



Supplement of

Five thousand years of fire history in the high North Atlantic region: natural variability and ancient human forcing

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1 Materials, reagents and instrumentation

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

6 1.1 Levoglucosan analysis

7 The samples were analyzed using high performance liquid chromatography/negative ion electrospray ioniza-
8 tion – tandem - mass spectrometry (HPLC/(-) ESI-MS/MS). Detailed information on the analytical method
9 is reported in the supplementary information of Zennaro et al. (2014), which modifies the method published
10 in Gambaro et al. (2008).

11 All ice core samples were defrosted immediately before analysis. Melted samples were spiked with a
12 standard solution of $^{13}\text{C}_6$ -labelled levoglucosan (Cambridge 20 Isotope Laboratories Inc., purity of 98%) as
13 an internal standard with a final concentration of 250 pg mL^{-1} . Response factors were determined every 10
14 samples as well as multiple response factors at the beginning and at the end of each instrumental run to
15 correct each potential instrumental deviation.

16 For the analysis, an aliquot of $100 \mu\text{L}$ was injected into the HPLC/MSMS system. Chromatographic sep-
17 aration was obtained using an Agilent 1100 series HPLC with a C-18 Synergy Hydro column (4.6 mm i.d., 50
18 mm length, 4 μm size particles; Phenomenex). A post-column addition of an ammonium hydroxide solution
19 (13mM ammonium hydroxide, LC-MS grade Sigma-Aldrich, in methanol, Romil ultrapure) was added using
20 a Waters 515 HPLC pump (Waters Corporation). The HPLC is coupled with API 4000 triple quadrupole
21 mass spectrometer (Applied Biosystems/MDS SCIEX) thought Turbo V ion spray source (ESI), operated
22 in negative mode. We quantified levoglucosan concentrations using isotope dilution mass spectrometry, by
23 comparing the levoglucosan peak area to the area of the $^{13}\text{C}_6$ isotopomer. The analysis was performed using
24 multiple reaction monitoring acquisition mode and we used the following transitions to quantify the analytes:
25 $161/113 \text{ m z}^{-1}$ for levoglucosan and $167/118 \text{ m z}^{-1}$ for the $^{13}\text{C}_6$ -labeled levoglucosan.

26 **2 RECAP levoglucosan, BC and ammonium concentration profiles and accumulation**
 27

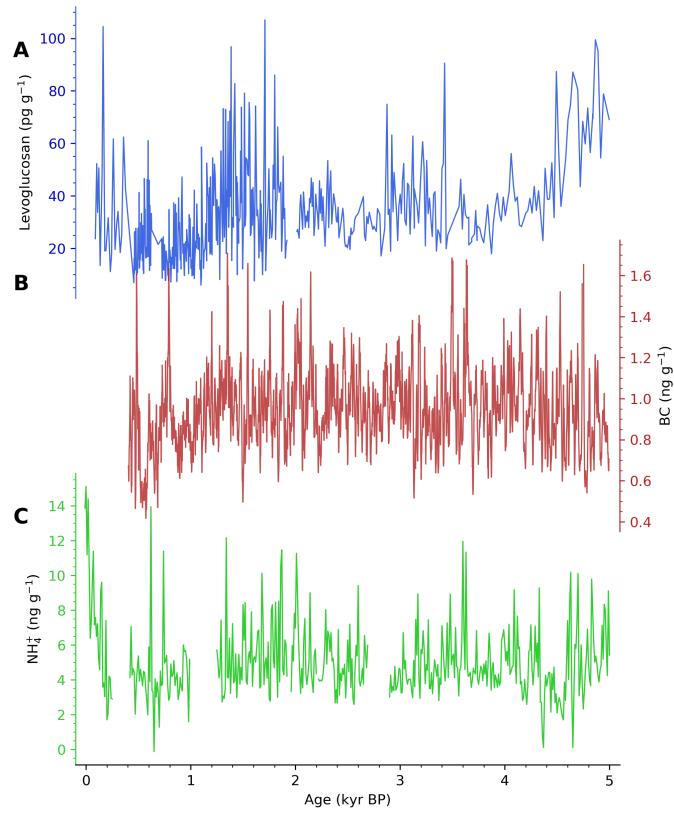


Figure S1: Concentration profiles of: (a) levoglucosan, pg g^{-1} ; (b) black carbon, ng g^{-1} ; (c) ammonium (NH_4^+), ng g^{-1} . The age scale is expressed in 1000 years before 2000 AD (kyr BP).

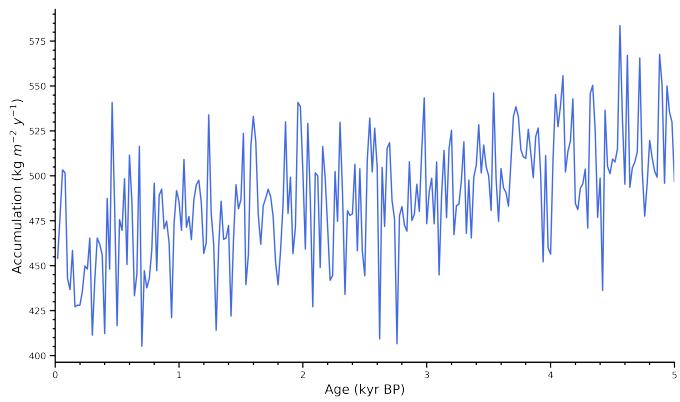


Figure S2: RECAP annual accumulation (in $\text{kg m}^{-2} \text{y}^{-1}$) calculated from diffusion and seawater corrected $\delta^{18}\text{O}$ (Hughes et al. 2020, Corella et al. 2019).

28 3 The Global Charcoal Database record

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

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

40 Charcoal data were transformed following the method described by Marlon et al. (2008), Power et al.
41 (2008) and Daniau et al. (2012). It comprehends:

- 42 (a) transforming non-influx data (e.g., concentration expressed as particles/cm³) to influx values (i.e.,
43 particles cm⁻² yr⁻¹) or quantities proportional to influx, by dividing the charcoal values by sample
44 deposition times.
- 45 (b) Box-Cox transformation to homogenize the variance of the samples.
- 46 (c) MinMax transformation to rescale data to a range between 0 and 1.
- 47 (d) Z-score calculated over the period 0 - 5 kyr BP.

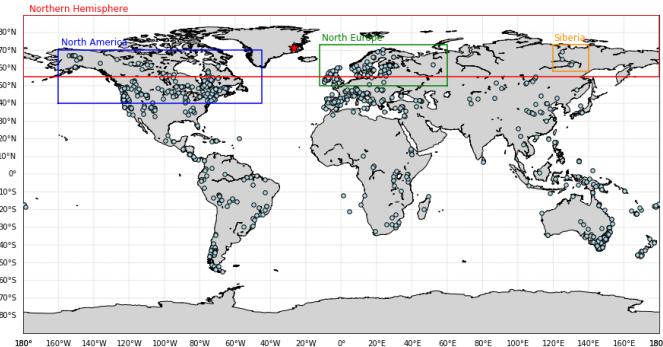


Figure S3: Location of charcoal records selected for regional composites. Source: <https://paleofire.org/>

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