1307 Ion, A.C., Vermeylen, R., Kourtchev, I., Cafmeyer, J., Chi, X., Gelencsér, A., Maenhaut, W.,
1308 Claeys, M., 2005. Polar organic compounds in rural PM_{2.5} aerosols from K-
1309 puszta, Hungary, during a 2003 summer field campaign: Sources and diel variations. *Atmos*
1310 *Chem Phys* 5, 1805-1814.
- 1311 Isaksson, E., Hermanson, M., Hicks, S., Igarashi, M., Kamiyama, K., Moore, J., Motoyama,
1312 H., Muir, D., Pohjola, V., Vaikmäe, R., van de Wal, R.S.W., Watanabe, O., 2003. Ice cores
1313 from Svalbard—useful archives of past climate and pollution history. *Physics and Chemistry*
1314 *of the Earth, Parts A/B/C* 28, 1217-1228.
- 1315 Isaksson, E., Kekonen, T., Moore, J., Mulvaney, R., 2005. The methanesulfonic acid (MSA)
1316 record in a Svalbard ice core. *Annals of Glaciology* 42, 345-351.
- 1317 Jaffrezo, J.-L., Clain, M.P., Masclet, P., 1994. Polycyclic aromatic hydrocarbons in the polar
1318 ice of greenland. Geochemical use of these atmospheric tracers. *Atmospheric Environment*
1319 28, 1139-1145.
- 1320 Jaffrezo, J.-L., Masclet, P., Clain, M.P., Wortham, H., Beyne, S., Cachier, H., 1993. Transfer
1321 function of polycyclic aromatic hydrocarbons from the atmosphere to the polar ice—I.
1322 Determination of atmospheric concentrations at dye 3, Greenland. *Atmospheric Environment*.
1323 *Part A. General Topics* 27, 2781-2785.
- 1324 Jaoui, M., Lewandowski, M., Kleindienst, T.E., Offenberg, J.H., Edney, E.O., 2007. β -
1325 caryophyllinic acid: An atmospheric tracer for β -caryophyllene secondary organic aerosol.
1326 *Geophysical Research Letters* 34.
- 1327 Jauhiainen, T., Moore, J., Perämäki, P., Derome, J., Derome, K., 1999. Simple procedure for
1328 ion chromatographic determination of anions and cations at trace levels in ice core samples.
1329 *Anal Chim Acta* 389, 21-29.
- 1330 Jimenez, J.L., Canagaratna, M.R., Donahue, N.M., Prevot, A.S., Zhang, Q., Kroll, J.H.,
1331 DeCarlo, P.F., Allan, J.D., Coe, H., Ng, N.L., Aiken, A.C., Docherty, K.S., Ulbrich, I.M.,
1332 Grieshop, A.P., Robinson, A.L., Duplissy, J., Smith, J.D., Wilson, K.R., Lanz, V.A., Hueglin,
1333 C., Sun, Y.L., Tian, J., Laaksonen, A., Raatikainen, T., Rautiainen, J., Vaattovaara, P., Ehn,
1334 M., Kulmala, M., Tomlinson, J.M., Collins, D.R., Cubison, M.J., Dunlea, E.J., Huffman, J.A.,
1335 Onasch, T.B., Alfarra, M.R., Williams, P.I., Bower, K., Kondo, Y., Schneider, J., Drewnick,
1336 F., Borrmann, S., Weimer, S., Demerjian, K., Salcedo, D., Cottrell, L., Griffin, R., Takami,
1337 A., Miyoshi, T., Hatakeyama, S., Shimojo, A., Sun, J.Y., Zhang, Y.M., Dzepina, K.,
1338 Kimmel, J.R., Sueper, D., Jayne, J.T., Herndon, S.C., Trimborn, A.M., Williams, L.R.,
1339 Wood, E.C., Middlebrook, A.M., Kolb, C.E., Baltensperger, U., Worsnop, D.R., 2009.
1340 Evolution of organic aerosols in the atmosphere. *Science* 326, 1525-1529.

- 1341 Johnsen, S.J., Clausen, H.B., Dansgaard, W., Fuhrer, K., Gundestrup, N., Hammer, C.U.,
 1342 Iversen, P., Jouzel, J., Stauffer, B., Steffensen, J.P., 1992. Irregular glacial interstadials
 1343 recorded in a new Greenland ice core. *Nature* 359, 311-313.
- 1344 Jouzel, J., 2013. A brief history of ice core science over the last 50 yr. *Clim. Past.* 9, 2525-
 1345 2547.
- 1346 Kahl, J.D.W., Martinez, D.A., Kuhns, H., Davidson, C.I., Jaffrezo, J.-L., Harris, J.M., 1997.
 1347 Air mass trajectories to Summit, Greenland: A 44-year climatology and some episodic
 1348 events. *Journal of Geophysical Research: Oceans* 102, 26861-26875.
- 1349 Kallenborn, R., Breivik, K., Eckhardt, S., Lunder, C.R., Manø, S., Schlabach, M., Stohl, A.,
 1350 2013. Long-term monitoring of persistent organic pollutants (POPs) at the Norwegian Troll
 1351 station in Dronning Maud Land, Antarctica. *Atmos. Chem. Phys.* 13, 6983-6992.
- 1352 Kang, J.H., Son, M.H., Hur, S.D., Hong, S., Motoyama, H., Fukui, K., Chang, Y.S., 2012.
 1353 Deposition of organochlorine pesticides into the surface snow of East Antarctica. *Sci Total*
 1354 *Environ* 433, 290-295.
- 1355 Kawamura, K., 1993. Identification of C2-C10 ω -oxocarboxylic acids, pyruvic acid,
 1356 and C2-C3 α -dicarbonyls in wet precipitation and aerosol samples by capillary GC and
 1357 GC/MS. *Analytical Chemistry* 65, 3505-3511.
- 1358 Kawamura, K., Bikkina, S., 2016. A review of dicarboxylic acids and related compounds in
 1359 atmospheric aerosols: Molecular distributions, sources and transformation. *Atmos. Res.* 170,
 1360 140–160. <https://doi.org/10.1016/j.atmosres.2015.11.018>
- 1361 Kawamura, K., Izawa, Y., Mochida, M., Shiraiwa, T., 2012. Ice core records of biomass
 1362 burning tracers (levoglucosan and dehydroabietic, vanillic and p-hydroxybenzoic acids) and
 1363 total organic carbon for past 300 years in the Kamchatka Peninsula, Northeast Asia.
 1364 *Geochim. Cosmochim. Acta* 99, 317 - 329.
- 1365 Kawamura, K., Suzuki, I., Fuji, Y., Watanabe, O., 1994. Ice core record of polycyclic
 1366 aromatic hydrocarbons over the past 400 years. *Naturwissenschaften* 81, 502-505.
- 1367 Kawamura, K., Suzuki, I., Fujii, Y., Watanabe, O., 1996. Ice core record of fatty acids over
 1368 the past 450 years in Greenland. *Geophysical Research Letters* 23, 2665-2668.
- 1369 Kawamura, K., Yokoyama, K., Fujii, Y., Watanabe, O., 1999. Implication of azelaic acid in a
 1370 Greenland Ice Core for oceanic and atmospheric changes in high latitudes. *Geophys. Res.*
 1371 *Lett.* 26, 871–874. <https://doi.org/10.1029/1999GL900116>
- 1372 Kawamura, K., Yokoyama, K., Fujii, Y., Watanabe, O., 2001. A Greenland ice core record of
 1373 low molecular weight dicarboxylic acids, ketocarboxylic acids, and α -dicarbonyls: A trend
 1374 from Little Ice Age to the present (1540 to 1989 A.D.). *J. Geophys. Res. Atmos.* 106, 1331–
 1375 1345. <https://doi.org/10.1029/2000JD900465>
- 1376 Kehrwald, N., Zangrando, R., Gabrielli, P., Jaffrezo, J.L., Boutron, C., Barbante, C.,
 1377 Gambaro, A., 2012. Levoglucosan as a specific marker of fire events in Greenland snow.
 1378 *Tellus Ser. B-Chem. Phys. Meteorol.* 64, 18196.

- 1379 Kesselmeier, J., Kuhn, U., Wolf, A., Andreae, M.O., Ciccioli, P., Brancaleoni, E., Frattoni,
1380 M., Guenther, A., Greenberg, J., De Castro Vasconcellos, P., de Oliva, T., Tavares, T.,
1381 Artaxo, P., 2000. Atmospheric volatile organic compounds (VOC) at a remote tropical forest
1382 site in central Amazonia. *Atmospheric Environment* 34, 4063-4072.
- 1383 Kirchgeorg, T., Schüpbach, S., Kehrwald, N., McWethy, D.B., Barbante, C., 2014. Method
1384 for the determination of specific molecular markers of biomass burning in lake sediments.
1385 *Org Geochem* 71, 1-6.
- 1386 Kourtchev, I., Fuller, S., Aalto, J., Ruuskanen, T.M., McLeod, M.W., Maenhaut, W., Jones,
1387 R., Kulmala, M., Kalberer, M., 2013. Molecular composition of boreal forest aerosol from
1388 Hyytiälä, Finland, using ultrahigh resolution mass spectrometry. *Environ Sci Technol* 47,
1389 4069-4079.
- 1390 Kourtchev, I., Fuller, S.J., Giorio, C., Healy, R.M., Wilson, E., O'Connor, I., Wenger, J.C.,
1391 McLeod, M., Aalto, J., Ruuskanen, T.M., Maenhaut, W., Jones, R., Venables, D.S., Sodeau,
1392 J.R., Kulmala, M., Kalberer, M., 2014. Molecular composition of biogenic secondary organic
1393 aerosols using ultrahigh-resolution mass spectrometry: Comparing laboratory and field
1394 studies. *Atmos Chem Phys* 14, 2155-2167.
- 1395 Kourtchev, I., Ruuskanen, T., Maenhaut, W., Kulmala, M., Claeys, M., 2005. Observation of
1396 2-methyltetrols and related photo-oxidation products of isoprene in boreal forest aerosols
1397 from Hyytiälä, Finland. *Atmos Chem Phys* 5, 2761-2770.
- 1398 Kroll, J.H., Donahue, N.M., Jimenez, J.L., Kessler, S.H., Canagaratna, M.R., Wilson, K.R.,
1399 Altieri, K.E., Mazzoleni, L.R., Wozniak, A.S., Bluhm, H., Mysak, E.R., Smith, J.D., Kolb,
1400 C.E., Worsnop, D.R., 2011. Carbon oxidation state as a metric for describing the chemistry of
1401 atmospheric organic aerosol. *Nat Chem* 3, 133-139.
- 1402 Kukučka, P., Lammel, G., Dvorská, A., Klánová, J., Möller, A., Fries, E., 2010.
1403 Contamination of Antarctic snow by polycyclic aromatic hydrocarbons dominated by
1404 combustion sources in the polar region. *Environ Chem* 7, 504.
- 1405 Lacorte, S., Quintana, J., Tauler, R., Ventura, F., Tovar-Sánchez, A., Duarte, C.M., 2009.
1406 Ultra-trace determination of Persistent Organic Pollutants in Arctic ice using stir bar sorptive
1407 extraction and gas chromatography coupled to mass spectrometry. *J. Chromatogr. A* 1216,
1408 8581–8589. <https://doi.org/10.1016/j.chroma.2009.10.029>
- 1409 Laliberté, F., Howell, S.E.L., Kushner, P.J., 2016. Regional variability of a projected sea ice-
1410 free Arctic during the summer months. *Geophysical Research Letters* 43, 256-263.
- 1411 Leck, C., Bigg, E.K., 2005. Source and evolution of the marine aerosol-A new perspective.
1412 *Geophysical Research Letters* 32, n/a-n/a.
- 1413 Legrand, M., De Angelis, M., 1995. Origins and variations of light carboxylic acids in polar
1414 precipitation. *Journal of Geophysical Research: Atmospheres* 100, 1445-1462.
- 1415 Legrand, M., De Angelis, M., 1996. Light carboxylic acids in Greenland ice: A record of past
1416 forest fires and vegetation emissions from the boreal zone. *J. Geophys. Res.* 101, 4129.
1417 <https://doi.org/10.1029/95JD03296>

- 1418 Legrand, M., De Angelis, M., Maupetit, F., 1993. Field investigation of major and minor ions
1419 along Summit (Central Greenland) ice cores by ion chromatography. *Journal of*
1420 *Chromatography A* 640, 251-258.
- 1421 Legrand, M., Hammer, C., De Angelis, M., Savarino, J., Delmas, R., Clausen, H., Johnsen,
1422 S.J., 1997. Sulfur-containing species (methanesulfonate and SO₄) over the last climatic cycle
1423 in the Greenland Ice Core Project (central Greenland) ice core. *Journal of Geophysical*
1424 *Research: Oceans* 102, 26663-26679.
- 1425 Legrand, M., Preunkert, S., Jourdain, B., Guilhermet, J., Fan, X., Alekhina, I., Petit, J.R.,
1426 2013. Water-soluble organic carbon in snow and ice deposited at Alpine, Greenland, and
1427 Antarctic sites: a critical review of available data and their atmospheric relevance. *Clim. Past.*
1428 9, 2195-2211.
- 1429 Levine, J.G., Wolff, E.W., Jones, A.E., Hutterli, M.A., Wild, O., Carver, G.D., Pyle, J.A.,
1430 2011a. In search of an ice core signal to differentiate between source-driven and sink-driven
1431 changes in atmospheric methane. *J. Geophys. Res.* 116, D05305.
1432 <https://doi.org/10.1029/2010JD014878>
- 1433 Levine, J.G., Wolff, E.W., Jones, A.E., Sime, L.C., Valdes, P.J., Archibald, A.T., Carver,
1434 G.D., Warwick, N.J., Pyle, J.A., 2011b. Reconciling the changes in atmospheric methane
1435 sources and sinks between the Last Glacial Maximum and the pre-industrial era. *Geophysical*
1436 *Research Letters* 38, n/a-n/a.
- 1437 Li, Q.L., Wang, N.L., Wu, X.B., Pu, J.C., He, J.Q., Zhang, C.W., 2011. Sources and
1438 distribution of polycyclic aromatic hydrocarbons of different glaciers over the Tibetan
1439 Plateau. *Sci. China-Earth Sci.* 54, 1189-1198.
- 1440 Lohmann, R., Gioia, R., Jones, K.C., Nizzetto, L., Temme, C., Xie, Z., Schulz-Bull, D.,
1441 Hand, I., Morgan, E., Jantunen, L., 2009. Organochlorine Pesticides and PAHs in the Surface
1442 Water and Atmosphere of the North Atlantic and Arctic Ocean. *Environmental Science &*
1443 *Technology* 43, 5633-5639.
- 1444 Ma, J., Hung, H., Tian, C., Kallenborn, R., 2011. Revolatilization of persistent organic
1445 pollutants in the Arctic induced by climate change. *Nat Clim Change* 1, 255-260.
- 1446 Macdonald, R.W., Barrie, L.A., Bidleman, T.F., Diamond, M.L., Gregor, D.J., Semkin, R.G.,
1447 Strachan, W.M.J., Li, Y.F., Wania, F., Alae, M., Alexeeva, L.B., Backus, S.M., Bailey, R.,
1448 Bewers, J.M., Gobeil, C., Halsall, C.J., Harner, T., Hoff, J.T., Jantunen, L.M.M., Lockhart,
1449 W.L., Mackay, D., Muir, D.C.G., Pudykiewicz, J., Reimer, K.J., Smith, J.N., Stern, G.A.,
1450 Schroeder, W.H., Wagemann, R., Yunker, M.B., 2000. Contaminants in the Canadian Arctic:
1451 5 years of progress in understanding sources, occurrence and pathways. *Sci Total Environ*
1452 254, 93-234.
- 1453 MacFarling Meure, C., Etheridge, D., Trudinger, C., Steele, P., Langenfelds, R., van Ommen,
1454 T., Smith, A., Elkins, J., 2006. Law Dome CO₂, CH₄ and N₂O ice core records extended to
1455 2000 years BP. *Geophysical Research Letters* 33.
- 1456 Marino, F., Castellano, E., Ceccato, D., De Deckker, P., Delmonte, B., Ghermandi, G.,
1457 Maggi, V., Petit, J.R., Revel-Rolland, M., Udisti, R., 2008. Defining the geochemical

- 1458 composition of the EPICA Dome C ice core dust during the last glacial-interglacial cycle.
1459 *Geochem. Geophys. Geosyst.* 9.
- 1460 Masclet, P., Hoyau, V., Jaffrezo, J., Legrand, M., 1995. Evidence for the Presence of
1461 Polycyclic Aromatic-Hydrocarbons in the Polar Atmosphere and in the Polar Ice of
1462 Greenland. *Analisis* 23, 250-252.
- 1463 Masclet, P., Hoyau, V., Jaffrezo, J.L., Cachier, H., 2000. Polycyclic aromatic hydrocarbon
1464 deposition on the ice sheet of Greenland. Part I: Superficial snow. *Atmospheric Environment*
1465 34, 3195-3207.
- 1466 McConnell, J.R., Edwards, R., Kok, G.L., Flanner, M.G., Zender, C.S., Saltzman, E.S.,
1467 Banta, J.R., Pasteris, D.R., Carter, M.M., Kahl, J.D.W., 2007. 20th-century industrial black
1468 carbon emissions altered arctic climate forcing. *Science* 317, 1381-1384.
- 1469 Mochida, M., Kitamori, Y., Kawamura, K., Nojiri, Y., Suzuki, K., 2002. Fatty acids in the
1470 marine atmosphere: Factors governing their concentrations and evaluation of organic films on
1471 sea-salt particles. *Journal of Geophysical Research: Atmospheres* 107, AAC 1-1-AAC 1-10.
- 1472 Muir, D.C.G., Teixeira, C., Wania, F., 2004. Empirical and Modeling Evidence of Regional
1473 Atmospheric Transport of Current-Use Pesticides. *Environ Toxicol Chem* 23, 2421.
- 1474 Muir, D.C.G., Wagemann, R., Hargrave, B.T., Thomas, D.J., Peakall, D.B., Norstrom, R.J.,
1475 1992. Arctic marine ecosystem contamination. *Sci Total Environ* 122, 75-134.
- 1476 Müller-Tautges, C., Eichler, A., Schwikowski, M., Hoffmann, T., 2014. A new sensitive
1477 method for the quantification of glyoxal and methylglyoxal in snow and ice by stir bar
1478 sorptive extraction and liquid desorption-HPLC-ESI-MS. *Anal Bioanal Chem* 406, 2525-
1479 2532.
- 1480 Müller-Tautges, C., Eichler, A., Schwikowski, M., Pezzatti, G.B., Conedera, M., Hoffmann,
1481 T., 2016. Historic records of organic compounds from a high Alpine glacier: Influences of
1482 biomass burning, anthropogenic emissions, and dust transport. *Atmos. Chem. Phys.* 16,
1483 1029–1043. <https://doi.org/10.5194/acp-16-1029-2016>
- 1484 Na, G., Liu, C., Wang, Z., Ge, L., Ma, X., Yao, Z., 2011. Distribution and characteristic of
1485 PAHs in snow of Fildes Peninsula. *Journal of Environmental Sciences* 23, 1445-1451.
- 1486 Nielsen, T., 1996. Traffic contribution of polycyclic aromatic hydrocarbons in the center of a
1487 large city. *Atmospheric Environment* 30, 3481-3490.
- 1488 Noziere, B., Kalberer, M., Claeys, M., Allan, J., D'Anna, B., Decesari, S., Finessi, E.,
1489 Glasius, M., Grgic, I., Hamilton, J.F., Hoffmann, T., Iinuma, Y., Jaoui, M., Kahnt, A.,
1490 Kampf, C.J., Kourtev, I., Maenhaut, W., Marsden, N., Saarikoski, S., Schnelle-Kreis, J.,
1491 Surratt, J.D., Szidat, S., Szmigielski, R., Wisthaler, A., 2015. The molecular identification of
1492 organic compounds in the atmosphere: state of the art and challenges. *Chem Rev* 115, 3919-
1493 3983.
- 1494 O'Dowd, C.D., Facchini, M.C., Cavalli, F., Ceburnis, D., Mircea, M., Decesari, S., Fuzzi, S.,
1495 Yoon, Y.J., Putaud, J.P., 2004. Biogenically driven organic contribution to marine aerosol.
1496 *Nature* 431, 676-680.

- 1497 O'Dwyer, J., Isaksson, E., Vinje, T., Jauhiainen, T., Moore, J., Pohjola, V., Vaikmäe, R., van
1498 de Wal, R.S.W., 2000. Methanesulfonic acid in a Svalbard Ice Core as an indicator of ocean
1499 climate. *Geophysical Research Letters* 27, 1159-1162.
- 1500 OECD, 2013. OECD/UNEP Global PFC Group, Synthesis on per- and polyfluorinated
1501 chemicals (PFCs), Environment, Health and Safety, Environment Directorate, OECD.
- 1502 Pancost, R.D., Boot, C.S., 2004. The palaeoclimatic utility of terrestrial biomarkers in marine
1503 sediments. *Mar Chem* 92, 239-261.
- 1504 Pavlova, P.A., Jenk, T.M., Schmid, P., Bogdal, C., Steinlin, C., Schwikowski, M., 2015.
1505 Polychlorinated Biphenyls in a Temperate Alpine Glacier: 1. Effect of Percolating Meltwater
1506 on their Distribution in Glacier Ice. *Environ Sci Technol* 49, 14085-14091.
- 1507 Pavlova, P.A., Schmid, P., Zennegg, M., Bogdal, C., Schwikowski, M., 2014. Trace analysis
1508 of hydrophobic micropollutants in aqueous samples using capillary traps. *Chemosphere* 106,
1509 51-56.
- 1510 Peel, D.A., 1975. Organochlorine residues in Antarctic snow. *Nature* 254, 324-325.
- 1511 Perrette, M., Yool, A., Quartly, G.D., Popova, E.E., 2011. Near-ubiquity of ice-edge blooms
1512 in the Arctic. *Biogeosciences* 8, 515-524.
- 1513 Peters, A.J., Gregor, D.J., Teixeira, C.F., Jones, N.P., Spencer, C., 1995. The recent
1514 depositional trend of polycyclic aromatic hydrocarbons and elemental carbon to the Agassiz
1515 Ice Cap, Ellesmere Island, Canada. *The Science of The Total Environment* 160-161, 167-179.
- 1516 Piazza, R., Gambaro, A., Argiriadis, E., Vecchiato, M., Zambon, S., Cescon, P., Barbante, C.,
1517 2013. Development of a method for simultaneous analysis of PCDDs, PCDFs, PCBs, PBDEs,
1518 PCNs and PAHs in Antarctic air. *Anal Bioanal Chem* 405, 917-932.
- 1519 Pokhrel, A., 2015. Studies on ice core records of dicarboxylic acids, ω -oxocarboxylic acids,
1520 pyruvic acid, α -dicarbonyls and fatty acids from southern Alaska since 1665AD: A link to
1521 climate change in the Northern Hemisphere. Hokkaido University.
- 1522 Pokhrel, A., Kawamura, K., Ono, K., Seki, O., Fu, P., Matoba, S., Shiraiwa, T., 2016. Ice
1523 core records of monoterpene- and isoprene-SOA tracers from Aurora Peak in Alaska since
1524 1660s: Implication for climate change variability in the North Pacific Rim. *Atmospheric*
1525 *Environment* 130, 105-112.
- 1526 Pokhrel, A., Kawamura, K., Seki, O., Matoba, S., Shiraiwa, T., 2015. Ice core profiles of
1527 saturated fatty acids (C12:0–C30:0) and oleic acid (C18:1) from southern Alaska since 1734
1528 AD: A link to climate change in the Northern Hemisphere. *Atmospheric Environment* 100,
1529 202-209.
- 1530 Preunkert, S., Jourdain, B., Legrand, M., Udisti, R., Becagli, S., Cerri, O., 2008. Seasonality
1531 of sulfur species (dimethyl sulfide, sulfate, and methanesulfonate) in Antarctica: Inland
1532 versus coastal regions. *Journal of Geophysical Research* 113.
- 1533 Prevedouros, K., Cousins, I.T., Buck, R.C., Korzeniowski, S.H., 2006. Sources, Fate and
1534 Transport of Perfluorocarboxylates. *Environmental Science & Technology* 40, 32-44.

- 1535 Ramanathan, V., Carmichael, G., 2008. Global and regional climate changes due to black
1536 carbon. *Nat Geosci* 1, 221-227.
- 1537 Rhodes, R.H., Bertler, N.A.N., Baker, J.A., Sneed, S.B., Oerter, H., Arrigo, K.R., 2009. Sea
1538 ice variability and primary productivity in the Ross Sea, Antarctica, from methylsulphonate
1539 snow record. *Geophysical Research Letters* 36.
- 1540 Rinne, H.J.I., Guenther, A.B., Greenberg, J.P., Harley, P.C., 2002. Isoprene and monoterpene
1541 fluxes measured above Amazonian rainforest and their dependence on light and temperature.
1542 *Atmospheric Environment* 36, 2421-2426.
- 1543 Rontani, J.F., Charriere, B., Vaultier, F., Garcia, N., Sempéré, R., Raimbault, P., 2012. Origin
1544 and degradation of lipids in aeolian particles from a coastal area of the north-western
1545 Mediterranean Sea. *Atmospheric Environment* 56, 124-135.
- 1546 Rubino, M., DOnofrio, A., Seki, O., Bendle, J.A., 2016. Ice-core records of biomass burning.
1547 *The Anthropocene Review* 3, 140-162.
- 1548 Ruggirello, R.M., Hermanson, M.H., Isaksson, E., Teixeira, C., Forsström, S., Muir, D.C.G.,
1549 Pohjola, V., van de Wal, R., Meijer, H.A.J., 2010. Current use and legacy pesticide
1550 deposition to ice caps on Svalbard, Norway. *Journal of Geophysical Research* 115, D18308.
- 1551 Saltzman, E.S., Dioumaeva, I., Finley, B.D., 2006. Glacial/interglacial variations in
1552 methanesulfonate (MSA) in the Siple Dome ice core, West Antarctica. *Geophysical Research*
1553 *Letters* 33, 1-4.
- 1554 Saltzman, E.S., Whung, P.Y., Mayewski, P.A., 1997. Methanesulfonate in the Greenland Ice
1555 Sheet Project 2 ice core. *Journal of Geophysical Research* 102, 26649-26657.
- 1556 Sankelo, P., Kawamura, K., Seki, O., Shibata, H., Bendle, J., 2013. n-Alkanes in Fresh Snow
1557 in Hokkaido, Japan: Implications for Ice Core Studies. *Arctic, Antarctic, and Alpine Research*
1558 45, 119-131.
- 1559 Sapart, C.J., Monteil, G., Prokopiou, M., van de Wal, R.S.W., Kaplan, J.O., Sperlich, P.,
1560 Krumhardt, K.M., van der Veen, C., Houweling, S., Krol, M.C., Blunier, T., Sowers, T.,
1561 Martinerie, P., Witrant, E., Dahl-Jensen, D., Rockmann, T., 2012. Natural and anthropogenic
1562 variations in methane sources during the past two millennia. *Nature* 490, 85-88.
- 1563 Scheringer, M., Stroebe, M., Wania, F., Wegmann, F., Hungerbühler, K., 2004. The effect of
1564 export to the deep sea on the long-range transport potential of persistent organic pollutants.
1565 *Environmental Science and Pollution Research* 11, 41-48.
- 1566 Schmid, P., Bogdal, C., Bluthgen, N., Anselmetti, F.S., Zwysig, A., Hungerbuhler, K., 2011.
1567 The missing piece: sediment records in remote Mountain lakes confirm glaciers being
1568 secondary sources of persistent organic pollutants. *Environ Sci Technol* 45, 203-208.
- 1569 Schmitt-Kopplin, P., Liger-Belair, G., Koch, B.P., Flerus, R., Kattner, G., Harir, M.,
1570 Kanawati, B., Lucio, M., Tziotis, D., Hertkorn, N., Gebefügi, I., 2012. Dissolved organic
1571 matter in sea spray: a transfer study from marine surface water to aerosols. *Biogeosciences* 9,
1572 1571-1582.

- 1573 Seki, O., Kawamura, K., Bendle, J.a.P., Izawa, Y., Suzuki, I., Shiraiwa, T., Fujii, Y., 2015.
 1574 Carbonaceous aerosol tracers in ice-cores record multi-decadal climate oscillations. *Scientific*
 1575 *Reports* 5, 14450.
- 1576 Sharkey, T.D., Wiberley, A.E., Donohue, A.R., 2008. Isoprene emission from plants: why
 1577 and how. *Ann Bot* 101, 5-18.
- 1578 Sharma, S., Chan, E., Ishizawa, M., Toom-Sauntry, D., Gong, S.L., Li, S.M., Tarasick, D.W.,
 1579 Leaitch, W.R., Norman, A., Quinn, P.K., Bates, T.S., Lévassieur, M., Barrie, L.A., Maenhaut,
 1580 W., 2012. Influence of transport and ocean ice extent on biogenic aerosol sulfur in the Arctic
 1581 atmosphere. *Journal of Geophysical Research: Atmospheres* 117, n/a-n/a.
- 1582 Sheldon, S.G., Steffensen, J.P., Hansen, S.B., Popp, T.J., Johnsen, S.J., 2014. The
 1583 investigation and experience of using ESTISOL™ 240 and COASOL™ for ice-core drilling.
 1584 *Annals of Glaciology* 55, 219-232.
- 1585 Shen, R.Q., Ding, X., He, Q.F., Cong, Z.Y., Yu, Q.Q., Wang, X.M., 2015. Seasonal variation
 1586 of secondary organic aerosol tracers in Central Tibetan Plateau. *Atmos Chem Phys* 15, 8781-
 1587 8793.
- 1588 Siggaard-Andersen, M.L., Gabrielli, P., Steffensen, J.P., Stromfeldt, T., Barbante, C.,
 1589 Boutron, C., Fischer, H., Miller, H., 2007. Soluble and insoluble lithium dust in the EPICA
 1590 DomeC ice core - Implications for changes of the East Antarctic dust provenance during the
 1591 recent glacial-interglacial transition. *Earth Planet. Sci. Lett.* 258, 32-43.
- 1592 Simon-Delso, N., Amaral-Rogers, V., Belzunces, L.P., Bonmatin, J.M., Chagnon, M.,
 1593 Downs, C., Furlan, L., Gibbons, D.W., Giorio, C., Girolami, V., Goulson, D., Kreutzweiser,
 1594 D.P., Krupke, C.H., Liess, M., Long, E., Mcfield, M., Mineau, P., Mitchell, E.A., Morrissey,
 1595 C.A., Noome, D.A., Pisa, L., Settele, J., Stark, J.D., Tapparo, A., Van Dyck, H., Van Praagh,
 1596 J., Van Der Sluijs, J.P., Whitehorn, P.R., Wiemers, M., 2015. Systemic insecticides
 1597 (Neonicotinoids and fipronil): Trends, uses, mode of action and metabolites. *Environmental*
 1598 *Science and Pollution Research* 22, 5-34.
- 1599 Simoneit, B.R.T., 2002. Biomass burning - A review of organic tracers for smoke from
 1600 incomplete combustion. *Appl. Geochem.* 17, 129-162.
- 1601 Sinclair, K.E., Bertler, N.A.N., Bowen, M.M., Arrigo, K.R., 2014. Twentieth century sea-ice
 1602 trends in the Ross Sea from a high-resolution, coastal ice-core record. *Geophysical Research*
 1603 *Letters* 41, 3510-3516.
- 1604 Slater, J.F., Currie, L.A., Dibb, J.E., Benner, B.A., 2002. Distinguishing the relative
 1605 contribution of fossil fuel and biomass combustion aerosols deposited at Summit, Greenland
 1606 through isotopic and molecular characterization of insoluble carbon. *Atmospheric*
 1607 *Environment* 36, 4463-4477.
- 1608 Sorooshian, A., Padró, L.T., Nenes, A., Feingold, G., McComiskey, A., Hersey, S.P., Gates,
 1609 H., Jonsson, H.H., Miller, S.D., Stephens, G.L., Flagan, R.C., Seinfeld, J.H., 2009. On the
 1610 link between ocean biota emissions, aerosol, and maritime clouds: Airborne, ground, and
 1611 satellite measurements off the coast of California. *Global Biogeochemical Cycles* 23, n/a-n/a.

- 1612 Steinlin, C., Bogdal, C., Scheringer, M., Pavlova, P.A., Schwikowski, M., Schmid, P.,
 1613 Hungerbuhler, K., 2014. Polychlorinated biphenyls in glaciers. 2. Model results of deposition
 1614 and incorporation processes. *Environ Sci Technol* 48, 7849-7857.
- 1615 Stortini, A.M., Martellini, T., Del Bubba, M., Lepri, L., Capodaglio, G., Cincinelli, A., 2009.
 1616 n-Alkanes, PAHs and surfactants in the sea surface microlayer and sea water samples of the
 1617 Gerlache Inlet sea (Antarctica). *Microchem. J.* 92, 37–43.
 1618 <https://doi.org/10.1016/j.microc.2008.11.005>
- 1619 Surratt, J.D., Lewandowski, M., Offenberg, J.H.; Jaoui, M., Kleindienst, T.E., Edney, E.O.,
 1620 Seinfeld, J.H., 2007. Effect of acidity on secondary organic aerosol formation from isoprene.
 1621 *Environ Sci Technol* 41, 5363-5369.
- 1622 Talalay, P.G., Gundestrup, N.S., 2002. Hole fluids for deep ice core drilling. *Memoirs of*
 1623 *National Institute of Polar Research. Special issue* 56, 148-170.
- 1624 Taylor, K.C., Mayewski, P.A., Twickler, M.S., Whitlow, S.I., 1996. Biomass burning
 1625 recorded in the GISP2 ice core: A record from eastern Canada? *Holocene* 6, 1-6.
- 1626 Thomas, E.R., Abram, N.J., 2016. Ice core reconstruction of sea ice change in the Amundsen-
 1627 Ross Seas since 1702 A.D. *Geophysical Research Letters* 43, 5309-5317.
- 1628 Trentmann, J., Luderer, G., Winterrath, T., Fromm, M.D., Servranckx, R., Textor, C.,
 1629 Herzog, M., Graf, H.F., Andreae, M.O., 2006. Modeling of biomass smoke injection into the
 1630 lower stratosphere by a large forest fire (Part I): reference simulation. *Atmos Chem Phys* 6,
 1631 5247-5260.
- 1632 Trostl, J., Chuang, W.K., Gordon, H., Heinritzi, M., Yan, C., Molteni, U., Ahlm, L., Frege,
 1633 C., Bianchi, F., Wagner, R., Simon, M., Lehtipalo, K., Williamson, C., Craven, J.S.,
 1634 Duplissy, J., Adamov, A., Almeida, J., Bernhammer, A.K., Breitenlechner, M., Brilke, S.,
 1635 Dias, A., Ehrhart, S., Flagan, R.C., Franchin, A., Fuchs, C., Guida, R., Gysel, M., Hansel, A.,
 1636 Hoyle, C.R., Jokinen, T., Junninen, H., Kangasluoma, J., Keskinen, H., Kim, J., Krapf, M.,
 1637 Kurten, A., Laaksonen, A., Lawler, M., Leiminger, M., Mathot, S., Mohler, O., Nieminen, T.,
 1638 Onnela, A., Petaja, T., Piel, F.M., Miettinen, P., Rissanen, M.P., Rondo, L., Sarnela, N.,
 1639 Schobesberger, S., Sengupta, K., Sipila, M., Smith, J.N., Steiner, G., Tome, A., Virtanen, A.,
 1640 Wagner, A.C., Weingartner, E., Wimmer, D., Winkler, P.M., Ye, P., Carslaw, K.S., Curtius,
 1641 J., Dommen, J., Kirkby, J., Kulmala, M., Riipinen, I., Worsnop, D.R., Donahue, N.M.,
 1642 Baltensperger, U., 2016. The role of low-volatility organic compounds in initial particle
 1643 growth in the atmosphere. *Nature* 533, 527-531.
- 1644 Tsigaridis, K., Daskalakis, N., Kanakidou, M., Adams, P.J., Artaxo, P., Bahadur, R.,
 1645 Balkanski, Y., Bauer, S.E., Bellouin, N., Benedetti, A., Bergman, T., Berntsen, T.K., Beukes,
 1646 J.P., Bian, H., Carslaw, K.S., Chin, M., Curci, G., Diehl, T., Easter, R.C., Ghan, S.J., Gong,
 1647 S.L., Hodzic, A., Hoyle, C.R., Iversen, T., Jathar, S., Jimenez, J.L., Kaiser, J.W., Kirkevåg,
 1648 A., Koch, D., Kokkola, H., Lee, Y.H., Lin, G., Liu, X., Luo, G., Ma, X., Mann, G.W.,
 1649 Mihalopoulos, N., Morcrette, J.J., Müller, J.F., Myhre, G., Myriokefalitakis, S., Ng, N.L.,
 1650 O'Donnell, D., Penner, J.E., Pozzoli, L., Pringle, K.J., Russell, L.M., Schulz, M., Sciare, J.,
 1651 Seland, Ø., Shindell, D.T., Sillman, S., Skeie, R.B., Spracklen, D., Stavrou, T., Steenrod,
 1652 S.D., Takemura, T., Tiitta, P., Tilmes, S., Tost, H., van Noije, T., van Zyl, P.G., von Salzen,
 1653 K., Yu, F., Wang, Z., Wang, Z., Zaveri, R.A., Zhang, H., Zhang, K., Zhang, Q., Zhang, X.,

- 1654 2014. The AeroCom evaluation and intercomparison of organic aerosol in global models.
1655 Atmos Chem Phys 14, 10845-10895.
- 1656 Uglietti, C., Zapf, A., Jenk, T.M., Sigl, M., Szidat, S., Salazar, G., Schwikowski, M., 2016.
1657 Radiocarbon dating of glacier ice: overview, optimisation, validation and potential. The
1658 Cryosphere 10, 3091-3105.
- 1659 UNEP, 2004. Stockholm Convention on Persistent Organic Pollutants. United Nations
1660 Environment Programme: Nairobi, Kenya.
- 1661 Vallelonga, P., Gabrielli, P., Balliana, E., Wegner, A., Delmonte, B., Turetta, C., Burton, G.,
1662 Vanhaecke, F., Rosman, K.J.R., Hong, S., Boutron, C.F., Cescon, P., Barbante, C., 2010.
1663 Lead isotopic compositions in the EPICA Dome C ice core and Southern Hemisphere
1664 Potential Source Areas. Quat. Sci. Rev. 29, 247-255.
- 1665 van Eijck, A., Opatz, T., Taraborrelli, D., Sander, R., Hoffmann, T., 2013. New tracer
1666 compounds for secondary organic aerosol formation from β -caryophyllene oxidation.
1667 Atmospheric Environment 80, 122-130.
- 1668 Vecchiato, M., Argiriadis, E., Zambon, S., Barbante, C., Toscano, G., Gambaro, A., Piazza,
1669 R., 2015. Persistent Organic Pollutants (POPs) in Antarctica: Occurrence in continental and
1670 coastal surface snow. Microchem J 119, 75-82.
- 1671 Vehvilainen, J., Isaksson, E., Moore, J.C., 2002. A 20th-century record of naphthalene in an
1672 ice core from Svalbard. Annals of Glaciology 35, 257-260.
- 1673 Vignati, E., Facchini, M.C., Rinaldi, M., Scannell, C., Ceburnis, D., Sciare, J., Kanakidou,
1674 M., Myriokefalitakis, S., Dentener, F., O'Dowd, C.D., 2010. Global scale emission and
1675 distribution of sea-spray aerosol: Sea-salt and organic enrichment. Atmospheric Environment
1676 44, 670-677.
- 1677 Virtanen, A., Joutsensaari, J., Koop, T., Kannosto, J., Yli-Pirila, P., Leskinen, J., Makela,
1678 J.M., Holopainen, J.K., Poschl, U., Kulmala, M., Worsnop, D.R., Laaksonen, A., 2010. An
1679 amorphous solid state of biogenic secondary organic aerosol particles. Nature 467, 824-827.
- 1680 von Schneidmesser, E., Schauer, J.J., Shafer, M.M., Hagler, G.S.W., Bergin, M.H., Steig,
1681 E.J., 2008. A method for the analysis of ultra-trace levels of semi-volatile and non-volatile
1682 organic compounds in snow and application to a Greenland snow pit. Polar Science 2, 251-
1683 266.
- 1684 Wang, W., Wu, M.H., Li, L., Zhang, T., Liu, X.D., Feng, J.L., Li, H.J., Wang, Y.J., Sheng,
1685 G.Y., Claeys, M., Fu, J.M., 2008. Polar organic tracers in PM_{2.5} aerosols from forests in
1686 eastern China. Atmos Chem Phys 8, 7507-7518.
- 1687 Wang, Z., Chappellaz, J., Martinerie, P., Park, K., Petrenko, V., Witrant, E., Emmons, L.K.,
1688 Blunier, T., Brenninkmeijer, C.A.M., Mak, J.E., 2012. The isotopic record of Northern
1689 Hemisphere atmospheric carbon monoxide since 1950: implications for the CO budget.
1690 Atmos Chem Phys 12, 4365-4377.
- 1691 Wang, Z., Chappellaz, J., Park, K., Mak, J.E., 2010. Large Variations in Southern
1692 Hemisphere Biomass Burning During the Last 650 Years. Science 330, 1663-1666.

- 1693 Wang, Z., Cousins, I.T., Scheringer, M., Buck, R.C., Hungerbuhler, K., 2014. Global
1694 emission inventories for C4-C14 perfluoroalkyl carboxylic acid (PFCA) homologues from
1695 1951 to 2030, part II: the remaining pieces of the puzzle. *Environ Int* 69, 166-176.
- 1696 Wang, Z., Xie, Z., Mi, W., Möller, A., Wolschke, H., Ebinghaus, R., 2015. Neutral Poly/Per-
1697 Fluoroalkyl Substances in Air from the Atlantic to the Southern Ocean and in Antarctic
1698 Snow. *Environmental Science & Technology* 49, 7770-7775.
- 1699 Wania, F., 2006. Potential of Degradable Organic Chemicals for Absolute and Relative
1700 Enrichment in the Arctic. *Environmental Science & Technology* 40, 569-577.
- 1701 Wania, F., Hoff, J.T., Jia, C.Q., Mackay, D., 1998. The effects of snow and ice on the
1702 environmental behaviour of hydrophobic organic chemicals. *Environ Pollut* 102, 25-41.
- 1703 Wania, F., Mackay, D., 1996. Peer reviewed: tracking the distribution of persistent organic
1704 pollutants. *Environ Sci Technol* 30, 390A-396A.
- 1705 Welch, K.A., Mayewski, P.A., Whitlow, S.I., 1993. Methanesulfonic acid in coastal Antarctic
1706 snow related to sea-ice extent. *Geophysical Research Letters* 20, 443-446.
- 1707 Whung, P.-Y., Saltzman, E.S., Spencer, M.J., Mayewski, P.a., Gundestrup, N., 1994. Two-
1708 hundred-year record of biogenic sulfur in a south Greenland ice core (20D). *Journal of*
1709 *Geophysical Research* 99, 1147.
- 1710 Wohrnschimmel, H., MacLeod, M., Hungerbuhler, K., 2013. Emissions, fate and transport of
1711 persistent organic pollutants to the Arctic in a changing global climate. *Environ Sci Technol*
1712 47, 2323-2330.
- 1713 Wolff, E.W., 2012. Chemical signals of past climate and environment from polar ice cores
1714 and firn air. *Chem. Soc. Rev.* 41, 6247. <https://doi.org/10.1039/c2cs35227c>
- 1715 Wolff, E.W., Fischer, H., Fundel, F., Ruth, U., Twarloh, B., Littot, G.C., Mulvaney, R.,
1716 Röthlisberger, R., De Angelis, M., Boutron, C.F., Hansson, M., Jonsell, U., Hutterli, M.a.,
1717 Lambert, F., Kaufmann, P., Stauffer, B., Stocker, T.F., Steffensen, J.P., Bigler, M., Siggaard-
1718 Andersen, M.L., Udisti, R., Becagli, S., Castellano, E., Severi, M., Wagenbach, D., Barbante,
1719 C., Gabrielli, P., Gaspari, V., 2006. Southern Ocean sea-ice extent, productivity and iron flux
1720 over the past eight glacial cycles. *Nature* 440, 491-496.
- 1721 Wurl, O., Ekau, W., Landing, W.M., Zappa, C.J., 2017. Sea surface microlayer in a changing
1722 ocean – A perspective. *Elem Sci Anth* 5, 31. <https://doi.org/10.1525/elementa.228>
- 1723 Wurl, O., Obbard, J.P., 2004. A review of pollutants in the sea-surface microlayer (SML): a
1724 unique habitat for marine organisms. *Mar. Pollut. Bull.* 48, 1016–1030.
1725 <https://doi.org/10.1016/j.marpolbul.2004.03.016>
- 1726 Xia, X., Hopke, P.K., 2006. Seasonal Variation of 2-Methyltetrols in Ambient Air Samples.
1727 *Environmental Science & Technology* 40, 6934-6937.
- 1728 Xie, S., Yao, T., Kang, S., Xu, B., Duan, K., Thompson, L.G., 2000. Geochemical analyses
1729 of a Himalayan snowpit profile: implications for atmospheric pollution and climate. *Org*
1730 *Geochem* 31, 15-23.

- 1731 Xie, Z., Wang, Z., Mi, W., Möller, A., Wolschke, H., Ebinghaus, R., 2015. Neutral Poly-
1732 /perfluoroalkyl Substances in Air and Snow from the Arctic. *Scientific Reports* 5, 8912.
- 1733 Xie, Z., Zhao, Z., Moller, A., Wolschke, H., Ahrens, L., Sturm, R., Ebinghaus, R., 2013.
1734 Neutral poly- and perfluoroalkyl substances in air and seawater of the North Sea. *Environ Sci*
1735 *Pollut Res Int* 20, 7988-8000.
- 1736 Yamamoto, S., Kawamura, K., Seki, O., 2011. Long-range atmospheric transport of
1737 terrestrial biomarkers by the Asian winter monsoon: Evidence from fresh snow from
1738 Sapporo, northern Japan. *Atmospheric Environment* 45, 3553-3560.
- 1739 Yamashita, N., Kannan, K., Taniyasu, S., Horii, Y., Petrick, G., Gamo, T., 2005. A global
1740 survey of perfluorinated acids in oceans. *Mar Pollut Bull* 51, 658-668.
- 1741 Yao, P., Schwab, V.F., Roth, V., Xu, B., Yao, T., Gleixner, G., 2013. Levoglucosan
1742 concentrations in ice-core samples from the Tibetan Plateau determined by reverse-phase
1743 high-performance liquid chromatography–mass spectrometry. *J Glaciol* 59, 599-608.
- 1744 Yassaa, N., Peeken, I., Zöllner, E., Bluhm, K., Arnold, S., Spracklen, D., Williams, J., 2008.
1745 Evidence for marine production of monoterpenes. *Environ Chem* 5, 391-401.
- 1746 You, C., Song, L., Xu, B., Gao, S., 2016. Method for determination of levoglucosan in snow
1747 and ice at trace concentration levels using ultra-performance liquid chromatography coupled
1748 with triple quadrupole mass spectrometry. *Talanta* 148, 534-538.
- 1749 You, C., Yao, T., Gao, S., Gong, P., Zhao, H., 2014. Simultaneous Determination of
1750 Levoglucosan, Mannosan and Galactosan at Trace Levels in Snow Samples by GC/MS.
1751 *Chromatographia* 77, 969-974.
- 1752 Young, C.J., Furdui, V.I., Franklin, J., Koerner, R.M., Muir, D.C.G., Mabury, S.A., 2007.
1753 Perfluorinated Acids in Arctic Snow: New Evidence for Atmospheric Formation.
1754 *Environmental Science & Technology* 41, 3455-3461.
- 1755 Yunker, M.B., Macdonald, R.W., 1995. Composition and Origins of Polycyclic Aromatic
1756 Hydrocarbons in the Mackenzie River and on the Beaufort Sea Shelf. *Arctic* 48, 118-129.
- 1757 Zangrando, R., Barbaro, E., Zennaro, P., Rossi, S., Kehrwald, N.M., Gabrieli, J., Barbante,
1758 C., Gambaro, A., 2013. Molecular Markers of Biomass Burning in Arctic Aerosols.
1759 *Environmental Science & Technology* 47, 8565-8574.
- 1760 Zennaro, P., Kehrwald, N., Marlon, J., Ruddiman, W.F., Brücher, T., Agostinelli, C., Dahl-
1761 Jensen, D., Zangrando, R., Gambaro, A., Barbante, C., 2015. Europe on fire three thousand
1762 years ago: Arson or climate? *Geophysical Research Letters* 42, 5023-2033.
- 1763 Zennaro, P., Kehrwald, N., McConnell, J.R., Schüpbach, S., Maselli, O.J., Marlon, J.,
1764 Vallenga, P., Leuenberger, D., Zangrando, R., Spolaor, A., Borrotti, M., Barbaro, E.,
1765 Gambaro, A., Barbante, C., 2014. Fire in ice: two millennia of boreal forest fire history from
1766 the Greenland NEEM ice core. *Clim. Past* 10, 1905-1924.
- 1767 Zhang, X., Meyer, T., Muir, D.C., Teixeira, C., Wang, X., Wania, F., 2013. Atmospheric
1768 deposition of current use pesticides in the Arctic: snow core records from the Devon Island
1769 Ice Cap, Nunavut, Canada. *Environ Sci Process Impacts* 15, 2304-2311.

1770 Zoccolillo, L., Amendola, L., Cafaro, C., Insogna, S., 2005. Improved analysis of volatile
1771 halogenated hydrocarbons in water by purge-and-trap with gas chromatography and mass
1772 spectrometric detection. *J. Chromatogr. A* 1077, 181–187.
1773 <https://doi.org/10.1016/j.chroma.2005.04.076>

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