1 Historical black carbon deposition in the Canadian High Arctic:

2 A >250-year long ice-core record from Devon Island

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29

30 Abstract.

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32 Black carbon aerosol (BC) emitted from natural and anthropogenic sources (e.g., wildfires, coal burning) can contribute to magnify climate warming at high latitudes by darkening snow- and ice-33 covered surfaces, thus lowering their albedo. Modelling the atmospheric transport and deposition 34 of BC to the Arctic is therefore important, and historical archives of BC accumulation in polar ice 35 can help to validate such modelling efforts. Here we present a >250-year ice-core record of 36 refractory BC (rBC) deposition on Devon ice cap, Canada, spanning the years 1735-1992, the first 37 such record ever developed from the Canadian Arctic. The estimated mean deposition flux of rBC 38 on Devon ice cap for 1963-1990 is 0.2 mg m⁻² a⁻¹, which is at the low end of estimates from 39 Greenland ice cores obtained by the same analytical method ($\sim 0.1-4 \text{ mg m}^{-2} \text{ a}^{-1}$). The Devon ice 40 cap rBC record also differs from Greenland records in that it shows only a modest increase in rBC 41 42 deposition during the 20th century, unlike in Greenland where a pronounced rise in rBC occurred from the 1880s to the 1910s, largely attributed to mid-latitude coal burning emissions. The 43 44 deposition of contaminants such as sulfate and lead increased on Devon ice cap in the 20th century but no concomitant rise in rBC is recorded in the ice. Part of the difference with Greenland could 45 46 be due to local factors such as melt-freeze cycles on Devon ice cap that may limit the detection 47 sensitivity of rBC analyses in melt-impacted core samples, and wind scouring of winter snow at 48 the coring site. Air back-trajectory analyses also suggest that Devon ice cap receives BC from more 49 distant North American and Eurasian sources than Greenland, and aerosol mixing and removal during long-range transport over the Arctic Ocean likely masks some of the specific BC source-50 51 receptor relationships. Findings from this study suggest that there could be a large variability in 52 BC aerosol deposition across the Arctic region arising from different transport patterns. This 53 variability needs to be accounted for when estimating the large-scale albedo lowering effect of BC deposition on Arctic snow/ice. 54

55 **1 Introduction**

The deposition of light-absorbing carbonaceous particles emitted by the incomplete combustion of biomass and fossil fuel can decrease the albedo of Arctic snow- and ice-covered surfaces, thereby amplifying high-latitude warming driven by the buildup of greenhouse gas emissions (AMAP, 2011; Bond et al., 2013). The widely used expression "black carbon" (BC) designates the insoluble, refractory fraction of these aerosols that is largely made of graphitic elemental carbon and strongly absorbs light at visible to near-infrared wavelengths (Petzold et al., 2013). Along with sulfate (SO_4^{2-}) , BC is one of the main short-lived climate pollutants being targeted for mitigation and control under multinational legal agreements (Quinn et al., 2008; AMAP, 2015).

64 In order to evaluate how past and future BC emissions have affected, and will affect, climate forcing in the Arctic, global atmospheric climate models can be used to simulate the transport and 65 deposition of BC aerosols in this region (Koch et al., 2011; Skeie et al., 2011; Lee et al., 2013; Jiao 66 and Flanner, 2016). At present, simulated BC dispersion suffers from large biases, either positive 67 or negative, compared with observational data on BC in Arctic air and snow (Jiao et al., 2014). 68 Validating model simulations is difficult because of the scarcity of such observations across the 69 70 Arctic. Direct monitoring of atmospheric BC is so far limited to a few decades and at a few stations 71 (Hirdman et al., 2010; Gong et al., 2010), and geographic surveys of BC in snow and ice are rare 72 and difficult to conduct over the vast Arctic region (e.g., Doherty et al., 2010).

Ice cores drilled from the accumulation area of glaciers and ice caps can be used as surrogates 73 74 for direct atmospheric observations, as they contain archives of BC and other aerosol species deposited in snow over many centuries (McConnell, 2010). At present, ice-core records of BC 75 76 deposition in the Arctic region are only available from Greenland (McConnell et al., 2007, 77 McConnell and Edwards, 2008; Zennaro et al., 2014; Sigl et al., 2015) and from Svalbard (Ruppel 78 et al., 2014). Here, for the first time, we present a historical record of BC deposition in the Canadian Arctic, developed from a core drilled on Devon Island ice cap, and spanning the years ~1735-1992. 79 The Devon ice cap BC record presents some striking differences from Greenland ice-core records 80 81 of rBC concentrations developed by the same methods. We discuss the possible reasons for these 82 differences, and consider the implications with respect to regional BC transport and deposition patterns in the Arctic region. 83

84 **2** Study site

At latitude 75° N, Devon ice cap (14,400 km²) occupies a central position in the eastern Canadian Arctic Archipelago and lies 275 km from the Greenland coast across northern Baffin Bay. The ice cap has been studied for half a century (Boon et al., 2010) and was previously drilled to obtain records of climate and atmospheric contaminants (e.g., Goto-Azuma and Koerner 2001; Shotyk et al., 2005; Kinnard et al., 2006). However, no record of BC deposition was ever developed from this or any other site in the Canadian Arctic. The core used in the present study (DV99.1) was obtained in April 1999 by the Geological Survey of Canada (GSC) at the top of a dome (75.32° N, 81.64° W, 1903 m.a.s.l.) located 25 km to the east of the ice cap's main dome and true summit (~1930 m.a.s.l) (**Fig. 1**). The coring site lies above the present-day equilibrium line which, based on long-term mass balance observations, has a mean altitude of 1150 m a.s.l.. The mean annual air temperature at the summit of Devon ice cap is -22 °C (Bezeau et al., 2013), and the estimated mean accumulation rate (\dot{A}) at the DV99.1 coring site is 0.14 m ice a⁻¹, or 0.16 m H₂O a⁻¹ (see below).

97 **3 Materials and methods**

98 **3.1 Core sampling and analyses**

99 The DV99.1 core was recovered in 0.4 to 1.1-m long increments (average 0.9 m), with a diameter of 9.8 cm. The uppermost 2.8 m of the core were made of crumbly firn, and were not be preserved 100 101 at the time of drilling. The solid-state DC electrical conductivity (EC) of the core was measured in 102 the field continuously using a hand-held system with parallel electrodes (Icefield Instruments Inc., 103 Whitehorse, Canada), as described in Zheng et al. (1998). The EC profiling started at a depth of 12.38 m, because sections of cores above this were of brittle firm that provided inadequate electrode 104 contact for the hand-held instrument. The core was shipped and stored in freezers at the GSC ice-105 core laboratory in Ottawa. There, it was sampled at 5- to 20-cm resolution for the determination of 106 stable oxygen isotope ratios (δ^{18} O) by mass spectrometry at the University of Copenhagen. Later, 107 57 discrete sub-samples from depths below 29 m were analyzed for lead (Pb) and other trace metals, 108 109 as reported in Zheng et al. (2007). The remaining cores were stored frozen (-20°C) inside sealed polyethylene bags, until archived core segments between 2.8 and 48 m depths were selected for 110 this study and shipped, still frozen, to Curtin University in Australia for BC analyses. These 111 112 combined core segments were estimated to span >250 years, as explained below.

Sample preparation and analysis was conducted between 6 and 11 Dec. 2012 at the Trace Research Clean Environmental facility at Curtin University. The facility consists of a large class 100 space containing multiple class 10 laboratory modules including a -20°C walk-in freezer within a general lab space (also class 10). The space was specifically designed for trace metal and particle work on ice cores (e.g., Burn-Nunes et al. 2011, Ellis et al., 2015, 2016; Tuohy et al., 2015; Vallelonga et al., 2017). The DV99.1 core sections were cut into sub-samples with a ~2.5 × 2.5 cm cross-section, which were processed in an ice-core melter coupled to a Continuous Flow

Analysis (CFA) system (see supplement, Fig. S1). Ice core preparation was carried out in the walk-120 121 in freezer, while processing in the CFA system was conducted in the general lab class 100 space. The CFA melter system was similar to that described by McConnell et al. (2002) with the exception 122 that the ice core melter head was made from aluminum. The method used to quantify BC in the ice 123 core was the same as used by others for the analysis of Greenland and Antarctic cores (Bisiaux et 124 al., 2012; McConnell et al., 2007, McConnell and Edwards, 2008; Zennaro et al., 2014). Meltwater 125 from the CFA system was aerosolized and desolvated with a U5000AT ultrasonic nebulizer 126 (CETAC Technologies, Omaha, NE, USA) and injected into a single-particle intracavity laser-127 induced incandescence photometer (Schwarz et al. 2010; SP2, Droplet Measurement Technologies, 128 Boulder, CO), which measured the mass concentration of BC particles in the meltwater flow. 129 130 Instrumental settings are given in the supplement (Table S1). Following Petzold et al. (2013), we refer to the BC fraction measured by this method as refractory BC (rBC), reported here in mass 131 concentration units of ng g⁻¹. 132

On each day of analysis, a log journal was created. The length of every piece of the DV99.1 133 134 core was carefully measured prior to analysis. During CFA, the time of each break between two ice core pieces was recorded, making it possible to reconcile the rBC record of each piece based 135 136 on the time-depth log. The flow rate of the CFA to the nebulizer was controlled by oversupplying a <1 mL debubbling vessel with excess water, allowing the instrument to maintain a very constant 137 138 flow rate. External calibration of the SP2 nebulizer system was achieved using eight standards of 100% carbon black pigment (MIS Ink Supply, Eboni-6K; Fig. S2) spanning a concentration range 139 140 of 0 to 20 ng g⁻¹. The standards were analyzed each day before and after ice core analysis and the results were compared to assess the stability, reproducibility, and measurement uncertainty of the 141 142 SP2. Additional details and calibration curves (Fig. S3-S6) are provided in the supplement, and potential sources of uncertanties in the results are discussed under section 3.3 below. 143

To compare the DV99.1 record of rBC with that of other deposited aerosol species, we used glaciochemical data obtained from two other cores drilled from the summit area of Devon ice cap in 1998 (core DV98.3) and 2000 (core DV2000) (**Fig. 1; Table 1**). The DV98.3 core was sampled continuously and analyzed for eight major ionic species by ion chromatography, as described in Kinnard et al. (2006). In this study, we used SO_4^{2-} , sodium (Na⁺), calcium (Ca²⁺), potassium (K⁺) and ammonium (NH4⁺) data obtained from the top 85 m of the core, which had been sampled at 3to 12-cm resolution. The non-sea salt fraction of sulfur (nssS) was estimated from Na²⁺ using the mean surface seawater composition of Pilson (2012), and the biomass burning fraction (BB) of K⁺ was estimated from Na²⁺ and Ca²⁺ as: $[K^+]_{BB} = [K^+] - (0.038 \text{ x} [Na^+]) - (0.04 \text{ x} [Ca^{2+}])$, following Legrand et al. (2016). The DV2000 core was drilled at the same site as the DV98.3 core, and was analyzed for Pb and other metals, as reported in Shotyk et al. (2005). The remaining archived volume from cores DV98.3 and DV2000 was, however, insufficient to carry out rBC analyses, which is why core DV99.1 was used for this purpose.

157 **3.2 Age models**

158 Annual layers are not easily resolved in cores from Canadian Arctic ice caps, partly owing to relatively low Å, but also to the effects of wind and/or summer surface melt. Therefore, age models 159 160 developed for these cores are commonly based on a variety of alternative methods. For the DV98.3 and DV99.1 cores, an ice-flow model (Dansgaard and Johnsen, 1969) was used, constrained by the 161 162 total ice thickness obtained from ice-radar measurements or from borehole depths, and by the estimated \dot{A} at each coring site. For the DV98.3 core, the age model was further constrained by 163 approximate layer counting using δ^{18} O and glaciochemical data at shallow depths, and, at greater 164 165 depths, using reference horizons from bomb radioactive fallout (1963; Pinglot et al. 2003) and from historical volcanic eruptions, including that of Laki, Iceland, in 1783 (All given dates are C.E.), 166 which is one of most recognizable historical volcanic signals recorded in EC and/or SO_4^{2-} records 167 168 of other Canadian Arctic ice caps (e.g., Zheng et al., 1998; Goto-Azuma et al., 2002). The age model in the upper 48 m of the DV99.1 core was constrained using a reference horizon provided 169 170 by a large EC (acidity) spike at a depth of 42.60 m (29.56 m ice equivalent), which was attributed to the 1783 Laki eruption (Fig. 2). This model gives an estimated maximum age of 1735 for the 171 172 section of the DV99.1 core used in the present study, and the last year in the record is 1992. The 173 age model also gave an acceptable agreement between profiles of various measured parameters in the DV98.3 and DV99.1 cores (Fig. S7-S8). The DV2000 core was drilled at the same site as the 174 DV98.3 core and used the same age model. The two cores were correlated using measurements in 175 176 the DV2000 that allowed identification of radioactive layers dated to 1958 (16.5 m depth) and 1963 (13.5 m depth) (Krachler et al., 2005). The DV2000 core was estimated to extend back to 1842. 177

Using the Laki 1783 reference layer, the estimated \dot{A} at the DV99.1 site is 0.14 m ice a⁻¹ (0.16 m H₂O a⁻¹) which is lower than at the ice cap summit (~0.25-0.28 m H₂O a⁻¹) or at sites elsewhere in the Devon ice cap accumulation zone (0.17-0.25 m H₂O a⁻¹; Colgan and Sharp, 2008). The most

likely explanation is partial scouring of winter snow layers by downslope winds at the DV99.1 site, 181 182 as also observed on parts of Agassiz ice cap (Fisher et al., 1983). This is supported by a comparison of the δ^{18} O measurements in the DV99.1 and DV98.3 cores, which shows that δ^{18} O variations in 183 the DV99.1 core are truncated of their most negative ("coldest") values relative to the DV98.3 core 184 (Fig. S9). An estimate of the amount of snow lost by wind scouring at the DV99.1 site can be made 185 from the difference in the amplitude of the δ^{18} O data at the DV98.3 and DV99.1 sites, and from \dot{A} 186 at the DV98.3 site, following Fisher and Koerner (1988). The calculation suggests that ~40-45 % 187 188 of the annual snow accumulation is removed by wind at this site, compared to the summit of Devon 189 ice cap.

190 **3.3 Quantifying uncertainties in the rBC record**

191 Analyses of rBC in the DV99.1 core were performed at high depth resolution, producing ~55-80 192 data points per meter over most of the core's length. The data were subsequently averaged over discrete depth increments equivalent to ~1- and ~10-year intervals, respectively, based on the core's 193 age model. In this paper, annually-averaged figures are used for illustrative purposes only, as 194 195 individual years can not be confidently resolved in the DV99.1 core. Down-core variations of rBC 196 in the ice core are the result of a combination of processes, including temporal changes in 197 atmospheric deposition rates (fluxes, abbreviated F), spatial variations of deposition of aerosols in snow, and post-depositional modifications (e.g., by wind scouring or summer surface melt). 198 199 Additional uncertainties in the rBC data come from the age model of the ice core (Fig. 2) and from 200 limitations of the analytical method.

201 The largest uncertainty with regards to the rBC analysis is due to the nebulization / 202 desolvation step before the SP2 analysis. At the time of this study we had adopted nebulizer / 203 desolvation systems used as a front end to inductively-coupled plasma mass spectrometers (ICP-204 MS). These systems are designed to deliver appropriate aerosol size distributions for analysis in 205 the ICP-MS. Schwarz et al. (2012) and Wendl et al. (2014) report rBC size-dependent losses during 206 nebulization / desolvation for several types of nebulizer desolvation systems. The study found that 207 the system used in this investigation has a poor transport efficiency for rBC particles with a volume equivalent diameter >500 nm. Hence rBC data from the DV99.1 core should be considered with 208 209 this limitation (see section 4.2 for a discussion). Other published ice core data sets from Greenland (for example Mc Connell et al., 2007) also suffer from this limitation, but are at least comparable. 210

Further research is required to assess the true size distribution of rBC deposition to the Devon ice cap and other Arctic sites.

Uncertainties in the DV99.1 age model are primarily due to the potential identification error 213 of the Laki 1783 layer in the EC profile, and to interannual variations in Å at the ice-coring site. 214 215 The relationship between true depth and ice-equivalent depth is nearly linear in the DV99.1 core down to 48 m, which suggests a steady firn densification rate over the corresponding time interval, 216 with no signs of dynamically-induced changes in the vertical strain rate. For the 1783 layer, we 217 conservatively assumed a possible dating error of ± 5 years, corresponding to a depth registration 218 error of $\sim \pm 1$ m at the 42.6 m EC peak. The interannual variability in \dot{A} was estimated from an array 219 220 of shallow cores (Colgan and Sharp, 2008) and from winter mass balance measurements since 1961 (data available through the World Glacier Monitoring Service). This information was used in a 221 222 Monte Carlo simulation in MatlabTM with 1000 realizations to compute confidence limits (CL) on the decadally-averaged rBC data. Briefly, a constrained random walk algorithm was used to 223 estimate the probabilistic distribution of the true age at any depth in the core from the surface down 224 to the Laki 1783 layer (Kinnard et al., 2006). Interannual variations in Å were considered to behave 225 as a stationary, autoregressive blue noise process with a lag-one serial autocorrelation coefficient 226 227 of -0.5 to -0.3, based on empirical data presented by Fisher et al. (1985). A population of 1000 alternative age models was thus generated. From each of these, 10-year averages of the rBC data 228 were computed, and 95 % CL were calculated for the geometric mean rBC concentration in each 229 230 decade (Fig. S10). Expressed as a coefficient of variation (CV), the estimated uncertainty on the 231 decadally-averaged rBC concentrations that arise from age model errors varies from 3 to 23 % 232 (median 6 %), depending on the decade considered.

The spatial variability of BC deposition on Canadian Arctic ice caps is unknown. An estimate 233 for Devon ice cap can be made from major ion analyses on shallow cores (Colgan and Sharp, 2008; 234 Fig. 1). In these cores, the spatial CV on the annual SO_4^{2-} deposition averages 42 % (range 17-100 235 %) over a period of ~40 years. Here, we make the assumption that deposition of BC on Devon ice 236 cap shares the same spatial variability as SO_4^{2-} , an aerosol species which, like BC but unlike others 237 such as nitrate (NO₃⁻), is not subject to re-emission from snow to air. While the spatial variability 238 may be large on an annual basis, Monte Carlo simulations results show that averaging the rBC data 239 240 over 10-year intervals reduces its effect on the geometric mean rBC uncertainty to a few % (CV)

in any decade (Fig. S10). The potential impact of post-depositional modifications in the rBC record
is discussed under section 4.2 below.

243 4 Results and discussion

244 **4.1 The DV99.1 record of rBC**

The depth profile of rBC measured in the DV99.1 core is shown in Fig. 3. The probability 245 distribution of rBC concentrations is approximately log-normal (Fig. S11), and we therefore use 246 both the arithmetic and geometric means (μ, μ_g) , as descriptive metrics for these data. Over the 247 entire core length, rBC concentrations average 1.8 ± 3.9 ng g⁻¹ ($\mu_g = 0.8$ ng g⁻¹) with a maximum 248 of 74.0 ng g⁻¹. The mean rBC concentration is approximately constant between 42 and 15 m depths, 249 and decreases gradually at shallower depths to reach ~1.0 ng g⁻¹ ($\mu_g = 0.5$ ng g⁻¹) in the uppermost 250 meter of core. Concentrations below 42 m show a comparatively larger variability and a greater 251 252 range of values (Fig. S12).

In Greenland cores, rBC deposition rose in the 1880s, peaked in the 1910s-20s, and decreased 253 254 thereafter (McConnell et al., 2007), in step with historical changes in coal-burning BC emissions from North America and Europe (Novakov et al., 2003; Bond et al., 2007; Lamarque et al., 2010). 255 256 In south-central Greenland, the early 20th century rise in rBC and nssS was also accompanied by increased deposition of Pb and other trace metals (McConnell and Edwards, 2008). Measurements 257 from the DV98.3 and DV2000 ice cores (Fig. 4) show that Devon ice cap also experienced 258 increased atmospheric deposition of SO₄²⁻ and Pb and during the 20th century, peaking between the 259 260 1960s and 1980s, and followed by a decline, consistent with trends in mid-latitude anthropogenic emissions from fossil fuel combustion. However, unlike in Greenland, the DV99.1 core shows no 261 large, sustained increase in rBC concentration concomitant with that of SO4²⁻ or Pb. There is a 262 modest rise in mean rBC concentrations from the early 1800s to the mid-20th century, but it is 263 much more gradual and of lesser magnitude than the rBC rise observed in ice-core records from 264 Greenland, although the relative timing and magnitude of these increases differ between core sites 265 (Fig. 5 and 6). In the DV99.1 ice core, the highest mean rBC concentrations for the 20th century 266 occur in the decade 1960-70 (μ = 4.7 ng g⁻¹, μ g = 1.7 ng g⁻¹), but these are not unprecedented, and 267 comparable mean concentrations occur in the earliest part of the record, in the decade 1780-1790 268 269 (Fig. S12).

The DV99.1 record also shows a pronounced decline in rBC concentration in the late 20th 270 271 century, but it occurs after the 1960s, which is later than in most Greenland cores, except at Humboldt (Fig. 5 and 6). This difference in timing could, however, be due to uncertainties in the 272 DV99.1 chronology compared to that of annually-dated Greenland cores. The DV99.1 mean rBC 273 concentrations over the period 1960-1990 ($\mu = 0.6$ -1.0 ng g⁻¹; $\mu_g = 0.3$ -0.5 ng g⁻¹) are lower than 274 in the early modern industrial period (early 19th century; $\mu = 1.0-3.0$ ng g⁻¹; $\mu_g = 0.7-1.6$ ng g⁻¹). 275 The only Greenland ice core in which a similar situation occurs is from the ACT2 site (66°N, Fig. 276 5). Neither winter mass balance measurements, nor reconstructed interannual changes in \dot{A} on 277 Devon ice cap (Colgan and Sharp, 2008) show any sustained long-term trend since the early 1960s, 278 and the decrease in rBC concentration in the DV99.1 core during this period can therefore not be 279 280 ascribed to changing precipitation rates on the ice cap. It seems more likely that the decrease is at 281 least in part due to a declining burden of atmospheric BC in the Canadian High Arctic since the 282 1960s (Gong et al., 2010). However, there are several methodological, site-specific and regionalscale factors that must be taken into account when interpreting the DV99.1 rBC record. These are 283 discussed below. 284

285 **4.2. Methodological and site-specific factors**

Observations of atmospheric BC at Alert on Ellesmere Island (82° N, Fig. 1) show a seasonal cycle 286 287 with airborne concentrations peaking during winter and spring months (December-March) and declining to their minimum in summer and early autumn months (June-September) (Gong et al., 288 2010). Most BC deposition in snow is thought to occur in spring and summer, when increased 289 cloudiness promotes in-cloud scavenging and wet deposition of BC-containing particles (Garrett 290 et al., 2011; Browse et al., 2012; Shen et al., 2017). In the interior of the Greenland ice sheet, the 291 292 seasonal cycle of BC deposition is well-preserved in snow and firn layers (e.g., McConnell et al., 2007). This is not the case at the DV99.1 core site on Devon Island. Even in the uppermost part of 293 the core, where some seasonal δ^{18} O variations can be detected, there is no recognizable seasonal 294 295 pattern of rBC concentration peaks (Fig. S13). This is likely the result of the combined effects of 296 wind scouring/mixing of surface snow (as described earlier) and of summer surface melt. The question therefore arises whether such processes could also have obliterated or masked a 20th 297 298 century anthropogenic signal in the DV99.1 rBC record.

The seasonally-resolved ice core record from site D4 in Greenland (71°N; Fig. 5) shows that 299 300 during the historical period of enhanced anthropogenic BC pollution in the Arctic, from the late 19th to mid 20th centuries, rBC deposition increased in both summer and winter (McConnell et al., 301 2007). If the Canadian High Arctic was impacted by airborne BC pollution in a similar way, one 302 would expect to find a marked increase in rBC concentrations in the DV99.1 core during the early 303 20th century, even if winter snow layers were scoured away by wind. To verify this, we performed 304 305 a simple simulation in which we generated synthetic time series of rBC deposition spanning the period 1800-1990, with a seasonal cycle superimposed on baseline inter-decadal variations similar 306 307 to those observed in the Greenland D4 ice-core record. Winter rBC deposition peaks in the series were represented using a log-Gaussian function, and their amplitude was allowed to vary from year 308 309 to year to produce a range of temporal variations comparable to, or lower than, that seen in the 310 Greenland D4 core. Winter deposition peaks were then randomly truncated by 30-60 % (mean 45 311 %) to simulate the effects of wind scouring on the record, and 5-year running means were computed from the resulting data, the smoothing being used to simulate the effects of post-depositional snow 312 313 layer mixing by wind. Results of these experiments show that even if the wintertime rBC deposition peaks between November to May were largely truncated by wind, the low-frequency baseline 314 315 variation would still persist, and should be recognizable above the remaining interannual signal 316 variance (Fig. 7). It therefore seems unlikely that wind scouring would completely obliterate this 317 rBC signal in the DV99.1 record, not unless the amplitude of the seasonal cycle of atmospheric BC 318 deposition on Devon ice cap is much lower than observed at Alert or in Greenland (Gong et al., 319 2010; Massling et al., 2015).

320 Unlike much of central Greenland, the summit of Devon ice cap is subject to partial melting 321 at the surface during summer months, and meltwater can percolate and refreeze into the underlying snow and firn to form infiltration ice features ("melt layers"). The volumetric percentage of melt 322 layers in core DV99.1 was measured by Fisher et al. (2012) as a proxy for past summer warmth. 323 324 These data show that surface melt rates at the coring site increased abruptly in the mid-19th century 325 following the end of the Little Ice Age cold interval, and have since averaged 22 % (median 19 %), 326 occasionally exceeding 50 % in the 20th century (Fig. 4). The DV99.1 coring site is above the present-day upper limit of the superimposed zone (~1400 m a.s.l.; Gascon et al., 2013) and the firm 327 there is >60 m thick, so it is very unlikely that there is any net loss by runoff at this location: any 328 meltwater produced in the summer must refreeze in the firn. However, even without net losses, one 329

must consider whether meltwater percolation and refreezing could account for the limitedvariability in the DV99.1 rBC record during the 19th and 20th centuries.

The post-depositional mobility of BC particles in melting snow is not well known, and likely 332 depends on the hydrophobicity of these particles, which is largely influenced by the presence or 333 absence of surface coatings, for e.g., with SO_4^{2-} (Liu et al., 2011, 2013). Doherty et al. (2013) 334 investigated the vertical redistribution of BC and other light-absorbing particles in snow and firn 335 near Dye 2 (66° N; ~2100 m a.s.l.; Fig. 5) in a part of the Greenland ice sheet's percolation zone 336 where melt layers >10 cm thick are now commonly found (de la Peña et al., 2015; Machguth et al., 337 338 2016). Only very limited vertical redistribution of BC was observed in the snow and firn, and surface melt and percolation did not obliterate seasonal variations of BC in the firn stratigraphy. 339 340 Doherty et al. (2013) attributed this result to the low scavenging efficiency of these particles by meltwater (~20-30 %). At the DV99.1 site on Devon Island, ice layers >10 cm are comparatively 341 very rare, but \dot{A} (0.14 m a⁻¹) is only half of that in the Dye 2 area (~0.32 m a⁻¹; Buchardt et al., 342 2012). Therefore surface melt could mask some seasonal variations of rBC in the firn. 343

The depth at which meltwater could percolate in firn at the DV99.1 site is not known 344 345 precisely over the time period covered in the rBC record. The thickness of the firn zone there (>60 m) is much greater than at Lomonosovfonna summit, Svalbard, for example (~25 m; Kekonen et 346 347 al., 2005). If we accept the estimated depth range of 0.5-2 m for meltwater-induced relocation of water-soluble ions at Lomonosovfonna summit for 2000-07 reported by Vega et al. (2016), then it 348 349 is highly unlikely than relocation of rBC particles could be deeper at the DV99.1 site. The summit of Devon ice cap is ~650 m higher than the Lomonosovfonna summit (1250 m a.s.l.), has a much 350 lower mean annual surface temperature (-22°C, compared to ~-10 to -12 °C at Lomonosovfonna; 351 W. van Pelt, pers. comm.), and the 10-m firn temperature on Devon ice cap summit was, in 2012, 352 < -15 °C (Bezeau et al., 2013), while at Lomonosovfonna it was -2 to -3° C in 1997 (van de Waal 353 et al., 2002). Attempts were also made to quantify post-depositional deposition of ions and/or 354 355 particles by melt/percolation on Penny ice cap on Baffin Island (66° N; Grumet et al., 1998; Zdanowicz et al., 1998), where estimated summer melt rates over the last 150 years are much 356 357 higher (40-100 %) than at the DV99.1 site (Zdanowicz et al., 2012). On Penny ice cap during the mid-1990s, ions and particles were estimated to be redistributed over depths of 3-5 m. A plausible, 358 conservative estimate of the maximum melt-induced relocation depth at the DV99.1 site for the 359 time period of interest might therefore be 3 m (firn depth). With a mean accumulation rate of 0.16 360

m H₂O a^{-1} at the site, soluble impurities could be offset by meltwater percolation in the core by 5-8 years relative to their true depositional depth/age, and probably less for BC particles given their hydrophobicity. In this paper, we focus on inter-decadal variations in rBC concentrations. At such a time-averaging window length, the effect of impurity relocation by melt should largely even out.

There is, however, another consideration. Unlike in the Doherty et al. (2013) study, rBC 365 concentrations in the DV99.1 core were measured by SP2, and the detection efficiency of this 366 method for BC in liquid samples depends on the type of nebulizer used for inflow. As previously 367 mentioned, Schwarz et al. (2012) and Wendl et al. (2014) showed that the relative areosolization 368 efficiency of rBC by the U5000AT ultrasonic nebulizer used in the analysis of the DV99.1 core 369 drops rapidly for particles with a volume-equivalent diameter >500 nm (~ 10% efficiency at a 370 371 volume-equivalent diameter of 600 nm). Coagulation and agglomeration is known to increase the 372 size of BC particles during thaw and refreezing of snow (Schwarz et al., 2013), and this raises the possibility that the SP2 may underestimate the true mass concentration of BC particles in those 373 parts of the DV99.1 that contain icy layers (Fig. 3). 374

375 To verify this, we examined the probability distribution of rBC particle mass in sections of the DV99.1 ice core with different percentages of melt layers. We compared core sections from 376 377 depths between 37-38 m (corresponding to the time interval ~1803-1814) which only had 1 % melt layers, with sections from depths 13-16 m (time interval ~1943-1963), which had up to 53 % melt 378 379 features (min. 9%), and found no significant differences between these core sections (Fig. S14). If rBC particles had coagulated to form larger clusters in sections of core where much percolating 380 381 meltwater refroze, the probability distribution or rBC mass in these sections should be positively 382 skewed relative to that in core sections unimpacted by meltwater, but our data show no evidence 383 of this. While it remains possible that melt-refreezing may have contributed to mask some historical variations in atmospheric BC deposition at the DV99.1 site, it seems unlikely, based on available 384 evidence, that this factor alone can account for the low rBC concentrations in the DV99.1 core, 385 386 when compared to Greenland records analyzed using the same methods.

Some of the central and northern Greenland sites (e.g., Summit, NEEM) from which ice-core rBC records were developed by the SP2 method (**Fig. 5**) experience less surface melt than Devon ice cap, and BC particles in firn at these sites are probably largely unaffected by post-depositional coagulation. Other coring sites located in southern Greenland (ACT2, D4) or at lower elevations (Humboldt) may experience some surface melt and refreezing in summer, but statistics on ice layerfrequency at these sites are unpublished, so this cannot be verified.

393 **4.3 Regional-scale factors**

394 Other reasons for the differences between the DV99.1 and Greenland rBC records (Fig. 6 and 7) 395 may be found in the atmospheric transport paths that deliver BC to the Canadian High Arctic, 396 relative to Greenland. Shindell et al. (2008) used multiple atmospheric transport models to 397 investigate the sensitivity of near-surface airborne BC concentrations in the Arctic to regional 398 anthropogenic emissions. They found that Europe and North America likely contribute equally to 399 BC deposition over Greenland, whereas the central and Russian sectors of the Arctic are more impacted by European emissions. Atmospheric BC in the Canadian High Arctic may be affected 400 401 by both European and North American emissions, but the region is expected to be less sensitive to changes in these emissions compared to other parts of the Arctic, partly because it is very remote 402 from all BC source regions (Shindell et al., 2008; their Fig. 9 and 10). 403

404 Sharma et al. (2006) and Huang et al. (2010) used air back-trajectory analyses to investigate the probable source regions of BC detected at Alert in winter and spring, and identified Russia and 405 Europe as dominant, followed by North America. The summit of Devon ice cap is 1000 km further 406 407 south and ~1.9 km higher, and could thus be affected by a different mix of BC source contributions 408 than Alert. To verify this, and also to contrast the situations of Devon ice cap and Greenland, we computed ensemble 10-day air back-trajectories from both Devon ice cap summit and from 409 410 Summit, Greenland, using the HYbrid Single-Particle Lagrangian Integrated Trajectory model (HYSPLIT v.4) of the NOAA Air Resources Laboratory (Draxler and Hess, 2014, Stein et al., 411 412 2015). As input, we used meteorological fields of the NCEP-NCAR 50-year reanalysis product, which are available on a global $2.5 \times 2.5^{\circ}$ grid at 6-hourly temporal resolution (Kistler et al., 2001). 413 414 Back-trajectories starting daily at 12:00 PM UTC were computed over the period 1948-1999. 415 Unlike Sharma et al. (2006) and Huang et al. (2010), however, we did not use trajectory clustering, because results are highly sensitive to the quality and density of meteorological data coverage used 416 in trajectory computations, and to the arrival height of trajectories (i.e., starting point of back-417 418 trajectories; Kassomenos et al., 2010; Su et al., 2015). Instead, we computed probability density maps or air parcel residence time from all combined trajectories over an equal area grid with 200 419 420 \times 200 km resolution, following a methodology analog to that of Miller et al. (2002).

421 Results (Fig. 8) show that for 10-day transport periods, air parcels arriving at Greenland 422 Summit are more commonly advected from the south-southwest than from other directions, and 423 frequently reach central Greenland after transiting over the North Atlantic, consistent with earlier findings by McConnell et al. (2007; Their Fig. S1). In contrast, air that reaches the summit of 424 Devon ice cap comes more frequently from the west-northwest, and transits over the Arctic Ocean, 425 426 which agrees with findings from analyses of low-level air transport to Devon ice cap by Colgan 427 and Sharp (2008) for the period 1979-2003. It is therefore likely that a large part of BC transported to Devon ice cap is from regional emission sources located in northwestern North America and/or 428 in the central or eastern parts of Eurasia. 429

Smoke plumes from forest or grassland fires, natural or provoked, can reach the Arctic and 430 431 contribute to BC pollution, particularly during summer (Stohl et al., 2006; Paris et al., 2009; Warnecke et al., 2009; Quennehen et al., 2012; Zennaro et al., 2014; Hall and Loboda, 2017). Back-432 trajectory analyses of BB aerosols detected at Eureka on Ellesmere Island (80° N; Fig. 1) indicate, 433 unsurprisingly, that boreal forest/grassland regions of Russia and Canada are the dominant source 434 435 regions for these long-range plume transport events, followed by north-central USA and Alaska (Viatte et al., 2015). To investigate the impact of forest/grassland fire emissions on BC deposition 436 437 to Devon ice cap, we compared the DV99.1 rBC record with reconstructed variations in fire frequency and/or burned area across Canada and Russia during the 19th and/or 20th centuries (Fig. 438 439 9; data from Girardin, 2007; Girardin and Sauchyn, 2008; Girardin et al., 2006; and Mouillot and Field, 2005). On an inter-decadal time scale, no statistically meaningful correlations (p < 0.05) 440 441 could be identified between the DV99.1 rBC record and the fire histories. If fire emissions 442 contribute to BC deposition on Devon ice cap, these contributions are either too small and/or mixed 443 in the DV99.1 record to be correlated with variations in fire frequency or burned area in the source regions. 444

Aerosol species such as K⁺ or NH₄⁺ are commonly associated with BB emissions, and are often used as BB tracers in polar snow (Simoneit, 2002; Legrand et al., 2016). Cheng (2014) identified sectors of south-central Russia and Kazakhstan as source regions for both BC and K⁺ aerosols transported to Alert between 2000 and 2002. However, we did not find any significant correlations (p < 0.05) between inter-decadal variations of rBC in the DV99.1 core and either (K⁺)_{BB} or NH₄⁺ in the DV98.3 record (**Fig. S15**). Whatever contributions BB emissions make to (K⁺)_{BB} or NH₄⁺ deposition on Devon ice cap, these do not covary directly with BC deposition, 452 possibly due to different post-depositional relocation of these impurities in the DV98.3 and DV99.1 453 cores, but also to mixing from multiple emission sources. For example, ammonia (NH₃) emissions 454 from seabird colonies near Baffin Bay may be a larger regional source of NH_4^+ to Devon ice cap 455 than distant wildfires (Wentworth et al., 2016).

456 **4.4 Atmospheric BC deposition rates**

In 90 % of the analyzed DV99.1 core, rBC concentrations are $< 3 \text{ ng g}^{-1}$, and in the uppermost 457 section of the core (depths 3-4 m), they are mostly ≤ 1 ng g⁻¹. These concentrations are very low 458 compared with the 8-14 ng g⁻¹ reported by Doherty et al. (2010) for seasonal snow sampled across 459 the Canadian Arctic in 2009. Part of the apparent discrepancy may be due to differences in 460 analytical methods: The BC concentrations in snow reported by Doherty et al. (2010) were 461 462 measured using a spectrophotometric technique which tends to yield larger mass concentrations relative to the SP2 method (Schwarz et al., 2012). Also, as stated earlier, rBC levels measured in 463 the DV99.1 core may underestimate actual deposition due to wind scouring of winter snow. 464 Atmospheric BC deposition over the summit region of Devon ice cap could also be lower than near 465 sea level, where most of Doherty et al.'s (2010) samples were obtained, because most of the ice 466 cap's accumulation area ($\geq \sim 1150$ m a.s.l.) is above the typical altitude range of low-level Arctic 467 stratocumulus cloud decks which promote aerosol scavenging (Browse et al., 2012). 468

469 Taking into account the aforementioned uncertainties, we estimated the average late 20th century atmospheric flux of rBC (F_{rBC}) over the summit region of Devon ice cap using 470 471 measurements of rBC concentrations in the DV99.1 core for 1963-1990, and data on spatial and temporal variations of A from Colgan and Sharp (2008) and from winter mass balance surveys 472 carried out over the ice cap since the early 1960s. The period 1963-1990 was selected because the 473 1963 radioactive layer in Devon ice cap firn provides a reference level to constrain estimates of 474 \dot{A} (Colgan and Sharp, 2008). Our calculations yield a mean F_{rBC} of 0.2 ± 0.1 mg m⁻² a⁻¹. If μ_{e} , rather 475 than μ , is used to estimate average rBC concentrations, the estimated F_{rBC} is slightly lower (0.1 mg 476 m⁻² a⁻¹). And if the measured concentrations of rBC are assumed to be underestimated by 60-80 %477 due to wind scouring of winter snow layers and/or inadequate detection by the SP2 instrument, the 478 adjusted figures for F_{rBC} are only slightly higher, ranging between 0.2 and 0.3 mg m⁻² a⁻¹. 479

480 These estimates are at the low end of measured net rBC deposition rates in Greenland ice 481 cores between the early 1960s and late 1990s, which vary from ~0.1 to ~2.3 mg m⁻² a⁻¹ (Lee et al.,

2013; see also Fig. S16). Compared to most of central and southern Greenland, the summit region 482 of Devon ice cap experiences low snow accumulation rates (0.17-0.25 m H₂O a^{-1} , or ≤ 0.31 m a^{-1} 483 in ice equivalent; Colgan and Sharp, 2008), and this probably accounts, at least in part, for the 484 lower rBC accumulation rates there, given the important role of precipitation scavenging in 485 controlling atmospheric BC deposition in the Arctic (Garrett et al., 2011; Browse et al., 2012). 486 Other reasons for the differences in rBC accumulation between Devon ice cap with Greenland may 487 be found in predominant patterns of air transport trajectories from source regions, as discussed 488 489 earlier.

490 **5** Summary and conclusions

491 We developed a >250-year time series of atmospheric rBC deposition from Devon ice cap spanning the years ~1735-1992. The rBC ice core record (core DV99.1) is the first from the Canadian Arctic, 492 493 and it supplements existing ice-core records of rBC from Greenland developed by the same 494 analytical methods. The DV99.1 record differs from Greenland records in that it only shows a very modest and gradual rise in rBC deposition through the 19th and early 20th century, unlike most 495 Greenland ice cores, in which there is large, well-defined rise in the 1880-90s, peaking in the 1910s. 496 497 This rise was attributed to BC emissions from coal combustion, which also emitted SO₂ and trace metals such as Pb (McConnell et al., 2007). Ice cores from Devon ice cap (DV98.3, DV2000) show 498 that the deposition of SO_4^{2-} and Pb also increased there during the 20th century, but the DV99.1 499 core shows no concomitant rise in rBC. 500

We suggest that differences between the DV99.1 and Greenland rBC records are due to a 501 combination of methodological, site-specific and regional-scale factors. The site DV99.1 coring 502 site is subject to summer melt-freeze cycles, and this may lead to some underestimation of true rBC 503 504 concentrations by the SP2 method. There is also evidence of wind scouring of snow at the site, which may lessen the amplitude and resolution of historical variations in BC deposition recorded 505 506 in the core. Air back-trajectory analyses suggest that, compared to Greenland, BC deposition on Devon ice cap is less sensitive to BC emissions from the North Atlantic sector (eastern North 507 508 America and western Europe) than Greenland is. We hypothesize that BC aerosols reaching Devon ice cap originate more frequently from north-central/northwestern North America, and/or from 509 510 Russia and central Asia. The relatively long transport trajectories over the Arctic Ocean allow for greater atmospheric mixing and deposition of aerosols to occur during transit, thus obscuring 511

512 source-receptor relationships. If correct, this interpretation implies that historical trends in BC 513 deposition over the Arctic, and the resulting albedo-climate forcing, are likely subject to large 514 spatial variability, even over the relatively short distance between Devon Island and Greenland. 515 This variability, which is probably linked to differences in BC aerosol transport patterns and 516 atmospheric residence time (Bauer et al. 2013), must be accounted for when attempting to model 517 the impact of past and future BC emission trends on the Arctic climate system.

This study also underscores the challenges of interpreting records of aerosol deposition 518 developed from firn or ice cores drilled on small ice caps or glaciers, where local topographic and 519 climatological effects can impact on the preservation of atmospheric signals, when compared with 520 521 the central regions of large ice sheets. A limitation of our study stems from the fact that the DV99.1 record of rBC deposition is from a different site than records of other aerosol species (SO_4^{2-} , Pb) 522 previously obtained from Devon ice cap summit. To verify our interpretation of the DV99.1 rBC 523 524 record, a new core should be drilled from the ice cap summit, or from another ice cap less affected by wind scouring and melt-freeze effects (e.g., on northern Ellesmere Island), and on which co-525 526 registered measurements of rBC and other aerosols could be made. This is particularly important when one considers the large amount of spatial variability inherent in ice core records, even in 527 528 areas of optimal preservation (e.g., Gfeller et al., 2014).

529 Acknowledgements

The recovery of the DV99.1 ice core was supported by the Geological Survey of Canada and the Polar Continental Shelf Project (Natural Resources Canada). Analysis of the core was funded by Curtin University (Curtin Research Fellowship to R. Edwards, # RES-SE-DAP-AW-47679-1), and by an Australian Endeavour Research Fellowship (# ERF_PDR_3051_2012) awarded to B.C. Proemse. N. Schaffer (Univ. of Ottawa) assisted with some of the illustrations. Insightful comments by three anonymous reviewers greatly contributed to improve earlier versions of this manuscript.

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Core	Lat.	Lon.	Max. depth	Approx. elevation	MAAT	Annual accum.	
	(N)	(W)	(m)	(m a.s.l.)	(°C)	(m H ₂ O)	Parameters measured
DV98.3	75.34°	82.14°	302	1930	-12	0.25-0.28	δ^{18} O, radioactivity, major ions, trace metals
DV99.1	75.32°	81.64°	169	1903	_	0.16	δ^{18} O, melt features, EC, rBC
DV2000	75.34°	82.14°	64	1930	-12	0.25-0.28	δ^{18} O, radioactivity, trace metals

Table 1. Details of the three Devon ice cap cores used in this study. MAAT = Mean annual surface air temperature. See text for specific references to published data.



Fig. 1. Location map of the Canadian Arctic Archipelago (left), with enlargement of Devon ice (right). The location of the various ice core sites mentioned in the text are shown. Sites A to E refer to the shallow core array of Colgan and Sharp (2008). Elevation contours on Devon ice cap are spaced at 100 m above sea level.



Fig. 2. Age models for parts of the DV98.3 and DV99.1 cores from Devon ice cap. The error bars on the age curve relative to ice-equivalent depths (red) bracket the 95 % confidence interval on the estimated age for discrete depths, as established from Monte Carlo simulations (see text).



Fig. 3. Profiles of physical properties and rBC in the top 48-50 m of the DV99.1 ice core. (a) Firn density and estimated mean annual layer thickness. (b) Frequency of discrete ice layers (>3 mm thick) per core section. (c) Solid-state electrical conductivity (EC) profile of the core from 12.8 to 50 m depth, smoothed to a vertical resolution of \sim 1 cm. The EC peak attributed to acidic fallout from the Laki 1783 eruption is labelled. (d) and (e) rBC concentrations plotted on linear and log scales. The bold red line is a 500-point (\sim 1-m) moving average.



Fig. 4. Environmental changes on Devon ice cap, 1740-1999, recorded in three cores from the summit region (DV98.3, DV99.1 and DV2000). (**a**) rBC concentrations in the DV99.1 core; (**b**) Pb concentrations in the DV99.1 core (~1740-1840) and DV2000 core (1840-2000); (**c**) $SO4^{2-}$ in the DV98.3 core; and (**d**) volumetric percentage of icy melt features in the DV99.1 core due to surface summer melt. Data are presented in ~1-, 5- and/or 10-year averages. For panels (**a**) to (**c**), 10-year geometric mean values of the data are also plotted in red on separate scales (left). The shaded grey bar identifies the Laki 1783 isochron used to correlate the different cores. The width of the bar denotes the maximum dating uncertainty at the corresponding depths in these cores. The Pb data are from Shotyk et al. (2005) and Zheng et al. (2007), the $SO4^{2-}$ data from Kinnard et al. (2006), and the melt feature data from Fisher et al. (2012).



Fig. 5. The record of atmospheric rBC and non-sea salt sulfur (nssS) deposition on Devon ice cap over the period 1800-2000 compared with similar records developed at various sites in Greenland by identical or nearly-identical methods. Full lines are rBC; stippled lines are nssS. Data from Summit, D4, ACT2 and Humboldt: McConnell et al. (2007) and Koch et al. (2011); data from NEEM: Zennaro et al. (2014) and Sigl et al. (2015). Also shown is the location of the ice-core record of elemental carbon (EC) deposition developed from Holtedahlfonna, Svalbard, by Ruppel et al. (2014), as well as other sites (Alert, Dye 2) mentioned in the text.



Fig. 6. (a) The DV99.1 record of atmospheric rBC deposition since 1800 compared with other records developed from sites in Greenland identified in **Fig. 5**. All records are presented in one-year averages. (b) As in (a) but for records of non-sea salt sulfur (nssS). Two volcanic eruption isochron used for correlation in the Greenland cores are highlighted.



Fig. 7. Simulation of the effects of snow wind scouring on the preservation of an anthropogenic signal of rBC deposition in a synthetic ice-core times series of rBC spanning the period 1800-1990. (a) The synthetic series, with a pseudo-seasonal cycle superimposed on the interdecadal baseline trend observed in the Greenland D4 record (McConnell et al., 2007). (b) The synthetic series after randomly truncating the amplitude of all winter deposition peaks (November-March) by 30-60 %. The bold red line in both panels is a 5-year running geometric mean.



Fig. 8. Maps of residence time probability for air arriving at (a) Devon ice cap and (b) Summit, Greenland over the period 1948-1999, computed using HYSPLIT4. Air residence probability densities were normalized to a scale of 0-1, and were spatially detrended by multiplying the original residence time grids (in hours) by the distance between each grid point and the coring site. This effectively removes the concentric increase in probability density near the back-trajectory start point (Ashbaugh et al., 1985). The spatial resolution of the grid is 200×200 km.



Fig. 9. (a) Historical variations in rBC concentration in the DV99.1 core, 1760-1992, compared with reconstructed historical trends in (b) fire frequency in the eastern boreal forest region of Canada (Girardin *et al.*, 2006), and (c) burned area across northern Canada (Girardin, 2007) and in the boreal and grassland regions of Russia and Central Asia (Mouillot and Field, 2005). All data were log-transformed to facilitate visual comparisons.