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A 300-Year High-Resolution Greenland Ice Record of Large-Scale Atmospheric Pollution by Arsenic in the Northern Hemisphere

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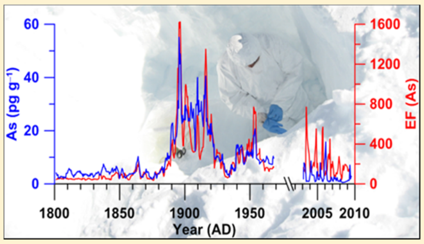
Supporting Information



ABSTRACT: We report the first high-resolution record of arsenic (As) observed in Greenland snow and ice for the periods 1711−1970 and 2003−2009 AD. The results show well-defined large-scale atmospheric pollution by this toxic element in the northern hemisphere, beginning as early as the 18th century. The most striking feature is an abrupt, unprecedented enrichment factor (EF) peak in the late 1890s, with an ∼30-fold increase in the mean value above the Holocene natural level. Highly enriched As was evident until the late 1910s; a sharp decline was observed after the First World War, reaching a minimum in the early 1930s during the Great Depression. A subsequent increase lasted until the mid-1950s, before decreasing again. Comparisons between the observed variations and Cu smelting data indicate that Cu smelting in Europe and North America was the likely source of early anthropogenic As in Greenland. Despite a significant reduction of ∼80% in concentration and ∼60% in EF from the 1950s to the 2000s, more than 80% of present-day As in Greenland is of anthropogenic origin, probably due to increasing As emissions from coal combustion in China. This highlights the demand for the implementation of national and international environmental regulations to further reduce As emissions.

1. INTRODUCTION

During recent decades, Greenland snow and ice records of changes in the occurrence of various trace elements (Cu, Zn, Rh, Pd, Pt, Cd, Hg, Tl, and Pb) have led to a better understanding of the anthropogenic influence on large-scale atmospheric cycling of these elements in the northern hemisphere over time scales of several tens of years to millennia.[1−8] These studies have revealed a noticeable increase in atmospheric depositions of Pb and Cu during Greco-Roman times,[2,3,8] the oldest hemispheric-scale atmospheric pollution ever reported, almost two millennia before the industrial revolution. Since the industrial revolution, well-established time-dependent patterns of hemispheric-scale anthropogenic perturbation have been observed for the investigated trace elements, with different peak periods. For instance, Pb concentrations in Greenland snow showed a dramatic increase in the 1950s, reaching a peak in the late 1960s (∼200-fold above natural values), because of the massive increase in the use of leaded gasoline, and a subsequent decline in response to a decrease in automotive emissions of Pb.[1,4,7] The concentrations of Cu, Zn, and Cd increased markedly until the middle of the 20th century, followed by a sustained decreasing trend during the following decades. Such temporal trends are linked to massive releases of these pollutants from nonferrous metal production and fossil-fuel combustion and subsequent reductions in emissions due to abatement measures applied in various countries in the northern hemisphere over the last few decades.[4,7] On the other hand, Tl concentrations show a maximum in the early 20th century because of incomplete combustion of coal, the exclusive source of Tl emissions into the atmosphere, at that time.[7]

Undoubtedly, the aforementioned Greenland snow and ice records provide critical information for quantifying the extent and impact of anthropogenic releases of trace elements of interest, which eventually reached the most remote areas of the northern hemisphere. Surprisingly, however, there are no detailed long-term data for arsenic (As) from Greenland snow and ice, despite the fact that the high toxicity of As can cause adverse health effects even at low exposure levels, raising global health concerns.[9,10] As is an element that the Environmental Protection Agency (EPA) and the World Health Organization

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(WHO) list as a carcinogen.[11] The lack of data is mainly because of the extremely low concentrations of As in polar snow and ice.[12,13] Ultraclean protocols are required throughout the analytical procedure and highly sensitive analytical methods must be used for the direct determination of As concentrations down to the subpicogram per gram level (1 pg $g^{-1} = 10^{-12}$ g g^{-1}).

Here, we present the first high-resolution record of As concentrations in an ice core from the North Greenland Eemian Ice Drilling (NEEM) camp in northwest Greenland, spanning the years from 1711 to 1970 AD; we used an ice core melter system for subannual sampling of continuous melting of discrete core sections. The data provide the opportunity to reconstruct the timing and amplitude of anthropogenic enrichment of As in one of the most remote areas of the northern hemisphere during the industrial era. Concentrations of As in Greenland Holocene ice and recent snow layers were also determined to characterize the natural Holocene and present-day As levels, respectively. In addition, we analyzed various discrete samples from an ice core from Summit, central Greenland, the period of which overlaps with that of the NEEM ice core, to check the efficiency of the continuous melting method by comparing the data between the two cores.

2. MATERIALS AND EXPERIMENTAL METHODS

2.1. Sample Description and Dating. In 2009, a 136-m-long ice core (hereafter, referred to as NEEM-2009-S1) was recovered at a site within 2 km from the NEEM deep ice coring site (77.45°N, 50.94°W, surface elevation 2461 m, mean annual snow accumulation rate of 22.5 g cm^{-2} yr^{-1}) in northwest Greenland,[14] as part of the NEEM project (Supporting Information, Figure S1), using the 3 in. diameter electromechanical drill. Each 55-cm-long core section from the upper 90 m was packed inside a low-density polyethylene (LDPE) bag and transported frozen to the Korea Polar Research Institute (KOPRI) for trace element measurements. The chronology of NEEM-2009-S1 was determined by counting the annual layers of the seasonal oxygen isotope ratio ($\delta^{18}O$) and soluble ions (sodium [Na^+] and nonsea-salt sulfate [nss-SO_4^{2-}]). The value of $\delta^{18}O$ is primarily dependent on the mean atmospheric temperature at the deposition site with less negative values in summer. Both Na^+ and nss-SO_4^{2-} concentrations in Greenland snow show peaks in winter to spring.[15] Counting the annual layers, NEEM-2009-S1 was found to cover the period 1711−2009 AD. Dating uncertainty was estimated to be ±2 years at the bottom of the core (90 m) based on the well-identified large volcanic nss-SO_4^{2-} depositions from the Krakatoa (1883), Tambora (1815), and Laki (1783) eruptions (Figure 2).

A continuous series of 70 snow samples from a 3.2-m snow pit was collected on June 26, 2009, at a site 3.5 km from the NEEM deep ice coring site. A snow pit was hand-dug by operators wearing full clean room garments and polyethylene gloves with metal shovels. About 10-cm-thick snow was then shaved away from the wall of the pit using acid-cleaned ultraclean low-density polyethylene (LDPE) scrapers. The snow samples were collected by horizontally pushing an acid-cleaned ultraclean Teflon tube (4.6 cm internal diameter, 35 cm in length) with an acid-cleaned plastic hammer and then transferred to an ultraclean 1 L LDPE bottle for storage.[16,17] Precautions were taken during the collection, handling, and storage of the samples to prevent the possibility of contamination, as previously reported in detail.[16,17] Combining the well-defined depth profiles of $\delta^{18}O$ and ionic species, the snow samples were dated from spring 2003 to summer 2009.[16,17]

Eight samples were selected from the 2540-m-long NEEM deep ice core.[14] The depths of these samples ranged from 1275.45 to 1330.45 m, corresponding to ages of ∼8840 to 9715 years before present (BP, where present is defined as 1950), respectively, the early Holocene time interval.

Finally, samples were selected from a 70.3-m-long ice core drilled at Summit, Greenland (72.34°N, 37.37°W, surface elevation 3283 m, the mean annual snow accumulation rate of 23 g cm^{-2} yr^{-1}) in 1989 as part of the European “Eurocore” program (Supporting Information, Figure S1), spanning a 217-year period (1722−1989 AD).[4]

2.2. Decontamination Method. The core sections of NEEM-2009-S1 were decontaminated by removing the outside of the core using an ultraclean continuous melter system described in detail elsewhere.[18] Briefly, each core section was first cut into parallel longitudinal subsamples with a cross-section of 4 × 4 cm^2 and lengths between 8 and 18 cm, dependent on core quality. These subsamples were then melted into discrete samples using a melting apparatus with a titanium (Ti) melting head that split the meltwater into two different channels, installed in a freezer inside a laminar flow class 100 clean booth in a clean laboratory (class 1000) at KOPRI.

For cores with a density of less than 0.58 g cm^{-3}, the melted sample from the inner part of the core appears to become mixed with that from the outer part during melting due to the capillary force caused by the material’s porosity.[18] Because the density of the upper 19.25 m was less than 0.58 g cm^{-3}, we therefore melted a total of 581 subsamples from 19.25 to 90.09 m in depth, covering a 260-year period between 1711 and 1970 AD. The time resolution of the individual melted subsamples varied from 0.2 to about 1 year of snow accumulation, with a mean value of 0.4 ± 0.15 year. Each of the melted samples was collected in an acid-cleaned LDPE bottle and kept frozen prior to analyses. Only the uncontaminated meltwater collected from the inner part of the core was used for analyses. The procedural blank for As was determined by processing an artificial ice core made by freezing ultrapure water (Millipore Milli-Q Element, Darmstadt, Germany) and was below the instrumental detection limit.[18] The aliquots (∼15 mL) of each melted sample were transported frozen to the State Key Laboratory of Cryospheric Sciences (SKLC) in China for ionic species measurements.

Each core section (4 × 4 cm^2 cross-section, 20 cm in length) from the NEEM deep ice core was mechanically decontaminated using sophisticated ultraclean procedures.[19] This involved the chiseling of successive veneer layers of the core in progression from the contaminated outside toward the center to obtain the contamination-free inner part of the core, using ultraclean stainless chisels or ceramic knives inside a laminar flow class 100 clean bench in a cold room at KOPRI. Then the inner core was divided into two pieces, each 10 cm long, and the upper piece was analyzed for this study. Each subsample covers a span time of ∼0.5 years of snow accumulation.

The Eurocore samples were mechanically decontaminated using different ultraclean procedures in a clean environment (class 100) at the Laboratoire de Glaciologie et Géophysique de l’Environnement (LGGE), France, as described in detail elsewhere.[4] The inner core so obtained integrated 1 or 2 years

Table 1. Statistical Summary of Mean Values (Expressed as Mean ± SD) and Ranges (in Parentheses) of Al and As Concentrations and Crustal Enrichment Factors (EFs) for As in Our Greenland Snow and Ice Samples, and Mean Values of Concentrations and EFs during Specific Periods and Increase Factors (IFs) As Defined in the Text

sample		Al (ng g^{-1})	As (pg g^{-1})/IF	EF (As)/IF	number of samples
snow pit (2003−2009 AD)		0.89 ± 1.05 (0.09−4.72)	2.63 ± 2.75 (0.50−15.8)	188 ± 138 (41.2−771)	70
NEEM deep ice core (8840−9715 years BP)		2.71 ± 0.84 (1.65−3.74)	2.15 ± 0.96 (0.54−3.34)	30 ± 8.9 (12.4−38.8)	8
eurocore ice core (1773−1965 AD)		2.18 ± 1.15 (0.60−4.13)	9.19 ± 6.0 (1.42−22.2)	236 ± 242 (30−1032)	20
NEEM-2009-S1 core					
the whole period (1711−1970 AD)		2.75 ± 2.25 (0.11−14.9)	7.79 ± 11.8 (0.36−147)	176 ± 308 (10.3−2437)	581
separated periods					
pre-1850		3.30	3.46/1.6	49/1.6	307
1850s		2.20	3.46/1.6	79/2.6	22
1860s		2.17	5.14/2.4	125/4.2	27
1870s		2.10	3.21/1.5	71/2.4	26
1880s	1881−1885	1.97	5.37/2.5	120/4.0	13
	1886−1890	2.41	14.3/6.7	264/8.8	12
1890s	1891−1895	1.74	22.0/10.2	755/25.2	13
	1896−1900	1.78	35.5/16.5	908/30.3	13
1900s	1901−1905	1.98	24.8/11.5	713/23.8	12
	1906−1910	2.88	29.1/13.5	474/15.8	10
1910s	1911−1915	2.88	29.6/13.8	532/17.7	11
	1916−1920	1.53	22.2/10.3	765/25.5	11
1920s	1921−1925	2.54	10.3/4.8	208/6.9	12
	1926−1930	2.00	8.67/4.0	221/7.4	11
1930s	1931−1935	2.64	4.82/2.2	96/3.2	12
	1936−1940	1.75	9.54/4.4	239/8.0	13
1940s		1.84	12.1/5.6	298/9.9	22
1950s		1.76	12.4/5.8	479/16.0	17
1960s		2.63	8.98/4.2	145/4.8	17

of snow accumulation. The samples used for this study were derived from the remaining aliquots of 20 inner core samples dated between 1773 and 1965 AD, which were transported frozen from LGGE to KOPRI after the previous study.[4]

2.3. Analytical Procedures. All sample handling and analytical procedures were performed in a class 10 clean booth in a class 1000 clean laboratory at KOPRI. The concentrations of Al and As in the samples were measured using ultrasensitive inductively coupled plasma sector field mass spectrometry (ICP-SF-MS) (Thermo Fisher Scientific, Bremen, Germany). To improve instrumental signal intensities, an APEX desolvation nebulizer (APEX, HF, ESI, Omaha, NE) and a Nafion membrane desolvation module (ACM, ESI, Omaha, NE) were used for the sample introduction system.

The samples were melted at room temperature before analyses and acidified to 1% with Fisher "Optima" grade ultrapure HNO_3. In addition, rhodium (Rh) was spiked as an internal standard. Detection limits, defined as three times the standard deviation of 10 measurements of the blank (1% "Optima" grade HNO_3 solution), were 92.3 pg g^{-1} for Al and 0.27 pg g^{-1} for As. Analyses of diluted solutions of certified riverine water reference materials, SLRS-6 (National Research Council, Canada), exhibited very good recovery versus certified values (in ng g^{-1}): 30.0 ± 5.9 versus 33.9 ± 2.2 for Al and 0.55 ± 0.04 versus 0.57 ± 0.08 for As.

The values of $\delta^{18}O$ and ionic species (Na^+ and SO_4^{2-}) in NEEM-2009-S1 samples were analyzed using Cavity Ring-Down Spectroscopy at KOPRI and ion chromatography at SKLC, respectively.

3. RESULTS AND DISCUSSION

3.1. Holocene Natural Background Level. To understand the perturbation of atmospheric cycles of trace elements linked to human activities, it is first necessary to know the natural background levels of these elements and to identify their sources. The As concentrations measured in the central part of each of the eight core sections from the NEEM deep ice core dated back to ∼8840−9715 years BP, as Holocene natural background samples, ranged from 0.54 to 3.34 pg g^{-1} (mean value: 2.1 pg g^{-1}) (Table 1). They are the first data ever obtained for Greenland old ice, and represent extremely low concentrations of As in Greenland Holocene ice, with intra-annual variation due to a span time of ∼0.5 year of snow accumulation for each analyzed core section. Interestingly, the mean Holocene As concentration in Greenland ice is comparable to that in Holocene ice (∼3 g g^{-1}) in Antarctica, the southernmost continent on Earth.[12]

We calculated the crustal enrichment factor (EF) to evaluate the degree to which As could be attributed to crustal input. The EF is defined as the concentration ratio of a given element to Al (a reference element for crustal dust) in snow or ice, normalized to the same concentration ratio in the upper continental crust (UCC).[20] The calculation of EF for As is as follows: EF = $[As/Al]_{ice}/[As/Al]_{crust}$. If the calculated values of EF are close to unity, crustal dust is a dominant source of As; conversely, EFs larger than unity indicate that contributions from other natural sources are important. Note that the selection of both a reference element (e.g., Al, Fe, and Sc) and crustal compositions can influence the result of the calculation of an EF.[21] Here, we used Al as a reference element, because it

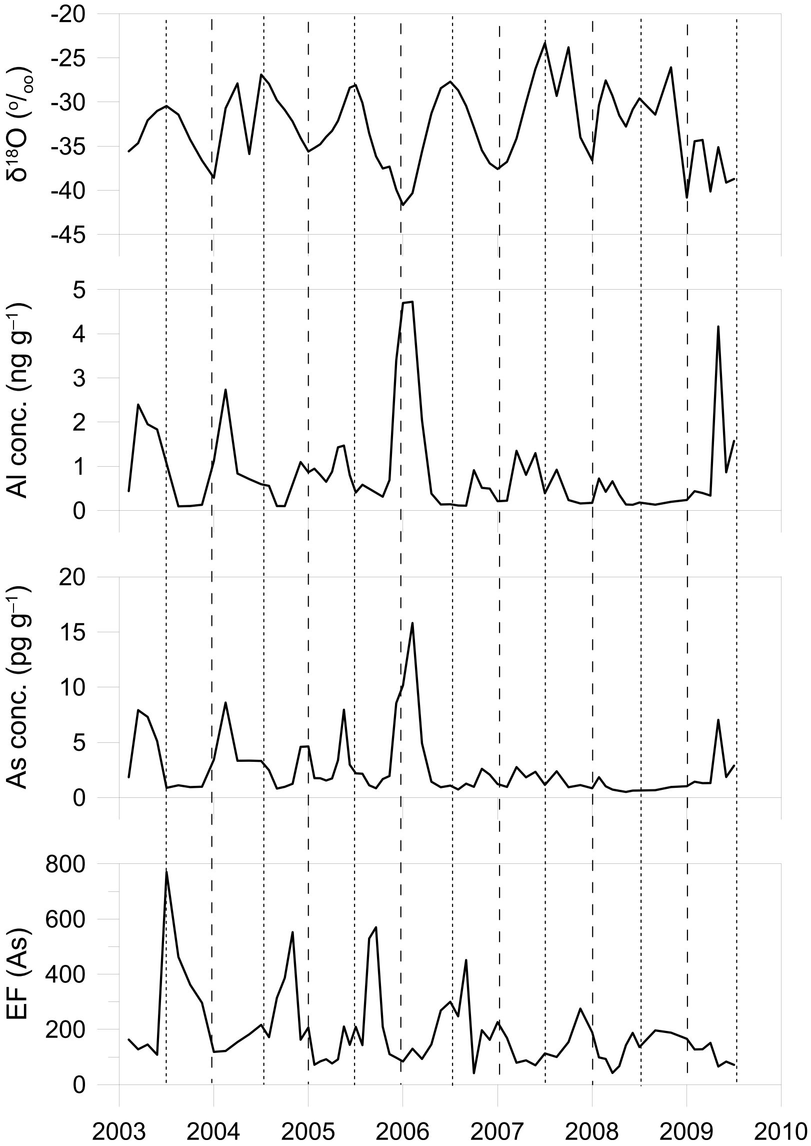

Figure 1. Depth profiles of $\delta^{18}O$, Al, and As concentrations and crustal enrichment factors (EFs) for As measured in our snow-pit samples from northwest Greenland. Dotted lines represent the maxima of $\delta^{18}O$ in summer and dashed lines represent the minima of $\delta^{18}O$ in winter during the period 2003–2009.

is a conservative element and a major constituent of clay minerals, a major contributor to continental mineral dust deposited in central Greenland.[22] Indeed, Al has been used successfully in evaluating crustal contributions to enrich trace elements in Greenland snow and ice.[2,3,5,23,24] The selection of appropriate crustal composition for dust transported to Greenland is also crucial in the calculation of an EF, because of the variable composition of the Earth's surface and the natural fractionation of elements through geochemical processes such as weathering and pedogenesis[21] and during the long-range atmospheric transport of mineral particles.[25] Due to the difficulties in addressing the above issues, we used the average composition of the UCC[20] as a crustal reference. It is believed that site-specific natural Holocene background levels of EFs for As allow us to quantify the extent to which human activities have affected the As cycles during the investigated industrial era (Table 1).

As shown in Table 1, the moderate EF values (mean ± standard deviation (SD): 30 ± 9) indicate that inputs from sources other than crustal dust were likely very significant. This is consistent with the suggestion that the most important natural sources for As in the atmosphere are volcanic emissions and continental and marine biogenic activity.[12,26]

3.2. Seasonal Variation in As in Recent Greenland Snow. Figure 1 shows the first comprehensive data obtained on the occurrence of As in Greenland snow layers dated from 2003 to 2009. The large variability in concentrations of As, ranging from 0.5 to 16 pg g^{-1} (mean value: 2.6 pg g^{-1}) (Table 1), reflects the strong seasonal variation. One striking feature is that enhanced concentrations of As appear to be linked to pronounced Al peaks in the winter and spring snow layers ($\delta^{18}O$ minima) (Figure 1). There was a very significant correlation between As and Al in snow with Pearson's correlation coefficient of 0.915 that is significant at p = 0.001, indicating a strong influence of crustal dust in transport and deposition of As to recent Greenland snow as found for other trace elements.[16,17,23] Interestingly, the most recent mean As concentration was slightly enhanced compared to the

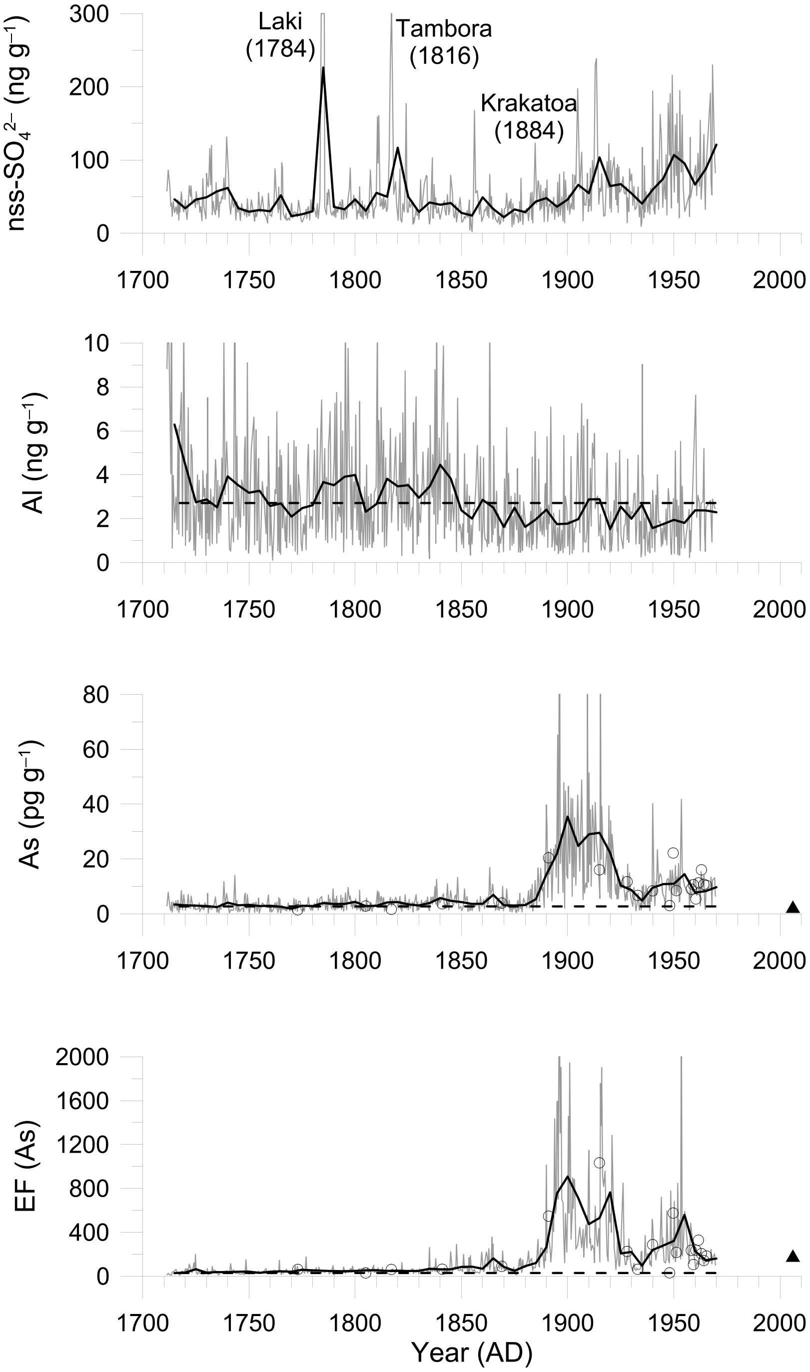

Figure 2. Continuous subannual records of nss-SO$_4^{2-}$, Al, and As concentrations and EFs for As between 1711 and 1970 AD based on NEEM-2009-S1. Solid lines represent 5-year-averaged values. The data determined from the discrete samples of the Greenland Eurocore ice core are shown by open circles. Also shown are the Holocene natural background levels from the NEEM deep ice core (dashed lines) and the mean values of As concentrations and EFs from snow-pit samples (solid triangles).

natural mean Holocene level (2.1 g g^{-1}). However, greater As concentrations during the winter and spring throughout the entire investigation period, reaching up to ~16 g g^{-1}, are about two to eight times above the natural Holocene level.

There is a paucity of data on the occurrence of As in Greenland snow and ice to compare our data. Very recently, concentrations of As and other elements in 22 shallow snow pits along a northwest Greenland transect were reported.[27] These As concentrations were an order of magnitude higher than those in our snow-pit samples. The reason for the discrepancy is uncertain given the lack of methodological details in ref 27. However, in our experience, As analysis is prone to contamination and ultraclean procedures are required to minimize the risk of sample contamination at the pg g^{-1} level throughout the entire analytical procedure from field sampling to laboratory analysis. It should also be noted that the Zn and Pb concentrations given in ref 27 are much higher than those previously obtained from Greenland snow,[1,4,17,23] which suggests systematic bias due to background contamination in the samples.

The EFs of As in the snow were within the range of 41−771, with a mean value of 188, which is about six times the mean

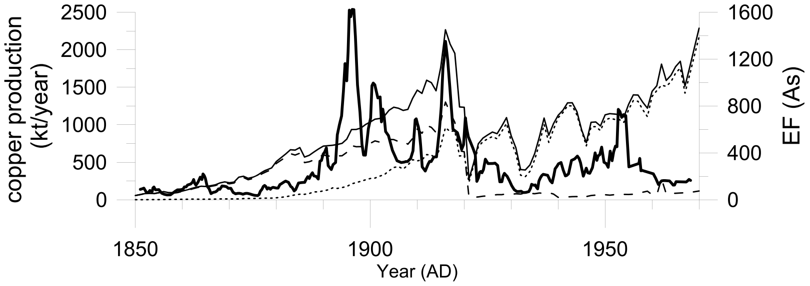

Figure 3. Comparison between 2-year-averaged EF values (thick solid line) and annual Cu production rates in Europe (dashed line) and North America (dotted line) between 1850 and 1970 AD.[29,30] The thin solid line indicates the total Cu production in the two regions.

Holocene natural level (Table 1). High EF values indicate that recent Greenland snow was greatly enriched with As relative to the crustal dust contribution, most likely due to a predominant anthropogenic source as well documented for other trace elements in recent Greenland snow.[16,17,23] The EF values tend to be inversely correlated with Al concentrations with much higher EFs (>200) when Al concentrations are relatively low in the summer and autumn snow layers (δ^{18}O maxima) (Figure 1), in contrast to the relationship between As and Al concentrations. Such a pattern implies a higher percentage of anthropogenic As in the summer to autumn snow layers.

3.3. Changes in As Concentrations and EFs over the Past 300 Years.

Figure 2 shows the first continuous high-resolution records of concentrations and EFs of As, as measured in the 581 innermost portions of NEEM-2009-S1 covering the period 1711−1970 AD. The large short-term variability in the concentrations is most likely associated with seasonal variation, as recorded in our snow-pit samples. We have thus averaged for the 5 years to compensate for inter- and intra-annual variation in concentrations (Figure 2). To validate the cleanness of our continuous melting decontamination procedures, we compared NEEM-2009-S1 averaged As concentrations and EF values with those obtained from discrete Eurocore samples, with a 1- or 2-year interval, over the period 1773−1965 AD. Because it was previously verified by full outside−inside concentration profiles of analyzed trace elements that there was no transfer of outside contamination into the center of the Eurocore samples,[4] it is considered that the As concentrations measured in the central part of each Eurocore sample represent the original snow or ice values. In Figure 2, the As concentrations and EFs and their temporal variability in both records show general agreement, despite differences in the geographic properties of the two drilling sites (Supporting Information, Figure S1). This confirms that there was no transfer of outside contamination into the inner part of individual NEEM-2009-S1 subsamples during the continuous melting process, giving us a high degree of confidence in the results.

As shown in Figure 2, the long-term time series of As concentrations and EFs between 1710 and 1970 AD are well characterized by the changing pattern of their values during the industrial era. Here, it must be noted that atmospheric As deposition fluxes (in pg cm^{-2} yr^{-1} as calculated from the As concentration measured in the ice and from the estimated snow accumulation rate in water equivalent per year for the corresponding sample) could differ from concentrations because snow accumulation rate can vary considerably with time. As shown in Figure S3, the As concentration record appears very similar to its flux record, because the estimated snow accumulation rates in our samples show no long-term temporal variability (mean ± SD: 22.5 ± 6.7 g cm^{-2} yr^{-1}), consistent with previous findings from four NEEM shallow ice cores covering the period 1725−2007.[28] Thus, these results suggest that the variability and trend in the As concentrations represent the history of changes in atmospheric depositions of As in central Greenland over the past 300 years.

Our data show that As concentrations and EFs remained relatively constant until 1850 with mean values ± SDs of 3.46 ± 2.34 pg g^{-1} and 49 ± 33, respectively (Table 1), exhibiting slightly higher mean levels by 1.6 times, respectively, relative to Holocene background natural levels. After a slight variation in As concentrations and EF values between the 1850s and 1870s, the 5-year averaged records show the most striking feature of abrupt, unprecedented increases after the mid-1880s, which then accelerate in the early 1890s, peaking in the late 1890s (Figure 3). In the 5-year-averaged maximum in the late 1890s (Table 1), the mean As concentration and EF are 35.5 pg g^{-1} and 908, with increase factors (IFs) of ∼17 and 30 relative to Holocene natural levels, respectively (Table 1). The IFs are defined as the ratios of the mean values of As concentrations or EFs between specific time periods and the early Holocene, calculated using the following equation: IF = $[X]_{specific}/[X]_{Holocene}$, where $[X]_{specific}$ and $[X]_{Holocene}$ refer to the mean values of As concentrations or EFs during the specific periods and the early Holocene, respectively. Profiles of As concentrations and EFs are then well defined with highly elevated levels until the ∼1910s, followed by a marked decline, reaching minima in the early 1930s of 4.82 pg g^{-1} and 96, respectively, almost pre-1880s levels. After the early 1930s, there is an apparent increase in concentrations and EFs, peaking in the mid-1950s, before decreasing again. Finally, the present-day As concentration and EF levels exhibit a contrasting situation. Compared to the 1960s, the present-day mean As concentration in recent Greenland snow is lower by a factor of 3.4, whereas the mean EF is at a level 1.3 times higher (Table 1).

Our long-term trend, characterized by significant increases in As concentrations and EFs relative to the Holocene natural levels during the specific periods, cannot be related to natural variation. As discussed before, one of the most important natural sources for As in the atmosphere is volcanic emissions.[12,26] However, there is no evidence that volcanic activities have increased during the past 300 years,[29] and our data show no synchronous increase in As concentrations in the volcanic layers linked to well-identified large volcanic nss-SO_4^{2-} depositions from the Krakatoa (1883), Tambora (1815), and Laki (1783) eruptions (Supporting Information, Figure S2). Marine biogenic emissions are also known to be a potentially important source of As in the atmosphere, accounting for ∼20% of the total As emissions from natural sources.[26] According to multicentury Greenland ice-core records of methanesulfonic acid (MSA), an oxidation product of dimethyl sulfide, produced by marine biota, a marked decline in MSA concentrations has occurred over the past two centuries, which was attributed to the significant decreasing trend in subarctic Atlantic primary productivity.[30] Thus, we can exclude the possible contribution of marine biogenic emissions to temporal patterns of As concentrations and EFs observed in our samples within at least the past 200 years. In addition, we have examined the relationship between our records and the North Atlantic Oscillation (NAO). The NAO is a primary source of inter-annual climate variability for the North Atlantic Ocean basin affecting the major atmospheric circulation patterns over much of Europe and parts of North America.[31,32] To compensate for short-term variability of the NAO index, we used the time series of the NAO index averaged over 5 years. As shown in Figure S4 of the Supporting Information, there are no obvious correlations between the 5-year-averaged values of As concentrations and EFs and those of the NAO indices, suggesting no significant influence of the NAO on As enrichments in our temporal record. Finally, the time series of Al concentrations exhibits generally lower values since the mid-19th century, which is in contrast to the increasing As concentrations and EFs during the corresponding period (Figure 2). Taken together, the enriched As concentrations and EFs in NEEM-2009-S1 are most likely a consequence of increased anthropogenic emissions of As during the industrial era.

As described before, both mean concentrations and EFs between 1710 and 1850 AD are enhanced by 1.6 times relative to Holocene mean natural levels (Table 1). This supports the large-scale atmospheric As pollution in the northern hemisphere as early as the beginning of the 18th century. A previous investigation of As in a Canadian Arctic ice core documented substantial enrichments of As exceeding natural levels during antiquity, ~3000 years ago, and suggested ancient atmospheric pollution for this element in remote areas of the northern hemisphere long before the 18th century.[33] However, this finding was deduced from eight discrete ice-core samples whose age ranged from 2000 to 4000 years BP, providing an incomplete low-resolution record. A highly resolved, continuous Greenland ice core record extending back to antiquity is required to substantially understand the extent and magnitude of ancient As pollution in the atmosphere of the northern hemisphere.

3.4. Legacy Impact of Cu Smelting on Greenland As Pollution. Nonferrous metal production, particularly Cu smelting processes, is the largest anthropogenic source for As emissions on a global scale.[13,34−37] We compared the temporal trends of 2-year-averaged EF values (as a surrogate for anthropogenic enrichment) with historical Cu smelting production data available for the period 1850−1970 AD in Europe and North America,[38,39] the candidates for the largest source regions (Figure 3).[4−8]

The variability in the EFs matches well with the Cu production record, except for the periods before ~1910 and after the mid-1950s. The observed discrepancy between the two records is likely because Cu smelting production data do not reflect substantial emission rates. The obvious difficulty in estimating temporal emission rates is the lack of data on emission factors of the past, which would have differed from current emission factors.[40] The emission factors of As for Cu smelting production were probably high until the beginning of the 20th century when improved furnaces and metallurgical technology began to spread.[40,41] In comparison, they have continuously decreased by orders of magnitude in more recent decades as a result of further improvements in metallurgical technology and the introduction of efficient control equipment in western countries.[34,36,42] Such a large decrease in emission factors resulted in a significant reduction in As emissions in Europe and North America after the mid-20th century.[43,44] Consequently, it would be reasonable to suggest that changes in EFs represent the legacy impact of historical Cu smelting production and the resultant As emissions in Europe and North America. Previous findings showed that ancient Pb pollution recorded in Greenland ice varied in parallel with emission changes in mining and smelting activities of Pb-containing ores in major source regions during the corresponding periods,[2,4,8] supporting the above hypothesis.

The relationship between the 2-year-averaged EF values and historical Cu rates was then used to deduce the most likely source regions of anthropogenic As enrichment in central Greenland during different periods. More than 70% of total Cu production was in Europe (particularly Germany) until the early 20th century, indicating Europe as a dominant source region. Thus, the peaks in As concentrations and EF values observed between the mid-1890s and the early 1900s reflect the highest emissions of anthropogenic As in Europe during that time, most likely associated with the poor emission control prior to the beginning of the 20th century.[40,41] Since then, Cu production in North America increased significantly, from 431 kt in 1905 to 920 kt in 1918, accounting for ~35 and 47% of total Cu production, respectively (Figure 3). After the First World War, Cu production rates decreased sharply in Europe and North America, from ~1030 kt in 1918 to 33 kt in 1922 and from ~920 kt in 1918 to ~457 kt in 1922, respectively, with a reduction in total production by a factor of 4, from ~1950 kt in 1918 to ~490 kt in 1922. The averaged EF values show a sudden decrease beginning in ~1918, by a factor of ~5 from 888 in 1918 to 165 in 1922. The striking similarity between the decreasing trends of EFs and total Cu production rates implies that the contributions from Europe and North America to anthropogenic As deposition in central Greenland were at similar levels between the mid-1900s and the early 1920s (Figure 3). The Cu production rate in Europe remained low at an average of ~74 kt yr^{-1} between 1921 and 1970, while it increased from ~800 kt in the mid-1920s to ~2170 kt in 1970 in North America.[38,39] This implies that anthropogenic As in Greenland originated mainly from North America after the mid-1920s. The minimum averaged EF value of ~96 in the early 1930s, corresponding to the Great Depression, is consistent with a notable dip in Cu production in North America (Figure 3), supporting the above assumption. Interestingly, the previous study found that EFs of Pb in central Greenland ice dropped greatly in the early 1930s, coinciding with the economic downturn and drastic declines in production during the Great Depression.[24] As a result, our Greenland ice-core record of EFs reflects historical emissions of As from the smelting of Cu in Europe and North America, eventually causing large-scale As pollution in the northern hemisphere. The same is true of the variability in As in Antarctic snow and ice, evidencing that historical large-scale As pollution in the southern hemisphere was associated with changes in Cu smelting production, particularly in Chile.[13,37]

An interesting feature observed in our records is that As concentrations and EF values increased again after the 1940s, reaching a peak in the mid-1950s, in parallel with nss-SO_4^{2-} concentrations (Figure 2), which were dominated by coal-burning emissions.[7] It should, therefore, be noted that the enrichment of As in central Greenland since the mid-20th century could be partially attributed to As emissions from coal combustion, a potential anthropogenic source.[34,36] According to global anthropogenic emission estimates,[36] the amount of As emitted from coal combustion accounted for a quarter of that from nonferrous metal production in the mid-1990s.

3.5. Projection of Future As Pollution. The temporal trend of As concentrations and EF values in our samples is characterized by a significant decrease from the 1950s to the 2000s, with a reduction of ~80% from 12.4 to 2.63 g g^{-1} for As concentration and ~60% from 479 to 188 for EF (Table 1). The mean concentration value in the 2000s is roughly similar to the Holocene natural level (2.15 g g^{-1}). As shown in the relationship between As and Al in the snow pit, crustal dust is the major transport medium for anthropogenic As input to snow. It is therefore likely that the relatively low present-day As concentration level is a consequence of reduced crustal dust inputs during the corresponding period (Table 1). In comparison, the present-day mean EF is enriched by a factor of ~6 relative to the Holocene natural level and by a factor of 1.3 relative to the 1960s level, indicating that more than 80% of present-day As deposited to central Greenland is anthropogenic in origin.

Since the mid-1970s, there has been a continuous reduction of As emissions due to progress in developing more efficient emission control equipment, particularly in Europe and North America,[36,43] along with a significant decrease in emissions from >10 000 t in the 1970s to 763 t in 2000 in Europe.[43] In contrast to this situation, emissions of As in East Asia, particularly China, have rapidly increased from 791 t in 1980 to 2501 t in 2006 due to the rapid economic growth and urbanization in the past decades.[45] More than 90% of the total amount of As emitted from China arises from coal combustion by power plants and industrial boilers,[46] which account for about half of present-day global anthropogenic As emissions.[47] Recently, the contribution from coal combustion in China has become growing for trace elements deposited on central Greenland snow.[7,16,17] Thus, the significantly enriched As observed in Greenland snow-pit samples is most likely attributed to a steadily increasing contribution from China in recent decades.[48]

The emissions trend of As from coal combustion in China declined after 2006, thanks to the increasing use of wet flue gas desulfurization and various air pollutant control devices in coal-fired power plants and industrial boilers.[45,46] Interestingly, the magnitudes of the peaks of EF values in the snow pit show a continuous decrease from 2006 to 2009 (Figure 1), probably due to decreasing As emissions from 2501 t in 2006 to 2326 t in 2009 in China.[45] Although further investigation is required to confirm this situation, our results highlight that the implementation of more rigorous emission controls and national ambient air quality standards in China will lead to a substantial reduction in pollutant emissions[45] and large-scale atmospheric As pollution in the northern hemisphere, with great benefits for public health. One example is the dramatic decline, down to the pre-1900 level, in As concentrations and its EFs after 2000 in Antarctic snow and ice.[13,37] This situation is closely linked to the introduction of governmental regulations, beginning in the mid-1990s, for reducing As emissions from the Cu industry in Chile, the most important anthropogenic source of As emissions in the southern hemisphere.[13,37]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.9b01805.

> Map of Greenland showing the sites of the NEEM2009S1 and the Eurocore ice cores; concentrations of nss-SO_4^{2-} and EF values for As measured at depths corresponding to the Laki (1783), Tambora (1815), and Krakatoa (1883) eruptions; 5-year-averaged As concentrations and fluxes in the NEEM2009S1 ice core between 1711 and 1970 AD; 5-year-averaged NAO indices, As concentrations, and EFs between 1860 and 1970 AD (PDF)

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