No inter-hemispheric $\delta^{13}CH_4$ trend observed

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To understand the reasons for global CH_4 changes since the 1990s, Kai *et al.*[1] evaluated a combined record of observed tropospheric CH_4 mole fractions as well as $\delta^{13}C$-CH_4 and δD-CH_4 measurements from mid latitudes of both hemispheres. Their data set shows a strongly decreasing inter-hemispheric difference (IHD) in $\delta^{13}C$-CH_4 from -0.24 ± 0.11‰ during 1989–1993 to -0.10 ± 0.04‰ during 2001–2005, which they largely attribute to decreasing rice emissions during the last two decades. Here we show that the experimental data used by Kai *et al.*[1] are probably biased because the authors used only one continental mountain station (Niwot Ridge, Colorado, USA) as representative of the entire Northern Hemisphere, thereby incorrectly determining the IHD of $\delta^{13}C$-CH_4. Our more comprehensive data set—representing background air in both hemispheres—shows that the IHD of $\delta^{13}C$-CH_4 has changed by less than 0.05‰ since 1990; the conclusion drawn by Kai *et al.*[1] of a significant reduction of NH microbial sources is, thus, not constrained by our data.

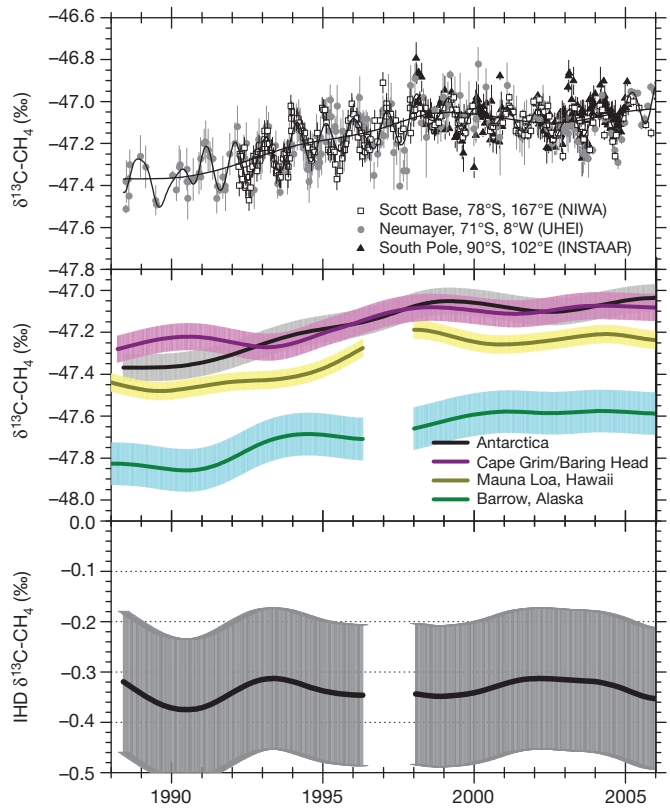

Figure 1 | Long-term trends in atmospheric $^{13}CH_4$. **a**, Three data sets from different laboratories adjusted to a common scale (Table 1). Individual points indicate single samples (NIWA, UHEI) or daily mean values (INSTAAR) with 1σ error bars. The solid lines are harmonic curves fitted through the merged data set with and without seasonal cycle[8]. **b**, De-seasonalised trend curves for the adjusted and merged data sets from **a** and those from Barrow and Mauna Loa[4,6,7], as well as combined from Cape Grim and Baring Head[4–6]. The shaded areas are the mean standard deviations of the de-seasonalised data around the trend curves. **c**, Inter-hemispheric difference (IHD) calculated from the trend curves in **b** as the difference of BRW + MLO minus CGO/BHD + Antarctica (shaded area is the $\pm 1\sigma$ uncertainty of the IHD).

Measuring stable isotopes in CH_4 with the precision needed for atmospheric CH_4 budgeting is difficult and only performed by a few laboratories worldwide. The large difference between atmospheric $\delta^{13}C$-CH_4 (approximately −47‰) and the primary $\delta^{13}C$ standard (NBS-19, +1.95‰) places stringent requirements on a laboratory's ability to maintain the integrity of an internal calibration scale over decades. Also modifications to analytical procedures are a potential source of bias in decade-long records. Without inter-laboratory comparisons, crucial for quality control, interpretation of combined $\delta^{13}C$-CH_4 records from different laboratories in modelling studies[2,3] may yield wrong conclusions.

One way of merging data from different laboratories is by comparing their colocated observations at global background sites. With the aim of establishing representative long-term $\delta^{13}C$-CH_4 trends, we combine measurements from University of Washington, Seattle, USA[4], University of Heidelberg (UHEI), Germany (unpublished), NIWA, New Zealand[5] and INSTAAR/NOAA, USA[6], from the Antarctic coast (Neumayer, 71°S, 8°W and Scott Base, 78°S, 167°E, SBO) and the South Pole (SPO), Cape Grim, Tasmania (41°S, 144°E, CGO) and Baring Head, New Zealand (41°S, 175°E, BHD), to determine mean $\delta^{13}C$-CH_4 offsets between these laboratories (see Methods and Table 1). Estimated offsets are then applied to the data from two sites in the Northern Hemisphere, Mauna Loa, Hawaii (20°N, 156°W, MLO) and Barrow, Alaska (71°N, 157°W, BRW), where long-term measurements exist[4,6,7] since 1988.

Combined data for Antarctica (Fig. 1a), adjusted to the NIWA scale according to the values given in Table 1, show deviations from the calculated mean harmonic fit curves[8] in the range of uncertainties of individual analyses in the different laboratories ($\pm$ 0.05 to 0.15‰, 1σ). Whereas NIWA and INSTAAR records from Antarctica, starting in 1992 (Scott Base) and 1998 (South Pole), can be extended backwards to 1988 with measurements from UHEI at Neumayer, outside Antarctica, that is, at Mauna Loa and Barrow, Alaska, only Quay *et al.*[4] data allow extending these records back to 1988. Their adjustment to the NIWA scale by −0.058‰ was achieved with overlapping data at BHD from 1993–1995 (refs 4, 5). This offset corresponds to a scale difference of 0.074‰ between the Quay *et al.*[4] and the INSTAAR[6] data. Note that disregarding this scale offset when evaluating combined records from Quay *et al.*[4] and INSTAAR[6], as was done in earlier modelling studies[2,3], yields an overestimation of the global long-term $\delta^{13}C$-CH_4 trend in the last two decades by about 30%.

Figure 1b shows the scale-adjusted long-term trends for BRW, MLO, 41°S, as well as for Antarctic sites. The calculated $\delta^{13}C$-CH_4 IHD was then estimated according to Patra *et al.*[9] as the difference between the mean of BRW and MLO data (NH) minus the mean from 41°S and Antarctica (SH) and is displayed in Fig. 1c. In contrast to Kai *et al.*[1], no significant change of the IHD is found between 1988 and 2005. This implies that our data set is more consistent with the control scenario in the Kai *et al.*[1] study, which assumes that both fossil fuel

Table 1 | Estimated offsets between $\delta^{13}CH_4$ scales in the different laboratories and the NIWA scale given as Laboratory minus NIWA (uncertainty is 1σ standard deviation)

Laboratory	Latitude (stations)	Overlapping period for comparison	Difference with NIWA $\delta^{13}CH_4$ (‰)
Ref. 4	41°S (Baring Head)	1993–1995	+0.058 ± 0.004
UHEI	Antarctica (SBO/Neumayer)	1992–2008	−0.169 ± 0.031
INSTAAR	Antarctica (SBO/South Pole)	1998–2008	+0.132 ± 0.022

and microbial sources remained mostly constant during the time period in question.

METHODS

We estimated the laboratory differences of $\delta^{13}C$-CH_4 between NIWA, INSTAAR and UHEI by comparing observations at SBO, Neumayer and SPO, as CH_4 gradients are not observed in Antarctica. Harmonic fit curves[8] were calculated through individual data sets (cut-off period: 54 months). Mean differences between de-seasonalised trend curves for the overlapping observational periods were calculated. No long-term changes in these differences were found, justifying constant values for adjusting the three data sets (Table 1). For adjustment of the Quay *et al.*[4] data see main text. Overlapping measurements in 1990–1992 were disregarded due to as yet unexplained excursions in the NIWA data.

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Levin *et al.*[1] report new methane data from Antarctica measured at the University of Heidelberg and combine these data with observations from two other networks to estimate long-term trends and the interhemispheric difference (IHD) in methane isotopes. These observations and the author's analysis suggest that the $\delta^{13}C$ IHD has been mostly uniform over the last three decades. This contrasts with the Niwot Ridge, Baring Head and Pacific Ocean time series that we analysed[2] and suggests that both fossil fuel and microbial sources remained mostly constant during the late 1980s and 1990s, following a trajectory of emissions that is more similar to the control scenario in our analysis (Fig. 2 and Supplementary Fig. 2 of Kai *et al.*[2]). The estimate of $\delta^{13}C$ inter-hemispheric difference is sensitive to different methods and selected observed sites. We note that the inter-hemispheric differences between Barrow and Cape Grim/Baring Head and between MLO and Cape Grim/Baring Head in Fig. 1 of Levin *et al.*[1] were largest near the beginning of the record (circa 1990) and are broadly consistent with comparisons we made in the Supplementary Information of our paper (Supplementary Fig. 9)[2]. Important next steps, in our opinion, are (1) to use all available observations from both the Kai *et al.*[2] and Levin *et al.*[1] studies to assess trends in methane isotopes and their dependence on the inclusion or exclusion of individual time series, and (2) to quantify changes in microbial and fossil sources consistent with the expanded set of observations presented by Levin *et al.*[1]. Even with a levelling off of both fossil and microbial sources during 1990–2005, our forward biogeochemical modelling analysis of rice agriculture provides evidence that emissions from this sector of the budget declined as a consequence of changes in fertilizer application and water management.

These two papers[1,2] highlight the value of isotope observations in constraining the global methane budget. To understand more recent changes in the global methane budget, including the causes of increases in mixing ratio that have occurred after 2005, intensified commitment to long-term funding support and cross-network calibration is needed for this crucial set of carbon cycle observations.

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