

5 kyr of fire history in the High North Atlantic Region: natural variability and ancient human forcing

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1 Materials, reagents and instrumentation

All pre-analytical steps were performed under a Class-100 clean bench located in a Class-100 clean room at the University of Venice. We used Purelab Ultra system (Elga, High Wycombe, U.K.) to produce the ultrapure water (18.2 M Ω cm, 0.01 TOC) utilized in all analytical and pre-analytical procedures (i.e. cleaning and decontamination procedures, standard solutions preparation) (Gambaro et al., 2008).

1.1 Levoglucosan analysis

The samples were analyzed using liquid chromatography/negative ion electrospray ionization–tandem-mass spectrometry (HPLC/(-) ESI-MS/MS). Detailed information on the analytical method is reported in the supplementary information of Zenaro et al. (2014), which modifies the method published in Gambaro et al. (2008).

All ice core samples were defrosted immediately before analysis. Melted samples were spiked with a standard solution of ¹³C6-labelled levoglucosan (Cambridge 20 Isotope Laboratories Inc., purity of 98%) as an internal standard with a final concentration of 250 pg mL⁻¹. Response factors were determined every 10 samples as well as multiple response factors at the beginning and at the end of each instrumental run to correct each potential instrumental deviation.

15 For the analysis, an aliquot of 100 μL was injected into the HPLC/MSMS system. Chromatographic separation was obtained
using an Agilent 1100 series HPLC with a C-18 Synergy Hydro column (4.6 mm i.d., 50 mm length, 4 μm size particles;
Phenomenex). A post-column addition of an ammonium hydroxide solution (13mM ammonium hydroxide, LC-MS grade
Sigma-Aldrich, in methanol, Romil ultrapure) was added using a Waters 515 HPLC pump (Waters Corporation). The HPLC
is coupled with API 4000 triple quadrupole mass spectrometer (Applied Biosystems/MDS SCIEX) through Turbo V ion spray
20 source (ESI), operated in negative mode. We quantified levoglucosan concentrations using isotope dilution mass spectrometry,
by comparing the levoglucosan peak area to the area of the $^{13}\text{C}_6$ isotopomer. The analysis was performed using multiple reaction
monitoring acquisition mode and we used the following transitions to quantify the analytes: 161/113 m/z^{-1} for levoglucosan
and 167/118 m/z^{-1} for the $^{13}\text{C}_6$ -labeled levoglucosan.

2 RECAP levoglucosan, BC and ammonium concentration profiles and accumulation

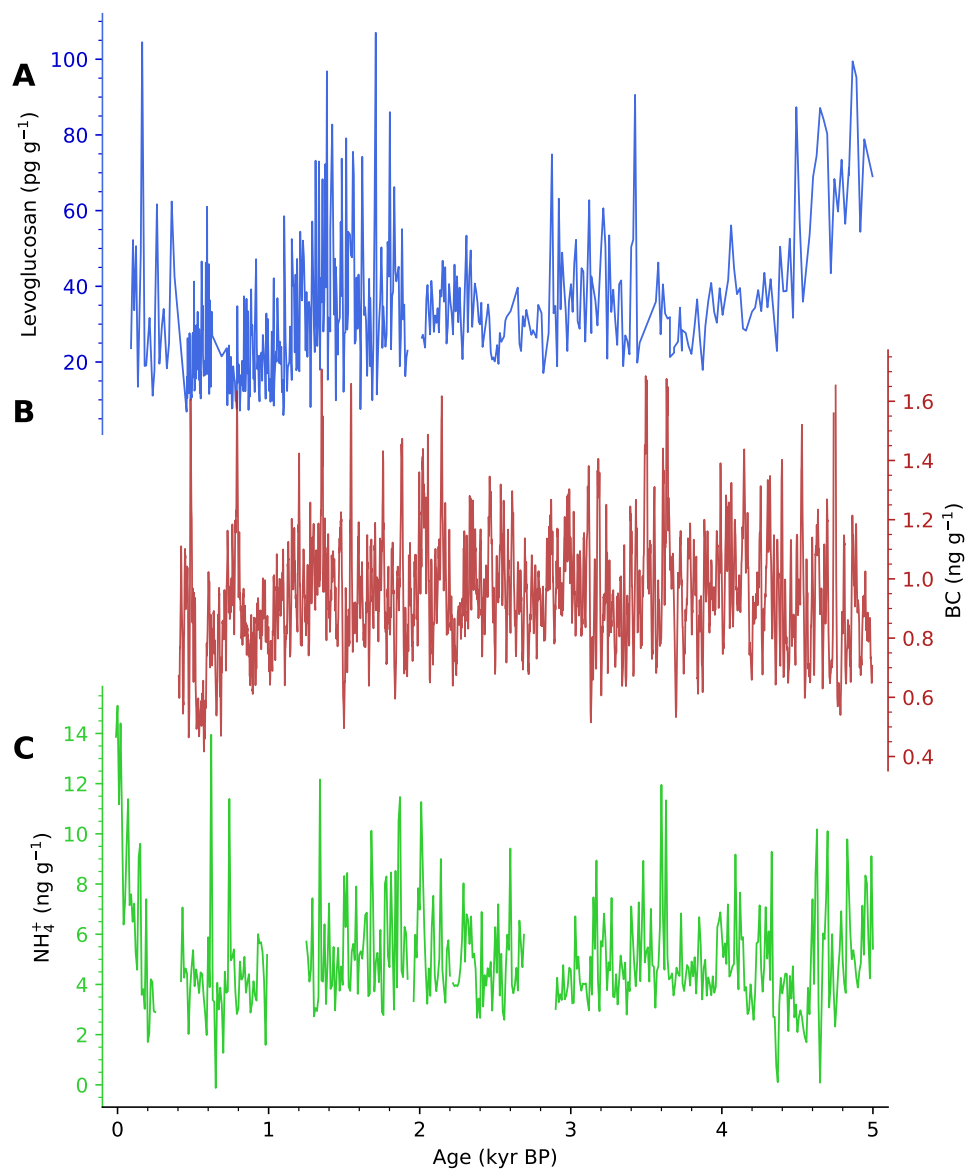


Figure S1. Concentration profiles of: (a) levoglucosan, pg g^{-1} ; (b) black carbon, ng g^{-1} ; (c) ammonium (NH_4^+), ng g^{-1} . The age scale is expressed in 1000 years before 2000 AD (kyr BP).

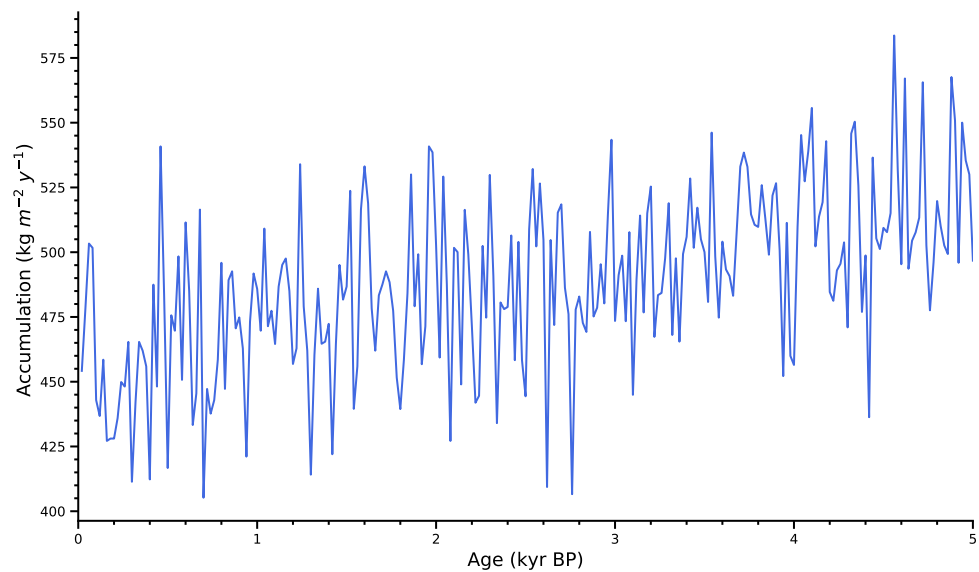


Figure S2. RECAP annual accumulation (in kg m⁻² y⁻¹) calculated from diffusion and seawater corrected $\delta^{18}\text{O}$ (Hughes et al., 2020; Corella et al., 2019).

25 3 The Global Charcoal Database record

Charcoal dataset has been retrieved from the Global Charcoal Database (GCDv4) (Marlon et al., 2016), available at <https://paleofire.org/> and analyzed with `paleofire` and `GCD R` packages. The `paleofire` package works in conjunction with the `GCD R` package that contains a simplified version of the charcoal dataset (Blarquez et al., 2014).

30 Fire signals derived from charcoal analysis are dependent on the applied technique that either measures microscopic charcoal ($< 100 \mu\text{m}$) in pollen slides or macroscopic charcoal ($> 200 \mu\text{m}$) by sieving sediments. Because of the limited spatial representativeness of charcoal records, several individual records must be assembled to derive a regional reconstruction of fire activity. In this way, paleo-fire records have been obtained at regional, continental, and global scales and can be compiled from the paleofire database for specific regions (Blarquez et al., 2014). Regional and global synthesis allows for the examination of broad-scale patterns in palaeofire activity (Marlon et al., 2013).

35 Charcoal data were transformed following the method described by Marlon et al. (2008); Power et al. (2008) and Daniau et al. (2012). It comprehends:

(a) transforming non-influx data (e.g., concentration expressed as particles/cm³) to influx values (i.e., particles cm⁻² yr⁻¹) or quantities proportional to influx, by dividing the charcoal values by sample deposition times.

(b) Box-Cox transformation to homogenize the variance of the samples.

40 (c) MinMax transformation to rescale data to a range between 0 and 1.

(d) Z-score calculated over the period 0 - 5 kyr BP.

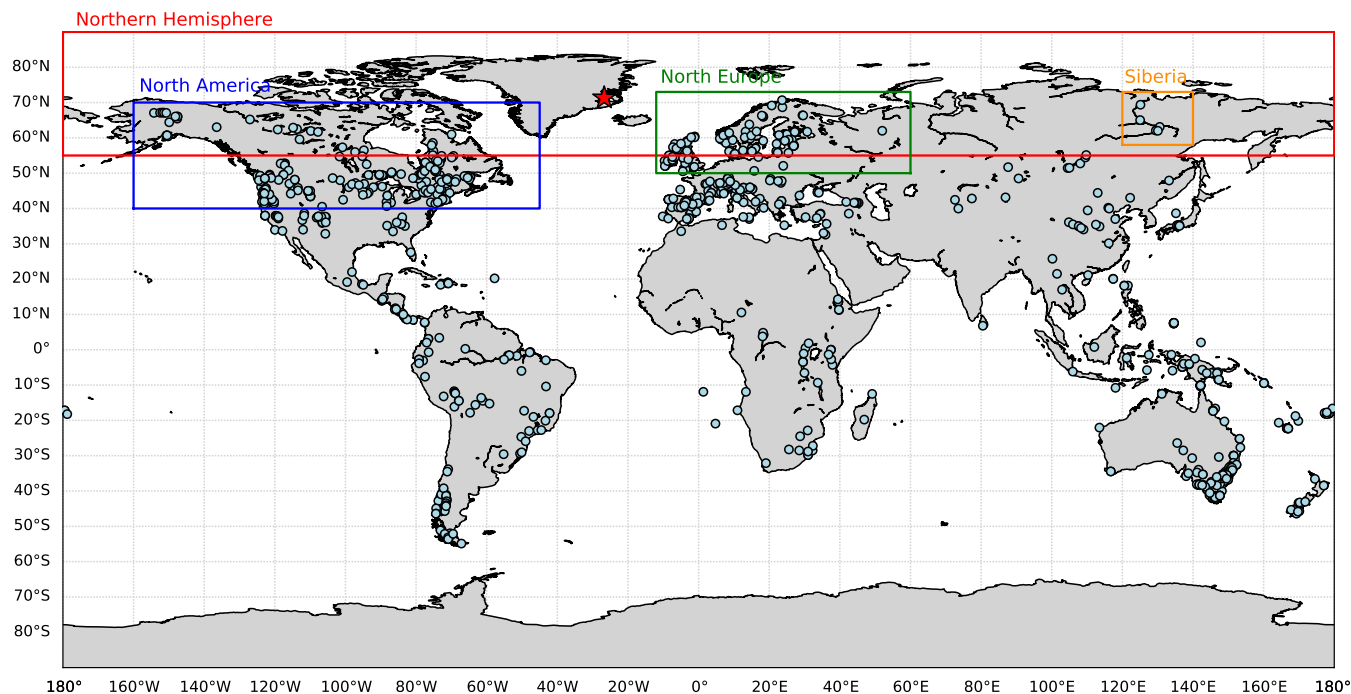


Figure S3. Location of charcoal records selected for regional composites. Source: <https://paleofire.org/>

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