The role of atomic chlorine in glacial-interglacial changes in the carbon-13 content of atmospheric methane

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Abstract

The ice-core record of the carbon-13 content of atmospheric methane ($\delta^{13}CH_4$) has largely been used to constrain past changes in methane sources. The aim of this paper is to explore, for the first time, the contribution that changes in the strength of a minor methane sink—oxidation by atomic chlorine in the marine boundary layer (Cl_{MBL})—could make to changes in $\delta^{13}CH_4$ on glacial-interglacial timescales. Combining wind and temperature data from a variety of general circulation models with a simple formulation for the concentration of Cl_{MBL}, we find that changes in the strength of this sink, driven solely by changes in the atmospheric circulation, could have been responsible for changes in $\delta^{13}CH_4$ of the order of 10% of the glacial-interglacial difference observed. We thus highlight the need to quantify past changes in the strength of this sink, including those relating to changes in the sea-ice source of sea salt aerosol.

1. Introduction

Methane (CH_4) is an important atmospheric constituent on account of its potency as a greenhouse gas and its strong influence on the tropospheric oxidizing capacity. We know from the polar-ice record that between the last glacial maximum (LGM; 21 kyr before present (BP)) and the pre-industrial Holocene (PIH; 1 kyr BP) its concentration, $[CH_4]$, rose from around 360 ppbv to about

700 ppbv [e.g. Loulergue et al., 2008], but how much of this change was source-driven, and how much was sink-driven, remains uncertain [see, e.g., Valdes et al., 2005; Kaplan et al., 2006; Fischer et al., 2008]. This study focuses on the $^{12/13}C$-isotopic composition of CH_4 trapped in polar ice, $\delta^{13}CH_4$, which provides a complementary constraint on the CH_4 budget and past changes therein [see, e.g., Ferretti et al., 2005; Fischer et al., 2008]. In the nomenclature of Schaefer and Whiticar [2008], $\delta^{13}CH_4$ can be expressed as the sum of the average isotopic composition of CH_4 sources, $\delta^{13}C_E$, and the average influence, by way of isotopic fractionation, of CH_4 sinks, ε_{WT} (equation 1). $\delta^{13}C_E$ can be broken down into the strength of each source, E_i, and its isotopic composition, $\delta^{13}C_{E_i}$ (equation 2). Similarly, ε_{WT} can be broken down into the fraction of CH_4 removed by each sink, F_j, and the fractionation coefficient associated with it, α_j (equation 3). Here, we explore the influence that CH_4-oxidation by atomic chlorine in the marine boundary layer (Cl_{MBL}) has on $\delta^{13}CH_4$ (encapsulated by the term, $(\alpha_{Cl}-1).F_{Cl}$, in equation 3), specifically the contribution that changes in the strength of this sink could make to glacial-interglacial changes in $\delta^{13}CH_4$.

$$\delta^{13}CH_4 = \delta^{13}C_E + \varepsilon_{WT} \qquad (1)$$

$$\delta^{13}C_E = \frac{\sum_{i=1}^{n} \delta^{13}C_{E_i}.E_i}{\sum_{i=1}^{n} E_i} \qquad (2)$$

$$\varepsilon_{WT} = \sum_{j=1}^{n} (\alpha_j - 1).F_j \qquad (3)$$

At present, about 80% of CH_4 is removed by the hydroxyl radical (OH) in the troposphere alone [e.g. Levy, 1971; Fung et al., 1991; Lelieveld et al., 1998]. Less than or similar to 10% is removed by soil uptake, and a similar fraction is removed by oxidants in the stratosphere [see, e.g., Fung et al., 1991; Lelieveld et al., 1998; Ridgwell et al., 1999]. It is estimated that Cl_{MBL} removes just 3-4% of CH_4 [e.g. Platt et al., 2004; Allan et al., 2007, 2010], yet owing to the strength of isotopic fractionation associated with this sink (α_{Cl}>1.06 [e.g. Saueressig et al., 1995] c.f. α_{OH}=1.0039 [Saueressig et al., 2001] and α_{soil}=1.017-1.025 [e.g., Reeburgh et al., 1997; Snover and Quay, 2000]), Cl_{MBL} could be responsible for an enrichment in $\delta^{13}CH_4$ of 2.6‰ relative to $\delta^{13}C_E$ [Allan et al., 2007]. Whilst changes in the strength of the Cl_{MBL} sink have been invoked to explain spatial and inter-annual variations in $\delta^{13}CH_4$ [Allan et al., 2005, 2007], their potential to contribute to glacial-interglacial changes has not been explored. Fischer et al. [2008], for example, did not consider Cl_{MBL} when attempting to explain the 3.5‰ enrichment in $\delta^{13}CH_4$ they measured at the LGM, relative to the pre-boreal Holocene (10 kyr BP). Schaefer and Whiticar [2008] did include Cl_{MBL} in their study of the glacial-interglacial $\delta^{13}CH_4$ record, but did not allow for changes in the strength of this sink. Here, we explore how sensitive the strength of the Cl_{MBL} sink is to a factor that could well have changed on glacial-interglacial timescales: the horizontal wind speed at the sea surface.

The main source of Cl_{MBL} is sea salt aerosol (SSA), which is produced by the action of the wind on wave crests, and from which BrCl and Cl_2 (that photolyse to give Cl_{MBL}) are liberated [see, e.g., Vogt et al., 1996; Platt et al., 2004]. The abundance of SSA in pseudo steady-state is determined by the rate of SSA production and the rate of SSA removal (e.g. by wet and dry deposition). The abundance of Cl_{MBL} derived from SSA then depends on the abundance of SSA, the acidity of the atmosphere, as BrCl and Cl_2 are believed to be liberated from SSA that has been acidified by the products of dimethyl sulfide (DMS) oxidation [Vogt et al., 1996; Platt et al., 2004], and the intensity of radiation of the wavelengths required to photolyse BrCl and Cl_2. However, as a first step in exploring the potential for Cl_{MBL} to contribute to glacial-interglacial changes in $\delta^{13}CH_4$, we explore the influence of the circulation alone, on the grounds that the production of SSA is highly sensitive to the wind speed [see, e.g., Monahan et al., 1986; Andreas et al., 1998; Witek et al., 2007], and several lines of paleodata, including the ice-core records of dust and sea salt [e.g.

Thompson and Mosley-Thompson, 1981; Petit et al., 1981; Hansson, 1994; Rothlisberger et al., 2002; and the recent review by Fischer et al., 2007], could indicate changes in this at the LGM.

We do so via a number of simple calculations employing a variety of model simulations of the PIH and LGM circulations. It is important we explore a variety of simulations, as there has been little consensus regarding the changes at the LGM, particularly in the region of the southern hemisphere westerlies (SHW), with estimates ranging from a 40% reduction in surface wind speeds [Kim et al., 2003] to a 25% increase in surface wind stress (implying a 12% increase in wind speeds) [Shin et al, 2003] in this region. Much of the literature has focused on changes in the strength (and position) of the SHW, owing to the bearing these could have on glacial-interglacial changes in CO_2 [see, e.g., Toggweiler, 1999; Toggweiler and Russell, 2008]. As the SHW exhibit some of the highest surface wind speeds globally and cover a broad swath of the Southern Ocean (see Figure 1), changes in their strength could also have bearing on the global strength of the Cl_{MBL} sink, and hence $\delta^{13}CH_4$. By employing a variety of simulations, we probe the range of influences circulation-driven changes in the strength of this sink could have had on $\delta^{13}CH_4$.

2. Calculations

We start by assuming that Cl_{MBL} removed the same fraction of CH_4 in the PIH as it is estimated to remove in the present, and hence was responsible for an equal enrichment in $\delta^{13}CH_4$ (relative to $\delta^{13}C_E$), namely 2.6(±1.2)‰ [Allan et al., 2007]. We thus equate $(\alpha_{Cl}-1).F_{Cl}$, integrated seasonally and globally in the PIH, to 2.6‰; see equation 3 and accompanying text. F_{Cl} is estimated to be between 0.03 and 0.04 [Platt et al., 2004; Allan et al., 2007, 2010], hence F_{Cl} is small compared to $1-F_{Cl}$ (the fraction of CH_4 removed by all other sinks) and a modest change in F_{Cl}, of up to say ±50%, will have little effect on F_{OH}, F_{soil} etc. It follows that, to a good degree of approximation, an

X% increase (decrease) in $(\alpha_{Cl}-1).F_{Cl}$ will be accompanied by a 0.026X‰ enrichment (depletion) in $\delta^{13}CH_4$. Assuming the rate of CH_4 removal by each CH_4 sink is first order with respect to $[CH_4]$, and again as F_{Cl} is small compared to $1-F_{Cl}$, we assume F_{Cl} is proportional to the product of $[Cl_{MBL}]$ and the rate coefficient for the reaction between Cl_{MBL} and CH_4, k_{Cl}. Accordingly, an X% increase (decrease) in $(\alpha_{Cl}-1).k_{Cl}[Cl_{MBL}]$ will be accompanied by a 0.026X‰ enrichment (depletion) in $\delta^{13}CH_4$. We can calculate α_{Cl} according to equation 4 [Saueressig et al., 1995], and k_{Cl} (molecules^{-1} cm^3 s^{-1}) according to equation 5 [Sander et al., 2003], where T is the temperature (K).

$$\alpha_{Cl} = 1.043 \times e^{\frac{6.455}{T}} \qquad (4)$$

$$k_{Cl} = 9.6 \times 10^{-12}.e^{\frac{-1360}{T}} \qquad (5)$$

To calculate $[Cl_{MBL}]$ (molecules cm^{-3}), we use a modified version (our equation 7) of the simple formulation with which Allan et al. [2007] explored the role of Cl_{MBL} in spatial and inter-annual variations in $\delta^{13}CH_4$ (our equation 6). Equation 6 expresses $[Cl_{MBL}]$ in terms of an average concentration of 18x10^3 molecules cm^{-3} and a seasonal variation governed by the time of year, t (day number). The tanh(3λ) term, where λ is the latitude (radians), simply ensures the seasonal cycles in the northern and southern hemispheres are six months out of phase. To explore the influence that the wind has on $[Cl_{MBL}]$, we add a factor of $N.V^P$, where V is the horizontal wind speed (ms^{-1}), P is the power to which this is raised and N is a normalization factor, of which our results are independent as we are only interested in percentage changes in $[Cl_{MBL}]$. We do so on the basis that Gong et al. [2002] suggest the column loading of SSA is proportional to V^P (with P=1.39 in the North Atlantic, 1.46 in the tropical Pacific, and 1.66 in the South Pacific). Assuming (1) the column loading of Cl_{MBL} is proportional to that of SSA, (2) the Cl_{MBL} is concentrated in the marine boundary layer (MBL), and (3) the height of the MBL does not change, $[Cl_{MBL}]$ should also be proportional to V^P. Though Gong et al. [2002] did not comment on it, their plots of loading versus wind speed [their Figure 2] indicate a proportionality to $V^{3.41}$, or similar, at wind speeds above about $5ms^{-1}$. We therefore employ (globally) P=1.39 at $V \leq 5ms^{-1}$ and 3.41 at $V > 5ms^{-1}$, but also explore the sensitivity of our results to variations in this formulation (see later).

$$[Cl_{MBL}] = 18 \times 10^3.\{1 + \tanh(3\lambda)\sin[2\pi(t-90)/365]\} \qquad (6)$$

$$[Cl_{MBL}] = 18 \times 10^3.\{1 + \tanh(3\lambda)\sin[2\pi(t-90)/365]\}.N.V^P \qquad (7)$$

With equations 4, 5 and 7, we can calculate $(\alpha_{Cl}-1).k_{Cl}[Cl_{MBL}]$ as a function of season and location during the PIH and LGM, provided we have the necessary wind and temperature data. Summarized in Table 1, these are taken from simulations with five general circulation models, more information on which can be found in our Auxiliary Material. Figure 1 illustrates the annual-mean surface wind speeds and temperatures in the PIH, and the changes in these at the LGM, according to each model. It also illustrates the percentage changes we calculate in $[Cl_{MBL}]$ at the LGM based on the wind data. Subject to the data from each model, we calculate the seasonally and globally integrated value of $(\alpha_{Cl}-1).k_{Cl}[Cl_{MBL}]$ throughout the MBL (treating areas of sea ice and open ocean alike; discussed later) in both the PIH and LGM, and hence the percentage change in this quantity on switching from PIH to LGM winds and temperatures, which we relate to a per-mil change in $\delta^{13}CH_4$.

We use mainly climatological monthly-mean data (based on 100-year integrations, or 20-year integrations in the case of HadAM3), these being arguably the most robust. However, we also repeat our calculations with CCSM3 and HadAM3 data, employing a full 100 years of monthly-mean data and a full 20 years of daily-mean data, respectively, to explore the sensitivity of our results to the degree of temporal averaging; see Table 1. To assess the sensitivity of our results to our formulation for P, we repeat all of these 'base' calculations (B) subject to an alternative value of P at $V \leq 5ms^{-1}$ (1.66; S1) and alternative values of V at which we switch from P=1.39 to P=3.41

($4ms^{-1}$ in S2 and $6ms^{-1}$ in S3). We also assess the sensitivity of our results to: the seasonality of $[Cl_{MBL}]$, by repeating the base calculations with the $\tanh(3\lambda)\sin[2\pi(t-90)/365]$ term in equation 7 set to zero (S4); and the changes in temperature between the PIH and LGM, by changing the winds whilst keeping the temperatures (PIH) constant (S5).

3. Results

The results of the base (B) and sensitivity (S1-5) calculations are given in Table 2; the numbers in parentheses correspond to the results obtained when less 'temporally averaged' data are employed (see Table 1 and accompanying text). We find that the effect on $\delta^{13}CH_4$ of switching from PIH to LGM winds and temperatures depends on which model data we use and the degree to which these are temporally averaged, with the base calculations yielding everything from a depletion of 0.46‰ to an enrichment of 0.14‰.

The S1 calculations show that our base results are insensitive to the value of P employed at $V \leq 5ms^{-1}$; we get the same results regardless of whether we employ the lowest value (1.39) or the highest value (1.66) Gong et al. [2002] reported based on calculations in the North Pacific and South Pacific respectively. Furthermore, the S2 and S3 calculations show that our results are reasonably robust to changes in the value of V at which we switch from P=1.39 to P=3.41, changing by less than or similar to 10% upon increasing or decreasing this by $1ms^{-1}$.

The effect of removing the $[Cl_{MBL}]$ seasonality in the S4 calculations is variable, depending on the model data used and the degree to which these are temporally averaged. Mostly, it has a modest effect (of the order of 10%), however it has a more pronounced effect in the calculations with IPSL-CM4 and HadAM3 climatological monthly-mean data. The change in $\delta^{13}CH_4$ we calculate could therefore be sensitive to the assumed [Cl_{MBL}] seasonality; we have employed the same [Cl_{MBL}] seasonality as Allan et al. [2007], reflecting that of the radiation required to photolyse BrCl and Cl_2; see equation 7 and accompanying text.

Finally, based on the S5 calculations, it would appear that the changes in temperature between the PIH and LGM are responsible for a depletion in $\delta^{13}CH_4$ of approximately 0.05-0.1‰, depending on the model data employed. The depletion reflects a reduction in the rate of reaction between Cl_{MBL} and CH_4 due to the reduction in temperatures at the LGM (see Figure 1 and equation 5), only marginally offset by an increase in the fractionation coefficient associated with this reaction (see equation 4).

4. Discussion

Our calculations suggest circulation-driven changes in the strength of the Cl_{MBL} sink could have a small but significant effect on $\delta^{13}CH_4$ on glacial-interglacial timescales. Depending on the model data employed, and the degree to which these are temporally averaged, we calculate changes in $\delta^{13}CH_4$ ranging from a depletion of 0.46‰ to an enrichment of 0.14‰, the magnitudes of which are of the order of 10% of the 3.5‰ glacial-interglacial difference observed [Fischer et al., 2008]. Factors not explored here, which could have also affected [Cl_{MBL}] and hence $\delta^{13}CH_4$ on these timescales, include: changes in the lifetime of SSA (e.g. due to changes in precipitation); changes in the acidity of the atmosphere (e.g. due to changes in DMS production linked to changes in biology, such as plankton type and/or abundance); and changes in the intensity of radiation required to photolyse BrCl and Cl_2 (e.g. due to changes in stratospheric ozone). $\delta^{13}CH_4$ could have also been affected by changes in F_{Cl} (and F_{soil}) accompanying changes in F_{OH}, also not explored here. If F_{OH}=0.9, F_{soil}=0.06 and F_{Cl}=0.04, and α_{OH}=1.0039‰, α_{soil}=1.02‰ and α_{Cl}=1.06‰, a 5% increase (decrease) in F_{OH} would lead to a 1.4‰ depletion (enrichment) in $\delta^{13}CH_4$ (assuming the change in F_{OH} is compensated for by changes in F_{soil} and F_{Cl}, and F_{Cl}=⅔ F_{soil}).

It is interesting that all of our calculations based on climatological monthly-mean data—arguably the most robust—suggest that the circulation-driven changes in the Cl_{MBL} sink would have led to a depletion in $\delta^{13}CH_4$ at the LGM relative to the PIH, primarily due to a reduction in the global abundance of Cl_{MBL}. Ice-core records show an increase in sea salt at the LGM, by a factor of 15 in the Arctic and 3 in the Antarctic [see Fischer et al., 2007, and references contained therein], which we would expect to have been accompanied by proportional increases in [Cl_{MBL}]. Of course, there could have been more Cl_{MBL} in polar regions but less at lower latitudes, yielding an overall reduction. However, our calculations yield percentage increases in [Cl_{MBL}] in some regions of the Arctic Ocean approaching, but still short of, the 15-fold increase we would expect, and generally capture less of the 3-fold increase expected in the Southern Ocean; see Figure 1. The calculations based on CCSM3 and HadAM3 data yield increases limited to the regions south of about 50°S and 60°S, respectively, accompanied by decreases to the north of these, whilst the remainder of the calculations predominantly show decreases in the Southern Ocean. This raises the question, what SSA source are we missing or underestimating in our calculations, and what influence does it have on $\delta^{13}CH_4$?

One possibility is that the simulations of the LGM circulation simply underestimate the wind speeds at high latitudes. If this were the case, it could call into question the validity of these simulations in other regions too. It certainly seems likely that at least part of the glacial-interglacial difference in sea salt (and dust) was the result of changes in wind speeds governing the strength of sea-salt sources, changes in wind patterns determining the efficiency of transport to Arctic and Antarctic ice-core sites and/or changes in precipitation affecting its atmospheric lifetime [see, e.g., Fischer et al., 2007; Petit et al., 2009]. However, there is some evidence that sea ice, as opposed to open ocean, is the dominant source of SSA reaching both coastal and continental Antarctic sites [e.g. Wagenbach et al., 1998; Rankin et al., 2002; Wolff et al., 2003, 2006]. In our calculations, we have assumed that sea ice is an equally strong source, showing the same dependence on wind speed. If however, sea ice were a stronger source on a per-unit-area basis, the increase in sea-ice at the LGM could have contributed to the 3-fold increase in sea salt seen in the Antarctic, and perhaps the 15-fold increase seen in the Arctic. A sea-ice driven increase in SSA, and hence Cl_{MBL}, at high latitudes would tend to strengthen the Cl_{MBL} sink, and hence enrich $\delta^{13}CH_4$ at the LGM. However, without knowing quantitatively how the strengths of the sea-ice and open-ocean sources compare, we cannot say what the net effect on $\delta^{13}CH_4$ would be if the increase in sea-ice were factored into our calculations.

What we can say is, irrespective of whether the net effect amounts to an enrichment or a depletion in $\delta^{13}CH_4$, a change in $\delta^{13}CH_4$ due to a change in the strength of the Cl_{MBL} sink would have implications for our interpretation of the glacial-interglacial $\delta^{13}CH_4$ record, and we have shown that $\delta^{13}CH_4$ is affected non-negligibly by circulation-driven changes alone. Fischer et al. [2008] attributed the enrichment in $\delta^{13}CH_4$ at the LGM to a near-complete shutdown of boreal wetland sources of relatively ^{13}C-poor CH_4, whilst biomass-burning sources of relatively ^{13}C-rich CH_4 were little or unchanged relative to the pre-boreal Holocene (10 kyr BP). A global synthesis of charcoal records by Power et al. [2008], however, has since shown that the last glacial period (16-21 kyr BP) was the period of least biomass burning in the last 21 kyr, suggesting we still have some enrichment in $\delta^{13}CH_4$ at the LGM to explain. An enrichment due to a strengthening of the Cl_{MBL} sink could potentially contribute to this, whilst a depletion due to a weakening of the Cl_{MBL} sink would further suggest the explanation offered by Fischer et al. [2007] is incomplete. Based on the results to our calculations, the influence that Cl_{MBL} has on $\delta^{13}CH_4$ cannot be ignored in future interpretations of the glacial-interglacial $\delta^{13}CH_4$ record, and hence further research is needed to quantify past changes in the strength of this sink, including those relating to changes in the sea-ice source of SSA.

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Wind and temperature data

Model	Resolution	Data	'Temporal averaging'
HadCM3	3.75°lon x 2.5°lat; 19 levels	10m winds; 1.5m temperatures	Climatological monthly means based on 100-year integrations
MIROC3.2	2.8°lon x 2.8°lat; 20 levels	10m winds; 2m temperatures	Climatological monthly means based on 100-year integrations
CCSM3	2.8°lon x 2.8°lat; 26 levels	1000mb winds and temperatures*	Climatological monthly means based on 100-year integrations (& 100 years of monthly means)
IPSL-CM4	3.75°lon x 2.5°lat; 19 levels	10m winds; 1.5m temperatures	Climatological monthly means based on 100-year integrations
HadAM3	3.75°lon x 2.5°lat; 19 levels	10m winds; 997mb temperatures	Climatological monthly means based on 20-year integrations (& 20 years of daily means)

Table 1. Main features of the data on which our calculations are based. *The wind and temperature data from CCSM3 correspond to the winds and temperatures on the lowest model level: mostly 1000mb, but in places 925mb or 850mb.

Changes in $\delta^{13}CH_4$

Model	B	S1	S2	S3	S4	S5
HadCM3	-0.46	-0.46	-0.44	-0.51	-0.39	-0.38
MIROC3.2	-0.25	-0.25	-0.24	-0.28	-0.22	-0.19
CCSM3	-0.15 (-0.22)	-0.15 (-0.22)	-0.15 (-0.23)	-0.14 (-0.22)	-0.13 (-0.22)	-0.02 (-0.10)
IPSL-CM4	-0.23	-0.23	-0.20	-0.26	-0.13	-0.15
HadAM3	-0.24 (0.14)	-0.24 (0.14)	-0.22 (0.14)	-0.25 (0.16)	-0.07 (0.12)	-0.17 (0.22)

Table 2. Changes in $\delta^{13}CH_4$ (‰) calculated in the base (B) and sensitivity (S1-5) calculations; the numbers in parentheses correspond to the results obtained when less 'temporally averaged' data are employed (see Table 1 and accompanying text for details).

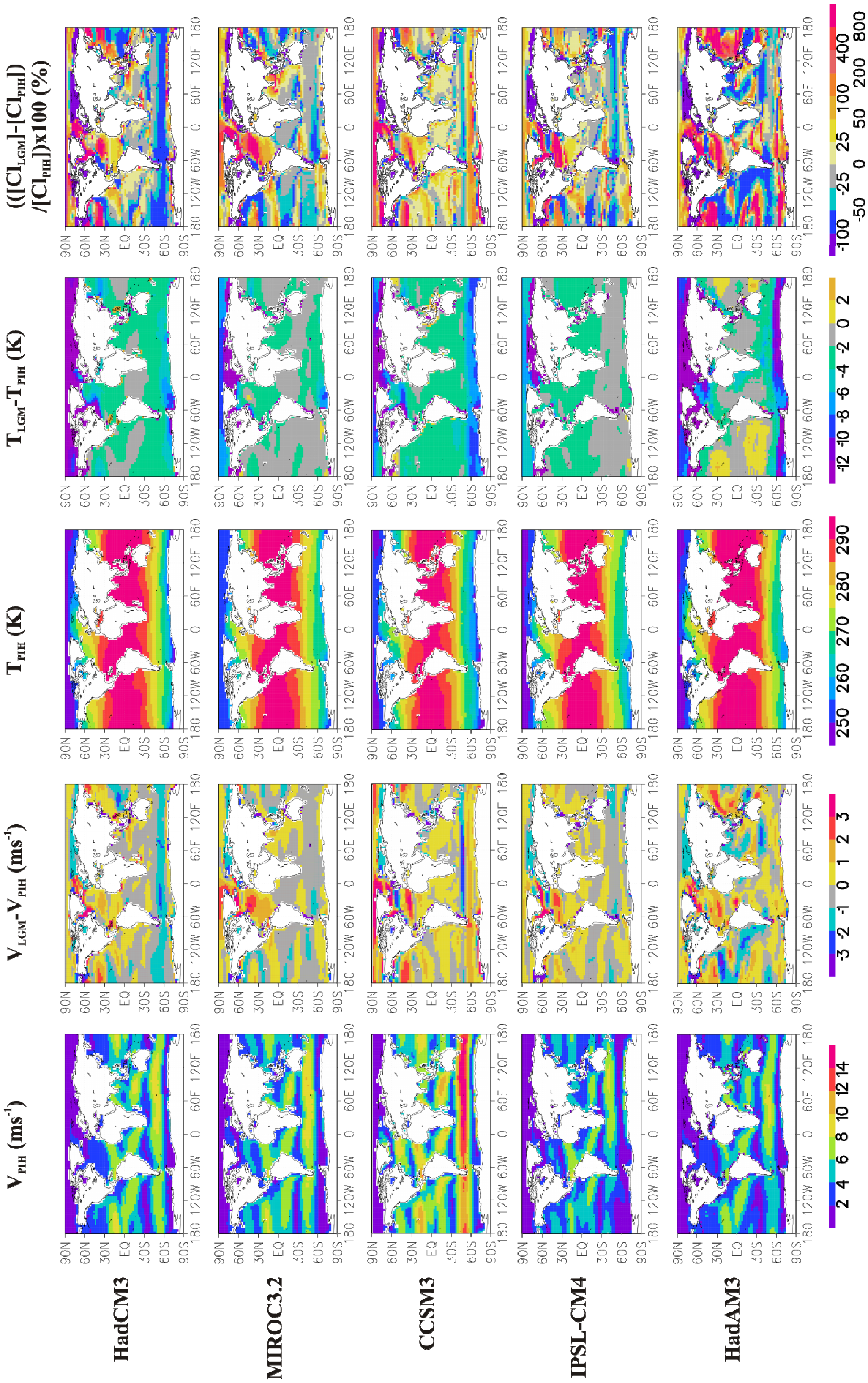

Figure 1. Annual-mean surface wind speeds (V_{PIH}) and temperatures (T_{PIH}) in the PIH, and the changes in these at the LGM (V_{LGM}-V_{PIH} and T_{LGM}-T_{PIH}), based on the climatological monthly-mean data from each model. Also, the percentage changes in [Cl_{MBL}] that we calculate at the LGM (((([Cl_{MBL}]$_{LGM}$-[Cl_{MBL}]$_{PIH}$)/[Cl_{MBL}]$_{PIH}$) x 100) based on the wind data.