High-resolution analyses of concentrations and sizes of refractory black carbon particles deposited on northwest Greenland over the past 350 years - Part 2. Seasonal and temporal trends in refractory black carbon originated from fossil fuel combustion and biomass burning

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Abstract. The roles and impacts of refractory black carbon (rBC), an important aerosol species affecting Earth's radiation budget, are not well understood owing to lack of accurate long-term observations. To study the temporal changes in rBC since the pre-industrial period, we analysed rBC in an ice core drilled in northwest Greenland. Using an improved technique for rBC measurement and a continuous flow analysis system, we obtained accurate and high temporal resolution records of rBC particle size and mass/number concentrations for the past 350 years. Number and mass concentrations, which both started to increase in the 1870s associated with inflow of anthropogenically derived rBC, reached their maxima in the 1910s–1920s and then subsequently decreased. On the basis of bBackward trajectory analyses, suggest we found that North America was likely the dominant source region of the anthropogenic rBC in the ice core. The increase in anthropogenic rBC shifted the annual concentration peaks of rBC from summer to winter–early spring. After rBC concentrations diminished to pre-industrial levels, the annual peak concentration of rBC returned to the summer. We found that anthropogenic rBC particles were larger than

32 biomass burning rBC particles. By separating the rBC in winter and summer, we reconstructed the temporal variations in rBC

33 that originated from biomass burning, including the period with large anthropogenic input. The rBC that originated from

34 biomass burning showed no trend of increase until the early 2000s. Finally, possible albedo reductions due to rBC are discussed.

35 Our new data provide key information for validating aerosol and climate models, thereby supporting improved projections of

36 future climate and environment.

1 Introduction

38 Black carbon (BC) particles, which are emitted by incomplete combustion of biomass and fossil fuels, play important roles

39 inaffect Earth's radiation budget and thus in climate change (Bond et al., 2013; Moteki, 2023; Matsui et al., 2022; Legrand et

40 al., 2016). In turn, changes in climate can affect emissions of BC from biomass burning through natural processes such as

41 wildfires. Global warming is considered a major cause of the recent increase in large wildfires globally that can cause serious

42 damage to ecosystems and human society (Calkin et al., 2023; Keeley and Syphard, 2021; Wang et al., 2021; Keane et al.,

43 2008). Increased occurrence of large wildfires in the future could affect Earth's radiation budget, and change the frequency at

44 which certain regions are exposed to serious hazard. Changes inIncreases of fossil fuel combustion since the Industrial

45 Revolution have changed Earth's radiation budget and contributed to the warming or cooling over the past century (Shindell

46 and Faluvegi, 2009; McConnell et al., 2007; Breider et al., 2017). To understand the effects of BC on the radiation budget and

47 of the impact of climate change on BC emissions, the long-term changes in the concentrations and size distributions of BC

48 particles should be   known. Data obtained since the pre-industrial period are particularly valuable because we cannot fully

49 understand the anthropogenic effects without characterizing BC in a pristine environment. The Arctic is the key region for

50 clearer elucidation of the roles of BC because the Arctic has warmed at a rate four times faster than that of the global average

51 over the past half century, leading to drastic changes such as sea ice retreat, enhanced glacier mass loss, and ecosystem changes

52 (Rantanen et al., 2022). Despite numerous studies based on observations and aerosol/climate models (e.g., Bond et al., 2013

53 and references therein), we have only limited knowledge on BC owing to lack of accurate long-term in situ observations (Mori

54 et al., 2019). For the Arctic region, data are particularly sparse and few long-term records of BC size distribution exist.

55   Although there have been no direct observations before the past few decades, ice cores drilled in the Arctic have

56 provided long-term records of BC. Development of the Single-Particle Soot Photometer (hereafter, SP2; Droplet Measurement

57 Technologies, USA) (Stephens et al., 2003; Baumgardner et al., 2004) enabled measurements of refractory BC (rBC), the

terminology used for incandesce-based BC measurements (Petzold et al., 2013; Lim et al., 2014), in Arctic ice cores, where

BC concentrations are low and sample volumes are limited (McConnell et al., 2007; Zdanowicz et al., 2018; Zennaro et al.,

2014; Osmont et al., 2018). A continuous flow analysis (CFA) system is often used with the SP2 for high-resolution analysis

of ice cores (McConnell et al., 2007; Zdanowicz et al., 2018; Zennaro et al., 2014). With an SP2 attached to a CFA system,

McConnell et al. (2007) reconstructed rBC mass concentrations in central and southern Greenland since the pre-industrial

period. They showed that rBC concentration began a gradual rise after 1850, which was followed by rapid increase around

1890, a peak at around 1910, and then erratic decline through the late 1940s, followed by a sharp drop in the 1950s. They

attributed the increase to rBC derived mainly from fossil fuel combustion in North America. Similar anthropogenic temporal

trends have been reported for other Greenland sites (McConnell, 2010). The rBC flux records presented by McConnell (2010)

suggest that the anthropogenically derived increase in rBC was substantially less in northern Greenland than in southern

Greenland, which is closer to the emission sources in North America and Western Europe. McConnell et al. (2007) also

reported that the greatest increase in anthropogenic rBC occurs in winter. However, no rBC particle size data from Greenland

ice cores have been published to date.

At Arctic sites outside Greenland, only a few ice cores have been analysed for BC. An ice core from Holtedahlfonna

(Svalbard) indicated that BC mass concentration started to increase after 1850 and peaked around 1910, similar to the rBC

record of ice cores from Greenland (Ruppel et al., 2014). BC concentrations in the Holtedahlfonna core increased again

between 1970 and 2004, reaching unprecedented values in the 1990s. This increase is not seen in Greenland ice cores, and

contradicts atmospheric BC observations from Svalbard and other Arctic sites (Sharma et al., 2013), which indicate declining

concentrations of atmospheric BC. Ruppel et al. (2014) attributed the differences partly to the different sources of

anthropogenic BC affecting Svalbard and Greenland attributable to different air mass trajectories. They also suggested that

changes in scavenging efficiency might have affected the Holtedahlfonna BC record. An ice core from Lomonosovfonna,

another site in Svalbard (Osmont et al., 2018), showed gradual increase in rBC during 1800–1859, followed by dramatic

increase from 1860. The concentrations displayed two maxima at around 1870 and 1895, before they started to decline.

Between 1910 and 1949, concentrations of rBC were low. In contrast to the concentrations of rBC in Greenland, another

notable increase was evident in the Lomonosovfonna core after 1940, and the concentrations were at their highest in the 1950s

and 1960s. The rBC concentrations started to decrease in the 1970s, i.e., much later than the start of the decline in Greenland.

84 The authors argued that the differences between Greenland and Lomonosovfonna are partly related to the different source

85 regions of the air masses reaching Greenland and Svalbard.

86 The differences between the Holtedahlfonna and Lomonosovfonna records might also reflect different methods used

87 for the measurement of BC mass concentration. The samples from the Holtedahlfonna ice core were filtered, and then the

88 filters were analysed for BC using a thermal–optical method (Osmont et al., 2018), whereas the Lomonosovfonna and

89 Greenland ice cores were analysed using an SP2. Uncertainties regarding the filtering efficiency (Ruppel et al., 2014) and the

90 effects of dust particles on the thermal–optical method could partly explain the differences in the long-term trends in BC

91 concentrations. Furthermore, melt–freeze cycles that commonly occur at ice coring sites in Svalbard would have affected the

92 rBC concentrations (Osmont et al., 2018). Moreover, melt–freeze cycles could have agglomerated the rBC particles to larger

93 sizes beyond the detection range of an off-the-shelf ~~standard~~ SP2 (Osmont et al., 2018; Wendl et al., 2014). An ice core rBC

94 record from the Devon Ice Cap in the Canadian Arctic was also found to differ from the records of Greenland ice cores

95 (Zdanowicz et al., 2018). Although such differences could be partly attributable to different rBC source regions, melt–freeze

96 cycles could have also affected the Devon Ice Cap record. To investigate whether melt–freeze cycles did affect the derived BC

97 concentrations, we need to know the sizes of the rBC particles.

98 Even for ice cores drilled at sites where summer melting seldom occurs, such as those from interior Greenland, it is

99 important to investigate the size distributions of rBC particles to verify whether they are within the detection range of the SP2

100 instrument. This is because the sizes of rBC particles in snow are often larger than those in the atmosphere (Schwarz et al.,

101 2013; Mori et al., 2019) and exceed the detection range of a traditional ~~standard~~ SP2. ~~, which~~The upper limit of detectable rBC

102 diameter is usually ~~between~~ approximately ~~70 and 850~~500 nm for the off-the-shelf SP2; that for SP2 modified by Moteki and

103 Kondo (2010) is approximately 850 nm (Moteki and Kondo, 2010; Mori et al.,2019); and that for the off-the-shelf SP2

104 Extended Range (SP2-XR) is 800 nm ~~(Mori et al., 2019)~~. If a large proportion of rBC particles have a diameter of >500 nm or

105 850 nm, the BC mass concentrations would be underestimated (Mori et al., 2019; Goto-Azuma et al., 2024~~submitted~~).

106 Furthermore, if an ultrasonic ~~nebuliser~~nebulizer, such as the U5000AT (CETAC Technologies, USA), was used with an off-

107 the-shelf ~~standard~~ SP2, as was the case in most previous studies of rBC in ice cores (McConnell et al., 2007; Kaspari et al.,

108 2011; Zennaro et al., 2014; Bisiaux et al., 2012a, b; Wang et al., 2015; Zdanowicz et al., 2018; Du et al., 2020), ~~the upper limit~~

109 ~~of detectable~~there would be large uncertainties in rBC ~~size would have been <850 nm~~mass concentrations (Wendl et al., 2014;

110 Goto-Azuma et al, ~~submitted~~2024). Because the nebulizing efficiency of this type of nebulizer varies markedly for rBC

particles < 850 nm~~within this size range~~ (Ohata et al., 2013; Mori et al., 2016; Goto-Azuma et al., 2024), variation in efficiency should be considered when calculating accurate mass concentrations and size distributions (Ohata et al., 2013). However, this was not taken into account in most previous ice core studies. It is therefore important to analyse Arctic ice cores using an instrumental set-up that allows detection of rBC particles with diameter of >850 nm, and also to consider the size-dependent efficiency of the nebulizer. We developed a CFA system that includes an rBC unit, which allows accurate high-resolution measurement of concentrations and size distributions of rBC particles with diameter between 70 nm and 4 μm. Using this system, we analysed an ice core drilled at the SIGMA-D site in northwest Greenland. The details of this new system and its performance are described in the companion paper (Goto-Azuma et al., 2024~~submitted~~). In this study, we analysed the data and investigated the temporal variability in concentration and size distribution of rBC that originated from fossil fuel combustion and biomass burning.

The BC detected in Arctic ice cores, together with NH_4^+ and specific organic materials (i.e., formate, levoglucosan, vanillic acid, and p-hydroxybenzoic acid), has been used to reconstruct past biomass burning (Ruppel et al., 2014; Zennaro et al., 2014; Grieman et al., 2017, 2018; Fischer et al., 2015; Pokhrel et al., 2020; Legrand et al., 2016). Although both BC and NH_4^+ have sources other than biomass burning (Osmont et al., 2018), levoglucosan, vanillic acid, and p-hydroxybenzoic acid primarily originate from biomass burning. However, the data regarding such organic materials usually have lower temporal resolution compared with that of rBC and NH_4^+ data owing to limitations of the measurement techniques. Furthermore, little is known about their changes during atmospheric transport and post-depositional processes (Hennigan et al., 2010). Different ice core proxies often show different temporal and spatial trends in biomass burning activities (Legrand and de Angelis, 1996; Legrand and Mayewski, 1997; Legrand et al., 1992, 2016; Kawamura et al., 2012; Grieman et al., 2017, 2018; Rubino et al., 2016; Zennaro et al., 2014). Compared with the Global Charcoal Database, which has been used widely to investigate changes in biomass burning on centennial to orbital time scales (Power et al., 2010; Marlon et al., 2016), ice core proxy records usually have higher temporal resolution. Even monthly or seasonally resolved continuous records of rBC and NH_4^+ for the past few centuries, millennia, and hundred thousand years have been derived from several Arctic ice cores, thereby allowing detection of high spikes in concentration in summer attributable to large boreal forest fires in northern North America and/or Siberia (Fischer et al., 2015; Zennaro et al., 2014). However, previous studies using rBC as a biomass burning tracer have been restricted to the pre-industrial period. This is because rBC originated from fossil fuel combustion contributed greatly to the total rBC concentrations and obscured the temporal trends in rBC related to biomass burning.

138   In this study, we reconstructed approximately monthly resolved concentrations and sizes of rBC particles in northwest

139   Greenland over the past 350 years. The rBC originated both from biomass burning and from fossil fuel combustion was

140   distinguished owing to their different seasonal variability. In this paper, we discuss the temporal trends in the concentration

141   and size of rBC particles originated from both sources, and we investigate the rBC source regions based on backward trajectory

142   analyses. We then estimated the potential albedo reductions based on the monthly mean rBC concentration data.

143   **2 Materials and Methods**

144   **2.1 Ice core processing, analyses, and dating**

145   A 222.7 m ice core was drilled at the SIGMA-D site (77.636° N, 59.120° W; 2100 m a.s.l.; Fig. 1) in northwest Greenland in

146   spring 2014 (Matoba et al., 2015). The annual mean air temperature and accumulation rate at the site were estimated to be

147   −25.6 °C and 0.23 w eq yra^{-1}, respectively (Nagatsuka et al., 2021). We examined the melt features (ice layers and thin crusts)

148   in the uppermost 20 meters of the SIGMA-D ice core, where increased summer melting would be expected due to recent

149   warming. We observed ice layers, with a maximum thickness of 10 mm, at only three depths. The 20-meter average melt

150   feature percentage (MFP) was 0.47%. The maximum MFP per meter was 1.7%, and 10 out of the 20 meters had no melt

151   features. Thus, the effects of melt-refreeze cycles are minimal at the SIGMA-D site.
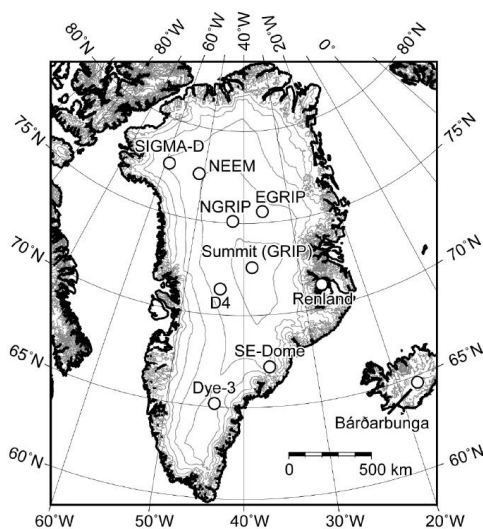
Figure 1: Location of the SIGMA-D site and that of other drill sites.

152   The details of the ice core processing and analyses are described in the companion paper (Goto-Azuma et al.,

153   submitted to Atmospheric Chemistry and Physics2024); therefore, we provide only a brief summary here. The top 175.77 m

154 of the core was divided into two vertical sections (Sections A and B) in the field. Section A was kept frozen and transported

155 to the National Institute of Polar Research (NIPR) in Japan; Section B was cut, melted, and bottled in the field.

156

157 Down to the depth of 112.87 m in Section A, we cut quadrangular prism samples with a cross section of 34 mm × 34

158 mm. For the depth interval between 6.17 and 112.87 m, we analysed rBC, stable isitopes of water isotopes, and six elements

159 (i.e., ^{23}Na, ^{24}Mg, ^{27}Al, ^{39}K, ^{40}Ca, and ^{56}Fe) using the NIPR CFA system. The top 6.17 m of Section A was too fragile to be

160 analysed using the CFA system; hence, we manually cut it into segments of approximately 0.1 m. These "discrete samples"

161 were decontaminated in a −20 °C cold room using a precleaned ceramic knife and then placed in powder-free plastic bags.

162 They were then melted and transferred to precleaned glass and polypropylene bottles in a class 10,000 clean room. The samples

163 in glass bottles were analysed for stable isotopes of water and rBC. For the discrete samples, stable isotopes of water were

164 analysed using a near-infrared cavity ring-down spectrometer (L2120-i, Picarro Inc., USA), a high-precision vaporizer (A0211,

165 Picarro Inc., USA), and an autosampler (PAL HTC9 - xt - LEAP, LEAP Technologies, USA). The precision of determination

166 was ±0:05‰ for δ^{18}O. The samples in the polypropylene bottles were analysed for six elements (i.e., ^{23}Na, ^{24}Mg, ^{27}Al, ^{39}K,

167 ^{40}Ca, and ^{56}Fe) using an inductively coupled plasma mass spectrometer (7700 ICP-MS, Agilent Technologies, USA) in a class

168 10,000 clean room at NIPR.

169 Both the CFA samples and the discrete samples were analysed for rBC using a Wide-Range SP2 (Mori et al., 2016),

170 which is a modified version of the SP2 (Droplet Measurement Technologies, USA), and a concentric pneumatic nebulizer

171 (Marin-5, Teldyne CETAC, USA). The combination of the Wide-Range SP2 and the pneumatic nebulizer enabled us to extend

172 the range of the size of rBC particles analysed (70 nm < diameter < 4 µm) to beyond that those of the off-the-shelfstandard

173 SP2 (70 nm < diameter < 600 850500 nm) and the modified SP2 (Moteki and Kondo, 2010) or off-the-shelf SP2-XR (50-70

174 nm<diameter<800-850 nm). This combination and a careful calibration procedure enabled us to measure not only the

175 concentration but also the diameter of rBC particles. The analytical errors of the rBC mass and number concentrations were

176 estimated to be <16% (Mori et al., 2016; Goto-Azuma et al., 2024). The reproducibility of the rBC number and mass

177 concentrations for repeated measurements was usually better than 10% (Mori et al., 2019; Goto-Azuma et al., 2024). The

178 detection limits of the rBC number and mass concentrations were approximately 10 0.35 counts µL^{-1} and 0.01 02 µg L^{-1},

179 respectively.

180 Depths of Section B above 61.2 m were analysed for Na$^+$, K$^+$, Mg^{2+} and, Ca^{2+}, Cl$^-$, NO$_3^-$, and SO$_4^{2-}$ using two ion

181   chromatographs (ICS-2100, Thermo Fisher Scientific, USA) at Hokkaido University (Japan), whereas depths between 61.2

182   and 112.87 m were analysed for NH_4^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, and SO_4^{2-} using two ion chromatographs (ICS-2000,

183   Thermo Fisher Scientific, USA) at NIPR. The limit of detection of Na^+ measured at Hokkaido University was 1~~0~~ µg L^{-1},

184   whereas that measured at NIPR was 0.2 µg L^{-1}. Stable ~~water~~ isotopes of water were analysed for all samples from Section B

185   using a near-infrared cavity ring-down spectrometer (L2130-i, Picarro, USA) and a high-throughput vaporizer (A0212, Picarro,

186   USA) at Hokkaido University. The precision of determination was ±~~0.08~~0.1‰ for $\delta^{18}O$. For dating purposes, tritium

187   concentrations were measured using a liquid scintillation counter (LSC-LB3; Aloka Co. Ltd., Japan) at 0.05 m intervals for

188   the depth interval 19.15–26.47 m (Nagatsuka et al., 2021).

189   Figure 2 shows the seasonal variability in Na and Na^+ concentrations, together with that in $\delta^{18}O$ ~~(Goto-Azuma et al.,~~

190   ~~submitted)~~. Concentrations of Na and Na^+ show maxima in winter and minima in summer, whereas the $\delta^{18}O$ shows maxima

191   in summer and minima in winter (Nagatsuka et al., 2021; Legrand and Mayewski, 1997; Mosher et al., 1993). ~~As reported in~~

192   ~~the companion paper (Goto-Azuma et al., submitted), w~~We dated Section B of the SIGMA-D core by annual layer counting

193   using mainly Na^+ (Nagatsuka et al., 2021), which exhibited clearer seasonal variation compared to $\delta^{18}O$ and other ionic species~~.~~

194   The seasonal variation of $\delta^{18}O$, typically used for annual layer counting, was often obscured by diffusion in the SIGMA-D

195   core. However, ~~W~~we supplementarily used Ca^{2+} and $\delta^{18}O$ data when annual peaks of Na^+ were not clearly observed.

196   Additionally, we used a tritium peak (1963) and volcanic SO_4^{2-} peaks (Katmai, 1912; Tambora, 1816, unknown, 1810; and

197   Laki, 1783) as reference horizons, as ~~(~~reported by Nagatsuka et al.~~,~~ (2021). Because the CFA data from Section B and the

198   discrete data from Section A agreed well (Fig. 2), we basically adopted the chronology of Section B for that of Section A~~.~~

199   ~~However, for the years before 1783, we made~~ with a few minor adjustments ~~where high SO₄²⁻ peaks did not match the volcanic~~

200   ~~eruptions reported from study of other Greenland ice cores (Sigl et al., 2013)~~. The uncertainties of dating were estimated to be

201   less than ±2 years. The CFA data covered 1653–2002 ~~(Goto-Azuma et al., submitted)~~, and the data from the top 6.1~~7~~ m covered

202   the period 2003–2013.

203   We divided one year into 12 months based on the assumption that the annual maxima and minima of Na^+

204   concentration correspond to 1 January and 1 July, respectively (Fig. 2). Each depth interval corresponding to a half year was

205   evenly divided into six months. Using the CFA data, we calculated the annual mean and the monthly mean values of the

206   number and mass concentrations of rBC particles. It is important to note that the months defined in this study may not align

207   exactly with calendar months for the following reasons: (1) precipitation is not evenly distributed throughout the year (Figs.

208 A1 and A2); (2) the minima and maxima of Na⁺ concentrations do not necessarily coincide with 1 January and 1 July,

209 respectively; and (3) dry deposition would have a small contribution. As a result, there is inherent uncertainty in this definition.

210 The discrepancy between the "months" defined in this study and actual calendar months could be one or two months.

211 Nevertheless, we will refer to these periods as "months" hereafter.
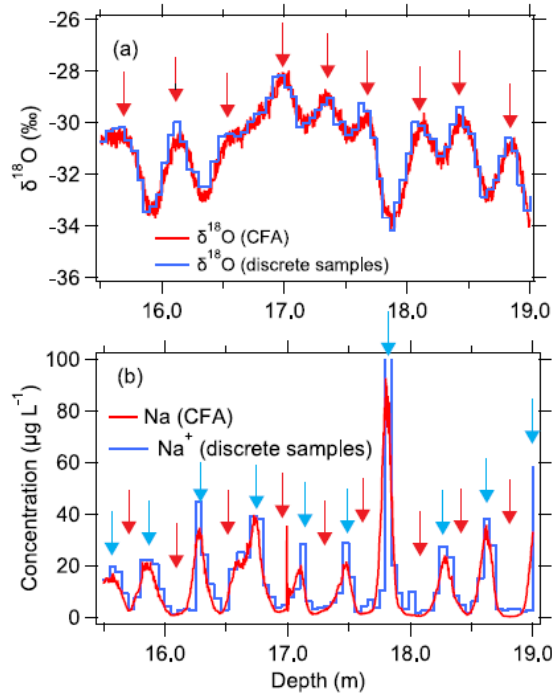
Figure 2: ~~Concentrations of~~ **(a) δ^{18}O and (b) Na (and Na⁺)** concentrations~~(Goto-Azuma et al., submitted)~~**. Red and blue curves represent data obtained from CFA measurements (this study) and discrete sample measurements (Nagatsuka et al., 2021) of the SIGMA-D core, respectively. Blue and red arrows indicate winter and summer, respectively. Winter and summer peaks were assumed to represent January 1 and July 1 of each year, respectively.**

212 As demonstrated in the companion paper (Goto-Azuma et al., 2024), the dispersion lengths of the CFA system are

213 ~35 and ~39 mm for Na and BC, respectively. However, we could usually resolve two peaks which were 10 mm apart, although

214 the signal dispersion might slightly reduce the heights of the seasonal peaks.

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219 **2.2 Backward trajectory analysis**

To estimate the contributions of different air masses affecting the SIGMA-D and D4 sites (Fig. 1), we performed 10-day backward trajectory analyses for the period 1958–2015. Dividing the globe into 21 regions (Fig. A1A3), we calculated the contribution from each region. We used the Single-Particle Lagrangian Integrated Trajectory (HySPLIT) model developed by the National Oceanographic and Atmospheric Administration (NOAA) (Stein et al., 2015). The initial air mass was set at three elevations at each site (i.e., 500, 1000, and 1500 m above ground level), and the accumulated probability of the air mass in each 1° grid cell was calculated. Assuming wet deposition of rBC at the ice core sites, the air mass probability was weighted with the local daily precipitation, i.e., if no precipitation occurred, the air mass was not considered, and vice versa. We used ERA5 precipitation data produced by the European Centre for Medium-Range Weather Forecasts (Hersbach et al., 2020). Details of the procedures are described in previous studies (Parvin et al., 2019; Nagatsuka et al., 2021; Nagatsuka et al., 2023). For comparison, we also calculated the regional contributions without weighted for precipitation, while accounting for dry deposition. However, we anticipate that dry deposition contributes only minimally compared to wet deposition (Appendix B).

3 Results and Discussion

3.1 Impacts of anthropogenic emissions on long-term trends in concentrations and sizes of rBC particles

Figure 3 displays annual and decadal averages of number and mass concentrations of rBC during the past 350 years. Notably, monthly mean values could have been affected by the values of the adjacent few one-two months, considering the resolution of the CFA data (10–40 mm) estimated from signal dispersion tests (Sect. 2.1 and Goto-Azuma et al., submitted2024). Because
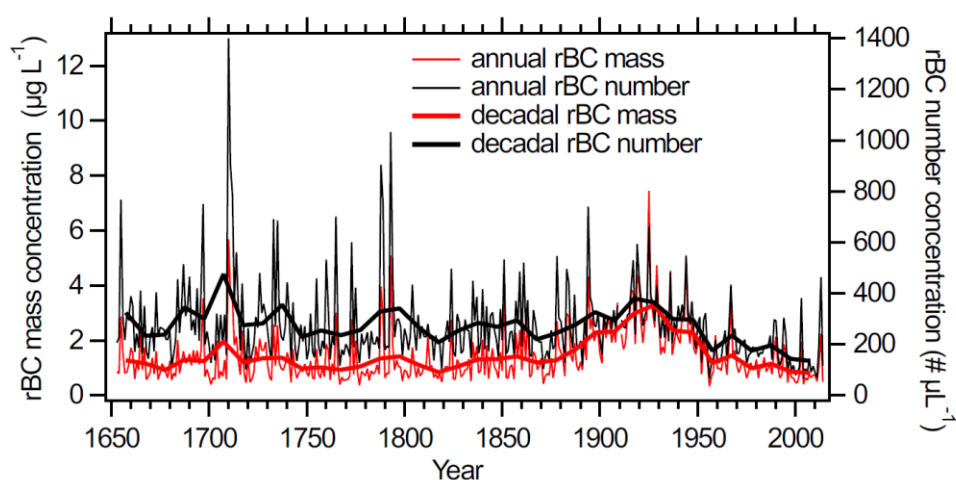
Figure 3: Annual mean (thin curves) and decadal mean (thick curves) concentrations of rBC. Red and black curves represent mass and number concentrations, respectively.

we melted the core from the bottom to the top, the data for ~~a few~~one-two months after large rBC concentration peaks could have been affected. However, the annual and decadal averages were unaffected by the CFA signal dispersion. We have also calculated annual rBC mass flux using annual mean rBC mass concentration data and annual accumulation rate data (Fig.A4). Since there are no long-term trends in annual accumulation rates, the temporal trends in rBC mass concentrations and rBC mass fluxes are consistent. Therefore, we used concentration data in the following discussion.

Many of the very high mass and number concentration peaks such as those in 1710 originated from large boreal forest fires, as discussed in Sect. 3.3. Apart from these sporadic sharp peaks in number and mass concentrations, their background levels started to increase in the 1870s, reached their maxima in the 1910s–1920s, and decreased again ~~after~~since the 1930s. Breakpoint analysis (Muggeo, 2003; de la Casa and Nasello, 2010) confirmed the timing of these increases and decreases. In the 1960s, rBC number and mass concentrations returned to their pre-industrial levels. In the 1980s and 1990s, number concentrations were below the pre-industrial level, whereas mass concentrations were similar to those of the pre-industrial level. Before 1850, the major sources of rBC in Greenland were likely to have been biomass burning emissions from boreal forest fires (Legrand et al., 2016; McConnell et al., 2007; Zennaro et al., 2014). The increases in rBC concentrations that occurred in the late 19th century to mid-20th century are likely attributable to inflow to Greenland of rBC of anthropogenic origin, as reported previously (McConnell, 2010; McConnell et al., 2007).

Direct comparison between the rBC concentrations in the SIGMA-D core and those in other Greenland ice cores is not strictly feasible owing to methodological differences. rBC measurements in other Greenland ice cores were conducted using the ~~standard~~ off-the-shelf SP2 coupled with an ultrasonic nebulizer (McConnell et al., 2007; McConnell, 2010; Zennaro et al., 2014). This setup allows for the measurement of rBC particles with diameter of less than ~~600~~500–650 nm (Goto-Azuma et al., ~~submitted~~2024). In contrast, the measurements of the SIGMA-D ice core could detect rBC particles with diameter up to 4 μm. Therefore, rBC concentrations in other Greenland ice cores might have been underestimated during periods when the diameter of large proportions of rBC particles exceeded approximately ~~650~~500 nm. Owing to lack of information on size distributions, the extent of the underestimation for other Greenland ice cores remains unknown. As described in the companion paper (Goto-Azuma et al., ~~submitted~~2024), if the ~~measurement method~~off-the-shelf SP2 used in the previous studies had also been used for the SIGMA-D ice core, the extent of underestimation would have depended on depth and hence on age. However, the general temporal trends in annual mean rBC concentrations at the SIGMA-D site did not change notably if rBC particles

264   with diameter of >~~650~~ 500 nm, the maximum measurable diameter of the off-the-shelf SP2, were excluded (Fig. 4). Therefore,

265   it is informative to compare the rBC concentration trends at the SIGMA-D site with those of other Greenland sites.

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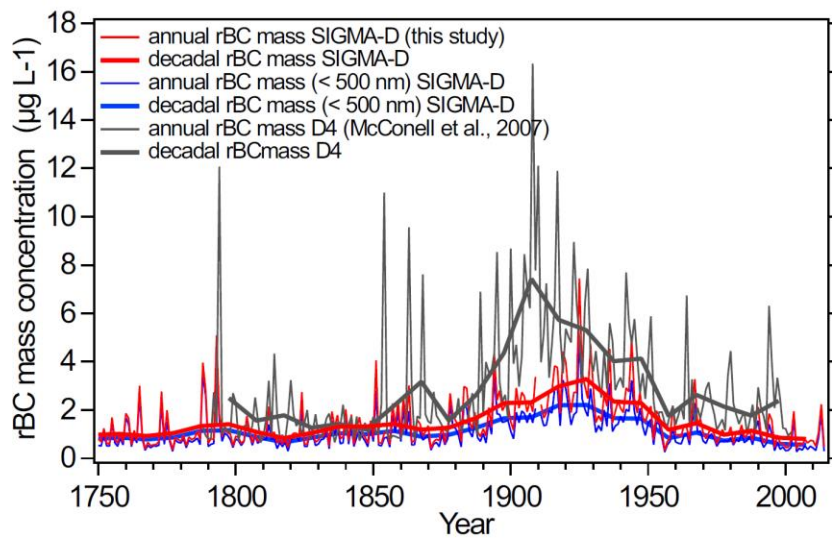
Figure 4: Annual mean (thin curves) and decadal mean (thick curves) mass concentrations of rBC. Red and

black curves represent rBC concentrations at the SIGMA-D and D4 sites, respectively. Blue curves show

~~annual~~ rBC concentrations for rBC particles with diameter of <~~650~~ 500 nm.

267

268   The long-term trends in rBC mass concentrations at the SIGMA-D site are broadly similar to those at other ice core

269   sites in Greenland (McConnell et al., 2007; McConnel., 2010), including the D4 site. However, the SIGMA-D core shows

270   much lower anthropogenic rBC concentrations, a later peak period, and later onset of the reductions in comparison with those

271   of the D4 core (Fig. 4). This is in accord with the studies by McConnel et al. (2007) and McConnel (2010), which indicate that

272   more southerly sites generally show higher anthropogenic rBC concentrations, an earlier peak period, and earlier onset of the

273   decline in anthropogenic rBC concentrations in comparison with those of more northerly sites. The BC emission inventories

274   for potential BC source regions indicate that emissions of anthropogenically derived BC started earlier in Europe than in North

275   America, and that the decline in anthropogenic BC concentrations started earlier in North America than in Europe or the former

276   USSR (Osmont et al., 2018). The emission inventories used by Osmont et al. (2018) were those adopted for the Coupled Model

277   Intercomparison Project phase 5 (CMIP 5; Bauer et al., 2013; Eckhardt et al., 2023; Lamarque et al., 2010). If those emission

278 inventories are reliable, then the slight difference in the temporal trends of rBC concentrations would indicate that southern

279 Greenland sites (e.g., the D4 site) had been influenced mainly by anthropogenic emissions from North America, whereas

280 northern Greenland sites (e.g., the SIGMA-D site) had been influenced by anthropogenic emissions from Europe and the

281 former USSR (in addition to those from North America), as was the case for anthropogenic sulphate (Goto-Azuma and Koerner,

282 2001). However, the results of our backward trajectory study do not support this hypothesis, as discussed below.

283   The 10-day precipitation-weighted backward trajectories for the SIGMA-D and D4 sites showed no contributions of

284 air masses from Antarctica (AT), Australia and New Zealand (AUS), South America (SAM), Southeast Asia (SEA), South

285 Asia (SA), the Antarctic Ocean (ATO), South Pacific Ocean (SPO), Indian Ocean (INO), and South Atlantic Ocean (SAO).

286 The four regions of the Middle East (ME), Africa (AF), East Asia (EA), and Central Asia (CA) (Fig. 5) showed maximum

287 contributions of <0.05%. In further analyses, we omitted the above 13 regions and focused on the eight regions of Europe

288 (EU), the Greenland Ice sheet (GrIS), Russia (RUS), North America (NA), the North Pacific Ocean (NPO), North Atlantic

289 Ocean (NAO), Arctic Ocean (AO), and Iceland (IC) (Fig. 5). Of these, GrIS, AO, NA, and NAO were found to be the major

290 sources of the air masses arriving at both the SIGMA-D site and the D4 site, although only NA represents a source of

291 anthropogenic BC emissions. Therefore, the temporal trends in anthropogenic rBC at both SIGMA-D and D4 appear to reflect

292 the trend of BC emission in NA.
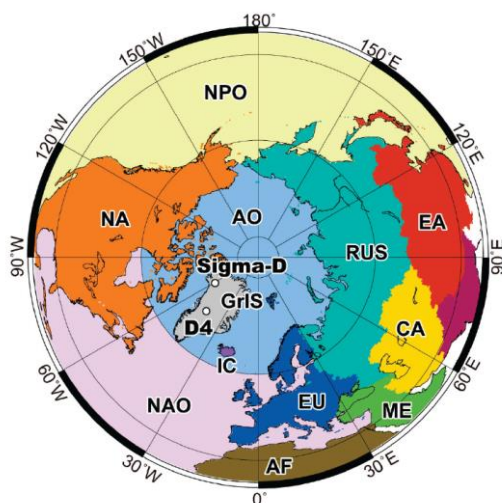
Figure 5: The 12 regions ~~used~~ showing non-zero contributions in ~~for~~precipitation-weighted backward trajectory analyses (GrIS: Greenland Ice Sheet, NA: North America, EU: Europe, RUS: Russia, CA: Central Asia, EA: East Asia, ME: Middle East, AF: Africa, NPO: North Pacific Ocean, NAO: North Atlantic Ocean, AO: Arctic Ocean, and IC: Iceland).

293 For precipitation-weighted trajectories, Tthe contributions of air masses from EU and RUS, which are regions with

294 high levels of emission of anthropogenic BC (Hoesly et al., 2018), were less than 4% and 1%, respectively, at both the SIGMA-

295 D site and the D4 site, even in winter

296 when their contributions are at their maxima. To investigate the influence of contributions from EU and RUS in more

297 detail, we recalculated the air mass contributions by excluding GriIS and the oceanic regions of NPO, NAO, and AO where

298 there are no sources of-BC emission. Although GrIS had the largest air mass contributions throughout the year and throughout

299 the 10 days, we excluded it because most of the region is covered with ice and has very minor BC sources. The temporal

300 variations in the contributions from NA, EU, RUS, and IC are plotted in Fig. 6 (for both precipitation-weighted and unweighted

301 trajectories), and the probability distributions of the air masses for the SIGMA-D and D4 sites are displayed in Fig. 7 (for

302 precipitation-weighted trajectories) and Fig. A5 (for precipitation-unweighted trajectories). In winter, when Except for the

303 initial few days at D4, the anthropogenic input of BC is greatest at both the SIGMA-D site (see Sect 3.2) and the D4 site

304 (McConnell et al., 2007), contributions from NA are the highest at both SIGMA-D and D4 sites for both precipitation-weighed

305 and unweighted trajectories throughout the year. The significant contributions of IC during the first few days at the D4 site are

306 likely due to its proximity to Greenland despite its small area, since IC is the only land region near Greenland that can

307 serve as a BC source region. However, if we include oceanic regions along with land regions, the contribution from IC

308 decreases substantially.

309 At both SIGMA-D and D4 sites, the contributions from EU and RUS increase in winter (Figs. 6, and 7, and A5) when

310 air masses from distant sources can more easily reach the Arctic (Jurányi et al., 2023) for both precipitation—weighted and

311 unweighted trajectories. Against our expectation based on CMIP 5 emission inventories, the contributions from EU were

312 slightly greater at D4 than at SIGMA-D. The contributions from RUS were similar at both sites and comprised approximately

313 20% of the total at most.Although backward trajectory analyses showed that contributions from EU were slightly different

314 between the SIGMA-D and D4 sites, the results suggested the opposite conclusion to that of an assumption based on the

315 regional difference in emission inventories to explain the slight differences in the temporal trend of rBC at the two sites. For

316 precipitation-weighted trajectories, the contributions from RUS were similar at both sites and comprised approximately 5% of

317 the total at most in winter, when the anthropogenic input of rBC is greatest at both the SIGMA-D site (see Sect 3.2) and the

318 D4 site (McConnell et al., 2007). While precipitation-unweighted trajectories in winter show higher contribution from RUS

319 compared with precipitation-weighted trajectories at both SIGMA-D and D4 sites, the contribution from RUS is greater at the

 SIGMA-D site than at the D4 site. The slight difference in temporal patterns of mass concentrations of anthropogenic rBC

 between the two sites might reflect the different contributions from RUS in winter. However, it should be noted that the 1958-

 2015 timeframe used for back trajectory calculations, a constraint given by availability of reanalysis data, is not

 necessarily representative of the entire 350-year period. Nagatsuka et al. (2021), based on the back trajectory studies for

 the SIGMA-D site, have shown that the interannual variability of contributions from different regions remained relatively

 constant during 1958-2013. Thus, we can discuss the source regions of rBC for this period based on our back trajectory

 calculations. For earlier periods, we can only hypothesize the back trajectories by assuming similar atmospheric

 circulations to those of the 1958-2015 period. This could lead to large uncertainties for the years before 1958.
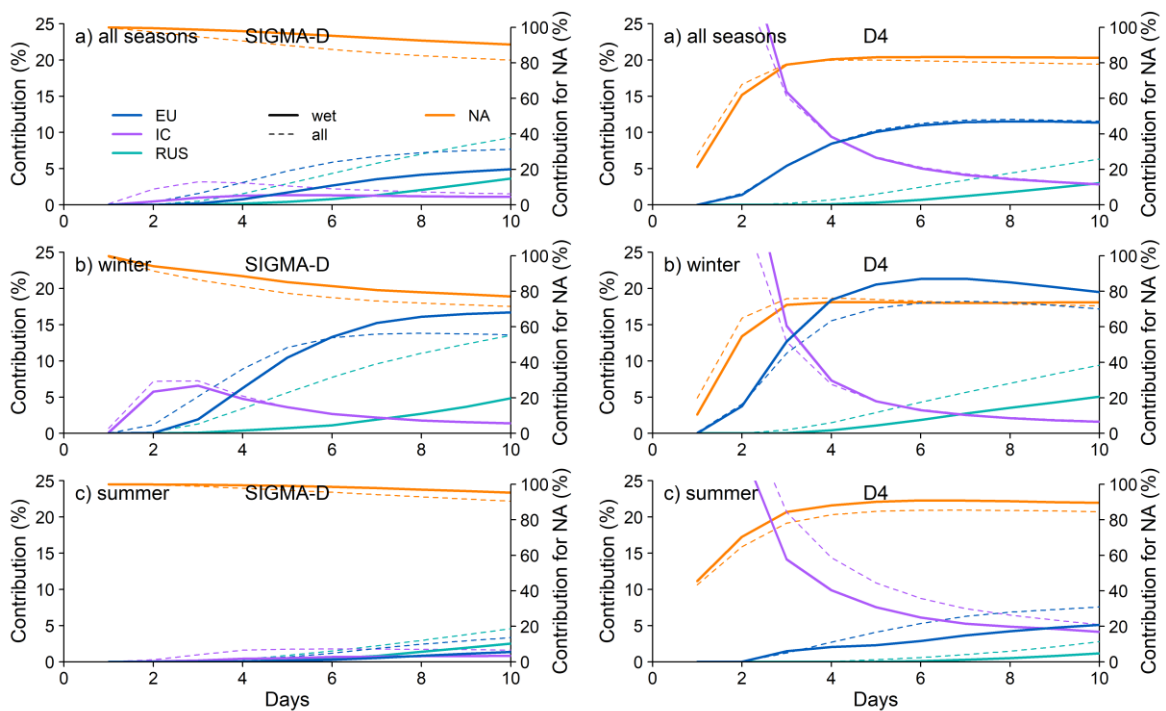
Figure 6: Temporal variability in contribution of air masses arriving at (left) the SIGMA-D site and (right) the D4 site from four regions: (a) averages of 12 months, (b) averages of winter months (December-February), and (c) averages of summer months (May-July). Right-hand axes indicate contributions from NA, and left-hand axes indicate contributions from the other regions. Solid and dashed curves denote results with and without weighing for the daily local precipitation, respectively.
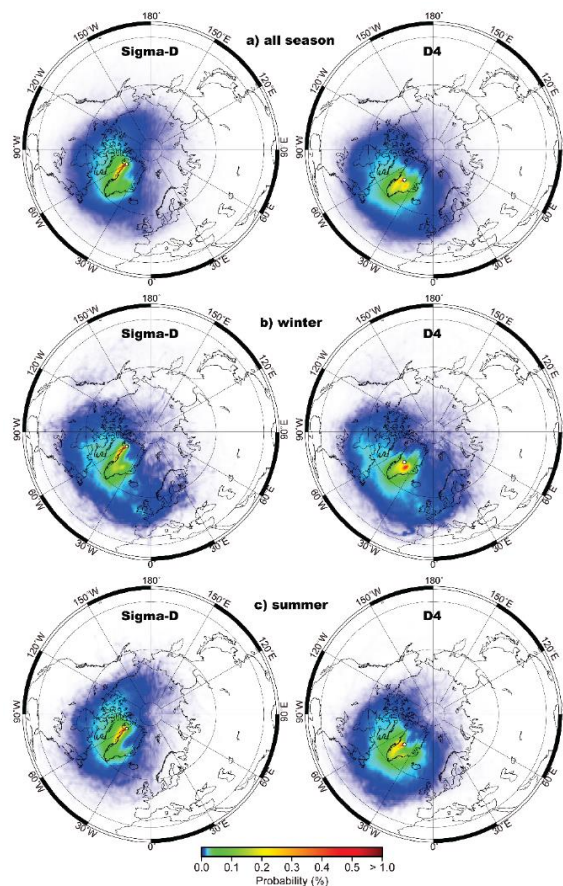
Figure 7: Probability distributions of air masses at (left) the SIGMA-D site and (right) the D4 site: (a) averages of all seasons, (b) averages of winter months (December–February), and (c) averages of summer months (May–July).

329   ~~Notably~~Additionally, there are large uncertainties in emission inventories. Although the CMIP 5 emission inventories

330   appear to reproduce the temporal patterns in concentrations and fluxes of rBC in Arctic ice cores better than those produced

331   using the Coupled Model Intercomparison Project phase 6 (CMIP 6) inventories, the reproduction of the magnitudes of the

332   concentrations and fluxes is better when using the CMIP 6 inventories (Eckhardt et al., 2023). A model intercomparison study,

333   which compared the modelling results obtained from 11 Earth System Models using CMIP 6 emission inventories with rBC

334   records from ice cores (Moseid et al., 2022), revealed errors in European emission inventories. However, the study also showed

335   that rBC concentrations in Northern Greenland ice cores reflected European emissions, contradicting our backward trajectory

336   analyses. It should be also noted that backward trajectory analyses are unable to capture the contributions of air masses

337   transported through the upper troposphere (Nagatsuka et al., 2021), which could be important when estimating the

338   contributions from distant sources. Currently, we are unable to explain the slightly different temporal trends in the rBC records

339   from different ice cores in Greenland. Further elucidation of this topic will require additional modelling studies constrained by

340   accurate rBC records from Greenland ice cores.

341   Figure 8 displays decadal mean mass and number size distributions of rBC for different periods with different

342   anthropogenic inputs. We assumed that the mass size distribution follows a ~~Gaussian~~ lognormal distribution and thus we

343   estimated the mass median diameter (MMD), which is one of the measures of an rBC size distribution. The decadal mean

344   MMD was 226 nm in the pre-industrial period of 1783–1792. It increased to 325 nm in the peak anthropogenic period of 1913–

345   1922, and subsequently decreased to 302 nm in 1993–2002 and 278 nm in 2003–2012. Number size distributions did not show

346   noticeable temporal change. To investigate the temporal changes in rBC size distribution, we used the average mass of rBC

347   particles (mBC) in addition to the MMD. The parameter mBC can be calculated by dividing the mass concentration by the

348   number concentration. Figure 9 shows the annual and decadal mean mBC and decadal mean MMD, together with the annual

349   and decadal mean rBC mass concentrations. ~~Of the two size parameters, mBC is easier to calculate than MMD; hence, it can~~

350   ~~be used to investigate changes with high temporal resolution.~~ Based on breakpoint analyses, we deduced the timing of rBC
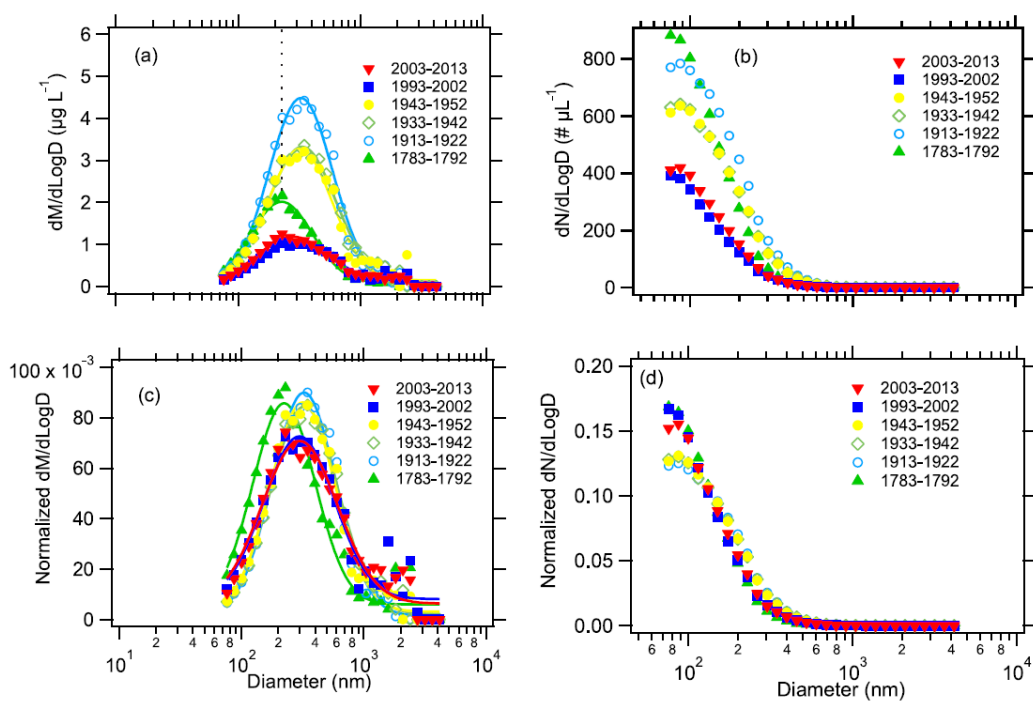
Figure 8: Temporal changes in decadal mean size distributions of rBC particles: (a) and (b) non-normalized

mass and number size distributions, respectively, and (c) and (d) ~~normalized~~ **mass and number size distributions**

normalized by total rBC mass and number concentrations, respectively. Dotted line in (a) indicates the mass

median diameter (MMD) for the period 1783–1792.

351   size changes. ~~Both the~~ The annual mean mBC and decadal mean mBC started to increase in the 1850s and the 1840s,
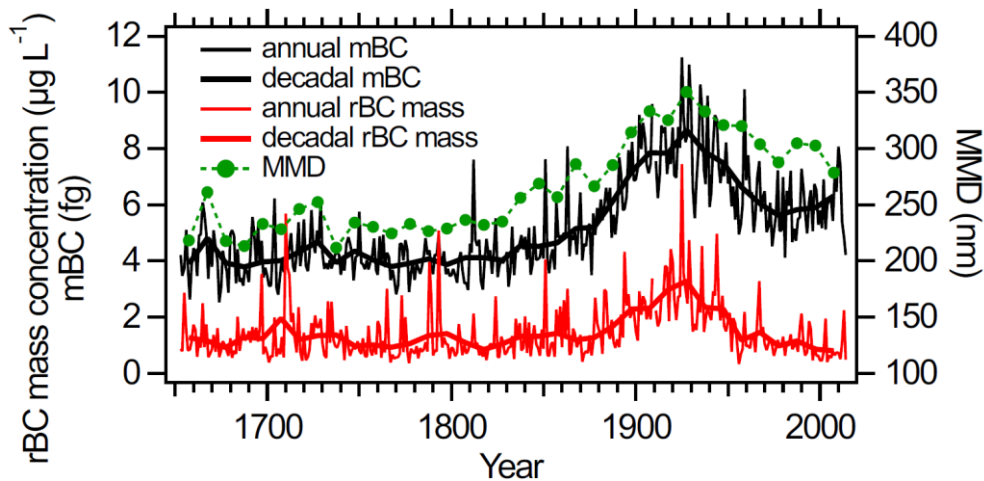
Figure 9: Annual and decadal mean mBC (black) and decadal mean MMD (green), together with annual and decadal mean rBC mass concentration (red). Thin and thick solid ~~lines~~ curves denote annual and decadal means, respectively.

respectively, while the decadal mean MMD started to increase in the 18~~2~~30s. Annual mean mBC, decadal mean mBC, and decadal mean MMD ~~and~~ peaked in the ~~1910s~~ 1920s, when the mass and number concentrations of rBC were at their maxima. The peak values of MMD and mBC were approximately twice and 1.5 times, as high as the corresponding pre-industrial values, respectively. Anthropogenically derived rBC particles that arrived in northwest Greenland appear to have been larger than rBC particles of biomass burning origin. This is contrary to our expectation because it has been reported that the sizes of rBC particles from biomass burning are larger than those from anthropogenic emissions near the sources (Bond et al., 2013). In the 1920s or 1930s, MMD and mBC both started to decrease, as did the mass and number concentrations of rBC particles. However, in contrast to rBC concentrations, neither MMD nor mBC returned to their pre-industrial levels; instead, they remained approximately 1.3 and 1.5 times higher than their pre-industrial levels, respectively. We also notice that the start of the increases in mBC and MMD appear to have occurred earlier than the increases in mass and number concentrations of rBC by ~~30~~20 ~~40~~ 30 years.

3.2 Temporal changes in seasonal variations in concentrations and sizes of rBC particles

Figure 10 compares the monthly mean rBC mass concentrations in three periods: the pre-industrial period, the period with high anthropogenic input, and recent years when concentrations decreased and returned to pre-industrial levels. Changes are
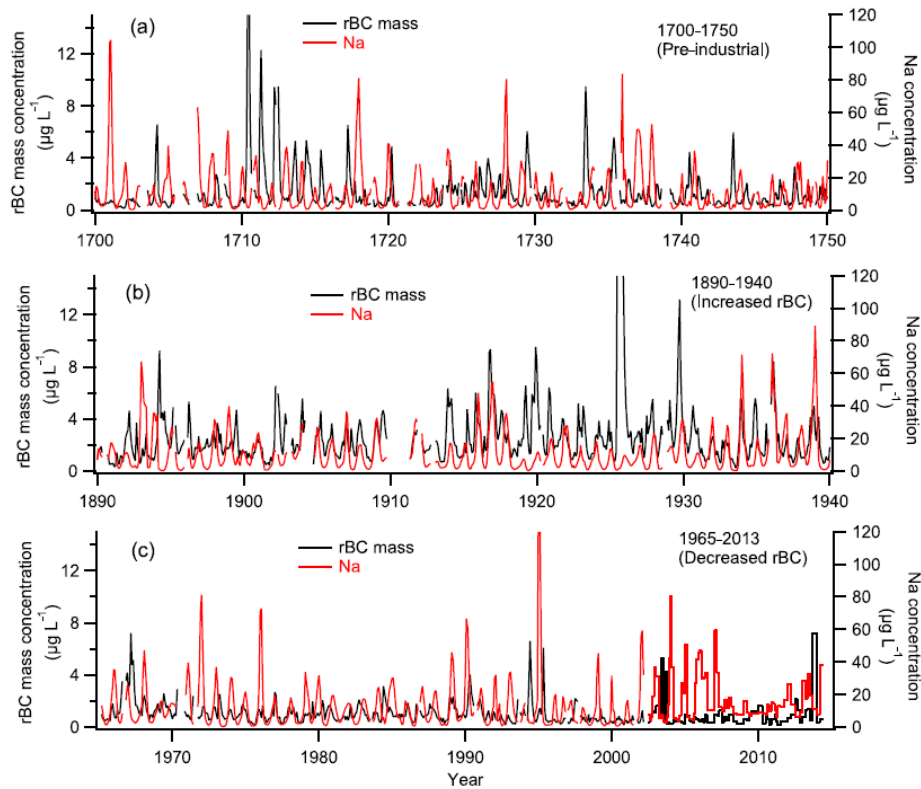
Figure 10: Monthly mean rBC mass concentrations and Na concentrations in three periods calculated from the CFA data, with the exception of 2003–2013 (concentrations for this period are raw data from the discrete samples that were analysed with monthly–bimonthly resolution).

367   evident in the seasonality of rBC concentrations with respect to Na concentrations, which peak in winter. As reported by

368   McConnell et al. (2007) in relation to the D4 core, rBC concentrations peaked in summer in the pre-industrial period, whereas

369   they peaked in late-winter to early spring during the peak industrial period. Figure 10 also indicates that in recent years after

370   the rBC concentrations returned to their pre-industrial levels, the peaks once again occurred in summer. During the transition

371   period between the pre-industrial and the peak anthropogenic periods, and that between the peak anthropogenic period and

372   recent years, concentrations show complex seasonal variability. ~~For example, i~~In some years, peaks occurred in both summer

373   and winter/early spring, whereas seasonal peaks were obscured or summer peaks and winter/early spring peaks appeared

374   alternately in other years.

375

376   To examine the general temporal trends in seasonal variations in rBC mass concentrations, we plotted 20-year

377   averages of rBC mass concentrations in each month for the years 1653–1992 and we plotted 10-year averages for 1993–2002

378   (Fig. 11). Up until the 20-year period of 1853–1872, rBC mass concentrations were elevated from March to September, peaking

379   in the late-spring to summer months (i.e., May–July). After the 20-year period of 1853–1872, rBC concentrations in autumn

380   to spring increased and became dominant. During the first half of the 20th century, rBC mass concentrations peaked in the

381   winter months of December and January. The autumn to spring increases in rBC concentrations are likely attributable to inflow

382   of anthropogenic emissions (McConnell et al., 2007). The seasonality of the anthropogenic rBC at SIGMA-D is consistent

383   with that of the present-day atmospheric rBC observations at Arctic sites such as Alert (Canadian high Arctic), Ny-Alesund

384   (Svalbard), Barrow (Alaska), and a Greenland coastal site (Sharma et al., 2006, 2019; Gong et al., 2010; Qi and Wang, 2019;
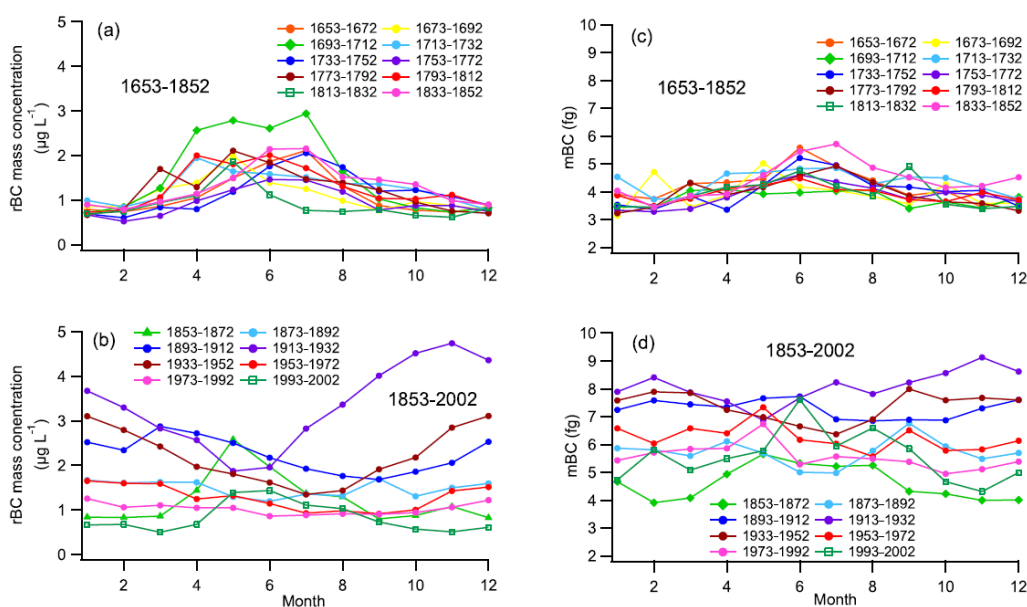
Figure 11: Twenty-year averages of (a) and (b) rBC mass concentrations and (c) and (d) mBC in each month

for the years 1653–1992 and the 10-year averages for 1993–2002.

385   Massling et al., 2015).

386

387   After the 20-year period of 1913–1933, when the anthropogenic input was at its maximum, the autumn to spring

388   concentrations decreased. During 1993–2002, the rBC mass concentration peaked in summer again. The recent seasonality of

389   rBC at the SIGMA-D site is the same as that observed at other Greenland ice-coring sites, including EGRIP (Du et al., 2020)

390   and Summit (Fig. 1) (Schmeisser et al., 2018), but it differs from that of atmospheric observations in the Arctic (including

391   Greenland), where rBC concentrations peak in winter/early spring (Sharma et al., 2006, 2019; Gong et al., 2010; Qi and Wang,

392 2019; Massling et al., 2015). Although we do not present the results for rBC number concentrations, they showed seasonal

393 variations similar to those found in mass concentrations. The influence of anthropogenic emissions in the recent two decades

394 appears to be much lower at the ice coring sites of SIGMA-D, EGRIP, and Summit, located at elevations of >2000 m a.s.l., in

395 comparison with that at atmospheric observation sites located near sea level where anthropogenic emissions remain dominant.

396 At the high-elevation sites on the GrIS, concentrations of rBC from biomass burning have exceeded those associated with

397 anthropogenic emissions since the late 20th century, which is likely attributable to reduced emissions of anthropogenically

398 derived rBC, primarily in NA and secondarily in EU (McConnell, 2010; McConnell et al., 2007; Moseid et al., 2022).

399 To understand the general temporal trends in seasonal variations in rBC size, we plotted 20-year averages of mBC

400 in each month for the years of 1653–1992 and we plotted 10-year averages for 1993–2002 (Fig. 11). Up until the 20-year

401 period of 1853–1872, mBC peaked in spring to the summer months (May–July) in most of the 20-year periods and it never

402 peaked in the winter months. After the 20-year period of ~~1873~~1853–~~1892~~1872, mBC in autumn–spring increased, and its

403 seasonality became obscured. After the peak anthropogenic period of 1913–1933, mBC in autumn–spring decreased. During

404 1993–2002, mBC once again peaked in summer. We see similar temporal trends in Figs. 12 and 13, i.e., both MMD and mBC

405 showed higher values in summer in the pre-industrial period. This seasonality would indicate that the sizes of rBC particles

406 originated from biomass burning are greater in summer than in winter. The winter and summer ~~values~~ mBC started to increase

407 in the ~~1830s~~1820s–~~1840s~~1830s with a larger ~~rates~~ of increase for winter ~~values~~mBC. Winter and summer values both peaked

408 in the ~~1910s~~1890s–194~~3~~0s and subsequently decreased, with ~~similar~~ a larger ~~rates~~ of decrease for winter ~~and summer~~. The

409 winter and summer MMD started to increase in the 1840s and 1810s, respectively, with larger rate of increase for winter MMD.

410 While winter MMD started to decrease in the 1900s – 1920s and has continued to decrease, the summer MMD did not exhibit

411 a clear downward trend. During the peak anthropogenic period, the summer and winter ~~values~~ mBC and MMD were close,

412 which obscured the seasonality in rBC particle size (Fig. 11~~(b)~~). We also note that during the peak anthropogenic period, rBC

413 particles larger than 1 μm in diameter increased in winter (Fig. 13). The winter values of MMD and mBC became lower than

414 the summer values in 1993–2002. Larger rBC particles in winter in the anthropogenic period support the argument that rBC

415 particles deposited at SIGMA-D were larger when originating from anthropogenic emissions than when associated with

416 biomass burning.

417 In the pre-industrial period, biomass burning would have been the predominant source of rBC. Backward trajectory

418 analyses (Figs. 6~~and~~, 7, and A5) indicate that boreal forest fires in NA would be the primary sources of rBC in summer at
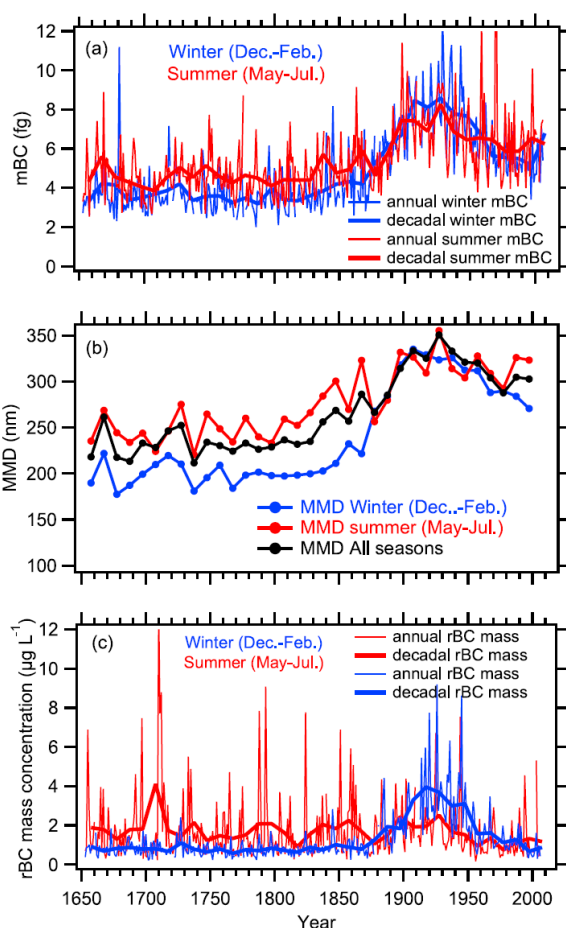
Figure 12: (a) Annual and decadal means of winter (December–February) and summer (May–July) mBC, (b) decadal means of winter, summer, and all-season (January–December) MMD, and (c) annual and decadal means of winter and summer rBC mass concentrations. In all panels, thin and thick solid lines denote annual and decadal means, respectively. Blue, red, and black curves denote winter, summer, and all-season means, respectively.

419   both the SIGMA-D site and the D4 site. Although the contributions of air masses from RUS are very small, especially in

420   summer (<3% at SIGMA-D; <1% at D4 for precipitation-weighted trajectories), Siberia has also been proposed as a potential

421   source of pyrogenic aerosols to Greenland (Zennaro et al., 2014). A recent study using the CAM-ATRAS global climate–

422   aerosol model (Matsui et al., 2022) showed that Siberia has made the largest contribution to rBC concentrations found in the

423   recent Arctic snow, although the contribution to Greenland snow specifically has not been reported. ~~We speculate that biomass~~

424   ~~burning in~~Therefore, Siberia could be a secondary source of rBC at the SIGMA-D site in summer ~~because the backward~~

425   ~~trajectory analyses showed that air masses originated from Siberia (Fig. 7)~~. In winter, the boreal forests in NA and Siberia are

426   covered with snow and thus there is little contribution of BC from boreal forest fires (Bond et al., 2013). However, rBC

427 concentrations are not zero, even in winter. Biomass burning in lower latitudes (Zennaro et al., 2014) could be a source of rBC

428 in winter, and the smaller sizes of rBC particles in pre-industrial winter periods suggest long-range transport of rBC that

429 supports this assumption.
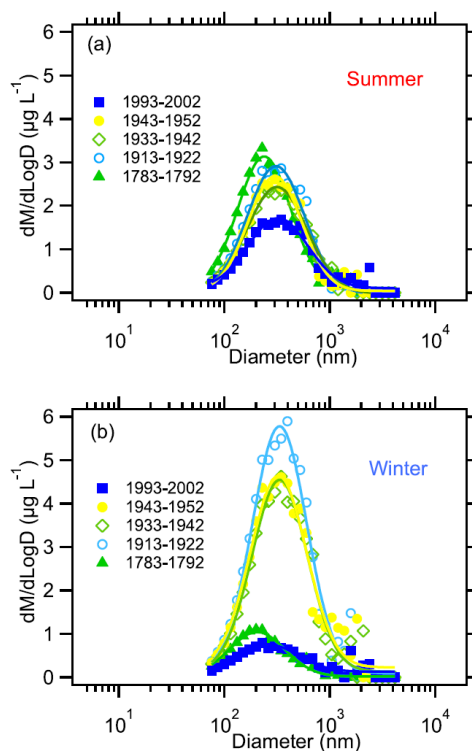
Figure 13: Temporal variability in mass size distributions of rBC particles during (a) winter (December–February) and (b) summer (May-July).

430

3.3 Historical changes in rBC originated from biomass burning

432 Figure 13 14 presents monthly mean rBC mass concentrations for the past 350 years, together with NH_4^+ concentrations.

433 Occasional high peaks in summer, which lasted for one-two months, likely originated from large boreal forest fires, mainly in

434 NA but with possible additional contributions from Siberia. Many of the high rBC peaks in summer coincide with high NH_4^+

435 concentration peaks in summer, which originate from large boreal forest fires (e.g., Legrand et al., 2016). Table A1 lists the

436 biomass burning events distinguished in the record of the SIGMA-D ice core, and in other ice cores and the surface snow of

437 Greenland. The events distinguished in the SIGMA-D core were defined using rBC mass concentration peaks and NH_4^+

438 concentration peaks. For rBC, peaks exceeding the summer (May–July) averages for 350 years + 2σ or 3σ were selected,

439 whereas for NH_4^+, summer peaks exceeding the annual averages for 350 years + 2σ or 3σ were selected. If an rBC or NH_4^+

summer peak in the SIGMA-D core with a concentration between the average + 1σ and 2σ was found in the same year as when a large biomass burning event was recorded at other Greenland sites, we also selected that peak as a biomass burning event. If the year of a biomass burning event reported by previous studies agreed with that in the SIGMA-D core to within ±2 years, taking account of dating errors in different ice cores, we assumed that the record in the different cores reflected the same event. In Fig. 1314(b), we marked only those events exceeding the average + 3σ. Most of the marked events (peaks in 1655, 1665, 1697, 1710, 1711, 1712, 1733, 1788, 1793, 1824, 1851, 1859, 1863, 1925, and 1944) occurred in May, June, or July; however, those in 1789, 1812, and 1894 occurred in April, the one in 1773 occurred in September, and the one in 1929 occurred in AugustSeptember-October. The peaks in 1925 occurred in July-August, and that in 1944 occurred in May and June, and we assumed that they originated from large biomass burning events. Nevertheless, we could not abandon the possibility that these summer peaks might have been affected by large peaks in the preceding winters owing to signal dispersion in the CFA system.

Most of the large events with rBC concentrations that exceeded the average + 3σ were also recorded in boreal forest fire records reconstructed from rBC, NH_4^+, or levoglucosan concentrations in other Greenland ice cores (Table A1). The high rBC concentration peaks in the summers of 1665, 1710, 1711, 1712, 1812, and 1824, accompanying high NH_4^+ peaks, and the high rBC peak in 1859 have not been reported previously. The high NH_4^+ concentration peaks in 1675, 1690, and 1750 have no corresponding rBC peaks in April, May, June, July, or August, while those in 16751697, 1710, 1712, 1715, and 1761 do have corresponding rBC peaks. As for the NH_4^+ concentration peak in 1690, the summer rBC data were missing and therefore comparison was not possible. Although Keegan et al. (2014) argued that the high summer rBC concentrations in 1889 and 2012 found at Summit were associated with widespread melt events in Greenland, no high rBC concentration peaks were found in 1889 or 2012 at the SIGMA-D site. As shown in Fig. 13 14 and Table A1, some of the large biomass burning events
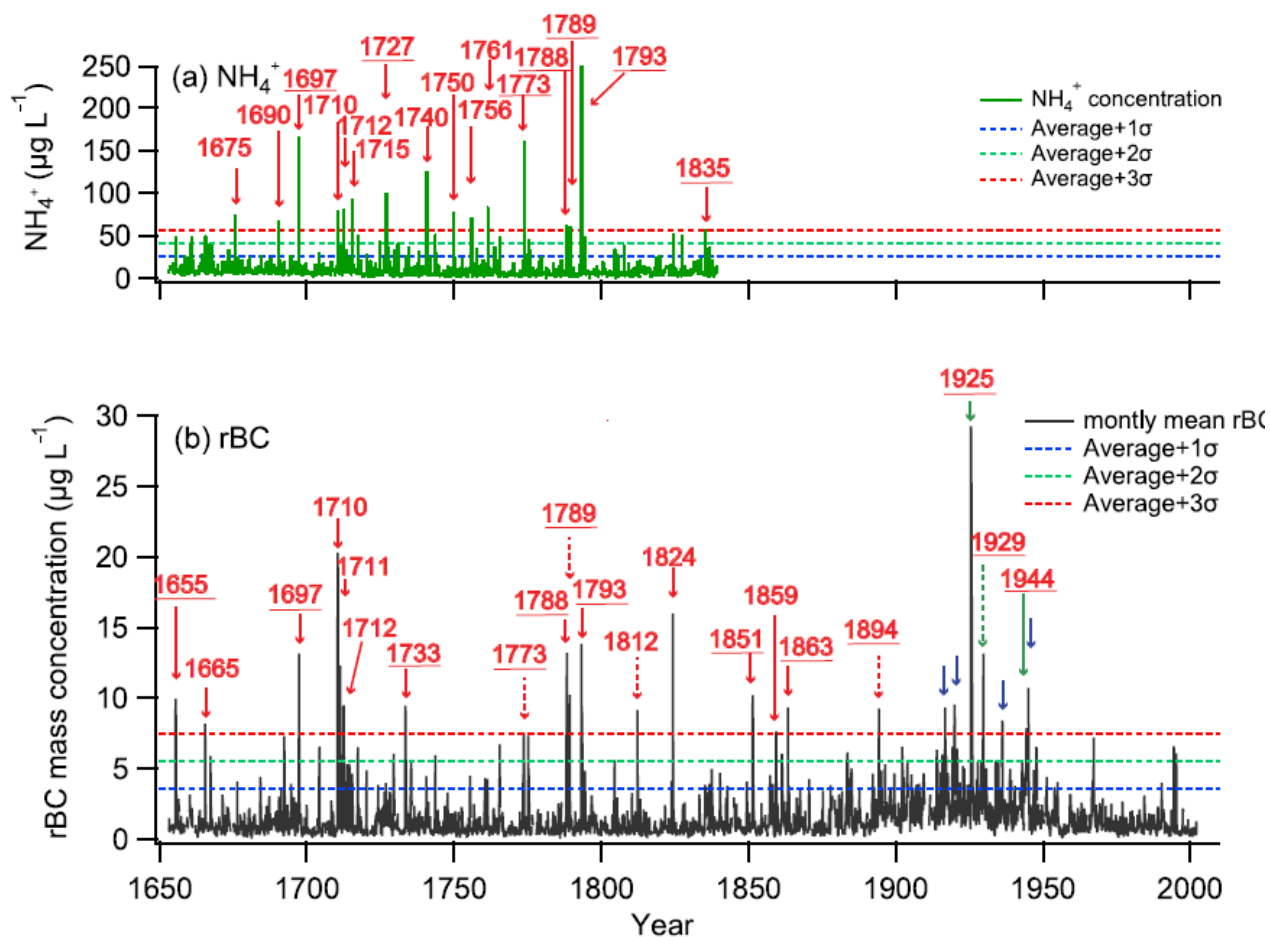
Figure ~~13~~14: (a) NH₄⁺ concentrations: ~~(a)~~ raw data, and **(b)** monthly mean **r**BC mass concentrations (calculated from CFA data. Red arrows in (a) show years when concentrations exceeded the average + 3σ in summer. Solid and broken arrows in (b) show years when concentrations exceeded the summer (May–July) average + 3σ in summer (May–July), and in spring or autumn months (April, August, and September), respectively. Blue arrows in (b) show years when concentrations exceeded the summer average + 3σ in winter. Solid and broken green arrows in (b) show years when concentrations exceeded the summer (May–July) average + 3σ in summer (May–July), and in spring or autumn months (April, August, and September), respectively, but those that might have been affected by winter peaks. Underlining denotes years when biomass burning events were also recorded in other Greenland ice cores/surface snow samples within 2 years. Dotted lines in (a) denote the concentration average over 350 years + 1σ (blue), + 2σ (green), and +3σ (red). Dotted lines in (b) denote summer (May–July) concentration average over 350 years + 1σ (blue), + 2σ (green), and +3σ (red).

459 recorded in other Greenland ice cores were not recorded in the SIGMA-D core, and vice versa. There are two possible reasons

460 for this: (1) different ice core sites are not always on the transport pathways of rBC from boreal forest fires (Legrand et al.,

461 2016), and (2) wind scour at a site can remove snow containing high concentrations of rBC. Despite the minor regional

462 differences within Greenland, most of the large rBC concentration peaks caused by large biomass burning events were recorded

463 widely across Greenland. This indicates that high rBC concentration peaks could be used to synchronize different ice cores in

464 Greenland as reference horizons for dating, as is usually carried out with volcanic sulphate peaks and their signatures detected

465 by DEP(dielectric profiling) and ECM (electrical conductivity measurement) peaks (Rasmussen et al., 2008; Sinnl et al., 2022).

466   The numbers of large biomass burning events in each 10 years are plotted in Fig. 14 15 using different definitions of

467 a "large" event. Figure 1415(a) displays the numbers of months with mass concentrations in summer (May–July) exceeding

468 the summer average + 1σ, 2σ, and 3σ; Fig. 1415(b) displays the number of months with number concentrations in summer

469 exceeding the summer average + 1σ, 2σ, and 3σ. Because large events in April, August, and September were not counted to

470 avoid the potential for impact of anthropogenic rBC, there would be minor underestimation of the number of large events.
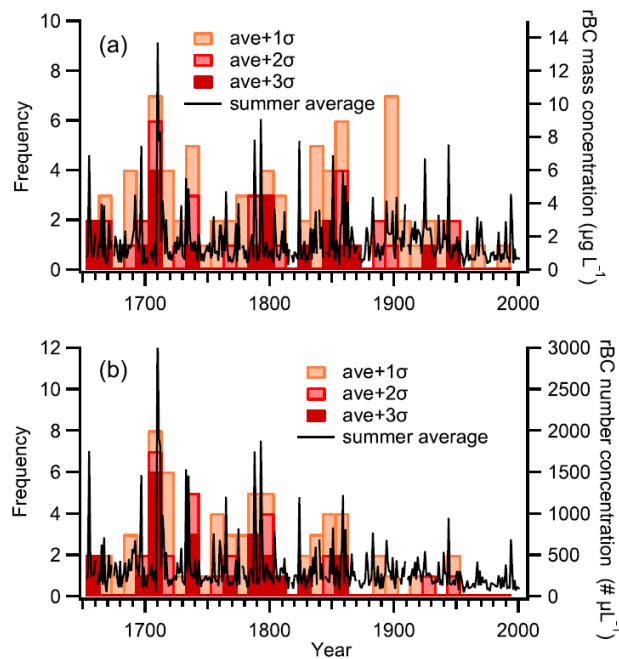
Figure 1415: Frequency of large biomass burning events. Black curves denote summer (May–July) averages of rBC concentrations. Bars show frequency of rBC summer peaks in each decade exceeding the average + 1σ, 2σ, and 3σ. (a) Mass concentrations of rBC were used to define peaks. (b) Number concentrations of rBC were used to define peaks.

471 Although the frequency of large events differs slightly between the different definitions, the general tendency is consistent.

472 Large events tended to be more frequent around the 1710s, 1790s, 1850s, 1900s, and 1950s. Moreover, there is no obvious

473   trend of increase up to the decade 1993–2002. To study the historical trends in concentrations of rBC originated from biomass

474   burning, we calculated the decadal averages of rBC mass and number concentrations for each month (Fig. 1516). During the

475   pre-industrial period, both mass and number concentrations were stable in the winter months (December–February), whereas

476   they showed large inter-decadal fluctuations in spring to autumn months (March–November). The fluctuations appear largest
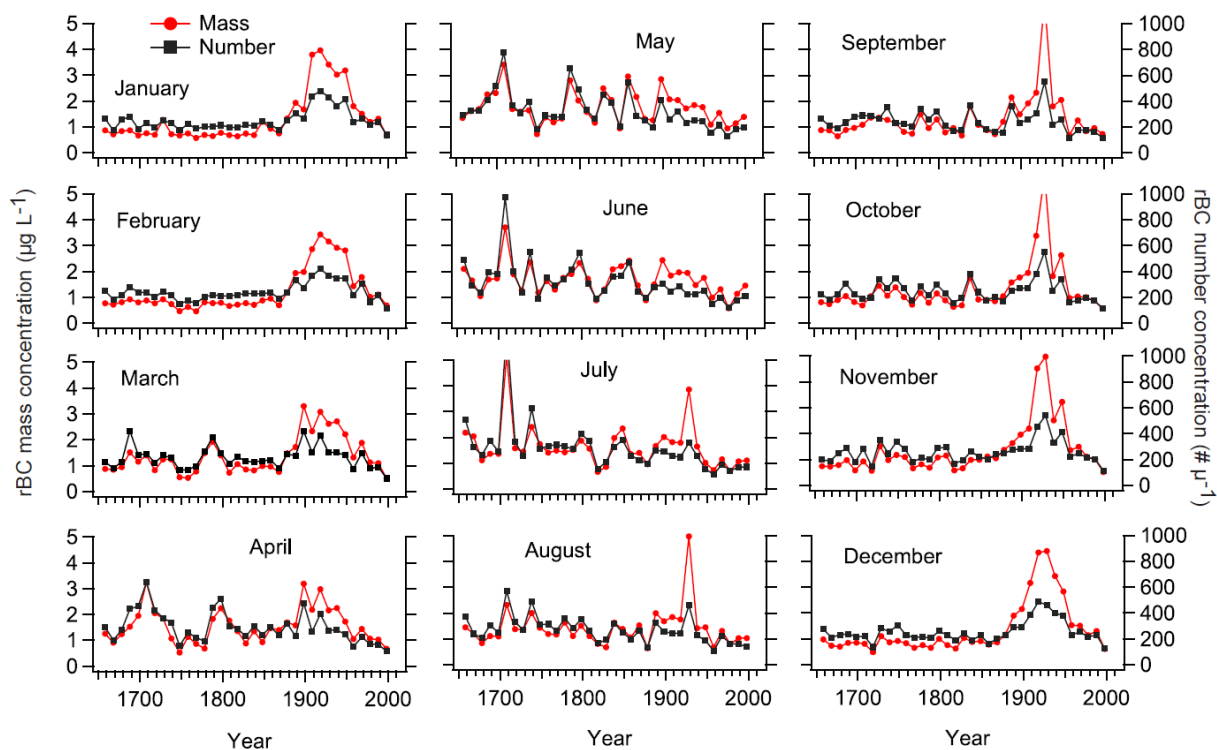
Figure 1516: Decadal averages of rBC mass (red) and number (black) concentrations for each month.

477   in spring–summer (April–July). Generally, the period of April–July is likely when the occurrence of large boreal forest fires

478   increases in NA (Whitman et al., 2018). The sporadic nature of the frequency of occurrence of large boreal forest fires would

479   explain the large fluctuations.

480   Since the 1870s, when anthropogenic rBC started to influence the SIGMA-D site, rBC mass and number

481   concentrations in September–April increased, as discussed in Sect. 3.32; however, there was little increase during the spring–

482   summer months. The same feature is also seen in Fig. 12(c). Although large inter-decadal variability in concentrations during

483   spring–summer obscured the temporal trends in spring–summer concentrations (Fig. 11), the general temporal trends are more

484   apparent in Fig. 1516. At the SIGMA-D site, we see slight trends of reduction in rBC mass and number concentrations during

485   spring–summer. Analysis of Fig. 1415 also suggests that the frequency of large boreal forest fires in NA showed a slight trend

of reduction over the past 350 years until the most recent decade (1993–2002). However, this trend has not been reported by previous studies on other ice cores from Greenland, partly owing to the different periods covered, the different temporal resolution of the analysis methods, and the different fire proxies used (Zennaro et al., 2014; Legrand et al., 2016; Parvin et al., 2019; Savarino and Legrand, 1998; Whitlow et al., 1994). Most previous studies used NH_4^+ as a fire proxy, with occasional use of levoglucosan and other organic materials; only a few studies have used rBC as a fire proxy for pre-industrial periods (Zennaro et al., 2014).

Since the 1950s, data on the area burned and the number of forest fires in Canada have become available (Hanes et al., 2018; Skakun et al., 2021). The SIGMA-D record does not appear to trace the Canadian forest fire database. Air masses arriving at the SIGMA-D site might not have passed over Canada during periods of large forest fires. Large uncertainties in fire data might also explain the disagreement. There are also large uncertainties and regional variability in sedimentary charcoal fire records (Marlon et al., 2012, 2013; Power et al., 2013). However, our results are consistent with the charcoal data from western NA, which show general decline in biomass burning since 1500, with a relatively enhanced fire period in the mid-19th century (Power et al., 2013). The biomass burning emission inventories for CMIP 6 also have large uncertainties (van Marle et al., 2017). Therefore, much more work is needed on the reconstruction of past biomass burning using ice cores.

3.4 Impacts of rBC on the ice sheet albedo

McConnell et al. (2007) calculated the quantitative impacts of rBC in snow on radiative forcing during early summer using rBC concentration from D4 ice core and the Snow, Ice, and Aerosol Radiative (SNICAR) model (Flanner et al., 2007), assuming an effective snow grain radius of 100 μm. They estimated the radiative forcing of 1.02 Wm^{-2} during the peak 5-year period from 1906 to 1910, representing a fivefold increase compared to which is a fivefold increase from preindustrial conditions. However, the radiative forcing of rBC in snow varies depending on both the assumed solar irradiance and snow grain size. Then, In this study, we calculated the possible albedo reduction due to rBC at the SIGMA-D site from the monthly mean rBC mass concentration data obtained in this study (Fig. 1617) using a physically based snow albedo model (Aoki et al., 2011). As the snow albedo reduction rate due to light absorbing particles is enhanced with an increase of snow grain size (Wiscombe and Warren, 1980), we assumed two effective snow grain radii r_s = 50 μm and 1000 μm, corresponding to new snow (defined as "precipitation particles" according to Fierz et al., 2009) and old melting snow (defined as "melt forms" according to Fierz et al., 2009) (Wiscombe and Warren, 1980) for clear sky and cloudy sky (overcast) conditions. The albedo

513   reductions under the cloudy sky are 20-48% larger than those under clear sky. These increases are related to the following two

514   factors: (1) the visible albedo depends on rBC concentration more strongly than the near infrared albedo (Wiscombe and

515   Warren, 1980); (2) the visible spectral fraction in solar irradiance at the snow surface under cloudy sky is larger than that under

516   clear sky (Aoki et al., 1999). Thus, the albedo reduction due to rBC under cloudy sky is enhanced more than clear sky.

517   Figure 16 17 demonstrates that the albedo reduction in case of new snow is consistently less than 0.01, even at the

518   maximum value for cloudy conditions in August 1925 (Fig. 16a17a). In contrast, for old melting snow, the albedo reduction

519   frequently exceeds 0.01 for both sky conditions (Fig. 16b17b). The maximum albedo reduction for cloudy conditions is 0.045

520   (r_s = 1000 µm) and 0.0098 (r_s = 50 µm) in August 1925, followed by the values of 0.034 (r_s = 1000 µm) and 0.0074 (r_s = 50

521   µm) in July 1710. The averaged albedo reduction for the overall period of 1650-2014 is 0.0031 (r_s = 1000 µm) and 0.0007 (r_s
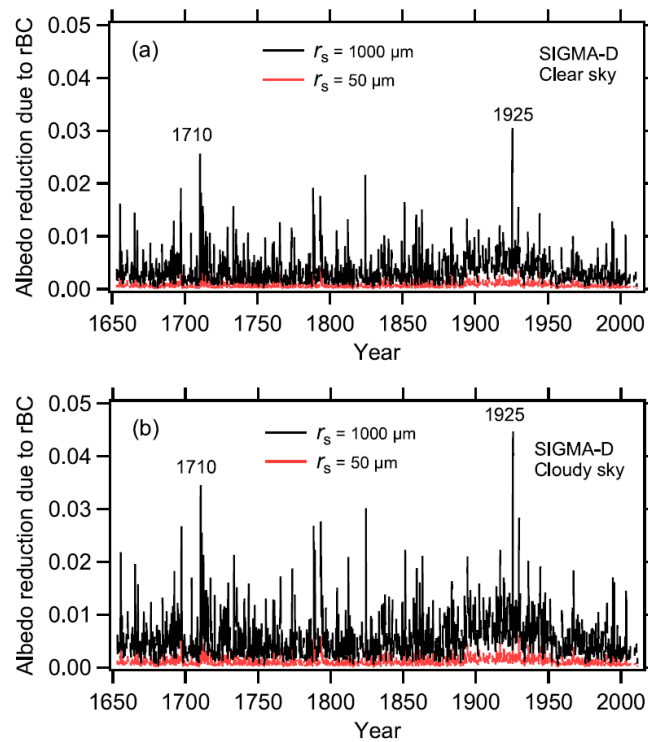
Figure 1617: Temporal variation of albedo reduction for (a) clear sky and (b) cloudy sky conditions, calculated from monthly mean rBC mass concentrations, for two effective snow grain radii: r_s = 50 µm (representing new snow, indicated by the red line) and r_s = 1000 µm (indicating old melting snow, shown by the black line). The albedo reduction values are calculated for solar zenith angle at local solar noon on the 15th of each month, excluding the polar night period from November to February. The maximum albedo reduction is simulated in 1925 and followed by 1710.

522 = 50 μm) for clear conditions, and 0.0054 (r_s = 1000 μm) and 0.0011 (r_s = 50 μm) for cloudy conditions. During the

523 anthropogenic concentration peak period of 1913-1933, the average albedo reduction increases to 0.0056 (r_s = 1000 μm) and

524 0.0012 (r_s = 50 μm) for clear conditions, and 0.0089 (r_s = 1000 μm) and 0.0019 (r_s = 50 μm) for cloudy conditions.

525   Warren ~~et al.~~ (2019) described that a~~n~~ rBC concentration of 20 parts per billion in weight can cause broadband snow

526 albedo reductions of 1-2%. They also noted that for a typical daily average solar irradiance of 400 W m^{-2} in the Arctic during

527 late spring and early summer, a 1% albedo reduction can lead to a positive forcing of 4 W m^{-2} locally, similar to the forcing

528 caused by doubling CO_2. Our calculation results indicate that a 1% of reduction in albedo can occur at numerous local spike-

529 like peaks for r_s = 1000 μm including the recent several decades after 1950. During the anthropogenic concentration peak

530 period (1913-1933), the average albedo reduction approaches 1% (0.0089) for r_s = 1000 μm under cloudy sky conditions.

531 Consequently, our simulations suggest that the amount of albedo reduction remains relatively small as long as new snow

532 conditions are maintained. However, if the surface snow grains ~~are~~ reach the size of old melting snow, which would have

533 occurred during summer months at the SIGMA-D site, the extent of albedo reduction becomes non-negligible.

534

4 Conclusions

536 We analysed the record of rBC over the past 350 years in the SIGMA-D ice core, which was drilled in northwest Greenland.

537 The improved technique for rBC measurement (Mori et al., 2016) and the CFA system built at NIPR allowed us to reconstruct

538 high temporal resolution records of the sizes and concentrations of rBC particles. Notably, this study marks the first

539 reconstruction of temporal changes in rBC size since the pre-industrial period.

540   The number and mass concentrations of rBC started to increase in the 1870s owing to anthropogenic input. The

541 concentrations reached their maxima in the 1910s–1920s, following which they decreased. By the 1960s, rBC concentrations

542 had reduced to levels close to or lower than those of the pre-industrial period. The trend of anthropogenic rBC at the SIGMA-

543 D site was generally similar to that reported previously for other ice core sites in Greenland, albeit with slight differences.

544 Backward trajectory analyses suggest that the major anthropogenic emission source that affected the SIGMA-D site was NA.

545 However, the backward trajectory analyses did not clearly explain the slight difference in the temporal trends of rBC between

546 the SIGMA-D site and the more southerly site D4. Anthropogenic rBC was transported to the SIGMA-D site mainly in the

547 winter half of the year, which was deduced by the changes in the seasonality of rBC concentrations. The backward trajectory

analyses produced consistent results, showing greater contributions from air masses from the industrial regions in NA, ~~and~~ EUR, and RUS in winter.

Pre-industrial rBC concentrations peaked in summer. In association with increased anthropogenic input, concentrations increased in winter to early spring, which shifted the annual peak in concentration to winter–early spring. When the anthropogenic input started to decline in the 1930s, concentrations in winter–early spring also decreased, which changed the seasonality of rBC concentrations; by the 1990s, rBC concentrations peaked in summer once again. This suggests that the major sources of rBC in recent years were not anthropogenic emissions but biomass burning. At the SIGMA-D site, rBC originated from anthropogenic emissions made only a minor contribution to the rBC concentrations in the summer months throughout the past 350 years. This enabled us to examine the temporal variability in biomass burning throughout the past 350 years, especially after the increase in anthropogenically derived rBC, which is a topic that has not been addressed by previous studies on rBC data from other ice cores in the Arctic.

The size distributions of rBC particles have also changed owing to anthropogenic impact. The seasonality of MMD and mBC also changed, ~~accompanying~~associated with the concentration changes. ~~Both MMD and~~Winter and summer mBC started to increase ~~around~~ in the 182~~3~~0s ~~or~~ 184~~3~~0s, peaked in the ~~1910s~~1890s ~~1940s~~ 1930s when rBC concentrations ~~were at their maxima~~peaked, and started to decline ~~after~~since the ~~1940s~~1930s. The winter and summer MMD started to increase in the 1840s and 1810s, respectively, with larger rate of increase for winter MMD. While winter MMD started to decrease in the 1900s – 1920s and has continued to decrease, the summer MMD did not exhibit a clear downward trend. Increases in winter MMD and mBC ~~accompanying~~ associated with the increase in winter rBC concentrations suggest that the diameter of rBC particles deposited over northwest Greenland were generally larger for anthropogenic rBC than for biomass burning rBC. ~~The seasonality of MMD and mBC also changed, accompanying the concentration changes. However, i~~In contrast to rBC concentrations, neither MMD nor mBC returned to their pre-industrial values; instead, they remained at higher values in the 1960s–2000s.

Pre-industrial rBC would have originated mainly from biomass burning. During the winters (December–February) of the pre-industrial period, decadal averages of monthly mean mass and number concentrations were stable, and the sizes of rBC particles were smaller than those in summer. This indicates that rBC in pre-industrial winters originated from biomass burning in low latitudes where there was no snow cover in winter, and that biomass burning in low latitudes that affected Greenland showed little change during the pre-industrial period. After the inflow of anthropogenic rBC started, it became difficult to

distinguish biomass burning rBC from anthropogenic rBC in winter, making it difficult to discuss the temporal changes in rBC originated from low-latitude biomass burning in winter. However, we could discuss the temporal changes in boreal forest fires that occur mainly in summer, the season with minimal anthropogenic input.

Sources of pre-industrial rBC were likely boreal forest fires primarily in NA. We investigated the temporal trend in the decadal frequency of large boreal forest fire events using high summer peaks of number and mass concentrations of rBC. We found no obvious trend of increase in the decadal frequency of large boreal forest fires until the decade of 1993–2002. Furthermore, we found no trends of increase in the decadal averages of monthly mean mass and number concentrations in summer during the past 350 years; we even found a trend of decrease for number concentrations. Although recent large fire events in NA are attributed to global warming (Brown et al., 2023), the effects of global warming do not seem to have left clear imprint in Greenland until the early 2000s. Therefore, we need further investigations using more recent ice core records of rBC.

We analysed the temporal variation of potential albedo reduction due to rBC at the SIGMA-D site during the past 350 years using a physically based snow albedo model. Albedo reductions under the assumption of consistently new snow grain size remained below 0.01, even at the peak rBC concentration in 1925. Conversely, under the assumption of old melting snow grain size, the albedo reduction frequently exceeded 0.01. Our calculation results reveal that a 1% of reduction in albedo can occur at numerous local spike-like peaks in the case of old melting snow, including the recent several decades after 1950. During the peak period of anthropogenic concentrations (1913-1933), the averaged albedo reduction approaches 1% for old melting snow cases. Consequently, our simulations suggest that the magnitude of albedo reduction remains relatively small as long as new snow conditions are maintained. However, if the surface snow grains are reach the size of old melting snow, the amount of albedo reduction becomes non-negligible.

Our new high temporal resolution records of rBC concentrations and sizes could contribute to evaluation of the impacts of both anthropogenically derived and biomass burning originated rBC on Earth's radiation budget, albedo, rBC–cloud interactions, and therefore rBC–climate interactions. They could also contribute to validation of emission inventories, and aerosol and climate models. High temporal resolution rBC data since 2002 are necessary to investigate the impact of global warming on boreal forest fires. Furthermore, high temporal resolution records of rBC concentrations and sizes during the early Holocene and the last interglacial period when it was warmer than the present day (NEEM community members, 2013; Vinther et al., 2009) should be obtained for better projections of rBC–climate interactions in a future warming world.

602

        Appendix A

Figure A1: Monthly snow height change observed with an automatic weather station (AWS) at the SIGMA-D site during the period May 2014 – September 2015 (Matoba et al., 2015). It appears that there was more precipitation in summer than in winter, which could introduce some bias in monthly dating of ~~an~~the SIGMA-D ice core. Although the AWS data indicated that precipitation occurred in all months (Fig. A2), there were a few months when snow height change was negative mainly owing to wind scouring. Moreover, the seasonal variation in precipitation seems to exhibit significant year-to-year variability. However, by averaging monthly mean concentrations over 10-20 years (Fig. 11), we can observe changes in the seasonality of rBC.
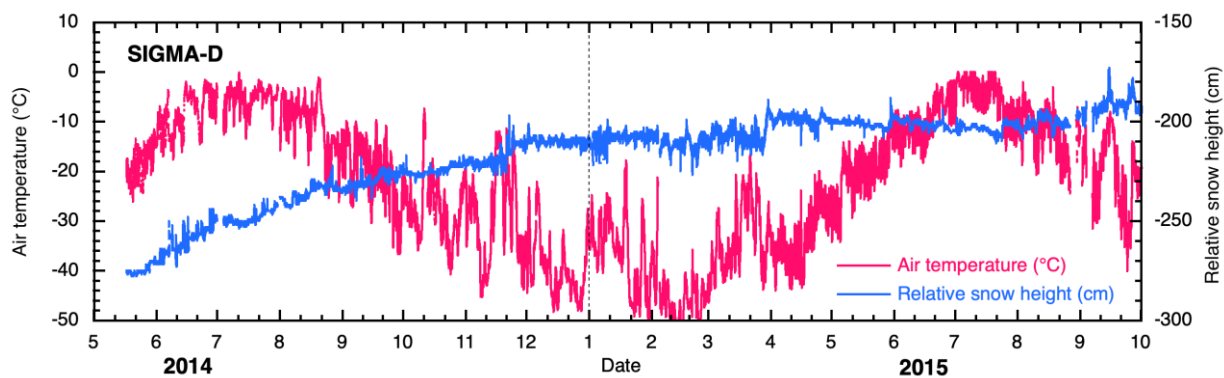
Figure A2. Seasonal variations of air temperature and relative snow height every 10 minutes observed at the SIGMA-D site during the period May 2014 – September 2015 (Matoba et al., 2015).

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605
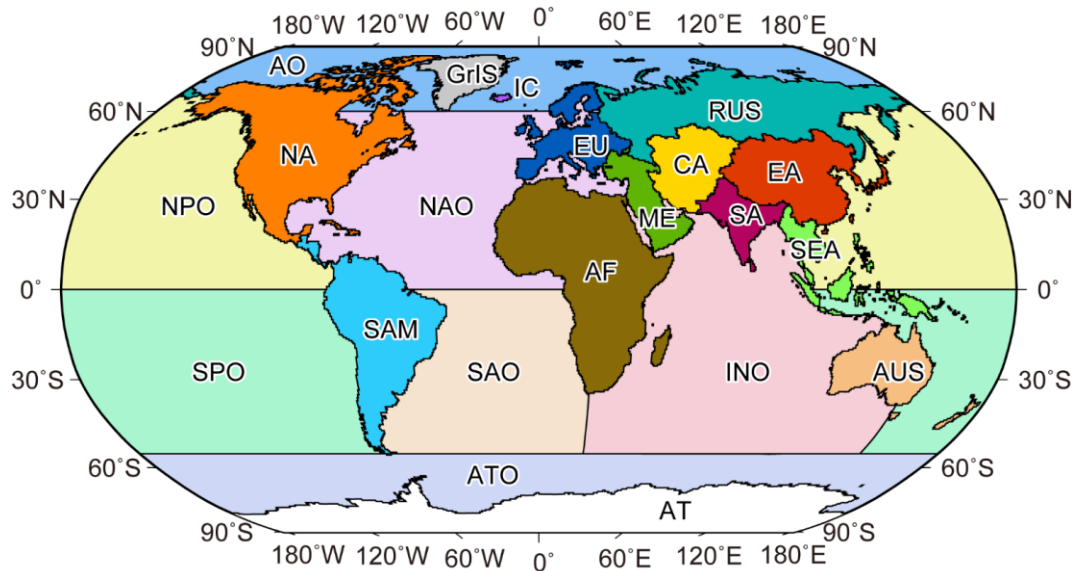
Figure A3: Map showing 21 regions used for calculating the regional contributions in backward trajectory analysis.

ME: Middle East, AT: Antarctica, AUS: Australia and New Zealand, SAM: South America, AF: Africa, EA: China and East Asia, EU: Europe, GrIS: Greenland Ice Sheet, SEA: Southeast Asia, SA: South Asia, CA: Central Asia, RUS: Russia, NA: North America, ATO: Antarctic Ocean, SPO: South Pacific Ocean, INO: Indian Ocean, NPO: North Pacific Ocean, SAO: South Atlantic Ocean, NAO: North Atlantic Ocean, AO: Arctic Ocean, IC: Iceland.

606
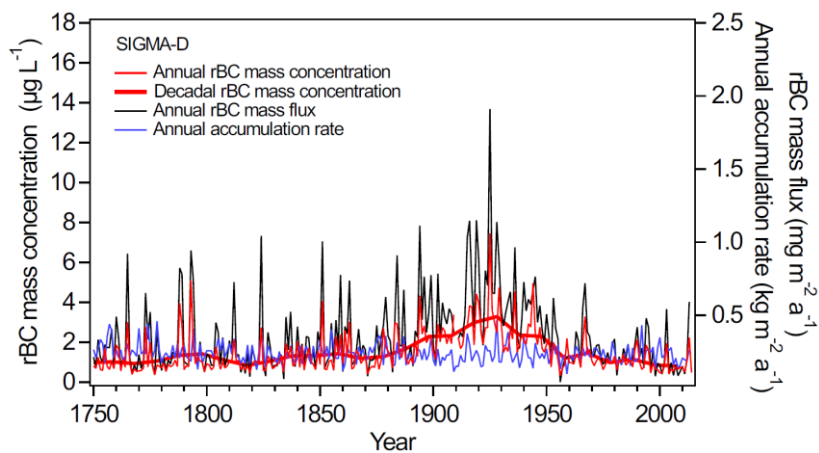
Figure A4: Annual mean and decadal mean rBC mass concentrations (thin and thick red curves, respectively), annual rBC mass flux (black), and annual accumulation rate (blue).
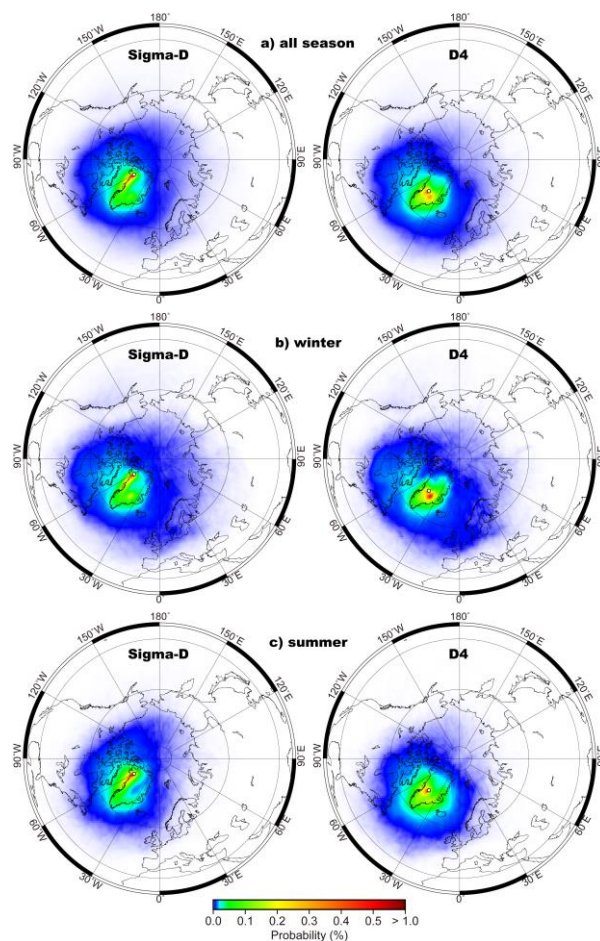
Figure A5: Probability distributions of air masses at (left) the SIGMA-D site and (right) the D4 site calculated without weighed with the local daily precipitation: (a) averages of all seasons, (b) averages of winter months (December-February), and (c) averages of summer months (May-July).

608

609 **Table A1 Biomass burning events distinguished in the SIGMA-D ice core record, and in the records of other ice cores**

610 **and surface snow from Greenland. Records from Greenland sites with temporal resolution of greater than 1 year were**

611 **not used. Events distinguished in the SIGMA-D core were defined using rBC mass concentration peaks and NH_4^+**

612 **concentration peaks. For rBC, peaks exceeding the summer (May–July) averages + 2σ or 3σ were selected; for NH_4^+,**

613 **peaks exceeding the annual average + 2σ or 3σ were selected. If a BC peak was found in April, August, or September,**

614 **the year is written in parentheses. If an rBC or NH_4^+ summer peak in the SIGMA-D core with a concentration between**

615 **the average + 1σ and 2σ was found in the same year when a large biomass burning event was recorded at other**

616 **Greenland sites, the peak was also selected as a biomass burning event. If a year with a biomass burning event reported**

617 **in previous studies agreed with that in the SIGMA-D core within 2 years, the records were considered to reflect the**

618 **same event, and are written on the same line in the table.**

619 **A: Year of the event in the SIGMA-D core**

620 **B: Magnitude of the rBC mass concentration peak**

621 **C: Magnitude of the NH_4^+ concentration peak**

622 **D: Year of the event in ice cores and surface snow from Greenland sites other than the SIGMA-D site**

623 **E: Location of the ice core or surface snow in Greenland**

624 **F: Biomass burning proxies**

625 **G: References**

626

SIGMA-D core (This study)			Ice cores and surface snow from Greenland sites other than the SIGMA-D site			
A	B	C	D	E	F	G
Year	Magnitude of rBC peak	Magnitude of NH_4^+ peak	Year	Location of ice core or surface snow	Proxy	Reference
1655	>average + 3σ	>average + 2σ	1654 1655	SUMMIT, NEEM SUMMIT	NH_4^+ NH_4^+, $HCOO^-$	(Legrand et al., 2016) (Savarino and Legrand, 1998)

1661	No data	>average + 2σ				
1665	>average + 3σ	>average + 2σ				
1667	>average + 2σ	>average + 1σ				
1675		>average + 3σ				
1684	>average + 1σ		1683	NEEM	NH$_4^+$	(Legrand et al., 2016)
1690		>average + 3σ				
1692	>average + 2σ					
1697	>average + 3σ	>average + 3σ	1699	SUMMIT	NH$_4^+$	(Legrand et al., 2016)
			1702–03	NEEM	NH$_4^+$	(Legrand et al., 2016)
			1702	NEEM	rBC	(Zennaro et al., 2014)
			1703	NEEM	rBC	(Zennaro et al., 2014)
1710	>average + 3σ	>average + 3σ				
1711	>average + 3σ	>average + 1σ				
1712	>average + 3σ	>average + 3σ				
1715	>average + 1σ	>average + 3σ				
1717	>average + 1σ	>average + 2σ	1719	NEEM	NH$_4^+$	(Legrand et al., 2016)
1724		>average + 2σ				
1727		>average + 3σ	1728	SUMMIT	NH$_4^+$	(Legrand et al., 2016)
1729	>average + 2σ					
1733	>average + 3σ		1732	NEEM	NH$_4^+$	(Legrand et al., 2016)
1735	>average + 2σ					
1740		>average + 3σ				
1743	>average + 1σ	>average + 2σ				
1750		>average + 3σ				
1756		>average + 3σ				
1761	>average + 1σ	>average + 3σ				

1765	>average + 2σ	>average + 2σ				
1773	>average + 1σ (>average + 3σ in September)	>average + 3σ	1771	NEEM	NH_4^+	(Legrand et al., 2016)
			1773	SUMMIT	NH_4^+	(Legrand et al., 2016)
			1773	SUMMIT	NH_4^+, $HCOO^-$	(Savarino and Legrand, 1998)
1775	>average + 1σ	>average + 2σ				
1788	>average + 3σ	>average + 3σ	1789	NEEM	rBC	(Zennaro et al., 2014)
1789	>average + 2σ (>average + 3σ in ~~August~~April)	>average + 3σ				
1793	>average + 3σ	>average + 3σ	1792	NEEM	NH_4^+	(Legrand et al., 2016)
1794	>average + 1σ	>average + 2σ	1794–95	SUMMIT	NH_4^+	(Legrand et al., 2016)
			1795	SUMMIT	NH_4^+, $HCOO^-$	(Legrand and De Angelis, 1996)
			1795	D4	NH_4^+	(Legrand et al., 2016)
1804	>average + 2σ	>average + 1σ				
1807		>average + 1σ	1807	SUMMIT, NEEM, D4	NH_4^+	(Legrand et al., 2016) (Legrand et al., 2016)
(1812)	(>average + 3σ in April)					
1824	>average + 3σ	>average + 2σ				
1827		>average + 2σ				
1835	>average + 1σ	>average + 3σ	1837	SUMMIT, NEEM, D4	NH_4^+ NH_4^+	(Legrand et al., 2016) (Legrand et al., 2016)
1840	>average + 1σ	No data	1839	SUMMIT	NH_4^+	(Legrand et al., 2016)
				SUMMIT	NH_4^+, HCOO	(Legrand and De Angelis, 1996)

			1846	SUMMIT	NH_4^+	(Legrand et al., 2016)
1849	>average + 1σ	No data	1847	D4	NH_4^+	(Legrand et al., 2016)
			1848	NEEM	NH_4^+	(Legrand et al., 2016)
1851	>average + 3σ	No data	1853	NEEM	NH_4^+	(Legrand et al., 2016)
		No data	1854	SUMMIT, D4	NH_4^+	(Legrand et al., 2016)
1859	>average + 3σ					
1861	>average + 2σ	>average + 1σ				
1863	>average + 3σ	No data	1863	SUMMIT, NEEM, D4	NH_4^+	(Legrand et al., 2016)
					NH_4^+	(Legrand et al., 2016)
				SUMMIT	NH_4^+, $HCOO^-$	(Savarino and Legrand, 1998)
		No data	1868	SUMMIT	NH_4^+	(Keegan et al., 2014)
			1869	D4	NH_4^+	(Legrand et al., 2016)
	No data	No data	1871	SUMMIT	NH_4^+	(Legrand et al., 2016)
			1872, D4	NEEM	NH_4^+	(Legrand et al., 2016)
1883	>average + 2σ	No data				
		No data	1886	SUMMIT, NEEM, D4	NH_4^+	(Legrand et al., 2016)
					NH_4^+	(Legrand et al., 2016)
				20D (Dye-3), GISP2 (SUMMIT)	NH_4^+	(Whitlow et al., 1994)
						(Legrand et al., 2016)
			1888	NEEM	NH_4^+	
		No data	1889	SUMMIT	rBC, NH_4^+	(Keegan et al., 2014)
				D4	NH_4^+	(Legrand et al., 2016)
			1890	SUMMIT	NH_4^+	(Legrand et al., 2016)

1894	>average + 1σ (>average + 3σ in April)	No data	1894–95 1894–95	SUMMIT, NEEM, D4	NH$_4^+$ NH$_4^+$	(Legrand et al., 2016) (Legrand et al., 2016)
			1895	SUMMIT	NH$_4^+$, HCOO$^-$	(Legrand and De Angelis, 1996)
1896	>average + 1σ	No data	1896	SUMMIT	NH$_4^+$, HCOO$^-$	(Savarino and Legrand, 1998)
1902	>average + 2σ	No data				
1909	>average + 1σ	No data	1908	SUMMIT, D4 SUMMIT	NH$_4^+$ NH$_4^+$, HCOO$^-$	(Legrand et al., 2016) (Savarino and Legrand, 1998)
				SUMMIT	rBC, NH$_4^+$	(Keegan et al., 2014)
		No data	1921	NEEM	NH$_4^+$	(Legrand et al., 2016)
1925	>average + 3σ	No data	1923	SUMMIT, D4	NH$_4^+$	(Legrand et al., 2016)
1927	>average + 1σ	No data	1927–28	NEEM	NH$_4^+$	(Legrand et al., 2016)
(1929)	(>average + 3σ in ~~August &~~ September___&___ October)		1929	SUMMIT, D4	NH$_4^+$	(Legrand et al., 2016)
1936	>average + 1σ	No data	1936–38 1938	SUMMIT SUMMIT, NEEM, D4	NH$_4^+$ NH$_4^+$	(Legrand et al., 2016) (Legrand et al., 2016)
1940	>average + 1σ	No data				
1944	>average + 3σ	No data	1942	NEEM, D4	NH$_4^+$	(Legrand et al., 2016)
		No data	1950	SUMMIT, NEEM, D4	NH$_4^+$	(Legrand et al., 2016)
				SUMMIT	NH$_4^+$, HCOO$^-$	(Savarino and Legrand, 1998)

		No data	1961	SUMMIT, NEEM, D4	NH_4^+	(Legrand et al., 2016)
				SUMMIT	NH_4^+, $HCOO^-$	(Savarino and Legrand, 1998)
				SE-Dome	Levoglucosan	(Parvin et al., 2019)
		No data	1964	SE-Dome	Levoglucosan	(Parvin et al., 2019)
		No data	1972	NEEM	rBC	(Zennaro et al., 2014)
			1973	NEEM	NH_4^+	(Legrand et al., 2016)
			1980	SUMMIT, NEEM, D4	NH_4^+	
1994	>average + 2σ	No data	1994	SE-Dome	Levoglucosan	(Parvin et al., 2019)
				SUMMIT	Levoglucosan, NH_4^+, $HCOO^-$, CH_3COO^-, $(C_2H_2O_4)^{2-}$	(Kehrwald et al., 2012; Dibb et al., 1996)
1995	>average + 2σ	No data				
		No data	1998	SE-Dome	Levoglucosan	(Parvin et al., 2019)
	No CFA data	No data	2012	SUMMIT	rBC, NH_4	(Keegan et al., 2014)
	No CFA data	No data	2013	SE-Dome	Levoglucosan	(Parvin et al., 2019)

627

628

Appendix B: Wet deposition vs dry deposition

We anticipate that the contribution of wet deposition was greater than that of dry deposition. It is difficult to estimate

the wet and dry deposition ratio directly since there are no observations at the SIGMA-D site, as at most of the sites in

the Arctic. Instead, we estimated the terminal velocity (V) of rBC particles falling onto the SIGMA-D site using the

equation $V=2\rho r^2 g/9\zeta$ assuming spherical rBC particles. Here ρ, r, g, and ζ denote the density of rBC particles, the radius

of rBC particles, the acceleration of gravity, and the viscosity coefficient of the atmosphere, respectively. We used the values 1800 kg m^{-3} and 1 μm for ρ and 2r (diameter), respectively. Assuming an atmospheric temperature of -40°C, ζ was calculated to be 1.5×10^{-5} N s m^{-2}. With these values, the terminal velocity was estimated to be 6 m day^{-1}. Given that the rBC particles fall from 500 m above the ice sheet surface at the SIGMA-D site, it would take approximately 100 days for the rBC particles to reach the ice sheet surface, indicating a very small dry deposition velocity at the SIGMA-D site. A study using the GEOS-Chem global chemical transport model (Breider et al., JGR, 2014) also indicated that the annual mean fraction of dry deposition in the Arctic was only 11 %. Furthermore, Sinha et al. (JGR, 2018) showed that the dry deposition was a small contributor (less than the uncertainties of the measurements, which were about 20%) to the total rBC deposition at Ny-Ålesund, Svalbard, where the total water equivalent snowfall amount during September-April was similar to the annual accumulation rate at the SIGMA-D site. Thus, it is reasonable to assume that the contribution of dry deposition is small.

Data availability

All the data used in this study will be submitted to the Arctic Data Archive System (ADS) as soon as the manuscript has been published.

Author contributions

KGA designed the study and led the manuscript writing. YOT was responsible for the BC measurements. YOT, MH, RD, and JO performed the CFA analyses of the SIGMA-D core. MH and SM measured the ion concentrations in the discrete samples. KoF, SM, AT, and NN dated the SIGMA-D ice core. MK calculated annual accumulation rates. KGA, YOT, and KaF analysed the CFA data. KGA, YOT, NM, TM, SO, YK, and MK interpreted the BC data. KoF performed backward trajectory analyses. TA analysed the AWS data. SM examined the melt features in the SIGMA-D ice core. TA designed and led the ice coring project at SIGMA-D. TA computed the impacts of BC on albedo. All the authors discussed the results.

Competing interests

The authors declare that they have no conflict of interest.

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Figure A1: Map showing 21 regions used for calculating the regional contributions in backward trajectory analysis.

ME: Middle East, AT: Antarctica, AUS: Australia and New Zealand, SAM: South America, AF: Africa, EA: China and East Asia, EU: Europe, GrIS: Greenland Ice Sheet, SEA: Southeast Asia, SA: South Asia, CA: Central Asia, RUS: Russia, NA: North America, ATO: Antarctic Ocean, SPO: South Pacific Ocean, INO: Indian Ocean, NPO: North Pacific Ocean, SAO: South Atlantic Ocean, NAO: North Atlantic Ocean, AO: Arctic Ocean, IC: Iceland.

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