High-resolution Holocene N_2O ice core record and its relationship with CH_4 and CO_2

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[1]   Nitrous oxide (N_2O) concentration records exist for the last 1000 years and for time periods of rapid climatic changes like the transition from the last glacial to today's interglacial and for one of the fast climate variations during the last ice age. Little is known, however, about possible N_2O variations during the more stable climate of the present interglacial (Holocene) spanning the last 11 thousand years. Here we fill this gap with a high-resolution N_2O record measured along the European Project for Ice Coring in Antarctica (EPICA) Dome C Antarctic ice core. On the same ice we obtained high-resolution methane and carbon dioxide records. This provides the unique opportunity to compare variations of the three most important greenhouse gases (after water vapor) without any uncertainty in their relative timing. The CO_2 and CH_4 records are in good agreement with previous measurements on other ice cores. The N_2O concentration started to decrease in the early Holocene and reached minimum values around 8 ka (<260 ppbv) before a slow increase to its preindustrial concentration of $\sim$265 ppbv.   INDEX TERMS: 0325 Atmospheric Composition And Structure: Evolution of the atmosphere; 0365 Atmospheric Composition And Structure: Troposphere–composition and chemistry; 1610 Global Change: Atmosphere (0315, 0325); 3344 Meteorology And Atmospheric Dynamics: Paleoclimatology; KEYWORDS: N_2O, CH_4, CO_2, nitrous oxide, greenhouse gases, Holocene

1.   Introduction

[2]   Carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O) are the three most important well-mixed greenhouse gases after water vapor, reaching global mean concentrations of 367 parts per million by volume (ppmv) [*Keeling and Whorf*, 2000], 1745 parts per billion by volume (ppbv), and 314 ppbv [*Intergovernmental Panel on Climate Change IPCC*, 2001], respectively, in the year 1998. They show an increasing trend since the beginning of the industrialization mainly due to increasing anthropogenic sources [*Barnola et al.*, 1995; *Battle et al.*, 1996; *Blunier et al.*, 1993; *Etheridge et al.*, 1996; *Machida et al.*, 1995]. However, questions arise about their natural variability and the possible climatic feedbacks affecting their future evolution under a global warming context. One way to obtain insight into the natural variability of these three greenhouse gases during a time period of relatively stable climate similar to today's is to reconstruct the concentrations back to 11 thousand years before present (11 ka) by measurements on polar ice cores. The records of CH_4 and CO_2 over this time period have provided interesting information about environmental changes in response to regional climate variations [*Blunier et al.*, 1995; *Chappellaz et al.*, 1997; *Indermühle et al.*, 1999]. Little is known about the evolution of the N_2O concentration during the Holocene apart from the last few hundred years [*Khalil and Rasmussen*, 1988; *Zardini et al.*, 1989]. From the high-resolution N_2O record presented in this paper we expect information about the global nitrogen cycle and changes of the main N_2O sources and sinks. In the modern global N_2O budget, natural N_2O sources are

nitrification and denitrification in soils (3–10 Tg N yr^{-1}) and in the ocean (3–6 Tg N yr^{-1}). About two thirds of the soil emissions occur in the tropics, and one third originates from temperate soils. The main sink for N_2O, on the other hand, is its decomposition in the stratosphere by photodissociation (90%) and reactions with excited oxygen (10%) [*IPCC*, 2001].

2.   Methods

[3]   For the N_2O and CH_4 measurements made in Bern the air trapped in polar ice samples is extracted with a melt-refreezing method [*Chappellaz et al.*, 1997; *Flückiger et al.*, 1999]. A sample of $\sim$40 g of ice is melted under vacuum in a glass container sealed with viton (water bath temperature of 50°C) and then refrozen from the bottom with an alcohol bath at −30°C to expel gases dissolved in the water (extraction efficiency: $\sim$99%). The extracted air is expanded into an evacuated sample loop and injected by the carrier gas (He) into the gas chromatograph. N_2+ O_2 + Ar, CH_4, and N_2O are separated on a Carboxen 1000 column (50 cm, 1.5 mm inner diameter). N_2+ O_2 + Ar is detected with a thermal conductivity detector (TCD), CH_4 is detected with a flame ionization detector (FID), and N_2O is detected with an electron capture detector (ECD). A falsification of the N_2O results due to a possible cross sensitivity of the ECD for N_2O and CO_2 can be precluded because these two gases are well separated on the Carboxen 1000 column. The N_2O results have to be corrected due to a loss of $(2.32 \pm 0.47) \times 10^{-8}$ mL of N_2O (at standard temperature and pressure) caused by the extraction corresponding to a concentration correction of $\sim$6 ppbv with a typical sample size of 40 g of ice. This correction was determined by tests with single-crystal ice and standard gas. N_2O measurements are calibrated with an air-based standard gas with a
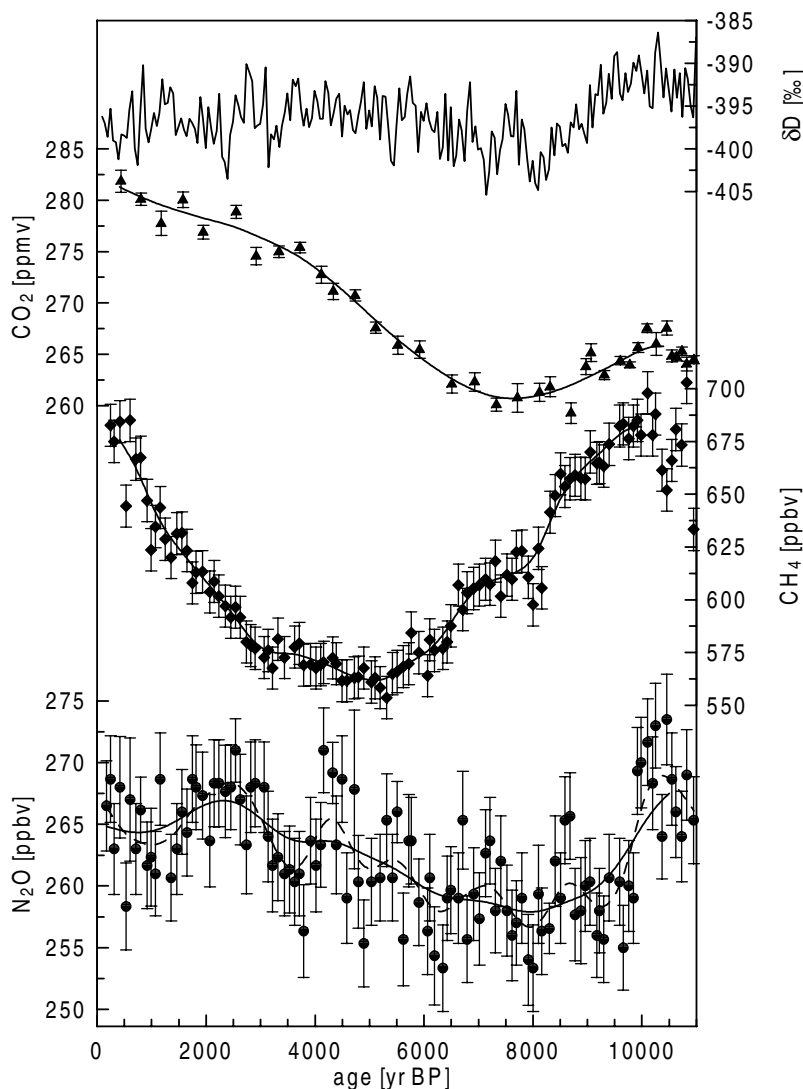
Figure 1. Dome C CO$_2$ (triangles), CH$_4$ (diamonds), N$_2$O (circles), and deuterium (top trace) [*Jouzel et al.*, 2001] records for the Holocene time period. The CO$_2$, N$_2$O, and CH$_4$ measurements are plotted together with their analytical reproducibility (1σ). Smoothed splines were calculated according to *Enting* [1987] with cutoff periods of 3000 years for CO$_2$, 3000 years (solid line) and 1500 years (dashed line) for N$_2$O, and 1500 years for CH$_4$, highlighting long-term trends of the three greenhouse gases. For CO$_2$ and N$_2$O it is believed that the splines with cutoff periods of 3000 years represent the long-term trends of the atmospheric concentration. The CH$_4$ spline was calculated with a smaller cutoff period (1500 years) because of a much shorter lifetime of CH$_4$ compared to CO$_2$ and N$_2$O. N$_2$O variations as indicated by the spline with a cutoff period of 1500 years are at the limit of significance given the analytical uncertainty of the data. The timescale for the ice and the enclosed air (which is younger than the surrounding ice because it is enclosed at the bottom of the firn layer), in years before 1950, is based on the timescale by *Schwander et al.* [2001]. The uncertainty of the absolute timescale for the ice is estimated to ±200 years. The gas-ice age difference is ∼2000 years with an estimated uncertainty of ∼10%. As all three gas records were measured on the air bubbles of the same core, there is no uncertainty in the relative timing of the gas records. The CO$_2$, CH$_4$, and N$_2$O data presented in Figure 1 can be downloaded from the World Data Centre-A for Paleoclimatology at Boulder, Colorado (http://www.ngdc.noaa.gov/paleo/data.html).

N$_2$O concentration of 304 ppbv. This concentration was cross-checked by measurements performed at the Laboratoire de Glaciologie et Géophysique de l'Environment in Grenoble, France, and at the Institut für Umweltphysik at the University of Heidelberg, Germany. While, for the intercalibration performed at Grenoble, a gas standard from the Commonwealth Scientific and Industrial Research Organisation (CSIRO) Division of Atmospheric Research was used, the Institut für Umweltchemie at

Heidelberg used a gas standard from the Atmospheric Lifetime Experiment (ALE) Global Atmospheric Gases Experiment (GAGE) network. The results of the intercalibration showed that the Bern standard is 1.1 ppbv higher on the CSIRO scale (305.1 ± 3.5 ppbv) and 3.0 ppbv lower on the ALE GAGE scale (301.0 ± 1.5 ppbv). For the calibration of the CH$_4$ measurements an intercalibrated air-based standard gas with a CH$_4$ concentration of 1050 ppbv is used [*Sowers et al.*, 1997]. An additional standard
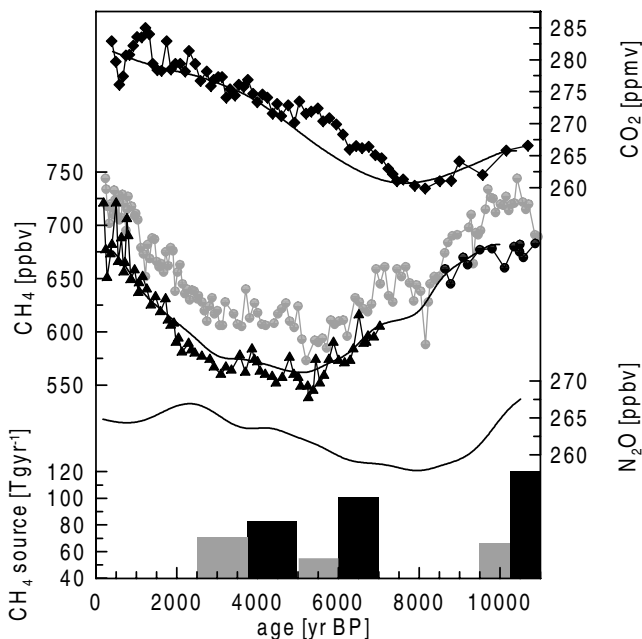
Figure 2. Comparison of the Dome C long-term trends of CO$_2$ (top trace, solid line), CH$_4$ (middle trace, solid line), and N$_2$O (bottom trace, solid line) from Figure 1 with previously published CO$_2$ and CH$_4$ data and published source distribution calculations for CH$_4$. The disagreement between the CO$_2$ data measured along the Taylor Dome ice core, Antarctica (solid diamonds, plotted on the original Taylor Dome timescale) [*Indermühle et al.*, 1999], and the Dome C CO$_2$ trend in the time period 4–8 ka can probably be attributed to differences in the timescales of the two ice cores [*Stauffer et al.*, 2002]. For CH$_4$ the Dome C trend agrees well with CH$_4$ results from the Antarctic ice cores D47 (solid triangles) and Byrd (solid circles) as well as with results from the GRIP ice core, Greenland (shaded circles), when taking the interpolar difference into account [*Chappellaz et al.*, 1997]. However, the used timescales are not synchronized. The GRIP, D47, and Byrd results are shown on a synchronized GRIP timescale [*Chappellaz et al.*, 1997; *Schwander et al.*, 1997], while the Dome C data are plotted on the original Dome C timescale [*Schwander et al.*, 2001]. In addition to the long-term trends of CO$_2$, CH$_4$, and N$_2$O, previously published source distribution calculations deduced from the interpolar gradient of CH$_4$ are shown for the periods 2.5–5, 5–7, and 9.5–11.5 ka [*Chappellaz et al.*, 1997]. Solid bars represent the tropical source (30°S-30°N), and shaded bars represent the source of the middle to high northern latitudes (30°–90°N). The source of the middle to high southern latitudes (30°–90°S) was assumed to be constant over the Holocene time period (15 Tg yr^{-1}) and is therefore not shown. Comparison of the long-term trends of CH$_4$ and N$_2$O to the CH$_4$ source distributions for the above mentioned time periods show that CH$_4$ was mainly controlled by drying of the tropics, while N$_2$O seems more related to the middle to high northern latitudes. Not shown are the source distribution calculations for the time period 0.25–1 ka because tentative results deduced from the gradient between the Dome C and the GRIP CH$_4$ measurements indicate a different source distribution than found by *Chappellaz et al.* [1997].

gas with N$_2$O and CH$_4$ concentrations of 201 and 408 ppbv, respectively, is used to check the linearity of the system. The analytical uncertainty of the N$_2$O results is determined by measuring single-crystal ice samples with standard gas and the scattering of three individual measurements per extracted ice core sample. The mean analytical uncertainty (1σ) for the Holocene time period is 3.6 ppbv for N$_2$O, while for CH$_4$ the analytical uncertainty (1σ) was estimated to be 10 ppbv [*Chappellaz et al.*, 1997].

[4] For the Bern CO$_2$ measurements, ice samples of 6–8 g are cracked under vacuum at low temperature (−30°C) with a needle cracker. The air from the opened bubbles expands over a cold trap (−70°C) into an absorption cell, where the CO$_2$ concentration is measured with an infrared laser absorption spectrometer. Calibration is done using air-based standard gases with CO$_2$ concentrations of 251.70, 321.06, and 342.03 ppmv. The CO$_2$ results shown here are an average over six individual samples for each depth. The given uncertainty reflects the 1σ reproducibility of the mean deduced from the scattering of the six individual measurements. The mean uncertainties (1σ) of the Holocene CO$_2$ measurements are 0.7 ppmv [*Monnin et al.*, 2001].

[5] Here we present new high-resolution Holocene records of N$_2$O, CH$_4$, and CO$_2$ concentrations measured on air extracted from bubbles trapped in the ice core from Dome Concordia (Dome C), Antarctica (75°06′06″S, 123°23′42″E, 3233 m above sea level.). This core was drilled in the framework of the European Project for Ice Coring in Antarctica (EPICA). Measurements were performed at 110, 112, and 36 different depth levels for N$_2$O, CH$_4$, and CO$_2$, respectively. The data presented in this study are not corrected for gravitational fractionation [*Schwander*, 1989]. The enrichment due to this fractionation is ∼2 ppbv for N$_2$O and 2 ppmv for CO$_2$, and for CH$_4$ the gravitational fractionation leads to a depletion of the order of ∼4 ppbv.

3. Results

[6] All three greenhouse gases show a concentration decrease in the first part of the Holocene, followed by a concentration increase to preindustrial values (Figure 1). N$_2$O and CO$_2$ concentrations started to decrease at around 10 ka, showing low values in the time periods 10 to 6 ka (below 260 ppbv) and 9 to 6 ka (below 263 ppmv), respectively. The CH$_4$ concentration decrease started around 9.5 ka and showed low concentrations (below 575 ppbv) between 6 and 3 ka.

[7] We briefly compare the new CO$_2$ and CH$_4$ records with records measured previously on other ice cores. The main focus is, however, the discussion of the high-resolution N$_2$O record.

3.1. Carbon Dioxide and Methane

[8] The CO$_2$ measurements performed along the Dome C ice core differ slightly from results measured along the Taylor Dome ice core [*Indermühle et al.*, 1999] (Figure 2). The difference between the two records is most pronounced between 4 and 8 ka. This disagreement is most likely due to uncertainties in the age scales of the two cores. [*Stauffer et al.*, 2002; B. Stauffer et al., High resolution records of CO$_2$, CH$_4$ and N$_2$O from polar ice cores, submitted to *Memoirs of National Institute of Polar Research*, 2001 (hereinafter referred to as Stauffer et al., submitted manuscript, 2001)]. Chemical artifacts in the Dome C CO$_2$ record are unlikely because the scattering of neighboring samples is within the expected analytical uncertainty. For a detailed review of possible artifacts, see *Monnin et al.* [2001, and references therein].

[9] The Dome C CH$_4$ record closes the gap in the Antarctic record between the D47 and the Byrd CH$_4$ record (7–9 ka) where high-resolution records were not yet available. For the other periods during the Holocene it compares well with records from Antarctica [*Chappellaz et al.*, 1997] and from Greenland [*Blunier*
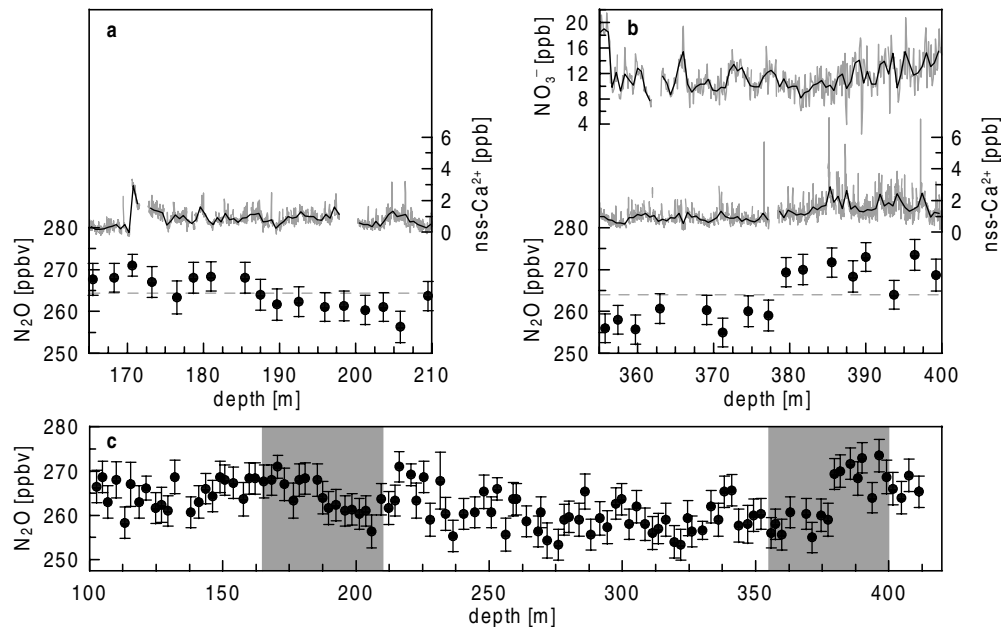
Figure 3. Dome C N₂O data compared to non-sea-salt calcium (nss Ca²⁺) and nitrate (NO₃⁻) measured along the same core for two depth intervals of rapid shifts in the N₂O concentration. The two depth intervals (a) 165–210 m and (b) 355–400 m, centered around 3 and 10 ka, respectively, on the gas age scale are marked as shaded areas in (c) the N₂O overview. The nss Ca²⁺ is shown in Figures 3a and 3b as 2 cm mean (middle trace, shaded line) and 55 cm mean (middle trace, solid line). NO₃⁻ was only measured in the deeper interval (Figure 3b) and is plotted as 10 cm mean (top trace, shaded line) and 55 cm mean (top trace, solid line). The N₂O results (solid circles) are complemented by the mean values over the corresponding depth interval (shaded dashed line). Neither non-sea-salt calcium (nss Ca²⁺) nor NO₃⁻ show an abrupt shift in the same depth interval as the N₂O record. It is therefore unlikely that the shifts in the N₂O record are due to an artifact produced by chemical compounds.

et al., 1995] when taking the interpolar difference into account (Figure 2). The only exception is at 8.2 ka, where records from Greenland show a sharp reduction in the CH₄ concentration for <200 years [*Blunier et al.*, 1995]. This relatively short event does not appear so clearly in the Dome C CH₄ record, most likely because of a larger smoothing of the atmospheric variations during the air enclosure process at Dome C as a result of the low accumulation rate (3 cm of ice per year, i.e., 8 times smaller than at Summit, Greenland). The time required to isolate the air bubbles at the firn-ice transition is roughly inversely proportional to the accumulation rate and lasts ~300 years at Dome C [*Schwander*, 1996]. Atmospheric variations shorter than this are therefore strongly attenuated.

3.2. Nitrous Oxide

[10] The only available precise N₂O data covering partly the same time period as the Dome C data presented here were measured along the EUROCORE and Greenland Ice Core Project (GRIP) ice cores, both from Summit, central Greenland [*Flückiger et al.*, 1999]. The data from these cores cover the last millennium and the beginning of the Holocene. In the Summit record a preindustrial value of 270 ppbv was determined. The mean value of the Dome C measurements over the last 1000 years, on the other hand, yields a value of 265 ppbv. Given today's small interhemispheric gradient of ~0.8 ppbv [*IPCC*, 2001], we expect that the interhemispheric gradient was also small during the past. Therefore the difference in the preindustrial levels of the Summit and the Dome C record cannot entirely be explained by the interhemispheric gradient. About half of the difference between the records can be explained by the relative dating uncertainties of the two cores, when the

lowest Dome C value in this time range is considered as an outlier. The remaining difference of ~2 ppbv is within the analytical uncertainty. However, we cannot exclude that the difference is caused by a small in situ production of N₂O in Greenland ice. A production of small amounts of trace gases by chemical reactions between impurities in the ice has been postulated for CO₂ and CO especially in Greenland ice, where the impurity concentrations are generally larger than in Antarctica [*Anklin et al.*, 1995; *Haan and Raynaud*, 1998]. Such in situ production may vary from depth to depth depending on the concentration of impurities. For instance, the difference between the GRIP and the Dome C records in the early Holocene is comparable to today's interhemispheric gradient. Therefore an in situ production in the GRIP core in this depth range can most likely be excluded.

[11] N₂O measurements in the older part of the Dome C core covering part of the last glacial period (20–14.5 ka) show a much larger disagreement to the GRIP record (Stauffer et al., submitted manuscript, 2001). While the GRIP record in this part shows a few elevated outliers [*Flückiger et al.*, 1999], the Dome C results show mostly too high values that are highly scattered, which is very likely the result of in situ production in the ice. A similarly high scattering was found in the Vostok ice core in the time period preceding the penultimate deglaciation [*Sowers*, 2001].

[12] This finding raises the question whether all the N₂O data measured along the Dome C ice core covering the Holocene reflect the atmospheric concentration or if some of the measurements are falsified by artifacts too. In general, ice from warm climate periods like the Holocene has much lower impurity concentrations than ice representing glacial epochs, and therefore possible artifacts are expected to be much smaller, but they cannot be excluded. To test

Table 1. Holocene Variations of N_2O, CH_4, and CO_2 Compared to the Concentration Changes During the Last Glacial-Interglacial Transition[a]

	Concentration Change Glacial-Interglacial,	Variation During the Holocene	Holocene Variation Compared to Transition, %
N_2O	70 (200–270) ppbv	10 (258–268) ppbv	14
CH_4	306 (368–674) ppbv	112 (562–674) ppbv	37
CO_2	76 (189–265) ppmv	20 (260–280) ppmv	26

[a] For CO_2 and CH_4 the data from the Dome C ice core were used [*Monnin et al.,*, 2001]. Data of the glacial- interglacial concentration change of N_2O are from *Flückiger et al.* [1999].

the possibility of artifacts in the Dome C Holocene ice caused by reactions involving impurities in the ice, we have compared the N_2O data to chemical compounds measured along the same core and at the same depths. The concentration of non-sea-salt calcium (nss Ca^{2+}) [*Röthlisberger et al.*, 2000] is an indicator of terrestrial dust input and possibly of the concentration of living bacteria in ice, when assuming that they are transported with the same air masses. The concentrations of ammonium (NH_4^+) (R. Röthlisberger, unpublished data, 2001) and nitrate (NO_3^-) [*Röthlisberger et al.*, 2000] are substrates, which could, in principal, lead to a N_2O production by chemical reactions or in the presence of bacteria. The N_2O record shows no correlation with nss Ca^{2+}, NO_3^- and NH_4^+ for the entire data set. Further, the detailed comparison of the N_2O data to nss Ca^{2+} and NO_3^- at two depth intervals of abrupt concentration changes of N_2O (∼3 and 10 ka) shows that no analogous abrupt shifts are found in the chemical compounds (Figure 3). The comparison of N_2O and NH_4^+ is based on tentative results, which are therefore not shown in Figure 3. We assume at this point, on the basis of available information, that the long-term trend in the N_2O record during the Holocene most likely represents atmospheric signals.

4. Discussion

[13] Compared with the glacial-interglacial concentration changes, the variations of the three greenhouse gases during the Holocene are small (see Table 1); the smallest variations are found in the N_2O record. The estimated atmospheric N_2O variations during the Holocene of ∼10 ppbv amount to only 14% of the glacial-interglacial change and are also much smaller than the anthropogenic increase (∼45 ppbv).

[14] All three greenhouse gases show variations on different timescales during the Holocene. The short-term fluctuations in the N_2O record, as shown in the spline with a cutoff period of 1500 years (Figure 1, bottom trace, dashed line) are at the limit of significance given the analytical uncertainty of the data. Therefore we restrict our discussion to the long-term trend of the record (Figure 1, bottom trace, solid line), which we consider more reliable and representative of the main atmospheric variations.

[15] To identify possible causes for the long-term trend in the N_2O record, we first estimate the necessary changes in the total source or the main sink required to explain the magnitude of the concentration change.

4.1. Magnitude of Changes in the N_2O Sources and Sinks

[16] Assuming a preindustrial N_2O concentration of 270 ppbv (which is a mean value of different data sets from *Machida et al.* [1995], *Flückiger et al.* [1999], and data presented in this paper), a preindustrial total source of 11×10^{12} g of nitrogen per year (11 Tg N yr^{-1}), and a constant lifetime of 120 years [*IPCC*, 2001] over the Holocene time period, the Holocene N_2O minimum corresponds to a total source decrease of ∼0.41 Tg N yr^{-1}, i.e., 3.7% of the total preindustrial source. About two thirds of the preindustrial source

are attributed to soils, and one third is attributed to the ocean [*IPCC*, 2001]. If only one source were responsible for the N_2O concentration change, this would correspond to either a decrease of 5.6% in the soil source or a decrease of 11.2% in the oceanic source compared to the preindustrial emissions.

[17] On the other hand, if we assume that the N_2O global source remained constant at the preindustrial level of 11 Tg N yr^{-1}, the stratospheric sink of N_2O (photodissociation and reaction with excited oxygen) had to be larger by 3.7% during the period of lowest Holocene N_2O concentration, implying a reduced lifetime by ∼4.4 years. Parameters which influence the lifetime of N_2O are the incoming solar UV radiation and the exchange of air masses between the troposphere and the stratosphere. It is assumed that ^{10}Be fluxes are a proxy for the solar irradiance [*Beer*, 2000]. For the Holocene time period, ^{10}Be fluxes based on ice core results show no significant variations [*Finkel and Nishiizumi*, 1997; J. Beer, unpublished data, 2001]. Therefore there is no indication that the N_2O variation during the Holocene is due to changing solar radiation. Furthermore, we are not aware of any significant change in the global exchange of air masses between the troposphere and the stratosphere during the Holocene.

[18] In addition to the above discussed mechanisms, a negative feedback between the N_2O, NO_x, and O_3 concentrations in the stratosphere [*Prather*, 1998] tends to mitigate a tropospheric N_2O variation and thus could lead to an underestimation of changes in the N_2O sources. A decreasing N_2O burden, for example, leads to a decrease in stratospheric NO_x and therefore to an increase in the midstratospheric O_3 concentration. This in turn reduces the solar UV radiation in the lower stratosphere. N_2O is therefore photo-lyzed less rapidly, implying a longer lifetime. During lowest Holocene N_2O concentrations this effect leads to a prolongation of the lifetime of 3 months compared to the preindustrial lifetime. With today's uncertainties in the N_2O budget and the N_2O measurements, a change in the lifetime by this order of magnitude can be neglected for the preindustrial part of the Holocene. We conclude that a variation of the sink can probably be neglected for the Holocene time period and that the observed variations in the N_2O concentration have to be attributed to changes in the soil emissions and/or to variations in the oceanic source.

4.2. Soils

[19] During the last glacial period and the transition from the last glacial to the Holocene, N_2O and CH_4 showed concentration changes in parallel with the fast climatic variations of the Northern Hemisphere [*Chappellaz et al.*, 1993; *Flückiger et al.*, 1999] similar to the $\delta^{18}O$ record, a proxy for paleotemperature, measured along the GRIP ice core from central Greenland [*Dansgaard et al.*, 1993]. By contrast, the CO_2 record showed a close relation with the paleotemperature record from Antarctica [*Indermühle et al.*, 2000; *Monnin et al.*, 2001]. The similarities of the N_2O and CH_4 records may point to partly similar primary causes, such as changes in the terrestrial biosphere due to, for example, changes in temperature, precipitation, and/or net primary productivity. During the Holo-

cene, however, the N$_2$O record is not in concert with the CH$_4$ record but rather parallel to the CO$_2$ concentration (Figure 1) as it was also observed for the anthropogenic increase over the last century [*Battle et al.*, 1996]. For the preindustrial part of the Holocene the variations in the CO$_2$ and CH$_4$ concentrations have both been attributed to changes in the terrestrial biosphere [*Chappellaz et al.*, 1997; *Indermühle et al.*, 1999] (for an alternative interpretation of the CO$_2$ record, see *Broecker et al.* [2001]). The comparison with the N$_2$O data could therefore give indications about causes of possible variations in the N$_2$O soil source.

[20] The main factors determining the CO$_2$ concentration during the Holocene are thought to be enhanced CO$_2$ uptake by the terrestrial biosphere in the early Holocene and a CO$_2$ release after 7 ka [*Indermühle et al.*, 1999]. Increased biological activity leading to a decrease in the atmospheric CO$_2$ concentration is in general related to higher temperature and moisture, conditions which favor in most soils higher N$_2$O emissions and vice versa. Therefore, if changes in the emissions due to buildup or decay of terrestrial biosphere dominated the N$_2$O and CO$_2$ concentration variations, we would expect rather opposite trends in these two records. Hence we conclude that it is unlikely that the Holocene CO$_2$ and N$_2$O concentration changes have the same origin in the terrestrial biosphere despite their similar evolutions.

[21] Are the differences between the CH$_4$ and N$_2$O records excluding a soil source for the observed N$_2$O variations during the Holocene? Like CH$_4$, N$_2$O has an important soil source which strongly depends on temperature and precipitation rates [*Bollmann and Conrad*, 1998; *Bouwman et al.*, 1993; *Potter et al.*, 1996]. However, a synchrony of the two records is not required because different soil conditions favor N$_2$O or CH$_4$ emissions. While the conditions for CH$_4$ production have to be at 100% water saturation, N$_2$O production ceases as the water-filled pore space in the soil approaches 100% [*Davidson*, 1991]. When assuming a constant sink, implying constant OH concentration during the preindustrial part of the Holocene, CH$_4$ is a proxy for the global extent of wetlands and therefore indirectly for precipitation minus evaporation. Source calculations using the interhemispheric gradient in atmospheric CH$_4$ [*Chappellaz et al.*, 1997] and comparison with terrestrial records [*Blunier et al.*, 1995] have suggested that the high concentrations of CH$_4$ in the early Holocene mainly reflect wet conditions in the tropics. Low concentrations in the mid-Holocene are reached after an ongoing drying in some parts of the tropics, mainly in the Sahel and Sahara regions. Emissions in the middle to high northern latitudes were lower in the period between 7 and 5 ka than in the period between 11.5 and 9.5 ka. After 5 ka, boreal wetlands started to grow and were at least partly responsible for the CH$_4$ increase after 5 ka.

[22] Comparing the N$_2$O record with the CH$_4$ data, it seems that the N$_2$O concentration is not primarily affected by the evolution of the wetness in the tropics, which mainly controlled the evolution of the atmospheric CH$_4$concentration from 11 until at least 5 ka. A slightly closer relation can be found between the wetness of the middle to high northern latitudes (Figure 2), derived from CH$_4$gradient calculations [*Chappellaz et al.*, 1997], and the N$_2$O concentration. The soils in these regions are possibly more sensitive to changes in moisture content than those in the tropics because conditions for N$_2$O production in middle to high northern latitudes are in general less favorable owing to lower temperatures and limited nitrogen availability [*Bouwman et al.*, 1993]. Both the period of drier conditions (less favorable for N$_2$O production) in the middle to high northern latitudes and the lowest N$_2$O concentrations in the Dome C ice core fall within the climatic optimum characterized by warm temperatures (more favorable for N$_2$O production) reported for different parts of the Northern Hemisphere, mainly the Atlantic sector and northern Eurasia [*Cheddadi et al.*, 1997; *Dahl-Jensen et al.*, 1998; *Foley et al.*, 1994;

Ganopolski et al., 1998; *MacDonald et al.*, 2000; *Webb et al.*, 1993]. Assuming that the middle to high northern latitudes were responsible for the N$_2$O variations during the Holocene, the evolution of the N$_2$O record suggests that the drier conditions have outweighed a possibly positive temperature effect.

4.3. The Ocean

[23] Apart from the soils, changes in the oceanic source could have contributed or even dominated the atmospheric N$_2$O changes during the Holocene. Model calculations based on ocean surface N$_2$O concentrations [*Nevison et al.*, 1995] have shown that in general, today's main oceanic sources are the Southern Ocean (40°–60°S), the northern Pacific Ocean, the equatorial upwelling zones, and the coastal upwelling zones predominantly in the tropical Northern Hemisphere. Apart from open ocean water column oxidation of organic matter under oxic conditions [*Suntharalingam and Sarmiento*, 2000], low-oxygen regions, e.g., the Arabian Sea and the eastern tropical North Pacific, are important N$_2$O sources [*Bange et al.*, 1996; *Dore et al.*, 1998; *Yoshinari et al.*, 1997]. Changes in the strength of these sources can derive from changes in the ocean biogeochemical cycle of nitrogen owing, for example, to changes in the wind- and buoyancy-driven circulations which determine the local nutrient availability and local temperature [*de Wilde and Helder*, 1997; *Dore et al.*, 1998].

[24] A very small effect is expected from changing sea surface temperatures and related changes in the solubility of N$_2$O in the water column. Using the solubility coefficients of *Wanninkhof* [1992] and modern annual mean ocean temperature and salinity data [*Levitus and Boyer*, 1994; *Levitus et al.*, 1994], a decrease of ~0.04 ppbv in the tropospheric N$_2$O concentration is calculated for a 1°C cooling in the mixed layer (upper 100 m) of the global ocean. Even if a 1°C cooling is applied to the upper 1000 m of the global ocean, the decrease in atmospheric N$_2$O does not exceed 0.5 ppbv. Global ocean temperature changes during the Holocene are thought to be small [see, e.g., *Marchal et al.*, 2002]. Possible changes in temperature-driven N$_2$O solubility of the ocean during the Holocene had therefore a minor impact on atmospheric N$_2$O concentration.

[25] The other mentioned effects influencing the oceanic N$_2$O sources and the resulting emissions to the atmosphere cannot be quantified for the Holocene time period with today's knowledge. For example, changes in wind and monsoon patterns have probably influenced regional and maybe even global ocean-atmosphere N$_2$O fluxes, but they could have produced opposing effects in different regions [*de Wilde and Helder*, 1997; *Dore et al.*, 1998]. Therefore possible changes in the strength of the oceanic source during the Holocene remain unknown.

4.4. Isotopes

[26] On the basis of the N$_2$O record and the previous discussions it is not yet possible to identify the mechanisms causing the N$_2$O concentration changes during the Holocene. This implies that at this point, it is difficult to assess how atmospheric N$_2$O will evolve in the future through climatic feedbacks associated with greenhouse warming. Measurements of the isotopic composition of N$_2$O extracted from polar ice cores may provide additional information. Using the box model of *Rahn and Wahlen* [2000], we estimate the isotopic shifts for the cases where the whole change in the N$_2$O concentration during the Holocene is attributed either to changes in the soil source or to changes in the ocean source. The δ^{15}N and δ^{18}O of N$_2$O emitted by natural soils range from − 34 to 2‰ and − 4 to 19‰, respectively, relative to atmospheric N$_2$ and O$_2$ (for an overview, see *Pérez et al.* [2000, and references therein]). The δ^{15}N and δ^{18}O of N$_2$O emitted by the ocean vary between 2 to 10‰ and 17 to over 30‰, respectively, relative to atmospheric N$_2$ and O$_2$ [*Dore et al.*, 1998; *Kim and Craig*, 1990; *Naqvi et al.*,

1998; *Yoshinari et al.*, 1997] (isotopic data from the top 1000 m of the ocean were used). Because of the large range of the isotopic signatures of the different sources we calculate the change in $\delta^{15}N$ and $\delta^{18}O$ of tropospheric N_2O for an ocean depleted and an ocean enriched scenario using the same isotopic signatures of the different sources as *Rahn and Wahlen* [2000] and assuming steady state conditions. The results from the different scenarios are used to estimate the range of the expected change. Focusing on the time period of lowest N_2O concentrations during the Holocene and assuming that the low N_2O concentrations were due to a reduced soil source, the calculated differences in $\delta^{15}N$ and $\delta^{18}O$ of tropospheric N_2O between the time of lowest N_2O concentrations and the preindustrial time are $\sim 0.3-0.4$ and $0.1-0.5$‰, respectively. For the case that a reduction in the N_2O flux from the ocean was entirely responsible for the low N_2O concentrations, the differences are about -0.5 to -0.8‰ for $\delta^{15}N$ and about -0.3 to -1.0‰ for $\delta^{18}O$. If reductions in both soil and ocean emissions were about equally responsible for the low N_2O concentrations, they would roughly cancel each other and result in nearly no isotopic change. Thus the sign of isotopic change may be a good indicator of soil versus ocean contribution in Holocene N_2O variability. However, the calculated changes in the isotopic signatures of tropospheric N_2O are small and require a high precision for isotopic measurements on N_2O extracted from polar ice. Furthermore, the expected changes are more than one order of magnitude smaller than the ranges of isotopic signatures of the natural sources. Therefore the isotopic signatures for the different natural N_2O sources and the strength of these sources must be better constrained in order to reduce the uncertainties in the above calculation and to better interpret future isotopic records of N_2O in terms of changes in the soil and ocean contributions to the atmospheric N_2O variations in the past.

5. Conclusions

[27] The N_2O concentration shows small but significant variations during the Holocene epoch. In contrast to the last glacial period and the last glacial-interglacial transition, the N_2O record exhibits more similarities with the CO_2 record than with the CH_4 record. To define the causes of the observed N_2O concentration changes, additional work is necessary to better understand the global climate during the Holocene in general as well as the influence of changing climate on the different N_2O sources. Measurements of $\delta^{15}N$ and $\delta^{18}O$ and intramolecular site preference in N_2O isotopomers [*Yoshida and Toyoda*, 2000] on N_2O extracted from polar ice together with better constrained natural sources and their isotopic signatures may be helpful in distinguishing between different N_2O sources and source strength in the past. Models of the nitrogen cycle in the terrestrial biosphere and in the ocean will help to quantify global N_2O fluxes under different environmental conditions.

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