Methane and nitrous oxide in the ice core record

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Polar ice cores contain, in trapped air bubbles, an archive of the concentrations of stable atmospheric gases. Of the major non-CO2 greenhouse gases, methane is measured quite routinely, while nitrous oxide is more challenging, with some artefacts occurring in the ice and so far limited interpretation. In the recent past, the ice cores provide the only direct measure of the changes that have occurred during the industrial period; they show that the current concentration of methane in the atmosphere is far outside the range experienced in the last 650 000 years; nitrous oxide is also elevated above its natural levels. There is controversy about whether changes in the pre-industrial Holocene are natural or anthropogenic in origin. Changes in wetland emissions are generally cited as the main cause of the large glacial–interglacial change in methane. However, changing sinks must also be considered, and the impact of possible newly described sources evaluated. Recent isotopic data appear to finally rule out any major impact of clathrate releases on methane at these time-scales. Any explanation must take into account that, at the rapid Dansgaard–Oeschger warmings of the last glacial period, methane rose by around half its glacial–interglacial range in only a few decades. The recent EPICA Dome C (Antarctica) record shows that methane tracked climate over the last 650 000 years, with lower methane concentrations in glacial than interglacials, and lower concentrations in cooler interglacials than in warmer ones. Nitrous oxide also shows Dansgaard–Oeschger and glacial–interglacial periodicity, but the pattern is less clear.

Keywords: ice cores; methane; nitrous oxide; Quaternary; glacial–interglacial cycles; pre-industrial

1. Introduction

After water vapour and carbon dioxide (CO2), methane (CH4) and nitrous oxide (N2O) are the most important long-lived greenhouse gases in the atmosphere. They are also important components of natural biogeochemical cycles, so that understanding changes in their concentration in the atmosphere is an indication of understanding of the underlying biogeochemistry and its reaction to external change. However, systematic measurements in the atmosphere began rather

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recently (e.g. in 1978 for CH4; Dlugokencky et al. 1994). Therefore, to establish the extent of recent increases in concentration, the context of natural variability and the processes underlying natural changes in these gases, it is necessary to find other ways to establish their evolution with time. Fortunately, we do not have to engage with proxy methods (where we measure one parameter to estimate the value of another) because a natural archive, polar ice, preserves samples of ancient atmospheric air, from which the concentrations of stable trace gases can be measured directly (Raynaud et al. 1993; Stauffer et al. 2002).

On the polar plateaus of Greenland and Antarctica, snow generally does not melt, but is compressed by the weight of overlying snow, eventually turning to solid ice with enclosed air bubbles. These bubbles become isolated from the overlying atmosphere at depths of typically 60–100 m, mainly depending on the local temperature and snow accumulation rate (Schwander & Stauffer 1984). They act as tiny, well-sealed canisters containing a sample of all the stable gases in the atmosphere, modified only slightly by fractionation processes in the firn column. If the air can be retrieved again, it can be treated as a sample of ancient air in exactly the same way as the contents of a flask of modern air, albeit with a much lower temporal resolution. All the stable components of the air, including (provided there is enough volume available) trace substances and isotopic compositions, can be measured.

CH4 concentrations have been measured frequently in polar ice for many years now (e.g. Stauffer et al. 1985; Chappellaz et al. 1990; Etheridge et al. 1998; Spahni et al. 2005). As well as providing a record of the evolution of CH4 concentrations, CH4 is an important contributor to the dating and synchronisation of ice cores. This is because it shows many rapid variations and these have to be recorded almost simultaneously in different ice cores, including ones from different hemispheres. N2O (e.g. Flückiger et al. 1999; Spahni et al. 2005) has been measured routinely in ice cores only more recently.

2. Methods

Common to all ice core gas measurements is the need to extract air from the ice; the measurement methods are often similar to those used for modern air samples. Different laboratories use different methods for gas extraction (and indeed some methods are appropriate only for certain gases). Generally the ice is placed in a container and this is evacuated to remove all modern air. The ice may then either undergo a melt–refreeze process (Raynaud et al. 1988) that expels the gases or may be crushed into tiny fragments with a ‘needle-cracker’ (Neftel et al. 1985) or a ‘cheese-grater’ technique (Etheridge et al. 1996). Deeper in the ice sheet, the air bubbles slowly become incorporated into the ice as clathrates and particular care is needed to extract the air as quantitatively as possible because there can be some fractionation between bubbles and clathrates during the period when both are present.

CH4 and N2O concentrations are measured in the extracted air by gas chromatography (typically with flame ionization detector for CH4 and electron capture detector for N2O). Analytical uncertainties of order 5–10 ppbv are quoted for CH4, and 2–4 ppbv for N2O, equivalent in each case to around 1% of the pre-industrial concentration. (Note: trace gas concentrations are generally presented as mixing ratios, e.g. as parts per billion by volume, ppbv.) In recent
years, the isotopic composition of the gases has also been measured using isotope ratio mass spectrometry; the small volumes of gas available from ice make this a challenging analytical task.

While ice with a high impurity content can give artefacts for CO₂ (Tschumi & Stauffer 2000), affecting Greenland but not Antarctic CO₂ measurements, there appear to be no such problems for CH₄, and artefact-free data can be obtained from both Greenland and Antarctica, and for glacial and interglacial periods. N₂O appears to suffer from artefact production, with a few outliers of high concentration in Greenland cores (Flückiger et al. 1999), and sections of unexpectedly high scattering of values in Antarctic ice (Spahni et al. 2005). It appears that only ice with high impurity concentrations suffers these effects, and it is not yet clear whether production within the ice (which appears to occur with all extraction methods) is chemical or biological (Sowers 2001). Most authors have dealt with this problem by removing artefacts statistically; this inevitably leads to gaps in the record of N₂O concentration and to some lingering uncertainty about the veracity of the data for this gas in certain time periods.

A few of the data discussed in this paper are derived from measurements of the air in the firn column above the depth where the ice encloses air bubbles. Such air can be sampled using a pump attached to a long tube attached to an inflatable bladder which ensures that air is drawn only from a limited depth range. Firn air sampling (e.g. Bernard et al. 2006) allows access to air just a few years to decades old and in much larger volumes than are usually available in ice cores themselves.

3. The last 2000 years

To determine the evolution of trace gas concentrations through the industrial era (and a context of variability from the preceding centuries), a record of very high time resolution is required which implies using a site with high snow accumulation rate. The Law Dome site on the edge of East Antarctica is particularly suitable; several cores have been used with snow accumulation rates of up to 1100 kg m⁻² yr⁻¹. The air at a particular depth in an ice core has a spread of ages, due to diffusion of air in the firn and the fact that air of a particular age becomes sealed at a range of depths. At sites in central Antarctica with very low snow accumulation rates, the age spread (and hence the practical temporal resolution) can be as high as several centuries (Schwander & Stauffer 1984); at Law Dome, the spread is 10–20 years (Etheridge et al. 1998), allowing production of well-resolved records and measurements within ice cores of recent decades.

(a) CH₄

The high-resolution CH₄ record for the last 1000 years (Etheridge et al. 1998) has recently been extended to 2000 years and supplemented with an N₂O dataset of the same length (MacFarling Meure et al. 2006). Other data from sites with lower resolution confirm the main conclusions (Blunier et al. 1993; Sowers 2001; Flückiger et al. 2002).

For CH₄, the background concentration in the centuries before AD 1800 was around 700 ppbv, albeit superimposed on centennial-scale fluctuations of order 40 ppbv and a slow increasing trend of order 5 ppbv per century (MacFarling Meure et al. 2006; figure 1). Given that the modern value in Antarctica is 1730 ppbv
(annual average for Antarctic sites for year 2005 in NOAA CMDL database at http://www.cmdl.noaa.gov/ccgg/), the concentration has increased by approximately 150% above the pre-industrial value. However, the value was only 870 ppbv in the year 1900, indicating that by far the majority of the increase occurred during the twentieth century. Modern measurements show that concentrations have stabilized in the early years of the twenty-first century (Bousquet et al. 2006).

During the last half of the twentieth century, CH$_4$ concentrations were increasing on average by more than 10 ppbv yr$^{-1}$ (figure 1). $^{13}$CH$_4$ data from atmospheric archives (e.g. Etheridge et al. 1998) as well as firn air and ice cores (Ferretti et al. 2005; Sowers et al. 2005) show methane became isotopically heavier during the twentieth century (values increasing from $-49\%e$ to just above $-47\%e$). This implies a shift in the balance of sources towards those that are isotopically heavy (fossil and pyrogenic) in comparison with the isotopically light biogenic sources. This is consistent with inventories of methane sources (e.g. IPCC 2001) that propose that natural sources are predominantly biogenic, while increased emissions arise from isotopically heavy direct anthropogenic sources (including energy usage and biomass burning) as well as biogenic sources under human influence such as increased numbers of
ruminants and increased rice cultivation. While the isotopic data are certainly helpful in pinpointing sources, we also have to explain the observation (Ferretti et al. 2005) of heavy isotopic values ($\delta^{13}C_{w}K_{47}\%$) in the first millennium AD and indeed apparently somewhat heavier values in the pre-Boreal period (11 kyr BP, where kyr BP denotes thousands of years before present; Schaefer et al. 2006). We will return to this topic in §8.

A further complication in interpreting both recent and natural changes is that the sources have not yet been well quantified. For example, a previously unconsidered natural source of methane from plants under aerobic conditions was recently announced (Keppler et al. 2006), although its source strength may be much less than originally proposed (Houweling et al. 2006; Kirschbaum et al. 2006). The potential importance of thaw lakes as part of the wetland source of CH$_4$ has also only recently been highlighted (Walter et al. 2006). Whatever the detailed causes, the change in concentration of CH$_4$ observed in the ice core record suggests that sources must have increased very strongly in the last 200 years; although the sinks (especially OH in the atmosphere) may also have changed, estimates are that the pre-industrial source strength was around 250 Tg yr$^{-1}$, increasing to near 600 Tg yr$^{-1}$ at the end of the twentieth century (Etheridge et al. 1998).

Figure 2. CH$_4$ and N$_2$O records over the last 650 kyr (Spahni et al. 2005 and references therein), based on data from Dome C (CH$_4$, purple line; N$_2$O, red line; excluding data believed to contain artefact) and Vostok (CH$_4$, blue line). Also shown are the $\delta D$ records from Dome C (black line; EPICA Community Members 2004) as well as from Vostok (grey line, $+42\%e$; Petit et al. 1999). Grey shaded areas highlight interglacial periods with a Dome C $\delta D$ value more than $-403\%e$ (EPICA Community Members 2004). Marine isotope stage numbers are shown at the bottom of the figure, and all data are on the EDC2 time scale.
The concentration of N$_2$O between AD 1000 and 1800 was close to 270 ppbv (figure 1; MacFarling Meure et al. 2006) and altered little in the last four millennia (Flückiger et al. 2002). This compares with a value of 319 ppbv for Antarctic sites for the year 2005 (NOAA CMDL database at http://www.cmdl.noaa.gov/ccgg/). The increase in the last 200 years has therefore been 20% for this gas. It really began only in AD 1850 (figure 1d) with concentrations exceeding 280 ppmv first observed in about AD 1905 and 300 ppmv being reached in the mid-1970s. The concentration of this gas therefore continues to rise sharply.

Isotopes of N$_2$O ($^{15}$N and $^{18}$O) measured in firn air and ice show decreasing values (Sowers et al. 2002; Ishijima et al. 2007) that are considered to be consistent with an increasing importance of agriculture (and in particular the use of fertilizers) for N$_2$O (Sowers et al. 2002). Recently, the first measurements of position-dependent $^{15}$N in firn air and ice have been reported along with further data for $^{18}$O (Bernard et al. 2006). The data remain quite scattered, but they support the earlier data, and open up the possibility that more precise measurements (including those of the position-dependent $^{15}$N) may in the future help to distinguish source and sink effects or the importance of natural and artificial fertilizers.

4. Glacial–interglacial cycles

The climate record of the last several hundred thousand years is dominated by the alternation between relatively short interglacial warm periods (such as the last 11 kyr) and much longer glacial cold periods. These cycles recur on about 100 kyr periods. Together with the cores covering a single glacial–interglacial cycle, there are three cores providing Antarctic climate records over multiple cycles: Dome Fuji covering three cycles (Watanabe et al. 2003); Vostok covering four cycles (Petit et al. 1999); and EPICA Dome C covering eight cycles (EPICA Community Members 2004). Greenhouse gas records have so far only been published to 650 kyr BP (Siegenthaler et al. 2005; Spahni et al. 2005). The pattern of Antarctic climate seen in these cores is that of glacial–interglacial cycles with a predominant period of 100 kyr (as also seen in other climate records around the globe; e.g. Lisiecki & Raymo 2005). The most recent four cycles show long glacials with short interglacials, and a range for Antarctica of around 10°C between warm and cold (Petit et al. 1999). The cycles preceding 450 kyr BP show somewhat longer but cooler interglacials (EPICA Community Members 2004).

The pattern of CH$_4$ concentrations (Petit et al. 1999; Spahni et al. 2005) has many similarities to that of the climate record (figure 2) and indeed to that of CO$_2$ (Siegenthaler et al. 2005). Concentrations are consistently high in interglacials and lower in glacials, with a range from approximately 360 ppbv in the last glacial maximum (LGM) up to 700 ppbv in the Early Holocene and the pre-industrial period. The highest value in the pre-industrial record (for marine isotope stage (MIS) 9) is 773 ppbv. The ‘weaker’ interglacials of the period before 450 kyr BP show lower interglacial CH$_4$ concentrations, maximizing at around 600 ppbv and scaling more or less with temperature (Spahni et al. 2005).

However, while the pattern for CO$_2$ is very similar indeed to that of Antarctic temperature, suggesting a dominant role for Southern Ocean processes in controlling atmospheric CO$_2$, CH$_4$ shows a much higher variability during...

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glacials. We examine this further in §5, but meanwhile we note that in the last glacial cycle, this variability follows that of the Dansgaard–Oeschger (D–O) temperature cycles that are so prominent in Greenland ice core records.

$N_2O$ shares some of the characteristics of the $CH_4$ record. Values tend to be higher (typically 270 ppbv) in interglacials than in glacials (minima around 200 ppbv are seen; Sowers 2001; Sowers et al. 2003; Flückiger et al. 2004; Spahni et al. 2005). However, there is no strong difference between the concentration in the ‘early interglacials’ and those seen after 450 kyr BP. Compared with $CH_4$, $N_2O$ concentrations remain elevated at interglacial levels for longer periods. There is also again strong variability (at D–O periods, see §5) during glacials. The $N_2O$ record is less complete than that of other trace gases because data where artefacts were suspected have been excluded.

5. Dansgaard–Oeschger events

The D–O events are the most important climate signal for the last glacial period in Greenland (North Greenland Ice Core Project Members 2004) and most Northern Hemisphere records; they also have weak Antarctic counterparts (EPICA Community Members 2006) which suggest that they involve changes in ocean heat transport (Stocker & Johnsen 2003). They consist of numerous sharp climate jumps, which in Greenland can have an amplitude as high as 15°C (Huber et al. 2006).

$CH_4$ shows a clear signal at every D–O event (figure 3; Brook et al. 1996, 2000; Flückiger et al. 2004). At the temperature increase that starts a D–O event, it has been shown (by the use of $^{15}N$ in $N_2$, which imprints a signal into the gas record for a rapid change in temperature due to the thermal gradient imposed on the firn column) that the start of the methane response typically lags the start of the temperature rise by less than 30–70 years (Severinghaus et al. 1998; Flückiger et al. 2004). The increase in $CH_4$ is completed in typically about a century.

The $CH_4$ response in D–O events is typically of order 100 ppbv (figure 4), but it does vary with each event and does not appear to be strongly related to the strength of the Greenland temperature change. For example, for D–O 10 and 11, $CH_4$ averages at over 100 ppbv higher than in the surrounding glacial periods (Flückiger et al. 2004); while for D–O 19 and 20, which show a stronger oxygen isotope signal in Greenland, the interglacial $CH_4$ is elevated by only approximately 50 ppbv. It has been pointed out (Brook et al. 1996; Flückiger et al. 2004) that the pattern of the amplitude of the $CH_4$ D–O signal resembles that of Northern Hemisphere low and mid-latitude summer insolation (i.e. it has a precessional signal).

$N_2O$ also shows a signal (figure 3) for every D–O event where it has been possible to produce reliable data (Sowers et al. 2003; Flückiger et al. 2004). The amplitude of the D–O changes is typically around 40 ppbv and shows no particular relationship with insolation or with $CH_4$ amplitudes (the amplitude is higher for D–O 19 and 20 than it is for D–O 10 and 11). Instead, the $N_2O$ amplitude seems to be correlated to the length of the D–O event (Flückiger et al. 2004). The D–O related $N_2O$ changes are smoother than those of $CH_4$ and indeed the rise in $N_2O$ often appears to pre-date the rise in $CH_4$ by some centuries. It should be remembered that, at least for long D–O events, the Antarctic
counterpart consists of a southern warming during the cold D–O phase (Blunier & Brook 2001). Thus, the N$_2$O rise might consist partly of a delayed response to the southern warming, followed by a response controlled by the north.

An important consequence of the D–O variability in both gases is that successful explanations of the glacial–interglacial amplitude must also be capable of explaining the fact that around half the amplitude of response occurred at intervals throughout the glacial and that, for CH$_4$, the response could occur within about a century. This is most clearly demonstrated for the Bølling–Allerød, Younger Dryas and the final warming into the pre-Boreal period (figure 5).

6. The causes of the observed glacial–interglacial and D–O CH$_4$ changes

Most analyses of the ice core data have tended to assume that changes in wetland emissions are responsible, with much of the discussion concentrating on apportioning those changes between the tropical and northern wetlands (e.g. Chappellaz et al. 1993a, b; Brook et al. 1996). However, changes in the concentrations of sinks may also be important and the possible influence of other sources (marine hydrates, biomass burning and vegetation) must also be considered.
There are a number of tools available for distinguishing different causes of the observed changes in atmospheric composition. Firstly, isotopic data ($^{13}$C, D, and eventually $^{14}$C) can provide constraints on the relative importance of different sources (as already discussed for the last 2000 years). Secondly, because the lifetime of methane (less than a decade) is not many times larger than the interhemispheric mixing time, we expect latitudinal inhomogeneity in the distribution of sources and sinks to lead to significant interhemispheric differences in concentration. Thus, by measuring the difference between Greenland and Antarctic concentrations, we can estimate the latitude of sources (assuming a uniform sink). As models of the Earth system become more complex, it has become possible to attempt bottom-up modelling in which climate changes drive changes in vegetation and emissions. Such exercises can test hypotheses about the influence of climate on sources and sinks to see whether they fit the data constraints. Finally, we can search for other constraints on the sinks of methane. As an example, there was a proposal that (Staffelbach et al. 1991) measurements of formaldehyde in polar ice could be used to indicate the strength of the atmospheric OH sink for CH$_4$; unfortunately, we now know that depositional and postdepositional effects control much of the variability in formaldehyde in ice cores (Hutterli et al. 2002), making this molecule currently impractical as an indicator of the sink. We will not discuss this further here, but there is still hope that other markers may be found that would provide constraint.

Figure 4. Oxygen isotope (North Greenland Ice Core Project Members 2004), temperature (red; Huber et al. 2006), CH$_4$ (green) and N$_2$O (Flückiger et al. 2004) data from NorthGRIP, Greenland over the period of 38–49 kyr BP on the SS09_sea time-scale (Johnsen et al. 2001). The period from D–O event 12 to 8 is shown (numbers at top of figure). The temperature curve was reconstructed using measurements of $^{15}$N$_2$ and firn air modelling (Huber et al. 2006).

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There have been strongly argued suggestions that emissions of marine hydrates (Nisbet 1992; Thorpe et al. 1996; Kennett et al. 2002) may have played a significant role in the changing methane record, and indeed as a trigger, in Late Quaternary climate change. Very large events, that would be observed as very high methane concentrations, can almost certainly be ruled out; no such very large spikes have been observed and the chance that they have been missed in the sampling regime to date is very low (Brook et al. 1996; Thorpe 1996). New data (Sowers 2006) on the deuterium content of CH$_4$ from the Greenland GISP2 core appear to rule out any significant role for marine hydrates in the last deglaciation or some D–O events. Specifically, the $\delta D$ value became more negative during warmings, while the expectation for the clathrate source would be that it would drive the signal more positive. Only if the clathrates had an unexpected isotopic signature, would they still be viable as an explanation for the observed changes. Although suitable isotopic data are not yet available for every change in CH$_4$ concentration, we consider it unlikely that the marine hydrates play any significant role at these time-scales.

Recently, $^{13}$CH$_4$ data have been obtained across the Younger Dryas/pre-Boreal warming (Schaefer et al. 2006), using the large volumes of ice available from old ice that outcrops near the west Greenland ice margin. No significant change was observed across the transition, suggesting that the increased source strength arises from increasing emissions from existing sources or at least from sources with similar isotopic content, rather than from new sources. However, the

Figure 5. Composite of CH$_4$ measurements from GRIP and NGRIP over the last 40 kyr (EPICA Community Members 2006 and references therein). The arrow shows a typical glacial–interglacial range, and the figure shows that the rapid events span a large part of that range. The figure is annotated to show the timing of some of the important climate features that are mentioned in the text and that are also manifested in changes in CH$_4$ concentration: YD, Younger Dryas cold period; B/A, Bølling–Allerød warm period; LGM, last glacial maximum; D–O 8, Dansgaard–Oeschger warm event number 8.
value of $\delta^{13}$C, at $-46\%$, is surprising, being somewhat heavier than that of recent air. This finding needs to be validated at other sites, and then its implications require further consideration.

The differences between CH$_4$ concentrations in Greenland and Antarctica have been assessed in a number of papers (Brook et al. 2000; Dällenbach et al. 2000). It is of course important to use records from both hemispheres that have the same calibration and to align the time-scales very carefully; both factors impose some uncertainty on the interhemispheric differences. The data have usually been analysed using a simple three box model (northern, southern and tropical sources), assuming changing sinks played little role. Since the southern source is assumed to be very small, for a CH$_4$ increase this method essentially assigns the majority of increased emissions to a tropical source when the interpolar gradient decreases and to a northern source when it increases.

Summarizing from these papers, one would estimate that the increased concentration of CH$_4$ from D–O cold to warm periods (between 25 and 46 kyr BP) was mainly due to increases in northern sources; the decrease from the Bølling–Allerød to the Younger Dryas would have to be due to a decrease in tropical sources and the final warming out of the Younger Dryas would require both sources to increase significantly (table 1). The implication is that both the tropics and high latitudes must be involved but that their relative influence may vary with time. Further work will be required on other time periods to confirm these conclusions and to assess their significance; for example, in the face of the apparent precessional influence on D–O CH$_4$ amplitude.

Bottom-up modelling studies have found that the expected changes in CH$_4$ sources are insufficient to fuel the glacial–interglacial changes observed in CH$_4$ concentration (Kaplan 2002; Valdes et al. 2005). Changes in the sink are also required; it was suggested that this might have arisen from a major increase in

Table 1. Estimated northern and tropical CH$_4$ source strengths for different time periods. This is based on a box model using the concentration and the interpolar gradient in concentration, with data from the ice cores at Taylor Dome and GISP2 (Brook et al. 2000), or at Byrd, Vostok and GRIP (Dällenbach et al. 2000). The emissions from the southern box are assumed steady at 15 Tg yr$^{-1}$ (warm periods, and Younger Dryas in Brook et al. (2000)) or 12 Tg yr$^{-1}$ (LGM and D–O cold periods). The northern box was taken as 30° N to 90° N, while the tropical box was from 30° N to 30° S.

<table>
<thead>
<tr>
<th>period</th>
<th>time-interval (ka BP)</th>
<th>north (Tg yr$^{-1}$)</th>
<th>tropics (Tg yr$^{-1}$)</th>
<th>reference</th>
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<td>31 ± 6</td>
<td>77 ± 6</td>
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<td>80 ± 11</td>
<td>Brook</td>
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<td>LGM</td>
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<td>16.7–20.3</td>
<td>14 ± 5</td>
<td>80 ± 5</td>
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<td>79 ± 23</td>
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isoprene (and other VOCs; volatile organic compounds) production in the Holocene compared with the LGM (Valdes et al. 2005; Kaplan et al. 2006). This would have led to a decrease in OH concentration and an increase in CH$_4$ lifetime. A model that includes this sink effect agrees reasonably well with the data, but it is not clear whether it can also account for the rapidity of changes or for the D–O changes in CH$_4$ concentration. It is interesting to note that, in the model discussed above (Valdes et al. 2005), the glacial–interglacial change is driven mainly by changes in the northern wetland source and in the tropical VOC-led sink.

While the studies above and others (Lathiere et al. 2005) all estimate a significant reduction in VOC emissions during the LGM, they neglect laboratory findings (Monson et al. 2007, presented at this meeting) that low CO$_2$ concentrations might lead to an increase in VOC emissions, possibly compensating other effects (Arneth et al. 2007). Changes in the geographical distribution of fire in the LGM would also be expected to affect the oxidizing capacity of the atmosphere, and hence CH$_4$ lifetime (Thonicke et al. 2005), but the magnitude of the effect has not been quantified. We conclude that there is currently little confirmed constraint, either from models or data, on the relative importance of source and sink changes. The inclusion of isotopic constraints in future modelling exercises would be one important advance in this respect.

In summary, we can conclude that the evidence against an important role for marine clathrates is now very strong, leaving the wetland source still as the main player in the observed changes, with both northern and tropical sources playing a role at different times. However, the bottom-up models cannot reproduce the size of source change that is required and appear to demand an important change in the sinks as well. Unfortunately, there are as yet no data constraints on this balance. Additionally, it will pose a major challenge to models to show why CH$_4$ changed by up to half its glacial–interglacial range many times during the glacial period; transient models will be required to establish whether explanations can account for the speed of many of the changes. Slow processes such as the exposure of land surface as the ice sheet retreated are clearly not capable of producing such fast variations.

7. Causes of N$_2$O changes

There is little additional information about the causes of the glacial–interglacial or D–O changes in N$_2$O. Isotopic data (Sowers et al. 2003) suggest that there was little change in the ratio of terrestrial to marine emissions of N$_2$O during the last 33 kyr. This implies that both sources increased by around 40% at the termination of the last glacial period. The shape of the D–O signal in N$_2$O, with its slow rise pre-dating the onset of the D–O event in Greenland climate and in methane, but culminating in a peak during the period of D–O warmth, would be consistent with both a southern (oceanic) and a northern (terrestrial) source being involved. One modelling study (Goldstein et al. 2003) that attempted to assess the change in N$_2$O that would result from an event such as the Younger Dryas cooling found that changes in the ocean could only account for about one-third of the 30 ppbv drop observed during this period; the authors inferred that terrestrial changes must also have been involved. Both modelling studies and further isotopic data will certainly be required to take this discussion beyond the rather qualitative statements made in this paragraph.
Although Holocene (pre-industrial) variability in CH$_4$ and N$_2$O is relatively small compared with the glacial–interglacial change, it is nonetheless significant and demands explanation.

N$_2$O concentrations reached approximately 270 ppbv in the Early Holocene (figure 6). They then fell to just below 260 ppbv at about 8 kyr BP before rising again to 270 ppbv in the last two millennia (Flückiger et al. 2002). The time pattern of these changes is somewhat similar to that of CO$_2$, and not the same as CH$_4$. However, there is not yet a clear explanation of the cause of the drop in concentration.

CH$_4$ shows a much stronger pattern of change, decreasing from approximately 700 ppbv at the start of the Holocene to a low of approximately 570 ppbv at about 5.5 kyr BP before increasing again to 700 ppbv in the pre-industrial (Blunier et al. 1995; Flückiger et al. 2002; figure 6). The changes in both directions are gradual. They are therefore not at all similar to the D–O changes of the glacial, although of comparable amplitude; as an aside, we mention that

8. The Holocene revisited

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there is one rapid methane excursion (reduction) associated with the 8.2 kyr cooling event which lasts for approximately 200 years (Blunier et al. 1995; Spahni et al. 2003) and is probably associated with changes in ocean heat transport. An analysis of the interhemispheric gradient in CH$_4$ concentrations for the Holocene suggests that the Mid-Holocene low might be mainly due to a reduction in tropical sources (drying of the tropics; Flückiger et al. 2002). The subsequent increase has been ascribed to an expansion of boreal wetlands, although this has yet to be substantiated.

Recently, it has been argued (Ruddiman 2003) that the rise in CH$_4$ between 5 kyr and the pre-industrial period is anomalous in the context of other interglacials and in relation to orbital forcing. It was then further suggested that increases in CH$_4$ (and indeed in CO$_2$) concentration even in this early period were the result of early agricultural activity in Eurasia, in particular forest clearance and rice agriculture (Ruddiman 2003). It is beyond the scope of this paper to discuss the CO$_2$ decrease during the Holocene, but it should be mentioned that this aspect of the so-called ‘early anthropogenic’ hypothesis has undergone significant criticism and modification (Claussen et al. 2005; Broecker & Stocker 2006; Masson-Delmotte et al. 2006; Ruddiman 2006). Most of the criticisms do not directly address the question whether agricultural changes could have been significant enough to induce the rise observed in CH$_4$ over the last 5 kyr. We do note however that, although MIS 5, 7 and 9 showed no phases of significantly increasing CH$_4$ concentrations, MIS 11 did see a very similar pattern to the Holocene with its early part (420–410 kyr BP) having a decline from 690 to 620 ppbv, followed by a rise back to 700 ppbv (Spahni et al. 2005). Although the orbital conditions are quite different (northern summer insolation falling during the Holocene fall and rise, and rising during the MIS 11 fall and rise), this nonetheless suggests that the Holocene rise is not necessarily anomalous.

However, a fully convincing explanation for the Holocene trends in CH$_4$ is still awaited. The story is further complicated by the finding that $\delta^{13}$CH$_4$ fell significantly during the period from about AD 1000 to 1800 in the absence of any major change in concentration, before beginning its anthropogenic rise (Ferretti et al. 2005). This was interpreted as implying significant amounts of biomass burning in the first millennium AD, which then decreased just as the industrial/anthropogenic increase in emissions became significant. While this explanation could be consistent with the data it has also to account for the finding of similarly high $\delta^{13}$C values in the pre-Boreal (Schaefer et al. 2006), when significant anthropogenically induced biomass burning is unlikely. Further $\delta^{13}$C data for the rest of the Holocene period are urgently needed, and more work is certainly needed to find a consistent explanation for all the Holocene changes in concentration and isotopic content, consistent with our knowledge of changing climate, land use and human activity.

9. Concluding remarks

Ice core data have shown that both CH$_4$ and N$_2$O show very significant glacial–interglacial changes, as well as variations at Dansgaard–Oeschger periods. New data (e.g. isotopic data) and modelling activities should allow the exact causes of the changes to be pinpointed in the next few years and placed in the context of the associated climate changes. The observed changes would lead to other
feedbacks in atmospheric chemistry, which need to be included in future coupled Earth system models. The pre-industrial Holocene also shows interesting and significant changes, and a debate still exists about their cause.

However, N\textsubscript{2}O is now well above any value so far seen in the (admittedly patchy) ice core record of the last 650 kyr. For CH\textsubscript{4}, an even stronger statement can be made: its concentration now sits above the range of natural variability for the last 650 kyr by a huge amount. The natural range appears to have been approximately 300 ppbv (from around 400–700 ppbv); the concentration is now approximately 1000 ppbv above that range, suggesting a huge perturbation of the relevant natural systems.

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