Towards reconstructing the Arctic atmospheric methane history over the 20th century: measurement and modeling results for the NGRIP firn

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Abstract. Systematic measurements of atmospheric methane (CH₄) mole fractions at the northern high latitudes only began in the early 1980s, and whilst CH₄ measurements from Greenland ice cores covered the period before ~1900, no reliable observational record is available for the intermediate period. In this study, we reconstruct the atmospheric CH₄ for that period, when the mole fraction started to increase rapidly. We use a set of trace gas data measured from firn (an intermediate stage between snow and glacial ice formation) air samples collected at the NGRIP (North Greenland Ice Core Project) site in 2001, in combination with a firn air transport model whose performance is validated by using a set of published firn air data at the NEEM (North Greenland Eemian ice Drilling) site. We examine a variety of possible firn diffusivity profiles using a suite of measured trace gases, and reconstruct the CH₄ mole fraction by an iterative dating method. We find that, given the currently available firn air data sets from Greenland, reliable reconstruction of the Arctic CH₄ mole fraction is possible only back to the mid 1970s. For the earlier period, it is difficult to identify the atmospheric CH₄ history that consistently reproduce the depth profiles of CH₄ in firn at both NGRIP and NEEM sites. Therefore, the currently proposed Arctic CH₄ history should still be considered preliminary and uncertain, and should not be treated as the known history for constraining firn-air transport models.

1 Introduction

Methane (CH₄) is an important atmospheric greenhouse gas emitted from both natural and anthropogenic sources. Despite great efforts for understanding its global budget, emission estimates of individual sources still have large quantitative uncertainties (e.g. Saunois et al., 2020; Chandra et al., 2021). Anthropogenic activities have enhanced CH₄ emissions globally and this resulted in the more than doubled abundance of atmospheric CH₄ over the industrial era (e.g. Etheridge et al., 1998). The CH₄ emission histories have been estimated based on human activity statistics combined with emission factors (Stern and
Kaufmann 1996; van Aardenne et al., 2001). Such historical emission inventories have been examined by atmospheric chemistry transport modeling (Houweling et al., 2000; Monteil et al., 2011; Ghosh et al., 2015), in combination with the records of atmospheric CH$_4$ mole fraction reconstructed from polar ice cores (Blunier et al., 1993; Nakazawa et al., 1993; Etheridge et al., 1998; MacFarling Meure et al., 2006; Sapart et al., 2012) and air extracted from porous snow layers at the top of ice sheets (firm) (Francey et al., 1999; Buizert et al., 2012; Sapart et al., 2013).

A large fraction of natural and anthropogenic CH$_4$ sources resides in the northern hemisphere, and thus the atmospheric CH$_4$ trend of the northern hemisphere can provide important information on the evolution of anthropogenic CH$_4$ emissions as well as the variations of natural CH$_4$ emission in response to climatic variability. The interhemispheric gradient of CH$_4$ mole fraction is also key to the allocation of CH$_4$ emissions between both hemispheres (e.g. Dlugokencky et al., 2003; Chandra et al., 2021).

![Figure 1: Atmospheric CH$_4$ mole fraction data covering the last 200 years. Symbols in grey are from the southern hemisphere; crosses and open circles are from the Law Dome ice core and firm, respectively (Etheridge et al., 1998; MacFarling Meure et al., 2006); open squares are from Cape Grim (CGO) (MacFarling Meure et al., 2006); dots are from South Pole (SPO) (ftp://aftp.cmdl.noaa.gov/). Colored data from the northern hemisphere; open squares, triangles and diamonds are from the Eurocore (Blunier et al., 1993), Eurocore and GISP2 (Etheridge et al., 1998) and Site J (Nakazawa et al., 1993) ice cores; red dots are the NEEM-S1 ice core (Rhodes et al., 2013); orange dots are from Alert, Canada (ALT) and Barrow, Alaska (BRW) (ftp://aftp.cmdl.noaa.gov/); light blue line is the atmospheric scenario prepared for the NEEM firn modeling (Buizert et al., 2012).](image-url)
Systematic measurements of atmospheric CH$_4$ mole fraction began in the 1980s. In Figure 1, CH$_4$ measurements at two Arctic sites Barrow, Alaska (BRW) and Alert, Canada (ALT) are shown (orange dots), whose records start in 1983 and 1985, respectively (data provided by National Oceanic and Atmospheric Administration/Earth System Research Laboratory/Global Monitoring Laboratory, NOAA/ESRL/GML). Although some sparse data from the 1970s are available (e.g. Rice et al., 2016), such “direct” measurements provide CH$_4$ data only since around 1980, which means that some reconstruction methodology is required to infer atmospheric CH$_4$ mole fraction variations before that. For this purpose, air extracted from ice cores and firn layers has been measured. Figure 1 also presents CH$_4$ mole fractions analyzed in ice cores from Greenland (open blue symbols), such as Eurocore (Blunier et al., 1993), Eurocore and GISP2 (Greenland Ice Sheet Project 2) (Etheridge et al., 1998) and Site J (Nakazawa et al., 1993). These data show fairly good agreements with each other until ~1900, after which the number of data and the consistency among the records are poor. Continuous measurements from NEEM-S1 ice core (Rhodes et al., 2013) presented CH$_4$ mole fractions before ~1960 (red in Figure 1), but their data are notably higher than the ice core data after ~1850. Therefore, the data gap between ~1900 and ~1980 is not covered reliably either by direct observations or ice core reconstructions.

In comparison to these data, higher-resolution CH$_4$ data are available from Antarctica (grey in Figure 1). The comprehensive Law Dome ice core and firn data set (Etheridge et al., 1998; MacFarling Meure et al., 2006) almost continuously covers the last 200 years and are well connected to the direct measurements at South Pole (SPO, data provided by NOAA/ESRL/GML) and Cape Grim (CGO) (Etheridge et al., 1998; MacFarling Meure et al., 2006). Such consistency and continuity among the datasets suggests that the Antarctic CH$_4$ data can serve as a good reference to represent the global atmospheric CH$_4$ trend over the past centuries. Buizert et al., (2012) used the Antarctic CH$_4$ trend with presumed interpolar difference (IPD) to propose the CH$_4$ history over Greenland (light blue in Figure 1), which in turn was used to constrain the gas diffusivity profile in firn at the North Greenland Eemian ice Drilling (NEEM) site. In their study, the Arctic CH$_4$ scenario was constructed by adding IPD to the Law Dome data, where the IPD was assumed to be proportionally correlated with the growth rate of CH$_4$. This seems reasonable assumption, given that the IPD and growth rate are both largely subject to changes in emissions from the northern hemisphere (Dlugokencky et al., 2003; Chandra et al., 2021). The Arctic CH$_4$ scenario by Buizert et al. (2012) is consistent with the direct measurements that started in the 1980s, and ice core reconstructions before ~1900 (Figure 1). It is thus considered as the most likely synthetic atmospheric CH$_4$ trend for the northern high latitudes, and is treated as a “known” history, by which the diffusivity profiles in firn are tuned in firn-air transport models (Witrant et al., 2012; Trudinger et al., 2013). It is however noted that this scenario has not been validated against independent estimates for the data gap period (from ~1900 to ~1980).

In this study, we present a set of mole fractions of CH$_4$ and other trace gases in firn air samples collected at the North Greenland Ice Core Project (NGRIP) site. Using the atmospheric scenarios by Buizert et al. (2012), we simulate the depth profiles of trace gases in the NGRIP firn with our firn-air transport model. We examine a variety of modeling cases for different diffusivity profiles and reconstruct the Arctic atmospheric CH$_4$ over the late 20th century using the iterative dating approach (Trudinger
et al., 2002). The reconstructed CH$_4$ trend is evaluated by comparison to the original atmospheric CH$_4$ scenario and to the NEEM firn air data. Uncertainty of the Arctic atmospheric CH$_4$ history for use in firn air modeling is discussed.

2 Experimental method

Firn air was sampled at the Greenland site NGRIP (75°10′N, 42°32′W, 2959 m AMSL) in May–June 2001. Accumulation, surface density, mean temperature and pressure are 179 kg m$^{-2}$ yr$^{-1}$, 300 kg m$^{-3}$, 241 K and 680 hPa, respectively. Details of the firn and firn-air sampling have been described elsewhere (Kawamura et al., 2006; Ishijima et al., 2007). At the NGRIP site, two shallow holes (EU and Japanese holes) were drilled (Kawamura et al., 2006; Landais et al., 2006), and the present data are from the firn air samples collected from the Japanese hole. The total number of air-sampling depths is 24. Since the technical details are reported in Kawamura et al. (2021), only brief descriptions of relevant data presented in this study are given here. CH$_4$ mole fractions of the firn air samples were measured using a gas chromatograph (Agilent 6890, Agilent Technologies Inc.) equipped with a flame ionization detector (GC-FID) at Tohoku University (TU), with a reproducibility of 2 ppb (Umezawa et al., 2014). The CH$_4$ mole fractions were determined against our working standard gases that were calibrated on the TU1987 CH$_4$ scale (Aoki et al., 1992; Umezawa et al., 2014; Fujita et al., 2018). The difference between the TU1987 CH$_4$ scale and the WMO CH$_4$ mole fraction scale (on which the NEEM CH$_4$ data were measured) is estimated to be ~0.5 ppb at the current atmospheric CH$_4$ levels (Fujita et al., 2018). Oyabu et al. (2020) reported that ice core data analyzed on the TU1987 and WMO scales showed good agreement within analytical uncertainties, indicating consistency of both scales, including for the lower mole fractions (e.g. ~700 ppb). It is therefore likely that the difference between both scales is well below the variations of interest in this study, and thus no correction is applied for use of the NGRIP and NEEM firn data.

The firn air samples were measured for CO$_2$ and SF$_6$ mole fractions respectively by using a nondispersive infrared gas analyzer (NDIR) and a gas chromatograph equipped with an electron capture detector (GC-ECD) at TU. The measurement reproducibility is estimated to be 0.02 ppm for CO$_2$ and 0.09 ppt for SF$_6$ and mole fractions of both gases are reported on the TU2010 CO$_2$ and TU2002 SF$_6$ scales, respectively (Sugawara et al., 2018).

The NGRIP firn air samples were also analyzed for selected halocarbons (CFC-11, CFC-12, CFC-113 and CH$_3$CCl$_3$) on the Vacuum Preconcentration and Refocusing-Gas Chromatography-Mass Spectrometry (VPR-GCMS) system, which was developed based on the work by Saito et al. (2006). An aliquot of the sample was transferred into an evacuated canister of ~0.3 L at around ambient pressure (~100 kPa) and the inner pressure of the canister was recorded. The air is extracted by a vacuum pump through a preconcentration trap filled with HayeSep D cooled to −135°C using a Stirling cooler. The preconcentration trap was heated to −70°C to release major atmospheric constituents and then up to 100°C to transfer the trapped compounds to a cryofocusing trap containing Carboxene 1000/Tenax TA at −100°C. The trap was then heated to 180°C to inject the trapped gases onto a PoraBOND Q separation column for subsequent analysis on MS. Mole fractions of individual halocarbons
are determined against a working standard gas (compressed dry air) that was calibrated against synthetic standards on the NIES-08 scales.

3 Firn air transport model

Since the gas diffusivity in firn layers is significantly lower than in the atmosphere, the movements of atmospheric constituents are driven mostly by molecular diffusion according to their vertical mole fraction gradients under the influence of gravity. In general, lighter air components (or isotopologues) diffuse faster under their mole fraction gradients, while heavier components accumulate in the deeper layers due to the gravitational effect. Hence the depth profiles of trace gas mole fractions in firn are determined by the atmospheric histories transferred towards depth in the firn by the molecular diffusion driven by the mole fraction gradient and gravity. At the bottom of firn, the air is trapped as bubbles in the ice sheet, which creates slow downward motion of firn air.

The firn column can be divided into three zones: a convective zone (CZ), a diffusive zone (DZ) and a lock-in zone (LIZ) (Sowers et al., 1992; Kawamura et al., 2006; Buizert et al., 2012). In CZ, primarily driven by surface winds and fluctuations of atmospheric pressure, air is mixed with the overlying atmosphere (Sowers et al., 1992; Kawamura et al., 2006). The CZ thickness at NGRIP is estimated to be below 2 m (Kawamura et al., 2006). In DZ, which is sufficiently isolated from the surface turbulence, movement of air is governed by molecular diffusion. Gravitational enrichment according to the barometric equation (i.e. linear increases of $\delta^{15}$N of N$_2$ and $\delta^{18}$O of O$_2$) occurs with depth, which stops at the top of LIZ (Sowers et al., 1992; Schwander et al., 1993; Kawamura et al., 2006). The top of LIZ (lock-in depth) at NGRIP is at depth 63 m (Kawamura et al., 2006). In LIZ, advection with the enclosing ice matrix dominates the transport of air, and air parcels are gradually isolated as bubbles. Traditionally, it was supposed that high-density impermeable ice layers stop diffusivity in LIZ completely, however, recent studies demonstrated finite diffusivity in LIZ (Severinghaus et al., 2010; Buizert et al., 2012; Trudinger et al., 2013). The deepest air sampling at NGRIP was successfully made at 77.71 m, and total pore closure is considered in the deeper layers in our modeling.

3.1 Modeling firn air transport

We use a one-dimensional diffusion model that has been used for the reconstruction of isotope ratios of CO$_2$ and N$_2$O (Sugawara et al., 2003; Ishijima et al., 2007). The model is conceptually similar to that developed by Trudinger et al. (1997); it is based on a theoretical formation of diffusion (Schwander et al., 1993) and a bubble trapping process (Rommelaere et al., 1997). Air movement in the firn is driven by molecular diffusion and a gravitational effect. Namely, a trace gas flux in firn is expressed by

$$ F = -D \left\{ \frac{s}{N_x} \left( \frac{\partial}{\partial x} \frac{c}{s} \right) - \frac{mge}{RT} \right\}, $$

(1)
where $D$ is the effective diffusivity of a trace gas molecule, the variables $s$, $c$, and $T$ are open porosity, trace gas molar concentration, and firn temperature, respectively, and the constants $m$, $g$, and $R$ are the mass number of the trace gas, the acceleration of gravity, and the gas constant, respectively. Vertical advection flux of the trace gas, caused by air trapping at the close-off zone and downward bulk motion of firn, is expressed by using the equation given by Rommelaere et al. (1997).

Conservation of the trace gas is given by

$$\frac{\partial c}{\partial t} + \frac{\partial (vc)}{\partial x} + \frac{\partial F}{\partial x} + rc = 0,$$

for the open pore space and

$$\frac{\partial c_b}{\partial t} + \frac{\partial (v_f c_b)}{\partial x} - rc = 0,$$

for bubbles. Here $c$ and $c_b$ are trace gas molar concentrations in the open pore space and bubbles, respectively. Vertical speed of air in the open pore space $v$ is distinguished from that of firn itself $v_f$. The vertical speed of firn $v_f(z)$ is simply given by dividing the accumulation rate by the firn density under the assumption of the steady-state densification of firn. At the transition zone where the open pore air is gradually trapped into bubbles, mass conservation is given by using a bubble trapping rate $r$ (s$^{-1}$), which simply means that a portion of the trace gas molar concentration in the open pore space ($rc$) is added to bubbles. The bubble trapping rate is given as a function of the open porosity, the total porosity, and the vertical speed of firn itself (Rommelaere et al., 1997). The total porosity was calculated from the firn density data. At the transition zone, the total porosity should be divided into the open and closed porosity. The closed porosity $s_c$ was calculated by the empirical equation given by Schawander (1989).

### 3.2 Effective diffusivity

We follow the previous firn-air studies in which the effective diffusivity in firn is optimized with an iterative method so as to minimize the difference between the simulated and observed depth profiles of CO$_2$ (Sugawara et al., 2003; Ishijima et al., 2007). An initial guess of the effective diffusivity for CO$_2$, $D_{init}(z)$, was calculated by:

$$D_{init}(z) = D_0 \left( \frac{T}{253} \right)^{1.85} \left( \frac{1013}{p} \right) [1.7 s(z) - 0.2],$$

where $s(z)$ and $D_0$ represent the open porosity at a depth $z$ and the diffusion coefficient of CO$_2$ at 253 K and 1013 hPa, respectively. $D_0$ was set to $1.247 \times 10^{-5}$ (m$^2$ s$^{-1}$) according to Trudinger et al. (1997). The bulk density was determined by measuring the dimension and weight of cylindrically cut firn core samples (Kawamura et al., 2006). The effective diffusivity of CO$_2$ thus obtained was converted to those of other trace gases by multiplying by scaling factors from Buizert et al. (2012). Therefore, the depth profile pattern of the effective diffusivity is identical among all gases, but the magnitude is gas-dependent due to the scaling factors. In this study, the effective diffusivity profile prepared for the NGRIP firn by Ishijima et al. (2007) is modified to improve the reproducibility of our newly measured trace gas profiles (section 4).
3.3 Performance of the firn air transport model

To validate our firn air transport model, we simulated depth profiles of various trace gases in the NEEM firn. Our model did not participate in the model intercomparison study using the NEEM data (Buizert et al., 2012). In this simulation, we employed the atmospheric scenarios prepared by Buizert et al. (2012) as per their model intercomparison. The diffusivity profile optimized for the CIC (Center for Ice and Climate, Niels Bohr Institute, University of Copenhagen) model was tuned for our model. The simulated depth profiles of various compounds are presented in Figure 2 and compared with those by other models presented in Buizert et al. (2012). The results confirm that performance of our model is comparable to those by other groups. As a measure of the model performance, Buizert et al. (2012) compared root mean square deviation (RMSD) between the model and data, which ranged from 0.73 to 0.92 for the six participating models. Following the same approach, our model yields the RMSD value of 0.83 of for the NEEM EU borehole.
Figure 2: Modeled depth profiles of various compounds in the NEEM firn. Open circles in black are the observed data with uncertainty estimated by Buizert et al. (2012). Our model results are shown in black solid lines and results from other models are in colors. Different models are labeled by institutions according to Buizert et al. (2012): CIC (Centre for Ice and Climate), CSIRO (Commonwealth Scientific and Industrial Research Organization), INSTAAR (Institute of Arctic and Alpine Research), LGGE (Laboratoire de Glaciologie et Géophysique de l'Environnement), OSU (Oregon State University) and SIO (Scripps Institution of Oceanography).
3.4 Modeling procedure

Our modeling procedure for reconstructing the atmospheric histories of trace gases was as follows:

(1) To represent atmospheric trace gas trends in the Arctic region, we began by employing atmospheric scenarios prepared for the NEEM firn air modeling (Buizert et al., 2012) for all the trace gases presented in this study (CH₄, CO₂, SF₆, CFC-11, CFC-12, CFC-113 and CH₃CCl₃). The firn transport model calculates depth profiles of these trace gases in the NGRIP firn with the initial effective diffusivity described in section 3.2.

(2) We examined the different sets of diffusivity profiles so as to improve overall reproducibility of the modeled profiles of the six trace gases except CH₄. In other words, we regarded these six trace gases as constraints to the diffusivity profile. Note that this step assumes that the atmospheric histories of the six gases are known with sufficient accuracy to infer a range of acceptable diffusivity profiles that reproduce the depth profiles of the firn air composition. We prepared 100 different sets of modified diffusivity profiles, and the overall model-data agreement for each set was evaluated based on the RMSD of the six gases.

(3) We ran the model with the 100 different sets of diffusivity profiles to calculate the depth profile of CH₄. Note that, based on the earlier steps, we know the diffusivity profiles that generate reasonable firn-air profiles for the six trace gases. Every diffusivity profile was used in combination with the firn-air CH₄ data for reconstructing an atmospheric CH₄ history. We employed an iterative dating approach (Trudinger et al., 2002) where the initial atmospheric scenario was modified to improve model reproducibility of the CH₄ depth profile (see below). The corrected atmospheric CH₄ scenarios were then compared to the initial scenario for further discussion.

The iterative dating for CH₄ was performed as follows:

(1) Depth profile of CH₄ was calculated with the initial atmospheric CH₄ scenario.

(2) Effective age at each sampling depth was calculated so that the modeled CH₄ mole fraction, at that depth, agreed with a value in the atmospheric CH₄ scenario.

(3) A new atmospheric CH₄ scenario was constructed by assigning the observed CH₄ mole fraction, at each depth, to the effective age.

(4) Depth profile of CH₄ was again calculated with the revised atmospheric CH₄ scenario.

(5) The above steps 2–4 were repeated until the model-data difference converged within an acceptable range (typically after a few iterations) (Trudinger et al., 2002; Ishijima et al., 2007). In this study, we made five iterations for each modified diffusivity case as we confirmed sufficient convergence of the result.
220  **4 Result**

**4.1 Initial and modified diffusivity simulations**

Figure 3 presents the initial simulation results in comparison to the observed profiles for the six trace gases (CO$_2$, SF$_6$, CFC-11, CFC-12, CFC-113 and CH$_3$CCl$_3$). As seen in this figure, measured profiles of these trace gases (except CH$_3$CCl$_3$) show gradual decreases with depth in the DZ and sharp decreases in the LIZ. In contrast, CH$_3$CCl$_3$ increases with depth in the DZ and sharply decreases in the LIZ. The difference of the depth profile pattern among species is due to their different historical atmospheric trends. It is known that the atmospheric mole fractions of the five trace gases (CO$_2$, SF$_6$, CFC-11, CFC-12 and CFC-113) have increased monotonically since the mid 20th century (Sturrock et al., 2002; Martinerie et al., 2009). In contrast, CH$_3$CCl$_3$ has increased until the early 1990s and has decreased since then (Sturrock et al., 2002; Rigby et al., 2017). Our simulation reproduces the observed depth profiles of these six trace gases in the NGRIP firn fairly accurately with the atmospheric scenarios prepared for modeling the NEEM firn air (Buizert et al., 2012).
It is interesting to note that the depth profiles of CH₃CCl₃ at NGRIP and NEEM are remarkably different. Whereas the NEEM data show a relatively sharp CH₃CCl₃ peak in the LIZ (~65 m, Figure 2), NGRIP does not show such a narrow peak. This is due to the timing of firn air sampling i.e. 2001 for NGRIP and 2008 for NEEM. When the NGRIP firn air was sampled, the signal of the maximum atmospheric CH₃CCl₃ in the early 1990s had only reached near the top of the LIZ at the site, thereby formulating the relatively gentle changes at the shallower depths. On the other hand, seven years later at the NEEM site, such signal was found deeper in the LIZ where the age of air changes rapidly with depth in both deeper and shallower sides. We emphasize that, despite the differences in the depth profiles of CH₃CCl₃ at the two sites, our simulations reproduce both profiles measured at both sites well, using the same atmospheric CH₃CCl₃ scenario.
Figure 3 shows that the model-data difference increases in the LIZ for all the trace gases. In particular, the model-data difference is pronounced as a dip around 70 m for all trace gases, implying that the mismatches may originate in a common factor in the modeling e.g. depth profile of diffusivity. To examine the impact of diffusivity modification on the simulated depth profiles and their agreements with the data, we prepared 100 sets of modified diffusivity profiles (Figure 4). The various diffusivity profiles were constructed by modifying the original profile at certain range of depths in a stepwise manner. Although this simple method does not guarantee identification of a best-match profile, we are confident that an acceptable range of the diffusivity profile is satisfactorily constrained. To reduce the model-data difference in the LIZ (Figure 3), we found that the diffusivity needs to be increased in the shallower layers than the top LIZ i.e. 50–65 m. The diffusivity was also modified in the deeper layers (>65 m) and simulations were made accordingly.

The simulated profiles for depths deeper than 50 m using the 100 diffusivity profiles are presented for the six trace gases (Figure 5). In this figure, the modeling results with the modified diffusivity profiles are shown in colors on the left axis, and the model-data differences of the respective cases are plotted on the right axis. It is clear that the model-data differences could be significantly reduced with some diffusivity cases. We calculated RMSD in the same manner as Buizert et al. (2012) with the measurement uncertainties of 0.2 ppm for CO$_2$, 0.2 ppt for SF$_6$, 1.1 ppt for CFC-11, 3.3 ppt for CFC-12, 0.6 ppt for CFC-113 and 3.2 ppt for CH$_3$CCl$_3$. The RMSD values are as little as 0.51 for a particular case. In Figure 4 and following figures, the model results with a RMSD of <0.75 and <1.0 are colored red and orange, respectively, and other cases are colored light blue.
Figure 5: Depth profiles of the six trace gases below 50 m depth in the NGRIP firn. Black circles indicate the measurements and solid lines in colors are the model results with different diffusivity profiles (left axis). Black lines are modeled results with the initial diffusivity. Also shown are the model-data differences (right axis). See text for difference in line colors.

Likewise, depth profiles of CH₄ are shown in Figure 6. These calculations were made with the 100 diffusivity profiles and the atmospheric CH₄ scenario for the NEEM firm-air modeling (Buizert et al., 2012). It is interesting to note that the characteristics of the model-data difference for CH₄ are different from those for the other six trace gases. For the other trace gases (Figure 5), the initial simulation showed increased model-data differences around 70 m, and they were reduced with some modified diffusivity profiles. For CH₄, the model run with the original diffusivity profile reproduces the observed CH₄ profile quite well down to ~73 m, but significantly overestimates by >20 ppb for the lowest three depths (the black solid line). Using the modified diffusivity profiles that allowed better agreements for the other six trace gases (orange and red lines), we actually find larger model-data CH₄ difference than in the initial simulation.
4.2 Reconstruction by iterative dating

We explore the possibility of reconstructing the Arctic CH₄ mole fractions by the iterative dating method. This approach sets the diffusivity profile fixed (assumed to be correct) and aims to find an acceptable atmospheric history to reproduce the firm-air depth profile. It is considered that the modified diffusivity profiles with the low RMSD values for the six trace gases are adequately evaluated and that the model-data mismatch in the CH₄ modeling is therefore attributable to uncertainty in the atmospheric CH₄ scenario. The atmospheric CH₄ scenarios obtained by the iterative dating method are presented in Figure 7 for the 100 modeling cases of the modified diffusivity. The different simulation cases are colored in the same manner as in the earlier figures (Figures 4–6). Note that the reconstruction cases colored in light blue are considered to be less likely, due to poorer reproduction of the depth profiles (Figures 5 and 6). The model results in red and orange are in good agreement with the initial atmospheric scenario by Buizert et al. (2012) after around 1980. For the earlier period, however, the upper bounds of the reconstructions matches with the initial scenario, and the overall range of acceptable histories is below the initial atmospheric CH₄ scenario (circles and shades in red and orange), suggesting that the CH₄ mole fractions may have been lower than the initial modeling scenario.
Figure 7: Results of reconstructions by the iterative dating method from the NGRIP firn air (colored circles) for the model cases with the 100 different diffusivity profiles (colored in the same manner as in Figures 5 and 6). The orange and red shades indicate the range of CH$_4$ mole fraction trends reconstructed using the diffusivity profiles that better reproduce the other six trace gases. Black solid line is the initial atmospheric CH$_4$ scenario (Buizert et al., 2012), and black dotted line is the smoothed Antarctic CH$_4$ mole fraction (spline curve) from the Antarctic data shown in Figure 1.

It should be stressed that the reconstructions for the time period before 1980 rely on the CH$_4$ data from the lowest three depths of the NGRIP firn air. The differences between the initial and corrected atmospheric CH$_4$ scenario from these three deepest data are up to ~100 ppb. As seen in Figure 7, such reduction in the Arctic atmospheric CH$_4$ scenario over the period would result in alignment with the atmospheric CH$_4$ trend in Antarctica inferred from the Law Dome and other datasets (black dotted line). It is again noted that all the reconstruction cases colored in orange and red used diffusivity profiles that yield relatively good model reproducibility with RMSD values of <1.0 and 0.75, respectively. It is therefore seen that iterative dating-based reconstruction from the NGRIP firn data suggests decreased CH$_4$ mole fraction from the 1950s to 1970s in any case, albeit with large uncertainty.

4.3 Comparison to the NEEM profile

To further evaluate consistency of the atmospheric CH$_4$ scenario reconstructed from the NGRIP firn, we ran the model for the NEEM firn using the corrected atmospheric CH$_4$ histories obtained from the iterative dating approach. The modeling results with the initial and modified atmospheric CH$_4$ histories are shown in Figure 8. With the initial scenario (black line), the model-data difference was <25 ppb, with relatively large differences appearing in the LIZ (>63 m). However, when the atmospheric
CH₄ histories reconstructed from the NGRIP firn were employed, the reconstruction cases based on the improved reproducibility for the NGRIP firn (orange and red lines) resulted in larger model-data differences of >50 ppb in the LIZ.

![Image](https://doi.org/10.5194/acp-2021-736)

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5 Discussion and conclusion

In section 4, we have shown that, with the atmospheric scenarios prepared for the NEEM firn, depth profiles of CO₂, SF₆, CFC-11, CFC-12, CFC-113 and CH₃CCl₃ in the NGRIP firn are accurately reproduced by using the modified diffusivity profiles (Figure 5). This suggests that the atmospheric scenarios of these trace gases used in the modeling are consistent with the depth profiles observed at both firn sites in Greenland (NEEM and NGRIP). In contrast, the observed CH₄ profile in the NGRIP firn was not reconciled using the atmospheric scenario prepared for the NEEM firn and the diffusivity profiles that allow adequate reproducibility for the above six trace gases. This suggests either that the Arctic atmospheric scenario of CH₄ is uncertain or that the diffusivity profile of the NGRIP firn is underconstrained.

We explored the correction of the atmospheric scenario of CH₄ by the iterative dating approach. This method improves agreement to the observed CH₄ depth profile in the NGRIP firn, with an implicit assumption that the diffusivity profile in each case is correct. Although uncertainty due to the under-constrained diffusivity profile in the LIZ is large, this attempt suggested...
that the CH₄ mole fractions over the period 1950–1980 could be decreased in comparison to the original scenario prepared for the NEEM modeling (Figure 7). However, the follow-up modeling with the corrected atmospheric CH₄ histories by the iterative dating based on the NGRIP data did not show improved reproducibility for the CH₄ profile at the NEEM site (Figure 8). It is therefore implied that neither the original CH₄ scenario by Buizert et al. (2012) nor the corrected CH₄ histories by this study, are well validated against the available two Greenland firn data sets (NGRIP and NEEM). The decrease of up to 100 ppb from the original scenario over the period 1950–1980, as suggested by the iterative dating in this study, would make the CH₄ mole fraction as low as that in Antarctica (Figure 7). We point out that such a nearly-zero IPD of the CH₄ mole fraction is highly unlikely, given that major fraction of both natural and anthropogenic CH₄ sources resides in the northern hemisphere in both preindustrial and industrial periods (Houweling et al., 2000; Ghosh et al., 2015; Saunois et al., 2020; Chandra et al., 2021).

It is important to note that the reconstructions for the period before 1980 were heavily influenced by the three deepest data in the LIZ (>74 m). Figure 9 shows distributions of the effective age of CH₄ at depths below 55 m in the NGRIP firn, colored the same as in the earlier figures. In addition, the spread of the effective age (σ_age) at each sampling depth is shown on the right axis. This figure shows that firn air samples collected at the three lowest sampling depths have effective ages corresponding to the period from ~1950 to the mid 1970s. In addition, even the acceptable diffusivities yield the spread of the effective age of >5 years at those depths (red and orange). This shows that the reconstruction of the CH₄ mole fraction for the period is subject to much uncertainty in effective age. The Antarctic atmospheric CH₄ record (see Figures 1 and 7) indicates that the atmospheric increase rate of CH₄ was 10–15 ppb yr⁻¹ over the period. The 5-year uncertainty in the age estimate for the NGRIP firn air samples could therefore be translated to an uncertainty of >50 ppb in the Arctic atmospheric CH₄ level. This is comparable to the IPD of CH₄ mole fraction during the 1950s to 1970s, which was assumed when Buizert et al. (2012) prepared the Arctic atmospheric CH₄ scenario for the NEEM modeling.
The IPD of the atmospheric CH$_4$ mole fraction is important for better understanding the evolution of the global CH$_4$ budget. Given that the Antarctic ice core and firn measurements have provided relatively reliable CH$_4$ records over the 20th century, improved reconstructions from Greenland ice cores and firn air should better constrain the changes in the IPD. To sufficiently constrain the historical global CH$_4$ budget, the reconstruction for Greenland needs to be accurate within ~10 ppb, corresponding to ~30 Tg CH$_4$ yr$^{-1}$ global emission. Unfortunately, based on the firn CH$_4$ data from NGRIP and NEEM, this study demonstrated that consistent reconstruction of the Arctic CH$_4$ mole fraction is achievable only back to the mid 1970s, and that the uncertainty of reconstruction is still very large (around 50 ppb) for the 1950s to 1970s.

Previous studies have used CH$_4$ as one of tracers that constrain diffusivity profiles in firn (Witrant et al., 2012; Trudinger et al., 2013). These studies have shown that CH$_4$ effectively contributed to constraining diffusivity for deep layers i.e. LIZ in the NEEM firn. However, the use of CH$_4$ as a strong constraint is valid only when its atmospheric scenario given as input to the models was assumed to be correct. Figures 5 and 6 show a larger spread in the model-data differences of CH$_4$ among the different diffusivity cases spread widely in the deepest layers of the LIZ, in comparison to the other six gases. This fact highlights that subtle changes of the diffusivity profile in the LIZ have a large impact on simulating CH$_4$, and it indeed indicates that the species could serve as an effective diffusivity constraint, if its atmospheric scenario was correctly given with low uncertainty. Although the currently proposed Arctic CH$_4$ history (Buizert et al., 2012) appears a useful choice in firn modeling at Greenland sites, it should be kept in mind that the use of CH$_4$ as a tuning tracer could lead to overfitting of the diffusivity profile.
Sapart et al. (2013) examined the reconstruction of stable carbon isotope ratio ($\delta^{13}C$) of atmospheric CH$_4$ using firn air measurements from both northern and southern hemispheres. They concluded that, with the available firn measurements and understanding of firn air transport, it is difficult to reliably reconstruct the past trend of $\delta^{13}C$ of CH$_4$ because of multiple reasons including uncertainty in the atmospheric CH$_4$ mole fraction scenario. Although there are many important and uncertain factors, the accurate reconstruction of the atmospheric CH$_4$ mole fraction is particularly important, because the trend in the mole fraction can lead to significant signal in the modeled $\delta^{13}C$ profile in firn due to the difference in the molecular diffusion coefficient, even in the absence of a temporal trend in atmospheric $\delta^{13}C$. This study revealed a large uncertainty in the Arctic CH$_4$ mole fraction trend over the 20th century, which supports the conclusion of Sapart et al. (2013) on the difficulty of reconstruction of $\delta^{13}C$ of CH$_4$ in the northern hemisphere. The NGRIP firn air samples were also analyzed for $\delta^{13}C$ and stable hydrogen isotope ratio ($\delta^D$) of CH$_4$ (Kawamura et al., 2021), but we regrettably report that reconstruction of $\delta^{13}C$ of CH$_4$ is difficult despite our best modeling efforts (not shown).

A possibility to improve the reproducibility of the depth profile of CH$_4$ in the NGRIP firn may come from additional constraint to the diffusivity profile along with those currently made by the six trace gases (CO$_2$, SF$_6$, CFC-11, CFC-12, CFC-113 and CH$_3$CCl$_3$). It could be performed by introducing additional effective tracers e.g. $^{14}$CO$_2$, although such measurements cannot be foreseen for the NGRIP samples. This study showed that, with the currently available firn data from Greenland (NGRIP and NEEM), reliable reconstruction of the Arctic CH$_4$ mole fraction history (independent of Antarctic records and assumed IPD) is possible back to the mid 1970s only. For the earlier period, consistent reconstruction with a small uncertainty of age estimate is currently difficult. Future sampling and measurements of ice cores at a high-accumulation site in Greenland (where age of air occluded can be determined accurately) may be the only way to reconstruct the atmospheric CH$_4$ trend over the 20th century.

Data Availability
The composition data of the NGRIP firn air samples are available on the Arctic Data archive System (ADS) of National Institute of Polar Research (https://ads.nipr.ac.jp/dataset/A20210609-001). The NEEM firn air data are available in the supplementary file of Buizert et al. (2012). Our modeling data are available upon request (umezawa.taku@nies.go.jp).

Author Contribution
TU, SS, KK and IO discussed on design of the study. KK, SA and TN conducted firn air sampling at the NGRIP site. SS, KK, TU and TS analyzed the firn air samples for trace gases. SJA set up the measurement system for the halocarbons. TU and SS made firn air model simulations. TU analyzed the measurement/modeling data and prepared the manuscript with contributions from all co-authors.
Completing interests

The authors declare that they have no conflict of interest.

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