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

3

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21 **Main Text:**

22 Atmospheric methane (CH₄) mixing ratios exhibited a plateau between 1995 and 2006 and have
23 been subsequently increasing. While there are a number of competing explanations for the
24 temporal evolution of this greenhouse gas, these prominent features in the temporal trajectory of
25 atmospheric CH₄ are expected to perturb the surface energy balance through radiative forcing,
26 largely due to CH₄'s infrared radiative absorption features. However, to date this has been
27 determined strictly through radiative transfer calculations. Here, we present a quantified
28 observation of the time-series of clear-sky radiative forcing by CH₄ at the surface from 2002-
29 2012 at a single site derived from spectroscopic measurements along with line-by-line
30 calculations using ancillary data. There was no significant trend in CH₄ forcing between 2002
31 and 2006, but since then, the trend in forcing was 0.026 ± 0.09 (99.7% CI) W/m²/yr. The
32 seasonal-cycle amplitude and secular trends in observed forcing are influenced by a
33 corresponding seasonal cycle and trend in atmospheric CH₄. However, we find that we must
34 account for the overlapping absorption effects of atmospheric water vapour (H₂O) and CH₄ to
35 explain the observations fully. Thus, the determination of CH₄ radiative forcing requires accurate
36 observations of both the spatiotemporal distribution of CH₄ and the vertically resolved trends in
37 H₂O.

38

39 **Atmospheric CH₄ and Its Radiative Forcing**

40 The globally-averaged atmospheric mixing ratio of CH₄ has risen since the pre-industrial epoch
41 from 722 ± 25 ppbv in 1750 to 1803 ± 2 ppbv in 2011⁽¹⁾. However, there is an unresolved debate
42 regarding the causes of the temporal trajectory of CH₄, and thus its sources and sinks, over the
43 last 30 years. The observed plateau in the CH₄ mixing ratio² and its end³ have been attributed to

44 some combination of changes in (1) hydroxyl (OH) radical destruction, (2) tropical wetland
45 emissions, (3) thawing permafrost and CH₄ hydrates, (4) agriculture, and (5) fossil-fuel
46 extraction and use, though their relative contributions are ambiguous given existing
47 observations⁴⁻¹⁰.

48
49 Rising atmospheric CH₄ mixing ratios are expected to change the distribution of atmospheric
50 radiative energy, and this is the essential justification for coordinated and prioritized scientific
51 inquiry regarding atmospheric CH₄. While substantial resources have been devoted to measuring
52 increasing atmospheric CH₄^(2,11) and understanding its anthropogenic contributions¹²⁻¹⁴, the
53 observational determination of its radiative forcing has, to date, been limited. Satellite
54 observations have inferred, but not quantified, the radiative forcing associated with rising mixing
55 ratios of this gas^{15,16}. Apart from those efforts, radiative forcing values have been strictly
56 calculated by radiative transfer models based on information gathered from laboratory
57 observations. The calculations performed for the IPCC Fifth Assessment report found that CH₄
58 has contributed to a stratospherically-adjusted longwave (5-20 μm) radiative forcing at the
59 tropopause of 0.48±0.05 W/m² from the pre-industrial epoch¹. However, the methods used by
60 that report were last revised in 1998⁽¹⁷⁾, and recent work has indicated that an upward revision to
61 the methane radiative forcing formulae and the determination of its global warming potential for
62 future Assessment Reports is necessary¹⁸, mostly due to the need to include shortwave effects.

63
64 The spectroscopy of CH₄, which is the foundation underlying the radiative forcing calculations,
65 is an active area of research¹⁹. This is because CH₄ exhibits a line structure of exceptional
66 complexity compared to other atmospheric greenhouse gases²⁰, and line-by-line calculations and

67 climate model radiation codes must capture this complexity to determine CH₄ 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 CH₄
71 infrared forcing^{22,23}, the scientific understanding of other potentially significant absorption
72 effects such as broadening dependencies²⁴ and H₂O continuum absorption^{18,25} is still advancing.
73 Alternatively, we can use field observations to establish the sufficiency of the approach by which
74 CH₄ 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) Program²⁶ 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 CO₂⁽²⁷⁾.

81

82 The time-series of weekly CH₄ surface flask measurements from SGP shows a high variability in
83 CH₄ at SGP, with boundary layer excursions sometimes exceeding 2300 ppbv (Figure 1). As
84 with other locations of high-precision atmospheric CH₄ measurements, the time-series of CH₄
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 CH₄ and ethane mixing
87 ratios^{28,29} (see Methods). Meanwhile, an analysis of these instantaneous CH₄ observations (see
88 Methods) shows (1) no significant trend in atmospheric CH₄ before 2007, (2) a break-point in

89 2007, and (3) that CH₄ mixing ratios have been rising at a rate of 7.5±4.4 (95% CI) ppbv/yr since
90 then.

91
92 While other studies have observed trends in the surface energy balance with broadband
93 radiometry^{30,31}, broadband observations are inadequate for attributing changes in that balance to
94 changes in atmospheric composition of specific gas species. Therefore, we use a long time-series
95 of clear-sky downwelling spectral infrared radiance observations to determine if changes in
96 atmospheric CH₄ mixing ratios have a discernible effect on the surface energy balance. We focus
97 here on longwave clear-sky flux changes since they are predicted to be the most sensitive
98 longwave radiative flux signal associated with rising greenhouse gases³² and since detailed all-
99 sky forcing calculations of the study site indicate that most of the forcing arises under clear-sky
100 conditions (see Methods).

101

102 **CH₄ Radiative Forcing Dependencies**

103 Figure 2(a) shows, through radiative transfer calculations, that the infrared emission by CH₄ that
104 contributes to its longwave surface radiative forcing occurs predominantly between 1200 and
105 1350 cm⁻¹. However, as the radiative transfer calculations in Figure 2(b) show, the determination
106 of CH₄ forcing is complicated by a significant H₂O and N₂O dependence of the downwelling
107 flux in the CH₄ absorption band, arising from the overlap of spectral absorption features of H₂O
108 and N₂O with those of CH₄. The downwelling flux is also highly temperature-dependent both
109 due to Planck function and absorption line temperature dependence. Fortunately, the surface
110 mixing ratios for N₂O are highly correlated with its mixing ratios throughout the column (Figure
111 2(c)), so the radiative effects of N₂O can be estimated using a near-surface measurement of its

112 mixing ratio. Radiosonde data at the ARM SGP site were used to control for variability in the
113 atmospheric thermodynamic state³³. Airborne measurements indicate that boundary-layer and
114 free tropospheric fluctuations in CH₄ mixing ratios are not highly correlated at subseasonal time-
115 scales. Therefore, surface observations of CH₄ mixing ratio alone are insufficient for calculating
116 CH₄ forcing at the time-scales of our analysis.

117
118 CH₄ surface radiative forcing was derived from 11 years' of infrared spectroscopic observations
119 made by the Atmospheric Emitted Radiance Interferometer (AERI)³⁴. The forcing was
120 determined by differencing AERI measurements with counterfactual line-by-line calculations²⁷
121 where the thermodynamic state is prescribed by concurrent radiosonde observations³³, but the
122 calculation used a pre-industrial CH₄ mixing ratio (see Methods). Detailed data quality control
123 and averaging methods were used to account for the effects of uncertainties in temperature, H₂O,
124 and N₂O, and the effect of instrumental noise, respectively (see Methods). The minimum
125 temporal resolution of the observations used here was 6 hours (see Methods). From this process
126 chain, we observe the direct, unadjusted, instantaneous radiative forcing at the surface, which,
127 while not biased by the effects of thermodynamics (see Methods), is still affected by them.
128 Ideally, measurements would be made under prescribed thermodynamic conditions, but we have
129 no means of controlling for these conditions in the field.

130
131 The mean spectral residuals were prominent only in the spectral region of CH₄ absorption (see
132 Methods) and therefore exclude the possibility that uncertainties in the atmospheric state and
133 instrument calibration were substantially affecting the results. Top-down validation of our
134 forcing estimates, based on *in situ* observations by simultaneous aircraft overflights³⁵, indicates

135 that we can observe instantaneous CH₄ forcing to within 0.14 W/m² (see Methods). Sensitivity
136 tests (see Methods) reveal that the transient plumes of boundary layer methane would lead to an
137 instantaneous surface radiative forcing signal of 0.05 W/m², so our analysis is unable to discern
138 the transient contribution of anthropogenic activity to observed forcing. However, suprasedasonal
139 time-series features of atmospheric CH₄ mixing ratios, which do contain contributions from
140 human activity⁴⁻¹⁰, are readily discernible in the observed radiative forcing.

141

142 **Observationally-Derived Forcing Time-Series and Influence of Thermodynamics**

143 Irrespective of the source of the atmospheric CH₄, we derive a time-series of CH₄ surface
144 longwave radiative forcing from observations that exhibits several prominent features (Figure 3).
145 During the multi-year atmospheric CH₄ plateau, the trend in this forcing did not differ
146 significantly from zero (p>0.1). The time-series exhibited a significant change around 2007 at
147 the end of the plateau (p<0.0001). From then onwards, the trend differed from zero at
148 0.026±0.006 W/m²/yr (99.7% CI). During the 11-year record, there was a large seasonal cycle,
149 with an amplitude of at least 0.2 W/m².

150

151 During the time period of the atmospheric CH₄ plateau, it is expected that there would not be
152 significant trends in surface radiative forcing from CH₄, and this was confirmed by observations.
153 However, the amplitude of the seasonal cycle in surface forcing throughout the time-series and
154 the forcing trend since 2006 cannot be fully explained by the atmospheric CH₄ mixing ratio at
155 SGP. The amplitude of the seasonal cycle in CH₄ dry atmospheric mixing ratio is 51.2±10.1
156 (99.7% CI) ppbv, and, based on the mean water vapor profile during the observational period at
157 the SGP, the seasonal cycle amplitude would be 0.012±0.002 (99.7% CI) W/m², 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 $\text{W/m}^2/\text{yr}$, significantly smaller than the observed trend of 0.026 ± 0.006 (99.7% CI) $\text{W/m}^2/\text{yr}$.
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

181 dependent on atmospheric state. The primary reason for this water vapour dependence is that
182 mid-IR CH₄ absorption occurs at the edge of a strong ν₂ H₂O absorption band. Therefore,
183 elevated H₂O mixing ratios saturate the CH₄ band³⁶ and reduce the latter molecule's radiative
184 forcing, as shown in Figures 4(d). Indeed, we performed a model-only computation based on
185 observed thermodynamics and CH₄ mixing ratios and obtain a trend of 0.020±0.009 (99.7% CI)
186 W/m²/yr, which is not distinguishable (p>0.05) from the observationally-derived trend.
187 Additionally, this effect is largely insensitive to the observed mid-tropospheric temperature
188 changes, as shown in Figure 4(c).

189
190 For the seasonal cycle, we find that the water vapour seasonal cycle of 7.7±0.03 g/kg helps
191 explain the seasonal cycle in observed CH₄ surface forcing. For trends, we note that a long-term
192 decreasing trend in moisture availability in the central US has been observed³⁷. This was also
193 observed in a 14-year analysis of AERI clear-sky radiances³⁸. At SGP, an analysis of radiosondes
194 coincidental to the CH₄ forcing observations is consistent with that finding and yields negative
195 trends in atmospheric moisture in the lowest 1 km, as shown in Figure 4(b). While no significant
196 change point in the vertically-resolved time-series is observed, column water decreased by 30%
197 since the end of the CH₄ plateau. This negative trend over the entire time-series and especially
198 since the end of the CH₄ plateau will tend to enhance CH₄ forcing, and provides the opportunity
199 to analyze the alternating effects of CH₄ and H₂O on the observed forcing. Figure 5 shows that
200 the observed forcing trends in CH₄ forcing could be reproduced only when we include nonlinear
201 predictors that include both CH₄ concentration and observed thermodynamic trends (R²=0.997,
202 see Methods). Specifically, trends in CH₄ surface flask measurements and trends in height-
203 resolved temporal profiles of temperature and humidity can be used to predict both plateau and

204 post-plateau surface radiative forcing trends after all variables are decomposed into frequency
205 noise (5a), a seasonal component (5b), and deseasonalized trends (5c), yielding a normally-
206 distributed residual signal (5d). The result is that the first temperature and moisture principal
207 components, covering the lower 5 km of the atmosphere, explain nearly all of the signal's
208 variance (5e and 5f).

209

210 **Broader Implications**

211 This study presents the first observational derivation and quantification of the effect of time-
212 varying CH₄ on the clear-sky surface energy balance, with a large seasonal cycle amplitude of
213 0.25 W/m² and a significant difference in forcing trends at SGP during and after the CH₄ plateau.
214 The decadal-averaged trend in surface forcing was larger for CO₂ than CH₄ at this site, but the
215 perturbation of the surface energy balance from rising CH₄ mixing ratios since the end of the
216 plateau was similar to the effect from rising CO₂ (0.02±0.007 W/m²/yr) at the site. Though this
217 difference was not statistically significant (p>0.3), it suggests that, since the end of the plateau,
218 the role of rising CH₄ in perturbing the surface energy balance can be highly dependent on local
219 water vapour trends³⁹⁻⁴². At SGP, CH₄ surface forcing trends are not necessarily inferior to that
220 of CO₂, even though forcing at tropopause by CO₂ is much more than CH₄⁽¹⁾.

221

222 These observations show a long-term trend in CH₄ surface radiative forcing, with variance from
223 a function of rising CH₄ mixing ratios and the non-negligible contribution that depends on the
224 vertical distribution of water vapour. This finding is related to tropopausal radiative forcing,
225 which figures prominently in the scientific discussion of how rising CH₄ impacts average
226 tropospheric temperatures¹, but spatial patterns in upper tropospheric moisture⁴³ mediate forcing

227 at the tropopause, while surface humidity more strongly affects surface forcing. For this
228 investigation, we find that trends in surface forcing from greenhouse gases are convolved with
229 the details of how the thermodynamic state of the atmosphere is evolving, and the local
230 thermodynamic conditions must be taken into account. Since local temperature and humidity
231 trends that are distinct from those at SGP exist at other sites, the relative contributions of
232 thermodynamics and mixing ratio changes to the forcing may also differ. Observed trends in
233 surface humidity have not been spatially or temporally uniform, nor have they been monotonic.
234 The magnitude of the globally-averaged land-surface humidity trend varies on decadal time-
235 scales while also exhibiting trends that are spatially variable over land and that show strong land-
236 ocean contrast³⁹⁻⁴². Therefore, the direct impact of greenhouse gases on the surface energy
237 balance cannot be predicted in isolation from thermodynamics. Nevertheless, as we have shown,
238 CH₄ surface radiative forcing trends can be derived from measurements and quantified
239 spectroscopically.

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354
355 **Author Contributions:** D.R.F. led the research, performed all calculations, and wrote the
356 manuscript; W.D.C. proposed the study concept, provided research guidance, and conceived
357 methods for isolating the CH₄ signal; S.C.B. provided CH₄ and N₂O data and associated support;
358 M.D.R. provided the statistical analysis; D.D.T. provided guidance on AERI instrument
359 performance and research focus; P.J.G. helped interpret AERI data; J.T. analyzed
360 thermodynamic contributions to the observed forcing. D.H. provided C₂H₆ data and associated
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362 sky error analysis; M.S.T. provided research feedback and guidance and served as P.I. of the
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364 manuscript.

365

366 **Competing financial interests:** The authors declare no competing financial interests.

367 **Figure Captions:**

368

369 **Figure 1:** Recent evolution of atmospheric methane at the surface study site.

370 Time-series of the annual distribution of surface flask measurements of CH₄ at DOE ARM SGP

371 site. Box-whisker plots show the mean (+), median (line), the box bounding the 25- and 75-

372 percentile and the whiskers set at the 0.1- and 99.9-percentile for weekly flask measurements

373 from a given year. Least-squares linear trend analyses are included for selected time periods

374 before and after 2007 (vertical dashed line). The 2007 change-point was determined from weekly

375 time-series data (see Methods).

376

377 **Figure 2:** Factors affecting CH₄ longwave surface instantaneous radiative forcing.

378 (a) Change in spectral flux for a 1 ppbv perturbation in CH₄ for a 1 km layer in a Mid-Latitude

379 Summer (MLS) profile⁴⁴. (b) Vertical sensitivity of downwelling surface flux in CH₄ absorption

380 band to 1 km perturbations in temperature, H₂O, N₂O, and CH₄ derived from LBLRTM radiative

381 transfer calculations with the MLS profile (c) Box-whisker diagrams of the vertical distribution

382 of CH₄ and N₂O, with inset of associated correlation coefficient in mixing ratio between the

383 surface and a given height, from aircraft observations³⁵ at SGP from flights 2002-2012. Box

384 spans 25th to 75th percentile, whisker spans 5th to 95th percentile of observations.

385

386 **Figure 3:** CH₄ longwave surface radiative forcing time-series.

387 Time-series (black), 2σ instantaneous uncertainty in CH₄ surface longwave radiative forcing

388 (gray; see Methods) and trends with 3σ uncertainty (red; *ibid.*) at DOE ARM SGP.

389

390 **Figure 4:** Thermodynamic dependence of CH₄ surface forcing.

391 (a) Vertically-resolved slope of ARMBE temperature measurements with the 99.7% confidence-
392 interval. (a) Same as (b) but for trends in the logarithm of specific humidity. (c) Surface radiative
393 forcing vs. tropospheric-averaged CH₄ as a function of temperature perturbations from 8 to 16.5
394 km from a mid-latitude summer atmosphere⁴⁴. The change in mid-level temperature over the
395 observed time-period was 0.4 ± 0.2 °K (99.7% CI) and is indicated on the plot (d) Same as (c) but
396 for humidity perturbations in g/kg from 0 to 1 km. The change in boundary-layer water vapour
397 over the observed time-period was -1.5 ± 1.0 g/kg (99.7% CI) and is indicated on the plot.

398

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

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

405 **Methods:**

406 CH₄ surface radiative forcing was determined by differencing measured spectra from the AERI
407 instrument⁴⁵, subject to quality control (see below), with radiative transfer calculations using 512
408 levels of temperature and humidity from radiosondes profiles as processed by the ARM Best
409 Estimates (ARMBE)^{33,46}, ozone from the Modern-Era Retrospective Analysis for Research and
410 Applications (MERRA)⁴⁷, CO₂ profiles from the nearest spatiotemporal grid point from
411 CarbonTracker-CO2 2013⁽⁴⁸⁾, monthly-averaged N₂O mixing ratios from the Mauna Loa
412 Observatory (MLO)⁴⁹, and pre-industrial (722 ppbv) CH₄ mixing ratios. This counterfactual
413 calculation, designed to simulate the spectrally-resolved radiance field at the Earth's surface, had
414 CH₄ mixing ratios remained at annually-averaged pre-industrial levels²⁷. The counterfactual was
415 created using the Line-by-Line Radiative Transfer Model (LBLRTM) version 12.2, using the
416 AER line parameter database version 3.1⁽⁵⁰⁾ based on HITRAN 2008⁽⁵¹⁾ with updated line-
417 mixing⁵² and the MT_CKD_2.5.2 H₂O continuum absorption model²⁵. Limb-brightening factors,
418 converting both observations and calculations from radiance to flux, were calculated with three-
419 point Gaussian quadrature over zenith angle⁵³. Supplementary Information Figure 1 shows a
420 schematic of this process chain.

421

422 **Data Quality Control**

423 AERI spectra were recorded every 8 minutes from the instrument's initial deployment to April
424 2004 (at SGP). Subsequently, spectra were recorded every 30 seconds, with only minor outages,
425 in order to provide higher temporal-resolution data for cloud studies⁵⁴. This analysis only
426 considered data starting in 2002 because the ARMBE data are derived from Vaisala RS-80
427 profiles prior to 2002 and that instrument suffered a known dry bias^{55,56}. The end of the analysis

428 period was the start of 2013, which was chosen because the AERI instrument at SGP
429 experienced a failure and was replaced in mid-2013. The analysis could be extended beyond
430 early 2013 but would have to address complications from changing instrumentation⁵⁷.
431

432 Only the subset of spectra recorded within 2 hours of a radiosonde launch were utilized. With 4
433 daily launches, each measurement is separated by a minimum of 6 hours and spans 4 hours.
434 Based on the radiosonde profile, a radiance spectrum was calculated using LBLRTM with 512
435 levels of temperature and relative humidity from the ARMBE product³³. All AERI spectra
436 recorded within 2 hours of the radiosonde launch were rank-ordered by the root-mean-squared
437 brightness temperature of the residual spectrum of the difference between the measurement and
438 the LBLRTM calculation between 600 and 980 cm^{-1} . This range was chosen to be sensitive to
439 thermodynamic conditions but insensitive to CH_4 or ozone, where the latter is strongly
440 influenced by MERRA biases⁵⁸. The rank-ordered spectra were averaged sequentially together
441 (i.e., the first two spectra were averaged, then the first three spectra were averaged, etc.) and the
442 RMS of the residual between that average and the LBLRTM calculation was recalculated. The
443 sequential average of the spectra that produced the minimum RMS of the residual relative to the
444 radiosonde-based LBLRTM calculation was used as the AERI spectral measurement for
445 subsequent analysis. The rationale for this approach is to average as many spectra together as
446 possible to minimize random measurement error, but to avoid biasing the spectra by averaging
447 observations during which clouds were present or where the thermodynamic conditions had
448 changed relative to the radiosonde.
449

450 Since the determination of CH₄ surface forcing is so dependent on an accurate specification of
451 the atmospheric thermodynamic profile, we apply additional tests of the sequentially averaged
452 spectra against the counterfactual calculations to remove cases where the thermodynamic or
453 condensate profiles differ substantially between the observation and the counterfactual. First, we
454 evaluate the RMS of the residual between the AERI spectral measurement and the LBLRTM
455 calculation between 790 and 810 cm⁻¹ (hereafter referred to as the 800 cm⁻¹ channel), because
456 this region is sensitive to atmospheric temperature, humidity, and condensates (see
457 Supplementary Information Figures 2(a) and 2(b)). These plots show the slope and correlation
458 coefficient of the least-squares relationship between the radiative flux sensitivity to moisture and
459 temperature perturbations for a given channel outside the CH₄ absorption feature (1200-1350 cm⁻¹)
460 and the average radiative flux sensitivity to moisture and temperature perturbations within the
461 CH₄ absorption feature. The least-squares relationship is derived from six model atmospheres,
462 which span a wide range of terrestrial thermodynamic conditions⁴⁴. The upper panels of Figures
463 (2a) and (2b) show that fluxes in the spectral region between 790 and 810 cm⁻¹ are more
464 sensitive to perturbations in temperature and moisture than fluxes in the CH₄ absorption band.
465 The lower panels show that perturbations in temperature and moisture produce flux perturbations
466 in the 790-810 cm⁻¹ spectral region and the CH₄ absorption band that are highly correlated.

467

468 We also utilize the RMS of the residual between 705 and 709 cm⁻¹ (hereafter referred to as the
469 707 cm⁻¹ channel), which is sensitive to the atmospheric boundary layer temperature.

470 Supplementary Information Figure 2(c) shows the gain and correlation coefficient for the
471 relationship between the variance of a spectral channel outside the CH₄ absorption feature and
472 the variance of the spectral channel within the CH₄ absorption feature, where both are calculated

473 with the measurements and calculations used in the aircraft validation cases (see below). This
474 figure shows that the 707 cm^{-1} variance is highly correlated with the variance within the CH_4
475 band across a range data wherein the 800 cm^{-1} tolerance criterion is satisfied below 5 K. A gain
476 of greater than unity, indicating high sensitivity to boundary-layer temperature perturbations, is
477 also shown at 707 cm^{-1} for the same 800 cm^{-1} tolerance criterion.

478

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

483

484 Supplementary Information Figure 4 shows the average residual spectrum featuring a large
485 deviation from zero where CH_4 has a prominent absorption due to the use of a pre-industrial CH_4
486 mixing ratio for the counterfactual calculation and deviations equivalent to less than 1 K in
487 temperature, 10 ppmv CO_2 , 5% percent H_2O , and 10% N_2O . The exception lies in the $9.6\text{ }\mu\text{m}$
488 ozone absorption band between 980 and 1080 cm^{-1} , indicating a systematic overestimation of
489 column ozone from the MERRA data products at SGP⁵⁸. The lack of prominent spectral
490 structures outside the CH_4 and O_3 bands excludes other possible explanations including cloud
491 contamination, water vapour or temperature bias, or instrument calibration, all of which produce
492 spectral residuals with characteristic features not solely in the CH_4 absorption band.

493

494 **Time-Series Decomposition**

495 We tested the hypothesis that the cause for the observed trend in radiative forcing could be
496 contained within a set of predictors including height-resolved trends in water vapour, height-
497 resolved trends in temperature, and ground level methane concentration measured by flasks. If
498 we cannot use these predictors to reproduce the observed forcing, we can infer that there are
499 other contributing factors to the forcing that we have not considered. For the reconstruction of
500 this time-series, we used a two-step decomposition of all predictors using a widely utilized and
501 flexible approach that avoids overfitting⁵⁹. First, we isolated the component of the unfiltered
502 signal that cannot be described as white noise or outlier data using a calibrated Random forest
503 with 100 weak learners⁵⁹. A calibrated Random forest was used to reproduce the signal at the
504 desired points in time, and the difference between the reproduced and actual signal was filtered
505 out. Second, the remaining noise and cyclical components of the signal were removed using
506 moving average filter with a 12-month window⁶⁰. The size of the moving-average filter window
507 was selected because the signal exhibited clear annual seasonal variations.

508

509 With this approach, we created a set of isolated trends for 1025 predictors (512 each for
510 temperature and humidity and 1 for flask CH₄ observations). To make the problem less
511 computationally expensive, and given the extreme level of redundancy in vertically-resolved
512 temperature and water-vapour predictors, we applied principal component analysis (PCA) for the
513 reduction of dimensionality⁶¹. The fraction of variance explain by the first 5 principal
514 components (out of 512) was found to be >99.99% for both temperature and humidity,
515 confirming the high-degree of redundancy in the predictors. With 5 PCs for temperature, 5 for
516 humidity, and 1 for methane concentration, we created a reduced set of 11 predictors to describe
517 the CH₄ radiative forcing trend. An ensemble of five back-propagation neural networks was then

518 trained to reproduce the trend component of the CH₄ radiative forcing⁶². To avoid over-fitting,
519 the training and reproduction of the radiative forcing was done in leave-one-out fashion, such
520 that the radiative forcing value to be reconstructed from the predictors is withheld from the
521 training set. Instead, ensemble neural networks are trained using the remaining data points, and
522 then the network is used to reproduce the withheld data point. The procedure was repeated
523 sequentially for all data points.

524

525 With this approach, the correlation coefficient between the observed trends in the entire CH₄
526 surface forcing time-series and the neural-network prediction where all 11 predictors are used is
527 0.9983 ($R^2=0.997$). Where only the CH₄ flask data is used as a predictor to train the network, the
528 correlation coefficient is 0.8907 ($R^2=0.793$). More specifically, we can explain ~80% of the
529 variance in radiative forcing using custom-designed non-linear predictor. However, we should
530 note that our signal is obtained from the difference between an observation and calculation,
531 which is not best possible non-linear predictor, so the amount of variance that can be explained
532 using only CH₄ concentrations is necessarily less than 80%. Rather, our results produce an
533 estimate of the minimum of the fraction of variance that cannot be explained using the
534 predictor(s) of interest. They also show that information from temperature and humidity, and not
535 just CH₄ flask concentration data, is needed to describe the observed trend in CH₄ surface
536 radiative forcing.

537

538 **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 CH₄ 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 CH₄ forcing for the SGP site at time $t = 1, \dots, T$. Our statistical model is:

544

$$545 \quad y_t = b_0 + b_1 t + b_2 X_t(t - t_0) + a_j + e_t + v_t, \quad (1)$$

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 CH₄ 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 coefficients⁶⁴. 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 models⁶⁴.

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) methods⁶⁶. MCMC output can be used
570 to compare the full and reduced models using Bayes factors⁶⁷.

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 N₂O**

593 The methods used to determine CH₄ surface radiative forcing can be biased by N₂O. Figure 2(b)
594 shows this due to the substantial amount of overlap in spectral radiance changes from
595 perturbations from N₂O and CH₄. However, the vertical profiles of N₂O collected by the ARM-
596 ACME missions³⁵ at SGP show that N₂O 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 CH₄ forcing
600 from utilizing monthly-averaged MLO N₂O observations instead of in situ ARM-ACME N₂O
601 observations was maximized at 1.2% of the CH₄ forcing.

602

603 N₂O can still bias CH₄ forcing because it is emitted after precipitation following the nearby fresh
604 application of nitrogen-based fertilizer⁶⁸, causing >5 ppbv deviations from the background N₂O
605 mixing ratio. NEXRAD data⁶⁹ 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, CO₂, or O₃ 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 CH₄ and N₂O 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/m², 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 (C₂H₆)
629 flask data. Non-Methane Hydrocarbon (NMHC) flask data from SGP were first filtered for

630 outliers; values that deviated more than $2\text{-}\sigma$ from a running median were excluded from trend
631 analyses. Filtered data were then uploaded to the NOAA server for filtering and trends were
632 determined using the method of Thoning et al.⁷⁰

633

634 **Clear-Sky Bias**

635 We evaluate the potential for clear-sky bias in the determination of CH_4 surface radiative
636 forcing. We estimate this bias by recalculating the Broadband Heating Rate Profile (BBHRP)⁷¹
637 profiles at SGP for 2010 based on pre-industrial CH_4 mixing ratios and comparing those to the
638 original BBHRP profiles, containing time-varying CH_4 derived from the nearest grid box from
639 CarbonTracker- CH_4 ⁽⁷²⁾. We then subset the data identified as clear-sky in the Radiatively
640 Important Parameters Best Estimate (RIPBE) product⁷³.

641

642 We find that most of the forcing is in the clear-sky but that the all-sky surface forcing is 0.065
643 W/m^2 , or 33%, less than the clear-sky forcing. This finding is expected because of non-negligible
644 overlap between broadband cloud absorption and CH_4 absorption, thereby masking CH_4 forcing.
645 This cloud-masking may vary year-to-year. Currently, the independent estimates of cloud
646 vertical profiles produce residual spectra with signatures of clouds, so the effect of CH_4 cannot
647 be isolated under all-sky conditions.

648

649 **Non-Methane Contributions to Observed Signal**

650 The possibility that condensates or non-methane gaseous atmospheric constituents are
651 contributing to the observed CH_4 surface forcing must be considered. The contribution of
652 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 HITRAN²¹, and found their contributions to be at least 5
656 orders of magnitude smaller than CH₄.

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 CH₄ and N₂O 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 CH₄-X2004 and N₂O
670 X2006A scales. Flask-based observations are shown to have uncertainties of less than 1.2 ppbv
671 for CH₄ and 0.4 ppbv for N₂O.

672

673 **Aircraft Validation**

674 Aircraft profiles of CH₄ and N₂O 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 work²⁷. For the CH₄ 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 CH₄ absorption
686 feature⁷⁵.

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 CH₄ 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**

698 The ARM data and radiative transfer codes used in this analysis are freely available to download
699 from <http://www.archive.arm.gov/discovery/> and <http://rtweb.aer.com>, respectively. The
700 following are URLs from which input data can be downloaded:

701 MERRA: <http://goldsmr3.sci.gsfc.nasa.gov/opensap/MERRA/MAI3CPASM.5.2.0/contents.html>

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

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

704 NOAA CH₄ data: <http://ds.data.jma.go.jp/gmd/wdcgg/pub/data/current/ch4/>

705 NOAA N₂O data:

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

707 NOAA C₂H₆ data: <http://ds.data.jma.go.jp/gmd/wdcgg/pub/data/current/vocs/ethane/event/>

708 Reprints and permissions information is available at <http://www.nature.com/reprints>

709

710 **Code Availability**

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

713 **References:**

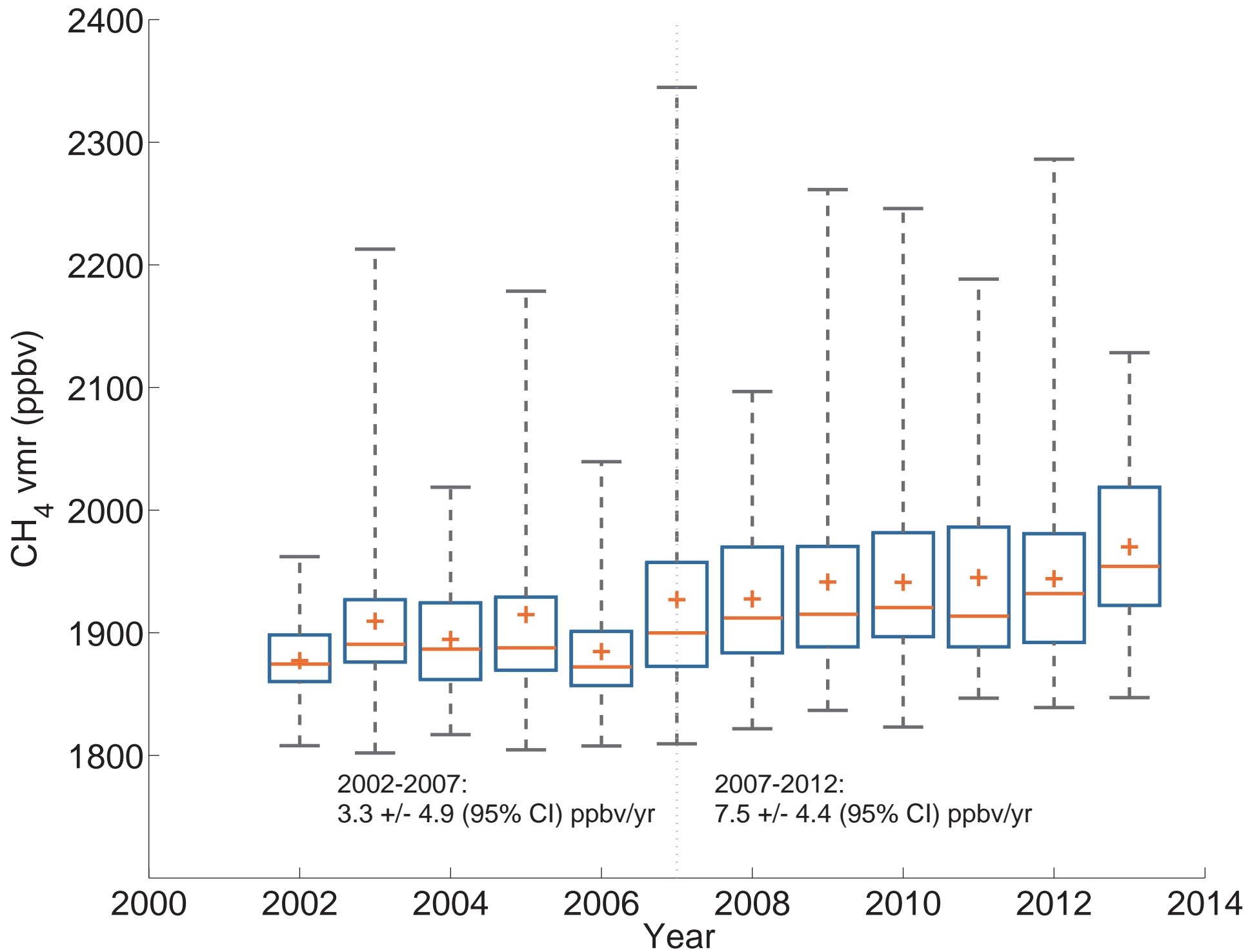
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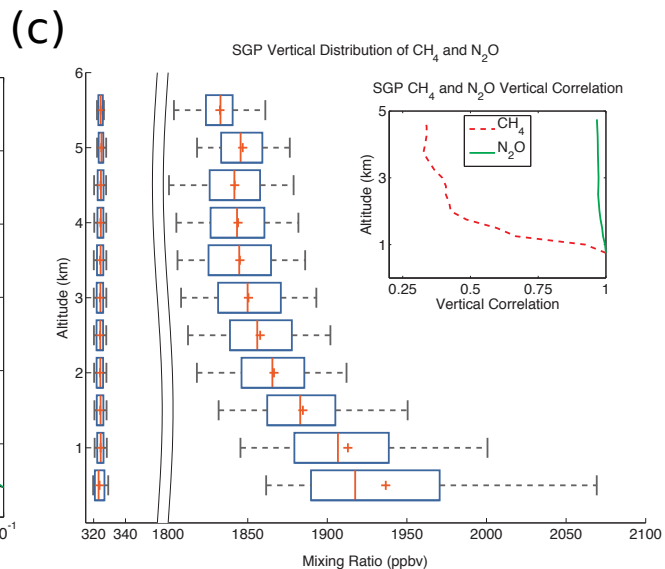
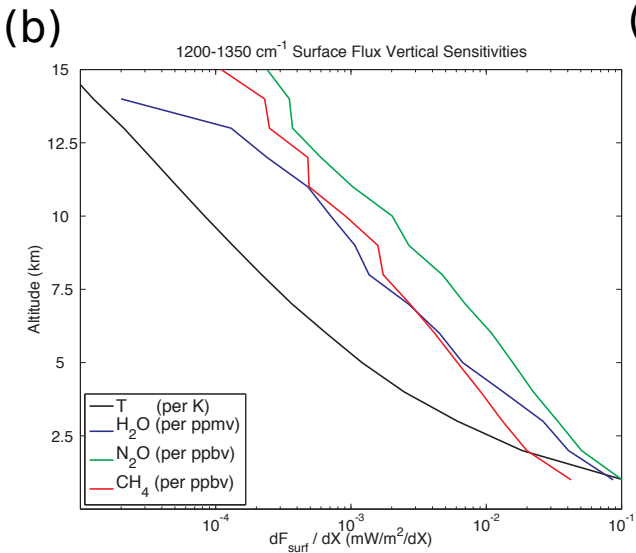
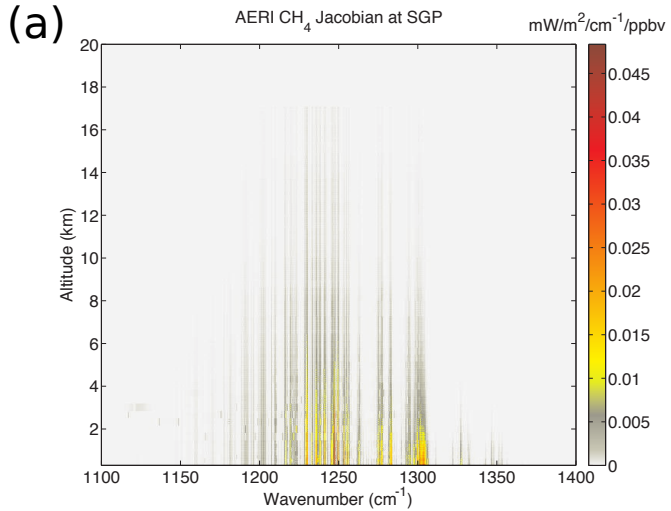
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SGP CH₄ Flask Measurements Box-Whisker Plot





SGP CH₄ Forcing

