Title
Observationally derived rise in methane surface forcing mediated by water vapour trends

Permalink
https://escholarship.org/uc/item/5qc4b6cq

Journal
Nature Geoscience, 11(4)

ISSN
1752-0894

Authors
Feldman, DR
Collins, WD
Biraud, SC
et al.

Publication Date
2018-04-01

DOI
10.1038/s41561-018-0085-9

Peer reviewed
Title:

Observationally-derived rise in methane surface forcing mediated by water vapour trends

Author Information:

D.R. Feldman\textsuperscript{1,*}, W.D. Collins\textsuperscript{1,2‡}, S.C. Biraud\textsuperscript{1}, M.D. Risser\textsuperscript{1}, D.D. Turner\textsuperscript{3}, P.J. Gero\textsuperscript{4}, J. Tadić\textsuperscript{1}, D. Helmig\textsuperscript{5}, S. Xie\textsuperscript{6}, E.J. Mlawer\textsuperscript{7}, T.R Shippert\textsuperscript{8} and M.S. Torn\textsuperscript{1,2}

Affiliations:

\textsuperscript{1} Lawrence Berkeley National Laboratory, Berkeley, CA, USA.
\textsuperscript{2} University of California-Berkeley, Berkeley, CA, USA.
\textsuperscript{3} National Oceanic and Atmospheric Administration Earth Systems Research Laboratory, Boulder, CO, USA.
\textsuperscript{4} University of Wisconsin-Madison, Madison, WI, USA.
\textsuperscript{5} Institute of Arctic and Alpine Research, University of Colorado-Boulder, Boulder, CO, USA.
\textsuperscript{6} Lawrence Livermore National Laboratory, Livermore, CA, USA.
\textsuperscript{7} Atmospheric and Environmental Research, Lexington, MA, USA.
\textsuperscript{8} Pacific Northwest National Laboratory, Richland, WA, USA.

\textsuperscript{*}Corresponding Author:1 Cyclotron Road, MS 74R-316C, Berkeley, CA 94720, USA.

\texttt{drfeldman@lbl.gov}

\textsuperscript‡ Denotes co-lead author.
Atmospheric methane (CH\textsubscript{4}) mixing ratios exhibited a plateau between 1995 and 2006 and have been subsequently increasing. While there are a number of competing explanations for the temporal evolution of this greenhouse gas, these prominent features in the temporal trajectory of atmospheric CH\textsubscript{4} are expected to perturb the surface energy balance through radiative forcing, largely due to CH\textsubscript{4}’s infrared radiative absorption features. However, to date this has been determined strictly through radiative transfer calculations. Here, we present a quantified observation of the time-series of clear-sky radiative forcing by CH\textsubscript{4} at the surface from 2002-2012 at a single site derived from spectroscopic measurements along with line-by-line calculations using ancillary data. There was no significant trend in CH\textsubscript{4} forcing between 2002 and 2006, but since then, the trend in forcing was 0.026±0.09 (99.7% CI) W/m\textsuperscript{2}/yr. The seasonal-cycle amplitude and secular trends in observed forcing are influenced by a corresponding seasonal cycle and trend in atmospheric CH\textsubscript{4}. However, we find that we must account for the overlapping absorption effects of atmospheric water vapour (H\textsubscript{2}O) and CH\textsubscript{4} to explain the observations fully. Thus, the determination of CH\textsubscript{4} radiative forcing requires accurate observations of both the spatiotemporal distribution of CH\textsubscript{4} and the vertically resolved trends in H\textsubscript{2}O.

Atmospheric CH\textsubscript{4} and Its Radiative Forcing

The globally-averaged atmospheric mixing ratio of CH\textsubscript{4} has risen since the pre-industrial epoch from 722±25 ppbv in 1750 to 1803±2 ppbv in 2011\textsuperscript{(1)}. However, there is an unresolved debate regarding the causes of the temporal trajectory of CH\textsubscript{4}, and thus its sources and sinks, over the last 30 years. The observed plateau in the CH\textsubscript{4} mixing ratio\textsuperscript{2} and its end\textsuperscript{3} have been attributed to
some combination of changes in (1) hydroxyl (OH) radical destruction, (2) tropical wetland
emissions, (3) thawing permafrost and CH₄ hydrates, (4) agriculture, and (5) fossil-fuel
extraction and use, though their relative contributions are ambiguous given existing
observations⁴⁻¹⁰.

Rising atmospheric CH₄ mixing ratios are expected to change the distribution of atmospheric
radiative energy, and this is the essential justification for coordinated and prioritized scientific
inquiry regarding atmospheric CH₄. While substantial resources have been devoted to measuring
increasing atmospheric CH₄(²,¹¹) and understanding its anthropogenic contributions¹²⁻¹⁴, the
observational determination of its radiative forcing has, to date, been limited. Satellite
observations have inferred, but not quantified, the radiative forcing associated with rising mixing
ratios of this gas¹⁵,¹⁶. Apart from those efforts, radiative forcing values have been strictly
calculated by radiative transfer models based on information gathered from laboratory
observations. The calculations performed for the IPCC Fifth Assessment report found that CH₄
has contributed to a stratospherically-adjusted longwave (5-20 μm) radiative forcing at the
tropopause of 0.48±0.05 W/m² from the pre-industrial epoch¹. However, the methods used by
that report were last revised in 1998¹⁷, and recent work has indicated that an upward revision to
the methane radiative forcing formulae and the determination of its global warming potential for
future Assessment Reports is necessary¹⁸, mostly due to the need to include shortwave effects.

The spectroscopy of CH₄, which is the foundation underlying the radiative forcing calculations,
is an active area of research¹⁹. This is because CH₄ exhibits a line structure of exceptional
complexity compared to other atmospheric greenhouse gases²⁰, and line-by-line calculations and
climate model radiation codes must capture this complexity to determine CH$_4$ radiative forcing. They do so by using line parameters in spectroscopic databases such as High Resolution Transmission (HITRAN)$^{21}$ and parameterizations of other absorption effects. These databases are frequently updated, and while the updates have produced only modest changes in CH$_4$ infrared forcing$^{22,23}$, the scientific understanding of other potentially significant absorption effects such as broadening dependencies$^{24}$ and H$_2$O continuum absorption$^{18,25}$ is still advancing. Alternatively, we can use field observations to establish the sufficiency of the approach by which CH$_4$ radiative forcing is solely determined from radiative transfer calculations.

The specialized, long-duration suite of observations collected at the U.S. Department of Energy Atmospheric Radiation Measurement (ARM) Program$^{26}$ at the Southern Great Plains (SGP) site (36° 36′ 18″ N, 97° 29′ 6″ W) provide a unique opportunity to observe greenhouse gases and their forcing, as indicated by the first observation of the increase in the greenhouse effect from rising atmospheric concentrations of CO$_2$.$^{27}$ The time-series of weekly CH$_4$ surface flask measurements from SGP shows a high variability in CH$_4$ at SGP, with boundary layer excursions sometimes exceeding 2300 ppbv (Figure 1). As with other locations of high-precision atmospheric CH$_4$ measurements, the time-series of CH$_4$ mixing ratios shows fine-scale temporal variability. At SGP, some of the excursions may be due to local hydrocarbon recovery, based on the correlation between CH$_4$ and ethane mixing ratios$^{28,29}$ (see Methods). Meanwhile, an analysis of these instantaneous CH$_4$ observations (see Methods) shows (1) no significant trend in atmospheric CH$_4$ before 2007, (2) a break-point in
2007, and (3) that CH$_4$ mixing ratios have been rising at a rate of 7.5±4.4 (95% CI) ppbv/yr since then.

While other studies have observed trends in the surface energy balance with broadband radiometry$^{30,31}$, broadband observations are inadequate for attributing changes in that balance to changes in atmospheric composition of specific gas species. Therefore, we use a long time-series of clear-sky downwelling spectral infrared radiance observations to determine if changes in atmospheric CH$_4$ mixing ratios have a discernible effect on the surface energy balance. We focus here on longwave clear-sky flux changes since they are predicted to be the most sensitive longwave radiative flux signal associated with rising greenhouse gases$^{32}$ and since detailed all-sky forcing calculations of the study site indicate that most of the forcing arises under clear-sky conditions (see Methods).

**CH$_4$ Radiative Forcing Dependencies**

Figure 2(a) shows, through radiative transfer calculations, that the infrared emission by CH$_4$ that contributes to its longwave surface radiative forcing occurs predominantly between 1200 and 1350 cm$^{-1}$. However, as the radiative transfer calculations in Figure 2(b) show, the determination of CH$_4$ forcing is complicated by a significant H$_2$O and N$_2$O dependence of the downwelling flux in the CH$_4$ absorption band, arising from the overlap of spectral absorption features of H$_2$O and N$_2$O with those of CH$_4$. The downwelling flux is also highly temperature-dependent both due to Planck function and absorption line temperature dependence. Fortunately, the surface mixing ratios for N$_2$O are highly correlated with its mixing ratios throughout the column (Figure 2(c)), so the radiative effects of N$_2$O can be estimated using a near-surface measurement of its
mixing ratio. Radiosonde data at the ARM SGP site were used to control for variability in the
atmospheric thermodynamic state\textsuperscript{33}. Airborne measurements indicate that boundary-layer and
free tropospheric fluctuations in CH\textsubscript{4} mixing ratios are not highly correlated at subseasonal time-
scales. Therefore, surface observations of CH\textsubscript{4} mixing ratio alone are insufficient for calculating
CH\textsubscript{4} forcing at the time-scales of our analysis.

CH\textsubscript{4} surface radiative forcing was derived from 11 years’ of infrared spectroscopic observations
made by the Atmospheric Emitted Radiance Interferometer (AERI)\textsuperscript{34}. The forcing was
determined by differencing AERI measurements with counterfactual line-by-line calculations\textsuperscript{27}
where the thermodynamic state is prescribed by concurrent radiosonde observations\textsuperscript{33}, but the
calculation used a pre-industrial CH\textsubscript{4} mixing ratio (see Methods). Detailed data quality control
and averaging methods were used to account for the effects of uncertainties in temperature, H\textsubscript{2}O,
and N\textsubscript{2}O, and the effect of instrumental noise, respectively (see Methods). The minimum
temporal resolution of the observations used here was 6 hours (see Methods). From this process
chain, we observe the direct, unadjusted, instantaneous radiative forcing at the surface, which,
while not biased by the effects of thermodynamics (see Methods), is still affected by them.

Ideally, measurements would be made under prescribed thermodynamic conditions, but we have
no means of controlling for these conditions in the field.

The mean spectral residuals were prominent only in the spectral region of CH\textsubscript{4} absorption (see
Methods) and therefore exclude the possibility that uncertainties in the atmospheric state and
instrument calibration were substantially affecting the results. Top-down validation of our
forcing estimates, based on \textit{in situ} observations by simultaneous aircraft overflights\textsuperscript{35}, indicates
that we can observe instantaneous CH$_4$ forcing to within 0.14 W/m$^2$ (see Methods). Sensitivity
tests (see Methods) reveal that the transient plumes of boundary layer methane would lead to an
instantaneous surface radiative forcing signal of 0.05 W/m$^2$, so our analysis is unable to discern
the transient contribution of anthropogenic activity to observed forcing. However, supraseasonal
time-series features of atmospheric CH$_4$ mixing ratios, which do contain contributions from
human activity$^{4-10}$, are readily discernible in the observed radiative forcing.

Observationally-Derived Forcing Time-Series and Influence of Thermodynamics
Irrespective of the source of the atmospheric CH$_4$, we derive a time-series of CH$_4$ surface
longwave radiative forcing from observations that exhibits several prominent features (Figure 3).
During the multi-year atmospheric CH$_4$ plateau, the trend in this forcing did not differ
significantly from zero ($p>0.1$). The time-series exhibited a significant change around 2007 at
the end of the plateau ($p<0.0001$). From then onwards, the trend differed from zero at
0.026±0.006 W/m$^2$/yr (99.7% CI). During the 11-year record, there was a large seasonal cycle,
with an amplitude of at least 0.2 W/m$^2$.

During the time period of the atmospheric CH$_4$ plateau, it is expected that there would not be
significant trends in surface radiative forcing from CH$_4$, and this was confirmed by observations.
However, the amplitude of the seasonal cycle in surface forcing throughout the time-series and
the forcing trend since 2006 cannot be fully explained by the atmospheric CH$_4$ mixing ratio at
SGP. The amplitude of the seasonal cycle in CH$_4$ dry atmospheric mixing ratio is 51.2±10.1
(99.7% CI) ppbv, and, based on the mean water vapor profile during the observational period at
the SGP, the seasonal cycle amplitude would be 0.012±0.002 (99.7% CI) W/m$^2$, significantly
smaller than the observed amplitude of 0.25±0.01 (99.7% CI) W/m². The observed trend in CH₄
since 2007 is 7.5±6.6 (99.7% CI) ppbv/yr which, again based on the mean water vapor profile
during the observational period at the SGP, would yield a trend of 0.002±0.0009 (99.7% CI)
W/m²/yr, significantly smaller than the observed trend of 0.026±0.006 (99.7% CI) W/m²/yr.

However, analyzing the time-series in isolation from thermodynamics is highly idealized, can
yield varying results depending on the choice of thermodynamic conditions, and is inconsistent
with actual conditions in the field. Nevertheless, this discrepancy must be resolved.

We can exclude several potential explanations for these findings; for example, the contributions
of observational error and analysis error would produce spectral residuals outside of the CH₄
absorption band and time-series statistics that are inconsistent with our findings. Possible
contributions from other radiatively-active trace gases in the CH₄ absorption band between 1200
and 1350 cm⁻¹ can also be excluded (see Methods).

Rather, we find that when we perform a multivariate signal decomposition analysis of the
deseasonalized time-series of CH₄ forcing constructed over the entire time-series using a
nonlinear predictor based solely on CH₄ concentrations, we can explain roughly 80% of the
variation in observed forcing (R²=0.793), implying that at least 20.7% of the variance is related
to other factors (see Methods).

Rather, we find that the contribution of trends and variability in water vapour to those in CH₄
surface forcing are significant. Even though the residual spectra indicate that we are not
imprecisely specifying atmospheric temperature and moisture, CH₄ forcing is nonetheless
dependent on atmospheric state. The primary reason for this water vapour dependence is that mid-IR CH$_4$ absorption occurs at the edge of a strong $\nu_2$ H$_2$O absorption band. Therefore, elevated H$_2$O mixing ratios saturate the CH$_4$ band$^{36}$ and reduce the latter molecule’s radiative forcing, as shown in Figures 4(d). Indeed, we performed a model-only computation based on observed thermodynamics and CH$_4$ mixing ratios and obtain a trend of 0.020±0.009 (99.7% CI) W/m$^2$/yr, which is not distinguishable (p>0.05) from the observationally-derived trend. Additionally, this effect is largely insensitive to the observed mid-tropospheric temperature changes, as shown in Figure 4(c).

For the seasonal cycle, we find that the water vapour seasonal cycle of 7.7±0.03 g/kg helps explain the seasonal cycle in observed CH$_4$ surface forcing. For trends, we note that a long-term decreasing trend in moisture availability in the central US has been observed$^{37}$. This was also observed in a 14-year analysis of AERI clear-sky radiances$^{38}$. At SGP, an analysis of radiosondes coincidental to the CH$_4$ forcing observations is consistent with that finding and yields negative trends in atmospheric moisture in the lowest 1 km, as shown in Figure 4(b). While no significant change point in the vertically-resolved time-series is observed, column water decreased by 30% since the end of the CH$_4$ plateau. This negative trend over the entire time-series and especially since the end of the CH$_4$ plateau will tend to enhance CH$_4$ forcing, and provides the opportunity to analyze the alternating effects of CH$_4$ and H$_2$O on the observed forcing. Figure 5 shows that the observed forcing trends in CH$_4$ forcing could be reproduced only when we include nonlinear predictors that include both CH$_4$ concentration and observed thermodynamic trends (R$^2$=0.997, see Methods). Specifically, trends in CH$_4$ surface flask measurements and trends in height-resolved temporal profiles of temperature and humidity can be used to predict both plateau and
post-plateau surface radiative forcing trends after all variables are decomposed into frequency
noise (5a), a seasonal component (5b), and deseasonalized trends (5c), yielding a normally-
distributed residual signal (5d). The result is that the first temperature and moisture principal
components, covering the lower 5 km of the atmosphere, explain nearly all of the signal’s
variance (5e and 5f).

Broader Implications

This study presents the first observational derivation and quantification of the effect of time-
varying CH4 on the clear-sky surface energy balance, with a large seasonal cycle amplitude of
0.25 W/m² and a significant difference in forcing trends at SGP during and after the CH4 plateau.
The decadally-averaged trend in surface forcing was larger for CO2 than CH4 at this site, but the
perturbation of the surface energy balance from rising CH4 mixing ratios since the end of the
plateau was similar to the effect from rising CO2 (0.02±0.007 W/m²/yr) at the site. Though this
difference was not statistically significant (p>0.3), it suggests that, since the end of the plateau,
the role of rising CH4 in perturbing the surface energy balance can be highly dependent on local
water vapour trends39-42. At SGP, CH4 surface forcing trends are not necessarily inferior to that
of CO2, even though forcing at tropopause by CO2 is much more than CH4(1).

These observations show a long-term trend in CH4 surface radiative forcing, with variance from
a function of rising CH4 mixing ratios and the non-negligible contribution that depends on the
vertical distribution of water vapour. This finding is related to tropopausal radiative forcing,
which figures prominently in the scientific discussion of how rising CH4 impacts average
tropospheric temperatures1, but spatial patterns in upper tropospheric moisture43 mediate forcing
at the tropopause, while surface humidity more strongly affects surface forcing. For this investigation, we find that trends in surface forcing from greenhouse gases are convolved with the details of how the thermodynamic state of the atmosphere is evolving, and the local thermodynamic conditions must be taken into account. Since local temperature and humidity trends that are distinct from those at SGP exist at other sites, the relative contributions of thermodynamics and mixing ratio changes to the forcing may also differ. Observed trends in surface humidity have not been spatially or temporally uniform, nor have they been monotonic. The magnitude of the globally-averaged land-surface humidity trend varies on decadal timescales while also exhibiting trends that are spatially variable over land and that show strong land-ocean contrast. Therefore, the direct impact of greenhouse gases on the surface energy balance cannot be predicted in isolation from thermodynamics. Nevertheless, as we have shown, CH$_4$ surface radiative forcing trends can be derived from measurements and quantified spectroscopically.
References:


dioxide, methane, and nitrous oxide: A significant revision of the methane radiative


20. Goody, R.M. & Yung, Y.L. *Atmospheric Radiation: Theoretical Basis Ch. 3* (Oxford


22. Kratz, D.P. The sensitivity of radiative transfer calculations to the changes in the
(2008).

23. Lu, P., Zhang, H. & Jing, X. The effects of different HITRAN versions on calculated


Acknowledgements: This material is based upon work supported by the Director, Office of Science, Office of Biological and Environmental Research of the U.S. Department of Energy (DOE) under Contract No. DE-AC02-05CH11231 as part of their Atmospheric System Research (ASR) Program and the Atmospheric Radiation Measurement (ARM) Program and Terrestrial Ecosystem Sciences Programs (TES), and the ARM Aerial Facility (AAF), and used resources of the National Energy Research Scientific Computing Center (NERSC) under the same contract. Work at LLNL was performed under the auspices of the U.S. DOE by Lawrence Livermore National Laboratory under contract No. DE-AC52-07NA27344. M. Alvarado, K. Cady-Pereira, L. Riihimaki, I. Simpson and P. Novelli also contributed. NOAA GMD provided flask CH₄, C₂H₆, and N₂O data.

Author Contributions: D.R.F. led the research, performed all calculations, and wrote the manuscript; W.D.C. proposed the study concept, provided research guidance, and conceived methods for isolating the CH₄ signal; S.C.B. provided CH₄ and N₂O data and associated support; M.D.R. provided the statistical analysis; D.D.T. provided guidance on AERI instrument performance and research focus; P.J.G. helped interpret AERI data; J.T. analyzed thermodynamic contributions to the observed forcing. D.H. provided C₂H₆ data and associated support; S.X. provided ARMBE data and associated support; E.J.M. and T.R.S. provided clear-sky error analysis; M.S.T. provided research feedback and guidance and served as P.I. of the grant supporting this research. All authors discussed the results and commented on the manuscript.

Competing financial interests: The authors declare no competing financial interests.
Figure Captions:

**Figure 1:** Recent evolution of atmospheric methane at the surface study site. Time-series of the annual distribution of surface flask measurements of CH$_4$ at DOE ARM SGP site. Box-whisker plots show the mean (+), median (line), the box bounding the 25- and 75-percentile and the whiskers set at the 0.1- and 99.9-percentile for weekly flask measurements from a given year. Least-squares linear trend analyses are included for selected time periods before and after 2007 (vertical dashed line). The 2007 change-point was determined from weekly time-series data (see Methods).

**Figure 2:** Factors affecting CH$_4$ longwave surface instantaneous radiative forcing. (a) Change in spectral flux for a 1 ppbv perturbation in CH$_4$ for a 1 km layer in a Mid-Latitude Summer (MLS) profile$^{44}$. (b) Vertical sensitivity of downwelling surface flux in CH$_4$ absorption band to 1 km perturbations in temperature, H$_2$O, N$_2$O, and CH$_4$ derived from LBLRTM radiative transfer calculations with the MLS profile (c) Box-whisker diagrams of the vertical distribution of CH$_4$ and N$_2$O, with inset of associated correlation coefficient in mixing ratio between the surface and a given height, from aircraft observations$^{35}$ at SGP from flights 2002-2012. Box spans 25$^{th}$ to 75$^{th}$ percentile, whisker spans 5$^{th}$ to 95$^{th}$ percentile of observations.

**Figure 3:** CH$_4$ longwave surface radiative forcing time-series. Time-series (black), 2$\sigma$ instantaneous uncertainty in CH$_4$ surface longwave radiative forcing (gray; see Methods) and trends with 3$\sigma$ uncertainty (red; ibid.) at DOE ARM SGP.
**Figure 4:** Thermodynamic dependence of CH₄ surface forcing.

(a) Vertically-resolved slope of ARMBE temperature measurements with the 99.7% confidence-interval. (a) Same as (b) but for trends in the logarithm of specific humidity. (c) Surface radiative forcing vs. tropospheric-averaged CH₄ as a function of temperature perturbations from 8 to 16.5 km from a mid-latitude summer atmosphere. The change in mid-level temperature over the observed time-period was 0.4±0.2 °K (99.7% CI) and is indicated on the plot. (d) Same as (c) but for humidity perturbations in g/kg from 0 to 1 km. The change in boundary-layer water vapour over the observed time-period was -1.5±1.0 g/kg (99.7% CI) and is indicated on the plot.

**Figure 5:** Forcing time-series decomposition and reconstruction from predictors

(a) Time-series of CH₄ forcing signal noise removed by Random forest with 100 weak learners. (b) Seasonal forcing signal. (c) Deseasonalized forcing signal. (d) Histogram of observed vs decomposed and reconstructed forcing. (e) First component of Principal Component Analysis (PCA) of temperature predictors. (f) First component of PCA for humidity predictors. See Methods for details.
Methods:

CH$_4$ surface radiative forcing was determined by differencing measured spectra from the AERI instrument$^{45}$, subject to quality control (see below), with radiative transfer calculations using 512 levels of temperature and humidity from radiosondes profiles as processed by the ARM Best Estimates (ARMBE)$^{33,46}$, ozone from the Modern-Era Retrospective Analysis for Research and Applications (MERRA)$^{47}$, CO$_2$ profiles from the nearest spatiotemporal grid point from CarbonTracker-CO2 2013$^{48}$, monthly-averaged N$_2$O mixing ratios from the Mauna Loa Observatory (MLO)$^{49}$, and pre-industrial (722 ppbv) CH$_4$ mixing ratios. This counterfactual calculation, designed to simulate the spectrally-resolved radiance field at the Earth’s surface, had CH$_4$ mixing ratios remained at annually-averaged pre-industrial levels$^{27}$. The counterfactual was created using the Line-by-Line Radiative Transfer Model (LBLRTM) version 12.2, using the AER line parameter database version 3.1$^{50}$ based on HITRAN 2008$^{51}$ with updated line-mixing$^{52}$ and the MT_CKD_2.5.2 H$_2$O continuum absorption model$^{25}$. Limb-brightening factors, converting both observations and calculations from radiance to flux, were calculated with three-point Gaussian quadrature over zenith angle$^{53}$. Supplementary Information Figure 1 shows a schematic of this process chain.

Data Quality Control

AERI spectra were recorded every 8 minutes from the instrument’s initial deployment to April 2004 (at SGP). Subsequently, spectra were recorded every 30 seconds, with only minor outages, in order to provide higher temporal-resolution data for cloud studies$^{54}$. This analysis only considered data starting in 2002 because the ARMBE data are derived from Vaisala RS-80 profiles prior to 2002 and that instrument suffered a known dry bias$^{55,56}$. The end of the analysis
period was the start of 2013, which was chosen because the AERI instrument at SGP experienced a failure and was replaced in mid-2013. The analysis could be extended beyond early 2013 but would have to address complications from changing instrumentation. Only the subset of spectra recorded within 2 hours of a radiosonde launch were utilized. With 4 daily launches, each measurement is separated by a minimum of 6 hours and spans 4 hours. Based on the radiosonde profile, a radiance spectrum was calculated using LBLRTM with 512 levels of temperature and relative humidity from the ARMBE product. All AERI spectra recorded within 2 hours of the radiosonde launch were rank-ordered by the root-mean-squared brightness temperature of the residual spectrum of the difference between the measurement and the LBLRTM calculation between 600 and 980 cm\(^{-1}\). This range was chosen to be sensitive to thermodynamic conditions but insensitive to CH\(_4\) or ozone, where the latter is strongly influenced by MERRA biases. The rank-ordered spectra were averaged sequentially together (i.e., the first two spectra were averaged, then the first three spectra were averaged, etc.) and the RMS of the residual between that average and the LBLRTM calculation was recalculated. The sequential average of the spectra that produced the minimum RMS of the residual relative to the radiosonde-based LBLRTM calculation was used as the AERI spectral measurement for subsequent analysis. The rationale for this approach is to average as many spectra together as possible to minimize random measurement error, but to avoid biasing the spectra by averaging observations during which clouds were present or where the thermodynamic conditions had changed relative to the radiosonde.
Since the determination of CH$_4$ surface forcing is so dependent on an accurate specification of the atmospheric thermodynamic profile, we apply additional tests of the sequentially averaged spectra against the counterfactual calculations to remove cases where the thermodynamic or condensate profiles differ substantially between the observation and the counterfactual. First, we evaluate the RMS of the residual between the AERI spectral measurement and the LBLRTM calculation between 790 and 810 cm$^{-1}$ (hereafter referred to as the 800 cm$^{-1}$ channel), because this region is sensitive to atmospheric temperature, humidity, and condensates (see Supplementary Information Figures 2(a) and 2(b)). These plots show the slope and correlation coefficient of the least-squares relationship between the radiative flux sensitivity to moisture and temperature perturbations for a given channel outside the CH$_4$ absorption feature (1200-1350 cm$^{-1}$) and the average radiative flux sensitivity to moisture and temperature perturbations within the CH$_4$ absorption feature. The least-squares relationship is derived from six model atmospheres, which span a wide range of terrestrial thermodynamic conditions$^{44}$. The upper panels of Figures (2a) and (2b) show that fluxes in the spectral region between 790 and 810 cm$^{-1}$ are more sensitive to perturbations in temperature and moisture than fluxes in the CH$_4$ absorption band. The lower panels show that perturbations in temperature and moisture produce flux perturbations in the 790-810 cm$^{-1}$ spectral region and the CH$_4$ absorption band that are highly correlated.

We also utilize the RMS of the residual between 705 and 709 cm$^{-1}$ (hereafter referred to as the 707 cm$^{-1}$ channel), which is sensitive to the atmospheric boundary layer temperature. Supplementary Information Figure 2(c) shows the gain and correlation coefficient for the relationship between the variance of a spectral channel outside the CH$_4$ absorption feature and the variance of the spectral channel within the CH$_4$ absorption feature, where both are calculated...
with the measurements and calculations used in the aircraft validation cases (see below). This figure shows that the 707 cm\(^{-1}\) variance is highly correlated with the variance within the CH\(_4\) band across a range data wherein the 800 cm\(^{-1}\) tolerance criterion is satisfied below 5 K. A gain of greater than unity, indicating high sensitivity to boundary-layer temperature perturbations, is also shown at 707 cm\(^{-1}\) for the same 800 cm\(^{-1}\) tolerance criterion.

Only spectral residuals with an RMS residual spectrum brightness temperature at 800 cm\(^{-1}\) of less than 3 K and a standard deviation at 707 cm\(^{-1}\) less than 0.3 K (after averaging) are considered for subsequent analysis. See Supplemental Information for the rationale for these threshold choices.

Supplementary Information Figure 4 shows the average residual spectrum featuring a large deviation from zero where CH\(_4\) has a prominent absorption due to the use of a pre-industrial CH\(_4\) mixing ratio for the counterfactual calculation and deviations equivalent to less than 1 K in temperature, 10 ppmv CO\(_2\), 5% percent H\(_2\)O, and 10% N\(_2\)O. The exception lies in the 9.6 µm ozone absorption band between 980 and 1080 cm\(^{-1}\), indicating a systematic overestimation of column ozone from the MERRA data products at SGP\(^{58}\). The lack of prominent spectral structures outside the CH\(_4\) and O\(_3\) bands excludes other possible explanations including cloud contamination, water vapour or temperature bias, or instrument calibration, all of which produce spectral residuals with characteristic features not solely in the CH\(_4\) absorption band.

**Time-Series Decomposition**
We tested the hypothesis that the cause for the observed trend in radiative forcing could be contained within a set of predictors including height-resolved trends in water vapour, height-resolved trends in temperature, and ground level methane concentration measured by flasks. If we cannot use these predictors to reproduce the observed forcing, we can infer that there are other contributing factors to the forcing that we have not considered. For the reconstruction of this time-series, we used a two-step decomposition of all predictors using a widely utilized and flexible approach that avoids overfitting. First, we isolated the component of the unfiltered signal that cannot be described as white noise or outlier data using a calibrated Random forest with 100 weak learners. A calibrated Random forest was used to reproduce the signal at the desired points in time, and the difference between the reproduced and actual signal was filtered out. Second, the remaining noise and cyclical components of the signal were removed using moving average filter with a 12-month window. The size of the moving-average filter window was selected because the signal exhibited clear annual seasonal variations.

With this approach, we created a set of isolated trends for 1025 predictors (512 each for temperature and humidity and 1 for flask CH₄ observations). To make the problem less computationally expensive, and given the extreme level of redundancy in vertically-resolved temperature and water-vapour predictors, we applied principal component analysis (PCA) for the reduction of dimensionality. The fraction of variance explain by the first 5 principal components (out of 512) was found to be >99.99% for both temperature and humidity, confirming the high-degree of redundancy in the predictors. With 5 PCs for temperature, 5 for humidity, and 1 for methane concentration, we created a reduced set of 11 predictors to describe the CH₄ radiative forcing trend. An ensemble of five back-propagation neural networks was then
trained to reproduce the trend component of the CH$_4$ radiative forcing$^{62}$. To avoid over-fitting, the training and reproduction of the radiative forcing was done in leave-one-out fashion, such that the radiative forcing value to be reconstructed from the predictors is withheld from the training set. Instead, ensemble neural networks are trained using the remaining data points, and then the network is used to reproduce the withheld data point. The procedure was repeated sequentially for all data points.

With this approach, the correlation coefficient between the observed trends in the entire CH$_4$ surface forcing time-series and the neural-network prediction where all 11 predictors are used is 0.9983 (R$^2$=0.997). Where only the CH$_4$ flask data is used as a predictor to train the network, the correlation coefficient is 0.8907 (R$^2$=0.793). More specifically, we can explain $\sim$80% of the variance in radiative forcing using custom-designed non-linear predictor. However, we should note that our signal is obtained from the difference between an observation and calculation, which is not best possible non-linear predictor, so the amount of variance that can be explained using only CH$_4$ concentrations is necessarily less than 80%. Rather, our results produce an estimate of the minimum of the fraction of variance that cannot be explained using the predictor(s) of interest. They also show that information from temperature and humidity, and not just CH$_4$ flask concentration data, is needed to describe the observed trend in CH$_4$ surface radiative forcing.

Statistical Analysis Methods
The statistical analysis of the time-series seeks to determine whether and when a change point occurred in the measured CH$_4$ surface radiative forcing, as well as the linear (temporal) trends and their significance. The following describes the methods used to perform this analysis.

Define $y_t$ as the CH$_4$ forcing for the SGP site at time $t = 1, \ldots, T$. Our statistical model is:

$$y_t = b_0 + b_1 t + b_2 X_t (t - t_0) + a_j + e_t + v_t,$$

(1)

where $\{b_k\}$ are unknown regression coefficients, $\{a_j\}$ represent (unknown) monthly effects, $e_t$ are independent and identically distributed (iid) $N(0, s^2)$ with $s^2$ unknown ($N(a, b)$ denotes a univariate Gaussian random variable with mean $a$ and variance $b$), and $v_t$ iid $N(0, w^2)$ with $w^2$ known (also, $e_t$ and $v_t$ are independent). The model (1) contains two error processes: first, $e_t$ represents error in the model specification and therefore $s^2$ is estimated; second, $v_t$ represents error introduced by the measurement process on $y_t$ and therefore $w^2$ will be considered fixed (see Statistical Analysis Results). The variable $X_t$ is defined to be 0 if $t \leq t_0$ and 1 if $t > t_0$, and the change point must fall between fixed bounds $T_U < t_0 < T_L$. Therefore, for $t \leq t_0$, the monthly-adjusted trend in expected CH$_4$ forcing has slope $b_1$; for $t > t_0$, the trend has slope $b_1 + b_2$. The unknown parameters in (1) and the change point can be estimated using a common (Frequentist) statistical technique called maximum likelihood (ML)$^{63}$, which also yields confidence intervals for the regression coefficients$^{64}$. Given the setup in (1), we can determine the significance of the change point $t_0$ by way of model selection: the full model (1) can be vs.
$H_1: b_2 \neq 0$. A test of $H_0$ can be done using a standard full vs. reduced model $F$-test for nested models.

The Frequentist analysis described above ignores any uncertainty in estimating the change point, and the model is not well suited to assess this uncertainty (outside of asymptotic evaluations).

Alternatively, a Bayesian approach can be used to determine the significance of the change point while accounting for its uncertainty (again using model comparison). Bayesian models that mirror the full (1) and reduced (2) models can be set up using noninformative prior distributions and estimated using Markov Chain Monte Carlo (MCMC) methods. MCMC output can be used to compare the full and reduced models using Bayes factors.

Statistical Analysis Results

The aforementioned models were fit for many different data sets from the SGP site. This data set was created by using values of the 800 cm$^{-1}$ brightness temperature (BT) residual threshold parameter ranging from 0.1 to 10 (see Data Quality Control). However, if the data set for a particular threshold value had fewer than 50 observations, the analysis was not conducted. The upper and lower limits of the change point were fixed to $T_L = 2004$ and $T_U = 2010$; any potential change points near the beginning or end of the time series are not of interest. The seasonal cycle of CH$_4$ due to hydroxyl radical destruction is captured via the monthly effects $\{a_j\}$; for comparison, all models were fit and results presented both with and without the monthly effects.

For the ML models, plots of the estimated change point, significance of the change point, and estimates of the slope parameters (with 99.7% confidence intervals) from both before and after
the change point are provided in Supplementary Information Figures 5 and 6. Results from the Bayesian models were approximately identical to the ML models and are omitted. Based on the similarity of results, the main text used the more familiar Frequentist results including the monthly adjustment.

Supplementary Information Table 1 numerically summarizes the results of the statistical analysis used in the main text where the 800 cm\(^{-1}\) BT threshold is 3 K.

**Controlling for N\(_2\)O**

The methods used to determine CH\(_4\) surface radiative forcing can be biased by N\(_2\)O. Figure 2(b) shows this due to the substantial amount of overlap in spectral radiance changes from perturbations from N\(_2\)O and CH\(_4\). However, the vertical profiles of N\(_2\)O collected by the ARM-ACME missions\(^{35}\) at SGP show that N\(_2\)O mixing ratios at altitude are highly vertically-correlated with the surface (see insets of Figure 2(c)) and vary by less than 1 ppbv seasonally.

Moreover, these differ very little from measurements at MLO. The error incurred in CH\(_4\) forcing from utilizing monthly-averaged MLO N\(_2\)O observations instead of in situ ARM-ACME N\(_2\)O observations was maximized at 1.2% of the CH\(_4\) forcing.

N\(_2\)O can still bias CH\(_4\) forcing because it is emitted after precipitation following the nearby fresh application of nitrogen-based fertilizer\(^{68}\), causing >5 ppbv deviations from the background N\(_2\)O mixing ratio. NEXRAD data\(^{69}\) were used to screen data to remove those observations for which precipitation had occurred in the previous 24 hours.
**Instantaneous Error**

There are several sources of error in the determination of the surface forcing from the AERI measurements. They include (1) spectroscopic error in LBLRTM; (2) AERI measurement error; (3) error in the temperature, water vapour, CO$_2$, or O$_3$ inputs to LBLRTM inputs; and (4) a contribution of unknown aerosol or cloud condensates to the AERI observations. While the error contributions from (1) are outside of the scope of this analysis, we can perform a top-down estimate of errors from (2) through (4) with AERI measurements and LBLRTM calculations using inputs from simultaneous aircraft profiles.

Surface radiative forcing time series from the aircraft data were derived from differencing AERI observations with counterfactual calculations. These were compared with the surface radiative forcing time series computed by differencing an LBLRTM calculation with the aircraft-observed profile of CH$_4$ and N$_2$O and the counterfactual calculation.

Supplementary Information Figure 8 show the standard deviation of AERI-observed and aircraft-derived surface radiative forcing. Figure 3 shows that an abscissa value of 3 K corresponds to an ordinate value of 0.14 W/m$^2$, which is thus our estimate of the 1-$\sigma$ instantaneous error in radiative forcing.

**Ethane Data Analysis**

Supplementary Information Figures 9(a) and 9(b) show time-series analyses of ethane (C$_2$H$_6$) flask data. Non-Methane Hydrocarbon (NMHC) flask data from SGP were first filtered for
outliers; values that deviated more than 2-σ from a running median were excluded from trend analyses. Filtered data were then uploaded to the NOAA server for filtering and trends were determined using the method of Thoning et al.70

Clear-Sky Bias
We evaluate the potential for clear-sky bias in the determination of CH4 surface radiative forcing. We estimate this bias by recalculating the Broadband Heating Rate Profile (BBHRP)631 profiles at SGP for 2010 based on pre-industrial CH4 mixing ratios and comparing those to the original BBHRP profiles, containing time-varying CH4 derived from the nearest grid box from CarbonTracker-CH4(72). We then subset the data identified as clear-sky in the Radiatively Important Parameters Best Estimate (RIPBE) product73. We find that most of the forcing is in the clear-sky but that the all-sky surface forcing is 0.065 W/m², or 33%, less than the clear-sky forcing. This finding is expected because of non-negligible overlap between broadband cloud absorption and CH4 absorption, thereby masking CH4 forcing. This cloud-masking may vary year-to-year. Currently, the independent estimates of cloud vertical profiles produce residual spectra with signatures of clouds, so the effect of CH4 cannot be isolated under all-sky conditions.

Non-Methane Contributions to Observed Signal
The possibility that condensates or non-methane gaseous atmospheric constituents are contributing to the observed CH4 surface forcing must be considered. The contribution of condensates can be excluded because they produce broadband signals that are not observed in the
residual spectra. We can also address the non-methane gaseous constituent question by determining the effects of perturbations in the atmospheric concentrations of 32 additional species with spectroscopy tabulated in HITRAN$^{21}$, and found their contributions to be at least 5 orders of magnitude smaller than CH$_4$.

**Flasks-Based Observations**

At the SGP site, a pair of 2.5 liters glass flasks is collected on a weekly basis from the top of the central facility 60m tower. Flask collection started in April 2002 and is currently ongoing. The collection of a pair of flasks allows basic quality assessment and control. These observations are part of the NOAA’s Global Greenhouse Gases Reference Network (REF)$^{74}$. Flasks are collected in the afternoon, when the planetary boundary layer is well-developed and observations are representative of a large area. Aircraft profiles of CH$_4$ and N$_2$O were recorded on approximately a bi-monthly basis from 2002 until the present (see Supplementary Information Figures 7(a) and 7(b)).

Ground-based and aircraft-based flasks are analyzed after they are collected at NOAA/ESRL by gas chromatography, and measurements are reported against WMO CH$_4$-X2004 and N$_2$O X2006A scales. Flask-based observations are shown to have uncertainties of less than 1.2 ppbv for CH$_4$ and 0.4 ppbv for N$_2$O.

**Aircraft Validation**

Aircraft profiles of CH$_4$ and N$_2$O above the SGP site were recorded on approximately a weekly basis with flask observations from 2002 until the present. Prior to 2006, the flasks were
collected only at 0.6 and 3.6 km, but since then, flasks were collected at 12 elevations between 0.5 km and 5.5 km above sea level (see Supplementary Information Figures 7(a) and 7(b)).

### Single-Site Analysis

The analysis presented here focused on the SGP site. Several other ARM sites exist, including the North Slope of Alaska (NSA) site, and AERI data from that site was analyzed for previous work\(^\text{27}\). For the CH\(_4\) analysis, however, differences in the instrumental noise in the AERI instrument at NSA greatly complicated the analysis there. In particular, the Extended—Range AERI at NSA has an expanded spectral range compared to the AERI at SGP, leading to higher instrumental (random) noise over 1200-1350 cm\(^{-1}\) spanning the dominant CH\(_4\) absorption feature\(^\text{75}\).

### Residual Brightness Temperature Threshold Rationale

The rationale for choosing a threshold of 3 K brightness temperature is based on balancing the number of data points with error in the CH\(_4\) surface forcing determination, both of which will increase with increasing threshold values. Another related factor for the determination of an appropriate threshold is the importance of observations throughout the year. The 3 K threshold enables a determination of the seasonal cycle in surface forcing at the SGP site and summertime multi-year trends at the NSA site. Supplementary Information Figure 3 shows the relationships between the 800 cm\(^{-1}\) brightness temperature residual threshold and the number of data points.

### Data Availability
The ARM data and radiative transfer codes used in this analysis are freely available to download from [http://www.archive.arm.gov/discovery/](http://www.archive.arm.gov/discovery/) and [http://rtweb.aer.com](http://rtweb.aer.com), respectively. The following are URLs from which input data can be downloaded:

- **MERRA**: [http://goldsmr3.sci.gsfc.nasa.gov/opendap/MERRA/MAI3CPASM.5.2.0/contents.html](http://goldsmr3.sci.gsfc.nasa.gov/opendap/MERRA/MAI3CPASM.5.2.0/contents.html)
- **NOAA N₂O data**: [ftp://aftp.cmdl.noaa.gov/data/hats/n2o/insituGCs/CATS/daily/mlo_N2O_Day.dat](ftp://aftp.cmdl.noaa.gov/data/hats/n2o/insituGCs/CATS/daily/mlo_N2O_Day.dat)

Reprints and permissions information is available at [http://www.nature.com/reprints](http://www.nature.com/reprints)

**Code Availability**

The computer code developed for this research was written in Matlab and will be made available upon request.
References:


49. Nitrous Oxide data from the NOAA/ESRL halocarbons in situ program. Calibration scale used: NOAA 2006A. More information about the calibration scale can be found at: [http://www.esrl.noaa.gov/gmd/ccl/](http://www.esrl.noaa.gov/gmd/ccl/)


64. Ravishanker, N. & Dey, D. *A First Course in Linear Model Theory* (Chapman and Hall/CRC, 2002).


2002-2007: 3.3 +/- 4.9 (95% CI) ppbv/yr
2007-2012: 7.5 +/- 4.4 (95% CI) ppbv/yr
2002-2007: -0.003 ± 0.006 W/m²/yr
2007-2012: +0.026 ± 0.006 W/m²/yr
(a) Noise removed by Random Forests (RF)

(b) Seasonal Component of CH$_4$ Surface Forcing

(c) Deseasonalized CH$_4$ Surface Forcing

(d) Histogram of Obs. vs. Reconstructed CH$_4$ Forcing

(e) First Temperature Reconstruction Eigenvector: 99.985 %

(f) First Humidity Reconstruction Eigenvector: 99.947 %