



RESEARCH ARTICLE

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Key Points:

- Biogenic sources dominate fossil-fuel sources of present-day summer organic carbon aerosol (70% vs. 30%) in south-eastern Europe
- Large pre-industrial variability of organic carbon aerosol in summer driven by vegetation emissions modulated by past temperatures
- Living biosphere with a small contribution from wood burning slightly exceeds present-day fossil-fuel sources of organic carbon in winter

Supporting Information:

Supporting Information may be found in the online version of this article.

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20th Century Changes of DOC and Its ^{14}C Signature Archived in Caucasus Ice-Core: Implications for Past Sources of Organic Carbon Aerosol in South-Eastern Europe

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Abstract To reconstruct the history of organic carbon (OC) aerosol over south-eastern Europe, dissolved organic carbon (DOC) and its ^{14}C signature (DO^{14}C) were investigated along an ice core drilled at the Mount Elbrus (ELB) in Caucasus. In summer, compared to pre-1945 levels, the DOC concentrations increased by 45% after 1960, the mean DO^{14}C depletion in recent ELB ice relative to atmospheric $^{14}\text{CO}_2$ of 32% being attributed to fossil-fuel sources. DO^{14}C content of ice deposited during the bomb-peak era (1955–1980) closely followed atmospheric $^{14}\text{CO}_2$ changes caused by atmospheric nuclear tests, suggesting the living biosphere as the main biogenic source of DOC in summer in this region. ELB data contrast with those previously obtained in summer Alpine (western Europe) ice in which a post-1950 doubling of DOC was observed and attributed to enhanced emissions of organic compounds from vegetation in France. This regional difference is discussed with respect to changes of biogenic organic compound emissions in response to past change of use-land and global warming. ELB data document, for the first time, changes of DOC and DO^{14}C in winter mountain ice showing an increase by 44% of DOC levels associated with a ^{14}C signature being 47% lower than that of atmospheric $^{14}\text{CO}_2$ in ELB ice deposited after 1960. The ^{14}C winter ELB ice record followed atmospheric $^{14}\text{CO}_2$ changes with a delay of ~ 3 years, suggesting that remaining emissions from the living biosphere, together with a small contribution from wood burning, are the main biogenic sources of DOC in winter in this region.

Plain Language Summary A good knowledge of past aerosol load and composition is important for climate change. In addition to sulfate, organic carbon aerosol (OC) is a major constituent of present-day aerosol but its budget remains far less understood. Ice-core chemical studies help to quantify natural versus anthropogenic sources over the past. Previous investigations of OC and its radiocarbon signature in Alpine ice had shown a doubling of summer OC due to enhanced emissions from vegetation contrasting with a weak impact of fossil-fuel emissions in western Europe. The regional character of biogenic emissions motivated, however, further studies conducted in other regions. Investigations of OC and its radiocarbon signature in an ice core extracted in the Caucasus permitted to reconstruct past OC changes in the south-eastern Europe. It is shown that, even in 1970, vegetation emissions still dominate fossil-fuel emissions as source of OC in summer. A quite large temporal variability of OC is observed and attributed to variations of vegetation emissions in response to past fluctuations of summer temperature in this region. After 1960, fossil-fuel emissions in winter became almost as large as biogenic emissions that were related to the living biosphere with a small contribution from wood burning at that season.

1. Introduction

The reconstruction of the changing atmospheric aerosol load and composition from present-day back to the pre-industrial period (PI), and the subsequent radiative impact are strongly needed to forecast future climate, particularly at regional scales. Although carbonaceous matter, black carbon (BC) and organic carbon (OC), is recognized as a major constituent of present-day aerosol in the lower and free troposphere over continents (see Pio et al., 2007; Putaud et al., 2004 for Europe), there are still major deficits in knowledge with respect to its sources. For instance, the relative contribution of natural versus anthropogenic sources to the present-day OC aerosol as well as the past variability of natural sources are not well known.

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Figure 1. Location of the Mt Elbus site: (a) The Caucasus, (b) Mt Elbus in the Caucasus mountains (Copyright: © 2014 National Geographic Society, i-cubed), and (c) the drill site on the western Mt Elbus plateau.

The study of chemical impurities trapped in solid precipitation accumulated over the past on cold glaciers represents a powerful way to reconstruct our changing atmosphere since PI (see Legrand & Mayewski, 1997 for a review). As an example, Moseid et al. (2022) recently compared the long-term trends of sulfate and BC between 15 ice cores and 11 Earth System Models over nine regions around the world. It was shown that simulated sulfate trends generally agree with ice-core data, whereas the BC model trends differ from the ice records suggesting underestimation of BC emissions during the early 20th century. Concerning OC aerosol, water-soluble OC (WSOC) generally dominates water-insoluble OC (WinOC) in the present-day European atmosphere (Pio et al., 2007). The reconstruction of past changes of WSOC preserved in ice is, however, a challenge since measurement of dissolved organic carbon (DOC) content of ice accounts for both WSOC aerosol and water-soluble organic gases. In spite of these difficulties, Legrand, Preunkert, May, et al. (2013) showed that analysis of DOC together with light carboxylates in Alpine ice allow reconstruction of past WSOC changes over western Europe. Discussions of the causes of WSOC changes observed in ice are hampered by the fact chemical species responsible for past WSOC changes are not yet fully identified (Legrand, Preunkert, May, et al., 2013), but investigations of the ^{14}C signature of DOC were shown to provide a powerful tool to quantify the fossil versus the contemporary DOC fraction (May et al., 2013). Applied to Alpine ice, these investigations of light carboxylates together with DOC and its ^{14}C signature demonstrated that the observed summer post-1950 increase by a factor of 2–3 of DOC and WSOC was mainly related to strengthened emissions of biogenic volatile organic compounds (BVOCs) from vegetation whereas the contribution of fossil-fuel burning remained limited to ~25% (Legrand, Preunkert, May, et al., 2013). Such a strong impact of biogenic emissions on the past budget of atmospheric OC aerosol in summer may be, however, regionally dependent on the nature of forested ecosystems and its past changes caused by use-land modifications. Furthermore, similar investigations for winter ice (not yet done in the Alps) are so far lacking.

Here we present a seasonally resolved ice-core record of DOC covering the 1910–1979 and ~30 years at the beginning of the 19th century extracted from an ice core drilled in 2009 at Mount Elbus (Caucasus). Together with measurements of light carboxylates, DOC data allow to reconstruct past changes of WSOC aerosol in south-eastern Europe. Highlighted by the ^{14}C signature of DOC in ice, these data are used to discuss changes of sources contributing to DOC and WSOC level by distinguishing between fossil-fuel combustion, living biosphere, or biomass burning. Finally, DOC data from ELB ice are compared to those previously obtained in summer Alpine ice.

2. Materials and Methods

2.1. Ice-Core Material and Dating

An ice core (182.6 m long) was drilled to bedrock in 2009 on the western plateau of Elbus (43°N, 42°E, 5,115 m elevation) in the Caucasus (Figure 1). The upper 168.5 m of the core were dated by annual layer counting primarily

Table 1

Summary of Determinations Done on ELB Ice Samples by Using IC (Major Ions and Light Carboxylates Including Ammonium and Succinate for Dating), and NDIR Analyzer (DOC)

| Depth (m) (mwe) | Time period | Net accumulation rate (mwe) | DOC Total samples (N) | IC Total samples (N) |
|---------------------------|-------------------------|-------------------------------|--------------------------|-------------------------|
| 60.14–87.22 (38.7–62.3) | 1949 to 1979 (31 years) | S: 0.42 W: 0.34 A: 0.76 | 389 (13) | 530 (18) |
| 90.2–118.8 (65.0–89.4) | 1910 to 1944 (35 years) | S: 0.49 W: 0.23 A: 0.72 | 348 (10) | 748 (21) |
| 133.2–139.3 (101.5–106.3) | 1875 to 1888 (14 years) | S: 0.20 W: 0.16 A: 0.36 | 82 (6.3) | 163 (12) |
| 154.4–161.6 (119.6–125.8) | 1782 to 1815 (33 years) | S: 0.14 W: 0.05 A: 0.19 | 153 (4.8) | 296 (9) |

Note. For each investigated time-period, we reported layer thickness (A: annual, S: half-year summer, and W: half-year winter), total number of samples, and mean number of samples per year (N). Uncertainties in the dating are detailed in Text S1 and shown in Figure S1 in Supporting Information S1.

using seasonal variations in ammonium and succinate concentrations, both exhibiting well-marked winter minima (Mikhaleiko et al., 2015; Preunkert et al., 2019). As a result of glacier ice flow, the annual ice layer thickness decreases with depth from 1.5 m water equivalent (mwe) near the surface to 0.46 mwe at ~100 m depth, and 0.18 mwe at 157 m depth (Preunkert et al., 2019). That renders more uncertain dating of the lower layers derived from annual layer counting. The annual counting was found to be very accurate (± 1 year) over the 20th century when anchored with the 1912 Katmai horizon located at 116.7 m depth (Mikhaleiko et al., 2015). The ice record of sulfate indicated that, in addition to the 1912 Katmai eruption, several other volcanic horizons were recorded in ELB ice but none of them has been unambiguously attributed to a particular event. Preunkert et al. (2019) proposed an age of 1774 at 168.5 m depth but the ice layer corresponding to the large 1815 eruption of Tambora was not identified and no dating uncertainty for years prior to 1912 was therefore estimated. Based on complementary data including the acidity, the dating was recently revisited by Mikhaleiko et al. (2024), suggesting the presence of the 1815 Tambora horizon either at 153.7 or 154.7 m depth and an age of 1752 at 168.5 m depth (Text S1 and Figure S1 in Supporting Information S1). Data reported in this work are reported with this new dating. Whereas the difference between the two datings did not exceed one or two years over the main part of the record (1910–1980) discussed in this study, it reached ~25 years in ice layers covering the beginning of the 19th century (Figure S1 in Supporting Information S1).

2.2. Analysis in ELB Ice

The DOC fraction related to solubilization of gaseous atmospheric species in Alpine ice was shown to be mainly related to light (C_1 – C_3) monocarboxylates (C_1 – C_3 RCOOH) and formaldehyde (HCHO) (Legrand, Preunkert, May, et al., 2013). It likely remains true for the ELB ice. To reconstruct past OC atmospheric aerosol in the Caucasus region, we therefore measured these species in ELB ice. From that, the WSOC ice content was estimated by subtracting from the DOC content the carbon levels corresponding to HCHO and C_1 – C_3 RCOOH concentrations. Whereas C_1 – C_3 RCOOH and HCHO represent most of the DOC fraction related to water-soluble gases, measurements of C_2 – C_5 dicarboxylic acids (R (COOH)₂) in Alpine ice were shown to only document a minor fraction of WSOC (Legrand, Preunkert, May, et al., 2013). That limits discussions on the possible cause of past WSOC changes in ice. Therefore, as done in Alpine ice, we complemented DOC, carboxylates, and HCHO data by investigations of the ¹⁴C signature of DOC in ELB ice in view to quantify past WSOC fractions related to fossil-fuel combustion, living biosphere, or biomass burning.

2.2.1. DOC Analysis

DOC was determined by using a commercial device (Teledyne Tekmar company), which was adapted to analyze DOC at a few ppbC level (Preunkert et al., 2011). After being mixed with phosphoric acid, samples

were sparged to drive off inorganic carbon and subsequently transferred to a reactor where a UV lamp together with synthetic air oxidize OC into CO₂ for quantification with a nondispersive infrared detector (NDIR). Three to five device blanks were made per day showing typical values of 25 ± 1.5 ppbC, leading to a detection limit (taken as twice the blank variability over a day) of ~ 5 ppbC. The typical uncertainty of DOC determination is less than 5% and 10% for summer and winter ELB ice, that contains more than 100 ppbC and 50 ppbC of DOC, respectively.

To remove contamination from ice before DOC analysis, we used a special glass-device developed by Preunkert et al. (2011) in which pieces of ice were washed with ultrapure water and kept melting. During melting, an inert gas atmosphere was maintained inside the glass receptacle to prevent contact of sample with ambient air of the lab. Due to rapid contamination of firn (a porous material) by gaseous organics (Legrand, Preunkert, Jourdain, et al., 2013), DOC investigations were restricted to the ice part of the core that covers the years prior to 1980. DOC measurements (~ 970 samples) were achieved on a quasi-continuous basis in ice layers covering the 1910–1979 years with additional measurements investigating the period from 1875 to 1888 and from 1782 to 1815 (Figure S2 in Supporting Information S1). Given available amounts of ice left after investigations of ions with ion chromatography (IC) (Preunkert et al., 2019; Kutuzov et al., 2019, see Section 2.2.2) and BC using a single particle soot photometer (Lim et al., 2017), the time resolution is twice lower for DOC than for IC (Table 1). Nevertheless, with at least 10 samples per year over the 20th century period, a seasonally-resolved record of DOC was derived. Further-down, whereas the sample resolution of a few samples per year is still adequate to document the summer record, it became too low for the deepest winter layers (from 154 to 162 m depth, i.e., 1782–1815) where the winter accumulation only represents a quarter of the annual layer thickness (Table 1). As a consequence, many of the winter ammonium/succinate minima used to define a winter layer were too thin to determine reliably winter DOC concentrations, and only seven winter values were calculated over these 33 years (Figure 2).

2.2.2. HCHO and Light (C1–C3) Monocarboxylates

HCHO was measured by a fluorimetric method based on the liquid phase reaction of HCHO with the Hantzsch reagent. The analyzer (Aerolaser AL4021) has a detection limit of 0.1 ppb. Blanks of the decontamination procedure were below 1 ppb (Legrand et al., 2007). Since previous investigation of HCHO in Alpine ice revealed an absence of seasonality, likely due to post-depositional diffusion of this volatile species (Legrand, Preunkert, May, et al., 2013), HCHO was measured in a very low time resolution (~ 3 samples per year). Seventy HCHO determinations were done in pooled aliquots of remaining samples from IC analysis done between 60.14 and 82.2 m depth (i.e., 1956–1979) (Figure S3 in Supporting Information S1).

Light carboxylates were quantified with a Dionex DX600 IC equipped with an AS11 separator column and a gradient pump system, allowing the determination of C₁–C₃ RCOOH including formate (HCOO[−]), lactate (CH₃CHOHCOO[−]), acetate (CH₃COO[−]), glycolate (CH₂OHCOO[−]), and glyoxylate (CHOCOO[−]), as well as C₂–C₅ dicarboxylates including oxalate (C₂O₄^{2−}), malate (CO₂CH₂CHOHCO₂^{2−}), malonate (CO₂CH₂CO₂^{2−}), succinate (CO₂(CH₂)₂CO₂^{2−}), and glutarate (CO₂(CH₂)₃CO₂^{2−}). Detection limits were close to 0.1 ppb for most carboxylates. Pieces of ice were subsampled and decontaminated at -15°C using a pre-cleaned electric plane tool to remove ~ 3 mm under a clean air bench (Preunkert & Legrand, 2013).

A total of 1750 subsamples were obtained along ice layers in which DOC was analyzed (Table 1). To minimize the loss of temporal resolution with depth along the core (Section 2.1), the sample depth resolution was decreased from 7 cm at 60 m depth to 4 cm between 90 and 119 m depth, and 2 cm between 154.5 and 161.6 m depth. As seen in Table 1, even in winter, such a sample resolution of at least ~ 10 samples per year permitted to derive a winter and summer record of DOC and WSOC back to the beginning of the 20th century.

2.2.3. DO¹⁴C Analysis

A major limitation of DO¹⁴C analysis in ice comes from high risk of sample contamination (Fang et al., 2021; Legrand, Preunkert, Jourdain, et al., 2013). A DOC extraction set-up for radiocarbon analyses was developed at the Institut des Géosciences de l'Environnement by coupling the DOC analyzer described in Section 2.2.1 to a cryogenic CO₂ extraction line in which CO₂ is piped through water traps at $T = -87^{\circ}\text{C}$ and a hot ($T = 700^{\circ}\text{C}$) Pt catalyst to reduce O₃. The oxidation efficiency of OC into CO₂ of the DOC analyzer was found to be very efficient for WSOC (Preunkert et al., 2011) including long-chain polyacids

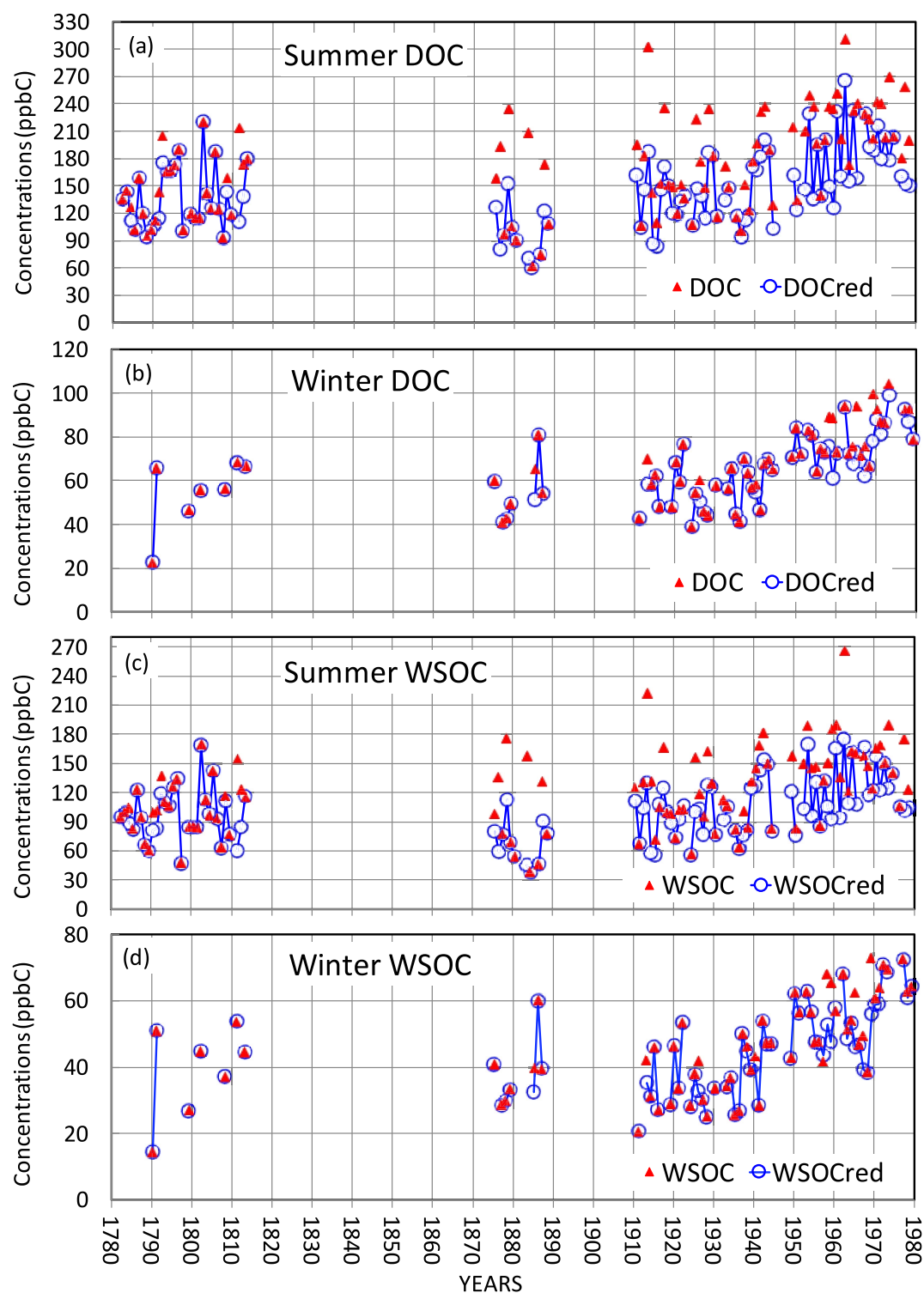


Figure 2. Half-year summer (a) and (c) and winter (b) and (d) concentrations of DOC and WSOC. DOC_{red} and WSOC_{red} are means calculated after removal of samples containing alkaline material (Section 3.2).

(humic-like substances) that significantly contribute to DOC levels in Alpine ice (Guilhermet et al., 2013; Legrand, Preunkert, May, et al., 2013). As for DOC analysis, contamination was removed by melting and washing ice pieces within a special glass device in which an inert gas atmosphere was maintained.

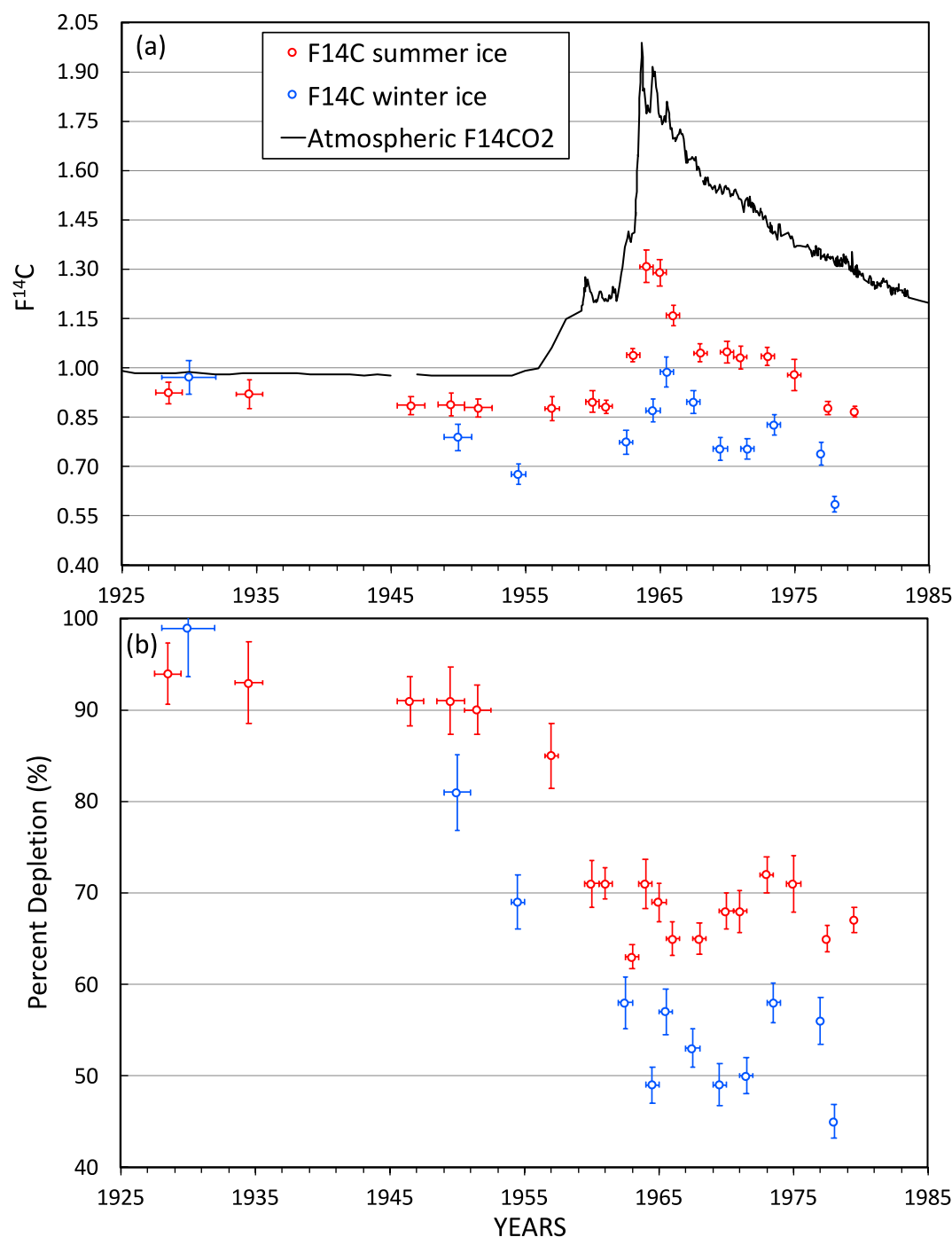


Figure 3. Comparison of the $DO^{14}C$ signature in ELB ice (red and blue dots refer to summer and winter, respectively) and the $F^{14}C$ of the atmospheric CO_2 (black line) (Levin et al., 2010). Vertical bars denote the $F^{14}C$ uncertainties, horizontal bars the dating uncertainties. Out of scale are values of 0.983 ± 0.05 for 1876/77 winter, of 1.11 ± 0.07 for 1876 summer. (a) Refers to $DO^{14}C$ values in ice, (b) to the percent depletion of ^{14}C in ice relative to the $F^{14}C$ of atmospheric CO_2 .

The CO_2 samples were then flame sealed into glass ampoules and ready for Accelerator Mass Spectrometer (AMS) measurement. The ^{14}C measurements were carried out at the accelerator mass spectrometer facility of the Curt-Engelhorn-Center Archeometry in Mannheim, Germany, the gas ion-source system allowing measurements in 2–10 μgC with an error of 3%–7% and $>10 \mu gC$ with an error of 1%–2% (Hoffmann et al., 2017). Given the blank variability, a detection limit (taken as 3σ) is close to 0.3 μgC per extraction done on 20 mL of ice (i.e., the

Table 2
Mean Summer and Winter Concentrations of DOC, WSOC and Water-Soluble Gases That Include C₁–C₃ Monocarboxylates Plus HCHO Over Preindustrial (PI) and Present-Day (PD)

| | Summer PI (1782–1944) | Summer PD (1960–1978) | Winter PI (1790–1944) | Winter PD (1962–1979) |
|---|-----------------------|-----------------------|-----------------------|-----------------------|
| DOC | 152.1 ± 46.5 | 227.0 ± 34.9 | 56.3 ± 11.8 | 85.3 ± 11.3 |
| DOC _{red} | 132.1 ± 34.8 | 191.6 ± 34.3 | 55.4 ± 11.6 | 79.6 ± 11.2 |
| WSOC _{red} | 91.5 ± 29.7 | 128.5 ± 26.7 | 35.5 ± 10.0 | 54.5 ± 10.9 |
| C ₁ –C ₃ RCOOH _{red} | 39.0 ± 10.9 | 60.9 ± 11.3 | 18.4 ± 4.5 | 22.9 ± 5.0 |
| HCHO | 1.6 | 2.2 | 1.6 | 2.2 |

Note. DOC_{red}, WSOC_{red}, and C₁–C₃ RCOOH_{red} refer to means for which samples containing alkaline material were removed (Section 3.2). All concentrations are in ppbC.

volume that can be handled by the DOC system). For winter samples containing 70 ppbC, four extractions provide 5.6 µgC compared to a detection limit of 1.2 µgC (for 4 extractions). In summer samples, typically containing 200 ppbC, two extractions provide 8 µgC compared to a detection limit of 0.6 µgC. All ¹⁴C data are expressed as fraction of modern (F¹⁴C) defined as the ¹⁴C/¹²C ratio of the sample divided by the ¹⁴C/¹²C ratio of the modern reference year 1950 (Reimer et al., 2004).

19 summer samples and 12 winter samples from ice layers covering the 20th century were measured for DO¹⁴C (Figure 3). Given the available ice-core sections of ~3 cm × 2.2 cm and to separately obtain winter and summer values, ice sections of 20–50 cm long were used to reach the required mass of carbon (Table S1 in Supporting Information S1). Most summer samples and all winter samples, except for winter layers deposited prior to 1950 for which ice covering two winter layers was needed, correspond to a half-year season (Table S1 in Supporting Information S1). One summer and one winter sample from ice corresponding to 1876 CE were also measured (Table S1 in Supporting Information S1). Working analytical conditions were, however, not as good as for other samples, likely explaining the unexpected high summer F¹⁴C value of 1.13 ± 0.07.

3. Data Presentation

In the following we examine winter and summer changes separately instead of examining annual (or multi-annual) trends for two reasons. First, it was shown that all chemical species exhibit a pronounced winter-to-summer contrast in the ELB ice, and that the ratio of winter to summer net snow accumulation rate decreased down the length of the core (Preunkert et al., 2019). Such changes with depth of snow deposition conditions can induce a non-atmospheric effect in chemical ice-records. Second, the strong summer-winter contrast seen at high-elevated mountain sites is primarily caused by enhanced atmospheric vertical mixing in summer compared to winter accompanied by seasonal change of source regions impacting the site. In the case of organic species whose natural sources often dominate anthropogenic sources, we may expect change of sources according to season as seen in the Alpine ice for HCOOH (Legrand et al., 2003) or long-chain polyacids (Guilhermet et al., 2013).

3.1. The Fraction of DOC Related to WSOC Aerosol

DOC present in ice comes from both WSOC aerosol and water-soluble organic gases such as short-chain monocarboxylic acids, and aldehydes. On the basis of an extended array of organic species including C₁–C₃ monocarboxylates, C₂–C₃ dicarboxylates, HCHO, and humic-like substances investigated in Alpine ice, Legrand, Preunkert, May, et al. (2013) chemically identified more than 50% of the DOC ice content. That permitted to decipher the fraction attributable to WSOC aerosol from the one related to organic gases. It was concluded that C₁–C₃ RCOOH together with HCHO represent most water-soluble organic gases contributing to the DOC content of ice, the fraction related to atmospheric WSOC aerosol being estimated by subtracting from the DOC content the contribution of water-soluble gases (i.e., HCHO and C₁–C₃ RCOOH). We here have used the same approach to calculate the WSOC contribution to the DOC content of ELB ice.

In contrast to C₁–C₃ RCOOH that were measured in all samples in which DOC was analyzed, HCHO was only measured in ELB ice layers covering the 1956–1979 years (Figure S3 in Supporting Information S1). The mean HCHO value (2.2 ± 1.0 ppbC) in the ELB ice deposited over that period is lower than that observed in the Alps (4.7 ± 1.0 ppbC) over the years 1971–1988 (Legrand, Preunkert, May, et al., 2013). This difference may be

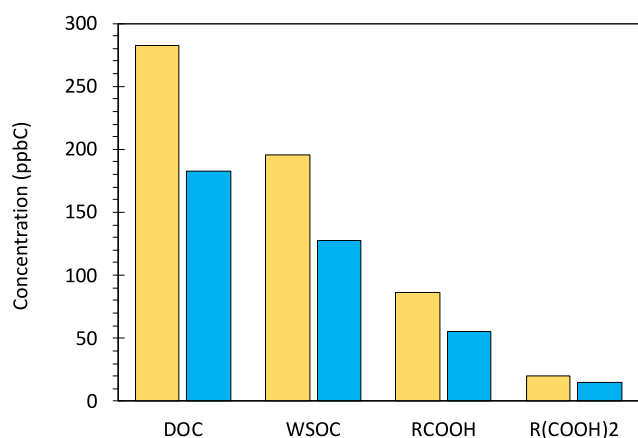


Figure 4. Comparison of the mean carbon content corresponding to DOC, WSOC, C₁–C₃ RCOOH, R(COOH)₂, formate and oxalate in ELB summer ice layers (1950–1979) characterized by high (in yellow) and low dust (in blue) inputs.

related to a stronger post-depositional loss of this volatile species at the ELB site where the surface net snow accumulation rate is lower (1.5 mwe, Preunkert et al., 2019) than at the Alpine site (3.3 mwe, Preunkert et al., 2000). No HCHO data are available in PI ice at ELB, so as a crude estimate we have assumed a concentration of 1.6 ppbC based on the decrease of HCHO observed in Alpine ice layers deposited over the 1971–1988 years (4.7 ppbC) compared to prior to 1950 (3.3 ppbC).

DOC and WSOC results are summarized in Table 2 and reported in Figure 2. We also report results in the Supporting Information (Table S2 and Figure S4 in Supporting Information S1) when the old dating from Preunkert et al. (2019) was considered. Whatever the considered dating, there is virtually no difference for winter data. In summer, the difference between the two DOC data set remains limited to ~1 ppbC for PI and less than 4 ppbC for PD time periods.

3.2. The Impact of Dust

Large dust plumes originating from the Middle East and Sahara reach the Caucasus (Kutuzov et al., 2013). Preunkert et al. (2019) had shown that deposition of these plumes that are characterized by high calcium content and a strong alkalinity, enhanced the level of numerous species in ELB ice because either they are present in dust at the emission stage or, being acidic, were taken up by the alkaline dust material during transport (Usher et al., 2003). Some of them like carboxylates contribute to the DOC level and since the amount of dust deposited at the ELB site had changed over time (Kutuzov et al., 2019), it is legitimate to examine the impact of dust on DOC ice concentrations. To evaluate the potential effect of dust events on deposition of organics, we compare averaged chemical composition in samples containing or not large dust inputs (Figure 4). As detailed in Preunkert et al. (2019), identification of layers in the ELB ice containing large dust inputs was done by examining the acidity (or alkalinity) of samples calculated from the ionic balance between anions and cations with concentrations expressed in micro-equivalents per liter (μEq L⁻¹):

$$[H^+] = ([F^-] + [Cl^-] + [NO_3^-] + [SO_4^{2-}] + [C_1-C_3 RCOO^-] + [R(COO)_2^{2-}]) - ([Na^+] + [K^+] + [Mg^{2+}] + [Ca^{2+}] + [NH_4^+]) \quad (1)$$

The large presence of dust in ELB ice, indicated by Ca²⁺ level of ~520 ppb and an alkalinity of 13.5 μEq L⁻¹ instead of 160 ppb of Ca²⁺ and an acidity of 1 μEq L⁻¹ in dust-free samples, leads to an enhancement by 50% of the DOC level (from 183 ± 84 ppbC to 282 ± 147 ppbC). This finding is not surprising since HCOOH, a weak acid contributing for 60% to the DOC fraction related to water soluble gases (Figure 3), is better incorporated in alkaline than acidic Alpine precipitation (Legrand et al., 2003). More unclear is the extent to which dust impacts

WSOC levels. Indeed, although Preunkert et al. (2019) reported a slight oxalate increase in dusty ELB ice (see also Müller-Tautges et al. (2016) for Alpine ice), this species only represents a few percents of WSOC (Figure 4). Thus, other chemical unidentified species contributing to WSOC levels were enhanced in samples containing large dust amount. Therefore, in the following we focus discussions on DOC_{red} and WSOC_{red} mean concentrations that were calculated after removal of samples containing large dust amounts, that is, containing more than 120 ppb of calcium and showing a decrease of the acidity (Preunkert et al., 2019). Samples dedicated to DO¹⁴C measurements were selected to be mostly free of large dust input (based on their Ca²⁺ content and acidity). Since large dust inputs preferentially reach the ELB site in April (Kutuzov et al., 2019), as seen in Table 2 and Table S2 in Supporting Information S1, dust mostly impacted DOC and WSOC levels of summer ice layers.

Table 3

Apportionment (Fossil Fuel Vs. Biogenic) of DOC, WSOC, Their Subfractions in Winter Ice Deposited Over Present-Day (1963–1979) and Prior to 1945

| Winter (ppbC) | Pre-industrial (PI) Prior to 1945 | Present-day(PD) 1963–1979 | PD-PI |
|---|-----------------------------------|---------------------------|-------|
| DOC | 55.45 | 79.6 | 24.2 |
| HCHO | ~1.6 | 2.2 | ~0.6 |
| C ₁ –C ₃ RCOOH _{red} | 18.4 | 22.9 | 4.5 |
| WSOC | 35.5 | 54.5 | 19.0 |
| DOC _{FF} | 0 | 37.4 | 37.4 |
| WSOC _{FF} | 0 | 32.3 | 32.3 |
| WSOC _{BIO} | 35.5 | 22.2 | –13.3 |

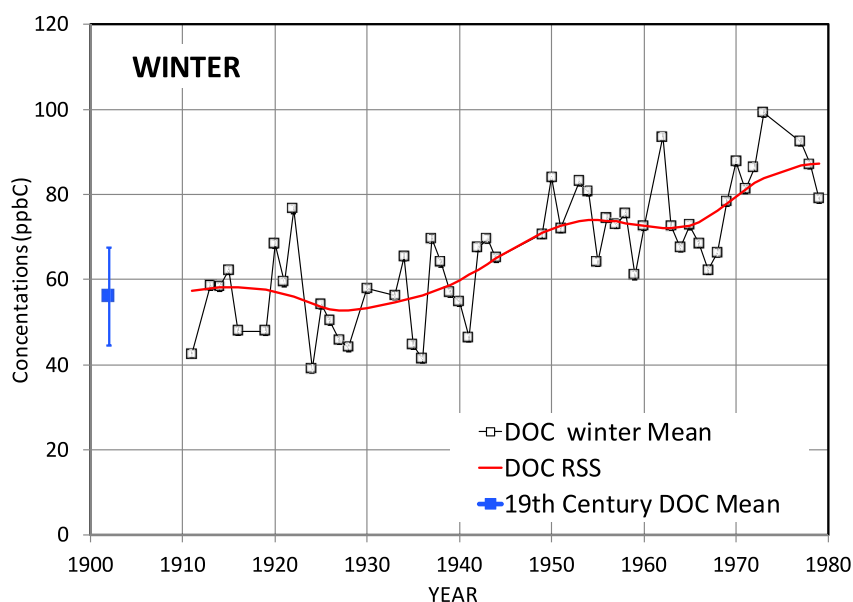


Figure 5. Winter DOC concentrations in ELB ice deposited between 1910 and 1980. Open squares are individual winter means. The blue square on the left is the averaged value over the 12 winters of the 19th century (see Figure 2b). The red line is a robust spline smoothing (RSS).

4. Discussions

4.1. The 20th Century Winter Trend of DOC and WSOC

DOC levels in winter ELB layers deposited prior to 1910 are poorly documented (see Section 2.2.1), and we focus discussions on the 20th century trend. On average over the 12 documented winters of the 19th century, DOC levels (56.0 ± 11.5 ppbC) were in the same range than those observed at the beginning of the 20th century (Figure 5). DOC concentrations then increased by some 24 ppbC (with WSOC accounting for 19 ppbC, Table 3). The DO^{14}C depletion relative to the atmospheric $^{14}\text{CO}_2$ value remained less than 5% in ~1876 and at the beginning of the 1930s, suggesting a dominance of biogenic source at these times. The DO^{14}C depletion relative to the atmospheric $^{14}\text{CO}_2$ value started to increase to 20%–30% at the beginning of the 1950s and reached on average 47% from 1962 to 1979 (Figure 3b). That suggests that 37.4 ppbC (47% of DOC, Table 3) are fossil-fuel in origin over that recent period.

To relate these DO^{14}C data to relevant information on past winter changes of WSOC aerosol, we need to make assumptions on the sources (i.e., on the ^{14}C signature) of organic gases, which also contribute to the DOC ice levels. For that, we assume that most of the increase of $\text{C}_1\text{-C}_3$ RCOOH (4.5 ppbC, Table 3) plus that of HCHO (0.6 ppbC) from PI to PD have a fossil fuel origin. The fraction of fossil-fuel WSOC (WSOC_{FF}) during PD was thus calculated by subtraction of 5.1 ppbC from the fossil-fuel DOC fraction (DOC_{FF}), the biogenic fraction of WSOC (WSOC_{BIO}) being calculated as the difference between WSOC and WSOC_{FF} (Table 3). WSOC concentrations were enhanced by 18.8 ppbC from PI to PD (Table 3), whereas DO^{14}C data indicate a larger increase of WSOC_{FF} (32.3 ppbC). This difference suggests that the WSOC_{FF} increase was counteracted by a WSOC_{BIO} decrease by 13.3 ppbC (Table 3).

After 1955, the living biosphere has been subject to a strong transient ^{14}C input from atmospheric CO_2 due to addition of bomb-produced radiocarbon (Levin et al., 2010). Examination of how close the DO^{14}C ice-record follows this atmospheric $^{14}\text{CO}_2$ perturbation helps to identify the main biogenic DOC source, either the fast-recycling living biosphere or the more slowly recycling biomass burning (wood combustion). In Figure 6a, we compared DO^{14}C ice data with the atmospheric $^{14}\text{CO}_2$ record reduced by 53% to account for a constant overall mean fossil contribution to the ice-core DOC over the 1960s and the 1970s. The DO^{14}C ice-record reached a maximum in winter 1964/65 (or winter 1965/66, Table S1 in Supporting Information S1) whereas the maximum of the atmospheric $^{14}\text{CO}_2$ perturbation occurred from mid-1963 to mid-1964. Applying a retrospective averaging of a few years (2–5 years) to the 0.53 times $^{14}\text{CO}_2$ atmospheric record, the best fit between the DO^{14}C ice record

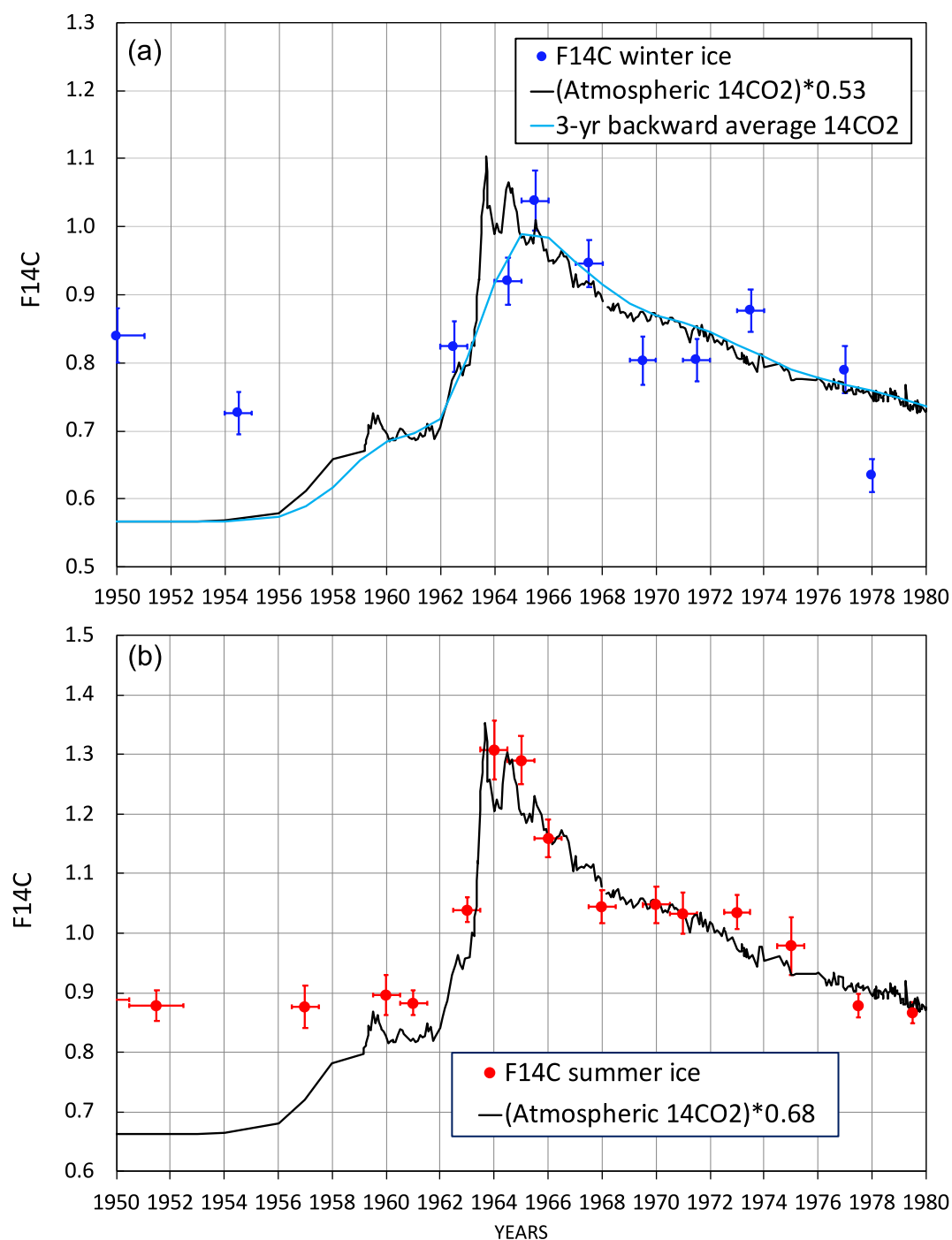


Figure 6. Ice-core DO^{14}C in Elbrus ice (squares) compared to the atmospheric $^{14}\text{CO}_2$ level (black lines). (a): Ice-core DO^{14}C values in Elbrus ice (blue squares) compared to 0.53 times the atmospheric $^{14}\text{CO}_2$ level (black line). The blue line is the smoothed $^{14}\text{CO}_2$ records calculated by averaging backwards over 3 years (b): Ice-core DO^{14}C (red squares) values in Elbrus summer ice compared to 0.68 times the atmospheric $^{14}\text{CO}_2$ level (black line).

and the atmospheric $^{14}\text{CO}_2$ signal is obtained for a period of 3 years, indicating that the DO^{14}C values fit most closely to a DOC source characterized by a turnover time of ~ 3 years. That suggests that remaining emissions from the winter living biosphere together with a small contribution from wood burning are the main biogenic sources of DOC in winter in this region.

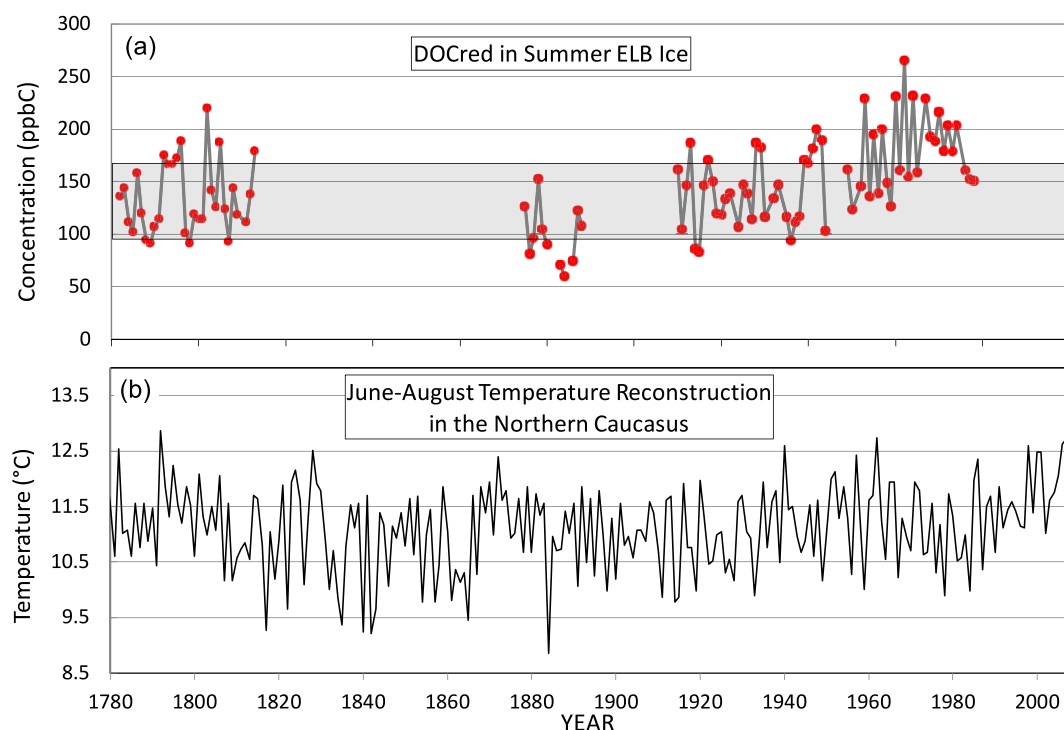


Figure 7. Past summer DOC_{red} concentrations in ELB ice (a) and June-September temperature reconstruction in the northern Caucasus (b) (Dolgova, 2016). The horizontal gray band denotes the mean ($\pm 1\sigma$) DOC_{red} value observed in ice deposited from ~1780 to 1945.

4.2. The 20th Century Summer DOC_{red} and WSOC_{red} Trends

As discussed in Section 3.2, we examine the trend of DOC and WSOC by considering only samples that were free of large dust inputs (DOC_{red} and WSOC_{red}). DOC_{red} concentrations remained close to 140 ppbC (136 ± 33 ppbC at the beginning of the 19th century, 140 ± 33 ppbC from 1910 to 1945). Although a rather large inter-annual variability can be observed (Figure 7, see further discussions in Section 4.3), DOC_{red} levels were then enhanced by 59.4 ppbC (with WSOC accounting for 37 ppbC, Table 4). The depletion of DO^{14}C relative to the atmospheric $^{14}\text{CO}_2$ remained less than 10% until 1935, suggesting a dominance of biogenic source at that time. The DO^{14}C depletion relative to the atmospheric $^{14}\text{CO}_2$ value started to increase to 15% at the end of the 1950s and reached on average 32% from 1962 to 1979, suggesting that 61.3 ppbC (32% of DOC_{red} , Table 4) are fossil fuel in origin over the PD time period.

Assuming that most of the increase from PI to PD of $\text{C}_1\text{-C}_3$ RCOOH (21.9 ppbC) and of HCHO (0.6 ppbC) (Table 4) have a fossil-fuel origin, we calculated the WSOC_{FF} fraction during PD by subtraction of 22.5 ppbC from the DOC_{FF} fraction. Note that the dominance of biogenic ($\sim 2/3$ of total) on anthropogenic ($\sim 1/3$ of total) sources of RCOOH in ice deposited during PD is in agreement with the global modern budget of formic and acetic acids (Paulot et al., 2011) that represent the most abundant atmospheric short-chain monocarboxylic acids. The WSOC_{BIO} was then calculated as the difference between WSOC and WSOC_{FF} (Table 4). WSOC concentrations were enhanced by 37 ppbC from PI to PD (Table 4), DO^{14}C data indicating a similar WSOC_{FF} increase (38 ppbC). That suggests that the increase of WSOC_{red} was mainly due to fossil-fuel burning and that biogenic sources were not significantly modified over the 1910–1980 years in this region.

Figure 6b compared DO^{14}C ice data with the atmospheric $^{14}\text{CO}_2$ record reduced by 68% to account for an overall mean fossil contribution to DOC ice levels over the 1960s and after. The DO^{14}C ice record reached a maximum in

Table 4
Apportionment (Fossil-Fuel Vs. Biogenic) of the DOC, WSOC, Their Subfractions in Summer Ice Over Present-Day and Prior to 1945

| Summer (ppbC) | Pre-industrial (PI) Prior to 1945 | Present-day (PD) 1962–1979 | PD-PI |
|---|--------------------------------------|-------------------------------|-------|
| DOC_{red} | 132.1 | 191.6 | 59.4 |
| HCHO | ~1.6 | 2.2 | ~0.6 |
| $\text{C}_1\text{-C}_3$ $\text{RCOOH}_{\text{red}}$ | 39.0 | 60.9 | 21.9 |
| WSOC_{red} | 91.5 | 128.5 | 37.0 |
| DOC_{FF} | 0 | 61.3 | 61.3 |
| WSOC_{FF} | 0 | 38.2 | 38.2 |
| WSOC_{BIO} | 91.5 | 90.3 | −1 |

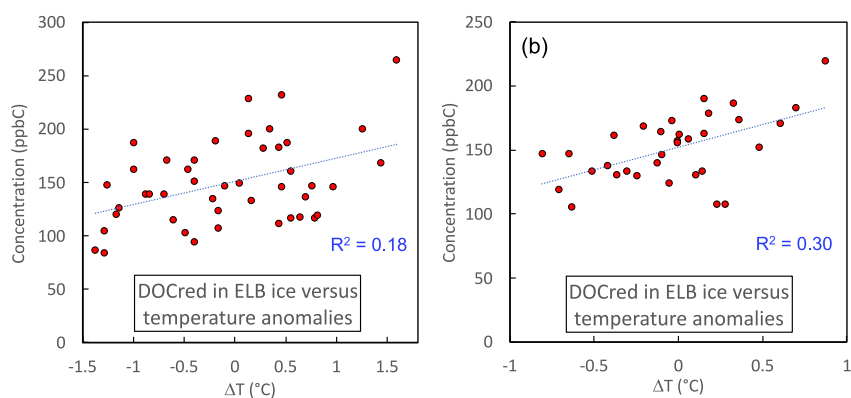


Figure 8. DOC_{red} in summer ELB ice deposited between 1910 and 1962 versus temperature anomalies (ΔT) relative to the 1901–2000 mean (11.15°C) in the northern Caucasus as reconstructed from tree-rings (Dolgova, 2016). (a) Raw annual data, (b) 3-year smoothed data.

summer 1964 (or summer 1965, Table S1 in Supporting Information S1), in phase with the maximum of the atmospheric $^{14}\text{CO}_2$ perturbation in mid-1964. That suggests that the living biosphere (BVOC emissions from vegetation) is the main biogenic source of OC in summer.

4.3. The Natural Variability of DOC_{red} and WSOC_{red} in Summer ELB Ice

Prior to 1950, when the DO^{14}C values indicate an insignificant anthropogenic fraction, there was a significant inter-annual variability of DOC_{red} levels in summer (132.1 ± 34.8 ppbC, Table 2). That is also observed for its two fractions, WSOC_{red} (91.5 ± 29.7 ppbC) and $\text{C}_1\text{--C}_3$ RCOOH (39.0 ± 10.9 ppbC). The DOC fraction related to water soluble gases is dominated by HCOOH and to a lesser extent CH_3COOH (Figure 4), two species that are mainly photochemically produced by oxidation of isoprene and monoterpenes (Paulot et al., 2011). The WSOC fraction is far less chemically documented than the $\text{C}_1\text{--C}_3$ RCOOH fraction, with only a small fraction of WSOC ($\text{C}_2\text{--C}_5$ dicarboxylates) being identified. As seen in Figure 4, oxalate represents a half of total $\text{C}_2\text{--C}_5$ dicarboxylates and is thought to mainly originate from isoprene oxidation (Legrand et al., 2007; Myriokefalitakis et al., 2011).

Emissions of isoprene and monoterpenes that likely strongly contribute to the DOC levels in ice are sensitive to light and temperature (Guenther et al., 1993). In Figure 8a (see also Figure S5 in Supporting Information S1) we compared DOC_{red} in ELB summer ice with June–September temperatures reconstructed in the northern Caucasus region in a dendroclimatic study of the latewood density of conifer tree-rings (Dolgova, 2016). We restricted the comparison to the 1910–1962 years, a period that is mainly free of anthropogenic DOC contribution (prior to 1962 as indicated by DO^{14}C values, Figure 3b) and for which dating uncertainty is minimal (± 1 year, Section 2.1). Although being scattered, the “DOC–T” relationship is found to be significant at the $P > 95\%$ confidence level. To minimize the 1-year dating uncertainty, we also examine the DOC–T relationship after having smoothed data over 3 years (Figure 8b). That improved the correlation with R^2 becoming equal to 0.30 instead of 0.18 when considering raw data. Although further works are clearly needed to confirm the link between past DOC levels in ice and summer air temperatures, this first study of DOC in ice deposited well before fossil-fuel emissions had started to impact DOC levels suggests, however, that past warm summer temperatures may have enhanced emissions of isoprene and monoterpenes from forested areas located around the Caucasus.

4.4. Comparison of the DOC Summer Ice-Record in the Alps and the Caucasus

The relative weak increase of DOC_{red} levels observed in ELB summer ice (45% from 132 ppbC prior to 1945 to 192 ppbC between 1962 and 1979, Table 4) differs from the more than doubling of levels (90 ppbC between 1921 and 1951, 200 ppbC between 1971 and 1988) previously reported in summer Alpine ice (Legrand, Preunkert, May, et al., 2013), whereas DO^{14}C data indicate a rather similar contribution of DOC_{FF} (50–60 ppbC) in both Caucasus and Alpine ice. The increase of DOC not related to fossil fuel (~ 60 ppbC) in summer Alpine ice was attributed by Legrand, Preunkert, May, et al. (2013) to an enhancement by $\sim 70\%$ of BVOC emissions during the second half of the 20th century in western Europe, though precise causes of such a change were not discussed. As seen in Figure 9, it is unlikely that the DOC increase in summer Alpine ice was related to the recent increase of

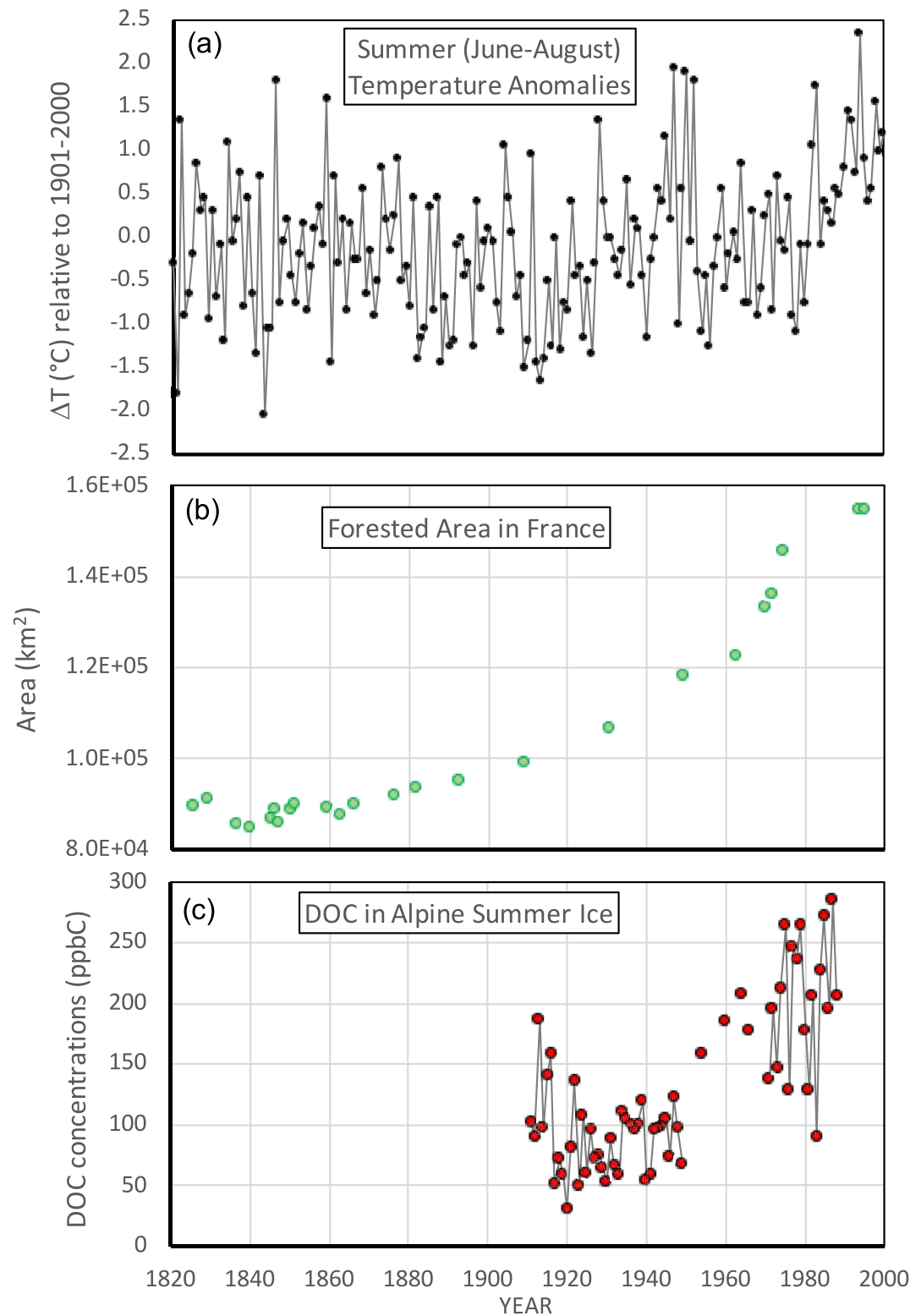


Figure 9. Environmental factors possibly influencing summer Alpine ice levels of DOC. (a) Temperature anomalies relative to 1901–2000 means in regions located west of the Alps (from 4 to 11.5°E, and from 43 to 49°N) (Auer et al., 2007; Böhm et al., 2010). (b) Change of the forested area in France since 1820 (Cinotti, 1996). (c) Adapted from Legrand, Preunkert, May, et al. (2013).

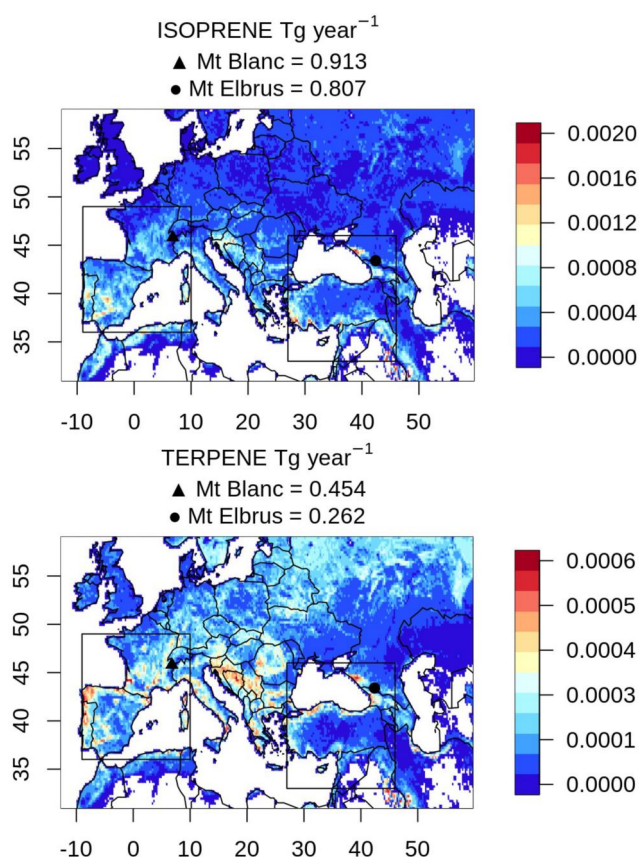


Figure 10. Annual emissions of isoprene (top) and the sum of terpenes (bottom) averaged over the 1982–2000 years as simulated by the MEGAN v2.1 model (Guenther et al., 2012; Sindelarova et al., 2014). Values reported on top of panels are mean values for regions (denoted with a rectangle) located south-west of the Caucasus (Mt Elbrus denoted with a black circle) and the Alps (Mt Blanc denoted with a black triangle).

valid if present-day conditions of deposition, in particular the precipitation rates, are similar at the two sites. Legrand et al. (2023) estimated a mean precipitation rate of 0.8 m of water in summer at the CDD site for present-day and no significant trend over the 20th century. At present, the ELB site encounters a very similar summer precipitation rate (0.87 m of water) without systematic changes over the 20th century. That legitimates the comparison of CDD and ELB ice concentrations with respect to biogenic emissions reported in Figure 10.

As a result of similar leaf area index (Figure S6a in Supporting Information S1), temperature (Figure S6b in Supporting Information S1) and light (Figure S6c in Supporting Information S1), emissions of isoprene that dominate BVOCs in regions influencing the two sites are almost identical (Figure 10a), those of the sum of terpenes being 70% higher in western than in south-eastern Europe (Figure 10b). Note that the resulting slightly higher emissions of BVOC precursors of DOC in western than south-eastern Europe would be in some extent balanced by the fact that emissions take place at higher elevation in south-eastern than western Europe (Figure S6d in Supporting Information S1). While these data suggest that BVOC emissions are similar in western and south-eastern Europe over the recent decades, DOC ice-core data suggest that they were some 50% lower at the beginning of the 20th century in western than south-western Europe. That is in line with our previous conclusion of a reduction back in time of the forested area in western Europe that did not occur in the Caucasus regions.

5. Conclusions

We developed a seasonally resolved ice-core record of DOC and its ¹⁴C signature from ice-cores extracted at the high-elevated glacier of Mt Elbrus located in the Caucasus. Data were used to document past atmospheric changes

temperatures. Indeed, even over the most recent decades (1980–1990) when the DOC levels were already high, the temperature anomalies (+0.5°C) did not exceed those over the 1942–1947 years (+0.7°C) (Figure 9). Instead, the averaged surface of forested areas has increased from 95,000 km² in the middle of the 19th century to 155,000 km² in the 1990s (Cinotti, 1996). The increase is even more pronounced on the western flank of the Alps (60%–110% between 1908 and 1981, <https://inventaire-forestier.ign.fr/IMG/pdf/IF31.pdf>).

Another interesting difference between the ELB and CDD sites are the PI summer ice DOC levels that were 45% higher in the Caucasus (132 ppbC) compared to the Alps (90 ppbC), whereas the recent levels were comparable (192 ppbC at ELB vs. 200 ppbC at CDD) with a similar anthropogenic contribution. The concentrations of DOC_{BIO} at the end of the 20th century were also similar at the two sites. These concentrations were influenced by present-day emissions of biogenic volatile organic compounds (BVOCs) from regions located around the sites, atmospheric transport pathways, and conditions of deposition at the sites. The emission sensitivity of the CDD site to deposition of submicron aerosols was investigated by running the Lagrangian particle dispersion model FLEXPART backward in time for wet and dry deposition. From that, it was suggested that France, Italy, Spain, Switzerland, and Germany are the main source regions in summer (Arienzo et al., 2021; Legrand et al., 2020). Using 10-day backward trajectories calculated from the HYSPLIT trajectory model, Kutuzov et al. (2019) concluded that the main regions impacting the deposition of aerosols in summer at the ELB site include Turkey, eastern and central Europe, the Middle East, and southern Russia. These findings were confirmed by the examination of ice-core records of submicron aerosols like sulfate at CDD and ELB (Preunkert et al., 2019).

On this basis, we reported in Figure 10 (and Figure S6 in Supporting Information S1) climatic parameters and present-day emissions of BVOCs from regions located south-west of sites that are thought to mainly influence aerosol deposition at CDD and ELB sites in summer. Such an approach that compares ice concentrations and emissions from relevant source regions is

of water-soluble organic carbon aerosol in south-eastern Europe in winter and summer. Radiocarbon DO^{14}C measurements in ice samples covering the bomb peak period permitted to investigate source apportionment of DOC and WSOC. It is shown that, whatever the time period, WSOC remained mainly of biogenic origin in this part of Europe in summer. Limited to $\sim 30\%$ in summer, the contribution of WSOC related to fossil-fuel burning emissions reached almost 50% in winter in the late 1970s. Examination of the time lag between changing DO^{14}C content of ice and atmospheric $^{14}\text{CO}_2$ indicates biogenic emissions of volatile organic compounds by the living biosphere in summer, the living biosphere together with a small contribution of wood burning in winter, as the main biogenic sources of DOC and WSOC in this region. A striking difference appears between the summer DOC records in the Caucasus and the Alps with an absence of significant recent increase of the biogenic fraction of DOC in south-eastern Europe contrasting with an increase by 70% in western Europe after ~ 1950 compared to pre-1945, as a result of large extensions of forested areas in France.

Data Availability Statement

Ice core data (Legrand et al., 2023) are available at NCEI (National Centers for Environmental Information) data base.

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