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

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Main Text:

Atmospheric methane (CH_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_4 are expected to perturb the surface energy balance through radiative forcing, largely due to CH_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_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_4 forcing between 2002 and 2006, but since then, the trend in forcing was 0.026±0.09 (99.7% CI) $W/m^2/yr$. The seasonal-cycle amplitude and secular trends in observed forcing are influenced by a corresponding seasonal cycle and trend in atmospheric CH_4. However, we find that we must account for the overlapping absorption effects of atmospheric water vapour (H_2O) and CH_4 to explain the observations fully. Thus, the determination of CH_4 radiative forcing requires accurate observations of both the spatiotemporal distribution of CH_4 and the vertically resolved trends in H_2O.

Atmospheric CH_4 and Its Radiative Forcing

The globally-averaged atmospheric mixing ratio of CH_4 has risen since the pre-industrial epoch from 722±25 ppbv in 1750 to 1803±2 ppbv in 2011[(1)]. However, there is an unresolved debate regarding the causes of the temporal trajectory of CH_4, and thus its sources and sinks, over the last 30 years. The observed plateau in the CH_4 mixing ratio[2] and its end[3] have been attributed to

some combination of changes in (1) hydroxyl (OH) radical destruction, (2) tropical wetland emissions, (3) thawing permafrost and CH_4 hydrates, (4) agriculture, and (5) fossil-fuel extraction and use, though their relative contributions are ambiguous given existing observations[4-10].

Rising atmospheric CH_4 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 CH_4. While substantial resources have been devoted to measuring increasing atmospheric CH_4[(2,11)] and understanding its anthropogenic contributions[12-14], 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 gas[15,16]. 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 CH_4 has contributed to a stratospherically-adjusted longwave (5-20 μm) radiative forcing at the tropopause of 0.48±0.05 W/m^2 from the pre-industrial epoch[1]. However, the methods used by that report were last revised in 1998[(17)], 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 necessary[18], mostly due to the need to include shortwave effects.

The spectroscopy of CH_4, which is the foundation underlying the radiative forcing calculations, is an active area of research[19]. This is because CH_4 exhibits a line structure of exceptional complexity compared to other atmospheric greenhouse gases[20], and line-by-line calculations and

67 climate model radiation codes must capture this complexity to determine CH_4 radiative forcing.
68 They do so by using line parameters in spectroscopic databases such as High Resolution
69 Transmission (HITRAN)[21] and parameterizations of other absorption effects. These databases
70 are frequently updated, and while the updates have produced only modest changes in CH_4
71 infrared forcing[22,23], the scientific understanding of other potentially significant absorption
72 effects such as broadening dependencies[24] and H_2O continuum absorption[18,25] is still advancing.
73 Alternatively, we can use field observations to establish the sufficiency of the approach by which
74 CH_4 radiative forcing is solely determined from radiative transfer calculations.
75
76 The specialized, long-duration suite of observations collected at the U.S. Department of Energy
77 Atmospheric Radiation Measurement (ARM) Program[26] at the Southern Great Plains (SGP) site
78 (36° 36′ 18″ N, 97° 29′ 6″ W) provide a unique opportunity to observe greenhouse gases and
79 their forcing, as indicated by the first observation of the increase in the greenhouse effect from
80 rising atmospheric concentrations of CO_2[(27)].
81
82 The time-series of weekly CH_4 surface flask measurements from SGP shows a high variability in
83 CH_4 at SGP, with boundary layer excursions sometimes exceeding 2300 ppbv (Figure 1). As
84 with other locations of high-precision atmospheric CH_4 measurements, the time-series of CH_4
85 mixing ratios shows fine-scale temporal variability. At SGP, some of the excursions may be due
86 to local hydrocarbon recovery, based on the correlation between CH_4 and ethane mixing
87 ratios[28,29] (see Methods). Meanwhile, an analysis of these instantaneous CH_4 observations (see
88 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_2O and N_2O dependence of the downwelling flux in the CH_4 absorption band, arising from the overlap of spectral absorption features of H_2O and N_2O 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_2O are highly correlated with its mixing ratios throughout the column (Figure 2(c)), so the radiative effects of N_2O 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[33]. Airborne measurements indicate that boundary-layer and free tropospheric fluctuations in CH_4 mixing ratios are not highly correlated at subseasonal time-scales. Therefore, surface observations of CH_4 mixing ratio alone are insufficient for calculating CH_4 forcing at the time-scales of our analysis.

CH_4 surface radiative forcing was derived from 11 years' of infrared spectroscopic observations made by the Atmospheric Emitted Radiance Interferometer (AERI)[34]. The forcing was determined by differencing AERI measurements with counterfactual line-by-line calculations[27] where the thermodynamic state is prescribed by concurrent radiosonde observations[33], but the calculation used a pre-industrial CH_4 mixing ratio (see Methods). Detailed data quality control and averaging methods were used to account for the effects of uncertainties in temperature, H_2O, and N_2O, 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_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 *in situ* observations by simultaneous aircraft overflights[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

158 smaller than the observed amplitude of 0.25±0.01 (99.7% CI) W/m^2. The observed trend in CH_4
159 since 2007 is 7.5±6.6 (99.7% CI) ppbv/yr which, again based on the mean water vapor profile
160 during the observational period at the SGP, would yield a trend of 0.002±0.0009 (99.7% CI)
161 W/m^2/yr, significantly smaller than the observed trend of 0.026±0.006 (99.7% CI) W/m^2/yr.
162 However, analyzing the time-series in isolation from thermodynamics is highly idealized, can
163 yield varying results depending on the choice of thermodynamic conditions, and is inconsistent
164 with actual conditions in the field. Nevertheless, this discrepancy must be resolved.
165
166 We can exclude several potential explanations for these findings; for example, the contributions
167 of observational error and analysis error would produce spectral residuals outside of the CH_4
168 absorption band and time-series statistics that are inconsistent with our findings. Possible
169 contributions from other radiatively-active trace gases in the CH_4 absorption band between 1200
170 and 1350 cm^{-1} can also be excluded (see Methods).
171
172 Rather, we find that when we perform a multivariate signal decomposition analysis of the
173 deseasonalized time-series of CH_4 forcing constructed over the entire time-series using a
174 nonlinear predictor based solely on CH_4 concentrations, we can explain roughly 80% of the
175 variation in observed forcing (R^2=0.793), implying that at least 20.7% of the variance is related
176 to other factors (see Methods).
177
178 Rather, we find that the contribution of trends and variability in water vapour to those in CH_4
179 surface forcing are significant. Even though the residual spectra indicate that we are not
180 imprecisely specifying atmospheric temperature and moisture, CH_4 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 ν_2 H_2O absorption band. Therefore, elevated H_2O 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_2O 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 CH_4 on the clear-sky surface energy balance, with a large seasonal cycle amplitude of 0.25 W/m^2 and a significant difference in forcing trends at SGP during and after the CH_4 plateau. The decadally-averaged trend in surface forcing was larger for CO_2 than CH_4 at this site, but the perturbation of the surface energy balance from rising CH_4 mixing ratios since the end of the plateau was similar to the effect from rising CO_2 (0.02 ± 0.007 $W/m^2/yr$) 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 CH_4 in perturbing the surface energy balance can be highly dependent on local water vapour trends[39-42]. At SGP, CH_4 surface forcing trends are not necessarily inferior to that of CO_2, even though forcing at tropopause by CO_2 is much more than CH_4[(1)].

These observations show a long-term trend in CH_4 surface radiative forcing, with variance from a function of rising CH_4 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 CH_4 impacts average tropospheric temperatures[1], but spatial patterns in upper tropospheric moisture[43] 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 time-scales while also exhibiting trends that are spatially variable over land and that show strong land-ocean contrast[39-42]. 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.

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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 CH_4 signal; S.C.B. provided CH_4 and N_2O 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 C_2H_6 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_2O, N_2O, 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_2O, 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), 2σ instantaneous uncertainty in CH_4 surface longwave radiative forcing (gray; see Methods) and trends with 3σ uncertainty (red; ibid.) at DOE ARM SGP.

Figure 4: Thermodynamic dependence of CH_4 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 CH_4 as a function of temperature perturbations from 8 to 16.5 km from a mid-latitude summer atmosphere[44]. 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 CH_4 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_2O 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_2O 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[57].

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[33]. 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[58]. 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_2O, and 10% N_2O. 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[59]. 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[59]. 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[60]. 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 CH_4 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[61]. 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 CH_4 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 ~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 that 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

539 The statistical analysis of the time-series seeks to determine whether and when a change point
540 occurred in the measured CH_4 surface radiative forcing, as well as the linear (temporal) trends
541 and their significance. The following describes the methods used to perform this analysis.
542
543 Define y_t as the CH_4 forcing for the SGP site at time $t = 1,\ldots, T$. Our statistical model is:
544
545 $$y_t = b_0 + b_1 t + b_2 X_t (t - t_0) + a_j + e_t + v_t, \quad (1)$$
546
547 where $\{b_k\}$ are unknown regression coefficients, $\{a_j\}$ represent (unknown) monthly effects, e_t are
548 independent and identically distributed (iid) $N(0, s^2)$ with s^2 unknown ($N(a, b)$ denotes a
549 univariate Gaussian random variable with mean a and variance b), and v_t iid $N(0, w^2)$ with w^2
550 known (also, e_t and v_t are independent). The model (1) contains two error processes: first, e_t
551 represents error in the model specification and therefore s^2 is estimated; second, v_t represents
552 error introduced by the measurement process on y_t and therefore w^2 will be considered fixed (see
553 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
554 change point must fall between fixed bounds $T_U < t_0 < T_L$. Therefore, for $t \leq t_0$, the monthly-
555 adjusted trend in expected CH_4 forcing has slope b_1; for $t > t_0$, the trend has slope $b_1 + b_2$.
556
557 The unknown parameters in (1) and the change point can be estimated using a common
558 (Frequentist) statistical technique called maximum likelihood (ML)[63], which also yields
559 confidence intervals for the regression coefficients[64]. Given the setup in (1), we can determine
560 the significance of the change point t_0 by way of model selection: the full model (1) can be vs.

561 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
562 models[64].
563
564 The Frequentist analysis described above ignores any uncertainty in estimating the change point,
565 and the model is not well suited to assess this uncertainty (outside of asymptotic evaluations)[65].
566 Alternatively, a Bayesian approach can be used to determine the significance of the change point
567 while accounting for its uncertainty (again using model comparison). Bayesian models that
568 mirror the full (1) and reduced (2) models can be set up using noninformative prior distributions
569 and estimated using Markov Chain Monte Carlo (MCMC) methods[66]. MCMC output can be used
570 to compare the full and reduced models using Bayes factors[67].
571
572 **Statistical Analysis Results**
573 The aforementioned models were fit for many different data sets from the SGP site. This data set
574 was created by using values of the 800 cm^{-1} brightness temperature (BT) residual threshold
575 parameter ranging from 0.1 to 10 (see Data Quality Control). However, if the data set for a
576 particular threshold value had fewer than 50 observations, the analysis was not conducted. The
577 upper and lower limits of the change point were fixed to T_L = 2004 and T_U = 2010; any potential
578 change points near the beginning or end of the time series are not of interest. The seasonal cycle
579 of CH_4 due to hydroxyl radical destruction is captured via the monthly effects $\{a_j\}$; for
580 comparison, all models were fit and results presented both with and without the monthly effects.
581
582 For the ML models, plots of the estimated change point, significance of the change point, and
583 estimates of the slope parameters (with 99.7% confidence intervals) from both before and after

584 the change point are provided in Supplementary Information Figures 5 and 6. Results from the
585 Bayesian models were approximately identical to the ML models and are omitted. Based on the
586 similarity of results, the main text used the more familiar Frequentist results including the
587 monthly adjustment.
588
589 Supplementary Information Table 1 numerically summarizes the results of the statistical analysis
590 used in the main text where the 800 cm^{-1} BT threshold is 3 K.
591
592 **Controlling for N_2O**
593 The methods used to determine CH_4 surface radiative forcing can be biased by N_2O. Figure 2(b)
594 shows this due to the substantial amount of overlap in spectral radiance changes from
595 perturbations from N_2O and CH_4. However, the vertical profiles of N_2O collected by the ARM-
596 ACME missions[35] at SGP show that N_2O mixing ratios at altitude are highly vertically-correlated
597 with the surface (see insets of Figure 2(c)) and vary by less than 1 ppbv seasonally.
598
599 Moreover, these differ very little from measurements at MLO. The error incurred in CH_4 forcing
600 from utilizing monthly-averaged MLO N_2O observations instead of in situ ARM-ACME N_2O
601 observations was maximized at 1.2% of the CH_4 forcing.
602
603 N_2O can still bias CH_4 forcing because it is emitted after precipitation following the nearby fresh
604 application of nitrogen-based fertilizer[68], causing >5 ppbv deviations from the background N_2O
605 mixing ratio. NEXRAD data[69] were used to screen data to remove those observations for which
606 precipitation had occurred in the previous 24 hours.

607

608 **Instantaneous Error**

609 There are several sources of error in the determination of the surface forcing from the AERI
610 measurements. They include (1) spectroscopic error in LBLRTM; (2) AERI measurement error;
611 (3) error in the temperature, water vapour, CO_2, or O_3 inputs to LBLRTM inputs; and (4) a
612 contribution of unknown aerosol or cloud condensates to the AERI observations. While the error
613 contributions from (1) are outside of the scope of this analysis, we can perform a top-down
614 estimate of errors from (2) through (4) with AERI measurements and LBLRTM calculations
615 using inputs from simultaneous aircraft profiles.

616

617 Surface radiative forcing time series from the aircraft data were derived from differencing AERI
618 observations with counterfactual calculations. These were compared with the surface radiative
619 forcing time series computed by differencing an LBLRTM calculation with the aircraft-observed
620 profile of CH_4 and N_2O and the counterfactual calculation.

621

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

626

627 **Ethane Data Analysis**

628 Supplementary Information Figures 9(a) and 9(b) show time-series analyses of ethane (C_2H_6)
629 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 CH_4 surface radiative forcing. We estimate this bias by recalculating the Broadband Heating Rate Profile (BBHRP)[71] profiles at SGP for 2010 based on pre-industrial CH_4 mixing ratios and comparing those to the original BBHRP profiles, containing time-varying CH_4 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) product[73].

We find that most of the forcing is in the clear-sky but that the all-sky surface forcing is 0.065 W/m^2, or 33%, less than the clear-sky forcing. This finding is expected because of non-negligible overlap between broadband cloud absorption and CH_4 absorption, thereby masking CH_4 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 CH_4 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 CH_4 surface forcing must be considered. The contribution of condensates can be excluded because they produce broadband signals that are not observed in the

653 residual spectra. We can also address the non-methane gaseous constituent question by
654 determining the effects of perturbations in the atmospheric concentrations of 32 additional
655 species with spectroscopy tabulated in HITRAN[21], and found their contributions to be at least 5
656 orders of magnitude smaller than CH_4.
657
658 **Flasks-Based Observations**
659 At the SGP site, a pair of 2.5 liters glass flasks is collected on a weekly basis from the top of the
660 central facility 60m tower. Flask collection started in April 2002 and is currently ongoing. The
661 collection of a pair of flasks allows basic quality assessment and control. These observations are
662 part of the NOAA's Global Greenhouse Gases Reference Network (REF)[74]. Flasks are collected
663 in the afternoon, when the planetary boundary layer is well-developed and observations are
664 representative of a large area. Aircraft profiles of CH_4 and N_2O were recorded on approximately
665 a bi-monthly basis from 2002 until the present (see Supplementary Information Figures 7(a) and
666 7(b)).
667
668 Ground-based and aircraft-based flasks are analyzed after they are collected at NOAA/ESRL by
669 gas chromatography, and measurements are reported against WMO CH_4-X2004 and N_2O
670 X2006A scales. Flask-based observations are shown to have uncertainties of less than 1.2 ppbv
671 for CH_4 and 0.4 ppbv for N_2O.
672
673 **Aircraft Validation**
674 Aircraft profiles of CH_4 and N_2O above the SGP site were recorded on approximately a weekly
675 basis with flask observations from 2002 until the present. Prior to 2006, the flasks were

676 collected only at 0.6 and 3.6 km, but since then, flasks were collected at 12 elevations between
677 0.5 km and 5.5 km above sea level (see Supplementary Information Figures 7(a) and 7(b)).
678
679 **Single-Site Analysis**
680 The analysis presented here focused on the SGP site. Several other ARM sites exist, including
681 the North Slope of Alaska (NSA) site, and AERI data from that site was analyzed for previous
682 work[27]. For the CH_4 analysis, however, differences in the instrumental noise in the AERI
683 instrument at NSA greatly complicated the analysis there. In particular, the Extended—Range
684 AERI at NSA has an expanded spectral range compared to the AERI at SGP, leading to higher
685 instrumental (random) noise over 1200-1350 cm^{-1} spanning the dominant CH_4 absorption
686 feature[75].
687
688 **Residual Brightness Temperature Threshold Rationale**
689 The rationale for choosing a threshold of 3 K brightness temperature is based on balancing the
690 number of data points with error in the CH_4 surface forcing determination, both of which will
691 increase with increasing threshold values. Another related factor for the determination of an
692 appropriate threshold is the importance of observations throughout the year. The 3 K threshold
693 enables a determination of the seasonal cycle in surface forcing at the SGP site and summertime
694 multi-year trends at the NSA site. Supplementary Information Figure 3 shows the relationships
695 between the 800 cm^{-1} brightness temperature residual threshold and the number of data points.
696
697 **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/ and 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

CarbonTracker-CO2: ftp://aftp.cmdl.noaa.gov/products/carbontracker/co2/molefractions/

CarbonTracker-CH4: ftp://aftp.cmdl.noaa.gov/products/carbontracker/ch4/molefractions/

NOAA CH_4 data: http://ds.data.jma.go.jp/gmd/wdcgg/pub/data/current/ch4/

NOAA N_2O data:

ftp://aftp.cmdl.noaa.gov/data/hats/n2o/insituGCs/CATS/daily/mlo_N2O_Day.dat

NOAA C_2H_6 data: http://ds.data.jma.go.jp/gmd/wdcgg/pub/data/current/vocs/ethane/event/

Code Availability

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

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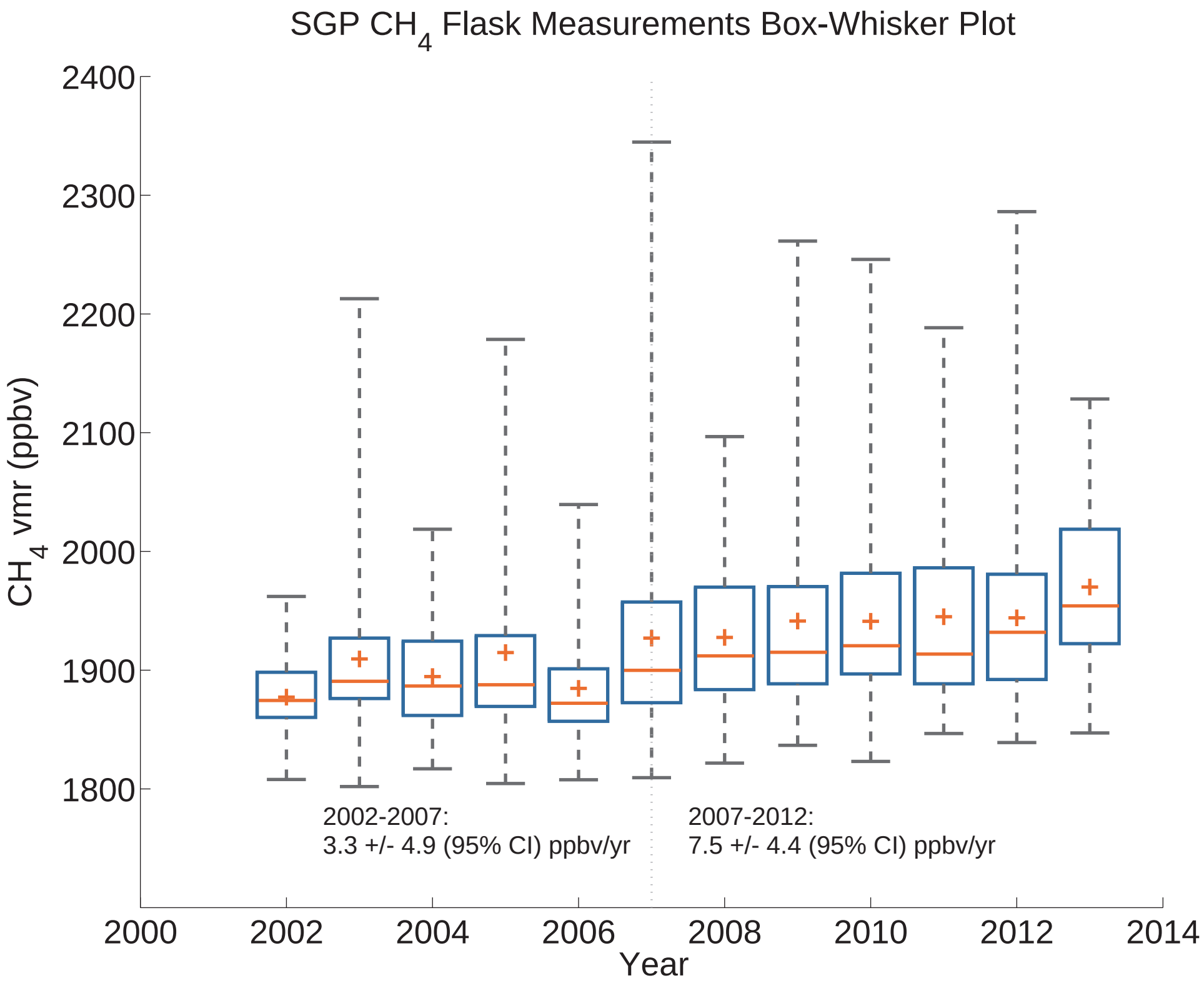
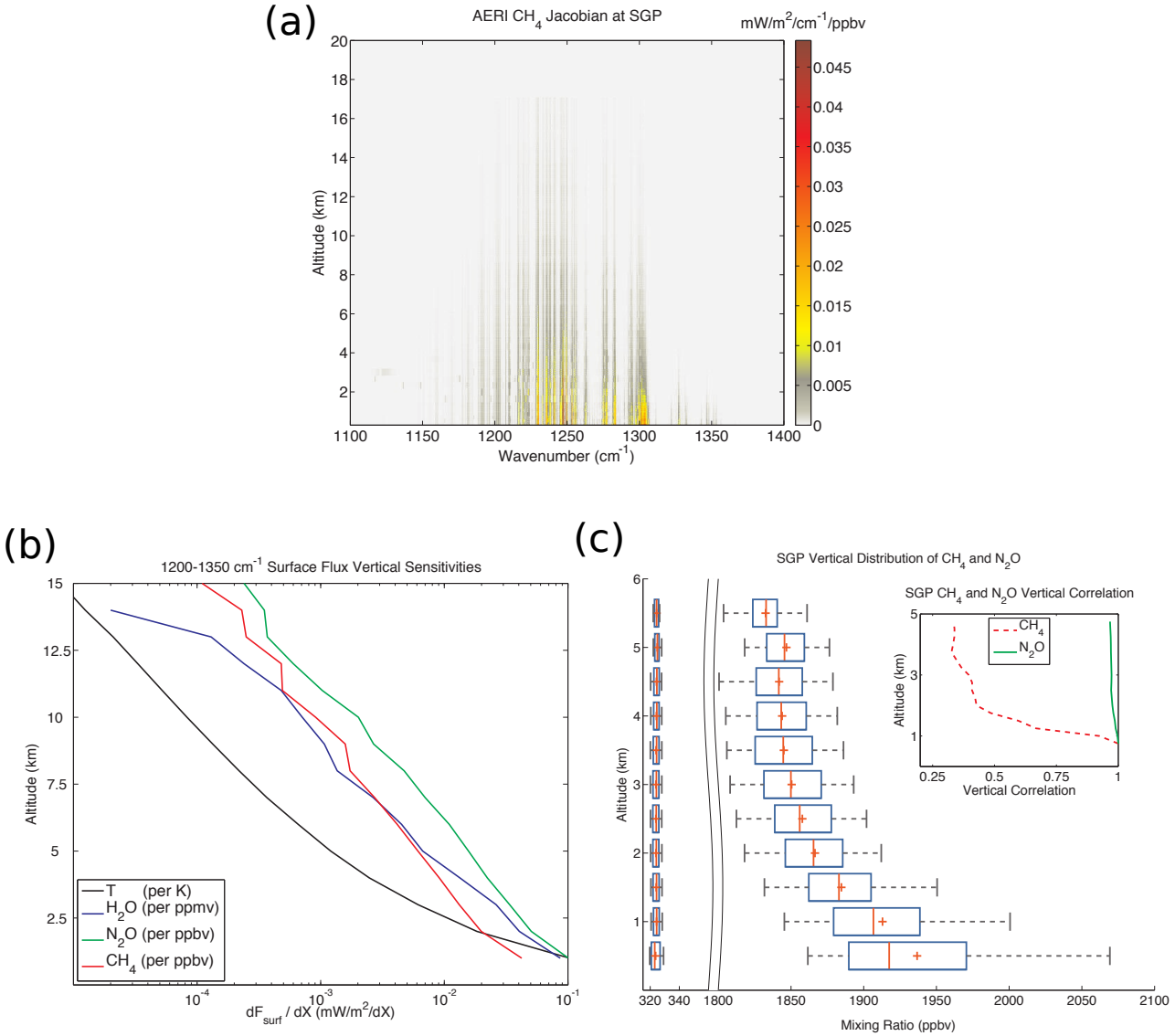
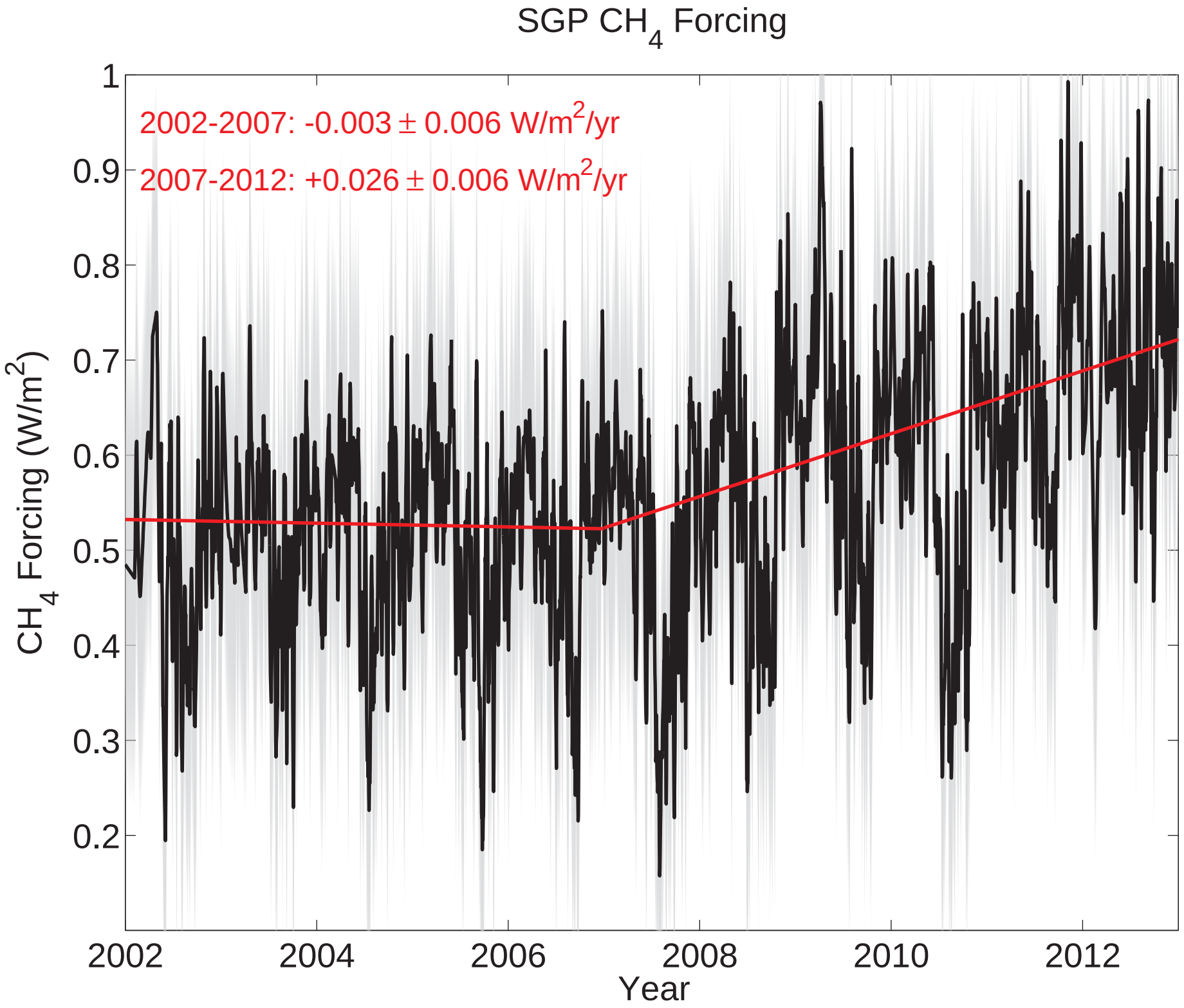
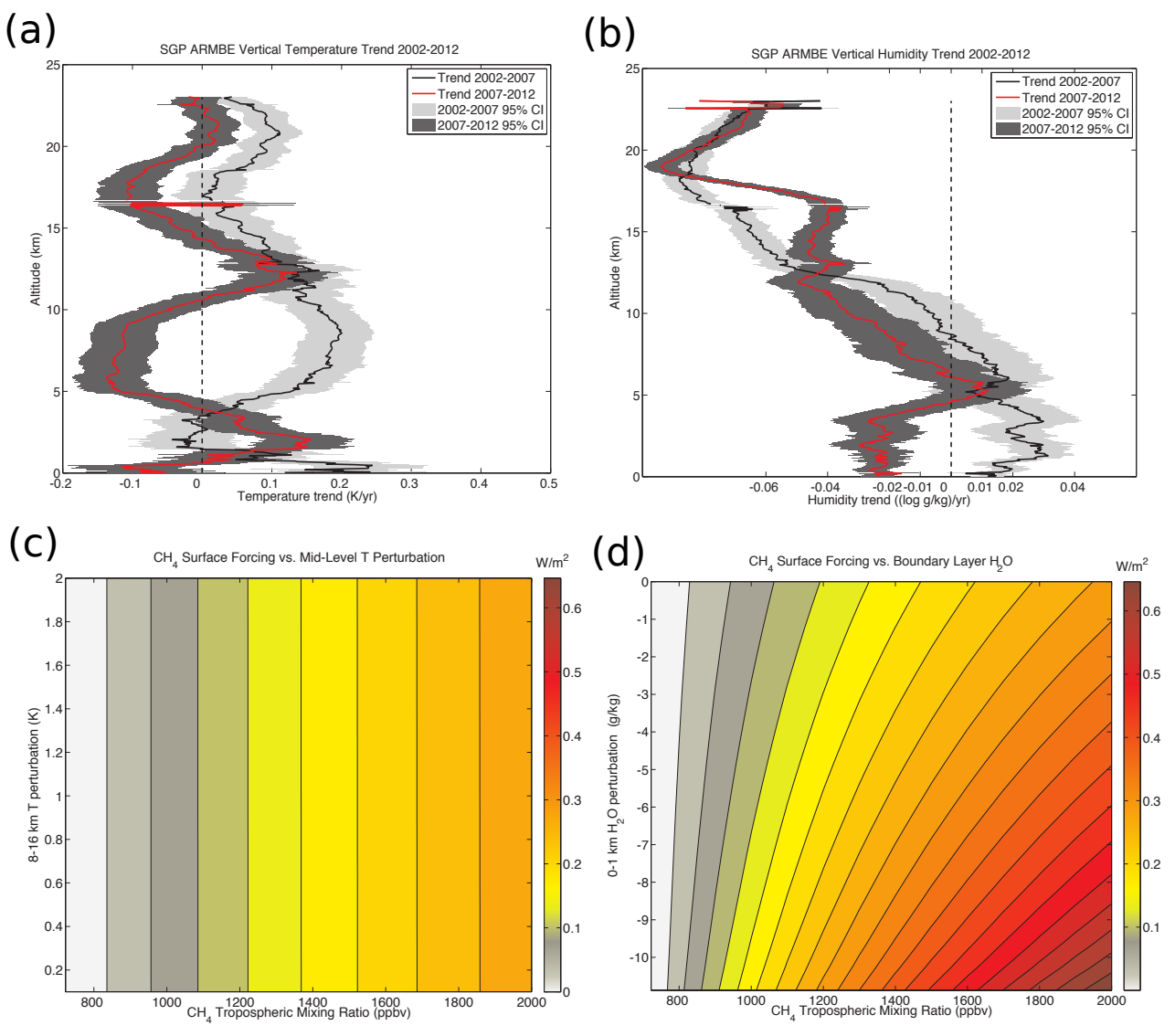
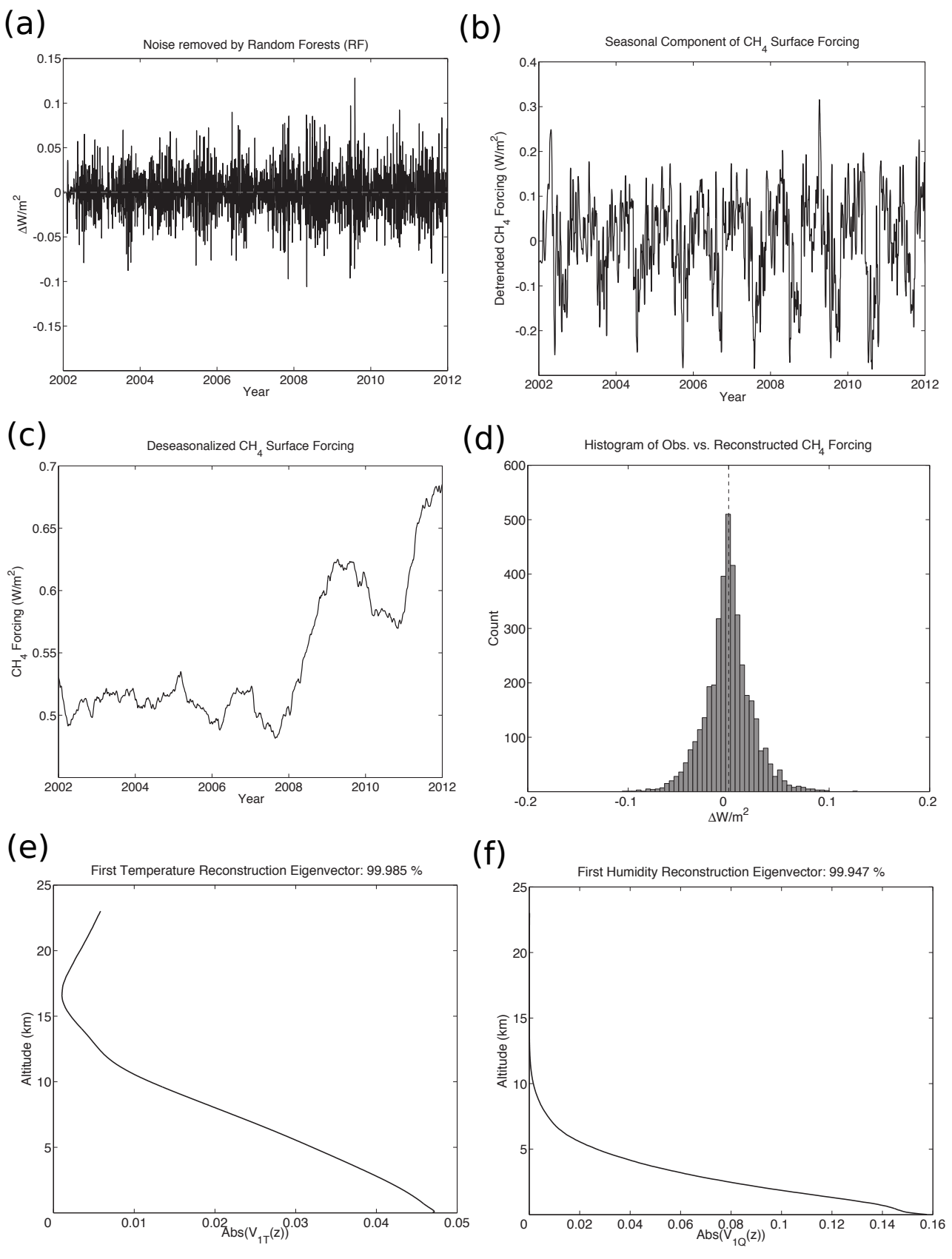

SGP CH4 Flask Measurements Box-Whisker Plot
CH4 vmr (ppbv)
2400
2300
2200
2100
2000
1900
1800
2000
2002
2004
2006
2008
2010
2012
2014
Year
2002-2007:
3.3 +/- 4.9 (95% CI) ppbv/yr
2007-2012:
7.5 +/- 4.4 (95% CI) ppbv/yr


(a)
AERI CH4 Jacobian at SGP
mW/m2/cm-1/ppbv
Altitude (km)
Wavenumber (cm-1)
(b)
1200-1350 cm-1 Surface Flux Vertical Sensitivities
Altitude (km)
dFsurf / dX (mW/m2/dX)
T (per K)
H2O (per ppmv)
N2O (per ppbv)
CH4 (per ppbv)
(c)
SGP Vertical Distribution of CH4 and N2O
Altitude (km)
Mixing Ratio (ppbv)
SGP CH4 and N2O Vertical Correlation
Vertical Correlation


SGP CH4 Forcing
2002-2007: -0.003 ± 0.006 W/m2/yr
2007-2012: +0.026 ± 0.006 W/m2/yr
CH4 Forcing (W/m2)
Year
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
2002
2004
2006
2008
2010
2012


(a)
SGP ARMBE Vertical Temperature Trend 2002-2012
Trend 2002-2007
Trend 2007-2012
2002-2007 95% CI
2007-2012 95% CI
Altitude (km)
Temperature trend (K/yr)
(b)
SGP ARMBE Vertical Humidity Trend 2002-2012
Trend 2002-2007
Trend 2007-2012
2002-2007 95% CI
2007-2012 95% CI
Altitude (km)
Humidity trend ((log g/kg)/yr)
(c)
CH4 Surface Forcing vs. Mid-Level T Perturbation
W/m2
8-16 km T perturbation (K)
CH4 Tropospheric Mixing Ratio (ppbv)
(d)
CH4 Surface Forcing vs. Boundary Layer H2O
W/m2
0-1 km H2O perturbation (g/kg)
CH4 Tropospheric Mixing Ratio (ppbv)


(a)
Noise removed by Random Forests (RF)
ΔW/m2
Year
(b)
Seasonal Component of CH4 Surface Forcing
Detrended CH4 Forcing (W/m2)
Year
(c)
Deseasonalized CH4 Surface Forcing
CH4 Forcing (W/m2)
Year
(d)
Histogram of Obs. vs. Reconstructed CH4 Forcing
Count
ΔW/m2
(e)
First Temperature Reconstruction Eigenvector: 99.985 %
Altitude (km)
Abs(V1T(z))
(f)
First Humidity Reconstruction Eigenvector: 99.947 %
Altitude (km)
Abs(V1Q(z))