

## 20th-Century Industrial Black Carbon Emissions Altered Arctic Climate Forcing

Joseph R. McConnell,<sup>1\*</sup> Ross Edwards,<sup>1</sup> Gregory L. Kok,<sup>2</sup> Mark G. Flanner,<sup>3</sup> Charles S. Zender,<sup>3</sup> Eric S. Saltzman,<sup>3</sup> J. Ryan Banta,<sup>1</sup> Daniel R. Pasteris,<sup>1</sup> Megan M. Carter,<sup>4</sup> Jonathan D. W. Kahl<sup>4</sup>

<sup>1</sup>Desert Research Institute, Nevada System of Higher Education, Reno, NV 89512, USA. <sup>2</sup>Droplet Measurement Technologies, Boulder, CO, USA. <sup>3</sup>Department of Earth System Science, University of California, Irvine, CA 92697, USA. <sup>4</sup>Department of Mathematical Sciences, University of Wisconsin-Milwaukee, Milwaukee, WI 53201, USA.

\*To whom correspondence should be addressed. E-mail: Joe.McConnell@dri.edu

**Black carbon (BC) from biomass and fossil fuel combustion alters chemical and physical properties of the atmosphere and snow albedo, yet little is known about its emission or deposition histories. Measurements of BC, vanillic acid, and non-sea-salt sulfur in ice cores indicate that sources and concentrations of BC in Greenland precipitation varied greatly since 1788 as a result of boreal forest fires and industrial activities. Beginning about 1850, industrial emissions resulted in a seven-fold increase in ice core BC concentrations with most change occurring in winter. BC concentrations after about 1951 were lower but increasing. At its maximum from 1906 to 1910, estimated surface climate forcing in early summer from BC in Arctic snow was about  $3 \text{ W m}^{-2}$ , eight times typical pre-industrial forcing.**

Emissions of BC particles result from incomplete combustion during the burning of biomass and fossil fuels (1). In the atmosphere, absorption of sunlight by BC contributes to global warming and alters cloud formation processes (2). Arctic climate is especially vulnerable to BC deposition because of its impact on the albedo of snow, glaciers, and sea ice—accelerating melting and increasing sensitivity to warming (3). Despite its importance, little is known about past natural or anthropogenic emissions of BC and its deposition. Glaciers and ice sheets contain a historical record of atmospheric deposition of aerosol-borne chemicals derived from natural and anthropogenic burning. Here we employ measurements in central Greenland ice cores to assess the origin and climate forcing of BC in snow during the past 215 years. Vanillic acid (VA) and non-sea-salt sulfur (nss-S) are used as indicators of forest fires and industrial pollution, respectively.

We used continuous melter analyses of BC, VA, a wide range of trace elements, and hydrogen peroxide (4–6). BC was analyzed using a laser-based atmospheric analyzer and VA using electrospray-triple quadrupole mass spectrometry (6). Measurements were made on an ice core collected in 2003 from a high snowfall region of west central Greenland,

the D4 site (6). Using the known mid-winter minimum in hydrogen peroxide concentration in Greenland snow (7) and assuming uniform snowfall rate within each year (6), we determined monthly and annual BC concentration in Greenland from 1788 through 2002 (Fig. 1A).

Black carbon concentrations varied significantly during the past 215 years and were highly seasonal, particularly during the period before industrialization beginning in the mid-1800s (Fig. 1A) (6). Average pre-industrial annual BC concentration was  $1.7 \text{ ng g}^{-1}$  with generally consistent low winter (defined as December through May) concentrations averaging  $1.3 \text{ ng g}^{-1}$  and highly variable summer (defined as June through November) concentrations averaging  $2.0 \text{ ng g}^{-1}$ . After 1850, annual BC concentrations began a gradual rise, followed by a rapid increase in ~1888. Annual average concentrations reached a peak of  $> 12.5 \text{ ng g}^{-1}$  in 1908 before beginning a general, although erratic, decline through the late 1940s followed by a sharp drop in 1952. Maximum winter BC concentration peaked in 1908 at more than  $20 \text{ ng g}^{-1}$ , with an average wintertime concentration of  $\sim 13 \text{ ng g}^{-1}$  during the highest five-year period (1906 through 1910), about ten times the mean winter concentration of  $1.3 \text{ ng g}^{-1}$  prior to 1850. During the period 1851 to 1951, annual average concentrations were  $4.0 \text{ ng g}^{-1}$ , with mean winter and summer concentrations of  $4.1$  and  $3.9 \text{ ng g}^{-1}$ , respectively. From 1952 to 2002, average annual concentrations were  $2.3 \text{ ng g}^{-1}$  and characterized by high year-to-year variability in summer and a gradual decline in winter BC concentrations through the end of the century (Fig. 1B). Although highly variable with season and year, monthly BC concentrations during the late 20th century (Fig. 1A) ranged from  $< 1 \text{ ng g}^{-1}$  to  $> 10 \text{ ng g}^{-1}$  and are in general agreement with published measurements of BC in Greenland snow (8–11).

While changes in BC measured in the D4 ice core are substantial, it is unclear from a single ice core record if the observed changes are representative of central Greenland or the larger Arctic region. As a first step in determining this, we made similar, although discontinuous, measurements from a second ice core collected at the D5 site ~350 km to the south

(6). Changes in BC during the last two centuries (Fig. 1B) were similar at both sites (6), suggesting that many of the large summer increases associated with boreal forest fires prior to industrialization, and the marked increases in winter and spring BC during and after industrialization, were regional and represent central Greenland and possibly much of the Arctic, including the seasonally snow-covered regions of northern and eastern Canada and sea-ice-covered areas of the North Atlantic.

To investigate BC sources in the Greenland records, we used ice core measurements (6) of the conifer-specific forest fire indicator, vanillic acid (VA) (12, 13), and measurements of non-sea-salt sulfur (nss-S) as an indicator of industrial emissions (mostly from fossil fuel combustion) (14, 6).

Comparisons of annual average BC and VA concentrations suggest that conifer combustion was the major source of BC in Greenland prior to 1850 (Fig. 2A) and a significant source during summer throughout the 215-year record. Before 1850, variations in BC concentrations closely matched changes in VA concentrations. Correlations between annual, winter, and summer concentrations of VA and BC were 0.87, 0.72, and 0.87 ( $p < 0.0001$ ), respectively. During the period 1850 to 1951, correspondence between VA and BC concentration dropped dramatically, particularly in winter. Although correlations between annual and summer average concentrations remained significant (annual:  $r = 0.56$ ,  $p < 0.0001$ ; summer:  $r = 0.34$ ,  $p < 0.0005$ ), winter concentrations showed no covariance. From 1951 to 2002, winter concentrations also were uncorrelated, while the correlation in summer concentrations remained at 0.44 ( $p < 0.0008$ ).

Air mass back-trajectory modeling suggests that eastern and northern U.S. and Canada are likely source regions of BC measured at the D4 ice core site (6). We used the NOAA/CMDL atmospheric trajectory model (15) driven by 1958 through 2002 velocity fields from the ERA-40 reanalysis (16). Modeling suggests that most BC is wet deposited and has an atmospheric lifetime of ~three days (11) so we used three-day trajectories corresponding only to major snowfall events. Given the model results and close correspondence between summer BC and VA, the likely source of BC from biomass burning is the conifer-rich boreal forest of eastern North America.

Northern Hemisphere industrial emissions of sulfur dioxide began in the mid-19th century with widespread burning of coal (17), and the ice core record clearly reflects this (Fig. 2B). Prior to 1850, nss-S concentrations were generally low and primarily attributed to biogenic emissions (14), although the entire ice core record is punctuated with very large, short-lived increases in nss-S resulting from fallout from well-known explosive volcanic eruptions. Long-term increases in nss-S began soon after 1850, accelerated sharply during the late 19th century, declined slowly from

~1910 to the late 1930s, and then increased strongly again through the early 1970s. In the early 1970s, implementation of the Clean Air Act lowered American sulfur emissions (other countries also began regulating emissions), resulting in a peak in nss-S in the D4 ice core record in ~1970 followed by a slow decline until ~1992 and a sharp drop almost to pre-industrial levels by 2002.

Prior to 1850 when correlations between BC and VA were high, concentrations of nss-S were not correlated to either BC or VA—suggesting that forest fires were not a significant source of atmospheric sulfur. After 1850, highly correlated increases ( $p < 0.0001$ ) in BC and nss-S concentrations indicate that industrial emissions became the primary source of BC. Correlations between annual, winter, and summer average BC and nss-S concentrations from 1850 to 1951 were 0.67, 0.74, and 0.59, respectively. Comparisons of BC and nss-S concentrations during winter when forest-fire-derived BC was at a minimum indicate that for every ton of pollution nss-S deposited in winter precipitation from 1850 to 1951, an average of ~0.3 tons of BC were deposited concurrently (6). After 1951, the positive correlation between nss-S and BC concentration decreased dramatically. Despite large increases in industrial SO<sub>2</sub> emissions (17) and nss-S concentrations in the ice core record, BC concentrations in the ice remained low. Some correlation between nss-S and BC concentrations, however, was still evident (annual:  $r = 0.30$ ,  $p < 0.02$ ), albeit substantially less significant than during the period of high BC concentrations.

Although not validated because of the paucity of historical 20th century BC measurements prior to this study, estimates of industrial BC emissions have been made based on records of fossil fuel combustion (18, 19). Such estimates were determined using fuel- and technology-dependent emissions factors that relate BC emissions to fuel combusted. Technological changes through time, however, mean that emissions factors are highly uncertain. Of the estimates of 20th century BC emissions reported by (18), our measurements of BC agree most closely with those from the U.S. In particular, estimates of U.S. emissions show a rapid increase in the late 18th century, a leveling off and decline in the early 20th century, followed by a sharp drop in the early 1950s, and a slow decline to the end of the century—very similar to the ice core measurements. Some models suggest that a large fraction of Arctic pollutants originate in south Asia (3). From results of air mass back-trajectory modeling (6) as well as comparisons of ice core measurements of BC and lead (20) with estimated BC and lead atmospheric industrial emissions, we conclude that most of the industrial BC deposited in central Greenland precipitation likely came from North American emissions, at least during the period of high BC concentrations from 1850 to 1951. Since 1951, the positive BC trend in the core record attributed to industrial

emissions (Fig. 2A) suggests that Asia may be the primary source today, consistent with other work (3).

This monthly resolved record of BC in Arctic precipitation allows quantitative estimation of the impacts on climate forcing of BC in snow from both forest fires and fossil fuel burning during recent centuries. We used the Snow, Ice, and Aerosol Radiative (SNICAR) model (11)—assuming an ice-grain effective radius of 100  $\mu\text{m}$  and mass distributions measured in the ice core (median particle mass of 1.82 femtograms geometric lognormal distribution width of 2.64) (6).

Because of large seasonal changes in incoming radiation at high latitudes and sometimes large seasonal changes in BC concentration in the ice core record, radiative forcing from BC in snow in central Greenland is highly seasonal (6) and increased markedly during the late 19th and early 20th centuries as a result of industrial pollution. Monthly averaged surface forcing (i.e., BC-induced heating) during the peak early summer period (June and July) was  $\sim 0.28 \text{ W m}^{-2}$ , with a median early summer forcing of  $\sim 0.20 \text{ W m}^{-2}$  prior to 1850,  $\sim 0.38 \text{ W m}^{-2}$  from 1850 to 1951, and  $\sim 0.22 \text{ W m}^{-2}$  after 1951. Forcing during the dark winter months was negligible. During the peak five-year period from 1906 to 1910, forcing at the D4 ice core site from BC in snow was  $1.02 \text{ W m}^{-2}$ , a five-fold increase from pre-industrial conditions with  $\sim 0.76 \text{ W m}^{-2}$  attributed to industrial pollution BC (Fig. 3A).

While enhanced radiative forcing from BC in snow results in warming and possibly summer melting on the permanently snow-covered Greenland ice sheet, potential impacts on seasonal snow covers are larger since additional warming leads to earlier exposure of underlying low albedo rock, soil, vegetation, and sea ice (19). Surface heating in seasonally snow-covered regions is primarily influenced by BC deposited during the snow accumulation period (December through May). Thus, early summer surface radiative forcing for a seasonally snow-covered site can be estimated using average BC concentration from December through July measured in the ice core and solar forcing conditions during the subsequent early summer (Fig. 3B). In simulations with these conditions, the radiative impact of industrial BC emissions is substantially greater since winter concentrations increased more than summer as a result of industrialization.

To estimate the impact of changes in BC measured in ice cores throughout the Arctic region during the past 215 years, we used global model simulations of 1998 and 2001 radiative forcing from BC in snow to extrapolate model results at the ice core site (11). The simulated average surface forcing of anthropogenic BC throughout the region  $60^{\circ}\text{N}$  to  $90^{\circ}\text{N}$  was 1.7 times that at the ice core site in Greenland. Assuming this ratio has been approximately constant in time, we scaled monthly average surface forcing for the seasonal snow-cover simulation to approximate changes in average Arctic surface

forcing during the same period (Fig. 3B). While in agreement with these results in central Greenland, 1983/84 spot measurements of BC indicated an Arctic/Greenland value of about 10 (21), suggesting that the impact from industrial BC emissions across the Arctic may have been significantly larger.

Pronounced increases in BC concentration in snow observed in the Greenland ice cores extrapolate to a marked impact on early summer climate forcing throughout the Arctic during and after industrialization, with changes largely attributed to winter industrial BC emissions (Fig. 3B). The median in estimated surface forcing in early summer throughout the Arctic was  $0.42 \text{ W m}^{-2}$  prior to 1850,  $1.13 \text{ W m}^{-2}$  during the period 1850 to 1951, and  $0.59 \text{ W m}^{-2}$  after 1951. During the five-year period of maximum industrial BC emissions from 1906 to 1910, estimated surface forcing in the Arctic was  $3.2 \text{ W m}^{-2}$ , about eight times typical early summer forcing prior to industrialization.

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### Supporting Online Material

[www.sciencemag.org/cgi/content/full/1144856/DC1](http://www.sciencemag.org/cgi/content/full/1144856/DC1)

Materials and Methods

Figs. S1 to S4

References

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**Fig. 1.** (A) Monthly (black) and annual (red) black carbon (BC) concentration from 1788 through 2002 measured in the Greenland D4 ice core. (B) Winter and summer BC concentrations show that long-term changes in BC were greater in winter (red) than summer (black) during the late 19th and early 20th centuries. Winter and summer BC concentrations measured in the D5 ice core (6) located ~350 km south of the D4 site (blue dashed) indicate that observed BC changes were at least regional in extent. The maximum monthly BC value of 58.8 ng g<sup>-1</sup> occurred in summer 1854.

**Fig. 2.** (A) Annual average concentrations of BC and vanillic acid (VA). The shaded region represents the portion of BC attributed to industrial emissions, not boreal forest fires. (B) Annual average concentrations of BC and non-sea-salt sulfur (nss-S). Large, short-lived increases in nss-S result from

explosive volcanism (e.g., Tambora, 1816; Krakatoa, 1883; and Katmai, 1912).

**Fig. 3.** (A) Surface radiative forcing from BC in snow during early summer (June and July) at the permanently snow-covered D4 ice core site. Forcing was modeled using SNICAR and monthly averaged total (black) and industrial (red) BC concentrations. (B) Estimated surface radiative forcing for a seasonal snow cover derived using mean winter BC concentration measured in the core and early summer solar forcing conditions (black). Average early summer surface forcing extrapolated throughout the Arctic region (blue). The dashed lines show five-year running means. Modeling of radiative forcing at the ice core site was for dry snow conditions since no surface melt occurs at D4. Although poorly known, redistribution of BC in a melting snow pack (22) may influence the impact of BC on forcing.





