

## Reconciling the changes in atmospheric methane sources and sinks between the Last Glacial Maximum and the pre-industrial era

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[1] We know from the ice record that the concentration of atmospheric methane, [CH<sub>4</sub>], at the Last Glacial Maximum (LGM) was roughly half that in the pre-industrial era (PI), but how much of the difference was source-driven, and how much was sink-driven, remains uncertain. Recent developments include: a higher estimate of the LGM-PI change in methane emissions from wetlands—the dominant, natural methane source; and the possible recycling of OH consumed in isoprene oxidation—the principal methane sink. Here, in view of these developments, we use an atmospheric chemistry-transport model to re-examine the main factors affecting OH during this period: changes in air temperature and emissions of non-methane volatile organic compounds from vegetation. We find that their net effect was negligible (with and without an OH recycling mechanism), implying the change in [CH<sub>4</sub>] was almost entirely source driven—a conclusion that, though subject to significant uncertainties, can be reconciled with recent methane source estimates.

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### 1. Introduction

[2] Methane (CH<sub>4</sub>) is an important atmospheric constituent on account of its potency as a greenhouse gas and its influence on the tropospheric oxidizing capacity. We know from the ice record that its concentration, [CH<sub>4</sub>], at the Last Glacial Maximum (LGM; 21kyr before present) was roughly half that in the pre-industrial era (PI; ~200 yr before present): about 360 ppbv compared to around 700 ppbv [e.g., *Loulergue et al.*, 2008]. But how much of this difference was source-driven and how much was sink-driven remains uncertain. Bottom-up model studies (employing dynamic global vegetation models) suggest the reduction in natural CH<sub>4</sub> sources at the LGM, the dominant one being wetlands, can at most account for roughly half the reduction in [CH<sub>4</sub>]

[e.g., *Valdes et al.*, 2005; *Kaplan et al.*, 2006]. These studies therefore suggest an increase in CH<sub>4</sub> sinks, of which oxidation by the hydroxyl radical (OH) is by far the greatest, is needed to explain the remainder of the reduction, appealing to an increase in [OH] due to a reduction in non-methane volatile organic compound (NMVOC) emissions. Recent calculations by *Weber et al.* [2010], however, suggest the reduction in CH<sub>4</sub> emissions from wetlands at the LGM was greater than previously simulated, implying a greater role for CH<sub>4</sub> sources. Meanwhile, the proposed recycling of OH consumed in the oxidation of isoprene [*Lelieveld et al.*, 2008]—the most abundant biogenic NMVOC [e.g., *Guenther et al.*, 2006]—could alter our understanding of the influence a reduction in NMVOC emissions at the LGM had on OH, and hence the size of the sink-driven component. Here, we use an atmospheric chemistry-transport model to (1) re-examine the main factors affecting the oxidizing capacity between the LGM and the PI, (2) estimate their net effect on [CH<sub>4</sub>], subject to an established, conventional isoprene oxidation scheme, with and without the addition of a possible OH recycling mechanism, and (3) show how these estimates can be reconciled with both the findings of *Weber et al.* [2010] and the observed change in [CH<sub>4</sub>].

[3] *Chappellaz et al.* [1993] estimated, based on a reconstruction of vegetation, that CH<sub>4</sub> emissions from wetlands were 44% lower at the LGM than in the PI, underpinning a 33% reduction in total CH<sub>4</sub> emissions (including emissions from termites, biomass burning and the ocean). ‘Top-down’ Monte-Carlo calculations, designed to explain ice-core measurements of both [CH<sub>4</sub>] and δ<sup>13</sup>CH<sub>4</sub>, suggest a reduction in wetland emissions of between 41 and 57% is plausible [see *Fischer et al.*, 2008, Table S2]. But until recently, bottom-up model studies have put the figure significantly lower, between effectively no change [*Kaplan et al.*, 2006] and a reduction of 27% [*Valdes et al.*, 2005], yielding reductions in total CH<sub>4</sub> emissions of just 16% and 23% respectively. *Weber et al.* [2010], however, have calculated reductions in wetland emissions of between 35 and 42%. Had *Valdes et al.* [2005] and *Kaplan et al.* [2006] simulated a 35–42% reduction in wetland emissions, they would have calculated reductions in total CH<sub>4</sub> emissions of 30–35% and 38–43% respectively. This opens up new possibilities regarding the explanation of the reduction in [CH<sub>4</sub>] at the LGM. Allowing for the small positive feedback between the concentration and atmospheric lifetime of CH<sub>4</sub> [see, e.g., *Prather*, 2007], the largest of these reductions in total CH<sub>4</sub> emissions, one of 43%, could account for practically the entire 49% reduction in [CH<sub>4</sub>], from 700 to 360 ppbv, without any increase in oxidizing capacity (besides that which would have been induced by the reduction in [CH<sub>4</sub>]). We note that a recent

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**Table 1.** Main Features of Experiments with p-TOMCAT<sup>a</sup>

Experiment	T <sub>Humidity</sub>	T <sub>Kinetics</sub>	E <sub>NMVOCS</sub>	OH Recycling	Resolution	[CH <sub>4</sub> ] <sub>AntBL</sub> (ppbv)	τ <sub>CH<sub>4</sub></sub> (years)
A	PI	PI	PI	None	2.8° × 2.8°; 31 lev	714	8.5
B	LGM	PI	PI	None	2.8° × 2.8°; 31 lev	763 (+7%)	9.1 (+7%)
C	LGM	LGM	PI	None	2.8° × 2.8°; 31 lev	840 (+18%)	10.0 (+18%)
D	PI	PI	None	None	2.8° × 2.8°; 31 lev	558 (−22%)	6.7 (−22%)
E	LGM	LGM	None	None	2.8° × 2.8°; 31 lev	637 (−11%)	7.6 (−11%)
F	LGM	LGM	LGM	None	2.8° × 2.8°; 31 lev	692 (−3%)	8.3 (−3%)
G	PI	PI	PI	None	5.6° × 5.6°; 19 lev	715	8.6
H	LGM	LGM	LGM	None	5.6° × 5.6°; 19 lev	703 (−2%)	8.5 (−2%)
I	PI	PI	PI	Fixed	5.6° × 5.6°; 19 lev	703	8.5
J	LGM	LGM	LGM	Fixed	5.6° × 5.6°; 19 lev	689 (−2%)	8.3 (−2%)
K	PI	PI	PI	T-dep.	5.6° × 5.6°; 19 lev	707	8.5
L	LGM	LGM	LGM	T-dep.	5.6° × 5.6°; 19 lev	692 (−2%)	8.3 (−2%)

<sup>a</sup>T<sub>Humidity</sub> and T<sub>Kinetics</sub> refer to the temperatures influencing the humidity and chemical kinetics; E<sub>NMVOCS</sub> refers to the NMVOC emissions from vegetation (as specified in Table 2); and ‘fixed’ and ‘T-dep.’ refer to fixed and temperature-dependent rate coefficients in the OH-recycling reactions (1 and 2). The [CH<sub>4</sub>]<sub>AntBL</sub> and τ<sub>CH<sub>4</sub></sub> calculated in each experiment are given (see Section 2 for definitions), as are the percentage changes in these quantities in each sensitivity experiment relative to the corresponding PI model run; see text for details.

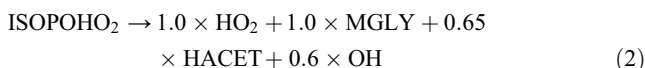
study by *Singarayer et al.* [2011] places a smaller emphasis on the role of CH<sub>4</sub> sinks than the studies of *Valdes et al.* [2005] and *Kaplan et al.* [2006].

[4] In principle, many factors could have affected the oxidizing capacity (see discussion in Section 4), but only two are identified in the literature as having had a significant influence between the LGM and the PI: the air temperature and NMVOC emissions from vegetation. The lower air temperatures at the LGM would have been accompanied by lower humidities, and hence lower [OH], as OH is formed from the reaction between excited oxygen atoms (O(<sup>1</sup>D)) and water vapor. *Martinerie et al.* [1995] estimated that, all else being equal, this would have increased the lifetime of CH<sub>4</sub>, τ<sub>CH<sub>4</sub></sub>, by 7%. The lower air temperatures would have also been responsible for slower rates of reaction between OH and CH<sub>4</sub>, which *Valdes et al.* [2005] estimated, together with the lower [OH], would have led to a 13% increase in τ<sub>CH<sub>4</sub></sub>; *Harder et al.* [2007] illustrated the sensitivity that τ<sub>CH<sub>4</sub></sub> shows to the degree of cooling at the LGM, calculating increases of 8%, 24% and 57% subject to three different representations of the glacial climate, based on data from *Climate: Long-Range Investigation, Mapping and Prediction (CLIMAP)* [1981], (see *Harder et al.* [2007] for details) and *Webb et al.* [1997] respectively. The physical effects of the lower temperatures at the LGM would thus have been to increase, not decrease, [CH<sub>4</sub>]. However, the cooler, drier climate of the LGM would have also seen lower NMVOC emissions from vegetation [e.g., *Adams et al.*, 2001; *Lathière et al.*, 2005; *Valdes et al.*, 2005; *Kaplan et al.*, 2006]. NMVOCs, such as isoprene, compete with CH<sub>4</sub> for reaction with OH, and hence a reduction in their emissions at the LGM would have tended to increase [OH] and reduce τ<sub>CH<sub>4</sub></sub>—by 17% according to *Valdes et al.* [2005]. There is, however, still considerable uncertainty regarding the degree to which the oxidation of isoprene ‘consumes’ OH; large discrepancies have been observed between modeled and measured [OH] in regions of high isoprene (and low nitrogen-oxide; NO<sub>x</sub> = NO + NO<sub>2</sub>) emissions [*Lelieveld et al.*, 2008; *Hewitt et al.*, 2010], and various so-called OH-recycling mechanisms have been proposed to resolve these [see, e.g., *Archibald et al.*, 2010]. One such mechanism, based on the calculations of *Peeters et al.* [2009], shows significant potential [*Archibald et al.*, 2010; *Stavrakou et al.*, 2010], and we therefore test

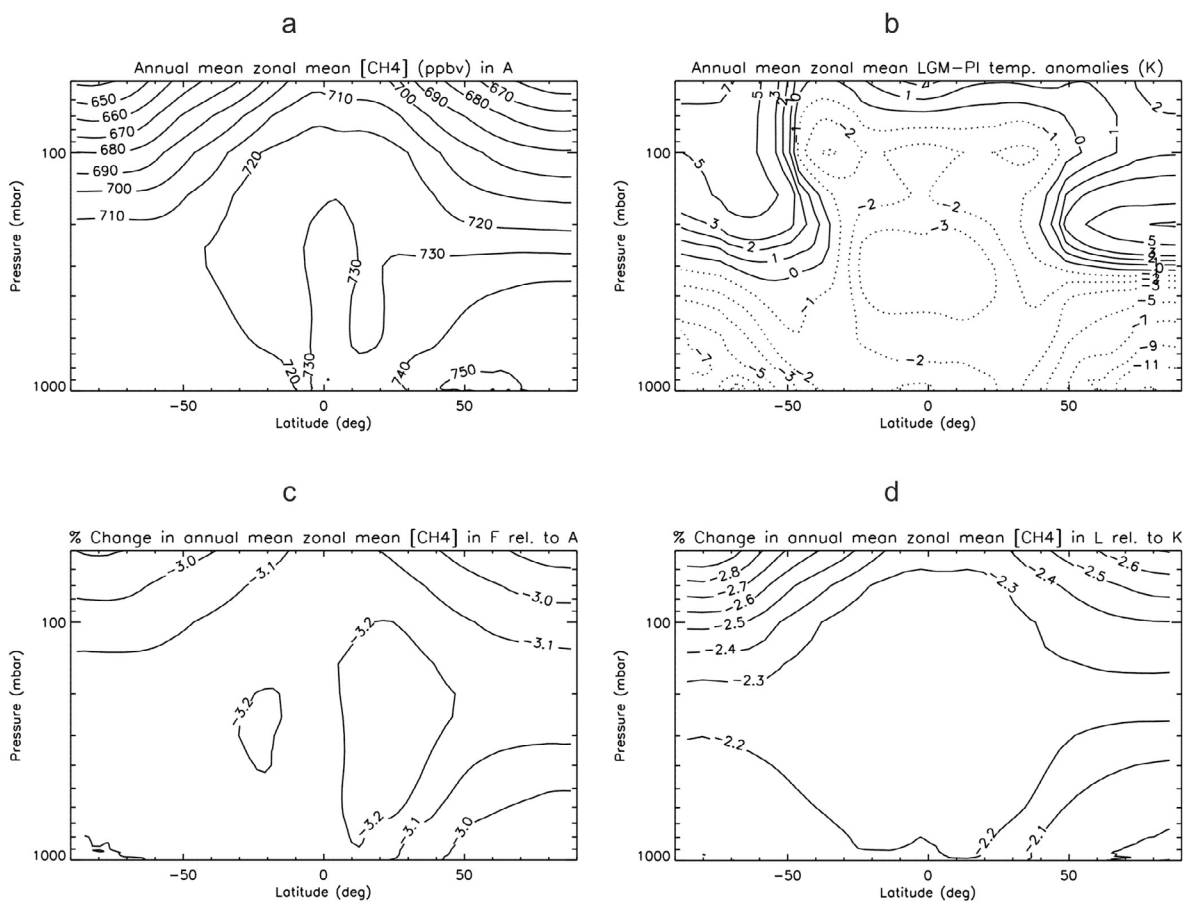
the sensitivity of our results, obtained with the conventional Mainz Isoprene Mechanism [*Pöschl et al.*, 2000], to its inclusion.

## 2. Model Experiments

[5] We carry out twelve experiments with the Cambridge parallelised-Tropospheric Offline Model of Chemistry and Transport (p-TOMCAT): the main features of these are summarized in Table 1. p-TOMCAT is a 3D global Eulerian model, run at a resolution of 2.8° × 2.8° on 31 levels (unless otherwise stated), and driven by wind, temperature and humidity data from the operational analyses of the European Centre for Medium-range Weather Forecasts (ECMWF). The model’s chemistry includes the HO<sub>x</sub>/NO<sub>x</sub> chemistries of methane, ethane, propane and isoprene, with the oxidation of isoprene following the Mainz Isoprene Mechanism [*Pöschl et al.*, 2000]; see *Levine et al.* [2011] for more details on both the physical and the chemical aspects of the model. In a number of the experiments, however, we add two reactions (equations (1) and (2)); ISOPOHO<sub>2</sub> = isoprene hydroxy peroxy radical, MACR = lumped C4 carbonyl, MGLY = methyl glyoxal, and HACET = hydroxyl-acetone), which together comprise an OH recycling mechanism based on the calculations of *Peeters et al.* [2009], previously implemented in the UKCA global chemistry-climate model [*Archibald et al.*, 2011]. To assess the sensitivity of our results to the temperature dependence of these additional reactions, we employ both fixed rate coefficients, as implemented by *Archibald et al.* [2011] ( $k_1 = 4.0 \times 10^{-3} \text{ s}^{-1}$  and  $k_2 = 8.0 \times 10^{-2} \text{ s}^{-1}$ ), and temperature-dependent ones, based on the calculations of *Peeters et al.* [2009] ( $k_1 = 2.1 \times 10^{11} e^{-8993/T}$  and  $k_2 = 5.9 \times 10^9 e^{-7366/T}$ , where T is the temperature in K).



[6] Experiment A (referred to by *Levine et al.* [2011] as the ‘PI model run’) employs PI trace gas emissions [*Valdes et al.*,



**Figure 1.** (a) Annual mean zonal mean [CH<sub>4</sub>] in experiment A, (b) annual mean zonal mean LGM-PI temperature anomalies, and (c, d) percentage changes in annual mean zonal mean [CH<sub>4</sub>] in experiments F and L, relative to A and K.

2005] and present-day meteorology (assuming recent meteorological analyses adequately represent the meteorology of the PI). The emissions include PI emissions of methane, which remain unchanged throughout the experiments in order to explore the impacts of changes in air temperature and NMVOC emissions (alone) on the oxidizing capacity. In experiment B, we modify the humidity in the model in line with LGM air temperatures, recalculating the saturated volume mixing ratio of water vapor with respect to ice according to *Marti and Mauersberger [1993]* and adjusting the water vapor volume mixing ratio so as to conserve relative humidity. In experiment C, we also use LGM air temperatures to influence the chemical kinetics. The LGM air temperatures are obtained by combining LGM-PI temperature

anomalies calculated with the Hadley Centre Atmosphere-only general circulation model, HadAM3 (see auxiliary material), and the ECMWF air temperatures employed in experiment A; the zonal-mean temperature anomalies are illustrated in Figure 1b.<sup>1</sup>

[7] In experiment D (referred to by *Levine et al. [2011]* as ‘Sink 2’), we remove all emissions from vegetation (as specified in Table 2), and in experiment E, we do so subject to LGM air temperatures (affecting both the humidity in the model and the chemical kinetics). In experiment F, instead of removing all emissions from vegetation, we reduce them

<sup>1</sup>Auxiliary materials are available in the HTML. doi:10.1029/2011GL049545.

**Table 2.** Trace-Gas Emissions<sup>a</sup>

Trace Gas	Biomass Burning	Oceans	Vegetation	Soils	Lightning	Wetlands	Termites	Total
NO <sub>2</sub>	1.4	-	-	5.1	4.8	-	-	11.3
CH <sub>4</sub>	11.0	13.0	-	-	-	147.9	27.0	198.9
CO	100.0	50.0	150.0 (100.5)	-	-	-	-	300.0 (250.5)
C <sub>2</sub> H <sub>6</sub>	0.7	-	3.5 (2.3)	-	-	-	-	4.2 (3.0)
C <sub>3</sub> H <sub>8</sub>	0.2	0.5	3.5 (2.3)	-	-	-	-	4.2 (3.0)
CH <sub>3</sub> COCH <sub>3</sub>	0.1	-	20.0 (13.4)	-	-	-	-	20.1 (13.5)
C <sub>5</sub> H <sub>8</sub>	-	-	673.7 (258.9)	-	-	-	-	673.7 (258.9)
HCHO	0.3	-	-	-	-	-	-	0.3
CH <sub>3</sub> CHO	0.8	-	-	-	-	-	-	0.8

<sup>a</sup>Trace-gas emissions are expressed in Tg molecular mass year<sup>-1</sup>, with the exception of NO<sub>2</sub> emissions, which are expressed in Tg N year<sup>-1</sup>. Numbers in parentheses refer to LGM emissions; all others refer to PI emissions [see *Valdes et al., 2005*].

in line with LGM estimates [Valdes *et al.*, 2005], based on calculations with the University of Sheffield Dynamic Global Vegetation Model [Woodward *et al.*, 1995; Beerling and Woodward, 2001] (see Table 2). Experiments I (K) and J (L) are repeats of experiments A and F, subject to OH recycling with fixed (temperature-dependent) rate coefficients,  $k_1$  and  $k_2$ . They are carried out at a lower resolution of  $5.6^\circ \times 5.6^\circ$  on 19 levels, having first repeated experiments A and F at this resolution (experiments G and H) to verify that the annual-mean [CH<sub>4</sub>] in the Antarctic boundary layer, [CH<sub>4</sub>]<sub>AntBL</sub> (defined to comprise all boxes in the lowest level of the model south of 70°S), and  $\tau_{CH_4}$  (defined as the annual-mean tropospheric burden of CH<sub>4</sub> divided by the annual CH<sub>4</sub> emission rate) are insensitive to the resolution.

### 3. Results

[8] The [CH<sub>4</sub>]<sub>AntBL</sub> and  $\tau_{CH_4}$  calculated in each experiment (once the model has reached equilibrium; see Levine *et al.* [2011] for definition) are given in Table 1. In experiments B–F, [CH<sub>4</sub>]<sub>AntBL</sub> and  $\tau_{CH_4}$  show very similar percentage changes relative to their values in experiment A; similarly, [CH<sub>4</sub>]<sub>AntBL</sub> and  $\tau_{CH_4}$  show very similar percentage changes in experiments H, J and L, relative to their values in experiments G, I and K, respectively. We therefore refer almost exclusively to changes in  $\tau_{CH_4}$ . Like Martinerie *et al.* [1995], we find that the lower humidity of the LGM leads to a 7% increase in  $\tau_{CH_4}$  (experiment B). Combined with the changes in chemical kinetics, we calculate an 18% increase in  $\tau_{CH_4}$  (experiment C); Valdes *et al.* [2005] calculated a 13% increase in  $\tau_{CH_4}$  in response to the cooling at the LGM, with trace-gas emissions fixed at LGM levels.

[9] In contrast, the removal of all NMVOC emissions from vegetation leads to a 22% reduction in  $\tau_{CH_4}$  (experiment D); this is an estimate of the maximum influence a reduction in NMVOC emissions at the LGM could have had on  $\tau_{CH_4}$ . Combined with the effects of the changes in air temperature, we calculate an 11% reduction in  $\tau_{CH_4}$  (experiment E), and when instead of removing all NMVOC emissions from vegetation, we reduce them in line with LGM estimates, we calculate a reduction of just 3% (experiment F). The percentage difference in annual-mean zonal-mean [CH<sub>4</sub>] in experiment F, relative to experiment A, is illustrated in Figure 1c.

[10] Repeating experiments A and F at lower resolution—experiments G and H—we calculate similar values of  $\tau_{CH_4}$  (8.6 years in G c.f. 8.5 years in A, and 8.5 years in H c.f. 8.3 years in F) and similar values of [CH<sub>4</sub>]<sub>AntBL</sub> (715 ppbv in G c.f. 714 ppbv in A and 703 ppbv in H c.f. 692 ppbv in F). We therefore also calculate a similar percentage change in the two quantities,  $\tau_{CH_4}$  and [CH<sub>4</sub>]<sub>AntBL</sub>, in response to the changes in air temperature and NMVOC emissions at the LGM (−2% in H relative to G c.f. −3% in F relative to A). Our results appear to be reasonably insensitive to model resolution.

[11] At the lower resolution, the addition of OH recycling to our PI climate/emission scenario (with both fixed and temperature-dependent rate coefficients) reduces  $\tau_{CH_4}$  by between 1 and 2%, from 8.6 years in experiment A to around 8.5 years in experiments I and K. This is similar to the 3% reduction calculated by Cooke [2010] with STOCHEM—

the UK Meteorological Office Global Three-Dimensional Lagrangian model—but contrasts with the 35% reduction calculated by Archibald *et al.* [2011] with UKCA. A further study is needed to understand the differences between the models in this regard. Here, we are primarily interested in the influence that recycling has on the change in  $\tau_{CH_4}$  in response to the changes in air temperature and NMVOC emissions at the LGM, relative to the PI. Subject to recycling (with both fixed and temperature-dependent rate coefficients), we find that the changes at the LGM result in just a 2% reduction in  $\tau_{CH_4}$  (experiments J and L relative to experiments I and K respectively). The influence of recycling in our calculations thus appears to be small, and its temperature-dependence non-critical. Figure 1d illustrates the percentage difference in annual-mean zonal-mean [CH<sub>4</sub>] in experiment L, relative to experiment K.

### 4. Discussion

[12] Our experiments with the Cambridge p-TOMCAT model suggest the net effect on  $\tau_{CH_4}$  of the changes in air temperature and NMVOC emissions at the LGM, relative to the PI, was negligible: their separate effects, though substantial, were roughly equal and opposite, resulting in a net change in  $\tau_{CH_4}$  of between 2 and 3%. This finding holds irrespective of whether we include an OH recycling mechanism based on the calculations of Peeters *et al.* [2009], previously shown to reduce modeled/measured [OH] discrepancies [Archibald *et al.*, 2010; Stavrakou *et al.*, 2010] of the sort identified by Lelieveld *et al.* [2008] and Hewitt *et al.* [2010]. If the changes in air temperature and NMVOC emissions were the only factors to significantly influence the oxidizing capacity during this period, the implication is that the LGM–PI change in [CH<sub>4</sub>] was almost entirely source-driven—a conclusion that, as outlined in Section 1, is consistent with recent estimates of CH<sub>4</sub> source strengths if CH<sub>4</sub> emissions from wetlands changed in line with Weber *et al.*'s [2010] highest estimate.

[13] In principle, other factors could have affected the oxidizing capacity. These include changes in: albedo, cloudiness, stratospheric ozone and NO<sub>x</sub> emissions. The increase in the amount of land and sea covered by ice at the LGM would have been accompanied by an increase in albedo at high latitudes, and hence an increase in the amount of UV radiation available here to photolyze tropospheric ozone to produce the excited oxygen atom, O(<sup>1</sup>D)—a key step in the production of OH. This would have tended to increase [OH] and reduce  $\tau_{CH_4}$  and [CH<sub>4</sub>]. However, given that only around 25% of CH<sub>4</sub> is oxidized outside of the tropics, and only a small fraction of this at high latitudes [see, e.g., Lawrence *et al.*, 2001; Labrador *et al.*, 2004], it is unlikely to have had a significant effect on  $\tau_{CH_4}$  globally. Similarly, changes in cloudiness, which would also affect the amount of UV radiation available to photolyze tropospheric ozone, are unlikely to have had a significant influence; Ramstein *et al.*, 1998, Figure 13] estimated that zonal-mean cloud cover changed by 5–10% at high latitudes and less than or similar to 1% at all other latitudes. Likewise regarding stratospheric ozone: a series of model studies has concluded that the total ozone column changed, at all latitudes, by less than or similar to 2% [see Pinto and Khalil, 1991; Crutzen and Brühl, 1993; Martinerie *et al.*, 1995; Karol *et al.*, 1995; Rind

*et al.*, 2009], though we note that these studies were only loosely constrained by ice-core measurements of [CH<sub>4</sub>], [CO<sub>2</sub>] and [N<sub>2</sub>O].

[14] Though NO<sub>x</sub> emissions play an important part in determining the oxidizing capacity, governing the formation of tropospheric ozone accompanying the oxidation of CH<sub>4</sub> and NMVOCs, it remains uncertain how they changed between the LGM and the PI. It is estimated that soils, lightning and biomass burning accounted for roughly 45%, 40% and 15%, respectively, of total NO<sub>x</sub> emissions in the PI [see, e.g., *Valdes et al.*, 2005] (Table 2). *Valdes et al.* [2005] estimated that NO<sub>x</sub> emissions from soils were 12% greater at the LGM whilst those from lightning were 19% lower, resulting in a small reduction in total NO<sub>x</sub> emissions that would have led, had all else been equal, to a 6% increase in  $\tau_{CH_4}$  at the LGM. They did so, however, using only an empirical (c.f. process-based) model of soil NO<sub>x</sub> fluxes [*Yienger and Levy*, 1995], and assuming NO<sub>x</sub> emissions from lightning, to which  $\tau_{CH_4}$  is especially sensitive (increasing/decreasing by more than a year in response to a 2.5Tg N year<sup>-1</sup> decrease/increase in emissions from this source [*Wild*, 2007]), scaled with the amount of convective precipitation simulated with an atmospheric general circulation model. Their estimates are therefore subject to significant uncertainties. It is also unclear how NO<sub>x</sub> emissions from biomass burning differed at the LGM: top-down Monte-Carlo calculations by *Fischer et al.* [2008] suggest there was little or no change in biomass burning whilst a recent global synthesis of charcoal records identifies the last glacial period (16–21kyr before present) as the period of least biomass burning in the last 21kyr [*Power et al.*, 2008]. What we can say, however, is that any reduction in total NO<sub>x</sub> emissions at the LGM would have tended to increase  $\tau_{CH_4}$ , and thus increase the reduction in CH<sub>4</sub> emissions needed at the LGM to explain the reduction in [CH<sub>4</sub>] observed.

[15] The changes in air temperature and NMVOC emissions that we have explored, not to mention the OH recycling mechanism employed [*Archibald et al.*, 2011], are also subject to uncertainties. We have explored changes in air temperature amounting to a cooling at the LGM of about two degrees in the tropics (see Figure 1b). This lies roughly in the middle of the coolings exhibited by state-of-the-art climate models [see *Braconnot et al.*, 2007, Figure 8], but as the latter exhibit a range of about a degree and are under-constrained by paleodata [see, e.g., *Braconnot et al.*, 2007; *Otto-Bliesner et al.*, 2009], it could be subject to an uncertainty of around  $\pm 25\%$ . The calculations of *Harder et al.* [2007] illustrate the sensitivity that  $\tau_{CH_4}$  shows to the degree of cooling at the LGM. Though we would generally expect a greater (lesser) cooling to result in a greater (lesser) reduction in NMVOC emissions, and hence the continued offsetting of one effect on the oxidizing capacity against the other, an extreme cooling (well beyond the bounds of a  $\pm 25\%$  uncertainty) could result in a net increase in  $\tau_{CH_4}$  at the LGM. For instance, *Harder et al.* [2007] found that the cooling estimated by *Webb et al.* [1997] led to a 57% increase in  $\tau_{CH_4}$ , whilst our calculations suggest the removal of all NMVOC emissions from vegetation would only reduce  $\tau_{CH_4}$  by 22%. The uncertainty surrounding the changes in NMVOC emissions is still harder to assess. There are uncertainties inherent to:

the dynamic global vegetation model with which the emissions are simulated; the simulations of the atmospheric circulation with which this is forced; and the estimates of present-day emissions [see, e.g., *Arnth et al.*, 2008], on which estimates of past emissions implicitly depend. A further notable uncertainty surrounds the degree to which the ‘CO<sub>2</sub>-suppression’ of isoprene emissions was reduced at the LGM relative to the PI [e.g., *Arnth et al.*, 2007; *Wilkinson et al.*, 2009], as a result of the lower [CO<sub>2</sub>] at the LGM [see, e.g., *Lüthi et al.*, 2008]. Any reduction in CO<sub>2</sub>-suppression at the LGM would have tended to increase  $\tau_{CH_4}$ , and thus increase the reduction in CH<sub>4</sub> emissions needed at the LGM to explain the reduction in [CH<sub>4</sub>] observed.

[16] In light of the significant uncertainties discussed above, we cannot assert that the LGM-PI change in [CH<sub>4</sub>] was definitely entirely source-driven. However, this is the implication of our calculations and such a conclusion is consistent with recent estimates of CH<sub>4</sub> source strengths, if CH<sub>4</sub> emissions from wetlands changed in line with *Weber et al.*’s [2010] highest estimate—close to the top-down estimate of *Fischer et al.* [2008], based on Monte-Carlo calculations designed to explain ice-core measurements of both [CH<sub>4</sub>],  $\delta^{13}CH_4$ , and  $\delta D(CH_4)$ ; Section 1. Furthermore, any reduction at the LGM in the total amount of NO<sub>x</sub> emitted, and/or the degree to which isoprene emissions were suppressed by CO<sub>2</sub>, would only imply a still larger total CH<sub>4</sub>-source change. We therefore conclude that it is plausible the LGM-PI change in [CH<sub>4</sub>] was entirely source-driven, and that the changes in CH<sub>4</sub> sources and sinks between the LGM and the PI could be reconciled thus.

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## References

- Adams, J. M., et al. (2001), An estimate of natural volatile organic compound emissions from vegetation since the Last Glacial Maximum, *Chemos. Global Change Sci.*, 3, 73–91, doi:10.1016/S1465-9972(00)00023-4.
- Archibald, A. T., et al. (2010), Impacts of mechanistic changes on HO<sub>x</sub> formation and recycling in the oxidation of isoprene, *Atmos. Chem. Phys.*, 10, 8097–8118, doi:10.5194/acp-10-8097-2010.
- Archibald, A. T., et al. (2011), Impacts of HO<sub>x</sub> regeneration and recycling in the oxidation of isoprene: Consequences for the composition of past, present and future atmospheres, *Geophys. Res. Lett.*, 38, L05804, doi:10.1029/2010GL046520.
- Arnth, A., et al. (2007), Process-based estimates of terrestrial ecosystem isoprene emissions: incorporating the effects of a direct CO<sub>2</sub>-isoprene interaction, *Atmos. Chem. Phys.*, 7, 31–53, doi:10.5194/acp-7-31-2007.
- Arnth, A., et al. (2008), Why are estimates of global terrestrial isoprene emissions so similar (and why is this not so for monoterpenes)?, *Atmos. Chem. Phys.*, 8, 4605–4620, doi:10.5194/acp-8-4605-2008.
- Beerling, D. J., and F. I. Woodward (2001), *Vegetation and the Terrestrial Carbon Cycle: Modelling the First 400 Million Years*, Cambridge Univ. Press, New York, doi:10.1017/CBO9780511541940.
- Braconnot, P., et al. (2007), Results of PMIP2 coupled simulations of the Mid-Holocene and Last Glacial Maximum—Part 1: Experiments and large-scale features, *Clim. Past*, 3, 261–277, doi:10.5194/cp-3-261-2007.
- Chappellaz, J. A., et al. (1993), The atmospheric CH<sub>4</sub> increase since the Last Glacial Maximum, (1). Source estimates, *Tellus, Ser. B*, 45, 228–241.

- Climate: Long-Range Investigation, Mapping and Prediction (CLIMAP) (1981), Seasonal reconstructions of the Earth's surface at the Last Glacial Maximum, *Map Chart Ser. MC-36*, Geol. Soc. of Am., Boulder, Colo.
- Cooke, M. C. (2010), Global modelling of atmospheric trace gases using the CRI mechanism, Ph.D. thesis, Univ. of Bristol, Bristol, U. K.
- Crutzen, P. J., and C. Brühl (1993), A model study of atmospheric temperatures and the concentrations of ozone, hydroxyl, and some other photochemically active gases during the glacial, the preindustrial Holocene, and the present, *Geophys. Res. Lett.*, *20*(11), 1047–1050, doi:10.1029/93GL01423.
- Fischer, H., et al. (2008), Changing boreal methane sources and constant biomass burning during the last termination, *Nature*, *452*, 864–867, doi:10.1038/nature06825.
- Guenther, A., et al. (2006), Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature), *Atmos. Chem. Phys.*, *6*, 3181–3210, doi:10.5194/acp-6-3181-2006.
- Harder, S. L., D. T. Shindell, G. A. Schmidt, and E. J. Brook (2007), A global climate model study of CH<sub>4</sub> emissions during the Holocene and glacial-interglacial transitions constrained by ice core data, *Global Biogeochem. Cycles*, *21*, GB1011, doi:10.1029/2005GB002680.
- Hewitt, C. N., et al. (2010), Overview: Oxidant and particle photochemical processes above a south-east Asian tropical rainforest (the OP3 project): Introduction, rationale, location characteristics and tools, *Atmos. Chem. Phys.*, *10*, 169–199, doi:10.5194/acp-10-169-2010.
- Kaplan, J. O., G. Folberth, and D. A. Hauglustaine (2006), Role of methane and biogenic volatile organic compound sources in late glacial and Holocene fluctuations of atmospheric methane concentrations, *Global Biogeochem. Cycles*, *20*, GB2016, doi:10.1029/2005GB002590.
- Karol, I. L., V. A. Frolkis, and A. A. Kiselev (1995), Radiative-photochemical modeling of the annually averaged composition and temperature of the global atmosphere during the last glacial and interglacial periods, *J. Geophys. Res.*, *100*(D4), 7291–7301, doi:10.1029/94JD02385.
- Labrador, L. J., R. von Kuhlmann, and M. G. Lawrence (2004), Strong sensitivity of the global mean OH concentration and the tropospheric oxidizing efficiency to the source of NO<sub>x</sub> from lightning, *Geophys. Res. Lett.*, *31*, L06102, doi:10.1029/2003GL019229.
- Lathière, J., D. A. Hauglustaine, N. De Noblet-Ducoudré, G. Krinner, and G. A. Folberth (2005), Past and future changes in biogenic volatile organic compound emissions simulated with a global dynamic vegetation model, *Geophys. Res. Lett.*, *32*, L20818, doi:10.1029/2005GL024164.
- Lawrence, M. G., et al. (2001), What does the global mean OH concentration tell us?, *Atmos. Chem. Phys.*, *1*, 37–49, doi:10.5194/acp-1-37-2001.
- Lelieveld, J., et al. (2008), Atmospheric oxidation capacity sustained by a tropical forest, *Nature*, *452*, 737–740, doi:10.1038/nature06870.
- Levine, J. G., E. W. Wolff, A. E. Jones, M. A. Hutterli, O. Wild, G. D. Carver, and J. A. Pyle (2011), In search of an ice-core signal to differentiate between source-driven and sink-driven changes in atmospheric methane, *J. Geophys. Res.*, *116*, D05305, doi:10.1029/2010JD014878.
- Loulergue, L., et al. (2008), Orbital and millennial-scale features of atmospheric CH<sub>4</sub> over the past 800,000 years, *Nature*, *453*, 383–386, doi:10.1038/nature06950.
- Lüthi, D., et al. (2008), High-resolution carbon dioxide concentration record 650,000–800,000 years before present, *Nature*, *453*, 379–382, doi:10.1038/nature06949.
- Marti, J., and K. Mauersberger (1993), Laboratory simulations of PSC particle formation, *Geophys. Res. Lett.*, *20*, 359–362, doi:10.1029/93GL00083.
- Martinerie, P. G., G. P. Brasseur, and C. Granier (1995), The chemical composition of ancient atmospheres: A model study constrained by ice core data, *J. Geophys. Res.*, *100*(D7), 14,291–14,304, doi:10.1029/95JD00826.
- Otto-Bliesner, B. L., et al. (2009), A comparison of PMIP2 model simulations and the MARGO proxy reconstruction for tropical sea surface temperatures at last glacial maximum, *Clim. Dyn.*, *32*, 799–815, doi:10.1007/s00382-008-0509-0.
- Peeters, J., et al. (2009), HO<sub>x</sub> radical regeneration in the oxidation of isoprene, *Phys. Chem. Chem. Phys.*, *11*, 5935–5939, doi:10.1039/b908511d.
- Pinto, J. P., and M. A. K. Khalil (1991), The stability of tropospheric OH during ice ages, inter-glacial epochs and modern times, *Tellus, Ser. B.*, *43*, 347–352.
- Pöschl, U., et al. (2000), Development and intercomparison of condensed isoprene oxidation mechanisms for global atmospheric modeling, *J. Atmos. Chem.*, *37*, 29–52, doi:10.1023/A:1006391009798.
- Power, M. J., et al. (2008), Changes in fire regimes since the Last Glacial Maximum: An assessment based on a global synthesis and analysis of charcoal data, *Clim. Dyn.*, *30*(7–8), doi:10.1007/s00382-007-0334-x.
- Prather, M. J. (2007), Lifetimes and time scales in atmospheric chemistry, *Philos. Trans. R. Soc. A*, *365*, 1705–1726, doi:10.1098/rsta.2007.2040.
- Ramstein, G., et al. (1998), Cloud processes associated with past and future climate changes, *Clim. Dyn.*, *14*(4), 233–247, doi:10.1007/s003820050220.
- Rind, D., J. Lerner, C. McLinden, and J. Perlwitz (2009), Stratospheric ozone during the Last Glacial Maximum, *Geophys. Res. Lett.*, *36*, L09712, doi:10.1029/2009GL037617.
- Singarayer, J. S., et al. (2011), Late Holocene methane rise caused by orbitally controlled increase in tropical sources, *Nature*, *470*, 82–85, doi:10.1038/nature09739.
- Stavrakou, T., et al. (2010), Improved global modelling of HO<sub>x</sub> recycling in isoprene oxidation: Evaluation against the GABRIEL and INTEX-A aircraft campaign measurements, *Atmos. Chem. Phys.*, *10*, 9863–9878, doi:10.5194/acp-10-9863-2010.
- Valdes, P. J., D. J. Beerling, and C. E. Johnson (2005), The ice age methane budget, *Geophys. Res. Lett.*, *32*, L02704, doi:10.1029/2004GL021004.
- Webb, R. S., et al. (1997), Influence of ocean heat transport on the climate of the Last Glacial Maximum, *Nature*, *385*, 695–699, doi:10.1038/385695a0.
- Weber, S. L., A. J. Drury, W. H. J. Toonen, and M. van Weele (2010), Wetland methane emissions during the Last Glacial Maximum estimated from PMIP2 simulations: Climate, vegetation, and geographic controls, *J. Geophys. Res.*, *115*, D06111, doi:10.1029/2009JD012110.
- Wild, O. (2007), Modelling the global tropospheric ozone budget: Exploring the variability in current models, *Atmos. Chem. Phys.*, *7*, 2643–2660, doi:10.5194/acp-7-2643-2007.
- Wilkinson, M. J., et al. (2009), Leaf isoprene emission rate as a function of atmospheric CO<sub>2</sub> concentration, *Global Change Biol.*, *15*(5), 1189–1200, doi:10.1111/j.1365-2486.2008.01803.x.
- Woodward, F. I., T. M. Smith, and W. R. Emanuel (1995), A global land primary productivity and phytogeography model, *Global Biogeochem. Cycles*, *9*, 471–490, doi:10.1029/95GB02432.
- Yienger, J. J., and H. Levy (1995), Empirical-model of global soil-biogenic NO<sub>x</sub> emissions, *J. Geophys. Res.*, *100*, 11,447–11,464, doi:10.1029/95JD00370.

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