Authors' response to referee comments

Anonymous Referee #1

General Comments:

The authors present valuable new BC data from the severely under-sampled Arctic. Historical BC records from different locations within the Arctic are essential for reliable model validation, and generally to understand the spatial and temporal variations in BC trends and processes affecting BC concentration and deposition patterns. Furthermore, discussion on post-depositional factors affecting BC records, such as wind scouring, is particularly welcome, as these are currently quite superficially known. The manuscript is well written and easy to follow. The used methods are appropriate, and the presented hypotheses are well justified and thoroughly discussed. I recommend publication if the following points are addressed in the revised manuscript.

Specific comments, and authors' responses:

Page 2, Line 14: Is the citation to Koch et al., 2011 and Lee et al. 2013 appropriate here, as these modelling papers don't present new ice core BC observations, as currently suggested by the sentence? For clarity, I'd suggest to replace these references with other appropriate work (e.g. McConnell 2010; Zennaro et al. 2014; Sigl et al. 2015) or modify the sentence. For instance, the Koch et al. (2011) cite McConnell et al. (2007), McConnell (2010) and McConnell and Edwards (2008) for the ice core observation data used in their modelling study.
P 6, l 27: Please, remove the citation to Koch et al. 2011, and replace e.g. with McConnell 2010 (if you like). Also, on P 6, l 28, Skeie et al. 2011 doesn't present any own BC emission inventory data, so please remove this citation as well.

Changes in the citations were made as suggested.

P 12, l 12: The citation to Ruppel et al. (2014) is incorrect in this context.

Removed.

P 3, l 19-23: Could you clarify what these microparticles are, i.e. for instance give examples on what type of particles are meant?

We decided to remove the microparticle data from the revised manuscript, and focus solely on the rBC data.

Section 3.3 discusses impressively the uncertainties caused by stochastic spatial variations of deposition of the aerosols in snow, and post-depositional modifications (e.g., by wind scouring) in the ice core record, while actual measurement uncertainties of the nebulizer and SP2 instrumentation are not included. However, there is reason to believe that the chosen analysis methodology itself may cause significant uncertainties for the rBC record as well. As the authors discuss in the last paragraph of Section 4.2 (P8, l 18-31) it is known that the used nebulizer doesn't effectively aerosolize larger rBC particles which however may constitute a notable part of the total BC in the studied ice core, as it is shown to be affected by post-depositional processes (e.g. summer melt) which are known to increase the BC particle size in snow (e.g. Schwarz et al., 2013). The manuscript should therefore determine clearly which size fraction of rBC is quantified here. It is understandable why the nebulization and SP2 quantification efficiency is only discussed in Section 4.2, after discussing summer melt of the ice core. However, these uncertainties should at

least be mentioned (if they are too difficult to be quantified) already in Section 3.3, and Section 4.2 referred for further discussion. Currently, in Section 3.3 the reader is erroneously led to believe that all uncertainties of the BC record are unrelated to the used rBC quantification methodology.

Uncertainties in the SP2 measurements, and from other sources, are now discussed in section 3.3, with additional material on the analytical data and quality control in the supplement to the revised article. The size range of rBC particles measured by the SP2 instrument in the DV99.1 core is unfortunately not know at present.

Finally, it would be good if the authors would present a total estimate (in numbers, %) of how large the uncertainties of the results are. P 5, l 27-28 says "Because the magnitude of ε_s is independent from that of errors that arise from ice core dating uncertainties (ε_t), the combined uncertainty was calculated as the quadratic sum of these terms ($\pm 2\sigma$).".Is the uncertainty seen in any of the figures? How large is the combined uncertainty? If these uncertainties ("s and "t) cannot be combined with the analytical method uncertainties, it would be good if these uncertainty percentages were presented separately (currently no uncertainty is given for the analytical methodology).

See response to above comment. On Fig 4 of the revised manuscript, we chose to remove the confidence limits, because they overcrowded the plots and made trends in the data (where they occur) difficult to see. However, we added plots of estimates for different sources of uncertainties (due, for e.g., to age model errors) in the supplement to the revised article .

P 12, l 16: For clarity, I'd suggest the following addition (in parenthesis): "The time series differs from the Greenland records (measured with the same analytical methodology as used here) in that it. . .". The addition could clarify that the differences of the Devon Island BC record to the Greenland records are surprising as they are analyzed with the same methodology, while differences to the Svalbard record may be expected due to different methodology.

The revised text as been modified as suggested.

Anonymous Referee #2

General Comments:

The authors present a reconstruction of black carbon and microparticle concentrations from an ice core from Devon Ice Cap in Canada covering the time period 1810-1990 AD. Where direct observations of atmospheric BC are scarce and limited to the most recent decades, ice-cores can – in principle – act as surrogates for direct observations and provide valuable information on the composition of the pre-industrial atmosphere and serve as benchmarks to assess the capabilities of models to realistically simulate the aerosol life-cycle and resulting forcing of past climate. In order to use such proxy reconstructions such glaciochemical records need to realistically represent the atmospheric impurity content through time. In this respect, the current manuscript falls short in providing sufficient evidence for the reasons summarized below: The authors provide virtually no information that would allow to assessing their ability to achieve reproducible BC concentrations from ice cores or to repeat their experiments. They fail to report how they calibrated their measurements and omit to discuss any metrics (e.g., detection limit, stability, linearity, stability, repeatability, reproducibility) commonly considered necessary when introducing new instrumentation in analytical chemistry (see for example (Lim et al., 2014; Wendl et al., 2014; Mori et al., 2016; Bigler et al., 2011). The same is true for the age-scales. The entire dating depends critically on the correct identification of the Laki signal in 1783 AD at this specific ice-core site and also for the other ice cores from Devon, but I can find in none of their cited papers a graph showing the full EC or SO4 record used to make this attribution. The same is true for the proxy signature of the 1963 AD nuclear bomb testing fallout. With no electrical or glacio-chemical signature of Laki provided in the manuscript and with having a huge sulfate spike recorded in 1847 AD which is not recorded in any other ice core from nearby Greenland, I consider it equally likely that the latter signal may as well be from Laki 1783, and your timescale off by over 60 years.

I consider it very unfortunate and not sufficiently well explained why you chose to limit your analyses to 1810-1990 AD and to only two new parameters. As stated above, Laki is crucial for the depth-age scale; the past 10 years would allow to have overlap with aerosol observations (e.g. from Alert); and analyzing additional aerosols in DV99.1 would allow you to 1) assess the effects of melting on your impurity records, 2) improve the relative dating among the different ice cores and timescales, and 3) to attribute specific sources to BC using for example NH4+ and SO42- as unique source tracers. The fact that the ice is fractured (>38m) or not consolidated (>4m) does not make measurements impossible, and half of an ice-core minus 2.5 x 2.5 cm consumed for your CFA measurements should provide you with enough material for additional analyses.

Authors' response:

First, some context needs to be provided. This has no incidence on the revisions to the paper as such, but it may help explain to the reviewer some of the shortcomings identified in the study. The analysis of the DV99.1 core for rBC was, to some extent, part of a "rescue operation" of the Canadian ice-core collection which, in 2011, was in danger of being permanently moth-balled as a result of the shutting down of the GSC ice-core laboratory in Ottawa (what remains of the collection eventually found a new home at the University of Alberta in 2017). At the time, an open call was sent to researchers interested in obtaining cores for various analyses. One outcome was that parts of the DV99.1 core were shipped to Curtin University for rBC analysis. Under more favorable circumstances, the core would also have been sampled and analyzed for ionic chemistry by IC at the GSC ice-core laboratory, where a core melter-sampling system had been set up. This, however, was not possible, which explains why we do not have co-registered ionic chemistry data to accompany the rBC and microparticle data for this core. This is admittedly not optimal, and it

reflects the conditions under which the study was initiated. Since the submission and review, we have been able to use additional, previously unprocessed analytical results, and to extend the rBC record to 1735, spanning the period including the Laki 1783 volcanic marker. Extending the record required a large additional effort. These new data are now included in the manuscript, and the plots and discussion have been updated accordingly.

The description of methods in the revised manuscript has been expanded, and additional include additional details are provided about instrumental settings, calibration, etc. A discussion of uncertainities in the SP2 analyses has been added in section 3.3. Some specific questions regarding data quality are answered below.

A number of minor mistakes and discrepancies in the paper were also corrected in the revised version. For example, the elevation of the DV99.1 site was incorrectly reported as 1750 m a.s.l. This has been revised to 1903 m a.s.l., and the altitude of the true summit of Devon ice ca, where the DV98.3 core was recovered, is actually 1930 m a.s.l.. These figures, and the coordinates of the coring sites, were verified with a recent detailed digital elevation model of the ice cap, and the correct values are now listed in Table 1.

Reviewer # 2 identified shortcomings and/or inconsistencies in the discussion of the age models of the DV99.1 and DV98.3 cores. To address some of these issues, we contacted Dr David Fisher, formerly with the GSC (now retired), who initially developed the age models for these cores. Dr Fisher kindly helped to clarify matters. To acknowledge his contribution, we added him as a co-author of the revised version of the manuscript.

Briefly: whenever an age model for a core is being developed, several iterations of the model are tested by choosing various plausible candidate volcanic marker peaks in EC and/or SO_4^{2-} profiles (as the case may be). The choice of the most plausible model is determined by several considerations. For e.g., the model should not result in changes in the age-depth relationship that would imply unrealistic changes in the mean accumulation rate at the coring site. And the model should be compatible with other information about conditions at the coring site such as the estimated snow accumulation rate obtained by radioactive measurements (when such data are available). Preference is also given to the model that provides the greatest coherence in the low-frequency variations of $\delta^{18}O$ records between cores and coring sites, as these variations are expected to be coherent and synchronous at regional scales (even if details may vary). The inconsistencies in the age model descriptions given in the submitted paper arose from some confusion between two different iterations of the age model used for the DV98.3 core. This was clarified in our exchanges with D. Fisher.

A more thorough and explicit description of the age models, with additional references, is now included in the revised manuscript, and the accompanying supporting information. The key points are discussed below, in order to avoid unnecessary repetitions in our response to the reviewer's detailed comments.

The age model of the **DV99.1 core** was developed in the manner described in Zheng *et al.* (2007), using a combination of ice flow model, EC measurements to identify volcanic signatures, and, at greater depth, the characteristic $\delta^{18}O$ step that marks the transition from glacial conditions into the early Holocene. The EC profile starts at a depth of 12.38 m: section of cores above this were of brittle firn that provided inadequate electrode contact for the hand-held instrument we used. An EC peak that was tentatively assigned to the Katmai 1912 eruption occurs at a depth of 25.50 m, but it is neither particularly large nor a truly distinctive peak, as it is superimposed on a "shoulder" in the baseline conductivity (starting at ~40 m depth) which likely corresponds to the rise in

acidifying aerosol deposition on Devon ice cap during the industrial era. It is known from other Canadian ice cores that this rise began ca 1870 on southern Baffin Island, and slightly later (ca 1900) on northern Ellesmere Island (Goto-Azuma *et al.*, 2002; Goto-Azuma and Koerner, 2001), so it probably occurred sometime between these dates on Devon Island. We did not show the presumptive 1912 Katmai marker in the DV99.1 age model plot of the submitted version of the paper, as its identification is uncertain, but it was used nonetheless to constrain the age model. This has now been added to the revised age model plots. The Katmai 1912 signal stands much more clearly in ice cores from Penny ice cap on Baffin Island (Goto-Azuma *et al.*, 2002). The EC peak in the DV99.1 core that was assigned to the Laki 1783 eruption is at a depth of 42.6 m (29.6 m ice-equivalent). It is the highest and sharpest peak in this part of the profile, and it clearly precedes the rise in baseline conductivity, just as it does in cores from Penny ice cap. There are no deeper EC peaks of comparable magnitude in this part of the DV99.1 core. There are a few shallower peaks between 33 and 40 m depth, but these are of lower magnitude, and could be ascribed to other eruptive events in the early 19th century, such as Tambora (1816), but they are not sufficiently distinctive to be confidently assigned to specific events. Hence we have no strong reasons to revise our assignment of the ECM peak at 42.6 m to Laki (1783). This identification is more reliable than that of the presumed Katmai 1912 EC marker at 25.5 m. Based on this assignment of the Laki 1783 marker, the mean accumulation rate at the DV99.1 site was estimated to be 0.14 m ice a^{-1} (~0.16 H_2O a^{-1}) over the period 1783-1992. (Note that in the submitted paper, the figure of 0.14 m a^{-1} was erroneously given as being in water equivalent).

The best fit of the ice-flow age model to the various volcanic (EC) and $\delta^{18}O$ markers in the entire DV99.1 core gives a predicted depth of 41.6 m for the 1783 layer, which is offset my one meter from the actual depth (42.6 m) at which the EC peak assigned to Laki occurs. This offset falls within plausible dating error limits if one allows for random interannual variations in the local snow accumulation rate. There is a larger (3.1 m) discrepancy between the model-predicted depth for Katmai 1912 (21.3 m) and the EC peak assigned to it (24.5 m), but as the identification of this EC marker is tentative at best, this discrepancy may not be meaningful. The manner in which the uncertainty of the age models were estimated (for both the DV99.1 and DV98.3 cores) is described below under our response to the reviewer's comment about page 5, L9-18.

The age model of the 302-m long **DV98.3** core (drilled near the true summit of Devon ice cap) was previously described in Kinnard *et al.* (2006) and also, more succinctly, in Krachler *et al.* (2005). No EC measurements were performed on this core, but there were measurements of radioactivity as well as high-resolution measurements of $\delta^{18}O$ and ionic chemistry data, including SO_4^{2-}. The radioactivity profile in firn/ice was measured by total beta (β) activity in the borehole, as well as by tritium (^3H) concentration and ^{137}Cs activity in the core itself. The ^3H profile can be seen in Clark *et al.* (2007), and the β and ^{137}Cs profiles in Pinglot *et al.* (2003). All of these profiles agree very well and show two clearly-separated peaks, the higher and shallower one centered at a depth of 16.6 m below the 1998 surface. This was assigned an age of 1963, in accordance with the chronology of Dibb *et al.* (1992) and Kudo *et al.* (1998) for radioactive fallout in the Arctic. The deeper, smaller peak is assumed to correspond to the earlier, mid-/late 1950s peak in radioactive fallout. The reviewer asked whether the radioactive peak in the DV98.3 core could be used to assess the effect of post-depositional melt on the glaciochemical records in this core. This analysis was in fact already done and reported by Pinglot *et al.* (2003), who derived a proxy melt index from the radioactive profiles in Arctic ice cores. This index should be equal to 1 in the absence of post-depositional changes in radionuclide distribution in snow and firn, and increase with higher melt rates. For the DV98.1 core site, the derived index value was 1.2. For comparison, it was estimated to be 2 at low-elevation Svalbard ice coring sites, where summer melt rates are far higher than on Devon ice cap. Comparison of the radioactivity profiles in the DV98.3 borehole/core and the ^{210}Pb activity profile at Summit, Greenland (Dibb *et al.*, 1992), shows very good agreement, suggesting limited post-depositional "smearing" at the DV98.3 site, although the

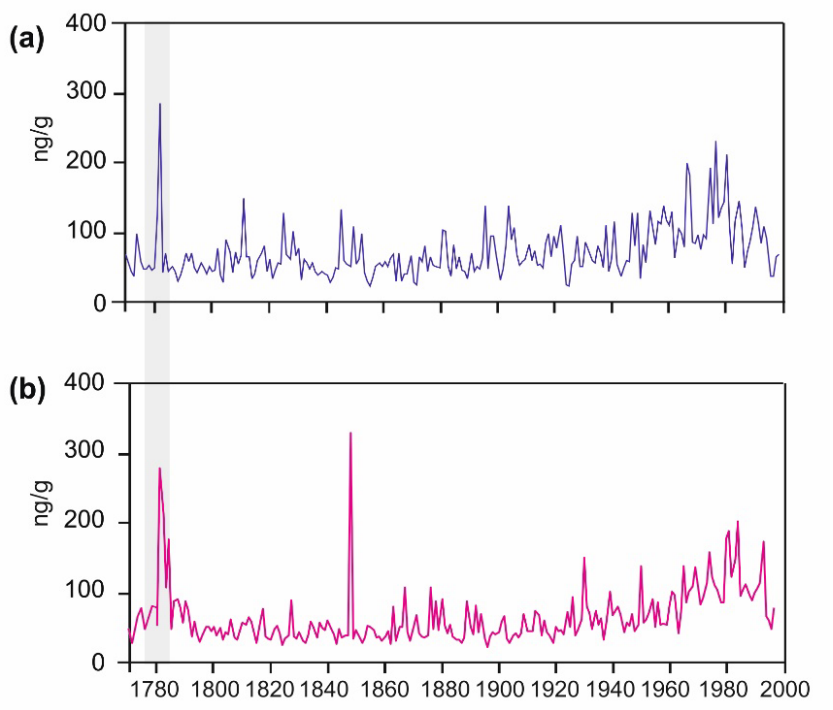
possibility remains that the position of the peaks at DV98.3 could have been slightly offset by melt relative to their initial stratigraphic location. (See also discussion on estimates of melt-percolation effects, below)

Based on the 1963 radioactive peak age assignment, the estimated mean accumulation rate at the DV98.3 coring site over the period 1963-1998 is ~0.25 ± 0.2 m ice a^{-1} (Kinnard *et al.*, 2006; Clark *et al.*, 2007). Seasonal or pseudo-seasonal variations in the $\delta^{18}O$ and SO_4^{2-} profiles are only recognizable in the uppermost part of the DV98.1 core (top ~15 m). Hence their usefulness for annual layer identification is limited. However, performing a cross-spectral analysis of these data (normalized to ice-equivalent depths) allows us to identify the frequencies at which most of the spectral power is concentrated. Applying this approach to the top ~11 m of the DV98.3 core (5 m in ice equivalent) reveals an unambiguous spectral peak at a frequency of 0.042 cm^{-1}, which corresponds to an approximate annual layer thickness of 0.24 m ice-equivalent, or an annual mean net accumulation rate of 0.26 m H_2O a^{-1} for the most recent decades in the record (see Kinnard *et al.*, 2006). In addition, there are over 50 years of continuous annual winter mass balance measurements available from the summit of Devon ice cap, and these constrain the mean accumulation rate there to 0.25-0.28 m H_2O a^{-1} for the latter part of the 20th century.

As described in Kinnard *et al.* (2006) one of the SO_4^{2-} peak that was used to constrain the age model for the DV98.3 occurs at an ice-equivalent depth of 25.5 m, and this was assigned to the 1912 eruption of Katmai. Using this marker gives an estimated mean accumulation rate for the 1912-1998 period of 0.29 m ice a^{-1}, or 0.32 m H_2O a^{-1}. Two other large SO_4^{2-} peaks occur at 61.55 and 81.55 m depths, respectively. The shallower one is narrow and sharp, the deeper of lesser amplitude and much broader. One of these peaks likely represents fallout from the Laki 1783 eruption. The atmospheric SO_4^{2-} flux in snow from this eruption over southern and western Greenland was much larger than that of other early 19th century eruptions such as those from 1809 and of Tambora in 1816 (Gao *et al.*, 2007). In SO_4^{2-} profiles of cores drilled on Penny ice cap (Baffin Island), the Laki 1783 signal is particularly prominent (Goto-Azuma et *al.*, 2002; Zdanowicz et al., 2015). The same is expected to be true on Devon ice cap, as it lies in the same broad latitude band of 65-75°N where maximum SO_4^{2-} deposition rate were detected in Greenland cores. There are arguments for, and against, each of the SO_4^{2-} peaks (61.55, 81.55 m) in the DV98.3 core as a potential marker for Laki. If we assign the deeper (81.55 m) peak to 1783, the inferred mean accumulation rate for 1783-1998 is 0.28 m ice a^{-1} (0.30 m H_2O a^{-1}). This agrees closely with the estimated mean accumulation rates for 1963-1998 and 1912-1998 based on radioactivity measurements and the Katmai SO_4^{2-} peak. If we assign instead the shallower (61.55 m), narrower SO_4^{2-} peak to 1783, the estimated accumulation rate for 1783-1998 is 0.21 m ice a^{-1} (0.23 m H_2O a^{-1}). This is lower than the figure for 1963-1998 and 1912-1998, but falls within the range of values obtained at various sites across the upper accumulation area of Devon ice cap (0.17 to 0.25 m H_2O a^{-1}; Colgan and Sharp, 2008).

In the age model that was finally developed, the shallower and sharper of the SO_4^{2-} peaks (at 61.55 m depth) was ascribed to Laki 1783 (as stated in Kinnard *et al.*, 2006). The nature of the deeper, broader SO_4^{2-} peak is uncertain: we found no corresponding broad peak in the DV99.1 EC profile within the range of depths at which it should have plausibly been detected. The choice of the 61.55 m EC peak for Laki was partly guided by the fact that resulting age model gave the best overall fit to other, deeper time EC markers in the core, and also resulted in a better agreement of the Holocene $\delta^{18}O$ profiles between the DV98.1 and DV99.1 cores (see supplement to the revised manuscript), and with other cores previously drilled on Devon ice cap in 1972-73. The confusion in the submitted manuscript arose from the fact that we used an earlier age model iteration in which the Laki 1783 signal had been assigned to the deeper (81.55 m) SO_4^{2-} peak. It is important to stress, however, that regardless of which of the two SO_4^{2-} peaks is assigned to Laki 1783, the main features of the DV98.3 SO_4^{2-} profile remain the same (see figure below), partly because the age model is also constrained by the 1963 radioactive marker. With either time scale,

the profile shows a rise in SO_4^{2-} in the mid-20th century, peaking in the 1970 or 1980s, followed by a decline. For the argumentation in the present study, this is the relevant point.



Above: The DV98.3 SO_4^{2-} profile, averaged over depth intervals corresponding to ~annual increments, and plotted using two different age models. Model (a) assigns the SO_4^{2-} peak at 61.55 m depth to the Laki 1783, while model (b) assigns the SO_4^{2-} peak at 81.55 m depth to this same eruption. The sharp SO_4^{2-} peak ca 1847 in (b) is the one that is assigned to Laki in (a).

The 63.72-m long **DV2000 core** was drilled at the same location (within GPS position error; ± 20 m) as the DV98.3 core. This core was used entirely for the analysis of trace metals such as Pb, and the mechanical decontamination protocol used (described in Zheng *et al.*, 2006) did not leave archive material for other analyses such as major ions or $\delta^{18}O$. The DV2000 core was correlated with the DV98.3 on the basis of measurements in the DV2000 that allowed identification of the 1958 (16.5 m depth) and 1963 (13.5 m depth) radioactive layers (Krachler *et al.*, 2005). The DV2000 core was estimated to extend back to 1842. In the detailed comments, the reviewer questions the validity of using the age model of the DV98.3 core for the DV2000 core. This would be a serious issue if our aim was to correlate interannual-scale (or higher-resolution) features in parallel cores, as the signal-to-noise ratio in $\delta^{18}O$ or glaciochemical signals can be large even with only a few meters of separation (e.g., Fisher *et al.*, 1998). However in this paper we are chiefly concerned with the longer-term (lower-frequency) variations in the ice-core data, which is why we present 10-year averages of the data in Fig. 4 of the manuscript. The reason we discussed the DV2000 Pb record was to emphasize the fact that both SO_4^{2-} and Pb ice-core records from the summit of Devon ice cap show clear evidence of enhanced anthropogenic aerosol deposition related to fossil fuel combustion emissions in the 20th century, peaking approximately in the 1970 or 1980s. Even if the chronology of the DV2000 was offset relative to that of the DV98.3 core by a few years, it would in no way invalidate this observation.

Regarding the potential effects of summer percolation on the signals in the DV99.1 core:

The long-term (~55-year) mean altitude of the equilibrium line (the ELA) in the summit region of Devon ice cap, based on mass balance measurements going back to the early 1960s, is 1150 m a.s.l.. The highest ELA measured in any given year during this period was 1700 m a.s.l. (D. Burgess, GSC, pers. comm.). Hence for most of the period considered in this study, the DV99.1 site probably lied above the ELA, but within the percolation zone where ice layers can be formed. A detailed core stratigraphic log of the DV99.1 core compiled by R. Koerner indicates that, apart from discrete ice layers and occasional ice glands, most firn layers did not have an icy matrix, i.e. they did not show evidence of being permeated by percolating meltwater. It is therefore likely that the DV99.1 site is, and has been, above the saturation zone for the time period considered here, and also above the superimposed ice zone, which only extends up to ~1400 m a.s.l. presently (Gascon *et al.*, 2013), and probably lower during the colder 19th century. At the summit of Penny ice cap (1930 m a.s.l.), where the firn is of comparable thickness as at the DV99.1 site (> 60 m) but summer melt rates are much higher, all meltwater refreezes in the firn, and there is no net less by runoff (Zdanowicz *et al.*, 2012). So it is very unlikely that there was any net loss of meltwater and impurities at the DV99.1 site in the late 1990s, or over the longer time interval considered in this study. Any summer meltwater produced at this site would have refrozen in situ inside the firn.

Note that the melt record in the DV99.1 core was incorrectly presented the submitted manuscript: the cited melt rates were too large. The original data can be found as an electronic supplement to Fisher *et al.* (2012) *Glob. Plan. Change* 84-85: 3–7. The record consists in data averaged over depth intervals corresponding to ~5-year steps, and extends to 1992. These data have been replotted on the correct scale in the revised manuscript. The estimated 5-year mean volumetric percentage of icy features in the DV99.1 core (the proxy used for summer melt rates) increased from 5 % (median 4 %) between 1783 and 1850, to 21 % (median 20 %) from 1850 to 1992. Within the latter period, there were three 5-year intervals during which the melt feature percentage exceeded 50 %.

The depth at which meltwater could percolate in firn at the DV99.1 site is not known precisely over the time period covered in the rBC record. As mentioned above, the thickness of the firn zone there is >60 m. This is much more than the ~25 m of the firn zone at Lomonosovfonna summit, Svalbard, for example (Kekonen *et al.*, 2005). If we accept the estimated depth range of 0.5-2 m for meltwater-induced ion relocation at Lomonosovfonna summit for 2000-07 reported by Vega *et al.* (2016), then it is highly unlikely than ion relocation could be deeper at the DV99.1 site. The summit of Devon ice cap is >600 m higher than the Lomonosovfonna summit (1250 m a.s.l.), has a much lower mean annual surface temperature (-22°C, compared to ~-10 to -12 °C at Lomonosovfonna; W. van Pelt, *pers. comm.)*, and the 10-m firn temperatures on Devon ice cap were, in 2012, < -15 °C (Bezeau *et al.*, 2013), while those at Lomonosovfonna were within -2 to -3° of zero C in 1997 (van de Waal *et al.*, 2002).

Attempts were also made to quantify post-depositional deposition of ions and/or 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 were much 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, conservative estimate of the maximum melt-induced relocation depth at the DV99.1 site for the time period of interest might therefore be 3 m (firn depth). With a mean accumulation rate of 0.16 m H_2O a^{-1} at

the site, this would imply that 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 rBC particles given their hydrophobicity. In this paper, we focus on inter-decadal variations in the ice-core parameters (10-averages of the rBC data). With such a wide time-averaging window length, the effects of impurity relocation by meltwater largely even out. Of course, melting-refreezing in the snow/firn may have impacted the rBC record otherwise, by reducing the detection sensitivity of large rBC particles in the melt-affected sections, as discussed in the paper. However we do not find a simple correlation between the rBC concentrations in the DV99.1 core and the melt index (see Fig. 4 in manuscript). Without additional evidence, we can not easily separate the possible effects of melt on the rBC record from those of possible changes (or lack thereof) in aerosol inputs. We therefore try to account for both types of factors in the paper.

As a footnote to the discussion above, decades of experience working with ice cores from Canadian Arctic ice caps have taught us that these records should *mostly, if not only, be analyzed for temporal trends at decadal or longer time scales*, owing to low accumulation rates, or the effects of melt, or both (see Koerner, 1997). Only in the uppermost few tens of meters of some cores from Devon and Ellesmere Island are isotopic or glaciochemical signals sufficiently well-preserved to allow for analysis of these records at interannual time scales (e.g., Kinnard *et al.*, 2006).

Bezeau *et al.* (2013) *J. Glaciol.* 59: 181-991.
Clark *et al.* (2007), *J. Geophys. Res.* 112, D01301, doi:10.1029/2006JD007471.
Colgan and Sharp (2008) *J. Glaciol.* 54, 28–40.
Fisher *et al.* (1998) *Science* 279(5351): 692-5.
Gascon *et al.* (2013) *J. Geophys. Res.* 118: 2380–2391.
Goto-Azuma and Koerner (2001) *J. Geophys. Res.* 206(D5): 4959–69.
Goto-Azuma *et al.* (2002) *Ann. Glaciol.* 35: 29-35.
Grumet *et al.* (1998) *Geophys. Res. Lett.* 25: 357–360.
Kekonen *et al.* (2002) *Ann. Glaciol.* 35: 261-265.
Kinnard *et al.* (2006) *Ann. Glaciol.* 44: 383-389.
Koerner (1997) *J. Glaciol.* 43(143): 90-97.
Krachler *et al.* (2005) *J. Environ. Monitor.* 7: 1169-1176.m
Kudo *et al.* (1998), *J. Environ. Radioactivity* 40 (3): 289-298.
Pinglot *et al.* (2003) *J. Glaciol.* 49: 149-158.
van de Waal *et al.* (2002) *Ann. Glaciol.* 35: 371-378.
Vega *et al.* (2016) *The Cryosphere* 10: 961–976.
Zdanowicz *et al.* (1998) *Tellus* 50B: 506-520.
Zdanowicz *et al.* (2012) *J. Geophys. Res.* 117, F02006, doi:10.1029/2011JF002248
Zdanowicz *et al.* (2015) *Sci. Tot. Environ.* 509-510: 104-114.
Zheng *et al.* (2006) *J. Environ. Monitor.* 8: 406-413.

Specific comments, and authors' responses:

Note: Many of the specific comments below are addressed in our discussion of the age models for the cores, given above. Therefore, where appropriate, we refer the reviewer to this discussion to avoid unnecessary repetition.

Page 2: L. 25: How deep was the core, did you reach bedrock. Is this the same 170.6 m long core as described by (Zheng et al., 2007) as D1999 core?

Yes it is. This information is now in Table 1 of the revised paper.

Page 3: L. 6: Surprising to see half of the core consumed for EC measurements and low resolution $\delta^{18}O$ analyses. What is the diameter of the cores?

To clarify: Few analyses were performed on the DV99.1 core *at the time it was drilled* (1999). Coring at the DV99.1 site had been done chiefly as a technical test for a drilling rig. The original core diameter was 9.8 cm. The topmost few meters were of very brittle firn and were not preserved at the time of drilling. Electrical conductivity (EC) measurements were done as a matter of routine using a hand-held device in the field, chiefly with the goal of detecting potential volcanic signatures. Sub-sections of the core wer e cut by band-saw and sent to the Univ. of Copenhagen for $\delta^{18}O$ analysis. This consumed about 1/3 of the core diameter. Later, in 2007, some archived cores were sampled at irregular depth intervals below 29 m by J. Zheng for trace metal analyses (see Zheng *et al.*, 2007; *Glob. Biogeochem. Cyc.* 21, GB2027, doi:10.1029/2006GB002897), and this consumed >1/2 of some parts of the remaining cores. Sampling for these trace metal analyses was done without an ice-core melter, and involved a lengthy decontamination procedure that used up a considerable volume of firn and ice for these sections, such that what remained of those sampled core sections for rBC/microparticle analysis was very limited.

L. 9: What is the reference for the initial age estimate?

See discussion of age models above. The initial age model development for the DV99.1 core is described in Kinnard *et al.* (2006) and Krachler *et al.* (2005), cited in the paper.

L. 10-11: Zheng et al., (2007) report that the core quality was good for the entire core D1999? Is this the same core? If so, which statement is correct? Why don't you add a table with all meta data for ice cores and analyses you discuss in your manuscript?

There was an error in the submitted manuscript on page 3, L8: The part of the DV99.1 archive core that was shipped to Curtin University for rBC analyses reached 48 m depth (not 38 m as was wrongly stated). This depth range was chosen based on the age model for the core to ensure that the rBC record thus produced would extend back to the early to mid-18th century. The uppermost 2.8 m of the DV99.1 core were made of very crumbly firn, and could not be preserved. Below this, the core was recovered in increments of length varying from 0.4 to 1.1 m (average 0.9 m for the part of the core considered in the present study). At depths greater than 48 m, some of the core archive pieces were fractured in many pieces inside the layflat bags.

A table with the metadata on ice cores and analyses was added to the revised manuscript, as suggested.

L.10: Why should unconsolidated snow not be useable for analyses? It is virtually impossible to contaminate with BC and analyses could have easily been performed with an SP2 on discrete samples.

The topmost 2.8 m of the core were not preserved at the time of drilling, as they were in poor condition. Hence they were simply not available for analysis. Concerning the physical state of the cores, see responses to previous three comments above. The reviewer's assertion that "it is virtually impossible to contaminate analyses with BC" is incorrect. BC aerosols are everywhere. Because BC has an atmospheric residence time on the order of days, the concentrations found in and on the polar ice caps are of course much lower than at other locations closer to sources. Extreme care is therefore still required for these analyses.

L12: When did the analysis take place? Over how many days, weeks, months? Did you observe sublimation on the ice surface after >15 years of storage?

Analyses were conducted between 6-11 December 2012. Despite being packed in thick, close-fitting lay-flat, sublimation/refrost was observed as is to be expected after >15 years of storage. The ice core pieces were therefore carefully cleaned with acid-cleaned ceramic knives and any loose refrozen material was scraped off prior to analysis. The core runs had also broken into several smaller pieces over time which were carefully measured and recorded. The ends of each core piece were also carefully cleaned to avoid contamination by particles. This work was carried out in a class 100 cold room.

L13: What was class 100? The cold room? The lab space?

See below.

L12-14: I am missing references and I have never heard of an Advanced Ultra-clean Environmental facility. Is this the first time you are performing this kind of analyses in this lab?

The name of the clean room facility changed from the Advanced Ultra-clean Environmental (ACE) facility to the Trace Research Clean Environmental facility (TRACE). A number of publications refer to the space as ACE and the newer publications as TRACE (see below). The facility consists of a large class 100 space containing multiple class 10 laboratory modules including a -20ºC 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). Ice core preparation was carried out in the walk-in freezer, while processing in the CFA system was conducted in the general lab class 100 space.

Tuohy *et al.* (2015) *J. Geophys. Res. Atmos.*, 120, 10,996–11,011, doi:10.1002/2015JD023293.
Burn-Nunes *et al.* (2011) *Cosmochim. Acta.* 75, 1-20, doi:10.1016/j.gca.2010.09.037.
Ellis *et al.* (2015) *Atmos. Meas. Tech.*, 8, 9, 3959-3969, doi:0.5194/amt-8-3959-2015.
Ellis *et al.* (2016) *Geophys. Res. Lett.*, 43(22),11875-11883, doi:10.1002/2016GL071042
Vallelonga *et al.* (2017) *Clim. Past.*, 13, 171-184, doi:10.5194/cp-13-171-2017.

L14: At which melt rates did you melt the ice? How do you assure the flowrate is constant? It must be difficult with the frequent change of sold ice lenses (40-60% on average) and soft firn. If the flowrate is not constant, how do you correct for this?

On each day of analysis, a log journal was created. Every piece of core was carefully measured in its length prior to analysis. During CFA, the time of each break between two ice core pieces was recorded, allowing us to adjust the rBC record of each piece based on the time-depth log. This is the same method that has been used for thousands of meters of ice core analysis in the USA at the Desert Research Institute in Reno Nevada and at other ice core analysis facilities within the USA and internationally. The flow rate to the nebulizer is controlled by oversupplying a <1 mL debubbling vessel with excess water allowing the instrument to maintain a very constant flow rate. Air bubbles from the ice core help to limit dispersion in the tubing up until the point that the ice core water reaches the debubbling vessel next to the BC instrumentation. The system is essential the same as described in McConnell *et al.* (2002) with the exception that the SP2 desolvation system replaces the ICP-MS.

L14-21: Provide a chart with the analytical setup of all instruments. Provide information on calibration (standard material, linearity, stability) and reproducibility of the results.

This has been added in the description of methods, discussion of uncertainties and in the paper's supplement.

L.17-18: These citations are all for a lab in the USA.

See responses to the four previous comments.

L.20: How does the microparticle content connect to your scientific problem? What is the motivation?

We decided to remove the microparticle data from the revised manuscript, and focus solely on the rBC data.

L. 24-25: Why did you not analyze these other aerosol species directly in DV99.1? There should be half of a core minus 2.5 x 2.5 cm of cross section left. This would allow you attribute with more confidence sources to biomass burning and coal burning. Comparisons to other ice cores drilled at different sites only allow you to compare some general trends. According to your age model you have but one common age marker between these ice-core records (the alleged 1783 signal), strong spatial gradients in accumulation caused by wind erosion and/or melting.

See discussion of age models above.

Page 4: L. 4-12: Is any of this age models published? If so, please add the citation and the timescale name for the ice cores, respectively. It appears 2 of 3 citations at the end of this section are based on Agassiz ice cap. I do not find any figure showing the signatures attributed to Laki and Katmai in Kinnard et al. (2006).

See discussion of age models above.

L. 4-12: Since your study is critically dependent on the correct identification of the two reference horizons 1783 and 1963, I expect to see all the data that was used for these attributions. It is very plausible that very large acidity in the Arctic were caused by the Laki eruption (Kekonen et al., 2005) but there may also other large acid layers recorded in the Arctic in e.g., 1765, 1815 (Wendl et al., 2015). Equally, the Arctic nuclear fallout signals are in general much broader (1954-1963, (Arienzo et al., 2016)) than described here. How sharp is your signal compared to these other ice cores? Maybe this could tell you something about potential redistribution of impurities caused by melting.

Most of these questions are addressed in our comments about the development of the age models (see above). The radioactive fallout signature in the DV98.3 core does not show strong evidence for post-depositional "smearing" due to melt (Pinglot *et al.*, 2003). However we do not have a corresponding radioactive profile at the DV99.1 coring site where the annual melt percentage is larger, so we can not use such information to quantify the possible effect of melt on ice-core impurities at the DV99.1 site.

We are aware that there are other plausible candidates for some of the SO_4^{2-} or ECM peaks seen in the DV98.3 and DV99.1 cores. The assignment of specific eruptions/dates to these peaks is of course presumptive in the absence of glass shards (a search done by S. Kuehn, Concord Univ., failed to produce any from these cores). The assignments are usually made in such a way

as to provide the greatest degree of coherence across cores and coring sites (for e.g., to synchronize Agassiz ice cap and Greenland cores; Vinther *et al.*, 2008, *J. Geophys. Res.* 113, D08115, doi:10.1029/2007JD009143), and also to produce depth-age models that are as smooth as possible (i.e., that do not, for example, require unrealistic changes in historical accumulation rates). It is the best that can be achieved in the absence of additional data to support these age assignments.

L. 15: Provide these EC measurements for the DV99.1 ice core. How reliable is this peak, if it was recorded in the fractured ice-core sections >38m. Was it reproduced by sulfate analyses?

As discussed above, neither SO_4^{2-}, nor any other major ions, were analyzed in the DV99.1 core.

L. 17: What accumulation rates to you get between year of drilling, 1963 and 1783 for each of the DV ice cores? Consider providing this information in supplement.

See discussion of age models above.

L. 24-26: Please show these common signatures from DV99.1, DV98.1, DV98.3

There is no core DV98.1. This was a typing error in the text. The SO_4^{2-} and EC signatures in the DV98.3 and DV99.1 cores are shown in the revised manuscript.

L. 26: What do you mean with adopted? How much depth-age models exist? Where are they published? Are there any isochrones between these age-models and ice cores?

See discussion of age models above.

L. 28: How much meters apart were DV98.3 and DV2000 drilled? Is it appropriate to use the same chronology for two different cores given that snow fall and snow conservation on summits are varying on very small spatial scales. I would only adopt a timescale for another ice core if this was supported by a number of isochrones.

See discussion of age models above.

L. 31: I doubt the true effective resolution of the measurements is at a mm scale. You may be recording data at a rate equivalent to mm in depth, but you need to account for the uncertainty in the depth registration and dispersion of the signals through mixing (Bigler et al., 2011).

This is probably correct, and the statement has been modified accordingly in the text. However since we subsequently average discrete measurements over depth intervals representing years to decades, the effect of the uncertainty in the specific depth registration of individual data points is negligible in the interpretation. We are not attempting to interpret features in the rBC record at sub-annual scales.

Page 5: L. 4-12: Add analytical uncertainties as well.

L. 6: (e.g. wind scouring, melt induced relocation). According to Kinnard et al. (2006) average melt rates in D99 are 50% after 1850 AD, which appears to me a significant factor that could modify the impurity records one way or the other.

See discussion of melt-percolation effects above.

L. 9-18: This approach assumes the layer thickness variation is the only source of uncertainty in estimating the age error. It assumes the Laki event is correctly attributed, and must take into account some prior knowledge of the snow accumulation rates and its variability. I don't see how you can estimate the variability "between reference layers of known age" without being able to count annual layers.

As we made clear in the submitted manuscript, when constructing estimates of the uncertainty for time-averaged ice-core parameters (rBC or other), we took into account multiple sources of error, not just the natural variability of the snow accumulation rate and its effect on dating. Dynamically-induced variations in the vertical strain rate over time at the coring site can also result in errors in the estimated ages, but we have no data for quantifying such effects over centuries. The density profiles in the DV98.3 and DV99.1 cores indicate that attenuation (layer-thinning) rates are very nearly linear over the range of depths of interest for this paper, so we have no basis for assuming important variations in vertical strain rate, such as those that might occur, for example, in the accumulation zone of a surging or tidewater-terminating mountain glacier.

The procedure for estimating the uncertainty in the core chronology between reference horizons of known or assumed age does not actually require that annual layers be identified. What we have done do is simulate, by a Monte Carlo procedure, how interannual stochastic variations in snow accumulation (with a plausible frequency spectrum) would cause the age-depth relationship to deviate from that predicted by either a constant accumulation rate model, or some other prescribed age model. By repeating the procedure thousands of times, a population of possible alternative age models is produced, and from these, an envelope of probability for the age of layers between reference horizons is constructed. Although this was not specified in the submitted manuscript (for brevity's sake), we also assigned, in this procedure, possible depth registration errors to the 1963 and/or 1783 age markers, and these errors were taken into account when building envelopes of age probabilities. The probbaility envelopes bracket, for each possible age, the depth interval within which the layer of corresponding age is most likely to be found (or the probable age interval that brackets each given depth). We then used these probabilities as input to a separate Monte Carlo simulation, in which we calculated, for each alternative age model, a resulting time-averaged data series (for example, or rBC). One issue that is not explicitly included in the procedure described above is the possible existence of discontinuities (hiatus) in the stratigraphy of the ice cores due to wind scouring. But since we allow for a broad range of possible variations in the accumulation rate, and we are only interested in the dominant features of the ice-core records at interdecadal scales, this is unlikely to have a large impact on our interpretation.

Note: To make Fig. 4 more easily readable, we removed, in the revised manuscript, the lines that represented the 95 % confidence limits which overcrowded the figure. For the rBC data, these are shown instead in the supplement to the revised manuscript.

Page 6: L. 17-18: Microparticle concentrations do not follow the same trend than nssS and Pb but have a clear step-function. On which observation do you base your attribution of "anthropogenic pollution"?

We removed the microparticle data from the revised manuscript, and focus solely on the rBC data.

L. 22: Such source attributions would strongly benefit of having all parameters analyzed on the same core.

Agreed, which is why we recommended, in our concluding comments, that this be done in a future ice-coring effort.

L. 23: Black carbon concentrations

Text has been changed.

Page 7: L. 12: Necessary not only legitimate

Text has been changed.

Page 8: L. 6-17: Are the sections in the ice with the increased melt layer occurrence believed to be the periods experiencing more melting? Or are they accumulating the meltwater (plus impurities) from the ice sections above? In other words: how deep does percolation go? Is there surface runoff carrying impurities away?

See discussion of melt-percolation effects above.

Given that DV is only 700 km away from NEEM and Humboldt ice cores and all ice cores agreeing on showing strong BC deposition in early 20th century I tend to believe the differences in BC deposition is not from differences in atmospheric burden, but from some aspect specific to the Devon ice cap. The low elevation and observed melt features appear to make a strong case that the impurities along the ice core may be subject to severe loss and/or redistribution in particular during warmer time periods (e.g. Arctic warming 1920-40s (Yamanouchi, 2011), which would smear and bias any atmospheric information.

There is a risk, in making such an argument, of assuming the answer. Our own analysis of air trajectories, presented in the paper, suggests that Devon ice cap is actually affected by a different mixture of aerosol sources than Greenland. In preparing this manuscript, we have tried to avoid making any presumptions about what the DV99.1 rBC record over the past two centuries *should look like*. We did not take it for granted that it should conform to what is observed in Greenland records. It is possible, as the reviewer suggests, that the DV99.1 record differs from the Greenland records due to post-depositional processes, and we acknowledged this possibility in the paper (see also discussion of melt-percolation effects above). But there are also reasons (described in the paper as well) to think that it may differ from Greenland records because of different aerosol source mixture and/or deposition history. Hence we can not simply dismiss the DV99.1 record on the grounds that it differs from those in Greenland. At present, this is the only ice-core record of rBC deposition available from the Canadian Arctic. Future efforts to duplicate it may prove it to be unreliable, or they may not. We present the DV99.1 rBC record for what it is, with its limitations and caveats, and offer possible competing explanations for why it should contrast with the Greenland records.

L. 18-28: Post-depositional coagulation moving BC sizes out of the detectable range also seems a very plausible explanation for reduced BC recovery during especially warm periods. Low reproducibility of replicate measurements when samples were subject to melting and freezing cycles is reported by several research groups performing BC analyses in ice and snow (apparent "loss" rates in the order of 50%); as a result performing BC analyses on samples that have been refrozen is strongly discouraged (see e.g. (Lim et al., 2014;Wendl et al., 2014)).

The ice-core samples used in this study were not subject to refreezing in the sense that they were not melted, then refrozen, prior to analysis. However the core itself contained melt features, which may have reduced the detection sensitivity of rBC particles, as we discussed. If this implies that any core containing substantial melt features is unsuitable for rBC analysis by the SP2 method, then similar rBC records that would be developed from Svalbard ice caps (for example), where annual mean temperatures are much higher than the Canadian High Arctic, should in the future be regarded as even less reliable than the DV99.1 record. But one way to establish if this is the case, or not, is to develop such records and compare them in order to establish their degree of coherence.

Page 9: L. 2-9: This may be true if you compared Devon Ice Cap with Central and Southern Greenland ice cores, but NEEM and Humboldt are just 700-800km away from Devon and are thought to have largely similar source regions for aerosols and precipitation (Zennaro et al., 2014).

See our response above to comment about page 8, L 6-17.

Page 10: L. 2-26: How meaningful is such a comparison given the low degrees of freedom (resulting from decadal data), dating uncertainties and the inability to differentiate industrial from BB BC in the Devon ice core? Are these correlation stables if you varied binning, removed the common declining trend over most of the 20th century?

We chose to remove the correlation maps and the corresponding part of the discussion (incl. Fig. 10) from the revised paper, as the correlations were weak, at best.

L. 29-31: This is not surprising; as you outline below: K+, NH4+ and BC have multiple sources and probably also different chemical properties making them more or less susceptible to melt-induced relocation.

The sentence was modified to express this more clearly.

Page 11: L. 2: Could these low numbers for the most recent time period indicate some loss from melting caused by the rapid warming of the Arctic? To my knowledge and supported by Figs. 5 and 6 concentrations of rBC lower than during the pre-industrial baseline are not recorded for any other ice-core in the Arctic.

The situation is not as unique as it seems: In the ACT2 record from southern Greenland (shown in our manuscript), average rBC levels in the first three decades of the 19th century (1800-1830) were lower than in the late 20th century (1960-2000). It is difficult to establish detailed comparisons because only annual averages of the arithmetic mean rBC concentration in Greenland cores have been reported. Comparing geometric mean concentrations would be more revealing. Net losses of water by runoff at the DV99.1 site are unlikely: see discussion of melt-percolation effects above. Also, in the 1960-1990 part of the core where the lowest rBC concentrations were measured, the frequency of ice layers was lower than in deeper core sections with higher rBC concentrations (see revised manuscript).

L. 15: Given the potential limitations from inadequate nebulization, potential loss and redistribution of impurities, I strongly doubt that this value is a realistic approximation of the true atmospheric BC influx.

We stressed in the revised text that our figures are likely lower-bound estimates.

L. 25: Note that you use the same abbreviation EC for both electrical conductivity and elemental carbon.

This has been corrected by avoiding EC to designate elemental carbon.

Page 12: L1-2: Does Humboldt show similar melt features than Devon Ice cap? The agreement between Humboldt and the other Greenland records (in both BC and nssS) seems very high.

This part of the text was removed to shorten and simplify section 4.4. of the manuscript. We are not aware of any published physical stratigraphic record from the Humboldt ice-coring site, or, for that matter, for many other Greenland cores in which rBC has been measured, so we can not comment on this aspect.

L9-12: None of the emission inventories or any ice core suggests that mean BC emissions from 1960-1990 were below preindustrial (i.e. before 1850) levels, as the Devon core seems to imply.

See response to comment about page 11, L2, above.

Figures:

Fig. 4: Extend the x-axis to include your only reference marker in 1783 AD. Units in panel b are missing and it is nssSO42-.

This Fig. 4 has been modified considerably to show the extended rBC record back to 1740, and also the 1783 marker in the DV98.3 SO_4^{2-} profile. The total SO_4^{2-} and nssSO_4^{2-} profiles in the DV98.3 are virtually identical over the part of the record considered here, so we have chosen to simply show the total SO_4^{2-} profile.

I do not see any signature related to the largest VEI 6 eruptions of Katmai, Krakatao, Tambora and 1809, but a huge SO4 signal around 1847 AD. Do you have any explanation? How do you know this is not from Laki 1783 or Tambora 1815?

The SO_4^{2-} peak at 1847 was the one that was ultimately assigned to Laki, as dicussed above. Unfortunately, we can not have absolute certainty concerning the identification of volcanic EC or SO_4^{2-} peaks since we do not have volcanic glass to confirm these assignments. Even if the SO_4^{2-} peak assigned to Laki is incorrectly identified and turned out to be from the 1809 or 1816 eruptions, this would have but a minor effect of the main features of the DV98.3 SO_4^{2-} record (see for e.g., figure in discussion of age models above).

How do you calculate K^+_{BB}?

The method that was employed was that of Legrand *et al.* (2016), as was specified in the submitted manuscript (p. 3): $[K^+]_{bb} = [K^+] - (0.038 \times [Na^+]) - (0.04 \times [Ca^{2+}])$. Legrand *et al.* (2016) *Clim. Past.* 12, 2033–2059, doi:10.5194/cp-12-2033-2016.

We have chosen not to show the NH_4^+ and K^+_{bb} profiles on the revised version of Fig. 4. These are, however, included these plots in the supplement.

Fig.4 and Fig.6: DV98.3 nssSO4 (panel b, Fig 4) appears to be different from nssS (Fig. 6), the latter is peaking in the 1960-1980s, the first starts to peak only after 1980. Which one is correct?

The discrepancy was due to a plotting error in one of the figures, and has been corrected.

Fig. S3: Check the lower panel. There should be only one y-value for a given depth value

Corrected in revised paper.

Historical black carbon deposition in the Canadian High Arctic: A >250-year long ice-core record from Devon Island

Christian M. Zdanowicz[1], Bernadette C. Proemse[2], Ross Edwards[3,4], Wang Feiteng[5], Chad M. Hogan[2], Christophe Kinnard[6] and David Fisher[7].

[1]Department of Earth Sciences, Uppsala University, Uppsala, 75646, Sweden

[2]School of Biological Sciences, University of Tasmania, Hobart, TAS7001, Australia

[3]Physics and Astronomy, Curtin University, Perth, WA6102, Australia

[4]Depart of Civil and Environmental Engineering, University of Wisconsin, Madison, WI, 53706, USA

[5]Cold and Arid Regions Environment and Engineering Research Institute, Chinese Academy of Sciences, Lanzhou, China

[6]Département des Sciences de l'Environnement, Université du Québec à Trois-Rivières, Trois-Rivières, G9A 5H7, QC, Canada

[7]Department of Earth Sciences, University of Ottawa, 120 University, Ottawa, K1N 6N5, ON, Canada

Correspondence to: Christian M. Zdanowicz (christian.zdanowicz@geo.uu.se)

Abstract.

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-covered surfaces, thus lowering their albedo. Modelling the atmospheric transport and deposition of BC to the Arctic is therefore important, and historical archives of BC accumulation in polar ice can help to validate such modelling efforts. Here we present a >250-year ice-core record of refractory BC (rBC) deposition on Devon ice cap, Canada, spanning the years 1735-1992, the first such record ever developed from the Canadian Arctic. The estimated mean deposition flux of rBC on Devon ice cap for 1963-1990 is 0.2 mg m^{-2} a^{-1}, which is at the low end of estimates from Greenland ice cores obtained by the same analytical method (~0.1-4 mg m^{-2} a^{-1}). The Devon ice cap rBC record also differs from Greenland records in that it shows only a modest increase in rBC 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 deposition of contaminants such as sulfate and Pb 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 be due to local factors such as melt-freeze cycles on Devon ice cap that may limit the detection sensitivity of rBC analyses in melt-impacted core samples, and wind scouring of winter snow at the coring site. Air back-trajectory analyses also suggest that Devon ice cap receives BC from more 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-receptor relationships. Findings from this study suggest that there could be a large variability in BC aerosol deposition across the Arctic region arising from different transport patterns. This variability needs to be accounted for when estimating the large-scale albedo lowering effect of BC deposition on Arctic snow/ice.

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).

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 deposition of BC aerosols in this region (Koch et al., 2011; Skeie et al., 2011; Lee et al., 2013; Jiao and Flanner, 2016). At present, simulated BC dispersion suffers from large biases, either positive or negative, compared with observational data on BC in Arctic air and snow (Jiao et al., 2014). Validating model simulations is difficult because of the scarcity of such observations across the Arctic. Direct monitoring of atmospheric BC is so far limited to a few decades and at a few stations (Hirdman et al., 2010; Gong et al., 2010), and geographic surveys of BC in snow and ice are rare 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 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 deposition in the Arctic region are only available from Greenland (McConnell et al., 2007, McConnell and Edwards, 2008; Zennaro et al., 2014; Sigl et al., 2015) and from Svalbard (Ruppel 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. The Devon ice cap BC record presents some striking differences from Greenland ice-core records of rBC developed by the same methods. We discuss the possible reasons for these differences, and consider the implications with respect to regional BC transport and deposition patterns in the Arctic region.

2 Study site

At latitude 75° N, Devon ice cap (14,400 km^2) 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 H_2O a^{-1} (see below).

3 Materials and methods

3.1 Core sampling and analyses

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 could not be preserved. At the time of coring, the solid-state DC electrical conductivity (EC) of the core was measured continuously using a hand-held system with parallel electrodes, as described in Zheng et al. (1998). The EC profiling started at a depth of 12.38 m, because section of cores above this were of brittle firn that provided inadequate electrode contact for the hand-held instrument. The core was shipped and stored in freezers at the GSC ice-core laboratory in Ottawa. There, it was sampled at 5- to 20-cm resolution for the determination of stable oxygen isotope ratios ($\delta^{18}O$) by mass spectrometry at the University of Copenhagen. Later, 57 discrete sub-samples from depths below 29 m were analyzed for lead (Pb) and other trace metals, as reported in Zheng et al. (2007). The remaining cores were stored frozen (-20ºC) inside sealed polyethylene bags, until archived core segments between 2.8 and 48 m depths were selected for this study and shipped, still frozen, to Curtin University in Australia for BC analyses. These 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 -20ºC 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-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 that the ice core melter head was made from aluminum. The method used to quantify BC in the ice core was essentially the same as used by others for the analysis of Greenland and Antarctic cores (Bisiaux et al., 2012; McConnell et al., 2007, McConnell and Edwards, 2008; Zennaro et al., 2014). Meltwater from the CFA system was aerosolized and desolvated with a U5000AT ultrasonic nebulizer (CETAC Technologies, Omaha, NE, USA) and injected into a single-particle intracavity laser-induced incandescence photometer (Schwarz et al. 2010; SP2, Droplet Measurement Technologies, Boulder, CO), which measured the mass concentration of BC particles in the meltwater flow. 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 concentration units of ng g^{-1}.

On each day of analysis, a log journal was created. Every piece of the DV99.1 core was carefully measured in its length 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 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 flow rate. External calibration of the SP2 nebulizer system was achieved using eight standards of 100% black carbon ink (Ebony MIS, EB6-4 K; **Fig. S2**) spanning a concentration range 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 SP2. Additional details and calibration curves (**Fig. S3**) are provided in the supplement, and potemtial sources of uncertanties in the results are discussed under section 3.3 below.

To compare the DV99.1 record of rBC with that of other 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 (Ca^{2+}), potassium (K^+) and ammonium (NH_4^+) data obtained from the top 85 m of the core, which had been sampled at 3- to 12-cm resolution. The non-sea salt fraction of sulfur (nssS) was estimated from Na^{2+} using the

mean surface seawater composition of Pilson (2012), and the biomass burning fraction (BB) of K^+ was estimated from Na^{2+} and Ca^{2+} as: $[K^+]_{BB} = [K^+] - (0.038 \times [Na^+]) - (0.04 \times [Ca^{2+}])$, following Legrand et al. (2016). The DV2000 core was drilled at the same site as the DV98.3 core, and was analyzed for lead (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.

3.2 Age models

Annual layers are not easily resolved in cores from Canadian Arctic ice caps, partly owing to relatively low $\dot{A}$, but also to the effects of wind and/or summer surface melt. Therefore, age models 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 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 approximate layer counting using $\delta^{18}O$ and glaciochemical data at shallow depths, and, at greater 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.], which is one of most recognizable historical volcanic signals recorded in EC and/or SO_4^{2-} records 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 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 section of the DV99.1 core used in the present study, and the last year in the record is 1992. The age model also gave an acceptable agreement between profiles of various measured parameters in the DV98.3 and DV99.1 cores (**Fig. S5-S6**). The DV2000 core was drilled at the same site as the DV98.3 core and used the same age model. The two cores were correlated using measurements in the DV2000 that allowed identification of the 1958 (16.5 m depth) and 1963 (13.5 m depth) radioactive layers (Krachler et al., 2005). The DV2000 core was estimated to extend back to 1842.

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 H_2O a^{-1}) which is lower than at the ice cap summit (~0.25-0.28 m H_2O a^{-1}) or at sites elsewhere in the accumulation zone (0.17-0.25 m H_2O 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, as also observed on parts of Agassiz ice cap (Fisher et al., 1983). This is supported by a comparison of the $\delta^{18}O$ measurements in the DV99.1 and DV98.3 cores, which shows that $\delta^{18}O$ variations in the DV99.1 core are truncated of their most negative ("coldest") values relative to the DV98.3 core (**Fig. S7**). An estimate of the amount of snow lost by wind scouring at the DV99.1 site can be made from the difference in the amplitude of the $\delta^{18}O$ data at the DV98.3 and DV99.1 sites, and from $\dot{A}$ at the DV98.3 site, following Fisher and Koerner (1988). The calculation suggests that ~40-45 % of the annual snow accumulation is removed by wind at this site, compared to the summit of Devon ice cap.

3.3 Quantifying uncertainties in the rBC record

Analyses of rBC in the DV99.1 core were performed at high depth resolution, producing ~55-80 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 age model. In this paper, annually-averaged figures are used for illustrative purposes only, as individual years can not be confidently resolved in the DV99.1 core. Down-core variations of rBC in the ice core are the result of a combination of processes, including temporal changes in 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). Additional uncertainties in the rBC data come from the age model of the ice core (**Fig. 2**), and from limitations of the analytical method.

The largest uncertainty with regards to the rBC analysis is due to the nebulization / desolvation step before the SP2 analysis. At the time of this study we had adopted nebulizer / desolvation systems used as a front end to inductively-coupled plasma mass spectrometers (ICP-MS). These systems are designed to deliver appropriate aerosol size distributions for analysis in the ICP-MS. Schwarz et al. (2012) and Wendl et al. (2014) report rBC size-dependent losses during nebulization / desolvation for several types of nebulizer desolvation systems. The study found that 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 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.

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 dating error of the Laki 1783 layer in the EC profile, and to interannual variations in the net accumulation rate at the ice-coring site. 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, with no signs of dynamically-induced changes in the vertical strain rate. For the 1783 layer, we assumed a possible dating error of ± 5 years, corresponding to a registration error of ~±1 m at the 42.6 m EC peak. The interannual variability in the accumulation rate was estimated from an array 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 Monte Carlo simulation in Matlab™ with 1000 realizations to compute confidence limits (CL) on the decadally-averaged rBC data. Briefly, a constrained random walk algorithm was used to estimate the probabilistic distribution of the true age at any depth in the core from the surface down to the Laki 1783 layer (Kinnard et al., 2006). Interannual variations in $\dot{A}$ were considered to behave as a stationary, autoregressive blue noise process with a lag-one serial autocorrelation coefficient 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 were computed, and 95 % CL were calculated for the geometric mean rBC concentration in each decade (**Fig. S8**). Expressed as a coefficient of variation (CV), the estimated uncertainty on the decadal rBC averages that arise from age model errors varies from 3 to 23 % (median 6 %), depending on the decade considered.

The spatial variability of BC deposition on Canadian Arctic ice caps is unknown. An estimate for Devon ice cap can be made from major ion analyses on shallow cores (Colgan and Sharp, 2008; **Fig. 1**). In these cores, the spatial coefficient of variation (CV) on the annual SO_4^{2-} deposition averages 42 % (range 17-100 %) over a period of ~40 years. Here, we make the assumption that deposition of rBC on Devon ice cap shares the same spatial variability as SO_4^{2-}, an aerosol species which, like BC but unlike others such as nitrate (NO_3^-), is not subject to re-emission from snow to air. While the spatial variability may be large on an annual basis, Monte Carlo simulations results show that averaging the rBC data over 10-year intervals reduces its effect on the geometric mean

rBC uncertainty to a few % (CV) in any decade (**Fig. S8**). The potential impact of post-depositional modifications in the rBC record is discussed under section 4.2 below.

4 Results and discussion

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 distribution of rBC concentrations is approximately log-normal (**Fig. S9**), and we therefore use both the arithmetic and geometric means (μ, μ_g), as descriptive metrics for these data. Over the entire core length, rBC concentrations average 1.8 ± 3.9 ng g^{-1} (μ_g = 0.8 ng g^{-1}) with a maximum of 74.0 ng g^{-1}. The mean rBC concentration is approximately constant between 42 and 15 m depths, and decreases gradually at shallower depths to reach ~1.0 ng g^{-1} (μ_g = 0.5 ng g^{-1}) in the uppermost meter of core. Concentrations below 42 m show a comparatively larger variability and a greater range of values (**Fig. S10**).

In Greenland cores, rBC deposition rose in the 1880s, peaked in the 1910s-20s, and decreased 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). 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 from the DV98.3 and DV2000 ice cores (**Fig. 4**) show that Devon ice cap also experienced increased atmospheric deposition of SO_4^{2-} and Pb and during the 20th century, peaking between the 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 large, sustained increase in rBC deposition concomitant with that of SO_4^{2-} or Pb. There is a modest rise in mean rBC concentrations from the early 1800s to the mid-20th century, but it is much more gradual and of lesser magnitude than the rBC rise observed in ice-core records from Greenland, although the relative timing and magnitude of these increases differ between core sites (**Fig. 5** and **6**). In the DV99.1 ice core, the highest mean rBC concentrations for the 20th century 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 comparable mean concentrations occur in the earliest part of the record, in the decade 1780-1990 (**Fig. S10**).

The DV99.1 rBC record also shows a pronounced decline in rBC deposition in the late 20th 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 DV99.1 chronology compared to that of well-dated Greenland cores. The DV99.1 mean rBC concentrations over the period 1960-1990 (μ = 0.6-1.0 ng g^{-1}; μ_g = 0.3-0.5 ng g^{-1}) are lower than in the early modern industrial period, in the early 19th century (μ = 1.0-3.0 ng g^{-1}; μ_g = 0.7-1.6 ng g^{-1}). The only Greenland ice core in which a similar situation occurs is from the ACT2 site (66°N, **Fig. 5**). Neither winter mass balance measurements, nor reconstructed interannual changes in $\dot{A}$ on Devon ice cap (Colgan and Sharp, 2008) show any sustained long-term trend since the early 1960s, and the decrease in rBC concentration in the DV99.1 core during this period can therefore not be ascribed to changing precipitation rates on the ice cap. It seems more likely that the decrease is at least in part due to a declining burden of atmospheric BC in the Canadian High Arctic since the 1960s (Gong et al., 2010). However, there are several methodological, site-specific and regional-scale factors that must be taken into account when interpreting the DV99.1 rBC record. These are discussed below.

4.2. Methodological and site-specific factors

Observations of atmospheric BC at Alert on Ellesmere Island (82° N, **Fig. 1**) show a seasonal cycle 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., 2010). Most BC deposition in snow is thought to occur in spring and summer, when increased cloudiness promotes in-cloud scavenging and wet deposition of the hydrophilic fraction of BC (Garrett et al., 2011; Browse et al., 2012; Shen et al., 2017). In the interior of the Greenland ice sheet, the 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 the core, where some seasonal $\delta^{18}O$ variations can be detected, there is no recognizable seasonal pattern of rBC concentration peaks (**Fig. S11**). This is likely the result of the combined effects of 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 20^{th} 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 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.,

2007). If the Canadian High Arctic was impacted by airborne BC pollution in a similar way, one would expect to find a marked increase in rBC concentrations in the DV99.1 core during the early 20th century, even if winter snow layers were scoured away by wind. To verify this, we performed 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 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 to year to produce a range of temporal variations comparable to, or lower than, that seen in the Greenland D4 core. Winter deposition peaks were then randomly truncated by 30-60 % (mean 45 %) 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 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 variation would still persist, and should be recognizable above the remaining interannual signal variance (**Fig. 7**). It therefore seems unlikely that wind scouring alone would completely obliterate this rBC signal in the DV99.1 record, not unless the amplitude of the seasonal cycle of atmospheric BC deposition on Devon ice cap is much lower than observed at Alert or in Greenland (Gong et al., 2010; Massling et al., 2015).

Unlike much of central Greenland, the summit of Devon ice cap is subject to partial melting 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 layers in core DV99.1 was measured by Fisher et al. (2012) as a proxy for past summer warmth. These data show that surface melt rates at the coring site increased abruptly in the mid-19th century following the end of the Little Ice Age cold interval, and have since averaged 22 % (median 19 %), 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 firn there is >60 m thick, so it is very unlikely that there is any net loss by runoff at this location: any meltwater produced in the summer must refreeze in the firn. However, even without net losses, one must consider whether meltwater percolation and refreezing could account for the limited variability 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 depends on the hydrophobicity of these particles, which is largely influenced by the presence or absence of surface coatings, for e.g., with SO_4^{2-} (Liu et al., 2011, 2013). Doherty et al. (2013) investigated the vertical redistribution of BC and other light-absorbing particles in snow and firn near Dye 2 (66° N; ~2100 m a.s.l.; **Fig. 5**) in a part of the Greenland ice sheet's percolation zone where melt layers >10 cm thick are now commonly found (de la Peña et al., 2015; Machguth et al., 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. 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 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., 2012). Therefore surface melt could mask some seasonal variations of rBC in the firn.

The depth at which meltwater could percolate in firn at the DV99.1 site is not known 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 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 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 lower mean annual surface temperature (-22°C, compared to ~-10 to -12 °C at Lomonosovfonna; W. van Pelt, pers. comm.), and the 10-m firn temperatures on Devon ice cap summit were, in 2012, < -15 °C (Bezeau et al., 2013), while those at Lomonosovfonna were within -2 to -3° of zero C in 1997 (van de Waal et al., 2002). Attempts were also made to quantify post-depositional deposition of ions and/or 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 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, conservative estimate of the maximum melt-induced relocation depth at the DV99.1 site for the time period of interest might therefore be 3 m (firn depth). With a mean accumulation rate of 0.16 m H_2O 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 rBC 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 concentrations in the DV99.1 core were measured by SP2, and the detection efficiency of this method for BC in liquid samples depends on the type of nebulizer used for inflow. As previously mentioned, Schwarz et al. (2012) and Wendl et al. (2014) have shown that the relative areosolization efficiency of rBC by the U5000AT ultrasonic nebulizer used in the analysis of the DV99.1 core drops rapidly for particles with a volume-equivalent diameter >500 nm (~ 10% efficiency at a volume-equivalent diameter of 600 nm). Coagulation and agglomeration is known to increase the 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 parts of the DV99.1 that contain icy layers (**Fig. 3**). 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**) certainly experience less or no summer surface melt, compared to Devon ice cap, and rBC 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 layer frequency at these sites are unpublished so this cannot be verified. While melt-refreezing may have contributed to mask some historical variations in atmospheric BC deposition at the DV99.1 site, it is uncertain if this alone can account for the low rBC concentrations in the DV99.1 core, when compared to Greenland records analyzed using the same methods. One conflicting observation is that the lowest rBC concentrations in the core are found in the uppermost 5 m, and this part of the core actually contains fewer ice layers than deeper sections (between 7-32 m) in which some of the highest rBC concentrations are measured (**Fig. 3**).

4.3 Regional-scale factors

Other reasons for the differences between the DV99.1 and Greenland rBC records (**Fig. 5** and **6**) may be found in the atmospheric transport paths that deliver BC to the Canadian High Arctic, relative to Greenland. Shindell et al. (2008) used multiple atmospheric transport models to investigate the sensitivity of near-surface airborne BC concentrations in the Arctic to regional

anthropogenic emissions. They found that Europe and North America likely contribute equally to 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 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 from all BC source regions (Shindell et al., 2008; their Fig. 9 and 10).

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 Europe as dominant, followed by North America. The summit of Devon ice cap is 1000 km further south and ~1.9 km higher, and could thus be affected by a different mix of BC source contributions 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 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., 2015). As input, we used meteorological fields of the NCEP-NCAR 50-year reanalysis product, which are available on a global 2.5 × 2.5° grid at 6-hourly temporal resolution (Kistler et al., 2001). Back-trajectories starting daily at 12:00 PM UTC were computed over the period 1948-1999. 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 in trajectory computations, and to the arrival height of trajectories (i.e., starting point of back-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 × 200 km resolution, following a methodology analog to that of Miller et al. (2002).

Results (**Fig. 8**) show that for 10-day transport periods, air parcels arriving at Greenland Summit are more commonly advected from the south-southwest than from other directions, and 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 Devon ice cap comes more frequently from the west-northwest, and transits over the Arctic Ocean, which agrees with findings from analyses of low-level air transport to Devon ice cap by Colgan 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 in the central or eastern parts of Eurasia.

Smoke plumes from forest or grassland fires, natural or provoked, can reach the Arctic and 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). Back-trajectory analyses of BB aerosols detected at Eureka on Ellesmere Island (80° N; **Fig. 1**) indicate, unsurprisingly, that boreal forest/grassland regions of Russia and Canada are the dominant source 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 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. 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 ($p < 0.05$) could be identified between the DV99.1 rBC record and the fire histories. If wildfire emissions contribute to rBC deposition on Devon ice cap, these contributions are either too small and/or mixed in the DV99.1 record to be correlated with variations in fire frequency or burned area in the source regions.

Aerosol species such as K^+ or NH_4^+ 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 NH_4^+ in the DV98.3 record (**Fig. S12**). Whatever contributions BB emissions make to $(K^+)_{BB}$ or NH_4^+ deposition on Devon ice cap, these do not covary directly with rBC deposition, possibly due to different post-depositional relocation of these impurities in the DV98.3 and DV99.1 cores, but also to mixing from multiple emission sources. For example, ammonia (NH_3) emissions from seabird colonies near Baffin Bay may be a larger regional source of NH_4^+ to Devon ice cap than distant wildfires (Wentworth et al., 2016).

4.4 Atmospheric BC deposition rates

In 90 % of the analyzed DV99.1 core, rBC concentrations are < 3 ng g^{-1}, and in the uppermost section of the core (depths 3-4 m), they are mostly ≤1 ng g^{-1}. These concentrations are very low

compared with the 8-14 ng g^{-1} reported by Doherty et al. (2010) for seasonal snow sampled across the Canadian Arctic in 2009. Part of the apparent discrepancy may be due to differences in analytical methods: The BC concentrations in snow reported by Doherty et al. (2010) were 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 the DV99.1 core may underestimate actual deposition due to wind scouring of winter snow. Atmospheric BC deposition over the summit region of Devon ice cap could also be lower than near sea level, where most of Doherty et al.'s (2010) samples were obtained, because most of the ice cap's accumulation area (≥ ~1150 m a.s.l.) is above the typical altitude range of low-level Arctic stratocumulus cloud decks which promote aerosol scavenging (Browse et al., 2012).

Despite 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 measurements of rBC concentrations in the DV99.1 core for 1963-1990, and data on spatial and temporal variations of $\dot{A}$ from Colgan and Sharp (2008) and from winter mass balance surveys carried out over the ice cap since the early 1960s. The period 1963-1990 was selected because the 1963 radioactive layer in Devon ice cap firn provides a reference level to constrain estimates of $\dot{A}$ (Colgan and Sharp, 2008). Our calculations yield a mean F_{rBC} of 0.2 ± 0.1 mg m^{-2} a^{-1}. If μ_g, rather than μ, is used to estimate average rBC concentrations, the estimated F_{rBC} is only slightly lower (0.1 mg m^{-2} a^{-1}). And if the measured concentrations of rBC are underestimated by 20-40 % due to selective wind scouring of winter snow layers and/or to inadequate detection by the SP2 instrument, the adjusted figures for F_{rBC} are only slightly higher, ranging from 0.2 to 0.3 mg m^{-2} a^{-1}.

These estimates are at the low end of calculated F_{rBC} in Greenland cores over the same period, which vary from ~0.1 to ~4 mg m^{-2} a^{-1} (Lee et al., 2013). They are also much lower than historical fluxes of elemental carbon in the Norwegian Arctic inferred from a Svalbard ice core, which range from ~3 to nearly 40 mg m^{-2} a^{-1} between 1960 and 2004 (Ruppel et al., 2014; see **Fig. 5** for location). Overall, rBC or elemental carbon concentrations in Arctic firn and ice cores increase with mean $\dot{A}$ (**Fig. S13**), likely reflecting the amount of precipitation scavenging in different geographic sectors (Garrett et al., 2011; Browse et al., 2012). Hence the low F_{rBC} at the DV99.1 site may be partly due to the low $\dot{A}$ on Devon ice cap (0.14-0.25 m a^{-1}; Colgan and Sharp, 2008), notwithstanding the effect of other factors.

5 Summary and conclusions

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, and it supplements existing ice-core records of rBC or elemental carbon from Greenland and Svalbard. The DV99.1 record differs from Greenland records developed by the same analytical methods in that it only shows a very modest and gradual rise in rBC deposition through the 19th and early 20th century, unlike most Greenland ice cores, in which there is large, well-defined rise in the 1880-90s, peaking in the 1910s. This rise was attributed to BC emissions from coal combustion, which also emitted SO_2 and trace metals such as Pb (McConnell et al., 2007). Ice cores from Devon ice cap (DV98.3, DV2000) show that the deposition of SO_4^{2-} and Pb also increased there during the 20th century, but the DV99.1 core shows no concomitant rise in rBC.

We suggest that differences between the DV99.1 and Greenland rBC records are due to a combination of methodological, site-specific and regional-scale factors. The site DV99.1 coring site is subject to summer melt-freeze cycles, and this may lead to underestimation of true rBC 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 rBC deposition recorded in the core. Air back-trajectory analyses suggest that, compared to Greenland, rBC deposition on Devon ice cap is less sensitive to BC emissions from the North Atlantic sector (eastern North 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 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 source-receptor relationships. If correct, this interpretation implies that historical trends in BC deposition over the Arctic, and the resulting albedo-climate forcing, are likely subject to large spatial variability, even over the relatively short distance between Devon Island and Greenland. This variability, which is probably linked to differences in BC aerosol transport patterns and atmospheric residence time (Bauer et al. 2013), must be accounted for when attempting to model 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 developed from firn or ice cores drilled on small ice caps or glaciers, where local topographic and climatological effects can impact on the preservation of atmospheric signals, when compared with

513 the central regions of large ice sheets. A limitation of our study stems from the fact that the DV99.1
514 record of rBC deposition is from a different site than records of other aerosol species (SO_4^{2-}, Pb)
515 previously obtained from Devon ice cap summit. To verify our interpretation of the DV99.1 rBC
516 record, a new core should be drilled from the ice cap summit, or from another ice cap less affected
517 by wind scouring and melt-freeze effects (e.g., on northern Ellesmere Island), and on which co-
518 registered measurements of rBC and other aerosols could be made. This is particularly important
519 when one considers the large amount of spatial variability inherent in ice core records, even in
520 areas of optimal preservation (e.g., Gfeller et al., 2014).

521 **Acknowledgements**

522 The recovery of the DV99.1 ice core was supported by the Geological Survey of Canada and the
523 Polar Continental Shelf Project (Natural Resources Canada). Analysis of the core was funded by
524 Curtin University (Curtin Research Fellowship to R. Edwards, # RES-SE-DAP-AW-47679-1), and
525 by an Australian Endeavour Research Fellowship (# ERF_PDR_3051_2012) awarded to B.C.
526 Proemse. N. Schaffer (Univ. of Ottawa) assisted with some of the illustrations.

527 **References**

528 AMAP. *Arctic Climate Issues 2015: Short-Lived Climate Pollutants: Summary for Policy-*
529 *Makers*. Oslo: Arctic Monitoring and Assessment Programme (AMAP), 16 pp., 2015.
530 AMAP. *The Impact of Black Carbon on Arctic Climate.* Oslo: Arctic Monitoring and
531 Assessment Programme (AMAP), 72 pp., 2011.
532 Ashbaugh, L.L., Malm, W.C., and Sadeh, W.Z.: A residence time probability analysis of
533 sulfur concentrations at Grand Canyon National Park: Atmos. Environ.,19, 1263–1270,
534 doi:10.1016/0004-6981(85)90256-2, 1985.
535 Bauer, S.E., Bausch, A., Makarenko, L., Tsigaridis, K., Xu, B., Edwards, R., Bisiaux, M. and
536 McConnell, J. : Historical and future black carbon deposition on the three ice caps: Ice-
537 core measurements and model simulations from 1850 to 2100. J. Geophys. Res. Atmos.,
538 118, 7948–7961, doi:10.1002/jgrd.50612, 2013.
539 Bezeau, P., Sharp,M., Burgess, D. and Gascon, G.: Firn profile changes in response to extreme

21st-century melting at Devon Ice Cap, Nunavut, Canada. J. Glaciol. 59, doi:10.3189/2013JoG12J208, 2013.

Bisiaux, M.M., Edwards, R., McConnell, J.R., Curran, M. A. J., Van Ommen, T.D., Smith, A.M., Neumann, T.A., Pasteris, D.R., Penner, J.E., and Taylor, K.: Changes in black carbon deposition to Antarctica from two high-resolution ice core records, 1850–2000 AD. Atmos. Chem. Phys., 12, 4107–4115, doi:10.5194/acp-12-4107-2012, 2012.

Bond, T.C., Doherty, S.J., Fahey, D.W., Forster, P.M., Berntsen, T., DeAngelo, B.J., Flanner, M.G., Ghan, S., Kärcher, B., Koch, D., Kinne, S., Kondo, Y., Quinn, P.K., Sarofim, M.C., Schultz, M.G., Schulz, M., Venkataraman, C., Zhang, H., Zhang, S., Bellouin, N., Guttikunda, S. K., Hopke, P.K., Jacobson, M.Z., Kaiser, J.W., Klimont, Z., Lohmann, U., Schwarz, J.P., Shindell, D., Storelvmo, T., Warren, S.G. and Zender, C.S.: Bounding the role of black carbon in the climate system: A scientific assessment. J. Geophys. Res. Atmos., 118, 5380–5552, doi:10.1002/jgrd.50171, 2013.

Bond, T. C., Bhardwaj, E., Dong, R., Jogani, R., Jung, S. K., Roden, C., Streets, D. G., and Trautmann, N. M.: Historical emissions of black and organic carbon aerosol from energy-related combustion, 1850–2000, Global Biogeochem. Cy., 21, Gb2018, doi:10.1029/2006gb002840, 2007.

Boon, S., Burgess, D.O., Koerner, R.M. and Sharp, M. J.: Forty-seven years of research on the Devon Island ice cap, Arctic Canada. Arctic, 63, 13–29, doi:10.14430/arctic643,2010.

Browse, J., Carslaw, K.S., Arnold, S.R., Pringle, K. and Boucher, O.: The scavenging processes controlling the seasonal cycle in Arctic sulphate and black carbon aerosol. Atmos. Chem. Phys., 12, 6775–6798, doi:10.5194/acp-12-6775-2012, 2012.

Buchardt, S.L., Clausen, H.B., Vinther, B.M. and Dahl-Jensen, D.: Investigating the past and recent ^{18}O-accumulation relationship seen in Greenland ice cores. Clim. Past, 8, 2053–2059, doi:10.5194/cp-8-2053-2012, 2012.

Burn-Nunes, L.J., Vallelonga, P., Loss, R.D., Burton, G.R., Moy, A., Curran, M., Hong, S., Smith, A.M., Edwards, R., Morgan, V.I. and Rosman, K.J.R.: Seasonal variability in the input of lead, barium and indium to Law Dome, Antarctica. Geochim. Cosmochim. Acta. 75, 1-20, doi:10.1016/j.gca.2010.09.037, 2011.

Cheng, M.D.: Geolocating Russian sources for Arctic black carbon. Atmos. Environ., 92, 398–410, doi:10.1016/j.atmosenv.2014.04.031, 2014.

571 Colgan, W. and Sharp, M.: Combined oceanic and atmospheric influences on net accumulation
572 on Devon Ice Cap, Nunavut, Canada. J. Glaciol., 54, 28–40,
573 doi:10.3189/002214308784409044, 2008.
574 Dansgaard, W. and Johnsen, S.J.: A flow model and a time scale for the ice core from Camp
575 Century, Greenland. J. Glaciol., 8, 215–223, doi:10.1017/S0022143000031208, 1969.
576 de la Peña, S., Howat, I.M., Nienow, P.W., van den Broeke, M.R., Mosley-Thompson, E.,
577 Price, S.F., Mair, D., Noël, B. and Sole, A.J.: Changes in the firn structure of the western
578 Greenland Ice Sheet caused by recent warming. Cryosphere, 9, 1203–1211, doi:
579 10.5194/tc-9-1203-2015, 2015.
580 Doherty, S.J., Grenfell, T.C., Forsström, S., Hegg, D.L., Brandt, R.E. and Warren, S.G.:
581 Observed vertical redistribution of black carbon and other insoluble light-absorbing
582 particles in melting snow. J. Geophys. Res. Atmos., 118, 5553–5569,
583 doi:10.1002/jgrd.50235, 2013.
584 Doherty, S. J., Warren, S. G., Grenfell, T. C., Clarke, A. D. and Brandt, R. E.: Light-
585 absorbing impurities in Arctic snow. Atmos. Chem. Phys., 10, 11,647–11,680,
586 doi:10.5194/acp-10-11647-2010, 2010.
587 Draxler, R.R. and Hess, G.D.: *Description of the HYSPLIT 4 modeling system.* NOAA
588 Technical Memorandum ARL-224. Air Resources Laboratory, Silver Spring, Maryland,
589 USA, 27 p., 2014.
590 Ellis, A., Edwards, R., Saunders, M., Chakrabarty, R.K., Subramanian, R., Van Riessen, A.,
591 Smith, A.M., Lambrinidis, D., Nunes, L.J., Vallelonga, P. and Goodwin, I.D.:
592 Characterizing black carbon in rain and ice cores using coupled tangential flow filtration
593 and transmission electron microscopy. Atmos. Meas. Tech., 8, 9, 3959-3969,
594 doi:0.5194/amt- 8-3959-2015, 2015.
595 Ellis, A., Edwards, R., Saunders, M., Chakrabarty, R.K., Subramanian, R., Timms, N.E., van
596 Riessen, A., Smith, A.M., Lambrinidis, D., Nunes, L.J. and Vallelonga, P.: Individual
597 particle morphology, coatings, and impurities of black carbon aerosols in Antarctic ice and
598 tropical rainfall. Geophysical Research Letters, 43(22),11875-11883,
599 doi:10.1002/2016GL071042, 2016.

Fisher, D. A. and Koerner, R. M.: The effects of wind on $\delta^{18}O$ and accumulation give an inferred record of seasonal amplitude from the Agassiz Ice Cap, Ellesmere Island, Canada. Ann. Glaciol., 10, 34–37, doi:10.1017/S0260305500004122, 1988.

Fisher, D.A., Zheng, J., Burgess, D., Zdanowicz, C., Kinnard, C.: Sharp, M. and Bourgeois, J. Recent melt rates of Canadian Arctic ice caps are the highest in four millennia. Global Planet. Change, 84–85, 3–7, doi:10.1016/j.gloplacha.2011.06.005, 2012.

Fisher, D.A., Reeh, N. and Clausen, H.B.: Stratigraphic noise in time series derived from ice cores. Ann. Glaciol., **7**, 76–83, doi:10.1017/S0260305500005942, 1985.

Fisher, D. A., Koerner, R. M., Paterson, W. S. B., Dansgaard, W., Gundestrup, N. and Reeh, N.: Effect of wind scouring on climatic records from ice-core oxygen-isotope profiles. Nature, 301, 205–209, doi:10.1038/301205a0, 1983.

Garrett, T.J., Brattström, S., Sharma, S., Worthy, D.E.J., and Novelli, P.: The role of scavenging in the seasonal transport of black carbon and sulfate to the Arctic. Geophys. Res. Lett., 38, L16805, doi:10.1029/2011GL048221, 2011.

Gascon, G., Sharp, M., Burgess, D., Bezeau, P. and Bush, A.B.G.: Changes in accumulation-area firn stratigraphy and meltwater flow during a period of climate warming: Devon Ice Cap, Nunavut, Canada. J. Geophys. Res. 118, 2380–2391, doi:10.1002/2013JF002838, 2013.

Gfeller, G., Fischer, H., Bigler, M., Schüpbach, S., Leuenberger, D. and Mini, O.: Representativeness and seasonality of major ion records derived from NEEM firn cores. Cryosphere, 8, 1855–1870, doi:10.5194/tc-8-1855-2014, 2014.

Giradin, M.P.: Interannual to decadal changes in area burned in Canada from 1781 to 1982 and the relationship to Northern Hemisphere land temperatures. Global Ecol. Biogeogr., 16, 557–566, doi:10.1111/j.1466-8238.2007.00321.x, 2007.

Girardin, M. and Sauchyn, D.: Three centuries of annual area burned variability in northwestern North America inferred from tree rings. Holocene, 18, 205–214, doi: 10.1177/0959683607086759, 2008.

Girardin, M.P., Bergeron, Y., Tardif, J.C., Gauthier, S., Flannigan, M.D. and Mudelsee, M.: 229-year dendroclimatic-inferred record of forest fire activity for the Boreal Shield of Canada. Int. J. Wildland Fire, 15, 375–388, doi:10.1071/WF05065, 2006.

Gong, S. L., Zhao,T. L., Sharma, S., Toom-Sauntry, D., Lavoué, D., Zhang, X. B., Leaitch, W. R.

631 and Barrie, L. A.: Identification of trends and interannual variability of sulfate and
632 black carbon in the Canadian High Arctic: 1981–2007. J. Geophys. Res., 115,
633 doi:10.1029/2009JD012943, 2010.
634 Goto-Azuma, K. and Koerner, R.M.: Ice core studies of anthropogenic sulfate and nitrate
635 trends in the Arctic. J. Geophys. Res., 206, D5, 4959–69, doi:10.1029/2000JD900635,
636 2001.
637 Goto-Azuma, K., Koerner, R.M. and Fisher, D.A.: An ice-core record over the last two centuries
638 from Penny Ice Cap, Baffin Island, Canada. Ann. Glaciol. 35, 29-25, 2002.
639 Grumet, N. S., Wake, C. P., Zielinski, G. A., Fisher, D. A., Koerner, R.M. and Jacobs, J. D.:
640 Preservation of glaciochemical time-series in snow and ice from the Penny Ice Cap, Baffin
641 Island. Geophys. Res. Lett. 25, 357-360, 1998.
642 Hirdman, D., Burkhart, J.F., Sodemann, H., Eckhardt, S., Jefferson, A., Quinn, P.K., Sharma, S.,
643 Ström, J. and Stohl, A.: Long-term trends of black carbon and sulphate aerosol in the
644 Arctic: changes in atmospheric transport and source region emissions. Atmos. Chem.
645 Phys., 10, 9351–9368, doi:10.5194/acp-10-9351-2010, 2010.
646 Huang, L., Gong, S. L., Sharma, S., Lavoué, D. and Jia1, C. Q.: A trajectory analysis of
647 atmospheric transport of black carbon aerosols to Canadian high Arctic in winter and
648 spring (1990–2005). Atmos. Chem. Phys., 10, 5065–5073,
649 doi:10.5194/acp-10-5065-2010, 2010.
650 Jiao C. and Flanner, M.G.: Changing black carbon transport to the Arctic from present day to the
651 end of 21st century. J. Geophys. Res. Atmos., 121, 4734–4750,
652 doi:10.1002/2015JD023964, 2016.
653 Jiao, C., Flanner, M.G., Balkanski, Y., Bauer, S.E., Bellouin, N., Berntsen, T.K., Bian, H.,
654 Carslaw, K.S., Chin, M., De Luca, N., Diehl, T., Ghan, S.J., Iversen, T., Kirkevåg, A.,
655 Koch, D., Liu, X., Mann, G.W., Penner, J.E., Pitari, G., Schulz, M., Seland, Ø., Skeie,
656 R.B., Steenrod, S.D., Stier, P., Takemura, T., Tsigaridis, K., van Noije, T., Yun, Y., and
657 Zhang, K.: An AeroCom assessment of black carbon in Arctic snow and sea ice. Atmos.
658 Chem. Phys., 14, 2399–2417, doi:10.5194/acp-14-2399-2014, 2014.
659 Kassomenos, P., Vardoulakis, S., Borge, R., Lumbreras, J., Papaloukas, C. and Karakitsios, S.:

660 Comparison of statistical clustering techniques for the classification of modelled
661 atmospheric trajectories. Theor. Appl. Climatol., 102, 1–12, doi:10.1007/s00704-009-
662 0233-7, 2010.
663 Kekonen, T., Moore, J., Paavo Perämäki, P., Mulvaney, R., Isaksson, E., Pohjola, V. and van de
664 Wal, R.S.W.: The 800 year long ion record from the Lomonosovfonna (Svalbard) ice
665 core. J. Geophys. Res. 110, D07304, doi:10.1029/2004JD005223, 2005.
666 Kinnard, C., Zdanowicz, C.M., Fisher, D.A., Wake, C.P. Calibration of an ice-core
667 glaciochemical (sea-salt) record with sea-ice variability in the Canadian Arctic. Ann.
668 Glaciol., 44, 383–390, doi:10.3189/172756406781811349, 2006.
669 Kistler, R., Kalnay, E., Collins, W., Saha, S., White, G., Woollen, J., Chelliah, M., Ebisuzaki,
670 W., Kanamitsu, M., Kousky, V., Van Den Dool, H., Jenne, R. and Fiorino, M.: The
671 NCEP-NCAR 50-year reanalysis: Monthly means CD-ROM and documentation. B. Am.
672 Meteorol. Soc., 82, 247-267, doi:10.1175/1520-
673 0477(2001)082<0247:TNNYRM>2.3.CO;2, 2001.
674 Koch, K., Bauer, S.E., Del Genio, A., Faluvegi, G., McConnell, J.R., Menon, S., Miller, R.L.,
675 Rind, D., Ruedy, R., Schmidt, G.A. and Shindell, D.: Coupled aerosol-chemistry–climate
676 twentieth-century transient model investigation: Trends in short-lived species and climate
677 responses. J. Climate, 24, 2693–2714, doi: 10.1175/2011JCLI3582.1, 2011.
678 Krachler, M., Zheng, J., Koerner, R., Zdanowicz, C., Fisher, D. and Shotyk, W.: Increasing
679 atmospheric antimony contamination in the northern hemisphere: snow and ice evidence
680 from Devon Island, Arctic Canada. J. Environ. Monitor. 7, 1169–1176, 2005.
681 Lamarque, J.F., Bond, T.C., Eyring, V., Granier, C., Heil, A., Klimont, Z., Lee, D., Liousse, C.,
682 Mieville, A., Owen, B., Schultz, M.G., Shindell, D., Smith, S.J., Stehfest, E.,Van
683 Aardenne, J., Cooper, O.R., Kainuma, M., Mahowald, N., McConnell, J.R., Naik, V.,
684 Riahi, R. and van Vuuren, D.P.: Historical (1850–2000) gridded anthropogenic and
685 biomass burning emissions of reactive gases and aerosols: methodology and application.
686 Atmos. Chem. Phys., 10, 7017–7039, doi:10.5194/acp-10-7017-2010, 2010.
687 Lee, Y.H., Lamarque, J.F., Flanner, M.G., Jiao, C., Shindell, D.T., Berntsen, T., Bisiaux,
688 M.M., Cao, J., Collins, W.J., Curran, M., Edwards, R., Faluvegi, G., Ghan, S., Horowitz,
689 L.W., McConnell, J.R., Ming, J., Myhre, G., Nagashima, T., Naik, V., Rumbold, S.T.,
690 Skeie, R.B., Sudo, K., Takemura, T., Thevenon, F., Xu, B. and Yoon, J.-H.: Evaluation of

preindustrial to present-day black carbon and its albedo forcing from Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP). Atmos. Chem. Phys., 13, 2607–2634, doi:10.5194/acp-13-2607-2013, 2013.

Legrand, M., McConnell, J. Fischer, H., Wolff, E. W., Preunkert, S., Arienzo, M., Nathan Chellman, N., Leuenberger, D., Maselli, O., Place, P., Sigl, M., Schüpbach, S. and Flannigan, M.: Boreal fire records in Northern Hemisphere ice cores: a review. Clim. Past., 12, 2033–2059, doi:10.5194/cp-12-2033-2016, 2016.

Liu, D., Allan, J., Whitehead, J., Young, D., Flynn, M., Coel, H., McFiggans, G., Fleming, Z.L. and Bandy, B.: Ambient black carbon particle hygroscopic properties controlled by mixing state and composition. Atmos. Chem. Phys., 13, 2015–2029, doi:10.5194/acp-13-2015-2013, 2013.

Liu, J., Fan, S., Horowitz, L.W. and Levy, H.: Evaluation of factors controlling long-range transport of black carbon to the Arctic. J. Geophys. Res., 116, D04307, doi:10.1029/2010JD015145, 2011.

Machguth, H., MacFerrin, M., van As, D., Box, J.E., Charalampidis, C., Colgan, W., Fausto, R.S., Meijer, H.A.J., Mosley-Thompson, E. and van deWal, R.S.W.: Greenland meltwater storage in firn limited by near-surface ice formation. Nat. Clim. Change, 6, doi:10.1038/NCLIMATE2899, 2016.

Massling, A., Nielsen, I. E., Kristensen, D., Christensen, J. H., Sørensen, L. L., Jensen, B., Nguyen, Q. T., Nøjgaard, J. K., Glasius, M. and Skov, H.: Atmospheric black carbon and sulfate concentrations in Northeast Greenland. Atmos. Chem. Phys., 15, 9681–9692, doi:10.5194/acp-15-9681-2015, 2015.

McConnell, J. R.: New directions: Historical black carbon and other ice core aerosol records in the Arctic for GCM evaluation. Atmos. Environ., 44, 2665–2666, 10.1016/j.atmosenv.2010.04.004, 2010.

McConnell, J. R. and Edwards, R.: Coal burning leaves toxic heavy metal legacy in the Arctic. P. Natl. Acad. Sci. USA, 105, 12,140–12,144, doi:10.1073/pnas.0803564105, 2008.

McConnell, J. R., Edwards, R., Kok, G. L., Flanner, M. G., Zender, C. S., Saltzman, E. S., Banta, J. R., Pasteris, D. R., Carter, M. M., and Kahl, J.D.: 20th-century industrial black carbon emissions altered Arctic climate forcing. Science, 317, 1381–1384, doi:10.1126/science.1144856, 2007.

McConnell, J. R., Lamorey, G. W., Lambert, S. W., Taylor, K. C. (2002). Continuous ice-core chemical analyses using inductively coupled plasma mass spectrometry. Environ. Sci. & Technol., 36(1), 7-11, doi:10.1021/es011088z, 2002.

Miller, J.E., Kahl, J.D.W., Heller, F. and Harris, J.M.: A three-dimensional residence-time analysis of potential summertime atmospheric transport to Summit, Greenland. Ann. Glaciol., 35, 403–408, doi:10.3189/172756402781816663, 2002.

Mouillot, F. and Field, C. B.: Fire history and the global carbon budget: a 1×1° fire history reconstruction for the 20th century. Glob. Change Biol., 11,398–11,420, doi:10.1111/j.1365-2486.2005.00920.x, 2005.

Novakov, T., Ramanathan, V., Hansen, J.E., Kirchstetter, T.W., Sato, M., Sinton, J.E. and Sathaye, J.A.: Large historical changes of fossil-fuel black carbon aerosols. Geophys. Res. Lett., 30, 1324, doi:10.1029/2002GL016345, 2003.

Paris, J.-D., Stohl, A., Nédélec, P., Arshinov, M. Yu., Panchenko, M.V., Shmargunov, V.P., Law, K.S., Belan, B.D. and Ciais, P.: Wildfire smoke in the Siberian Arctic in summer: source characterization and plume evolution from airborne measurements. Atmos. Chem. Phys., 9, 9315–9327, doi:10.5194/acp-9-9315-2009, 2009.

Petzold, A., Ogren, J.A., Fiebig, M., Laj, P., Li, S.-M., Baltensperger, U., Holzer-Popp, T., Kinne, S., Pappalardo, G., Sugimoto, N., Wehrli, C., Wiedensohler, A. and Zhang, X.-Y.: Recommendations for reporting “black carbon” measurements. Atmos. Chem. Phys., 13, 8365–8379, doi:10.5194/acp-13-8365-2013, 2013.

Pilson, M. E. O.: *An Introduction to the Chemistry of the Sea*, 2nd edition. Cambridge: Cambridge University Press, 533 pp., 2012.

Pinglot, J.F., Vaikmäe, R.A., Kamiyama, K, Igarashi, M., Fritzsche, D., Wilhelms, F., Koerner, R., Henderson, L., Isaksson, E., Winther, J.-G., van de Wal, R.S.W., Fournier, M., Bouisset, P. and Meijer, H.A.J.: Ice cores from Arctic sub-polar glaciers: chronology and post-depositional processes deduced from radioactivity measurements. J. Glaciol. 49, 149-158, doi:10.3189/172756503781830944, 2013.

Quennehen, B., Schwarzenboeck, A., Matsuki, A., Burkhart, J.F., Stohl, A., Ancellet, G. and Law, K.S.: Anthropogenic and forest fire pollution aerosol transported to the Arctic: observations from the POLARCAT-France spring campaign. Atmos. Chem. Phys., 12, 6437–6454, doi:10.5194/acp-12-6437-2012, 2012.

753 Quinn, P.K., Bates, T.S., Baum, E., Doubleday, N., Fiore, A.M., Flanner, M., Fridlind, A.,
754 Garrett, T.J., Koch, D., Menon, S., Shindell, D., Stohl, A. and Warren, S.G.: Short-lived
755 pollutants in the Arctic: their climate impact and possible mitigation strategies. Atmos.
756 Chem. Phys., 8, 1723–1735, doi:10.5194/acp-8-1723-2008, 2008.
757 Ruppel, M.M., Isaksson, I., Ström, J., Beaudon, E., Svensson, J., Pedersen, C.A. and Korhola,
758 A.: Increase in elemental carbon values between 1970 and 2004 observed in a 300-year ice
759 core from Holtedahlfonna (Svalbard). Atmos. Chem. Phys., 14, 11,447–11,460,
760 doi:10.5194/acp-14-11447-2014, 2014.
761 Ruth, U., Wagenbach, D., Steffensen, J. P. and Bigler, M.: Continuous record of microparticle
762 concentration and size distribution in the central Greenland NGRIP ice core during the last
763 glacial period. J. Geophys. Res., 108, 1–12, doi:10.1029/2002JD002376, 2003.
764 Schwarz, J.P., Gao, R.S., Perring, A.E., Spackman, J.R. and Fahey, D.W.: Black carbon aerosol
765 size in snow. Sci. Rep., 3, 1356, doi:10.1038/srep01356, 2013.
766 Schwarz, J. P., Doherty, S. J., Li, F., Ruggiero, S. T., Tanner, C.E., Perring, A. E., Gao, R. S.,
767 and Fahey, D. W.: Assessing single particle soot photometer and integrating sphere /
768 integrating sandwich spectrophotometer measurement techniques for quantifying black
769 carbon concentration in snow. Atmos. Meas. Tech., 5, 2581–2592, doi:10.5194/amt-5-
770 2581-2012, 2012.
771 Schwarz, J.P., Spackman, J.R., Gao, R.S., Perring, A.E., Cross, E., Onasch, T.B., Ahern, A.,
772 Wrobel, W., Davidovits, P., Olfert, J., Dubey, M.K., Mazzoleni, C., and Fahey, D.W.: The
773 detection efficiency of the single particle soot photometer. Aerosol Sci. Tech., 44, 612–
774 628, doi:10.1080/02786826.2010.481298, 2010.
775 Sharma, S., Andrews, E., Barrie, L. A., Ogren, J. A. and Lavoué, D.: Variations and sources of
776 the equivalent black carbon in the High Arctic revealed by long-term observations at
777 Alert and Barrow: 1989–2003. J. Geophys. Res., 111, D14208,
778 doi:10.1029/2005JD006581, 2006.
779 Shen, Z., Ming, Y., Horowitz, L.W., Ramaswamy, V. and Lin, M.: On the seasonality of
780 Arctic black carbon. J. Climate, 30, 4429-4441, doi:1 0.1175/JCLI-D-16-0580.1, 2017.
781 Shindell, D.T., Chin, N., Dentener, F., Doherty, R.M., Faluvegi, G., Fiore, A.M., Hess, P.,
782 Koch, D.M., MacKenzie, I.A., Sanderson, M.G., Schultz, M.G., Schulz, M., Stevenson,
783 D.S., Teich, H., Textor, C., Wild, O., Bergman, D.J., Bey, I., Bian, H., Cuvelier, C.,

784 Duncan, B.N., Folberth, G., Horowitz, L.W., Jonson, J., Kaminski, J.W., Marmer, E.,
785 Park, R., Pringle, K.J., Szopa, S., Takemura, T., Zeng, G., Keating, T.J. and Zuber, A.: A
786 multi-model assessment of pollution transport to the Arctic. Atmos. Chem. Phys., 8,
787 5353–5372, doi: 10.5194/acp-8-5353-2008, 2008.
788 Shotyk, W., Zheng, J., Krachler, M., Zdanowicz, C., Koerner, R. and Fisher, D.: Predominance of
789 industrial Pb in recent snow (1994–2004) and ice (1842–1996) from Devon Island, Arctic
790 Canada. Geophys. Res. Lett., 32, doi:10.1029/2005GL023860, 2005.
791 Simoneit, B.R.T. :Biomass burning: A review of organic tracers for smoke from incomplete
792 combustion. Appl. Geochem., 17: 129–162, doi:10.1016/S0883-2927(01)00061-0, 2002.
793 Skeie, R.B., Berntsen, T., Myhre, G., Pedersen, C.A., Ström, J., Gerland, S. and Ogren, J.A.:
794 Black carbon in the atmosphere and snow, from pre-industrial times until present. Atmos.
795 Chem. Phys., 11, 6809–6836, doi:10.5194/acp-11-6809-2011, 2011.
796 Sigl, M., Winstrup, M., McConnell, J.R., Welten, K.C., Plunkett, G., Ludlow, F., Büntgen, U.,
797 Caffee, M., Chellman, N., Dahl-Jensen, D., Kipfstuhl, S., Kostick, C., Maselli, O.J.,
798 Mekhaldi, F., Mulvaney, R., Muscheler, R., Pasteris, D.R., Pilcher, J.R., Salzer, M.,
799 Schüpbach, S., Steffensen, J.P., Vinther, B.M. and Woodruff, T.E. : Timing and climate
800 forcing of volcanic eruptions for the past 2,500 years. Nature, 523, 543–549,
801 doi:10.1038/nature14565, 2015.
802 Stein, A. F., Draxler, R. R., Rolph, G. D., Stunder, B. J. B., Cohen, M. D. and Ngan, F.: NOAA's
803 HYSPLIT atmospheric transport and dispersion modeling system. B. Am. Meteorol. Soc.,
804 96, 2050-2077, doi:10.1175/BAMS-D-14-00110.1, 2015.
805 Stohl, A., Andrews, E., Burkhart, J.F., Forster, C., Herber, A., Hoch, S.W., Kowal, D., Lunder,
806 C., Mefford, T., Ogren, J.A., Sharma, S., Spichtinger, N., Stebel, K., Stone, R., Ström,
807 J.,Tørseth, K., Wehrli, C. and Yttri, K.E.: Pan-Arctic enhancements of light absorbing
808 aerosol concentrations due to North American boreal forest fires during summer 2004. J.
809 Geophys. Res., 111, doi:10.1029/2006JD007216, 2006.
810 Su, L., Yuan, Z., Fung, J.C.H. and Lau, A.K.H.: A comparison of HYSPLIT backward
811 trajectories generated from two GDAS datasets. Sci. Total Environ., 506–507, 527–537,
812 doi:10.1016/j.scitotenv.2014.11.072, 2015.

Tuohy A, Bertler N, Neff P, Edwards R, Emanuelsson D, Beers T, Mayewski P.: Transport and deposition of heavy metals in the Ross Sea Region, Antarctica. J. Geophys. Res. Atmos., 120, 10,996–11,011, doi:10.1002/2015JD023293, 2015.

Vallelonga, P., Maffezzoli, N., Moy, A.D., Curran, M.A., Vance, T.R., Edwards, R., Hughes, G., Barker, E., Spreen, G., Saiz-Lopez, A. and Corella, J.P.: Sea-ice-related halogen enrichment at Law Dome, coastal East Antarctica. Clim. Past, 13, 171-184, doi:10.5194/cp-13-171-2017, 2017.

van de Wal, R.S., Mulvaney, R., Isaksson, E., Moore, J.C., Pinglot, J.-F., Pohjola, V.A. and Thomassen, M.P.A.: Reconstruction of the historical temperature trend from measurements in a medium-length borehole on the Lomonosovfonna plateau, Svalbard. Ann. Glaciol. 35: 371-378, doi:10.3189/172756402781816979, 2002.

Vega, C.P., Pohjola, V.A., Beaudon, E., Claremar, B., van Pelt, W.J.J. Pettersson, R., Isaksson, E., Martma, T., Schwikowski, M. and Bøggild, C.E.: A synthetic ice core approach to estimate ion relocation in an ice field site experiencing periodical melt: a case study on Lomonosovfonna, Svalbard. The Cryosphere, 10, 961-976, doi:10.5194/tc-10-961-2016, 2016.

Viatte, C., Strong, K., Hannigan., J., Nussbaumer, E., Emmons, L.K., Conway, S., Paton-Walsh, C., Hartley, J., J. Benmergui, J. and Lin, J.: Identifying fire plumes in the Arctic with tropospheric FTIR measurements and transport models. Atmos. Chem. Phys., 15, 2227–2246, doi.org/10.5194/acp-15-2227-2015, 2015.

Warneke, C., Bahreini, R., Brioude, J., Brock, C.A., de Gouw, A. Fahey, D.W., Froyd, K.D., Holloway, J.S., Middlebrook, A., Miller, L., Montzka, S., Murphy, D.M., Peischl, J., Ryerson, T.B., Schwarz, J.P., Spackman, J.R. and Veres. P.: Biomass burning in Siberia and Kazakhstan as an important source for haze over the Alaskan Arctic in April 2008. J. Geophys. Res., 36, doi:10.1029/2008GL036194, 2009.

Wendl, I.A., Menking, J.A., Färber, R., Gysel, M., Kaspari, S.D., Laborde, M.J.G. and Schwikowski, M. : Optimized method for black carbon analysis in ice and snow using the Single Particle Soot Photometer. Atmos. Measur. Tech., 7, 2667–2681, doi:10.5194/amt-7-2667-2014, 2014.

Wentworth, G.R., Murphy, J.G., Croft, B., Martin, R.V., Pierce, J.R., Côté, J.-S., Courchesne, I., Tremblay, J.-É., Gagnon, J., Thomas, J.L., Sharma, S., Toon-Saundry, D., Chivulescu,

A., Levasseur, M. and Abbatt, J.P.D.: Ammonia in the summertime Arctic marine boundary layer: sources, sinks, and implications. Atmos. Chem. Phys., 16, 1937–1953, doi:10.5194/acp-16-1937-2016, 2016.

Zdanowicz, C., Smetny-Sowa, A., Fisher, D., Schaffer, N., Copland, L. and Eley, J.: Summer melt rates on Penny ice cap, Baffin Island: Past and recent trends, and implications for regional climate. J. Geophys. Res. Earth Surf. 117, F02006, doi:10.1029/2011JF002248, 2012.

Zdanowicz, C., Zielinski, G. and Wake, C.: Characteristics of modern atmospheric dust deposition in snow on Penny Ice Cap, Baffin Island, Arctic Canada, Tellus 50B: 506-520, doi:10.3402/tellusb.v50i5.16234, 1998.

Zennaro, P., Kehrwald, N., McConnell, J.R., Schüpbach, S., Maselli, O.J., Marlon, J., Vallelonga, P., Leuenberger, D., Zangrando, R., Spolaor, A., Borrotti, M., Barbaro, E., Gambaro, A. and Barbante, C.: Fire in ice: two millennia of boreal forest fire history from the Greenland NEEM ice core. Clim. Past, 10, 1905–1924, doi:10.5194/cp-10-1905-2014, 2014.

Zheng, J., Shotyk, W., Krachler, M. and Fisher, D.A.: A 15,800-year record of atmospheric lead deposition on the Devon Island Ice Cap, Nunavut, Canada: Natural and anthropogenic enrichments, isotopic composition, and predominant sources. Glob. Biogeochem. Cyc. 21, GB2027, doi:10.1029/2006GB002897, 2007.

Zheng, J., Kudo. A., Fisher. D., Blake. E. and Gerasimoff. M.: Solid electrical conductivity (ECM) from four Agassiz ice cores, Ellesmere Island NWT, Canada: high-resolution signal and noise over the last millennium and low resolution over the Holocene. Holocene, 8, 413–421, doi: 10.1191/095968398676187747, 1998.

Core	Lat. (N)	Lon. (W)	Max. depth (m)	Approx. elevation (m a.s.l.)	MAAT (°C)	Annual accum. (m H_2O)	Parameters measured
DV98.3	75.34°	82.14°	302	1930	-12	0.25-0.28	$\delta^{18}O$, radioactivity, major ions, trace metals
DV99.1	75.32°	81.64°	169	1903	–	0.16	$\delta^{18}O$, melt features, EC, rBC
DV2000	75.34°	82.14°	64	1930	-12	0.25-0.28	$\delta^{18}O$, 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.

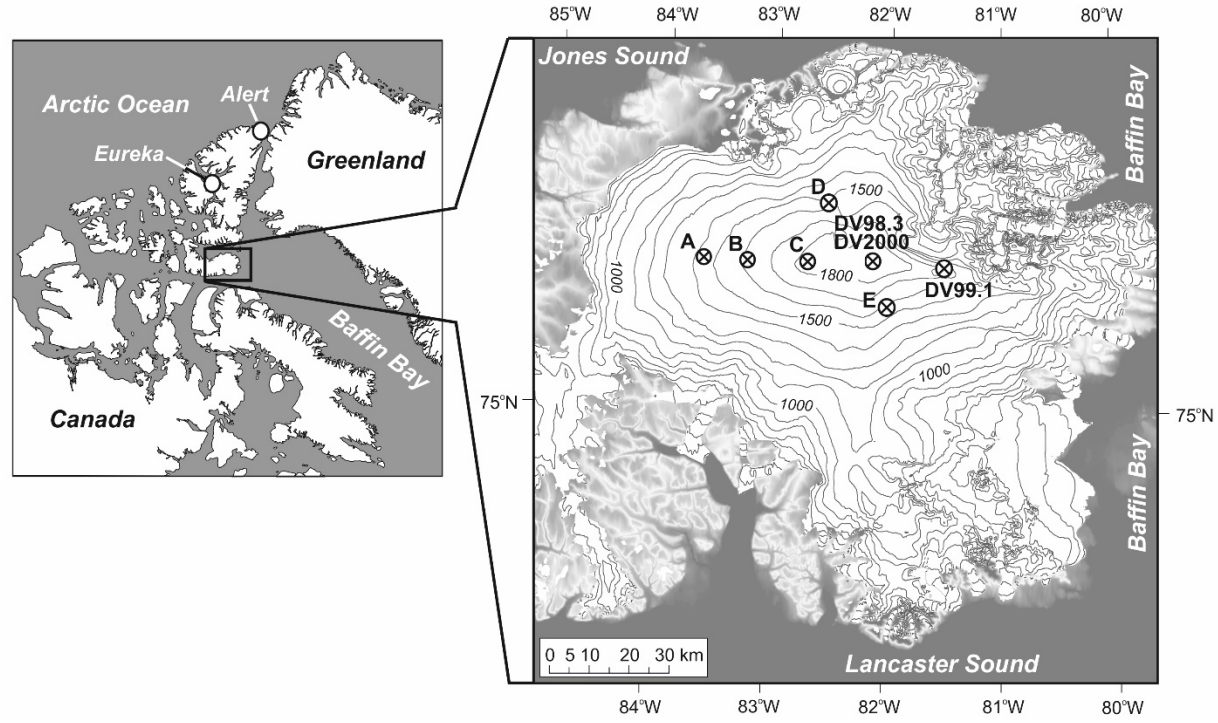


Fig. 1. Location map of the Canadian Arctic Archipelago (left), with enlargement of Devon ice (right). The location of the various ice core sites mentioned in the text are shown. Sites A to E refer to the shallow core array of Colgan and Sharp (2008). Elevation contours on Devon ice cap are spaced at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

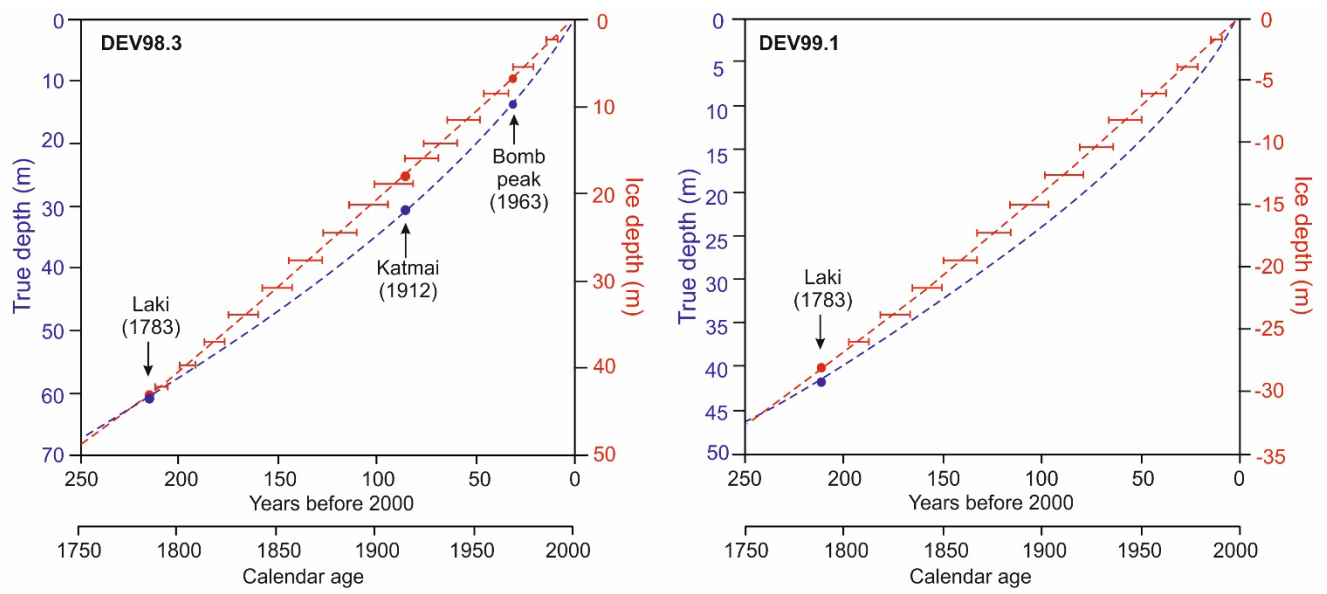


Fig. 2. Age models for parts of the DV98.3 and DV99.1 cores from Devon ice cap. The error bars on the age curve relative to ice-equivalent depths (red) bracket the 95 % confidence interval on the estimated age for discrete depths, as established from Monte Carlo simulations (see text).

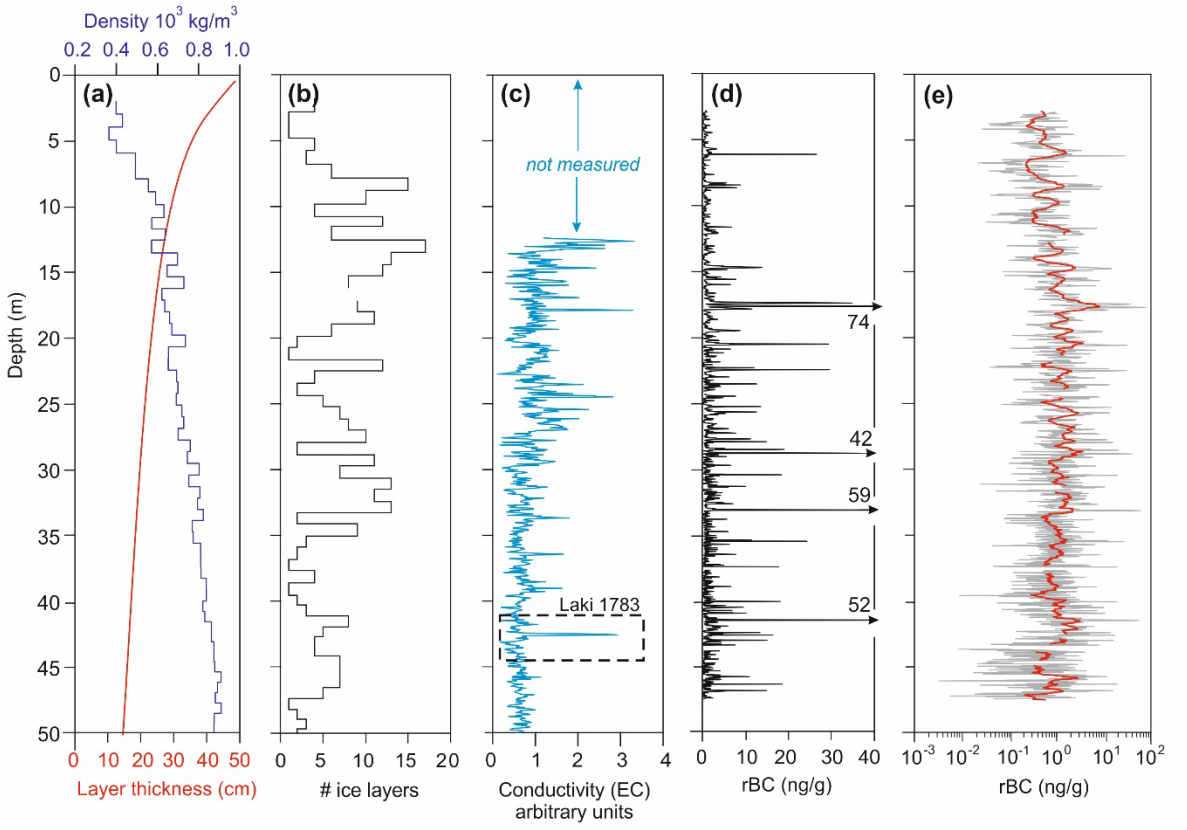


Fig. 3. Profiles of physical properties and rBC in the top 48-50 m of the DV99.1 ice core. **(a)** Firn density and estimated mean annual layer thickness. **(b)** Frequency of discrete ice layers (>3 mm thick) per core section. **(c)** Solid-state electrical conductivity (EC) of the core from 12.8 to 50 m depth. 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 (~1-m) moving average.

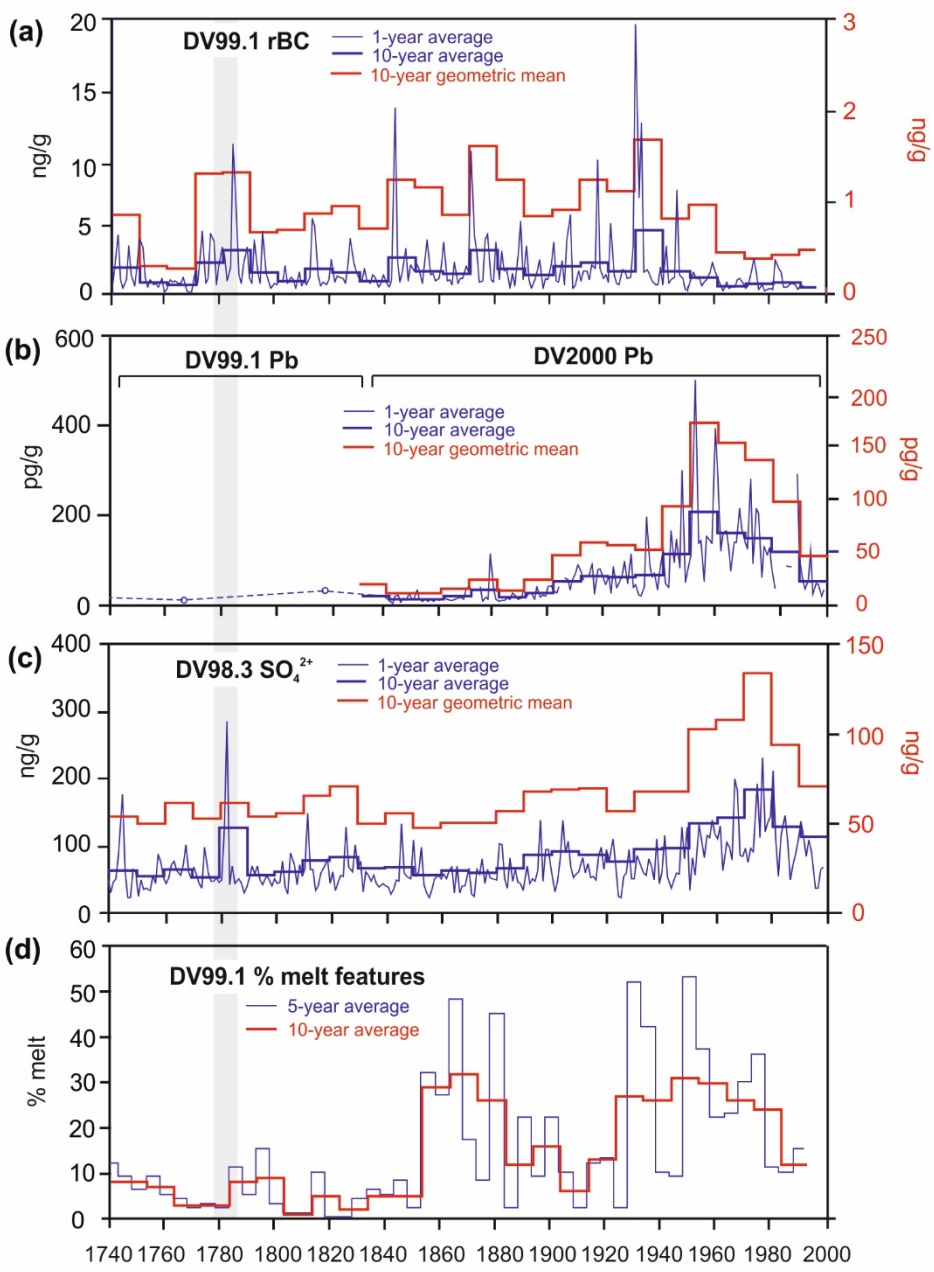


Fig. 4. Environmental changes on Devon ice cap, 1740-1999, recorded in three cores from the summit region (DV98.3, DV99.1 and DV2000). **(a)** rBC concentrations in the DV99.1 core; **(b)** Pb concentrations in the DV99.1 core (~1740-1840) and DV2000 core (1840-2000); **(c)** SO_4^{2-} in the DV98.3 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 SO_4^{2-} data from Kinnard et al. (2006), and the melt feature data from Fisher et al. (2012).

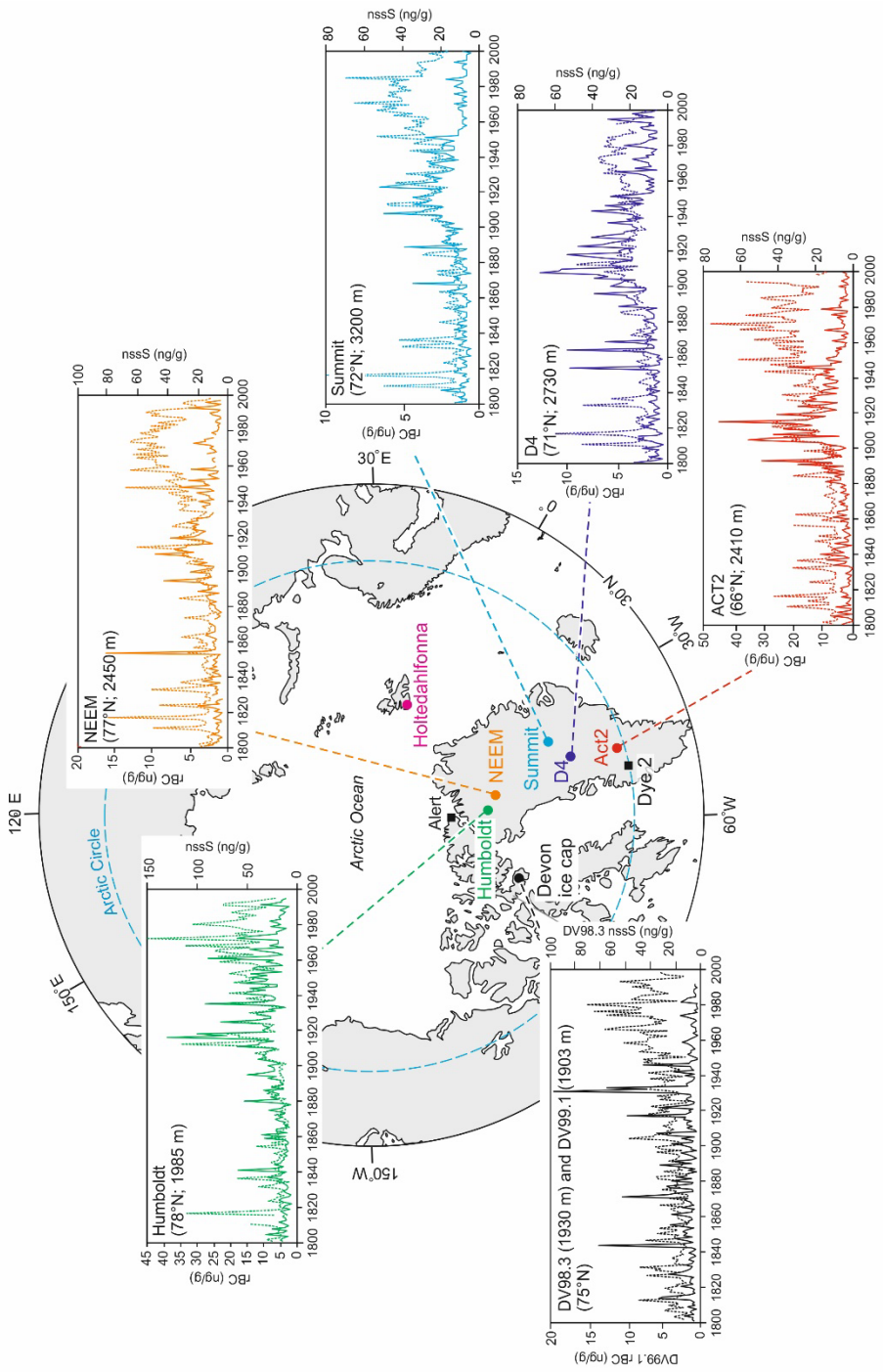


Fig. 5. The record of atmospheric rBC and non-sea salt sulfur (nssS) deposition on Devon ice cap over the period 1800-2000 compared with similar records developed at various sites in Greenland by identical or nearly-identical methods. Full lines are rBC; stippled lines are nssS. Data from Summit, D4, 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.

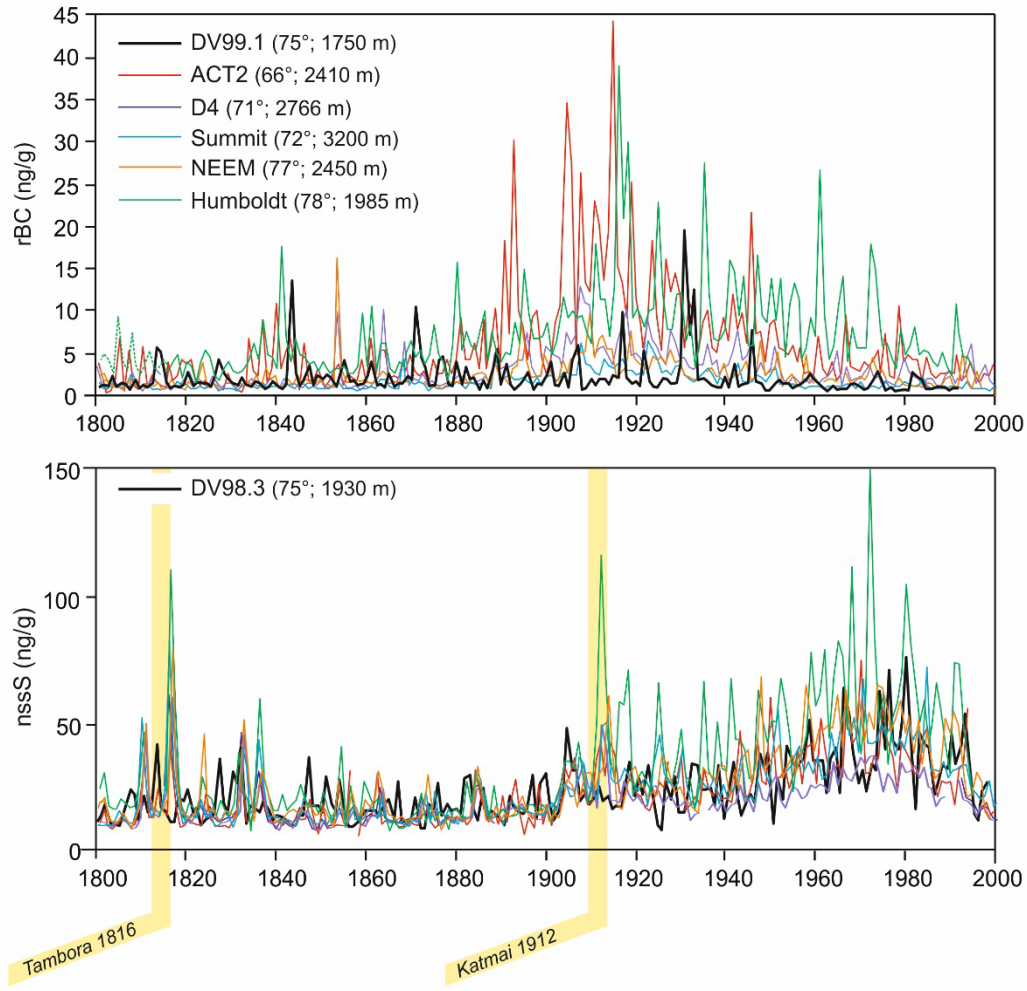


Fig. 6. (a) The DV99.1 record of atmospheric rBC deposition since 1800 compared with other records developed from sites in Greenland identified in **Fig. 5**. All records are presented in one-year averages. **(b)** As in (a) but for records of non-sea salt sulfur (nssS). Two volcanic eruption isochron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

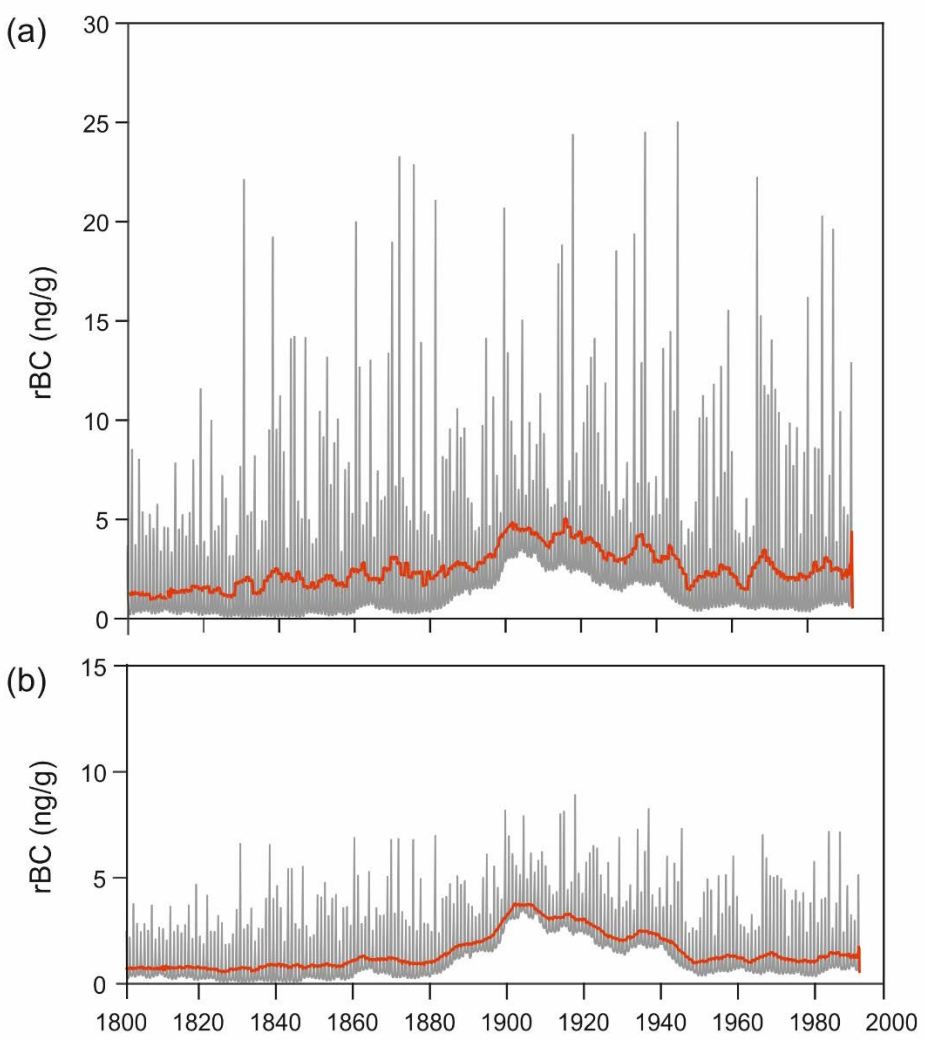


Fig. 7. Simulation of the effects of snow wind scouring on the preservation of an anthropogenic signal of rBC deposition in a synthetic ice-core times series of rBC spanning the period 1800-1990. **(a)** The synthetic series, with a pseudo-seasonal cycle superimposed on the interdecadal baseline trend 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.

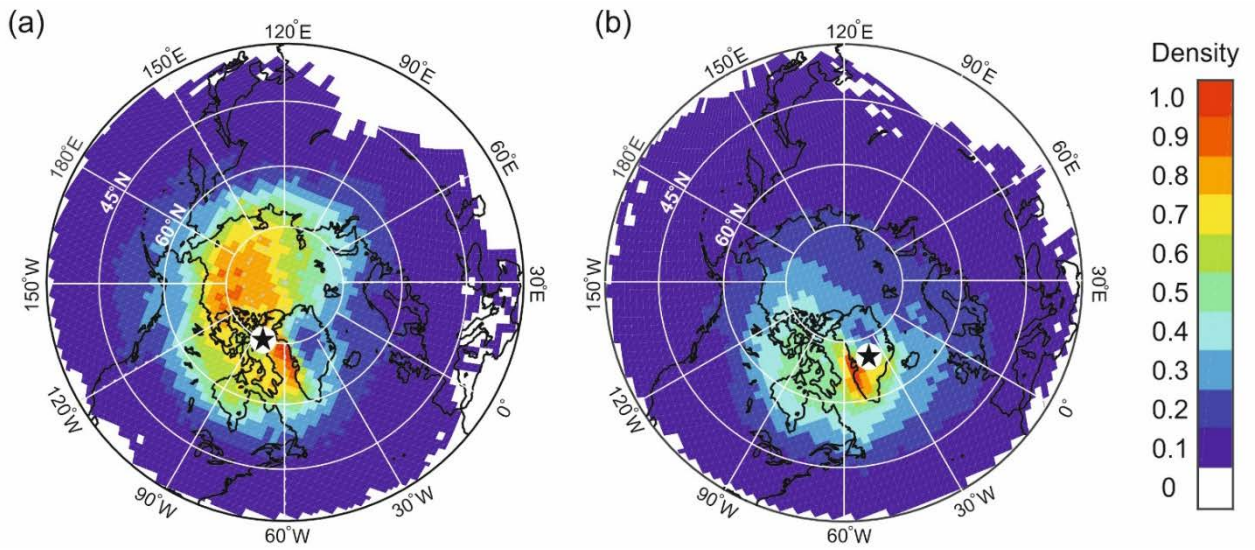


Fig. 8. Maps of residence time probability for air arriving at **(a)** Devon ice cap and **(b)** Summit, Greenland over the period 1948-1999, computed using HYSPLIT4. Air residence probability densities were normalized to a scale of 0-1, and were spatially detrended by multiplying the original residence 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.

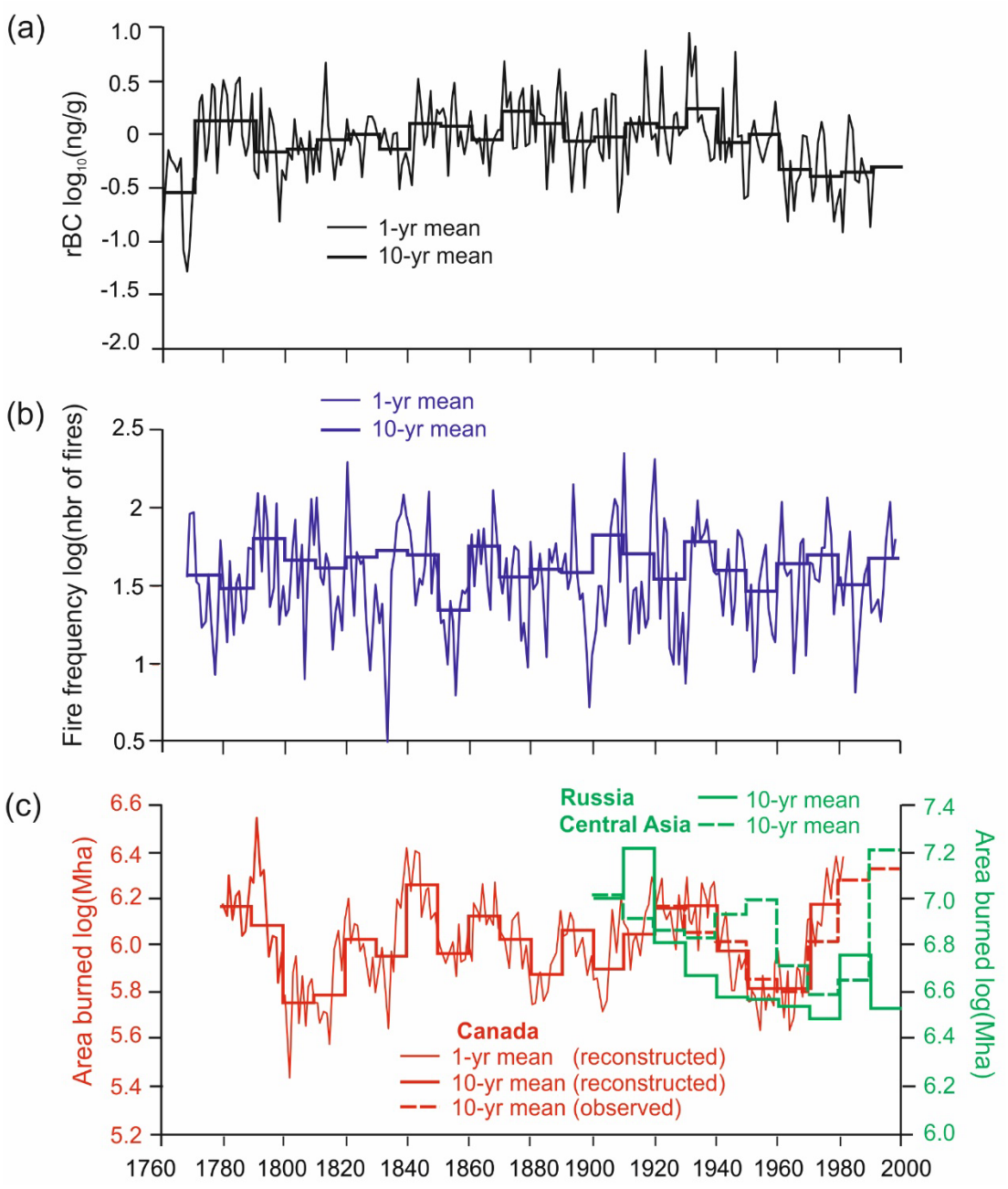


Fig. 9. (a) Historical variations in rBC concentration in the DV99.1 core, 1760-1992, compared with reconstructed historical trends in **(b)** fire frequency in the eastern boreal forest region of Canada (Girardin *et al.*, 2006), and **(c)** burned area across northern Canada (Girardin, 2007) and in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

Supplement of

Historical black carbon deposition in the Canadian High Arctic: A >250-year long ice-core record from Devon Island

Christian M. Zdanowicz et al.
Correspondence to: Christian M. Zdanowicz (christian.zdanowicz@geo.uu.se)

Black Carbon - Continuous flow analysis (CFA)

Determination of rBC concentrations in the Devon Island DV99.1 ice core archive were performed within the Curtin University Trace Research Advanced Clean air facility (TRACE) using a continuous flow ice core melting system coupled to an intracavity laser-induced single particle incandescence soot photometer (Droplet Measurement Technologies). Sections of ice core used for the study were logged, measured and sectioned into square longitudinal samples of ice inside a class 100 walk-in freezer in the TRACE facility. The ends of samples were carefully scraped with a ceramic chisel blade and the samples relocated to a chest freezer next to the CFA melter system. The system is similar to the ice core melter system used by McConnell and Edwards et al. (2008) with the exception that the melter head was made out of aluminium rather than silicon carbide. A schematic of the system is provided below (**Fig. S1**).

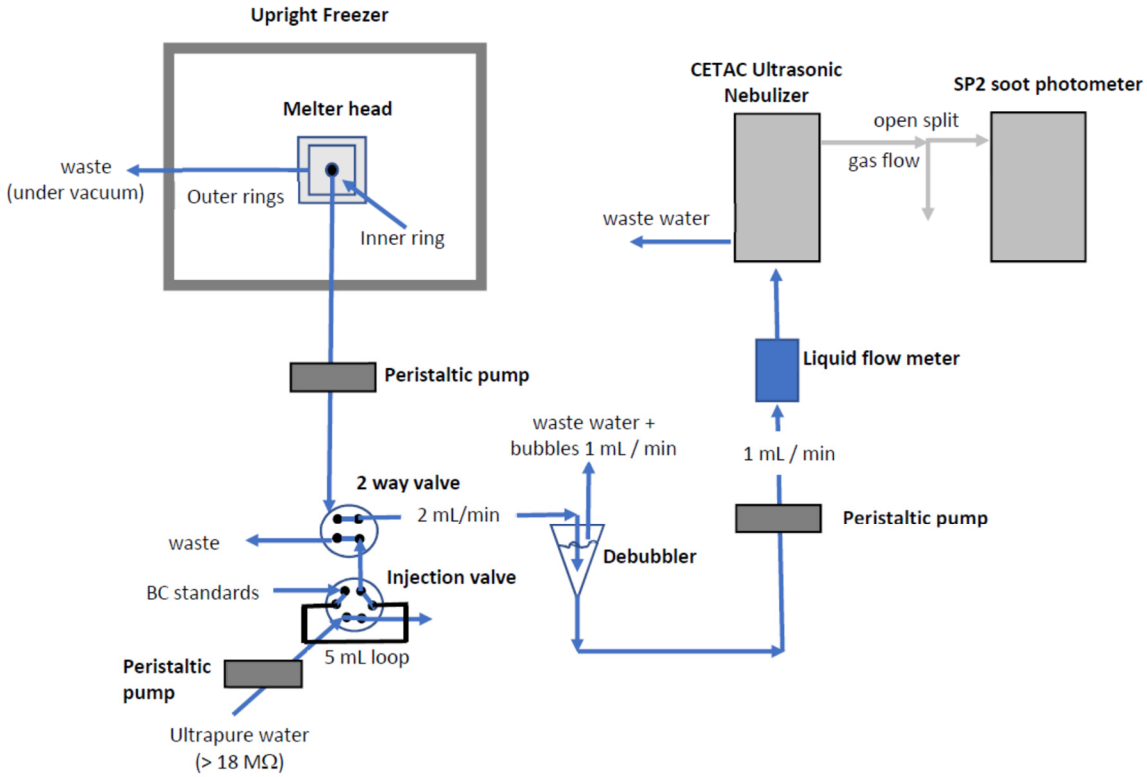


Figure S1: Schematic of the Continuous Flow Analysis (CFA) - SP2 system used for the analysis of the DV99.1 core at the Trace Research Clean Environmental facility, Curtin University.

The ice core sections were continuously loaded into the melter stand in sequence. Only melt water from the inner most ring of the melter head was used for the study. From the inner ring, melt water containing bubbles of air (from the ice core) was pumped through Teflon PFA capillary lines (inner diameter 0.3 in, or 7.62 mm), by a peristaltic pump, into a 2-way four port valve (VICI) and a small debubbling system. The debubbling system was used to remove air bubbles from the line and to decouple the liquid flow from the ice core melter to the ultrasonic nebulizer and desolvation system. The 4-port valve was used to select ice core melter flow or rBC standards and/or ultrapure water via a 2-way, 6-port injection valve (VICI). The injection loop was ~5 mL. Debubbled water flowing into the ultrasonic nebulizer (U5000AT; CETAC Technologies, Omaha, NE, USA) was measured using an inline water flow meter (Truflo, Glass Expansion). The efficiency of the nebulizer was evaluated by weighing water pumped from the systems primary waste line. The efficiency was typically ~25%. Instrumental settings are shown in **Table S1**.

SP2 settings	
Sample gas flow rate	120 cm^3 / min
Sheat gas flow rate	1000 cm^3 / min
Purge gas flow rate	276 cm^3 / min
Laser power setting	4.1
Nebulizer settings	
Gas flow rate	980 cm^3 / min
Liquid flow rate	1013 μL / min

Table S1. Instrumental settings for the SP2 and nebulizer used in this study.

The colloidal BC standards used for the study were derived from a commercially available 100% carbon ink (MIS, Eboni-6-K). This material was used in preference to the standards used by Mc Connell et al. (2007) because of its larger rBC particle size, which is closer to the geometric mean volume equivalent diameter (~200 nm) of rBC found in the remote atmosphere. Electron microscope images of the standard rBC particles are shown in **Fig S2**. Standards were prepared by serial dilution with ultrapure water.

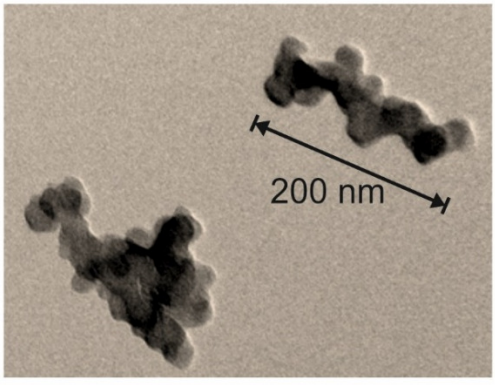


Figure S2: Transmission Electron Microscope image of colloidal rBC particles (MIS EB6-4K) used as standards for calibration of the SP2.

A typical calibration sequence, run at the beginning and at the end of the melt sequence is show in **Fig. S3a**. The linear calibration is shown in **Fig. S3b**, and incorporates both the standard sequence run at the beginning and at the end of the days melt sequence ~ 5 hours apart. Standards run during pauses in the melting were relatively stable (**Fig. S3c**).

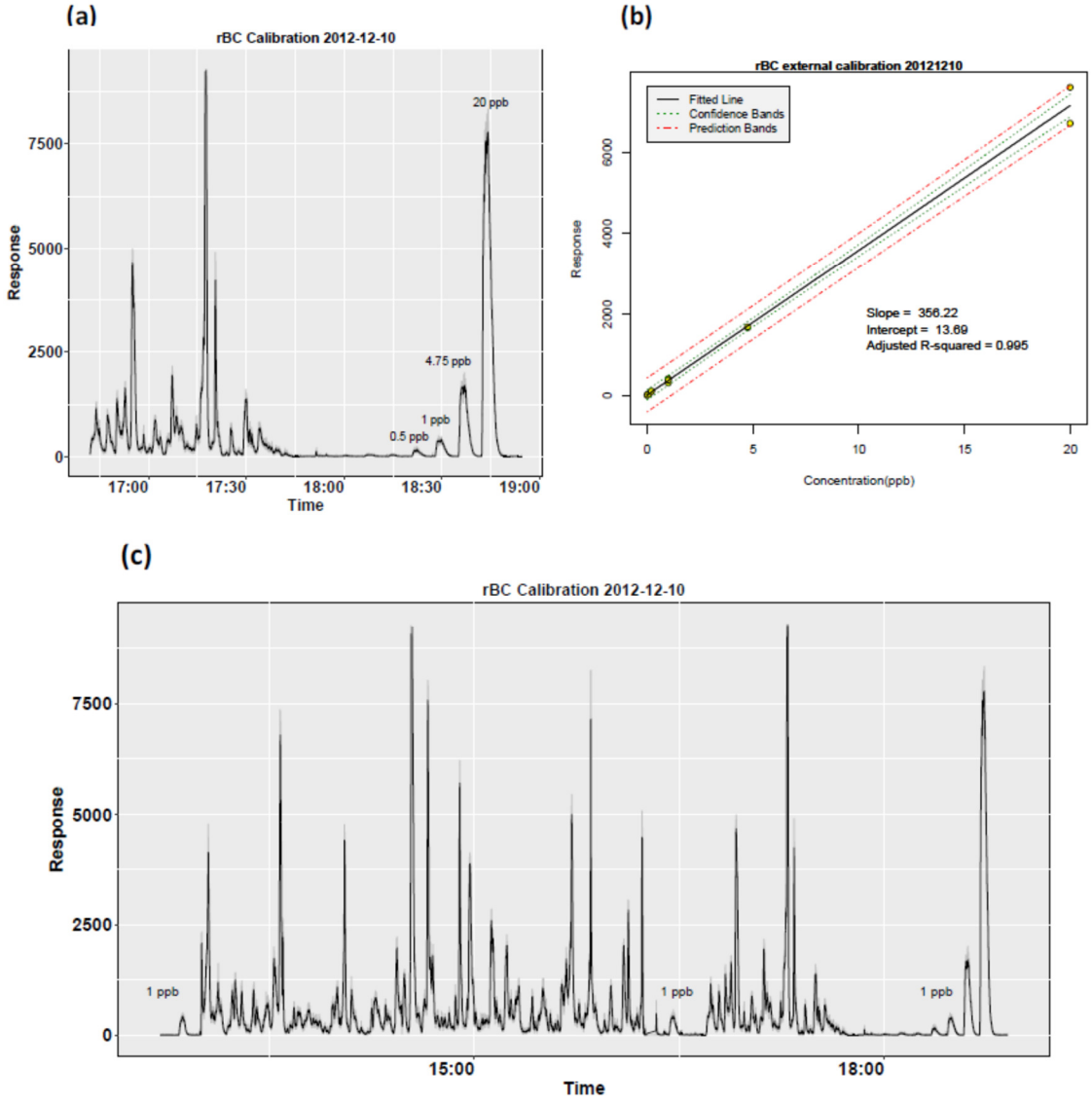


Figure S3: rBC External calibration for 10 Dec., 2012. **(a)** Calibration sequence at the end of the melt run; **(b)** linear calibration comprising all of the days standards; **(c)** plot showing 1 ng/g (ppb) rBC external standards run during pauses in the core melting sequence.

Analyses were conducted over the course of five days (5-11 Dec., 2012) with the same set of standards. The sensitivity of the analytical system remained stable on 6-7 Dec. with linear calibration slopes of ~ 434 and 444, respectively. However the calibration slopes from 10-11 Dec. were 356 and 360, respectively. This step in sensitivity is related to a change within the SP2 instrument and not due to aggregation of the standard. While the change in slope is roughly 19 %, the rBC concentrations either side of the step in sensitivity were essentially the same (**Fig. S4**).

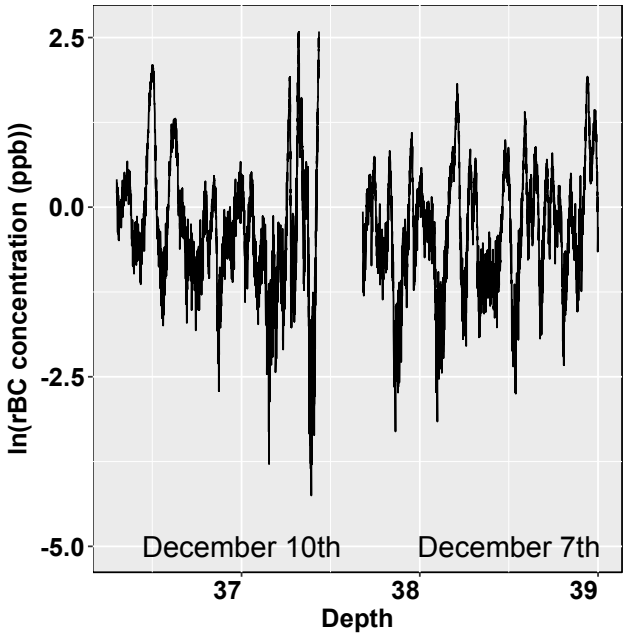


Figure S4. Comparison of rBC concentrations determined on 7 and 10 December, 2012. The data are plotted on a logarithmic scale to better compare the geometric mean concentrations.

For example the geometric mean rBC concentration was 0.773 ng g^{-1} (n = 2618) for depths 37.68 to 39.00 m (determined on 7 Dec.) and 0.722 ng g^{-1} (n = 2671) for depths 37.44 to 36.00 m (determined on 10 Dec.). For depths 37.00 to 37.44 m the geometric mean rBC concentration was 0.656 ng g^{-1} (n = 1301, from 10 Dec.) and for depths 37.68 to 38.31 m it was 0.661 ng g^{-1} (n = 1310, from 7 Dec.). Since the difference between the ice sections bridging the sensitivity shift is < 2% we conclude that the SP2 instrument sensitivity dropped and that the external standards remained relatively constant in colloidal mass.

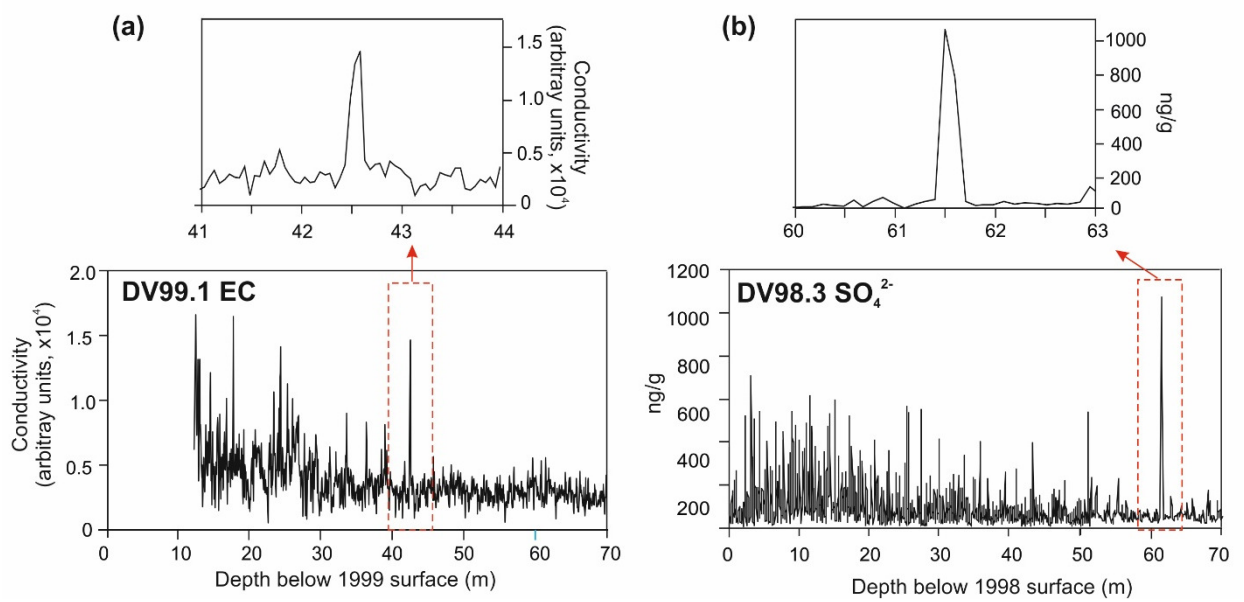


Figure S5: Profiles of EC in the DV99.1 core (**a**; profile starts at 12.4 m) and of SO_4^{2-} concentrations in the DV98.3 core **(b)** down to 70 m depth. Enlargements above each plot show peaks in these profiles that were ascribed to fallout from the Laki 1783 eruption, and were used to correlate the two cores.

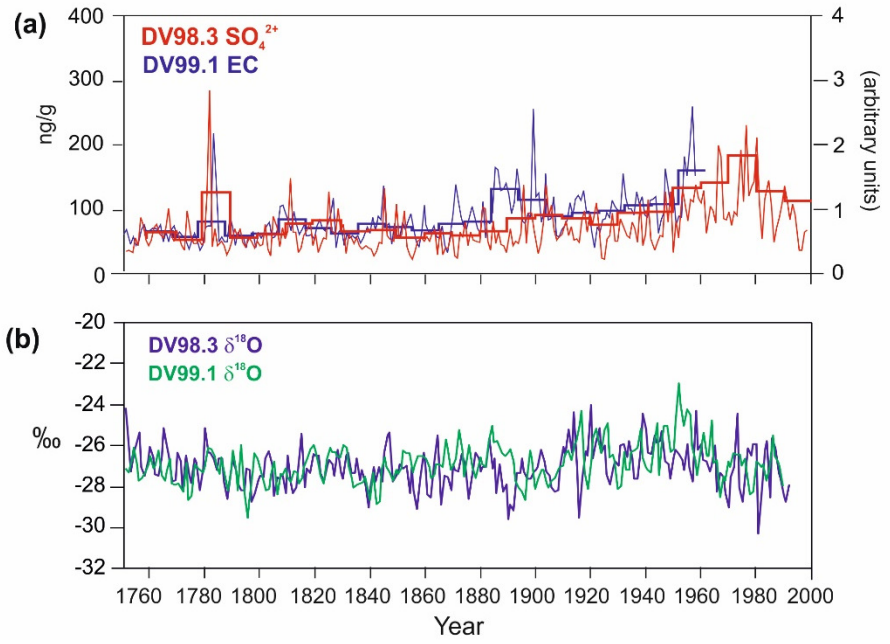


Figure S6: (a) The DV99.1 record of EC (right-hand scale) overlaid on the DV98.3 record of SO_4^{2-} concentrations (left-hand scale) over the period 1740-1998 . Data are shown in averages of ~one year (thinner lines) and ~10 years (bolder, stepped lines), the latter starting with the last year in each record. (b) Overlaid $\delta^{18}O$ records from the DV99.1 and DV98.3, averaged over intervals of ~one year. On this figure, the mean $\delta^{18}O$ of the DV99.1 record was offset by -2.2 ‰ to show the degree of matching between the two records. See also next figure.

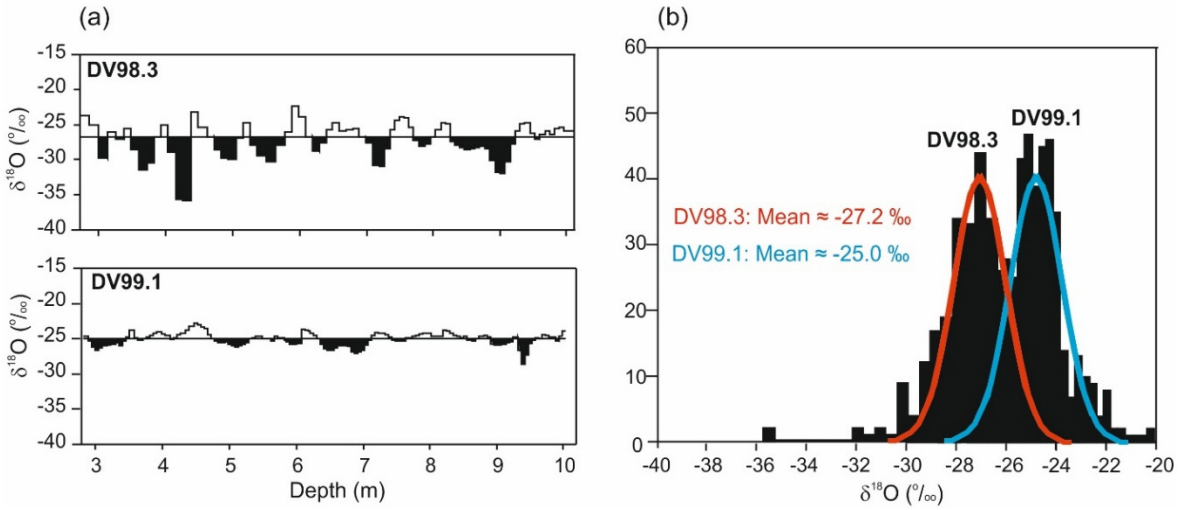


Figure S7: (a) Compared $\delta^{18}O$ profiles in two shallow sections of the DV98.3 and DV99.1 cores from Devon ice cap, showing the attenuation of seasonal variations in the DV99.1 core relative to the DV98.3 core. **(b)** Overlaid histograms of $\delta^{18}O$ values in the core sections shown in (a), with Gaussian models fitted to each.

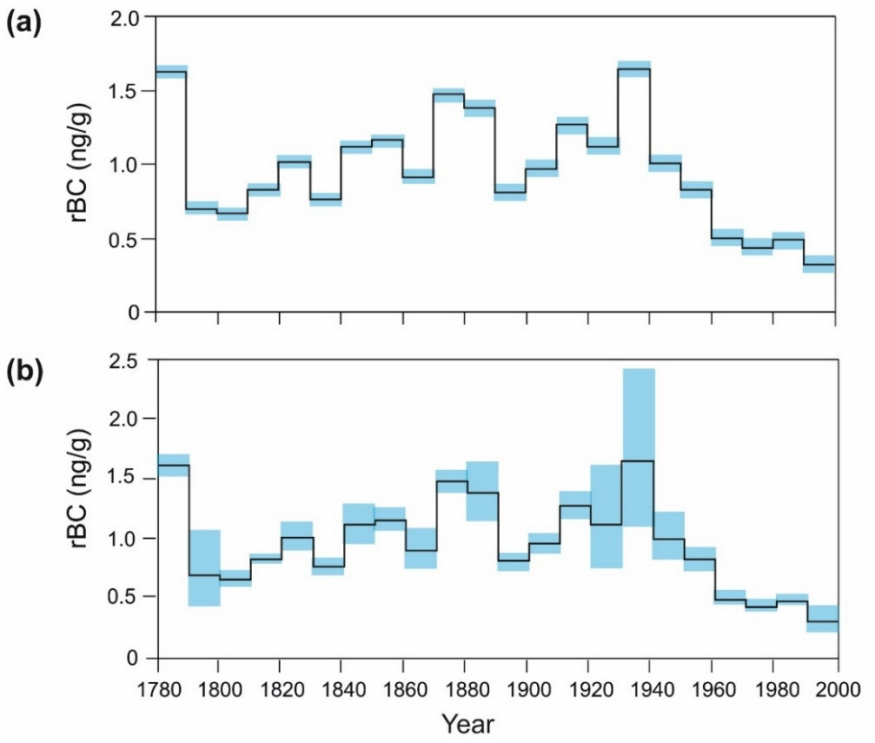


Figure S8: Uncertainties on 10-year averages (geometric mean) of rBC concentrations in the DV99.1 core over the period 1780-2000 arising from various error sources, and estimated by Monte Carlo methods. **(a)** Uncertainties arising from spatial variability of rBC deposition across the summit area of Devon ice cap. **(b)** Uncertainties arising from potential errors in the age model used for the DV99.1 core. The range of uncertainties for any decade in the rBC data is shown as blue shading bounded by 95 % confidence limits (CL). Note that the estimated mean rBC concentration in the last decade (1990-2000) is based on ~2 years of data only.

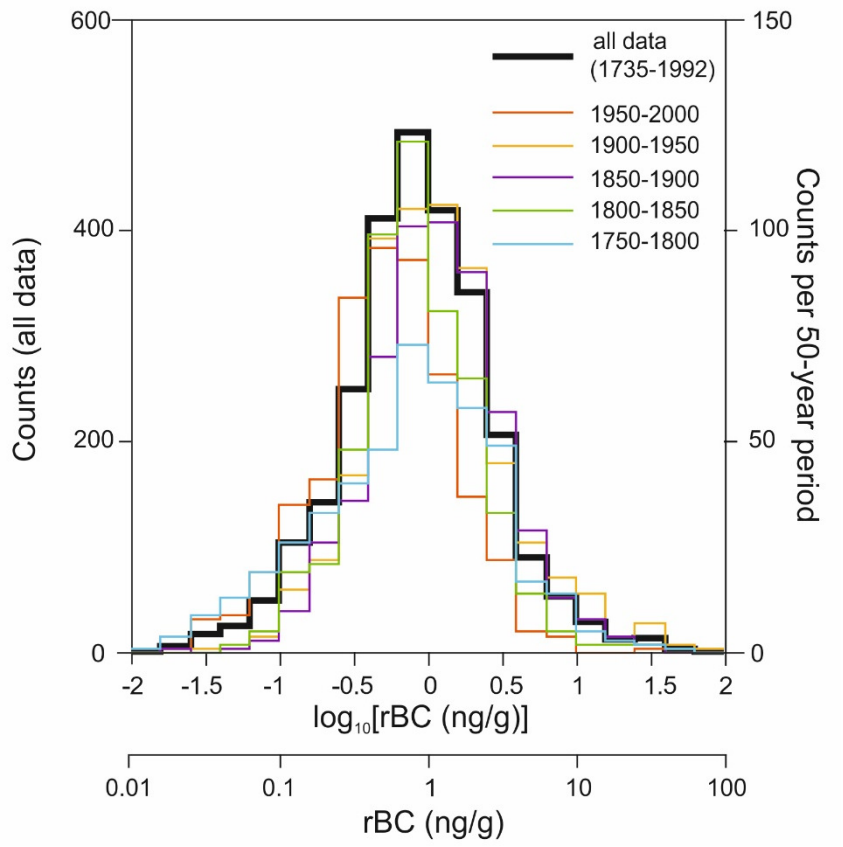


Figure S9: Probability distribution of rBC concentrations measured in the DV99.1 core. The bold dark line includes all data (scale at left), while the coloured lines include data over discrete 50-year intervals (scale at right).

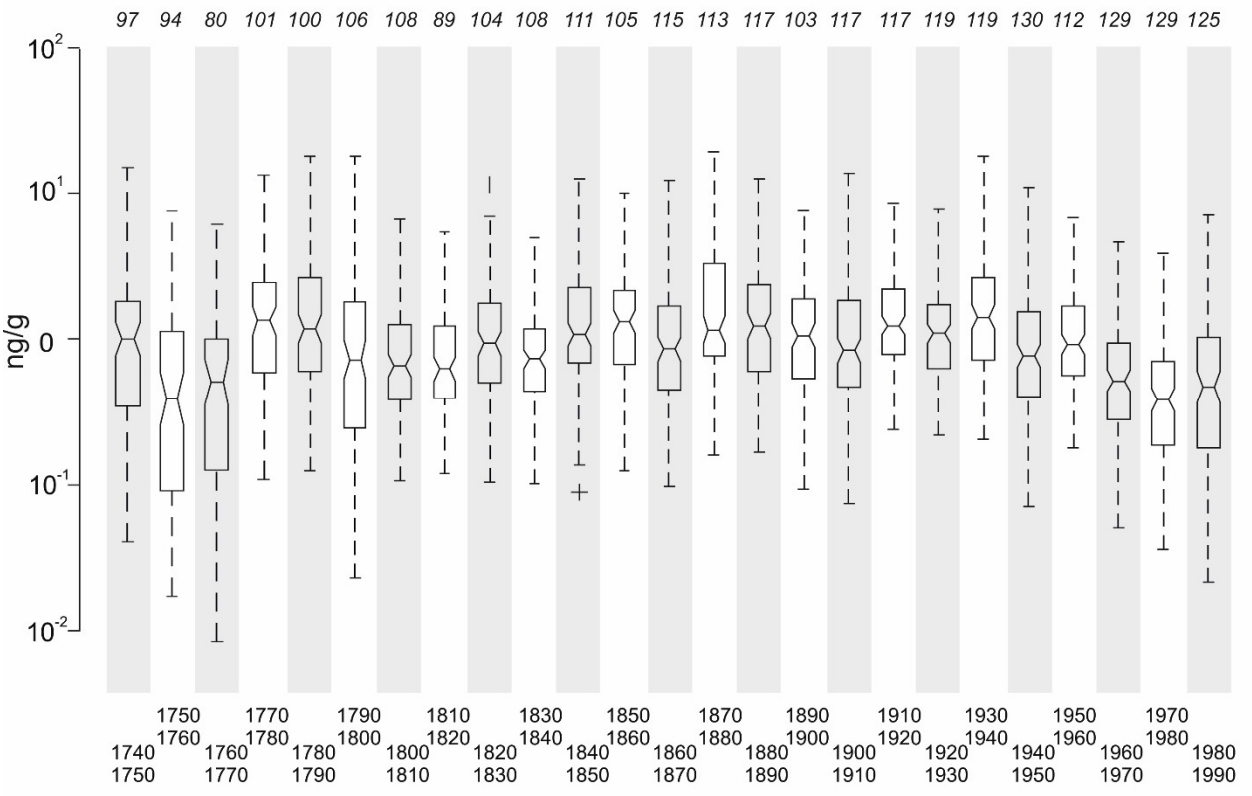


Figure S10: Notched box plots of rBC concentrations in the DV99.1 core, grouped by estimated decadal intervals from 1740 to 1990. Figures in italics at top of plot are the number of data points included in each decadal interval. Notches in the box plots denote the 95 % confidence intervals of the estimated median concentration in each decade.

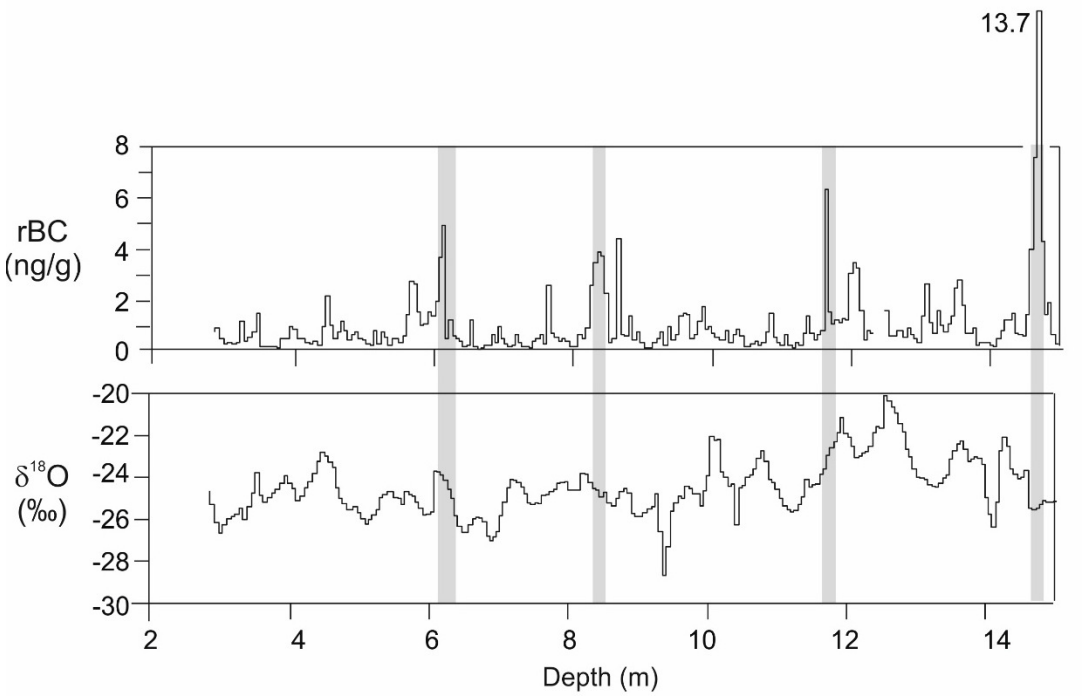


Figure S11: Variations of rBC concentrations and $\delta^{18}O$ measured in the uppermost 14.5 m of the DV99.1 core. Some of the most outstanding peaks in rBC concentrations are highlighted by grey shading.

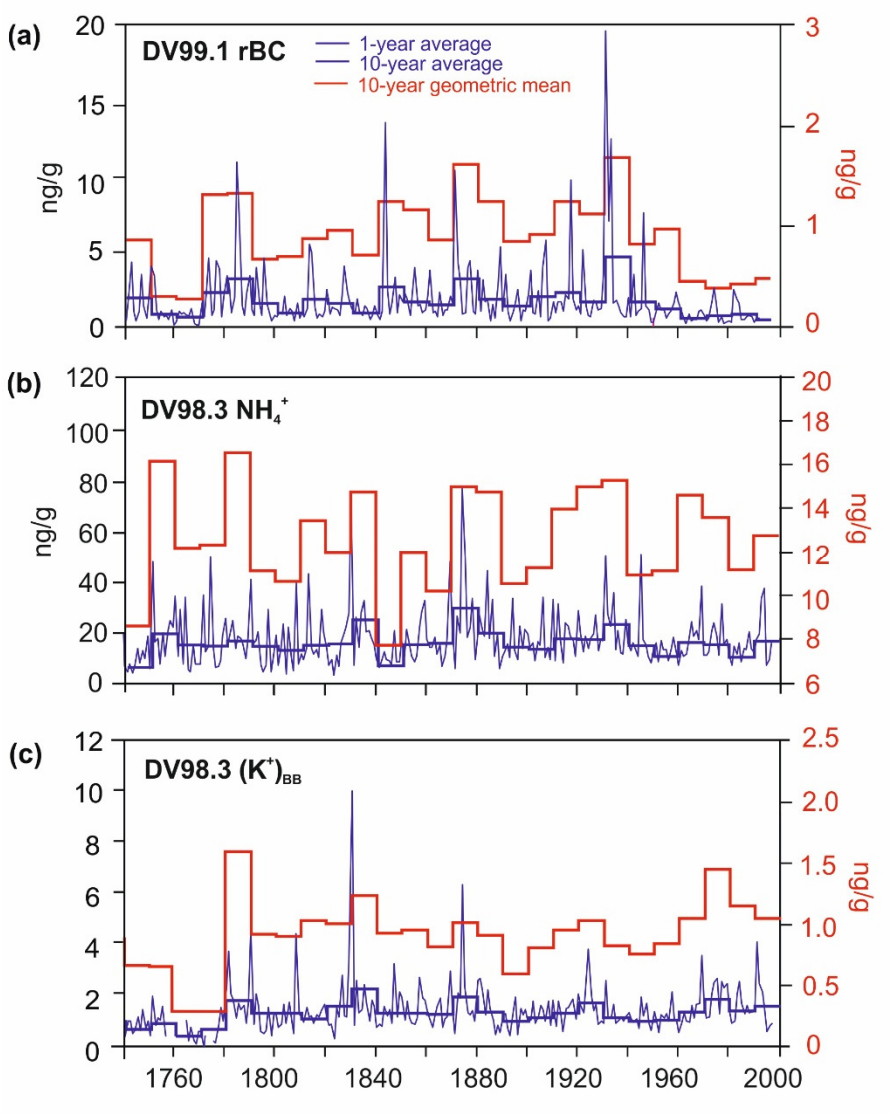


Figure S12. **(a)** rBC concentrations in the DV99.1 core, 1740-1992; **(b)** Ammonium (NH_4^+) and **(c)** the estimated biomass burning fraction of potassium $(K^+)_{BB}$ in the DV98.1 core over the same time period. Two large outliers were removed from the $(K^+)_{BB}$ data. As in Fig. 4 in the paper, the blue lines represent ~1- and 10-year arithmetic averages of the data (scale at left), while the red stepped lines show the geometric mean of the data over 10-year intervals (scale at right).

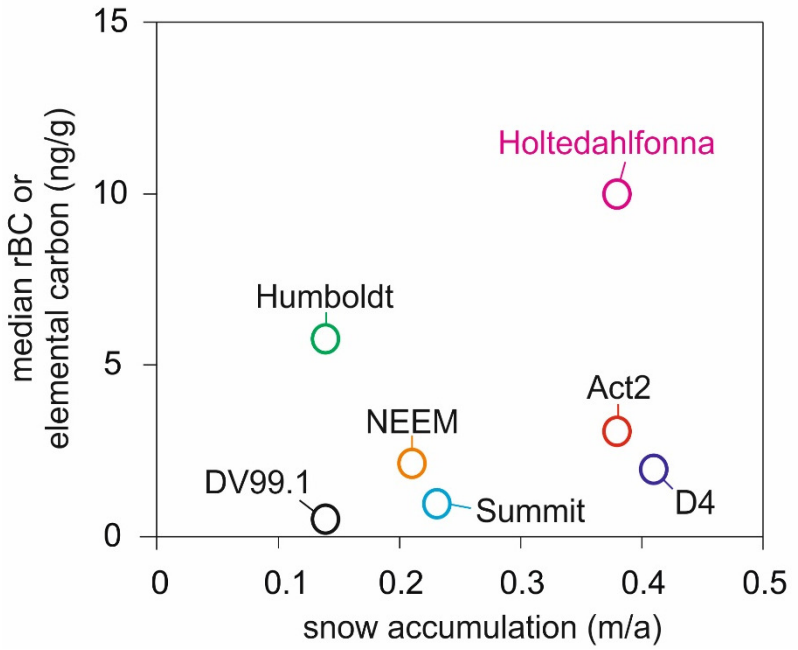


Figure S13: Scatter plot of median rBC or elemental carbon concentrations in firn and glacial ice vs. mean snow accumulation rates over the period ~1960-1990 at the Arctic sites shown on Fig. 5. Data sources for BC elemental carbon: McConnell et al. (2007), Koch et al. (2011), Zennaro et al. (2014), Ruppel et al. (2014) and Sigl et al. (2015). Data sources for snow accumulation rates: Banta and McConnell (2007) and Bales et al. (2009).

References

Banta, J.R. and McConnell, J.R.: Annual accumulation over recent centuries at four sites in central Greenland, J. Geophys. Res., 112, D10114, doi:10.1029/2006JD007887, 2007.

Bales, R.C., Guo,Q., Shen, D., McConnell, J.R., Du,G., Burkhart, J.F., Spikes, V.B., Hanna, E. and Cappelen, J.: Annual accumulation for Greenland updated using ice core data developed during 2000–2006 and analysis of daily coastal meteorological data, J. Geophys. Res., 114, D06116, doi:10.1029/2008JD011208, 2009.

Koch, K., Bauer, S.E., Del Genio, A., Faluvegi, G., McConnell, J.R., Menon, S., Miller, R.L., Rind, D., Ruedy, R., Schmidt, G.A. and Shindell, D.: Coupled aerosol-chemistry–climate twentieth-century transient model investigation: Trends in short-lived species and climate responses, J. Clim., 24, 2693–2714, doi: 10.1175/2011JCLI3582.1, 2011.

McConnell, J. R. and Edwards, R.: Coal burning leaves toxic heavy metal legacy in the Arctic. P. Natl. Acad. Sci. USA, 105, 12,140–12,144, doi:10.1073/pnas.0803564105, 2008.

McConnell, J. R., Edwards, R., Kok, G. L., Flanner, M. G., Zender, C. S., Saltzman, E. S., Banta, J. R., Pasteris, D. R., Carter, M. M., and Kahl, J.D.: 20th-century industrial black carbon emissions altered Arctic climate forcing. Science, 317, 1381–1384, doi:10.1126/science.1144856, 2007.

Ruppel, M.M., Isaksson, I., Ström, J., Beaudon, E., Svensson, J., Pedersen, C.A. and Korhola, A.: Increase in elemental carbon values between 1970 and 2004 observed in a 300-year ice core from Holtedahlfonna (Svalbard), Atmos.
Chem. Phys., 14, 11,447–11,460, doi:10.5194/acp-14-11447-2014, 2014.

Sigl, M., Winstrup, M., McConnell, J.R., Welten, K.C., Plunkett, G., Ludlow, F., Büntgen, U., Caffee, M., Chellman, N., Dahl-Jensen, D., Kipfstuhl, S., Kostick, C., Maselli, O.J., Mekhaldi, F., Mulvaney, R., Muscheler, R., Pasteris, D.R., Pilcher, J.R., Salzer, M., Schüpbach, S., Steffensen, J.P., Vinther, B.M. and Woodruff, T.E.:Timing and climate forcing of volcanic eruptions for the past 2,500 years, Nature 523, 543–549, doi:10.1038/nature14565, 2015.

Zennaro, P., Kehrwald, N., McConnell, J.R., Schüpbach, S., Maselli, O.J., Marlon, J., Vallelonga, P., Leuenberger, D., Zangrando, R., Spolaor, A., Borrotti, M., Barbaro, E., Gambaro, A. and Barbante, C.: Fire in ice: two millennia of boreal forest fire history from the Greenland NEEM ice core, Clim. Past, 10, 1905–1924, 10.5194/cp-10-1905-2014, 2014.