High-Resolution Tritium Profile in an Ice Core from Camp Century, Greenland

Qiao, Jixin; Colgan, William; Jakobs, Gunnar; Nielsen, Sven

Published in:
Environmental Science and Technology

Link to article, DOI:
10.1021/acs.est.1c01975

Publication date:
2021

Document Version
Publisher's PDF, also known as Version of record

Environmental Science & Technology

pubs.acs.org/est

Article

High-Resolution Tritium Profile in an Ice Core from Camp Century, Greenland

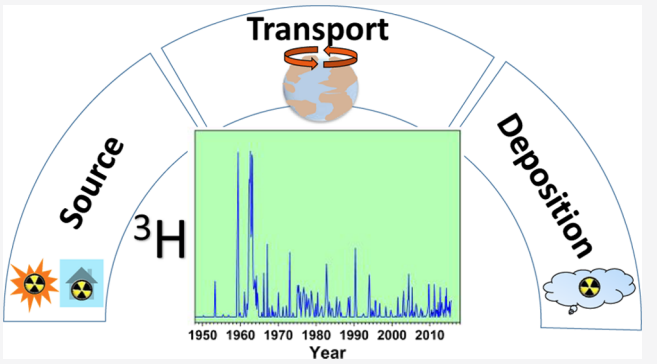
Jixin Qiao,* William Colgan, Gunnar Jakobs, and Sven Nielsen

Cite This: *Environ. Sci. Technol.* 2021, 55, 13638−13645

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: We measure ^{3}H in an ice core from Camp Century. The temporal distribution of ^{3}H concentration in the ice core corresponds generally well with the historical record of explosive yields of atmospheric nuclear weapons tests. Maximum ^{3}H values observed in 1962−1963 are comparable to those in ice core or precipitation in many other locations in the Northern Hemisphere. There is no indication that significant ^{3}H contamination was locally released into the air during the operation of the Camp Century reactor. It is, however, somewhat surprising that several prominent ^{3}H peaks are still observed after 1980. We suggest that these are associated with airborne ^{3}H releases from the civil nuclear industry. A wavelet analysis during 1970−2017 indicates the primary frequency of variability in the ^{3}H record is annual ^{3}H peaks. These annual peaks can be combined with the ^{3}H spikes from global fallout of known nuclear weapons tests to benchmark and evaluate theoretical ice core dating scales back to the 1950s. A positive correlation is observed between annual ^{3}H average concentration and variability of Arctic Oscillation (AO). This highlights the value of ^{3}H as a potential tracer for air masses and airborne pollutants in the Arctic.



KEYWORDS: *tritium, Camp Century, ice core, source, tracer application*

INTRODUCTION

During 1960−1964, a portable nuclear reactor of moderate size, type PM-2A, operated below the surface of the ice sheet at Camp Century in Northwest Greenland. The reactor had a thermal power of 10 MW that was used for electricity (1.5 MW) and heating. Conventional and radioactive liquid wastes arising from the operation of the camp were discharged into the Greenland Ice Sheet. The Danish-American agreement permitted discharge of liquid radioactive waste into the ice sheet of up to 2 GBq/year (50 mCi/year), whereas all solid radioactive wastes had to be removed from Greenland.[1]

An environmental monitoring program was carried out by Camp Century staff during the operation of the reactor that included $\alpha/\beta/\gamma$ measurements of background radiation and measurements of radioactivity in discharged coolant, surface air and snow, and the subsurface drinking water supply. In 1961 and 1962, α and β radioactivity in the air and snow showed increased levels due to fallout from atmospheric nuclear weapons testing by the Soviet Union.[2−4] The measurement data was shared with Danish authorities, who concluded in 1964 that the reactor operation had not resulted in any significant increase in levels of radiation or radioactivity at Camp Century or its surroundings.[5]

Today, some concern exists regarding the potential remobilization of the liquid radioactive waste at Camp Century, and its impact on the surrounding environment, in the context of climate change in the Arctic region.[6] Therefore, reevaluation of radioactivity at the abandoned reactor site is necessary to deliver policy-relevant information. In this work, we present an investigation carried out for the distribution of radioactivity (primarily tritium (^{3}H)) in an ice core recovered about 150 m from the reactor ventilation stack. Besides using ^{3}H as an important vector for evaluating the local radioactive contamination, we also explore the broader applicability of ^{3}H as an atmospheric tracer in the Arctic.

Sources of ^{3}H in the Environment. ^{3}H is a pure β emitter with a half-life of 12.32 years. Natural ^{3}H is mainly produced at a rate of ca. 71 PBq/year (0.2 kg/year) by the interaction of cosmic radiation with nitrogen in the upper atmosphere, with a steady-state global inventory of ca. 1285 PBq (3.6 kg)[7] and occurs in the form of water molecules (HTO). Natural tritium background concentration is typically very low, with reported values of between 1.18 and 2.36 Bq/kg in precipitation at Thule, Greenland during 1945−1950.[7]

Received: March 26, 2021
Published: September 29, 2021

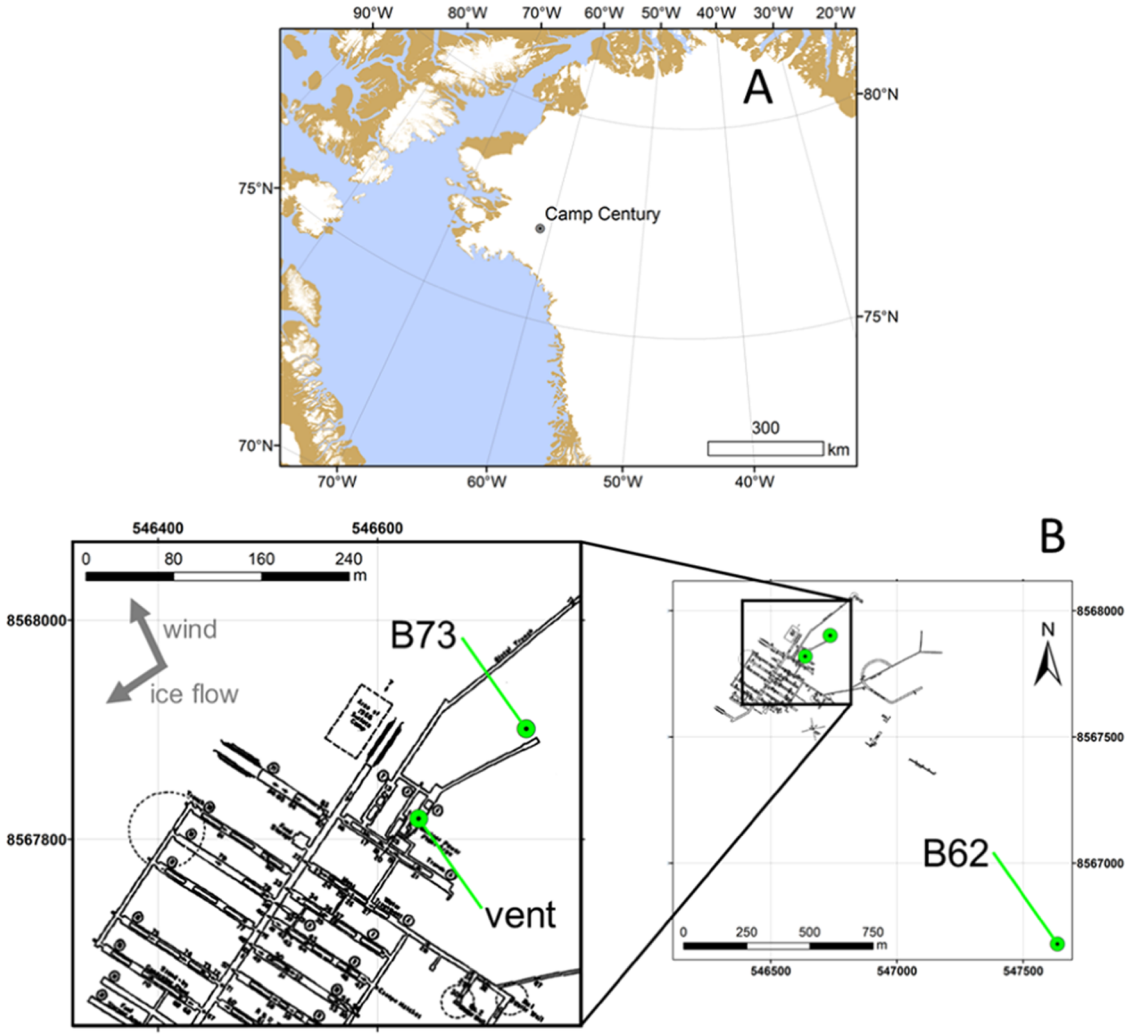


Figure 1. Location of Camp century (A) and the ice core sampling site (B73) in this study relative to the estimated reactor vent position (B). The contemporaneous remote undistributed ice core (B62) was not analyzed in this study. As-built site map from Kovacs[11] georeferenced in EPSG:3413 coordinate system by Karlsson et al.[14] Vectors show prevailing wind (toward 336°) and ice flow (toward 255°) directions.

Since 1954, a total of ca. 187 425 PBq (525 kg) of ^{3}H, mainly in the form of HTO, has been injected into the upper troposphere and the stratosphere via atmospheric detonations of thermonuclear devices.[8] Approximately 4641 PBq (13 kg) of tritium gas (HT) was also released by military tritium facilities and leaks from underground testing of nuclear weapons during 1950−2000.[7,9] Most atmospheric nuclear weapons tests took place in the Northern Hemisphere, with three major sites including Novaya Zemlya in the Russian Arctic, Bikini and Eniwetok Islands (U.S.) in the Pacific Ocean, and the Nevada Test Site in the continental U.S. A reported 85 tests took place on the island of Novaya Zemlya.[10]

In today's atmosphere, ^{3}H is mainly released from the nuclear power industry. These emissions are primarily associated with nuclear power plants and nuclear fuel reprocessing.[9] Compared to the global fallout from atmospheric nuclear weapons testing, the ca. 125 PBq (0.35 kg) ^{3}H inventory from civil nuclear industry has been relatively minor during 1950−2000.[8]

MATERIALS AND METHODS

Ice Core Sampling. The present-day location of Camp Century's subsurface infrastructure was estimated prior to fieldwork by georeferencing a historical site map.[11] This georeferencing used a single tie-point, the location of the original drill tower, corrected for motion since its last precise survey in 1986.[12] The nuclear reactor vent is assumed to be located directly above the nuclear power plant trench. The general ice core location was preselected to be downwind of this estimated reactor vent position. The final ice core location (B73 at 77.1826°N, 61.1125°W and 1887 m above sea level) was selected using ice-penetrating radar to find a gap in the subsurface debris field that was suitable for ice drilling. We estimate that the ice core was recovered 150 m from the reactor vent (Figure 1). A remote reference ice core B62 (77.1826°N, 61.1125°W) was contemporaneously recovered 1.5 km away at an undisturbed upwind site to compare the near-surface ice-sheet density profiles inside and outside of the Camp Century debris field.[13]

The ice cores were recovered using a University of Wisconsin Eclipse2 ice drilling system during July 2017. This relatively lightweight (800 kg) tip-drill system operates without drilling fluid to depths of approximately 300 m.[15] The B73 ice core was sampled from between 180 and 4000 cm depth, although drilling continued without sampling to a total depth of 73 m. Core sections were cut into samples of 10.0 cm in length, or 9.9 cm accounting for saw loss, and weighed for density on an open-air

https://doi.org/10.1021/acs.est.1c01975
Environ. Sci. Technol. 2021, 55, 13638−13645

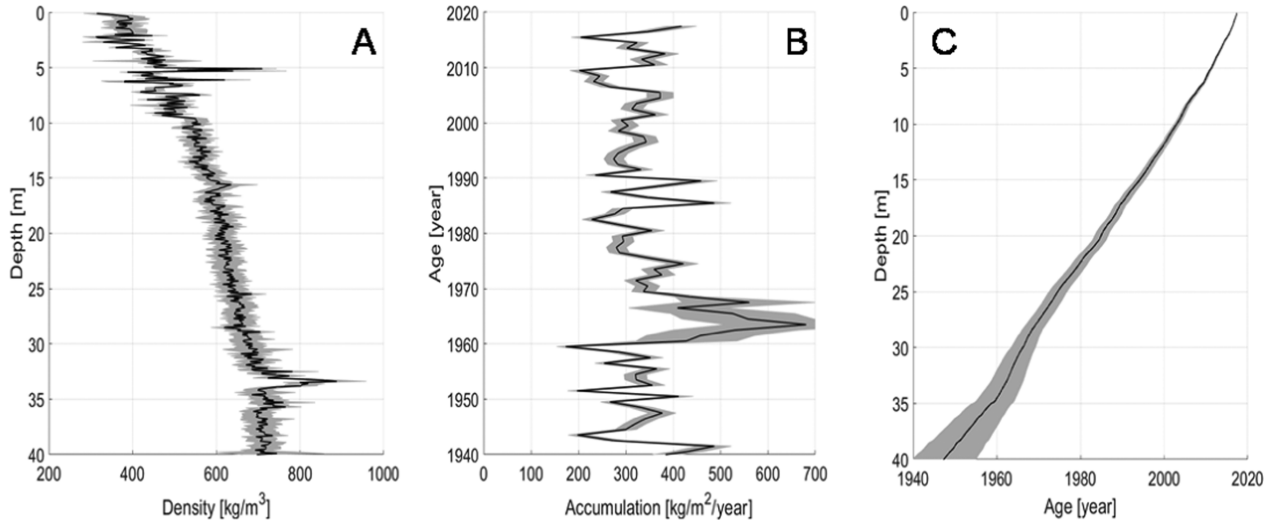


Figure 2. (A) Previously described ice-sheet density profile of core B73 at Camp Century.[13] (B) Previously described annual accumulation rate history at Camp Century.[16] (C) Novel age-depth relation for core B73 modeled here. In all subplots, shaded areas denote associated uncertainty.

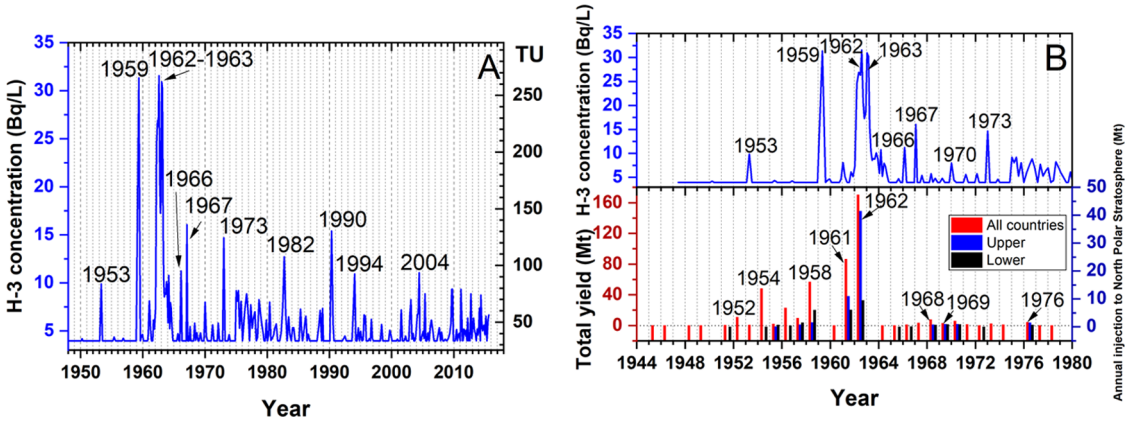


Figure 3. Distribution of ^{3}H activity concentrations in the Camp Century ice core B73 (A) and its correlation to global atmospheric nuclear weapons test explosion yields, as well as estimated injection to upper and lower layers of North Polar stratosphere[8] (B). ^{3}H concentrations below the limit of detection (LOD) are presented as LOD (3.94 Bq/L). Tritium units (TU) is used to express the ^{3}H concentration on the right of *Y*-axis in (A), wherein 1 TU = 0.118 Bq/L.[18] All of the data of ^{3}H concentration are decay-corrected to 28th July 2017.

core logging table. Given an internal drill diameter of 8.0 cm, each sample was equivalent to between 145 mL (at 300 kg/m^3 firn density) and 440 mL (at 915 kg/m^3 pure ice density) of water. Samples from the top 40 m of the core were sealed into individual Whirlpak bags within approximately 15 min of extraction. The samples were allowed to melt in transit back to Copenhagen.

Determination of ^{3}H. Aliquots of 10 mL from each water sample were analyzed using low-level scintillation counting (liquid scintillation counter, LSC: Tri-Carb 3170 TR/SL and Quantulus, PerkinElmer) by direct measurements. Blank samples were prepared using tritium dead water. The standards were prepared with 10 mL of NIST-SRM-4361 Hydrogen-3 standard. The samples, standards, and blanks were transferred to a 20 mL plastic vial, and 10 mL Ultima Gold LLT scintillation cocktail (PerkinElmer) was added to each sample. The samples were measured using LSC for 50 min in three cycles. With the above-described process, the detection limit for tritium is about 4 Bq/L, which is calculated as 4.65 σ_b, with σ_b referring to the standard counting error of ^{3}H concentrations in blank samples (n = 6). The uncertainty of ^{3}H concentration is obtained as an expanded uncertainty that consists of counting statistic errors of sample, standard, and blank in LSC measurement and the uncertainty of the certified value of the standard (about 2.5%), with a coverage factor of k = 1. Standard uncertainties range from 11% (highest measured activities) to 34% (close to detection limit). All of the data of ^{3}H concentration presented in this work were decay-corrected to 28th July 2017 (the end-date of the ice core sampling).

RESULTS AND DISCUSSION

Age-Depth Relation. The age-depth relation of the ice core and its samples was estimated by combining the measured accumulation-depth profile with a previously described annual accumulation rate history for the site.[16] The measured accumulation-depth profile, in meters of water equivalent (mWE), was derived from depth integration of individual sample densities (Figure 2). As each sample represents 10 cm in length, the time interval covered by each sample varies from 0.1 ± 0.1 year in the surface layers to 0.2 ± 7.6 year in the bottom layers of the ice core. Uncertainties in the accumulation-depth profile and accumulation rate history, which are assumed to be independent, were summed in quadrature. Date uncertainty increases from 2015.7 ± 0.1 at 180 cm depth to 1968.0 ± 2.5 at

https://doi.org/10.1021/acs.est.1c01975
Environ. Sci. Technol. 2021, 55, 13638−13645

2870 cm depth and to 1947.4 ± 7.6 at 4000 cm depth. The accumulation-depth profile was derived from the B73 core recovered within the subsurface debris field (Figure 1). The accumulation rate at this site is clearly increased due to enhanced snow deposition associated with drifting snow during the active period of Camp Century. Based on historical descriptions and modern experiences, we estimate this accumulation enhancement to be 50 ± 50% during the 1960−1967 period.[11,13] The propagation of this substantial uncertainty is evident in the associated dating model uncertainty.

This age-depth relation for B73 suggests that ice deposited during the nuclear power plant operational period (1960−1964) is now located between 3100 and 3450 cm depth. Comparison of the B73 density-depth profile with that of ice core B62, highlights that densities inside the debris field are significantly higher than outside the debris field between 3200 and 3500 cm depth (Figure S1).[13] This high-density layer, which is discolored slightly yellow in appearance and contains visible macroscopic particulates, likely reflects enhanced local compaction and pollution during the Camp Century active period. The recovered ice samples therefore clearly span the entire Camp Century active period.

^{3}H Depth Profile. The overall analytical results obtained in this work for ^{3}H are summarized in Table S1. Graphic illustrations of ^{3}H concentration distribution along the dated ice core are shown in Figure 3A. Notably high ^{3}H concentrations (17−32 Bq/L) are observed in the depth range 3230−3320 cm, which corresponds to the period of 1963.0 ± 3.7 to 1962.2 ± 3.9. Another sharp ^{3}H peak at 1959.4 ± 4.6 (depth of 3480−3490 cm), along with several smaller peaks (^{3}H concentration ≥10 Bq/L) from the late 1960s until 2004, are also marked in Figure 3A. Our record clearly captures a huge increase in ^{3}H concentration in the 1950s−1960s, followed by a steady decrease over time since ca. 1963. The overall variability of ^{3}H concentration along the ice core is fundamentally composed of (1) source variability, (2) transport variability, and (3) deposition variability.[17]

^{3}H Source Terms. To understand the source terms of ^{3}H in the Camp Century ice core, we plotted the measured ^{3}H temporal distribution, together with the historical record of global atmospheric nuclear weapons testing yields in 1945−1980, as well as the estimated annual injection of nuclear debris into upper and lower layers of North Polar stratosphere in Figure 3B. Due to differing patterns of air mass movement between the upper and lower stratospheres, nuclear debris injected above the upper stratosphere are widely dispersed, contributing to global fallout, whereas those injected to the lower stratosphere mostly form regional and local fallout.[8] During 1945−1980, a total of 543 atmospheric nuclear weapons tests, corresponding to 440 Mt (trinitrotoluene [TNT] equivalents) explosive yields, were conducted.[8] The most active years of testing from the standpoint of the total explosive yields are 1962, 1961, 1958, and 1954, respectively (Figure 3B).

^{3}H Peaks before 1961. As seen from Figure 3B, prior to 1961, the two notable peaks (1953.3 ± 6.2 and 1959.4 ± 4.6) for ^{3}H concentration in the Camp Century ice core correspond well with the high explosion yield of atmospheric nuclear weapons test in 1954 (48.3 Mt) and 1958 (56.8 Mt), respectively, considering the uncertainties in the age model. The ^{3}H peak signal in 1959.4 ± 4.6 is much more intense than the one in 1953.3 ± 6.2. This could be related to: (1) the total fusion yield (the primary production path for ^{3}H) for the tests in 1958 (30.3 Mt) is nearly 2 times higher than that in 1954 (17.4 Mt), resulting in much higher ^{3}H fallout in 1958; (2) the bomb tests in 1954 were mostly carried out in the Pacific Ocean, while in 1958 tests occurred both in the Pacific and Arctic regions, with the total annual denotation at Novaya Zemlya of 16.1 Mt.[10] Therefore, a much greater injection of nuclear debris into the North Polar stratosphere is expected in 1958 (7.6 Mt) compared to 1954 (0.01 Mt).[8] This indicates that the main transport pathway for historical global fallout ^{3}H at Camp Century was via airborne stratospheric injection. Similar observations of elevated ^{3}H levels in 1954 and 1959 have been reported in an ice core from Spitsbergen and a precipitation record from Ottawa (Canada).[19] Earlier studies in snow samples from Greenland have also observed a notable ^{3}H peak in 1959,[20] which is consistent with the historical record for other radionuclides, such as ^{137}Cs in precipitation in Tromsø, Norway.[21]

^{3}H Peak during 1962−1963. The ^{3}H peak observed in the Camp Century ice core in 1962−1963 corresponds to the most intensive atmospheric nuclear weapons tests during 1961−1962, especially a series of tests conducted in September−November 1961 (totaling 86 Mt) and August−December 1962 (totaling 133 Mt) at Novaya Zemlya.[8] The branching peak shape may be explained by the tests ejecting tritium into the stratosphere, with subsequent transfer to the troposphere which is seasonally dependent (e.g., occurring mostly in spring) and potential interferences (e.g., snow removal, disturbance, etc.) from local activities at the Camp Century site during 1960−1964.

Similar temporal trends in atmospheric deposition of radionuclides occur at most Arctic sites,[22] with many studies observing maximum deposition in 1963 at the Greenland ice sheet,[23] Mount Logan (Yukon Territory, Canada),[24] Devon Island (Canada), Svalbard (Norway), and Severnaya Zemlya (Russia).[25] Since the Nuclear Test Ban Treaty came into force in 1963, tritium levels in precipitation in the Northern Hemisphere have been steadily decreasing due to radioactive decay and dilution within the vast environmental reservoir.[25] Our observations support this notion of a steady decrease in the atmospheric reservoir since the Nuclear Test Ban Treaty came into force.

^{3}H peak concentrations in 1963 from Devon Island, Svalbard and Severnaya Zemlya ice cores have been reported in the range of 350−800 Bq/L,[25] corresponding to 17−38 Bq/L (decay-corrected to 28th July 2017). Our observed peak values are consistent with these previous observations. Additional observations of ^{3}H concentrations in precipitation from Greenland (Station Nord, Kangilinnguit), Iceland (Reykjavik), Norway (Isfjord (Svalbard)) and Denmark (Ødum, Askov, Tystofte) also show peak levels of up to 600−1200 Bq/L in 1963[26] (Figure S2). This corresponds to present-day levels of 30−60 Bq/L, when corrected for temporal decay between atmospheric deposition and ice-core sampling. The local ^{3}H concentrations (up to 30 Bq/L) from the Camp Century ice core correspond well with the regional concentrations in precipitation observed in Greenland in the 1960s from the nuclear weapons fallout. This suggests no additional local radionuclide contributions resulting from the operation of the nuclear reactor at Camp Century.

^{3}H Peaks in 1965−1980. Several moderate ^{3}H peaks during the 1965−1980 period are observed in the Camp Century ice core. Only some of these peaks appear correlated to the atmospheric nuclear weapons testing events in this period. On the one hand, this could be due to the very low explosion yields of these bomb tests. On the other hand, this could be associated with the uncertainties (about 2−3 years) in the age model. The

https://doi.org/10.1021/acs.est.1c01975
Environ. Sci. Technol. 2021, 55, 13638−13645

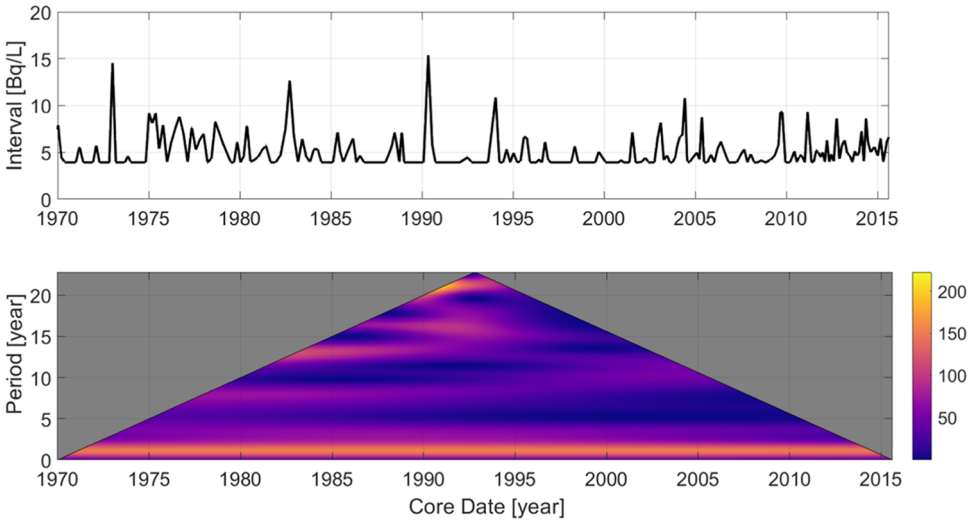


Figure 4. Wavelet power spectrum for ^{3}H activity concentrations with time in the Camp Century ice core for the period of 1970−2015. Power spectrum units shown below are years squared (year^2). ^{3}H concentrations below the limit of detection (LOD) are presented as LOD (3.94 Bq/L).

last high-yield (>4 Mt) detonation was the Chinese test (total yield of 4.12 MT) over Lop Nor on 17 November 1976, releasing ca. 2 kg of ^{3}H with most HTO (85%) injected into the stratosphere below 20 km altitude.[27] Several ^{3}H peaks observed in the late1970s might be attributed to this detonation.

^{3}H Levels after 1980. Although atmospheric nuclear weapons testing ended in 1980, it is somewhat surprising that several ^{3}H pronounced peaks are still observed in the Camp Century ice core during 1980−2017. Based on tritium vertical profiles in stratospheric water vapor (mainly at 32°N latitude) during 1975−1983, Ehhalt et al.[28] obtain a decay time of 7.7 ± 2.0 years for HTO in the middle and upper stratosphere. This decay time, which is solely due to the transport of HTO into the troposphere, is much longer than the estimated residence times of HTO in the lower stratosphere (2 ± 0.2 years).[29] Thus, while it is possible that there may have been remnant ^{3}H in the stratosphere in the decade immediately following the termination of nuclear weapons testing, it is unlikely that there was remnant ^{3}H after ca. 1990.

Since the 1970s, nuclear installations for both civil and military use have become an additional source of tritium, mostly in the form of HTO. ^{3}H release from the civil nuclear industry is likely now the dominant present-day ^{3}H source for the Arctic,[30] as the atmospheric legacy of nuclear weapons testing has vanished since ca. 1990. The civil nuclear industry releases ^{3}H through both nuclear reprocessing plants and nuclear reactors.[8,31] ^{3}H discharges from nuclear reprocessing plants, however, are primarily in the liquid phase. For example, >90% of ^{3}H releases (141 PBq in total during 1970−1997) from the European reprocessing plants were discharged as liquid effluents into the Atlantic Ocean.[8,31,32]

Airborne ^{3}H can be more readily transported to Northwest Greenland. In recent decades, the greatest source of airborne ^{3}H emissions has been heavy water reactors (HWRs).[8] Canada is responsible for the greatest proportion of reported ^{3}H airborne releases.[8,31] These releases are associated with the operation of several Canadian HWRs located between 40°N and 48°N latitude.[8,31] During the 1991−1997 period, annual airborne ^{3}H release from Canada (1780−3773 TBq/year) was on average 47 ± 6% of the global ^{3}H annual airborne emission (4196−11 000 TBq/year).[8,31] HWRs in India were also responsible for a nontrivial amount of airborne ^{3}H releases (2184−3457 TBq/year) but only in the period of 1990−1994.[8] Other individual nuclear facilities from North America, Europe, and Asia had less significant contributions.

Considering the variable residence times and pathways in atmospheric transport, simple statistical analysis cannot reveal an alignment between ice-core ^{3}H variability and known ^{3}H discharges from the civil nuclear industry. Nevertheless, the persistently high ^{3}H inventories in the past decades in the Camp Century ice core, despite the 12-year half-life of ^{3}H, clearly indicate that the ice core is preserving "recent" ^{3}H emissions signals that do not reflect leftover ^{3}H from pre-1980 atmospheric weapons testing. We suggest that atmospheric transport is consistently bringing mid-latitude Canadian ^{3}H emissions to Camp Century in recent decades. In this context, ^{3}H appears to be a good tracer to study the movement of North American air masses and pollutants into the High Arctic.

^{3}H Annual Cycle. From Figure 3A, it is apparent that regular ^{3}H annual peaks occur in the ice-core during 1970−2017. A wavelet analysis was performed to confirm that the primary frequency of variability in the tritium record is centered on 1 year (Figure 4). For this wavelet analysis, the ^{3}H record was interpolated to a standard 0.1-year time-step over the post-1970 portion of the ice core record. During this one-dimensional (1D) linear interpolation, the limit of detection (LOD = 3.94 Bq/L) was used for any samples in which values were below the LOD. This wavelet power spectrum ("wave∧2") was analyzed with the continuous wavelet transform function ("contwt.m") in MATLAB.[33] This power spectrum confirms that annual frequency is the unambiguous primary mode of temporal ^{3}H variability in post-1970. An analogous analysis of depth ^{3}H variability with a 0.1-m depth-step similarly provides an independent estimate of the annual net accumulation at the site. The primary frequency in depth variability of ^{3}H is ca. 0.6 m/year, which is equivalent to 0.3 m of water equivalent per year assuming a bulk core density of 500 kg/m, over the 1970−2016 period (Figure S3).

Clearly, continuous along-core sampling with a lower ^{3}H detection limit would permit detailed annual layer counting using ^{3}H concentration. Several previous studies have reported similar annual ^{3}H patterns. For example, tritium profiles of

https://doi.org/10.1021/acs.est.1c01975
Environ. Sci. Technol. 2021, 55, 13638−13645

annual resolution recovered from Carrefour, Greenland, in 1967[34] as well as Dye-3, Greenland, in 1971[35] also showed annual peaks. The depth resolution in this work is significantly better than these earlier Greenland tritium studies.[34] Acknowledging radioactive decay over the decadal time scale, ^{3}H can clearly serve as a conservative atmospheric isotope tracer, like ^{18}O in, ice core studies.[17] ^{18}O and other isotope species can be influenced by post-depositional redistribution by meltwater.[36,37] Camp Century, however, presently resides in the "percolation zone" of the ice sheet, which experiences limited summer melt that percolates and refreezes within the annual snow layer. At Camp Century, there is insufficient meltwater to warm the entire annual snowpack to the pressure melting point and permit percolation into underlying annual layers, which is characteristic of the "wet snow zone".[16] While surface meltwater has been observed to form deep pipes of preferential flow through intervening cold snow and firn layers elsewhere in the ice-sheet accumulation area, this piping requires substantially more surface meltwater than is available at Camp Century.[38] Therefore, while our ^{3}H record may reflect limited post-depositional meltwater redistribution, it is reasonable to expect that any meltwater redistribution remains within the annual layer.

While we cannot confirm the precise seasonality of the annual ^{3}H peak, we speculate that it corresponds to photochemical reactions associated with polar sunrise in each spring.[17] Yasunari et al.[39] measured the maximum tritium concentration in late spring in an ice core from Mount Wrangell, Alaska, during 1992−2002. Fourré et al.[7] also observed that the annual ^{3}H peak in snow from central Greenland, as well as in Arctic precipitation, occurs in spring. This follows the similar seasonal pattern generally observed in mid-latitudes of the Northern Hemisphere. As ^{3}H is defined as a "stratospheric tracer", the annual cycle we observed should somehow be related to stratospheric processes.[39] It has been suggested that ^{3}H fallout in the Arctic is the result of the dominant spring mixing of stratospheric and tropospheric air at mid-latitudes, which is consistent with the deposition of other stratospheric tracers such as ^{7}Be, ^{10}Be, and ^{14}C.[40,41] For example, Meijer et al. compared the very detailed $^{14}CO_2$ time series at different atmospheric monitor stations and observed a profound seasonal cycle (maximum in July−August) after the 1962−1963 detonation peaks.[41]

Atmospheric Transport and Deposition of ^{3}H. The Arctic Oscillation (AO) refers to an atmospheric circulation pattern over the mid-to-high latitudes of the Northern Hemisphere. The relative strength of the north−south sea-level pressure gradient measured by the AO controls the latitudinal position of the mid-latitude jet stream. The mid-latitude jet stream circles the planet, flowing west to east, along the north−south boundary where the polar and mid-latitude cells of global atmospheric circulation converge.[42] A more positive AO means lower-than-average air pressure over the Arctic and higher-than-average pressure over the Atlantic. So, under AO+ conditions, the jet stream shifts northward toward the pole. While the polar cell circumscribed by the jet stream decreases in area under AO+ conditions, the strength of the jet stream increases and potentially better insulates high-latitude regions from mid-latitude air masses.[43,44]

In Figure 5, we explore the relations between variability in ^{3}H concentration and variability in AO index during 1970−2017. Statistical evaluation was performed using a Pearson correlation test (Table S2). Annual ^{3}H average concentration is positively

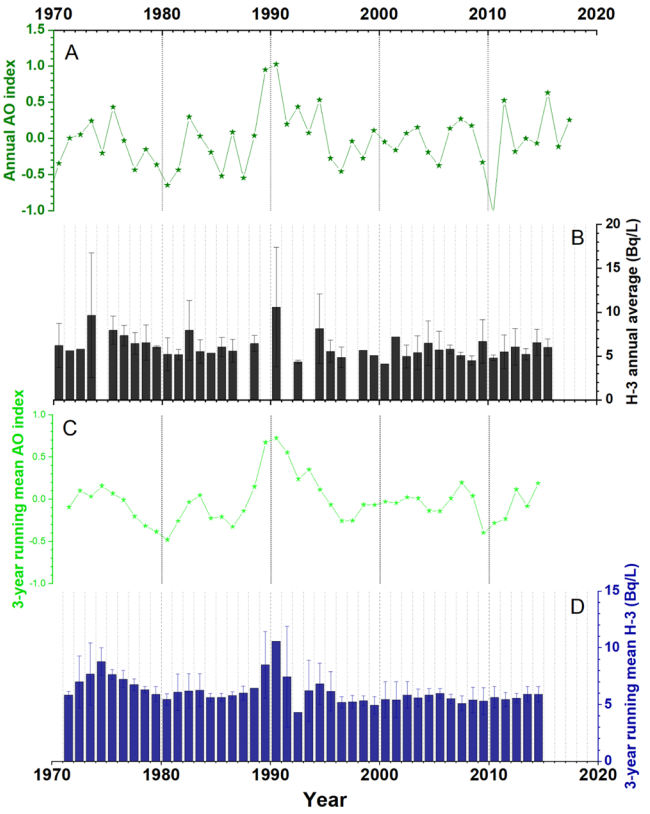


Figure 5. Temporal variabilities of (A) annual average Arctic Oscillation (AO) index, (B) annual average ^{3}H activity concentrations in the Camp Century ice core, (C) 3-year running mean AO index, and (D) 3-year running mean ^{3}H concentration in the Camp Century ice core. Data of AO indexes were obtained from National Weather Service (NOAA).[47] All of the data of ^{3}H concentration are decay-corrected to 28th July 2017.

correlated to annual AO index ($r = 0.43$, $p < 0.01$, $n = 40$). This positive correlation between annual AO index and annual ^{3}H average concentration appears to suggest that more ^{3}H-enriched mid-latitude air masses reach Camp Century in AO+ years. In this context, however, we must acknowledge substantial dating uncertainty, which can introduce red-noise (or autocorrelated) biases when comparing an ice-core-dated record with an independent observational record.[45] To compensate for this dating uncertainty, we apply a running mean to both the ice core and AO records and evaluate statistical uncertainty under correspondingly reduced degrees of freedom. The 3-year running mean ^{3}H concentration and the 3-year running mean AO index is also significantly correlated ($r = 0.60$, $p < 0.01$, $n_{eff} = 20$). For these 3-year running means, we reduce our effective sample size (n_{eff}) by $1.5/w = 0.5$, wherein w (=3) is the number of points used in the running mean.[46]

The AO can also influence the variability of atmospheric tracers in ice core by influencing their deposition through snowfall. As hydrogen is a constituent of ice, ^{3}H should be primarily deposited at Camp Century via "wet" deposition, meaning in snowfall, as opposed to via "dry" deposition, meaning independent of precipitation (e.g., via ^{3}H association to larger aerosol particles).[17] Therefore, the notion of wet deposition creates an expectation for the annual ^{3}H inventory to be correlated to net snow accumulation, as reported in earlier studies.[20,25] Snowfall on the Greenland ice sheet is known to vary with North Atlantic Oscillation (NAO) phase (The NAO is

https://doi.org/10.1021/acs.est.1c01975
Environ. Sci. Technol. 2021, 55, 13638−13645

closely related to the AO.[48,49]). While snowfall across the majority of the Greenland ice sheet exhibits a negative correlation with NAO, Northwest Greenland exhibits a positive correlation with the NAO.[49,50] We, however, find no significant correlation between annual ^{3}H inventory and either annual snowfall accumulation or NAO index (Figure S4). This lack of correlation may be explained by noise in ice-core record associated with dating uncertainties and/or compensating NAO feedbacks.

The compensating influences of AO on the atmospheric transport and snowfall deposition make it difficult for us to speculate the physical processes underlying the positive correlation between AO and ^{3}H concentration that we observed. For example, under AO+ conditions, there is generally less atmospheric transport from Canada to Northwest Greenland, but there is also generally more snowfall deposition in Northwest Greenland. Vice versa under AO- conditions. Additionally, the local deposition of ^{3}H may also be influenced by seasonal effects, such as photochemical reactions in the spring[17] or seasonality of snowfall,[43] that vary over the reconstruction period. These diverse and sometimes competing effects of deposition variability make it challenging to conclusively discern the AO's role in deposition variability. At present, our data simply suggest that ^{3}H concentration at Camp Century is significantly correlated with AO phase.

PERSPECTIVES

In the context of ice core interpretation, our results suggest that high-resolution ^{3}H profiles are useful as a conservative atmospheric tracer species, similar to ^{18}O, for annual layer counting and independent evaluation of age-depth models and accumulation rates. In addition to resolving annual layers, the ^{3}H record also resolves individual events. Several years that are known to have high ^{3}H emissions associated with historical thermonuclear detonations are clearly reflected in the ice-core-derived ^{3}H record. Based on the presence of abundant recent ^{3}H at Camp Century, ^{3}H appears to be a potential tracer for the movement of air masses and pollutants into the High Arctic. While it is difficult to conclusively discern the influence of the Arctic Oscillation on atmospheric transport and/or snowfall deposition variability in the ^{3}H record at Camp Century, the positive correlation between ^{3}H annual average concentration and annual AO index suggests a promising archive for understanding variability in atmospheric transport and/or snowfall deposition. Finally, with current technology, it is conceivable to both increase the temporal resolution of ice-core samples and decrease the analytical ^{3}H sensitivity limit to produce an ice-core-derived ^{3}H record with monthly resolution. This would not only help address some present ambiguity in subannual atmospheric transport and snowfall deposition mechanisms but also provide valuable insight into the life cycle of ^{3}H in the high-latitude cryosphere.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.1c01975.

Overall analytical results for ^{3}H activity concentration in the ice core (Table S1); statistical correlation efficiencies between the variability of ^{3}H concentration and Arctic Oscillation (Table S2); near-surface density profiles of the sampling site (Figure S1); tritium concentrations in precipitation in 1961−1963 from selected locations (Figure S2); wavelet power spectrum for ^{3}H concentrations with depth in 1970−2015 (Figure S3); and interannual variabilities of North Atlantic Oscillation, snowfall net accumulation and ^{3}H inventory in the Camp Century ice core (Figure S4) (PDF)

AUTHOR INFORMATION

Corresponding Author

Jixin Qiao − *Department of Environmental Engineering, Technical University of Denmark, 4000 Roskilde, Denmark;* orcid.org/0000-0001-5409-4274; Phone: +45 46775367; Email: jiqi@env.dtu.dk

Authors

William Colgan − *Geological Survey of Denmark and Greenland, 1350 Copenhagen, Denmark*

Gunnar Jakobs − *Department of Environmental Engineering, Technical University of Denmark, 4000 Roskilde, Denmark*

Sven Nielsen − *Department of Environmental Engineering, Technical University of Denmark, 4000 Roskilde, Denmark*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.est.1c01975

Author Contributions

J.Q. performed data analysis and wrote the manuscript. W.C. sampled the ice core and performed the age-depth modeling. G.J. performed measurement of tritium. S.N. assisted with project management. All authors contributed to reviewing and editing the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

J.Q. thanks the Danish Ministry of Health for financial support. W.C. was supported by the Camp Century Climate Monitoring Programme, which is jointly funded by Geological Survey of Denmark and Greenland (GEUS) and the Danish Cooperation for Environment in the Arctic (DANCEA) within the Danish Ministry for Energy, Utilities and Climate. The authors warmly thank Allan Pedersen, Daniel Binder, Horst Machguth, Jakob Abermann, and Mike Jayred for assistance in drilling and processing ice cores B62 and B73. Open access publication made possible through support from Greenland Climate Network (GC-Net) ice-sheet monioring program at GEUS.

REFERENCES

(1) Nielsen, H.; Nielsen, K. H. *Camp Century*; Aktuel Naturvidenskab, 2017; pp 38−41.

(2) Ølgaard, P. L. *Report No. 3 on: Surroundings of PM-2A Reactor in Camp Century, Thule, Greenland*; Risø: Roskilde, Denmark, 1962.

(3) Ølgaard, P. L. *Report No. 1 on: Surroundings of PM-2A Reactor in Camp Century, Thule, Greenland*; Risø: Roskilde, Denmark, 1961.

(4) Ølgaard, P. L. *Report No. 2 on: Surroundings of PM-2A Reactor in Camp Century, Thule, Greenland*; Risø: Roskilde, Denmark, 1962.

(5) Ølgaard, P. L. *Report No. 4 on: Surroundings of PM-2A Reactor in Camp Century, Thule, Greenland*; Risø: Roskilde, Denmark, 1964.

(6) Colgan, W.; Machguth, H.; MacFerrin, M.; Colgan, J. D.; van As, D.; MacGregor, J. A. The Abandoned Ice Sheet Base at Camp Century, Greenland, in a Warming Climate. *Geophys. Res. Lett.* **2016**, *43*, 8091−8096.

(7) Fourré, E.; Jean-Baptiste, P.; Dapoigny, A.; Baumier, D.; Petit, J. R.; Jouzel, J. Past and Recent Tritium Levels in Arctic and Antarctic Polar Caps. *Earth Planet. Sci. Lett.* **2006**, *245*, 56−64.

(8) UNSCEAR. *Sources and Effects of Ionizing Radiation*, UNSCEAR 2000 Report to the General Assembly, with Scientific Annexes; United Nations Scientific Committee on the Effects of Atomic Radiation, 2000, Vol. *I*.
(9) Happell, J. D.; Östlund, G.; Mason, A. S. A History of Atmospheric Tritium Gas (HT) 1950−2002. *Tellus B* **2004**, *56*, 183−193.
(10) Khalturin, V. I.; Rautian, T. G.; Richards, P. G.; Leith, W. S. A Review of Nuclear Testing by the Soviet Union at Novaya Zemlya, 1955−1990. *Sci. Global Secur.* **2005**, *13*, 1−42.
(11) Kovacs, A. *Campus Century Resivited: A Pictorial View—June 1969*, Special Report; U.S. Army Cold Regions Research and Engineering Laboratory, 1970.
(12) Gundestrup, N. S.; Clausen, H. B.; Hanse, B. L.; Rand, J. Camp Century Survery 1986. *Cold Reg. Sci. Technol.* **1987**, *14*, 281−288.
(13) Colgan, W.; Pedersen, A.; Binder, D.; Machguth, H.; Abermann, J.; Jayred, M. Initial Field Activities of the Camp Century Climate Monitoring Programme in Greenland. *Geol. Surv. Den. Greenl. Bull.* **2018**, *41*, 75−78.
(14) Karlsson, N. B.; Colgan, W. T.; Binder, D.; Machguth, H.; Abermann, J.; Hansen, K.; Pedersen, A. Ice-Penetrating Radar Survey of the Subsurface Debris Field at Camp Century, Greenland. *Cold Reg. Sci. Technol.* **2019**, *165*, No. 102788.
(15) Blake, E. W.; Wake, C. P.; Gerasimoff, M. D. The ECLIPSE Drill: A Field-Portable Intermediate-Depth Ice-Coring Drill. *J. Glaciol.* **1998**, *44*, 175−178.
(16) Vandecrux, B.; Colgan, W. T.; Solgaard, A.; Steffensen, J. P.; Karlsson, N. B. Firn Evolution at Camp Century, Greenland: 1966-2100. *Front. Earth Sci.* **2021**, *9*, No. 578978.
(17) Legrand, M.; Mayewski, P. Glaciochemistry of Polar Ice Cores: A Review. *Rev. Geophys.* **1997**, *35*, 219−243.
(18) IAEA. *Statistical Treatment of Data on Environmental Isotopes in Precipitation*; International Atomic Energy Agency, 1992.
(19) Van Der Wel, L. G.; Streurman, H. J.; Isaksson, E.; Helsen, M. M.; Van De Wal, R. S. W.; Martma, T.; Pohjola, V. A.; Moore, J. C.; Meijer, H. A. J. Using High-Resolution Tritium Profiles to Quantify the Effects of Melt on Two Spitsbergen Ice Cores. *J. Glaciol.* **2011**, *57*, 1087−1097.
(20) Merlivat, L.; Ravoire, J.; Vergnaud, J. P.; Lorius, C. Tririum and Deuterium Content of the Snow in Greenland. *Earth Planet. Sci. Lett.* **1973**, *19*, 235−240.
(21) Wright, S. M.; Howard, B. J.; Strand, P.; Nylén, T.; Sickel, M. A. K. Prediction of 137Cs Deposition from Atmospheric Nuclear Weapons Tests within the Arctic. *Environ. Pollut.* **1999**, *104*, 131−143.
(22) Wilson, C. *Radioactive Fallout in the North Region*; Cold Regions Research and Engineering Laboratory, 1967; Vol. DA Project.
(23) Koide, M.; Michel, R.; Goldberg, E. D.; Herron, M. M.; Langway, C. C., Jr. Characterization of Radioactive Fallout from Pre- and Post-Moratorium Tests to Polar Ice Caps. *Nature* **1982**, *296*, 544−547.
(24) Holdsworth, G.; Pourchet, M.; Prantl, F. A.; Meyerhof, D. P. Radioactivity Levels in a Firn Core from the Yukon Territory, Canada. *Atmos. Environ. (1967)* **1984**, *18*, 461−466.
(25) 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.; Meijer, H. A. J. Ice Cores from Arctic Sub-Polar Glaciers: Chronology and Post-Depositional Processes Deduced from Radioactivity Measurements. *J. Glaciol.* **2003**, *49*, 149−158.
(26) IAEA. *Environmental Isotope Data No. 1: World Survey of Isotope Concentration in Precipitation (1984−1987)*; International Atomic Energy Agency, 1969; Series No. 96.
(27) Mason, A. S.; Hut, G.; Telegadas, K. Stratospheric HTO and ;95Zr Residence Times. *Tellus* **1982**, *34*, 369−375.
(28) Ehhalt, D. H.; Rohrer, F.; Schauffler, S.; Pollock, W. Tritiated Water Vapor in the Stratosphere: Vertical Profiles and Residence Time. *J. Geophys. Res.: Atmos.* **2002**, *107*, No. 4757.
(29) Mason, A. S.; Ostlund, H. G. Vertical Transport of Water in the Stratosphere. *J. Geophys. Res.* **1976**, *81*, 5349−5352.
(30) IAEA. *Behaviour of Tritium in the Environment*; International Atomic Energy Agency, 1979.
(31) UNSCEAR. *Sources and Effects of Ionizing Radiation*; United Nations Scientific Committee on the Effects of Atomic Radiation, 2008; Vol. *1*.
(32) Hou, X. Tritium and 14C in the Environment and Nuclear Facilities: Sources and Analytical Methods. *J. Nucl. Fuel Cycle Waste Technol.* **2018**, *16*, 11−39.
(33) Erickson, J. Continuous Wavelet Transform and Inverse. MATLAB Central File Exchange. https://ch.mathworks.com/matlabcentral/fileexchange/20821-continuous-wavelet-transform-and-inverse (retrieved March 4, 2021).
(34) Ambach, W.; Dansgaard, W. Fallout and Climate Studies on Firn Cores from Carrefour, Greenland. *Earth Planet. Sci. Lett.* **1970**, *8*, 311−316.
(35) Theodorsson, P. In *40-Year Tritium Profiles in a Polar and a Temperate Glacier*, International Association of Hydrological Sciences Publication 118 (Symposium at Grenoble 1975—Isotopes and Impurities in Snow and Ice), 1977; pp 393−398.
(36) Goto-Azuma, K.; Koerner, R. M. Ice Core Studies of Anthropogenic Sulfate and Nitrate Trends in the Arctic. *J. Geophys. Res.: Atmos.* **2001**, *106*, 4959−4969.
(37) Koerner, R. M.; Fisher, D. A.; Goto-Azuma, K. A 100 Year Record of Ion Chemistry from Agassiz Ice Cap Northern Ellesmere Island NWT, Canada. *Atmos. Environ.* **1999**, *33*, 347−357.
(38) Humphrey, N. F.; Harper, J. T.; Pfeffer, W. T. Thermal Tracking of Meltwater Retention in Greenland's Accumulation Area. *J. Geophys. Res.: Earth Surf.* **2012**, *117*, No. F01010.
(39) Yasunari, T. J.; Shiraiwa, T.; Kanamori, S.; Fujii, Y.; Igarashi, M.; Yamazaki, K.; Benson, C. S.; Hondoh, T. Intra-Annual Variations in Atmospheric Dust and Tritium in the North Pacific Region Detected from an Ice Core from Mount Wrangell, Alaska. *J. Geophys. Res.: Atmos.* **2007**, *112*, No. D10208.
(40) Dibb, J. E.; Meeker, L. D.; Finkel, R. C.; Southon, J. R.; Caffee, M. W.; Barrie, L. A. Estimation of Stratospheric Input to the Arctic Troposphere: 7Be and 10Be in Aerosols at Alert, Canada. *J. Geophys. Res.: Atmos.* **1994**, *99*, 12855−12864.
(41) Meijer, H. A. J.; van der Plicht, J.; et al. Comparing Long-Term Atmospheric 14C and H Records near Groningen, the Netherlands with Fruhojmen, Norway and Izana, Canary Islands 14C Stations. *Radiocarbon* **1995**, *37*, 39−50.
(42) Atmospheric Circulation. https://en.wikipedia.org/wiki/Atmospheric_circulation.
(43) Sjolte, J.; Hoffmann, G.; Johnsen, S. J.; Vinther, B. M.; Masson-Delmotte, V.; Sturm, C. Modeling the Water Isotopes in Greenland Precipitation 1959-2001 with the Meso-Scale Model REMO-Iso. *J. Geophys. Res.: Atmos.* **2011**, *116*, No. D18105.
(44) Fischer, H.; Mieding, B. A 1,000-Year Ice Core Record of Interannual to Multidecadal Variations in Atmospheric Circulation over the North Atlantic. *Clim. Dyn.* **2005**, *25*, 65−74.
(45) Colgan, W.; Sharp, M. Combined Oceanic and Atmospheric Influences on Net Accumulation on Devon Ice Cap, Nunavut, Canada. *J. Glaciol.* **2008**, *54*, 28−40.
(46) Moore, J.; Kekonen, T.; Grinsted, A.; Isaksson, E. Sulfate Source Inventories from a Svalbard Ice Core Record Spanning the Industrial Revolution. *J. Geophys. Res.: Atmos.* **2006**, *111*, No. D15307.
(47) NOAA. https://www.cpc.ncep.noaa.gov/.
(48) Cohen, J.; Barlow, M. The NAO, the AO, and Global Warming: How Closely Related? *J. Clim.* **2005**, *18*, 4498−4513.
(49) Bjørk, A. A.; Aagaard, S.; Lütt, A.; Khan, S. A.; Box, J. E.; Kjeldsen, K. K.; Larsen, N. K.; Korsgaard, N. J.; Cappelen, J.; Colgan, W. T.; Machguth, H.; Andresen, C. S.; Peings, Y.; Kjær, K. H. Changes in Greenland's Peripheral Glaciers Linked to the North Atlantic Oscillation. *Nat. Clim. Change* **2018**, *8*, 48−52.
(50) Mosley-Thompson, E.; Readinger, C. R.; Craigmile, P.; Thompson, L. G.; Calder, C. A. Regional Sensitivity of Greenland Precipitation to NAO Variability. *Geophys. Res. Lett.* **2005**, *32*, No. L24707.

https://doi.org/10.1021/acs.est.1c01975
Environ. Sci. Technol. 2021, 55, 13638−13645