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METHANE AND THE CH_4–RELATED GREENHOUSE EFFECT OVER THE PAST 400 MILLION YEARS

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ABSTRACT. Natural variations in the tropospheric CH_4 concentration, excluding short bursts from geospheric reservoirs, have been estimated for the past 400 Ma by scaling a wetland CH_4 emission estimate for the middle Pliocene (ca. 3.6–2.6 Ma) by the relative rate of coal basin deposition at any given time in the past. Wetland CH_4 fluxes were used as inputs into the Cambridge 2-D chemistry-transport model to determine the equilibrium atmospheric response. The approach suggests tropospheric CH_4 concentrations reached exceptionally high values of ~12,000 ppb during the Permo-Carboniferous, when tropical swamplands were widespread, fell to minimum levels (~100 ppb) during the Triassic 'coal gap', averaged around 2000 to 4000 ppb during the Mesozoic and < 1000 ppb in the Cenozoic. Peak Permo-Carboniferous CH_4 levels could have contributed additional radiative forcing of ~3 to 4 W m^{-2}, after accounting for the indirect effects of increased stratospheric H_2O and tropospheric ozone. Assuming co-variance of N_2O with CO_2 and CH_4, we predict a combined additional forcing by these two trace greenhouse gases of up to 4 W m^{-2} during the warm Mesozoic. Although variations in Earth's Phanerozoic CH_4 history probably played a secondary role to atmospheric CO_2 and the evolution of the Sun in driving climate change, the combined effects CH_4 and N_2O appear to be sufficiently large to warrant incorporation into global modeling studies of past warm climates.

INTRODUCTION

Anthropogenic perturbation of the natural methane cycle over the past century (Cicerone and Oremland, 1988; IPCC, 2001, 2007) has contributed to a rise in the concentration of atmospheric CH_4. Ice-cores and geochemical evidence indicate natural variations in the atmospheric CH_4 concentration have also occurred in the geological past. Studies of air bubbles enclosed in glacial ice indicate that atmospheric CH_4 has at least doubled in concentration from the last glacial maximum to pre-industrial time (Raynaud and others, 1988; Chappellaz and others, 1990; Spahni and others, 2005). In addition, natural CH_4 emissions from the breakdown of geospheric reservoirs (for example, methane hydrates and thermal decomposition of organic matter) have been called upon to explain relatively sudden and large changes in the carbon isotopic composition of the ancient oceans and atmosphere linked to climatic change events (Dickens and others, 1995; Svensen and others, 2004; Bowen and others, 2006; Beerling and Brentnall, 2007).

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Changes in the global atmospheric CH_4 are a significant contributor to the overall greenhouse effect because on a molar basis methane is about 20 times more effective as a greenhouse gas than carbon dioxide (IPCC, 2001, 2007). CH_4 entering the stratosphere is a significant source of stratospheric water vapor through a set of reactions involving hydroxyl radical (OH) and excited atomic oxygen (O^1D) (Lelieveld and others, 1993, 1998). Atmospheric CH_4 is therefore the most significant climate forcing greenhouse gas after CO_2, and including its indirect effects on tropospheric ozone and stratospheric H_2O gives it a net forcing equivalent to about half that of CO_2 (Hansen and others, 2000, 2007; Hansen and Sato, 2004). Variations in CH_4 concentrations in the atmosphere, and hence water vapor in the stratosphere, may also lead to climate feedbacks through changes in the frequency, area and optical thickness of polar stratospheric clouds (Blake and Rowland, 1988; Thomas and others, 1989; Sloan and others, 1992; Sloan and Pollard, 1994).

The question therefore arises as to whether changes in CH_4 at different times in the Phanerozoic could have exerted an important influence on global climate (for example, Sloan and others, 1992; Schmidt and Shindell, 2003). This issue is beginning to be addressed with three-dimensional (3-D) Earth system modeling approaches to characterize the nature of a possible Permo-Triassic atmospheric perturbation (Lamarque and others, 2006), and for quantifying the contribution of CH_4 to early Eocene global warmth (Beerling and Valdes, 2002, 2003). Analyses of atmospheric CH_4 changes over the entire Phanerozoic are also addressing this issue by adopting a necessarily more simplified modeling philosophy to estimate CH_4 fluxes to the atmosphere from biological sources, and a simple model of atmospheric CH_4 oxidation (Bartdorff and others, 2008).

Here, we adopt a Phanerozoic perspective on the evolution of the CH_4 cycle, with the aim of investigating the theoretical bounds on the climatic effect of CH_4 relative to variations in atmospheric CO_2 and solar radiation over the past 400 million years, the time since the rise of large land plants. Our approach scales a new Pliocene estimate of wetland CH_4 emissions with changes in the relative deposition rate of coal basin sediments over time (Ronov, 1976; Budyko and others, 1987) to estimate potential long-term historical variations in wetland CH_4 inputs to the atmosphere. Corresponding atmospheric CH_4 concentrations are calculated with a two-dimensional (2-D) chemistry-transport model (CTM) that includes a reasonably complete treatment of the atmospheric chemical sources and sinks of CH_4, and allows realistic representation of the oxidizing capacity of the troposphere, particularly in the tropics where hydroxyl radicals (OH) are produced by photolysis of water vapor (Harwood and Pyle, 1975; Law and Pyle, 1993a, 1993b; Harfoot and others, 2008).

THE GLOBAL CH_4 CYCLE: PAST AND PRESENT

An outline of the natural, or pre-human, methane cycle is shown in figure 1. This interpretation is derived from the data of Fung and others (1991), Hein and others (1997), Cao and others (1998), Lelieveld and others (1998), Petit and others (1999), Houweling and others (1999), Kvenvolden and Lorenson (2001), and Prather and others (2001). The most important sources of atmospheric CH_4 are continental wetlands, with only minor (<15 Tg CH_4 yr^{-1}) additional emissions from other sources including the oceans, wildfires, termites, hydrates and volcanoes (IPCC, 2007). Hydrate emissions could, of course, be very variable but this variability is not considered here. Methane is produced by strictly anaerobic members of the Archaea that inhabit terrestrial wetland soils and sediments where they decompose organic matter. It is likely that for much of the past 400 million years, the contribution of CH_4 to the atmosphere from enteric fermentation by ruminants has been modest (Bartdorff and others, 2008). This implies that the relative contribution from wetlands has been larger than that given in figure 1 since swamplands originated and became widespread in the

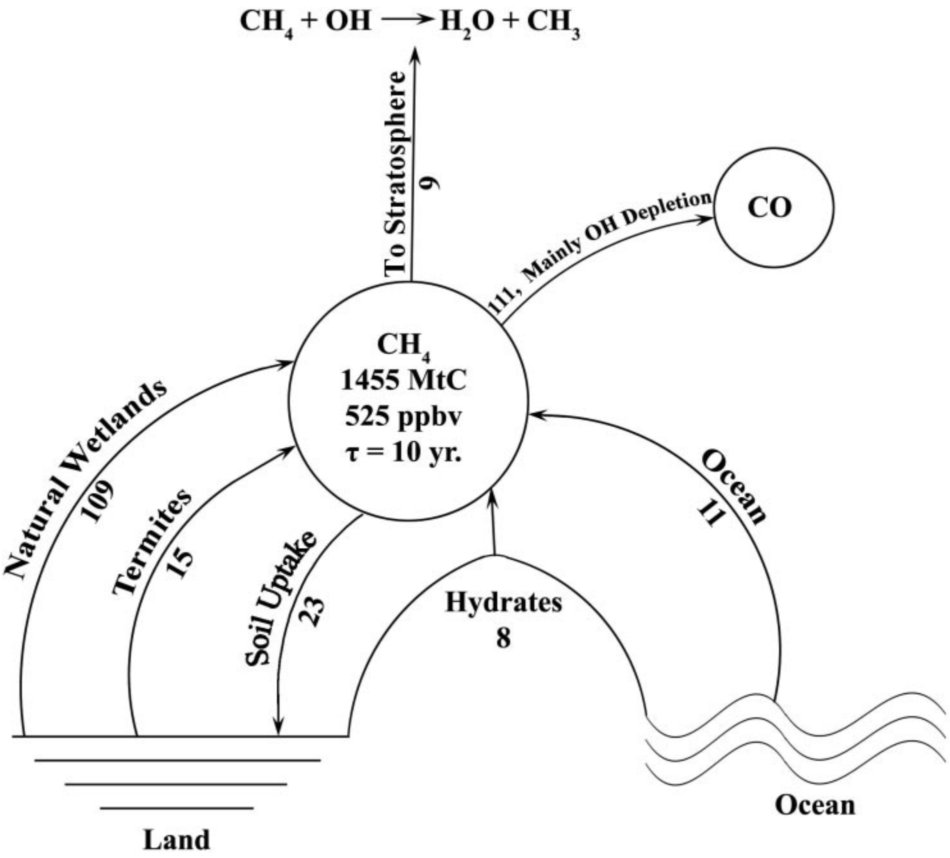

Fig. 1. Pre-human biogeochemical cycle of methane. Fluxes are in units of millions of tons of carbon as CH_4 per year. τ = atmospheric lifetime of CH_4. See text for discussion.

mid- to late Devonian as a result of the rise of large land plants (Greb and others, 2006).

As depicted (fig. 1), the major control on the production of methane under natural conditions is the abundance of wetlands, such as swamps, marshlands, bogs and lakes. In wetlands, the presence of standing water allows the development of anoxic conditions in the underlying sediments or soils that are necessary for the anaerobic production of methane by methanogens. Methane production in swamps is also favored by the low concentration of dissolved sulfate in freshwater because sulfate reducing bacteria can out compete methanogens for the breakdown products of organic matter (H_2, acetate, organic acids and alcohols) (Schimel, 2004). In anoxic marine sediments, methane production and accumulation occur only at depths in sediments below the zone of sulfate reduction, which can be large because of the high sulfate content of seawater (for example, see Berner, 1980). This makes it difficult for the methane to escape from the sediment, especially since the upward diffusing methane is consumed by reaction with aerobic methanotrophs (Oremland and Culbertson, 1992).

The abundance of wetlands in the geologic past is not known, although their evolutionary history is well documented in the fossil record (Greb and others, 2006). However, because coal is the fossil residue of swamp vegetation and mire floral

Table 1

Percent of coal basin sediments as a proportion of total clastics as a function of time. Data from Ronov (1976) and Budyko and others (1987). Relative clastic deposition rates from Berner and Kothavala (2001). Time scale after Gradstein and others (2004)

Period	Midpoint Age (Ma)	% Coal Basins	Rel. clastics deposition rate	Rel. Coal Basin deposition rate
Pliocene	3.5	2	1.00	0.020
Miocene	13	1	1.58	0.016
Oligocene	28	0 2	1.76	0.035
Eocene	45	0 3	0.91	0.027
Paleocene	60	3	0.61	0.018
Upper Cretaceous	83	0 5	1.02	0.051
Lower Cretaceous	120	0 3	0.99	0.030
Jurassic	170	0 4	0.75	0.030
Upper Triassic	215	1	0.56	0.006
Middle Triassic	236	1	0.50	0.005
Lower Triassic	248	0.5	1.16	0.006
Upper Permian	262	6	1.40	0.084
Lower Permian	285	10	0.48	0.048
Upper and Middle Carboniferous	310	22	0.63	0.139
Lower Carboniferous	335	8	0.65	0.052
Upper Devonian	375	<<1	1.27	0.001
Middle Devonian	392	0	0.87	0
Lower Devonian	408	0	0.75	0

communities, coal together with the associated more abundant but non-commercial disseminated organic matter in coal basin sediments (Berner and Canfield, 1989), can be taken to serve as a proxy for the relative abundance of the spatial and temporal extent of wetlands (Bartdorff and others, 2008).

The relative abundance of coal basin sediments, as a proportion of total clastic sediments, for the major Phanerozoic geologic periods has been estimated by Berner and Canfield (1989) based on the data of Ronov (1976) and Budyko and others (1987) (table 1) (fig. 2). The data of table 1 are in general agreement with independent estimates of the relative abundance of economic coal deposits (Bestougeff, 1980). Note that the maximum impact of coal formation occurred during the Upper and Middle Carboniferous Periods centered around 300 Ma. As this period of time appears to represent a maximum for the entire Phanerozoic, it may be possible to calculate the maximum concentration for Phanerozoic atmospheric CH_4 over the last 400 Ma.

Sediment is lost over time via erosion and subduction meaning present masses are less than those originally deposited (Veizer and Jansen, 1979; Wold and Hay, 1990; Berner and Kothavala, 2001). Obtaining a reasonable estimate of the mass of originally deposited coal requires correcting for changes in clastic sedimentation rates over time (compare Bartdorff and others, 2008). Total global sedimentation rate in the Carboniferous, for example, may have been half that of today (Wold and Hay, 1990). We calculate the relative coal basin deposition rate as the product of percentage coal basin sediments and the rate of original total clastic sedimentation, with the latter normalized to the Pliocene value (Berner and Kothavala, 2001, fig. 2A). Rather than using raw Pliocene data, which over-represents long-term erosive loss, original clastic sedimentation rate for the Pliocene was obtained by extrapolating to $t = 3$ Ma the best fit

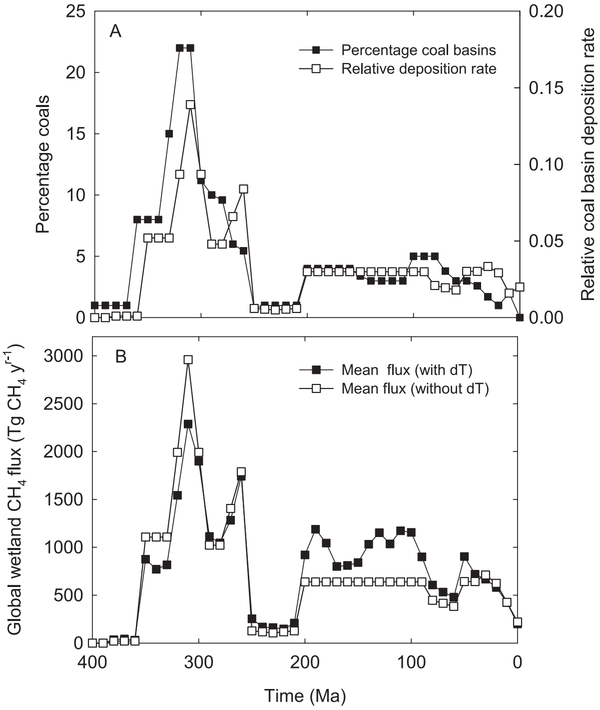

Fig. 2. Changes in (A) percentage coal basin sediments and relative deposition rate (table 1), and (B) modeled changes in global wetland fluxes based on scaling a middle-Pliocene wetland CH_4 emission estimate with the relative coal basin deposition rate in (A). Also shown in (B) is the effect of temperature-dependence (eq. 1) on emission rates.

exponential decay of Phanerozoic sediment masses (Berner and Kothavala, 2001). These calculations also assume that the content of total reduced carbon in coal basin sediments, and not just coal itself which is defined in terms of economics, has not changed greatly over time, which is reasonable (Berner and Canfield, 1989).

Conversion of relative coal basin deposition rates into wetland CH_4 emission flux, *J*, for each 10 Ma time step over the past 400 Ma, was achieved by scaling an estimate of wetland CH_4 fluxes during the Pliocene. This was obtained following the modeling protocol established by Valdes and others (2005), in which the Hadley Centre atmospheric general circulation model simulated a representative global 'average' Middle Pliocene (*ca.* 3.6–2.6 Ma) climate with revised boundary conditions derived from the United States Geological Survey's PRISM2, particularly new sea surface temperature and sea-ice fields (Dowsett and others, 1999; Dowsett, 2006). The resulting climate is generally well validated against a range of terrestrial and marine palaeoclimate datasets with global geographical coverage (Haywood and Valdes, 2006; Salzmann and others, 2008) and was used to drive a global terrestrial carbon cycle model (Beerling and Woodward, 2001) coupled to a wetland emissions model (Cao and others, 1998). This coupling of climate and carbon cycle models yielded a global wetland methane flux of 425 Tg yr^{-1}, around four times larger than obtained for the pre-industrial biosphere by adopting the same approach (table 2) (Valdes and others, 2005). The higher Pliocene wetland emissions result from more extensive tropical and northern hemisphere wetlands than were present during the pre-industrial period due to a more vigorous hydrological cycle in a warmer world with a reduced cryosphere.

Table 2

Simulated Pre-Industrial and Middle Pliocene wetland CH_4 fluxes by region. All fluxes in Tg CH_4 yr^{-1}

	Northern hemisphere 90-30ºN	Tropics 30ºN-30ºS	Southern hemisphere 30ºS-90ºS	Total
Pre-industrial				
Wetland area (10^6 km^2)	7.5	6.6	0.5	14.6
Wetland CH_4 fluxes	63.5	144.3	2.8	210.7 (163-179)[1]
Middle Pliocene				
Wetland area (10^6 km^2)	10.0	10.7	0.7	21.4
Wetland CH_4 fluxes	150.0	270.3	5.7	426.0

[1] estimated min-max range for the pre-industrial terrestrial biosphere from the recent modeling studies of Harder and others (2007) and Kaplan and others (2006).

The evolution of global wetland CH_4 emissions to the atmosphere over the Phanerozoic was obtained by scaling the Pliocene value with the relative coal basin sedimentation rates, calculated every 10 Ma as the weighted value either side of the mid-point of a geological epoch. Finally, we included a temperature dependence of the global wetland CH_4 flux, *J*, for a particular 10 Ma time-slice with an exponential temperature relationship fitted to field observations of CH_4 emissions (Christensen and others, 2003), normalized to the average global surface temperature of 14.3°C (fig. 2B), to give

$$fT_{wetland} = \frac{\exp(0.1678 \times T)}{11.07} \qquad (1)$$

the final wetland flux $J(t) = J \times fT_{wetland}$, where T in eq. (1) is global mean temperature (°C), calculated after accounting for changes in atmospheric CO_2 concentration, the evolution of the solar constant and palaeogeography (Berner and Kothavala, 2001).

MODELING EARTH'S LONG-TERM ATMOSPHERIC CH_4 VARIATIONS

We computed the atmospheric CH_4 concentration for a given wetland CH_4 flux, *J(t)* taken to be representative of each 10 Ma time step by releasing it into the lowest tropospheric layer of the Cambridge 2-D atmospheric chemistry-transport model (CTM). Because the time scale for CH_4 turnover is only about 10 years (Khalil and Rasmussen, 1989), we assume that the concentration of CH_4 is at steady state at any given time in the geologic past.

The 2-D CTM has been extensively described elsewhere (Harwood and Pyle, 1975, 1980; Law and Pyle, 1993a, 1993b) and its set-up for variable molecular O_2 levels are detailed in Harfoot and others (2007). In brief, the model calculates its own zonal mean circulation consistent with forcing by radiative, latent and sensible heating. Transport and mixing is divided into advection due to zonal mean circulation, and eddy transport arising from departures from the zonal mean. Eddy transport is parameterized as an eddy diffusion process, with appropriate diffusion coefficients (Harwood and Pyle, 1975, 1980). The model has been used extensively to consider the chemistry and dynamics of the middle atmosphere (Harwood and Pyle, 1980; Haigh, 1984; Bekki and Pyle, 1992; Bekki and others, 1994), the region of interest for this investigation.

The basic model used here includes a reasonably detailed tropospheric chemistry scheme. The major removal mechanism of atmospheric CH_4 is its temperature-dependent reaction with gaseous OH radical to form CO and subsequently CO_2 and is represented by an oxidation scheme for CH_4 and other representative non-methane hydrocarbons, as well as the gas phase chemistry of the O_x, HO_x, NO_y, ClO_y, BrO_y, SO_x families (Law and Pyle, 1993a, 1993b). The CTM also includes a detailed stratospheric chemistry scheme (Bekki and Pyle, 1992; Bekki and others, 1994). Details of calculation procedures, including the treatment of stratospheric photolysis, cloud, aerosol and tropospheric water vapor schemes, are given in Harfoot and others (2007). Pre-industrial trace gas emissions are held constant for all simulations and were: 0.7 Tg S yr^{-1} (0.5 Tg wetlands, 0.2 Tg soils), 483 Tg yr^{-1} CO, and 8 Tg N yr^{-1} (4 Tg soils, 4 Tg lightning).

Radiative heating is calculated interactively for the stratosphere: in the long wave from the mixing ratios of CO_2, H_2O, O_3, SO_2 and N_2O (Haigh, 1984), and, in the shortwave, from O_2 and O_3 mixing ratios. This formulation allowed us to include the feedback of climate on stratospheric chemistry. The model's atmosphere is heated from below by prescribed pre-industrial mean monthly sea-surface temperatures (SSTs). SSTs influence surface-to-air heat fluxes in the lowermost level and, following the adiabatic lapse rate, the temperature up to the tropopause. Radiative cooling is fixed at 1.5 K d^{-1} in the lower troposphere and 0.75 K d^{-1} in the upper troposphere.

All model calculations were run to steady-state and performed either with atmospheric O_2 variations concentration predicted over the past 400 Ma by a coupled long-term carbon and sulfur cycle geochemical model (Berner, 2006; see also Harfoot and others, 2007), or with a constant atmospheric O_2 content of 21 percent.

RESULTS AND DISCUSSION

Modeled variations in the tropospheric CH_4 levels over the past 400 Ma vary in proportion to CH_4 flux estimated to have been released from terrestrial wetlands for different eras (figs. 2 and 3, table 1). In particular, the global tropospheric CH_4 concentration peaks during the Permo-Carboniferous, when tropical wetlands were most abundant (ca. 10,000–12,000 ppb), and dips (ca. 100–200 ppb) during the Triassic 'coal gap', when they almost disappeared from the terrestrial realm with the extinction of peat-forming plants at the Permo-Triassic boundary (fig. 3A) (Retallack and others, 1996). For much of the Mesozoic, we predict tropospheric CH_4 concentrations of 2000 to 4000 ppb and for the Cenozoic, $<$1000 ppb.

The large changes in tropospheric CH_4 concentrations between the Carboniferous and Triassic are associated with a correspondingly large fall and rise, respectively, in the oxidizing capacity of the lower troposphere and ozone (figs. 3A-C). In the presence of adequate NO_x ($NO + NO_2$), oxidation of CH_4 and CO is an important mechanism for the production of tropospheric ozone (Lelieveld and others, 1993, 1998), a potent greenhouse gas and a major secondary air pollutant. Variations in global NO_x from lightning and soils over the Phanerozoic are unknown (Raven and Yin, 1998), but with pre-industrial N-sources held constant over the last 400 Ma, the variable wetland CH_4 emissions produced peak tropospheric ozone concentrations of about 80 to 100 ppb at around 300 Ma, with a slightly lower range of values for the Mesozoic and Cenozoic (60–80 ppb) (fig. 3B). We note however that for 0 Ma, the Cambridge 2-D CTM simulates a global average surface ozone concentration of ca. 40 ppb in the lowest model layer (0–4 km), which is higher than that found in the (usually much thinner) surface layer of other global chemistry models simulating a pre-industrial atmosphere (15–20 ppb) (Mickley and others, 2001), indicating that the ozone estimates in figure 3B may lie towards the upper bound. Nevertheless, our results suggest that for much of their evolutionary history, terrestrial ecosystems experienced potentially adverse surface ozone concentrations (Ashmore, 2005), with values similar to those predicted for 2100 AD (Prather and others, 2003).

A chemically and climatically important consequence of the modeled high Permo-Carboniferous atmospheric CH_4 is a corresponding peak in stratospheric CH_4

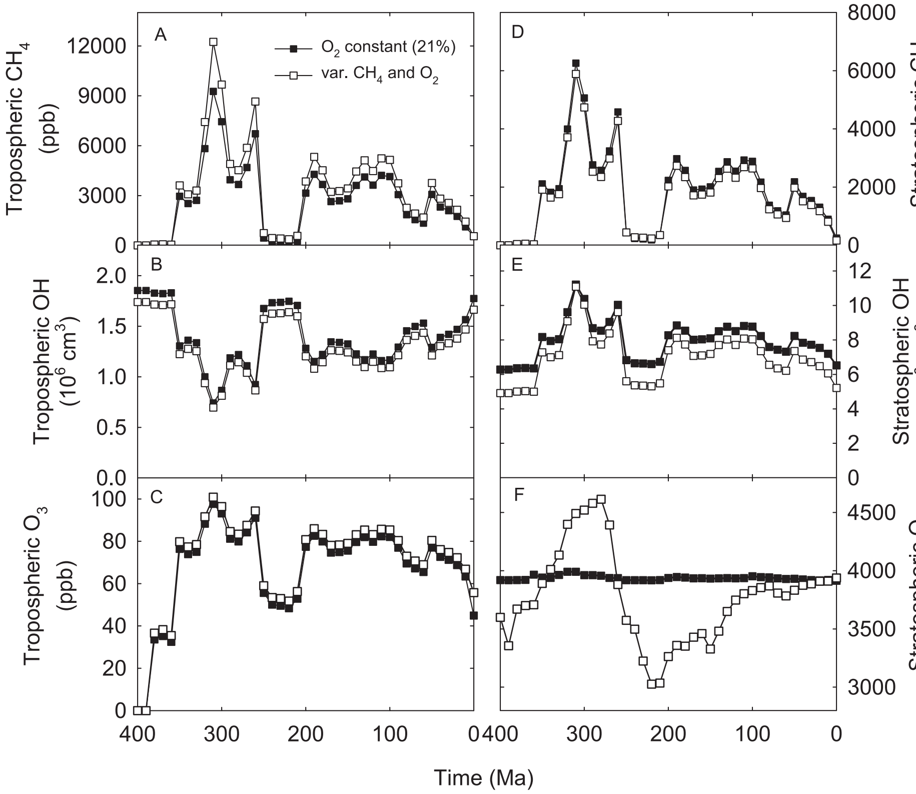

Fig. 3. Changes in the tropopsheric and stratospheric concentrations of CH_4 (A and D), hydroxyl radical (OH) abundance (B and E), and ozone (O_3) concentration (C and F) over the past 400 Ma. Calculations were made either with O_2 held at a constant 21 % (21 % O_2), or with a variable atmospheric O_2 content (Berner, 2006). See text for further details.

concentrations (fig. 3D) because more of it escapes oxidation due to the reduced tropospheric hydroxyl radical abundance (fig. 3B). At around 12,000 ppb, the CH_4 concentration (and subsequent production of stratospheric water vapor) is around the level suggested to have promoted the formation of type II polar stratospheric clouds (PSCs) in the early Eocene (Sloan and others, 1992; Sloan and Pollard, 1994). High tropospheric CH_4 concentrations, and more extensive stratospheric PSCs, might therefore constitute a previously underappreciated positive climate feedback during this interval. It could allow for an ice-free Siberian landmass at lower atmospheric CO_2 levels than estimated by coupled climate-ice sheet models that neglect this effect (Hyde and others, 2006), bringing ice-sheet model-derived CO_2 estimates closer in line with those of carbon cycle models (Berner, 2006) and fossil leaf-based paleo-CO_2 proxies (Beerling, 2002; Royer, 2006).

Variations in wetland CH_4 fluxes over the past 400 Ma have minor impacts on the ozone concentration in the stratosphere, when the atmospheric oxygen concentration is held at 21 percent (fig. 3F). For example, stratospheric ozone falls by 2.5 percent (<100 ppb) with 7 to 8 fold increase in wetland CH_4 emissions, which compares to the 20 percent reduction reported by Schmidt and Shindell (2003) in their 2-D model calculations with linearized stratospheric chemistry that lacked ozone transport by advection. Large variations are evident when CH_4 fluxes co-vary with modeled varia-

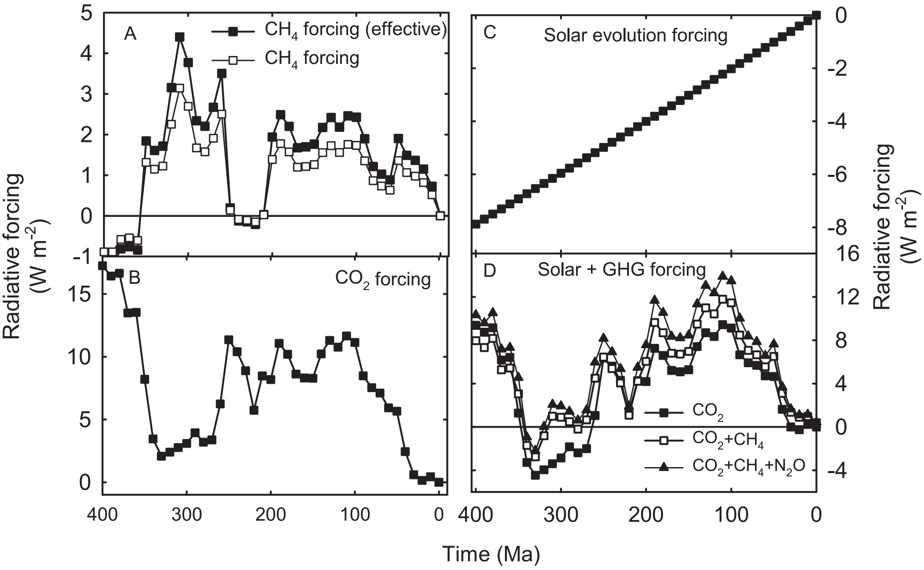

Fig. 4. Calculated changes in radiative forcing of climate by (A) CH_4, (B) CO_2 (Berner, 2006), (C) solar output (Sc) individually, and (D) collectively with and without N_2O after accounting for increased forcing by the rising solar output. See text for further details.

tions in atmospheric O_2 over the past 400 Ma (Berner, 2006), but this is simply an effect of O_2 changes (fig. 3F) (Harfoot and others, 2007). Stratospheric ozone production depends on the photolysis frequency and concentration of O_2, so that at higher O_2 concentrations the rate in the upper stratosphere leads to more ozone (Harfoot and others, 2007).

The climatic forcing F(GHG, W m^{-2}) for modeled changes in CH_4 can be estimated and compared with those for modeled CO_2 changes over the past 400 Ma using analytic expressions for individual gases derived from the 3-D Goddard Institute of Space Studies climate model radiative transfer calculations (Hansen and others, 2000):

$$F(CH_4 = 0.0406(\sqrt{m_t} - \sqrt{m_o}) - [g(m_t, n_o) - g(m_o, n_o)] \qquad (2)$$

$$F(CO_2) = f(C_t) - f(C_o), \text{ where } f(C) = 4.996 \ln(C + 0.0005C^2) \qquad (3)$$

where $g(m, n) = 0.5 \ln[1 + 2 \times 10^{-5}(mn)^{0.75}]$ $C = CO_2$ (ppm), $m = CH_4$ (ppb), $n = N_2O$ (ppb), and the subscript o refers to the (pre-human) present, and t some time in the past. Including the additional indirect forcing of CH_4 caused by increases in tropospheric ozone and stratospheric H_2O raises $F(CH_4)$ by 40 percent (Hansen and others, 2007). In our calculations, we conservatively assume a pre-industrial value for n_o of 265 ppb, and m_o of 700 ppb (IPCC, 2007).

Equation (2), modified by a factor of 1.4, indicates that at ~3 to 4 W m^{-2} the thermal forcing owing to the peak CH_4 in the Permo-Carboniferous of 10,000 to 12,000 ppb is about double that for CO_2 during this interval (2 W m^{-2}) (figs. 4A and 4B). Radiative forcing by CH_4 is therefore quite high for this interval. In addition, for most of the Mesozoic and Cenozoic, forcing by variations in tropospheric CH_4 is on the order of 1 to 2 W m^{-2}, a value that is roughly a fifth of that calculated for modeled changes in atmospheric CO_2 over much of the Phanerozoic (Berner, 2006) (fig. 4B).

For comparison, CO_2 forcing is estimated to range from the relatively low pre-industrial value to up to 16 times this level at around 16.0 Wm^{-2} (fig. 4B).

In addition to changes in greenhouse gas (GHG) concentrations, the evolution of global climate over the past 400 Ma has been driven by the gradual increase in solar radiation with the evolution of the Sun (for example, Crowley, 1993; Berner, 2004). Increased solar output is estimated to have increased thermal forcing by 7 to 8 W m^{-2} during this time, a forcing that has to be summed with those arising from variations in the concentration of the greenhouse gases CH_4 and CO_2 (fig. 4C). The resulting net forcing patterns indicate that atmospheric CH_4 still exerts a significant effect during the Permo-Carboniferous, and strengthens CO_2-related forcing during warm intervals through the Phanerozoic (fig. 4D). Methane is likely to have played a more significant role in global warming at times when CO_2 forcing was low and solar radiation was similar to today, such as during the Pliocene and interglacials in the Quaternary (Raynaud and others, 1988; Hansen and others, 2007).

To this point, calculated climate forcings by atmospheric greenhouse gases over the Phanerozoic have neglected the contribution of the nitrous oxide (N_2O), another important long-lived trace greenhouse gas. However, from analyses of glacial-interglacial greenhouse gases determined from ice-core records (Hansen and others, 2005; Spahni and others, 2005), Hansen and others (2007) proposed the effective forcing of N_2O is approximately 15 percent of the sum of the effective forcing by CO_2 and CH_4, because warmer wetter climates caused by high CO_2 and CH_4 stimulate microbial N_2O production. Assuming this relationship holds over longer timescales, figure 4D reveals that including N_2O adds a further 1 to 2 W m^2 of forcing during the high CO_2 warm Mesozoic era.

The relative global mean temperature response for CH_4 and CO_2 can be estimated from a simple greenhouse function for CO_2 and CH_4 (Berner and Kothavala, 2001; Beerling and Berner, 2002), modified to include the evolution of the Sun's luminosity:

$$dT = \Gamma_{mc} \ln\left[\frac{C + \lambda M}{C_0 + \lambda M_0}\right] - Ws \times \left(\frac{t}{570}\right) \tag{4}$$

where C_0 and M_0 are the atmospheric masses of CO_2 and CH_4 (in 10^{18} mol) at $t = 0$, given 1ppm $CO_2 = 1.6 \times 10^{-4}$, and 1ppb $CH_4 = 1.67 \times 10^{-4}$, C and M are the masses of CO_2 and CH_4 respectively at some time in the past, Γ_{mc} refers to the combined CH_4 plus CO_2 greenhouse response (4 °C), and λ is the ratio of the greenhouse response of CH_4 per molecule to that of CO_2 (25). The negative term in the right hand expression accounts for the effect of increased solar luminosity on temperature, with $Ws = 7.4$ (Berner, 2004).

According to equation 4, peak tropospheric CH_4 concentrations of the Permo-Carboniferous could raise global mean surface temperatures by approximately 2 °C, and 0.5 to 1.0 °C throughout most of the Mesozoic and Cenozoic (fig. 5A). Inclusion of a CH_4-related greenhouse effect in coupled climate-ice sheet modeling for the Siberian landmass during the Permo-Carboniferous might therefore be improved (Hyde and others, 2006). Calculated CH_4-related warming is not insubstantial of itself (fig. 5A), but is quantitatively less than that of the combined effects of CO_2 and the solar constant (fig. 5B). Radiative forcing by N_2O in the Mesozoic and Cenozoic of 1 to 2 W m^2 could add a further 0.5 to 2 °C, given present-day climate model sensitivity ranges of 0.5 °C/(W/m^2) to 1 °C/(W/m^2) (IPCC, 2001, 2007; Schmidt and Shindell, 2003). These numbers clearly indicate that together N_2O and CH_4 could contribute a combined warming of up to 3 °C during peak Mesozoic warmth, for example, mid-Cretaceous 100 Ma, and point to the need for their representation in modeling studies of past climates.

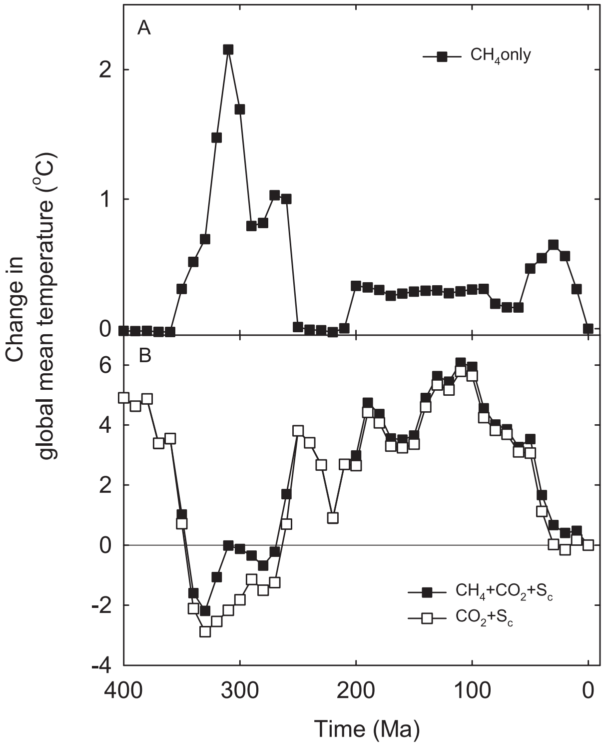

Fig. 5. Calculated change in global mean surface temperature caused by modeled changes in tropospheric CH_4 concentration (A), and (B) CH_4 plus CO_2 (fig. 3), after accounting for the evolution of the solar constant (S_c). Effective forcing in (A) accounts for methane's contribution to stratospheric water vapor and tropospheric ozone, both greenhouse gases that together raise its radiative forcing by ca. 40% (Hansen and others, 2000)

It is also important to recognize that regional greenhouse gas forcings by, for example, elevated ozone and secondary organic aerosols derived from volatile organic compounds emitted by vegetation over continental regions, may be significant feedbacks on climate (for example, Claeys and others, 2004; Beerling and others, 2007). Notwithstanding this point, compared to all the errors inherent in constructing models for CO_2 and climate over Phanerozoic time, it appears that changes in tropospheric CH_4 concentration have not exerted an effect on ancient climates as important as changes in atmospheric CO_2 and the evolution of the Sun (fig. 5).

Comparison with Earlier Phanerozoic CH_4 Calculations

Our Phanerozoic reconstruction of wetland CH_4 fluxes can be compared with that reported by Bartdorff and others (2008) (fig. 6), a comparison indicating we consistently predict the highest fluxes of the two studies, despite both using similar approaches based on relative coal basin sedimentation rates. The difference arises because Bartdorff and others (2008) predict CH_4 emissions from ancient wetlands as a function of coal basin sedimentation rates normalized to the Pliocene, the most recent period of coal deposition in Ronov's compilation (table 1), but adopt a global emission value of modern wetland soils and swamps (ca. 100 Tg CH_4 yr^{-1}). However, paleodata, and model simulations, indicate a generally warmer, wetter Middle Pliocene climate than today (Dowsett and others, 1999; Salzmann and others, 2008) favoring extensive

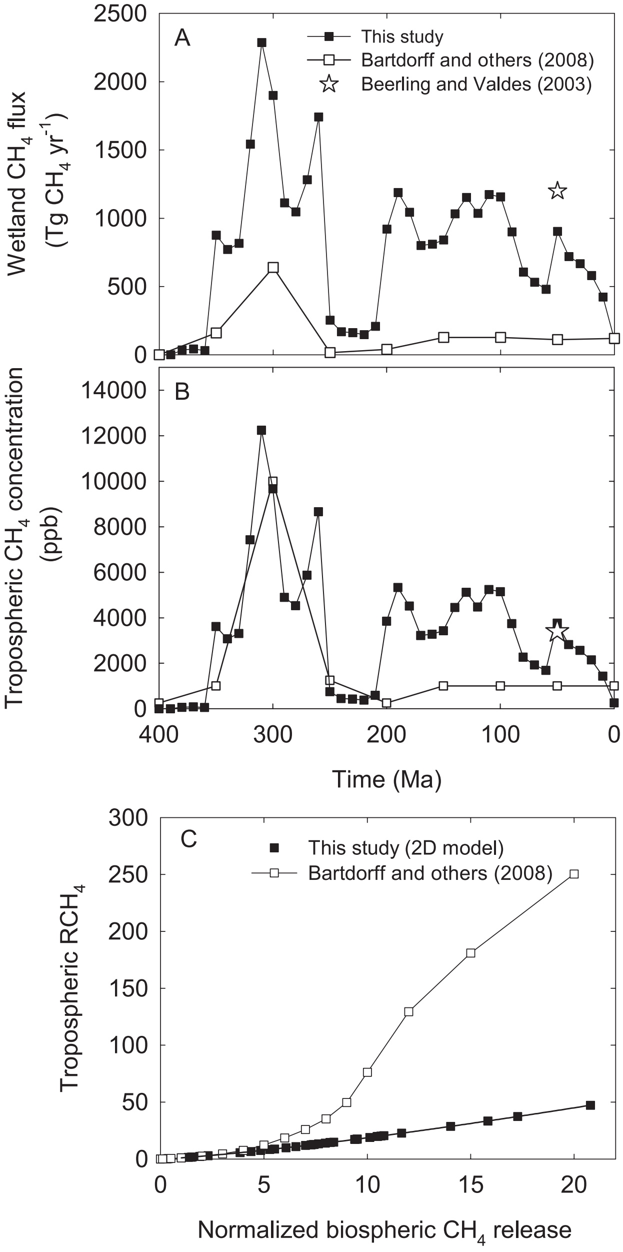

Fig. 6. Comparison of (A) wetland CH_4 fluxes, (B) tropospheric CH_4 concentrations and (C) modeled CH_4 flux-concentration relationship between the present study and that of Bartdorff and others (2008).

wetland formation and anaerobic CH_4 production (table 2). Normalizing Pliocene coal deposition against a value for modern wetlands may therefore significantly underestimate the strength of this source term in the global CH_4 budget.

Nevertheless, the tropospheric CH_4 concentration prediction of Bartdorff and others (2008) for the Permo-Carboniferous is similar to ours (fig. 6B). The similarity emerges because of large differences in the sensitivity of the relationship between wetland CH_4 emissions and the corresponding tropospheric concentration (fig. 6C), with the 2-D CTM predicting lower tropospheric CH_4 concentrations by an order of magnitude than the simple one-step oxidation approach of Bardtdorff and others (2008). We suggest this is because the CTM captures the latitudinal and seasonal variations in the atmospheric chemical processes that allow the maintenance of a much higher oxidizing capacity in the tropics where the generation of OH via reaction of H_2O with $O(^1D)$ is most important (Harfoot and others, 2008).

For the early Eocene, 50 Ma, coal basin deposition derived wetland emissions, and corresponding tropospheric CH_4 concentrations, can be evaluated against results obtained with a 3-D Earth system model employing a 3-D global atmospheric chemistry model coupled to the AGCM (Beerling and Valdes, 2002, 2003). In these simulations, the wetland flux at 50 Ma was at around 1200 Tg CH_4 yr^{-1} reasonably similar to that obtained from our scaling procedures and gave a tropospheric concentration identical to our results, but which is somewhat at odds with those of Bartdorff and others (2008) (fig. 6, A-C).

Modeling Caveats

We emphasize that our 400 Ma atmospheric CH_4 curves, and conclusions concerning the resulting CH_4-related forcing of climate, must be regarded as first-order estimates based on 2-D model calculations initialized with the sedimentary record of fossil wetlands. Modeled variations in CH_4 exclude the impact of variations in trace gases that can significantly alter its concentration and lifetime. Biogenic emissions of NO_x and volatile organic compounds (VOCs) will have changed in concert with the evolution of atmospheric CO_2 and climate over the past 400 Ma, as well as the productivity of the terrestrial biosphere (Beerling and Woodward, 2001; Beerling and others, 2007). VOCs and NO_x exert a major influence on tropospheric CH_4 chemistry and ozone abundance via their effects on OH, which is consumed by oxidation of VOCs and NO_x. Three-dimensional Earth system model simulations of the global CH_4 concentrations for the last glacial maximum, 21 ka, for example showed reduced emissions of VOCs from the terrestrial biosphere owing to a drier, cooler climate and contraction of forests, which amplified the chemical sink for CH_4 (Valdes and others, 2005; Kaplan and others, 2006; Harder and others, 2007). These studies also demonstrated that changes in the CH_4 sink strength are especially important when changes in climate and the absolute CH_4 are large, as is likely to have been the case over the past 400 Ma.

CONCLUSIONS

We conclude that the evolution of Earth's natural global CH_4 cycle over the Phanerozoic has been dominated by CH_4 inputs from the geographical and ecological expansion of swamps and other wetland communities since the mid to late Devonian. These major CH_4 inputs to the atmosphere are, to a first approximation, reflected in the relative rate of coal basin deposition, because coals are the fossil record of wetland environments. During the Permo-Carboniferous, when tropical mires and swamplands were widespread, the CH_4 input to the atmosphere was probably substantial, raising global tropospheric concentrations up to ca. 12,000 ppb and increasing radiative forcing by about 3 to 4 W m^{-2}, double that of CO_2 at this time. Mesozoic and Cenozoic wetlands, which were comprised of very different plant communities, are estimated to have produced tropospheric CH_4 concentrations to 2000 to 4000 ppb, adding 1 to 2 W m^{-2} of radiative forcing. The co-variance of N_2O with CO_2 and CH_4 observed in Quaternary ice cores implies by extension that N_2O was probably also higher in the past, and we estimate it supplied a further 1 to 2 Wm^{-2} for much of the past 200 Ma. Although these results suggest the trace greenhouse gases CH_4 and N_2O are clearly second-order drivers of climate change over much of the Phanerozoic compared to CO_2 and solar variability, their combined effects are sufficiently large to warrant incorporation into global modeling studies of past climates.

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