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Carbon Monoxide and Ultra-Trace Gases from Ice Cores

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Abstract

Air trapped in polar ice cores is a valuable archive for determining paleoatmospheric levels of ultra-trace gases that have weak emissions and are removed quickly from the atmosphere, resulting in abundances ranging from parts per billion (ppb) down to parts per trillion (ppt). Despite very low atmospheric abundances, ultra-trace gases have profound influence on the chemistry of the atmosphere and impact global climate. In this article, firn air and ice core measurements of carbon monoxide, carbonyl sulfide, ethane, acetylene, methyl chloride, and methyl bromide are reviewed and discussed.

Keywords

Acetylene; Carbon monoxide; Carbonyl sulphide; Ethane; Firn air; Ice core; Methyl bromide; Methyl chloride.

Key points

- Air trapped in polar ice cores is a valuable archive for determining the paleoatmospheric levels of ultra-trace gases, which influence atmospheric chemistry and indirectly impact global climate.
- Ultra-trace atmospheric gases investigated in ice archive during the last decade include carbon monoxide, ethane, acetylene, carbon sulfide, methyl chloride and methyl bromide.
- This article reviews firn air and ice core measurements of ultra-trace atmospheric gases, and points out promising avenues for future analyses and researches.

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1. Introduction

Air trapped in polar ice cores has proven to be a valuable archive for determining paleoatmospheric levels of trace gases such as carbon dioxide (CO₂), methane (CH₄), and nitrous oxide (N₂O). The ultra-trace gases (e.g., carbon monoxide, non-methane hydrocarbons, carbonyl sulfide, methyl chloride; methyl bromide) have weaker emissions and are removed faster from the atmosphere, resulting in abundances as low as a few parts per trillion (ppt) in the most extreme cases. Despite very low atmospheric abundances, ultra-trace gases have a profound influence on the chemistry of the atmosphere and impact global climate, drawing interest from a wide range of scientific disciplines. The ambient mixing ratios of many ultra-trace gases are routinely measured as part of atmospheric sampling networks (e.g., <http://www.esrl.noaa.gov/gmd>). Establishing the past atmospheric variability of ultra-trace gases will contribute to our understanding of the feedback mechanisms between the global biogeochemical systems and the climate, as well as providing opportunities to observe past variability in the chemistry of the atmosphere.

Ice core ultra-trace gas measurements present many analytical challenges. Ice cores contain only 10% air by volume. Using large amounts of ice is often not feasible because of both practical limitations on extraction techniques and the fact that these procedures require destructive sampling of rare and valuable ice cores. In most cases, ice core gas analyses are carried out with considerably smaller samples than typically used in atmospheric measurements. As a result, even minor levels of contamination can present significant problems and lead to experimental artifacts. Contaminants can be introduced during drilling, transport, storage, sampling, extraction, and analysis phases. Implementing clean handling procedures and using the right materials for the application throughout these phases are often the most critical components in ultra-trace gas measurements.

Potential causes of measurement artifacts are not limited to external contaminants. Chemically reactive gases can be produced or lost while still in the snow, in the firn before getting trapped in ice cores, or within the ice core matrix. Such in situ effects can be very difficult to identify. Direct

verification of the ice core measurements with contemporaneous real-time atmospheric data can be difficult to achieve. Shallow ice cores from high accumulation rate sites contain air from the second half of the twentieth century and represent the only means for direct verification of ice core measurements. Often, confirming the fidelity of the ice core ultra-trace gas records requires an indirect approach, in which determining the atmospheric composition of the recent past through analysis of firn air plays a crucial role. Firn air gas records can overlap with both the realtime atmospheric measurements and the youngest (most recent) time periods that can be studied with the ice core records. Ultimate confirmation requires agreement between multiple firn air and ice core records.

Measurement difficulties can also apply to atmospheric sampling and in-situ measurements. Sample containers can modify the CO concentration of the contained air and small corrections (typically less than 1%) may need to be applied, especially for remote sampling sites such as Antarctica where the samples may not be analyzed back at laboratories for up to a year. Potential drift in CO concentrations must also be allowed for calibration gases at measurement sites or at central laboratories. Firn and ice core samples have the advantage that they can be measured within a short period soon after collection and the effects of these drifts can be reduced.

The last decade has seen considerable improvements in the measurement of ultra-trace gases in ice cores, although this research is still in its early stages. The following sections include a review of the published literature on ice core measurements of six such ultra-trace gases: carbon monoxide, ethane, acetylene, carbonyl sulfide, methyl chloride, and methyl bromide.

2. Carbon Monoxide

Carbon monoxide (CO) is a reactive short-lived trace gas that plays a crucial role in the interactions between climate and atmospheric chemistry. CO acts on the budgets of both hydroxyl radical (OH) and ozone (O₃) and thus has a strong impact on the global oxidative capacity of the atmosphere. With up to 40 % of the OH radicals reacting with CO in the modern troposphere (Lelieveld et al., 2016), CO is the principal sink for tropospheric OH. Consequently, CO indirectly affects the lifetime of many atmospheric constituents such as methane (CH₄), volatile organic compounds (VOCs), and hydrofluorocarbons (HFCs). Oxidation of CO by OH in the presence of high levels of nitrogen oxides (NO_x) can result in significant production of tropospheric ozone and ultimately leads to CO₂ production (Crutzen, 1973).

CO is produced by atmospheric oxidation of different gaseous precursors and emitted by various surface processes. Atmospheric oxidation of CH₄ and VOCs represents about half of the modern sources (Duncan et al., 2007). CO is emitted from a variety of anthropogenic and natural sources, which include incomplete combustion of anthropogenic fossil fuels and biofuels (Hoesly et al., 2018), biomass burning (van der Werf et al., 2017), oxidation of methane and nonmethane hydrocarbons (Duncan et al., 2007), and to a lesser degree, plants leaves (Bruhn et al., 2013; Tarr et al., 1995) and oceans (Conte et al., 2019). Anthropogenic emissions, which comprise more than half of the total CO emissions today, occur mostly in the northern hemisphere. The uneven distribution of sources coupled with a short lifetime (tropospheric mean ~2 months) results in large interhemispheric gradients. Typical annual mean surface CO concentrations range from ~120 ppb in the Northern Hemisphere (NH) to ~40 ppb in the Southern Hemisphere (SH) (Petron et al., 2023). In the absence of anthropogenic emissions, source-driven variations in atmospheric CO levels would likely be due to

changes in biomass burning emissions and atmospheric methane (CH₄) levels. Any change in the oxidative capacity of the atmosphere would also impact the abundance of CO in the preindustrial atmosphere.

2.1. CO studies from Northern Hemisphere firn and ice

Ground based and satellite-derived CO data are only available for the last three decades. Ancient air preserved in glacial ice and firn is thus a unique archive for reconstructing the past atmospheric [CO] record prior to the 1990s. The first NH firn air study of [CO] was conducted at the small Devon ice cap in the Canadian Arctic (Clark et al., 2007). This study found [CO] monotonically increasing with depth in the firn, and an unrealistically high value of 186 ppb for the deepest sample. Clark et al. (2007) concluded that CO in the Devon firn was likely affected by in situ production. By analyzing [CO] depth profiles collected from firn air at three different Greenland sites (NGRIP, Summit, and NEEM), Petrenko et al. (2013) obtained the first reliable reconstruction of atmospheric [CO] spanning 1950-2010 CE. This reconstruction has been recently extended back to 1700 CE with the high-resolution Continuous Flow Analyses (CFA, see analytical section below) analysis of 700 m of ice from 4 different Greenland ice cores (NGRIP, PLACE, NEEM, and D4) (Faïn et al., 2022). These new records revealed high and variable concentrations that cannot be interpreted as changes in atmospheric but most likely related to in situ production occurring within the ice archives themselves after bubble closure (Faïn et al., 2014). Additional measurements conducted on individual discrete samples allowed to rule out the possibility of rapid CO production during the CFA analytical process. However, the possibility that the Greenland ice archive CO reconstruction could be slightly positively biased by in situ production occurring within the Greenland ice cannot be fully excluded. Therefore, the atmospheric [CO] history extracted from Greenland should be considered as an upper bound of the past [CO] abundance in the Arctic (Faïn et al., 2022). This recent and multi-sites CO record could not be reconciled with the prior Eurocore dataset (Haan et al., 1996; Haan and Raynaud, 1998), calling the accuracy of the relatively low and stable CO values reported for the period 1650-1950 CE by these pioneering studies. The continuous history of past atmospheric [CO] at high northern latitudes, based on multi-site firn air sampling and CFA-based ice core record, spans 1700-2010 CE and is shown on Fig. 1. The temporal changes depicted by this historical [CO] record probably have a larger spatial significance than the Arctic context alone. From 1700 to 1875 CE, the Arctic CO record reveals stable or slightly increasing values in the 100–115 ppb range. From 1875 to the 1970s CE, the record indicates a monotonic increase from ~115 to ~155 ppb. After ~1980, [CO] declined by ~40 ppb to present-day levels (Fig. 1).

2.2. CO studies from Antarctic firn and ice

Ice archives from Antarctica have also been investigated: CO was collected in firn air at seven sites (Lock In, DE08-2, DSSW19K, DSSW20K, South Pole, ABN, and Berkner Island) to reconstruct [CO] in the Antarctic atmosphere from 1898 CE to present (Fig. 1; Faïn et al., 2023). CFA analyses conducted on three ice cores (DC12, ABN, and TaldIce) extended this reconstruction back for three millennia starting 1897 CE (Fig. 2; Faïn et al., 2023). Overall, this recent record of past atmospheric [CO] at the southern latitudes, which appears to be unaffected by in situ CO production, reveals (i) stable levels prior to 1500 CE at levels of about 40 ppb, (ii) a ~ 5 ppb decrease between the medieval period and the Little Ice Age (LIA), and (iii) a progressive increase from a minimum of 32 ± 4 ppb in ~1700 CE to near-present day levels of 54 ± 2 ppb by 1985 CE. This trend is based on an excellent agreement between 10 firn air and ice core [CO] records and links with modern [CO] atmospheric monitoring (Fig. 1). Finally, the Antarctic ice [CO] reconstruction is representative of the 45-90°S atmosphere, with

temporal changes having probably a larger spatial significance, including at least the 30-90°S latitudinal band.

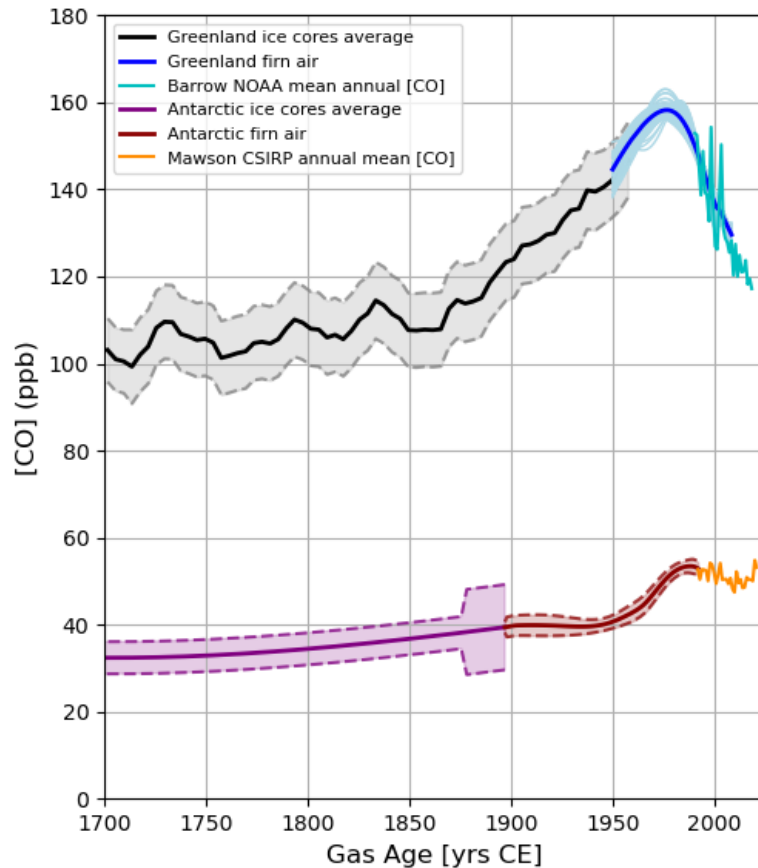


Figure 1. Greenland and Antarctic atmospheric [CO] from ice cores and firn air reconstructions (Fain et al., 2023, 2022; Petrenko et al., 2013), and from NOAA and CSIRO atmospheric monitoring at Barrow (Alaska) and Mawson (Antarctica) stations. The envelopes on the firn and ice core records represent 2σ uncertainties. The envelope on the Greenland ice core record represents 1σ uncertainty.

For pre-industrial time, the recent CO record from Fain et al. (2023) exhibits substantial differences with the previously published CO data from the D47, SP, and VST ice cores (Haan et al., 1996; Haan and Raynaud, 1998; Wang et al., 2010). It exhibits overall lower levels (e.g., ~ 10 ppb lower prior to 1400 CE), a minimum during the LIA occurring about 100 years later, and no maximum in [CO] in the late 1800s. The preindustrial variations in atmospheric CO imply changes in either the atmospheric lifetime or biomass burning emissions of CO. The lifetime of atmospheric CO is determined primarily by reaction with tropospheric OH ($>90\%$), and there is no evidence to suggest that OH variability in the preindustrial atmosphere was larger than the 10% upper limit suggested for the preindustrial to modern change (Stevenson et al., 2020). Thus, the minimum in [CO] reconstructed during the LIA (Fig. 2) is likely related to lower CO fire emissions during this period. Wang et al. (2010) reported the first measurements of CO stable isotopes (i.e., $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) from the SP ice core, with lower isotopic values associated with lower [CO] during the LIA. Wang et al. (2010) also concluded that the combination of [CO] and CO stable isotopes identified large changes in biomass burning emissions as the main driver of the observed trends. Although the [CO] patterns reported by Wang et al. (2010) could not be reproduced by a more recent and comprehensive study (Fain et al., 2023), it demonstrated that the analysis of stable CO isotopic ratios in air trapped in polar ice cores (Wang and Mak, 2010) is a promising approach to provide additional powerful clues for the interpretation of the

past evolutions of the CO budget. Finally, the absence of a [CO] peak around the turn of the century (Fig. 1) argues against there being a peak in Southern Hemisphere biomass burning at this time, which is in agreement with (i) other paleofire proxies such as ethane or acetylene (Nicewonger et al., 2018, 2020a) and (ii) conclusions reached by paleofire modelling (e.g., Hamilton et al., 2018; van der Werf et al., 2013).

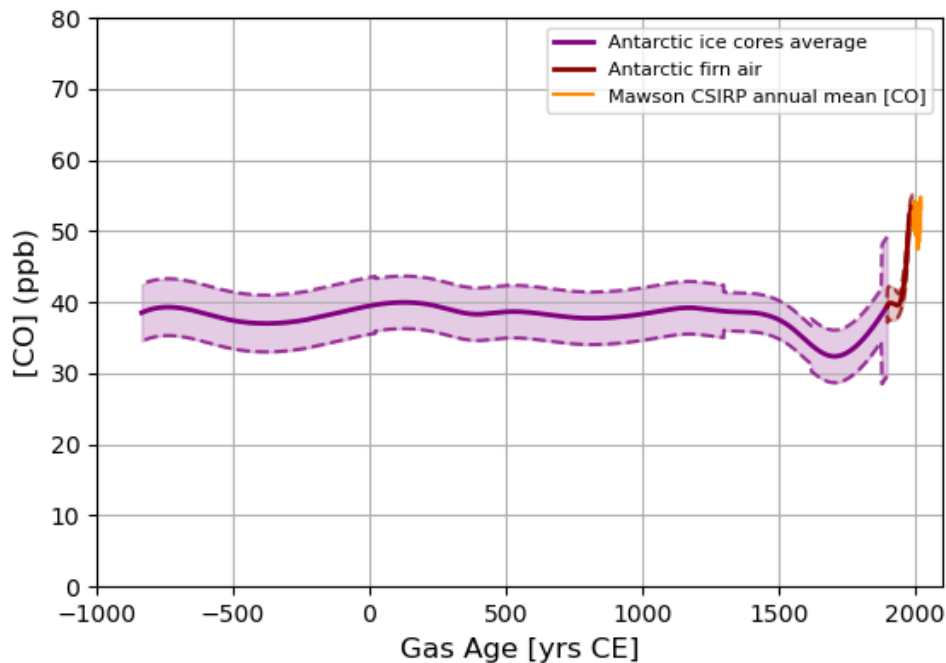


Figure 2. Reconstructed CO mixing ratio in the Antarctic atmosphere for the last 3000 years showing a multi-site ice core composite (purple line), spanning –835 to 1897 CE, and the multi-site firn air reconstruction from Fig. 1 (red line), spanning 1897 to 1992 CE. The envelopes represent 2σ uncertainties. Annual mean [CO] at Mawson Station is shown in orange (Faïn et al., 2023).

2.3. Comparing ice archives and global model CO reconstructions during the industrial era

Bipolar atmospheric [CO] extracted from Greenland and Antarctica ice archives for the period 1850-present (Fig. 1) were used as a benchmark for the Aerosol Chemistry Model Intercomparison ensembles (AerChemMIP, CMIP6; Collins et al., 2017) to assess together the global chemistry-climate models and the emission datasets they used (Faïn et al., 2024). Most models underestimate [CO] at high northern latitudes (Faïn et al., 2024). Figure 3 reports a comparison of ice archive and multimodel [CO] changes, defined as [CO] anomalies relative to the 2000 CE [CO] level. Over the period 1980-2010 CE, CO changes from ice archives and AerChemMIP multimodel outputs are in excellent agreement at both northern and southern high latitudes. Such agreement suggests that the surface emissions of CO (including anthropogenic emissions), as well as in the main CO sink (OH oxidation), are now accurately represented within models. Over the 1920 to 1975 CE, a mismatch in [CO] remains between the AerChemMIP multimodel mean and the ice archive dataset in the Arctic, with the multimodel mean showing lower growth rate before 1945, and higher growth rate after 1945. Although Greenland ice archive record should only be considered as an upper bound of the past CO abundance, as we cannot fully rule out in situ production artifacts (Faïn et al., 2022), the mismatch between modeled and observed CO trends at high NH latitudes could be related to uncertainties in anthropogenic CO emission factors (EFs), specifically EFs for Residential commercial and other (RCO) and for transportation sectors. A better evaluation of these EFs would be an area of improvement for future

modeling of the past NH [CO]. In the Southern Hemisphere, AerChemMIP models simulate an increase in atmospheric [CO] from 1850 to 1980 CE closely reproducing the observations (22 ± 10 ppb and 13 ± 7 ppb, respectively). Such agreement supports CMIP6 biomass burning CO emission inventories which do not reveal a peak in CO emissions in the late 19th century. Both SH models and observations show an accelerated growth rate in [CO] during 1945–1980 CE relative to 1980–1945 CE, likely linked to increased anthropogenic transportation emissions. Finally, the models closely reproduce the cessation of [CO] growth by the 1980s in both hemispheres and subsequent [CO] decline (stronger in the NH) (Faïn et al., 2023; Petrenko et al., 2013). Such decline was attributed to improved fossil fuel combustion and the broad introduction of catalytic converters in the transport sector by stable isotopes analyses of CO (i.e., $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) conducted on firn air samples from the Greenland NEEM site (Wang et al., 2012).

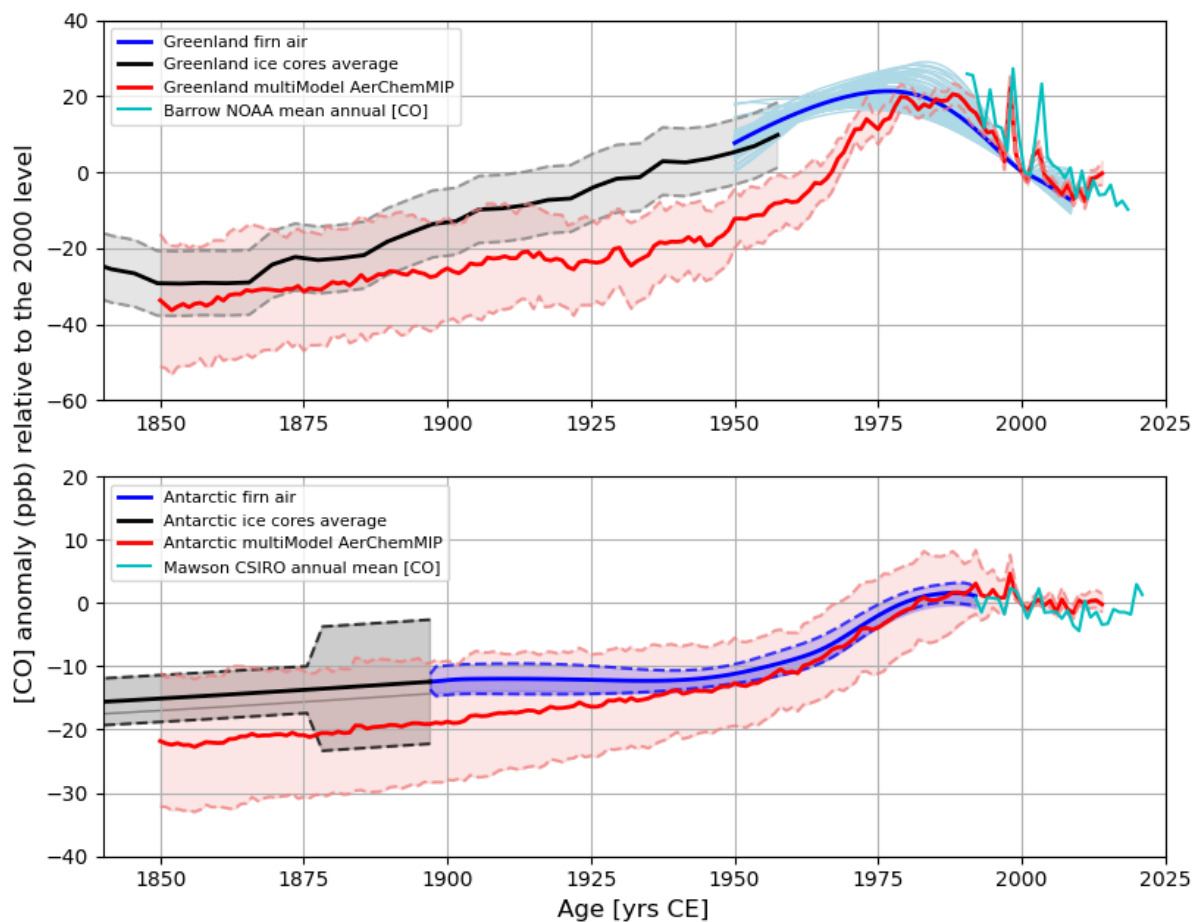


Figure 3. Anomaly of Greenland (upper panel) and Antarctic (lower panel) atmospheric [CO] from ice cores and firn air reconstructions (Faïn et al., 2023, 2022; Petrenko et al., 2013), from NOAA and CSIRO atmospheric monitoring ; and from Multimodel AerChemMIP historical simulations (red line), with the red envelope showing a 1-sigma uncertainty. All data are reported as anomalies relative to annually-averaged 2000 levels. Adapted from Faïn et al. (2024).

3. Ethane

Ethane (C_2H_6) is the most abundant non-methane hydrocarbon in the atmosphere and is an important atmospheric pollutant. Ethane is emitted in the modern atmosphere by the production and use of oil and natural gas, burning of biofuels and biomass, and natural geologic seeps (Etiope and Ciccioli, 2009;

Helmig et al., 2016), where recent results for very low geological emissions of methane in preindustrial times (Hmiel et al., 2020) also suggest a rather small geological ethane source. About two thirds of the present-day budget of ethane is from human use of fossil fuels and biofuels, while the largest natural source of ethane is from biomass burning emissions. The major sink of atmospheric ethane is via oxidation with the OH radical, resulting in a global mean lifetime of roughly 2 months (i.e., comparable to the lifetime of CO; Burkholder et al., 2015). Ethane is also oxidized by chlorine atoms which are produced in the marine boundary layer by reactions involving marine aerosols and polluted air (Wang et al., 2019). Such a reaction with chlorine may constitute a significant portion (~20%) of the ethane sink.

Currently, ethane emissions are primarily situated in the Northern Hemisphere, a consequence of fossil fuel production and utilization (Xiao et al., 2008). Between 2000 and 2010 CE, the average annual ethane concentrations were 1300–1400 ppt over Greenland and 200–250 ppt over Antarctica (Aydin et al., 2011; Simpson et al., 2006). This substantial north/south interpolar ratio of ethane (roughly 6:1) results from the uneven geographical distribution of ethane sources coupled with its relatively short atmospheric lifetime.

Ethane was analyzed in the air extracted from ice core samples from Greenland (GISP2B and GISP2D cores) and Antarctica (WDC05A, WDC06A, and SPC14 ice cores) with mean gas ages ranging from ~0 CE to 1900 CE (Nicewonger et al., 2020b, 2018, 2016). Ethane in Greenland samples ranges from 446 ppt to 610 ppt, while Ethane in Antarctic samples range from 65 ppt to 167 ppt (Fig. 4). The resulting preindustrial north/south interpolar ratio is $\sim 4.6 \pm 0.4$ (Nicewonger et al., 2018). The ice core ethane records display clear temporal variability over the last two millennia. Ethane is highest during the Medieval Period, with a mean of 534 ± 26 ppt over Greenland and 130 ± 17 ppt over Antarctica. Ethane is lowest during the LIA, when the mean ethane level is 474 ± 36 ppt over Greenland and 96 ± 15 ppt over Antarctica. Using a 3D chemical transport model (UCI-CTM), Nicewonger et al. (2018) demonstrated that the ice core ethane records are sensitive to biomass burning emissions, with Greenland ethane levels highly sensitive to boreal burning and Antarctic levels sensitive to non-boreal regions and primarily affected by tropical burning. Overall, the ethane record suggests stable biomass burning emissions in the period spanning 1000 to 1500 CE and a gradual decline in fire emissions from the MP to the LIA in the 1500s, with the LIA as a minimum in burning, in agreement with the CO record (Faïn et al., 2023). This decline is estimated to be 30 %–45 % by the ethane dataset (Nicewonger et al., 2018).

After 1850 CE, ethane levels begin to rise in both the Greenland and Antarctic records (Fig. 4), accordingly with higher ethane levels revealed by firn air records (Aydin et al., 2011; Helmig et al., 2014; Simpson et al., 2012; Worton et al., 2012). Atmospheric impacts of industrialization start to become apparent after 1850 CE, with the bulk of the changes occurring during the 20th century. Analysis of polar firn air samples from both hemispheres indicates indeed significant increases in atmospheric ethane during the first half of the 20th century, attributed to rising anthropogenic emissions, followed by a decline from 1980 to 2000 (Aydin et al., 2011; Helmig et al., 2014; Simpson et al., 2012; Worton et al., 2012). Atmospheric ethane levels have exhibited stability in the early 21st century (Simpson et al., 2012).

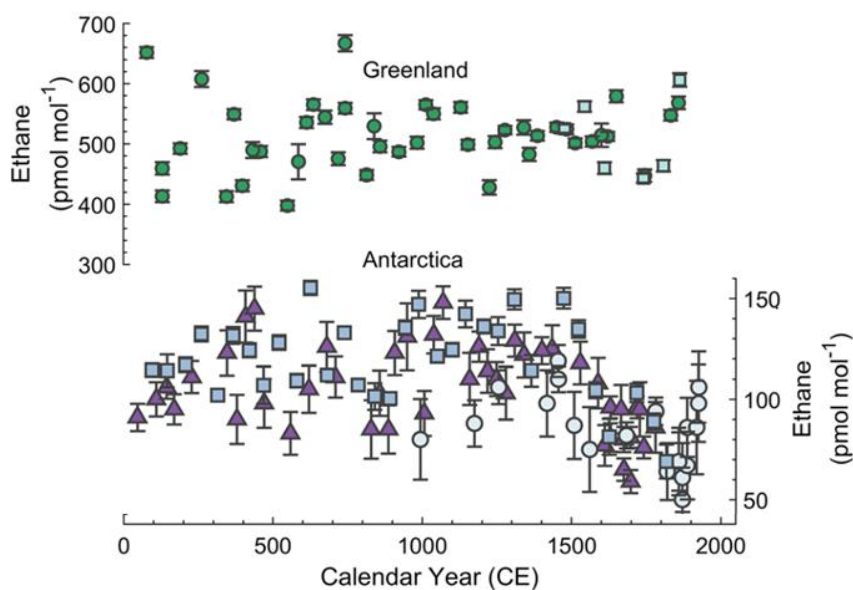


Figure 4. Ice core ethane over the last 2,000 years. (upper panel) Greenland ice core ethane from GISP2B (squares) and GISP2D (circles), (lower panel) Antarctic ice core ethane from WDC05A (circles), WDC06A (triangles) and SPC14 (squares). Error bars on the ethane measurements represent 1σ uncertainties. Reproduced from Nicewonger et al. (2020b).

4. Acetylene

Acetylene (C_2H_2) is released from incomplete combustion processes including fossil fuel, biofuel burning and biomass burning. About half of the acetylene emissions arise from biofuel burning, while the remaining half split equally between fossil fuel and biomass burning (Xiao et al., 2007). Acetylene may also have a small source from partial combustion of methane through geologic outgassing, but this is likely only a minor component of the budget (Nicewonger et al., 2020a). Acetylene is lost in the atmosphere via reaction with the OH radical, resulting in a global mean lifetime of roughly 2–3 weeks (Burkholder et al., 2015; Xiao et al., 2007). Biomass burning has been reported as the only major source of acetylene to the preindustrial atmosphere (Nicewonger et al., 2020a).

Very limited measurements of acetylene in ice archives have been conducted so far. Acetylene was measured in the same core analyzed for ethane: the GISP2B and GISP2D ice cores from Summit, Greenland; the WDC05A, WDC06A and SPC14 ice cores from Antarctica (Nicewonger et al., 2020a). The ice core acetylene records reveal significant temporal variability in atmospheric levels over the past 2,000 years (Fig. 5). The Greenland ice core data show preindustrial acetylene levels that are considerably lower than the modern atmosphere throughout the 2,000-year record, indicating less acetylene emissions in the preindustrial Northern Hemisphere. The Greenland record displays a slow long-term increase during the first 1,000 years and later stabilizes, averaging 104 ± 2 ppt (mean \pm 1 SE) from 0 to 1500 CE. There is a clearly resolved minimum centered around 1700 CE, following a decline that starts near 1500 CE. Greenland levels rise sharply after 1750 CE. The Antarctic acetylene data show a similar stability to Greenland over 0–1500 CE, with a sharp long-term decline that starts around 1500 CE. The Antarctic acetylene averages 36 ± 1 ppt from 0 to 1500 CE, which is roughly twice the modern mean acetylene level over Antarctica. After 1650 CE, acetylene declines by more than 50% to a minimum of 17 ± 2 ppt during 1650–1750 CE. Modeling results suggest that pyrogenic acetylene emissions during 1000–1500 CE were sustained at rates significantly greater than modern day and declined by over 50% during the LIA (Nicewonger et al., 2020a). However, large uncertainties

remain on preindustrial fire history, with implications for the PI to modern evolution in aerosol radiative forcing (Hamilton et al., 2018). Nicewonger et al. (2020b) used chemical transport models to investigate if a single global burning history could be extracted from the three hydrocarbon ice core records. They could not find a consistent fire history, even when assuming unrealistic changes in the spatial distribution of fire and biomes.

After 1750 CE, Greenland acetylene levels rise sharply. An Arctic atmospheric history of acetylene concentration was reconstructed from NGRIP firn air (Greenland) for the period 1950-2000, also revealing an ~50% increase between 1950 and 1980, a maximum in ~1980 at ~600 ppt, followed by a ~100% decrease from 1980 et 2000 CE (Worton et al., 2012). No Acetylene data are available for the period 1850-1950 CE. The acetylene trend over the last decade is similar to the one observed for other NMHC (e.g., ethane and propane; Helmig et al., 2014; Worton et al., 2012) as well as for CO (Fig. 1 and previous section; Petrenko et al., 2013), suggesting that emission reductions that have been implemented since the 1970s had the effect of reducing both CO and the NMHC emissions. Unlike Greenland, the Antarctic record does not display a sharp rise during the nineteenth century.

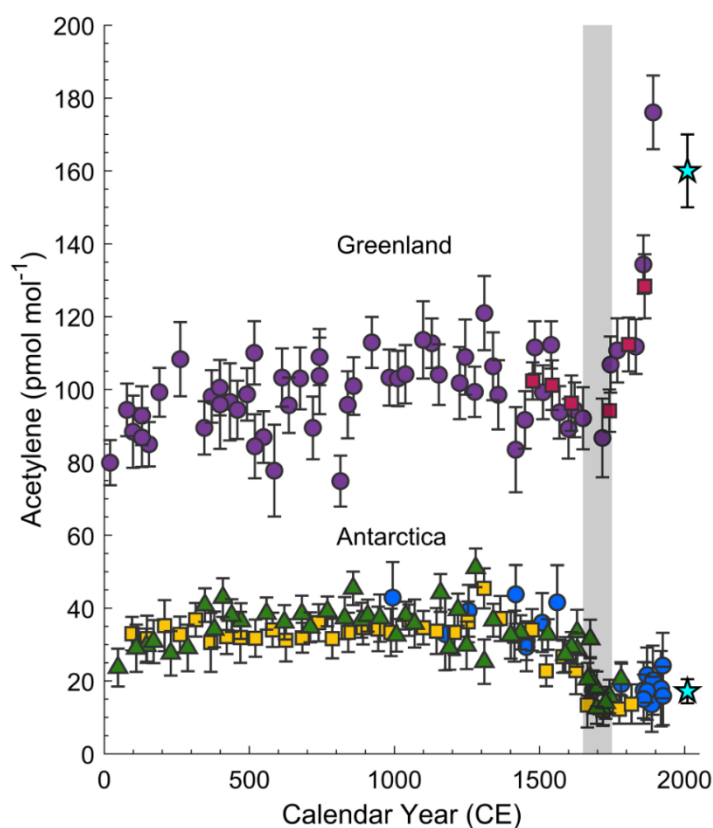


Figure 5. Ice core acetylene levels over the last 2,000 years. Greenland samples are from GISP2B (pink squares) and GISP2D (purple circles). Antarctic samples are from WDC05A (blue circles), WDC06A (green triangles), and SPC14 (yellow squares). Error bars represent $\pm 1\sigma$ analytical uncertainty. Mean acetylene levels over Greenland and Antarctica from 2012 to 2018 (cyan stars) are also shown. The gray bar delineates the acetylene minimum in both records from 1650 to 1750 CE. pmol mol^{-1} and ppt are equivalent units. Reproduced from Nicewonger et al. (2020a).

5. Carbonyl Sulfide

Carbonyl sulfide (COS) is the most abundant sulfur gas in the troposphere. Its tropospheric lifetime is 2–4 years, allowing for mixing between hemispheres. The mean COS mixing ratio was ~480 ppt in the southern and 490 ppt in the northern hemispheres based on atmospheric measurements over the 5 years between 2000 and 2005 (Montzka et al., 2007). In the stratosphere, COS oxidizes to form sulfate aerosols, which reduce the amount of solar radiation that reaches the earth. It is estimated that COS contributes about half of the background stratospheric sulfate during periods of volcanic inactivity (Weisenstein et al., 2006), implying that large variations in the atmospheric COS levels would have an impact on global climate.

Natural COS sources include terrestrial and oceanic emissions. Anthropogenic emissions are linked to industrial production of synthetic fibers. COS is oxidized by OH in the troposphere and taken up by soils but the most significant removal process is uptake by terrestrial vegetation through gross primary production (GPP) (Kettle et al., 2002; Montzka et al., 2007). The removal of COS by terrestrial biota has drawn considerable scientific interest (Campbell et al., 2008; Sandoval-Soto et al., 2005; Seibt et al., 2010; Xu et al., 2002). COS is taken up by plants during photosynthesis alongside CO₂. This process represents a net COS uptake, because unlike CO₂, COS is not respired back into the atmosphere. Consequently, ice core COS records could potentially reveal atmospheric COS variability caused by changes in global photosynthetic activity and therefore help constrain the causes of past CO₂ variations in the atmosphere.

First data on atmospheric COS variability during the periods that predate the instrumental record were obtained from polar firn air measurements at two sites in Antarctica and one in the Canadian Arctic (Sturges et al., 2001b). This study was followed up by additional firn air measurements at South Pole and Megadunes, Antarctica, and Summit and Renland, Greenland (Aydin et al., 2020; Montzka et al., 2004). These observations offer evidence that mean COS levels increased from a stable preindustrial background level of ~300–350 ppt starting in the 19th century and peaked at ~550 ppt around 1975 CE over Greenland and around 1987 CE over Antarctica, presumably as a result of rising anthropogenic emissions (Aydin et al., 2020). These firn air based atmospheric histories are consistent with independent surface air time series data from the corresponding sites and the Antarctic ice core COS records during periods of overlap (Aydin et al., 2020, 2008; Montzka et al., 2004)

More recent measurements from a South Pole ice core provide a continuous COS record for the last 2000 years when combined with the earlier Siple Dome record (Aydin et al., 2008; Figure 6). The Siple Dome and South Pole data display consistency where they overlap and most neighbouring data points within both data sets exhibit agreement. These are strong indicators that the COS levels measured in these two ice cores from Antarctica reflect true atmospheric mixing ratios over the last 2000 years. There are a few cases when the measured COS mixing ratio in individual samples is elevated with respect to the overall trend and the neighbouring data points. It is unlikely these outliers reflect true atmospheric levels. Instead, they may be due to intermittent contamination introduced during extraction and analysis of the ice core samples or in situ production of COS via a yet unidentified chemical mechanism. Excluding the outliers, the average COS mixing ratio in the South Pole record is 310–350 ppt, with an overall increasing trend of ~1.8 ppt per 100 years (Aydin et al., 2008). One major concern about COS ice core measurements has been potential in situ loss of COS via hydrolysis in liquid-like layers within the ice matrix (Assonov et al., 2005). It is possible that this long-term increasing trend is linked to slow hydrolysis of COS in the ice sheet. However, when this trend is extrapolated to the present day, the calculated COS increase between the preindustrial times and the end of the twentieth century is much smaller than what is apparent in the ice core and firn air records, providing strong evidence that anthropogenic emissions during the twentieth century had a profound impact

on the atmospheric mixing ratio of this gas. The South Pole record also displays higher than average COS levels between 1000–1200 CE and 1500–1700 CE, and lower than average mixing ratios between 100 and 700 CE. Such anomalies may be due to changes in the biogeochemical cycling of COS as a response to variations in the global climate. Longer-term measurements from different ice cores will help determine whether these really are periods of COS variations in the atmosphere that are climatically driven.

More recently, COS measurements were extended back to 8000 years before present (8 kyr BP) in the Antarctic ice cores from Byrd, Siple Dome, Taylor Dome and West Antarctic Ice Sheet (WAIS) (Aydin et al., 2014; Fig. 6). These measurements demonstrated decreases with depth at varying rates for each ice core and were attributed to temperature-dependent in situ loss of COS by hydrolysis. Corrections based on the (quite different) temperature histories of each core resulted in reconstructed COS records from each core that were broadly consistent (Figure 10 of Aydin et al., 2014). A minimum in COS levels in the mid-Holocene was followed by a steady rise to a pre-industrial level of about 350 ppt, similar to previous studies. The rise indicates a decline in terrestrial productivity during the late Holocene.

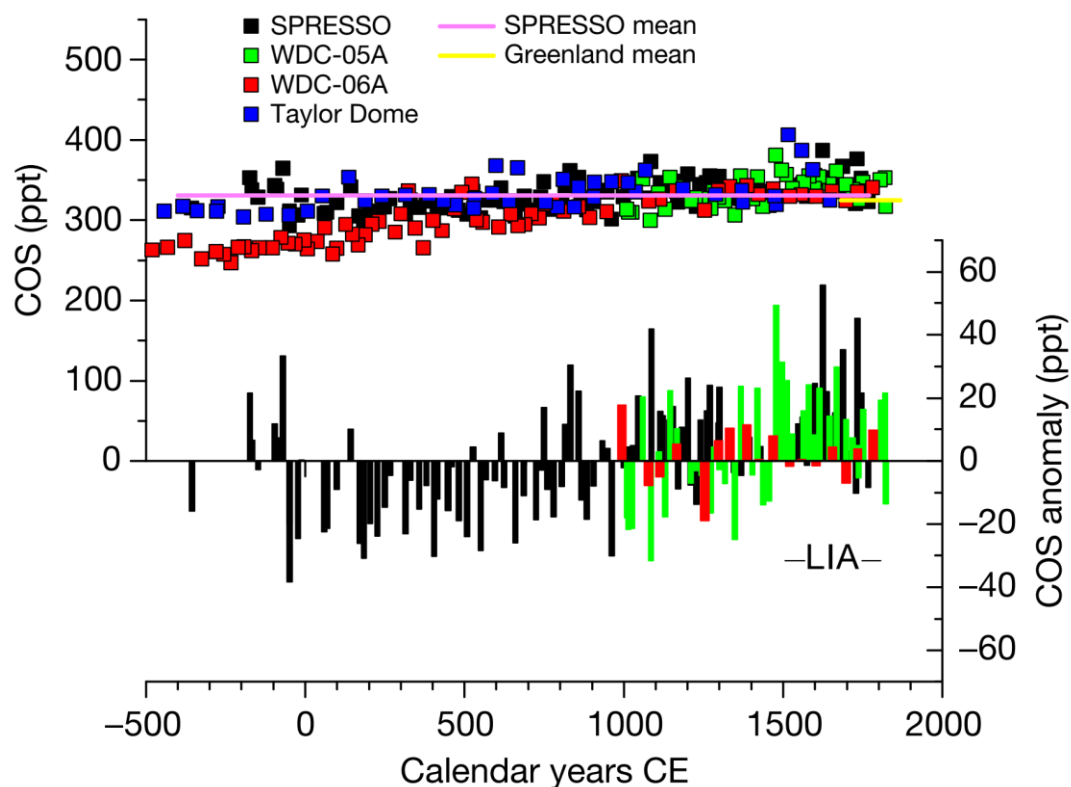


Figure 6. COS measurements in the SPRESSO ice core from South Pole (black squares), WDC-05A (green squares) and WDC-06A (red squares) ice cores from WAIS Divide, and Taylor Dome (blue squares) ice core. The mean of South Pole measurements (magenta line) is 331 ppt. The mean of the Greenland ice core measurements (yellow line) is 325 ppt. Greenland measurements are not shown for clarity. COS anomalies shown in the bottom panel are calculated as difference from the mean of the South Pole data for both the South Pole and WAIS Divide data sets. The anomalies are plotted using the same color code as the ice core data. Little Ice Age (LIA) is also shown. Reproduced from Aydin and Petrenko (2018).

COS measurements from the last glacial and through the deglaciation to the Holocene were made on the WAIS and Taylor Dome ice cores (Aydin et al., 2016). Corrections were made for hydrolysis in

bubble and clathrated (bubble-free) ice. COS varied from 200-300 ppt for much of the last glacial period, declined to below 200 ppt in the early Holocene and rose to 300 ppt in the late Holocene as found earlier. The glacial-Holocene decline was attributed to an increase in GPP as the biosphere regrew (causing greater loss of COS) and a possible decrease in oceanic COS emissions. Recently, a COS record spanning the 52.5 kyr before present was recovered at high resolution from a South Pole (SP14) ice core using both dry and wet extraction methods (Aydin et al., 2023). Interpretation of the SP14 COS record, and its comparison with the WAIS and Taylor Dome records, is complex. While the cold mean annual surface temperatures at the South Pole (-50°C) might mean that SP14 COS measurements do not require a correction for loss to hydrolysis, the SP14 COS glacial record is impacted by impurity-related COS production in the ice sheet. On-going investigations may assess how to correct for such COS in situ production, and if similar processes affect other glacial COS records (Aydin et al., 2023).

Studies involving COS measurements have been applied to understanding two important features of the carbon cycle over recent centuries. The first (Rubino et al., 2016) modelled the measured COS increase in ice cores from South Pole and Siple Dome during the Little Ice Age (1500-1750 AD) to find the cause of a concurrent CO₂ decrease and d¹³CO₂ increase measured in Law Dome ice (Etheridge et al., 1996; Rubino et al., 2019). The decrease in COS was explained by lower temperatures causing GPP to decrease but terrestrial autotrophic respiration to decrease even more (due to its larger temperature sensitivity) with a net draw-down of atmospheric CO₂, further characterised by the d¹³CO₂ signal as terrestrial biospheric in origin. This provided observational confirmation of the positive terrestrial carbon-climate feedback implied by global models (Arora et al., 2020). It also provides an alternative explanation of the CO₂ decrease at 1610 AD being caused by regrowth of agricultural lands and marking the start of the Anthropocene (Koch et al., 2019; Lewis and Maslin, 2015). Second, the changes in COS compiled from measurements of the Siple Dome ice core, South Pole firn air and South Pole atmosphere were used to infer its main sources and sinks since 1900 AD (Campbell et al., 2017). Of interest is the response of the carbon cycle to increased atmospheric CO₂ concentrations, changing climate, nutrients and land use. After allowing for the role of the growth in industrial sources on the observed 30% increase in COS concentrations since pre-industrial levels, the uptake of COS by plants was found to have increased with an estimated increase in GPP of 31% (+/- 5%) at the global scale during the 20th century.

These long term records of COS, in particular those just before and during the industrial period and the substantial perturbation on the carbon cycle and climate, provide important observational constraints for carbon cycle models that simulate future terrestrial carbon fluxes and atmospheric CO₂ concentrations.

6. Methyl Chloride

Methyl chloride (CH₃Cl) is the most abundant naturally occurring halocarbon with a mean tropospheric mixing ratio of 550+/-30 ppt. It is the largest source of chlorine in the stratosphere, thus considered an important ozone-depleting gas (Montzka et al., 2003b). Emissions from tropical vegetation and biomass burning are considered to be the two most important sources of CH₃Cl. Direct emissions linked to industrial activities are deemed insignificant and oceanic emissions are large but balanced with oceanic uptake that is almost equally large, resulting in a relatively small net source. Oxidation with OH is the most important loss pathway for CH₃Cl, with additional removal by oceanic uptake and

degradation in soils, resulting in a tropospheric lifetime of just over 1 year (Hamilton et al., 2003; Khalil and Rasmussen, 1999; Tokarczyk et al., 2003; Yokouchi et al., 2002).

There have been several CH₃Cl firn air studies at various sites in Antarctica (Aydin et al., 2004; Butler et al., 1999; Kaspers et al., 2004; Trudinger et al., 2004). The firn air records consistently displayed evidence that atmospheric CH₃Cl levels rose about 40–50 ppt during the twentieth century, despite relatively small discrepancies regarding the mean levels measured at different Antarctic sites (Trudinger et al., 2004). First measurements in a shallow ice core from Siple Dome, Antarctica, showed that mean CH₃Cl levels were 500 ppt between CE 1700 and 1900, in agreement with the inferred CH₃Cl abundance in the preindustrial atmosphere based on the firn air measurements (Aydin et al., 2004). A longer CH₃Cl record was obtained from a South Pole ice core (Williams et al., 2007). These measurements provide a continuous CH₃Cl record for the last 2000 years when combined with the earlier Siple Dome observations, and a more recent Holocene dataset collected along the Taylor Dome ice core (Fig. 7; Verhulst et al., 2013). There is consistency between the three data sets. The average CH₃Cl mixing ratio in the South Pole ice core is 460 ppt, or 70–80 ppt lower than the annual mean levels observed in Antarctica today. The South Pole data reveal centennial scale variability that appears to be correlated with climatic shifts during the last millennia, suggesting a warming global climate may lead to increased CH₃Cl levels in the atmosphere (Williams et al., 2007). The South Pole ice core data also exhibit a positive trend of 3 ppt per 100 years over the last 2000 yrs (Williams et al., 2007). The Taylor Dome CH₃Cl record reveals that such a trend extends to the mid-Holocene (Fig. 7; Verhulst et al., 2013).

The CH₃Cl atmospheric record was extended to the entire Holocene by the measurements of three deep ice cores from Siple Dome, West Antarctica (Saltzman et al., 2009), Dome Fuji, East Antarctica (Saito et al., 2007), and Taylor Dome, East Antarctica (Verhulst et al., 2013). The latest record drastically improved in resolution, and reveals a CH₃Cl variability throughout the Holocene similar to that of atmospheric CH₄, with higher levels in the early and late Holocene, and a well-defined minimum during mid-Holocene at about 450 ppt (Fig. 7). The Taylor Dome data suggest that natural CH₃Cl variability was on the order of 15–20% during the preindustrial Holocene. This is small compared to the fourfold increase in equivalent effective stratospheric chlorine that occurred during the twentieth century due to the anthropogenic emissions of CFCs and other chlorinated compounds (Montzka and Reimann, 2010). The Taylor Dome CH₃Cl Holocene record is not affected by in situ production, as observed for the Siple Dome record (Saltzman et al., 2009) or for a short preindustrial record measured in two shallow Greenland ice cores which indicated in situ production of CH₃Cl that likely occurred in the firn (Aydin et al., 2007). While Greenland ice cores contain high levels of impurities, Siple Dome is a warmer site compared to Taylor Dome. The potential impacts of site temperature and ice impurity levels on CH₃Cl production in the firn still need to be examined with additional firn air and ice core measurements.

Over the last glacial, The Dome Fuji CH₃Cl dataset exhibits a large enhancement compared to Siple Dome and Taylor Dome records. It has been shown that the excess CH₃Cl in the entrapped bubbles is correlated with elevated dust levels in the enclosing ice from the last glacial period at the Dome Fuji site (Saito et al., 2007). It cannot be ruled out that the existing Taylor Dome and Siple Dome measurements from the last glacial period also include a small positive bias due to dust related in situ production of CH₃Cl since the entire Antarctic continent experienced enhanced dust deposition during the last glacial period (Lambert et al., 2008). There is intriguing evidence in the glacial Taylor Dome data that CH₃Cl and CH₄ may be correlated during interstadial events (Verhulst et al., 2013). The sources and sinks of atmospheric CH₃Cl and CH₄ are located primarily in the tropics, and covariations

in their atmospheric levels likely reflect changes in tropical conditions. However, measurements from Taylor Dome show that the mean CH_3Cl level did not change between the last glacial (50–30 kyr B.P.) and interglacial (11–0 kyr B.P.) periods, a pattern different from atmospheric CH_4 mixing ratio (e.g., Rhodes et al., 2015). This supports the hypothesis that CH_4 rise during the last glacial-interglacial transition also relates to boreal wetland emissions. However, further interpretations of the CH_3Cl ice core glacial record would require a better understanding of the impacts of ice core dust on CH_3Cl levels: further research with higher resolution CH_3Cl data from multiple sites during periods of high and variable dust flux are needed.

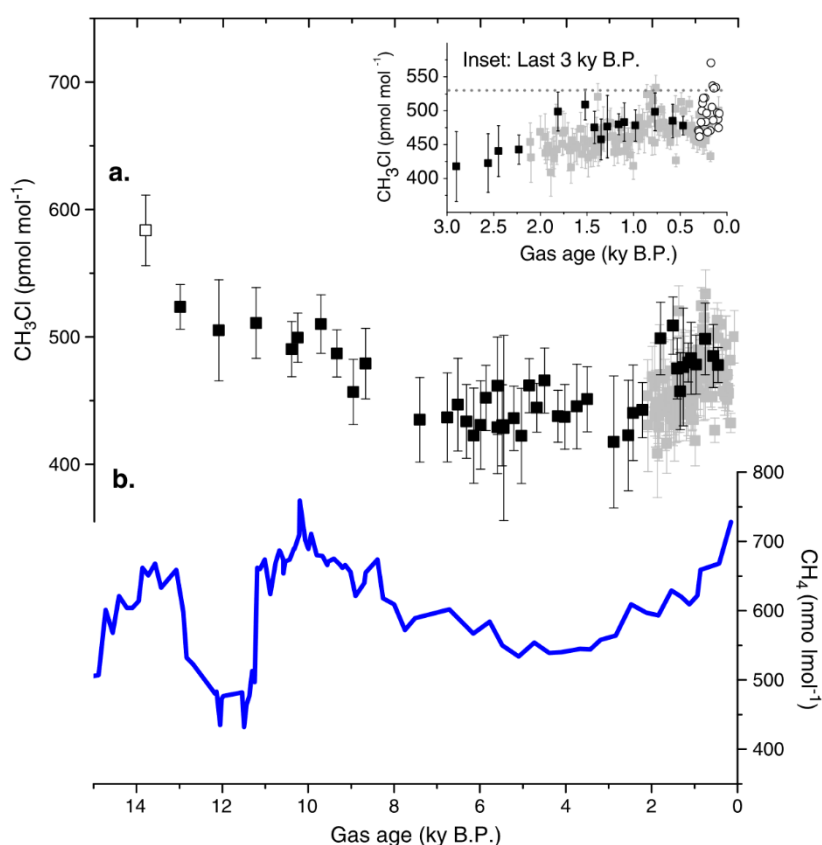


Figure 7. (a) Atmospheric history of CH_3Cl during the Holocene from the Taylor Dome (black squares, Verhulst et al., 2013) and South Pole ice cores (gray squares : Williams et al., 2007). All data are plotted with $\pm 1\sigma$ errors. The open square at 13.8 kyr B.P. is a Taylor Dome sample with high calcium content. (inset) Comparison of Taylor Dome CH_3Cl measurements covering the last 3000 years (black squares, this study) with prior shallow ice core measurements from South Pole (filled grey squares) and Siple Dome (open circles) (Aydin et al., 2004; Williams et al., 2007). Dashed line represents the modern-day mean level over Antarctica (530 ppt; Aydin et al., 2004). pmol mol⁻¹ and ppt are equivalent units. (b) Atmospheric history of CH_4 from Taylor Dome (Brook et al., 2000). nmol mol⁻¹ and ppb are equivalent units. Reproduced from Verhulst et al. (2013).

7. Methyl Bromide

Methyl bromide (CH_3Br) is a stratospheric ozone-depleting substance with both natural and anthropogenic sources. It is produced naturally in oceanic and terrestrial biogeochemical systems, and during biomass burning. In addition, it has been industrially manufactured to be used as a fumigant in agriculture and other industries during the twentieth century (Clerbaux and Cunnold, 2006). It is taken up by oceans and soils, and oxidized in the atmosphere by OH, resulting in a mean atmospheric

lifetime of 0.7 years (Yvon-Lewis and Butler, 1997). Following the recognition of its prominent role in depletion of the stratospheric ozone layer, it was included in the Montreal Protocol and its amendments. Restrictions on CH₃Br use as a fumigant started in 1998. Consistent with the timing of the regulatory actions, the atmospheric abundance of CH₃Br peaked in 1998–1999 at 10–11 ppt in the northern hemisphere and 8–8.5 ppt in the south (Montzka et al., 2003a, 2003b). Since then, its atmospheric mixing ratio declined considerably, especially in the north where most of the anthropogenic emissions used to occur (Montzka et al., 2003a, 2003b; Yokouchi et al., 2002; Yvon-Lewis et al., 2009).

CH₃Br measurements in firn air at four different sites in Antarctica revealed that the atmospheric mixing ratio of this gas increased by about 3 ppt during the twentieth century, with 2 ppt of the increase occurring after the 1950s. In contrast, measurements in firn air from the Canadian Arctic and Greenland displayed increasing CH₃Br mixing ratios in deeper firn, suggesting in situ CH₃Br production close to the base of the firn (Butler et al., 1999; Sturges et al., 2001a). These results indicate that it could be possible to develop a southern hemisphere CH₃Br record with measurements in Antarctic ice cores, but it was unlikely that the same could be done in the northern hemisphere.

The first ice core CH₃Br measurements from a shallow core from Siple Dome, Antarctica, displayed first direct evidence that the CH₃Br abundance in the pre-twentieth century atmosphere was below 6 ppt (Saltzman et al., 2004). In contrast, CH₃Br mixing ratios from two Greenland shallow ice cores were higher than the peak northern hemisphere levels in all the samples, displaying high scatter with little or no consistency between neighboring data points (Aydin et al., 2007). These first sets of measurements suggest it is highly unlikely that a northern hemisphere CH₃Br record will be recovered using ice cores from Greenland and the Canadian Arctic

CH₃Br was analyzed in the same South Pole ice core that was used in COS and CH₃Cl measurements. The South Pole data provide a continuous CH₃Br atmospheric history for the last 2000 years when combined with the shorter Siple Dome record from Antarctica (Fig. 8). The mean CH₃Br mixing ratio in the South Pole ice core is 5.4 ± 0.6 ppt (1σ), with no discernable long-term trend but variations at 10–20% level are evident over centennial time scales (Saltzman et al., 2008). This centennial variability could be driven by changes in climate or may be related to artifactual CH₃Br enhancement due to unknown factors. The lack of a long-term trend in the 2000 year-long record is strong evidence against a time-dependent chemical loss or production within the ice cores. The stability of the CH₃Br mixing ratios over the measurement periods provides a strong constraint on how low we can expect atmospheric CH₃Br levels to drop as a result of the measures taken under the Montreal Protocol. Longer records from Antarctic ice core records are needed to investigate the impacts of significant changes in global climate on the atmospheric CH₃Br levels and the state of the stratospheric ozone layer.

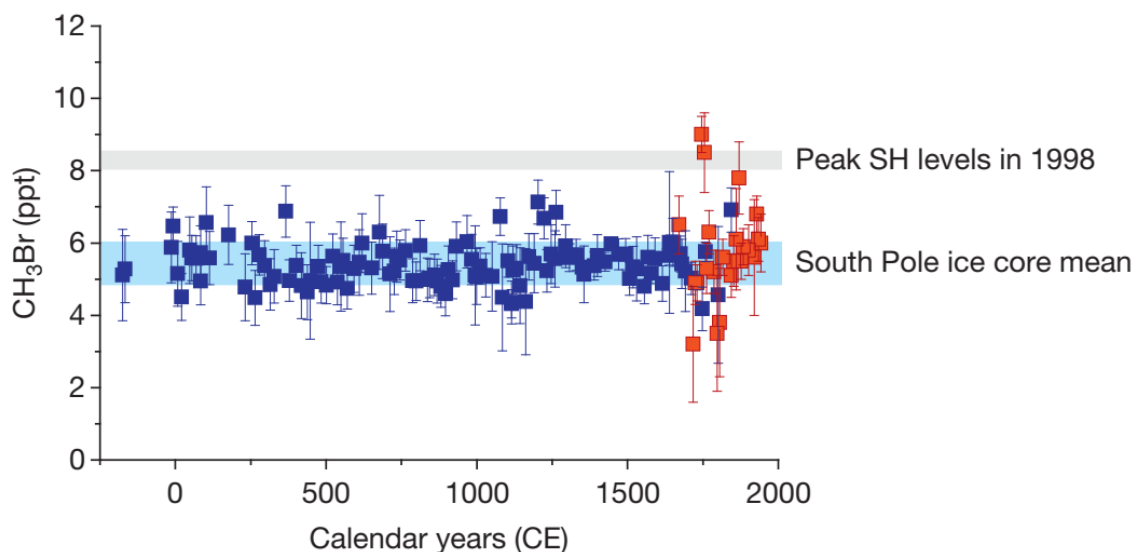


Figure 8. CH₃Br measurements in polar ice cores. The Siple Dome (red squares) and the South Pole (blue squares) data are consistent during the period of overlap. The gray band represents the peak annual mean CH₃Br mixing ratios observed in the southern hemisphere during 1997–1999 (Montzka et al., 2007). The blue band represents the mean CH₃Br mixing ratio in the South Pole ice core. The thicknesses of the gray and blue bands represent the estimated uncertainty in the reported means.

The global budget of methyl bromide has never been fully understood as evidenced by the significant budget gap between the bottom-up source estimates and calculated atmospheric losses (Saltzman et al., 2022). The methyl bromide levels in preindustrial Antarctic ice cores show a similar budget gap, assuming that the natural components of the preindustrial budget (sources and sinks) were similar to the present day (Saltzman et al., 2004).

8. Ice Core Air Extraction Methods

COS, CH₃Cl, and CH₃Br measurements are conducted using a ‘dry’ extraction method, in which the entrapped air is liberated in a cold vacuum chamber without melting the ice core samples (Aydin et al., 2007). After cleaning the outer surfaces, ice core samples (400–500 g) are placed on a sharp cutting surface welded inside a stainless-steel vacuum chamber. Once the chamber is isolated and pumped out, it is put into linear motion device that results in the sample sliding back and forth over the cutting surface. In 15 min, most of the ice core sample is shredded and the liberated air is collected in the vacuum chamber. This method results in 70% recovery of the air trapped in the ice core.

A ‘wet’ extraction technique was used for the pioneering CO measurements (Haan et al., 1996; Haan and Raynaud, 1998). Ethane and acetylene measurements are also conducted with a ‘wet’ extraction method (Nicewonger et al., 2020a, 2016). Prior to the extraction, the outer surface of an ice core sample (1–2 mm) is shaved off for eliminating potential contaminants on the surface. The sample is then placed under vacuum in a glass extraction vessel. During the first stage of the extraction, the ice core sample is melted by immersing the glass vessel in a hot water bath. While the sample melts, the air trapped inside the sample collects in the headspace inside the glass vessel. Once melting is complete, the hot bath is replaced with a cold one. The extracted air is cryogenically transferred into a stainless steel sample tube immersed in liquid helium (269°C). Elevated ethane levels were detected in dust-rich ice core sections measured discreetly with a ‘wet’ extraction method, pointing to a process sensitive to the melt extraction technique (Mühl et al., 2023). However, the ethane data described in

this chapter are not impacted by this ‘in-extractu’ artifact, considering the low dust content in Holocene ice. More recently, wet extraction was also developed for COS analyses (Aydin et al., 2023). Continuous flow analysis (CFA) of CO is now routinely applied to CO analyses along ice cores. Briefly, ice core sticks are cut at a 34 mm × 34 mm cross section and processed on a melter head located in a cold room. The melter head is composed of inner and outer collection areas, with the inner area dedicated to sample collection. The water and gas bubble mixture is continuously pumped and the gas is extracted along the sample line after the debubbler by applying a pressure gradient across a gas permeable membrane. Then, the gas is dried by a Nafion (Perma Pure) dryer. Finally, CO mixing ratios are continuously measured by a laser spectrometer. CFA CO analyses have greatly improved over the past decade, including lowering the CO blank and characterizing how CO is preferentially dissolved during the CFA process so as to establish an absolute calibration (Faïn et al., 2022). The excellent precision of CO analyses has been confirmed, and the designs of CFA setups themselves have been optimized to limit the instrumental smoothing and improve signal resolution. Regardless of the extraction technique that has been used, very small amounts of air are available for measurements, requiring highly sensitive analytical instrumentation. The COS, Ethane, acetylene, CH₃Cl, and CH₃Br have been measured in a gas chromatogram-mass spectrometer (GC–MS) system that makes use of high-resolution mass spectrometry for improved sensitivity, which enables ppt level measurements in ice core air samples that often do not exceed 20–30 ml STP (standard temperature and pressure) in size (Aydin et al., 2007). The CO measurements are presently carried out with SARA OF-CEAS (optical feedback enhanced spectrometer) spectrometers (e.g., Faïn et al., 2023).

9. Conclusion and outlook

The potential of the ice cores in preserving a true archive of past atmospheric ultra-trace gas variations remains unexplored. In addition to the compounds covered in this article, a range of nonmethane hydrocarbons (Helmig et al., 2014) have been measured in ice core air. In the coming years, it is likely that more will be learnt about the past Earth climate and climate drivers from ultra-trace measurements from ice archives. Promising avenues include new CO datasets from high-accumulation ice cores to characterize decadal variations in atmospheric CO and constrain further CO evolution of emissions and sinks during the industrial period, new isotopic CO dataset to characterize the past evolution of the CO budget, or the use of innovative proxies such as ¹⁴CO to better assess the past OH trends. Also, extending ice core records of paleofire proxies such as ethane, acetylene, or CO to glacial periods, and glacial/interglacial transitions, would be warranted. As an example, assessing the evolution of atmospheric [CO] during the last Termination would provide new insights on the evolution of the oxidative capacity during a glacial - interglacial transition, and thus help to constrain the evolution of major greenhouse gases such as methane during such transitions.

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