

Responses to the Editor

I find that overall the author's responses cover the points raised by the reviewers well, and the manuscript is now worthy of publication. However a few points remain to address:

Response to Anonymous Referee #1:

General comments: I find that the authors argue well in response to these comments and provide valid answers to the reviewer's concerns, however these responses seem to be mainly only in the response and have not been sufficiently incorporated into the article. Particularly the response to the second general comment does not mention any point at which this information has been incorporated into the article; the response to the first general comment has resulted in some but insufficient changes. Please incorporate all important points presented in the response into the revised article.

[Response] Thanks a lot for your careful review and comments. Following your suggestion, [for the first general comment](#), we added several sentences to the fourth paragraph of the *Introduction* section to address the importance of all target species presented in this study and their potential scientific connections (Lines 130–140). We also added a sentence in the second paragraph of the *Conclusions* section to emphasize the different SF₆ emission pattern in the Indian sub-continent compared to those of the USA and EU countries suggested by our study (Lines 1007–1010). The distinct N₂O emission pattern in the Indian sub-continent has already been addressed in the same paragraph (Lines 1001–1004).

[For the second general comment](#), we added more details to *Section 2.1* (Lines 199–209) and *Section 2.3.1* (Lines 365–372), as well as Table S5 and Figure S1 in the supplement, to clarify the potential influence of local emissions on PON and our approaches to minimize it.

Page 7193 L13: As with the response to the second general comment on a similar point – the response presents information which should be included in the revised manuscript in sufficient detail to convince the reader of the measurement time selection protocol and the potential local influences at PON.

[Response] As mentioned for the second general comment, we added more details to *Section 2.1* (Lines 199–209) and *Section 2.3.1* (Lines 365–372), as well as Table S5 and Figure S1 in the supplement, to clarify the potential influence of local emissions on PON and our approaches to minimize it.

Response to Anonymous Referee #2:

2.2.1 Flask sampling, page 7179: It should be mentioned in the revised article that the magnesium perchlorate drier has been tested for compound losses. The points made in response to the next two comments (P7180 L2–4 and L6) should also be incorporated into the revised manuscript.

[Response] Following your suggestions, we incorporated these points into the revised manuscript (Lines 252–253, 262–263, 266).

Conclusions, page 7203 L7-9: Perhaps the article title should also be moderated in response to this valid comment?

[Response] Following your suggestions, we revised the title to “Flask measurements of long-lived trace gases at three ground stations in India”. We also revised *Abstract* accordingly to make it more precise (Lines 30–32).

Response to Anonymous Referee #3:

Point 6: It seems that this is a very important point made by the reviewer; the authors have provided significant answers to the reviewer’s query in the response but there are very little changes made in the article. Please ensure all important points from the response are reflected in changes to the article.

[Response] Following your suggestions, we added a few sentences in *Section 3.1.2* to describe the anticyclone in the upper troposphere over the monsoon region (Lines 496–501). We also clarified in *Section 3.1.4* (Lines 663–672) the mechanisms that account for the summer enhancements of SF₆ observed by the CARIBIC flights in the upper troposphere, which is in contrast to the results derived from the flask measurements at HLE.

Point 7: This point was also raised by the other reviewers and I found it was addressed well in the response but insufficiently in changes to the manuscript – given it is brought up numerous times by the reviewers, ensure it is very well covered in changes to the manuscript.

[Response] As mentioned before, we added more details to *Section 2.1* (Lines 199–209) and *Section 2.3.1* (Lines 365–372), as well as Table S5 and Figure S1 in the supplement, to clarify the potential influence of local emissions on PON and our approaches to minimize it.

Page 7174 L11: Is this information now presented in the article?

[Response] No, we didn’t incorporate this information in the article, since it may not be very relevant to the context of the first paragraph of the *Introduction* section (focusing on anthropogenic GHG emissions rather than natural emissions).

List of changes in the revised manuscript

Changes to the main text

Page 1: change the title “Five-year flask measurements of long-lived trace gases in India” to “Flask measurements of long-lived trace gases at three ground stations in India”.

Page 2, Line 30: remove “five-year”.

Page 2, Line 30: remove “(2007–2011)”

Page 2, Line 31: add “over the period 2007–2011” after “at these three stations”.

Page 6, Line 121: add “major” before “GHGs”.

Page 6, Lines 128–130: change “For each station, four GHG species (CO₂, CH₄, N₂O, SF₆) and two additional trace gases (CO, H₂) are measured to characterize the annual means and seasonal cycles, with results and discussions presented in Sect.3.” to “For each station, we measure the atmospheric concentrations of four major GHG species (CO₂, CH₄, N₂O and SF₆) and two additional trace gases (CO and H₂).”.

Page 6, Lines 130–143: add the following sentences before “Gradients between different stations”: “Among these trace gases, CO₂, CH₄ and N₂O are the three most abundant GHGs in the atmosphere, and the UNFCCC requires each Non-Annex I Party to regularly report anthropogenic emissions of these gases (MoEF, 2012). Sulfur hexafluoride (SF₆) is widely considered as a good tracer for anthropogenic activities with a long atmospheric lifetime and almost purely anthropogenic sources (Maiss et al., 1996), and the Non-Annex I Parties are also encouraged to provide information on its anthropogenic emissions (MoEF, 2012). Although CO and H₂ are not GHGs by themselves, both of them play critical roles in the CH₄ budgets through reaction with the free OH radicals (Ehhalt and Rohrer, 2009). Besides, CO and H₂ are good tracers for biomass/biofuel burning (Andreae and Merlet, 2001), an important source of GHG emissions that is quite extensive in India (Streets et al., 2003; Yevich and Logan, 2003). Time series of atmospheric concentrations of all these trace gases are analyzed for each station to characterize the annual means and seasonal cycles, with results and discussions presented in Sect. 3.”.

Page 9, Lines 199–202: add the following sentences after “west of the stations.”: “Given its proximity to an urban area and a highway, PON can be influenced by local emissions. Although the highway nearby has a low traffic flow, in-situ measurements at PON (not presented in this paper) do show that this site is heavily polluted by local emissions during nighttime.”.

Page 9, Line 204: add “(actually 97% of flask samples taken between 12:00 and 14:00 LT)” after “between 12:00 and 18:00 local time (LT)”.

Page 9, Lines 206–209: add “Further, we also remove outliers that are likely polluted by local emissions and not representative of regional background concentrations (see Sect. 2.3.1 for details). We believe that through these two approaches the local influences at PON should be sufficiently minimized.” before “Flask sampling at PON”.

Page 11, Lines 252–253: add “Tests have shown that use of the magnesium perchlorate drier doesn’t result in any loss of the target compound.” before “To prevent entrainment”.

Page 12, Lines 261–264: change “On average the flasks arrive at LSCE, France about 150 days after the sampling date, and are analyzed for CO₂, CH₄, N₂O, SF₆, CO, and H₂ with two coupled gas chromatograph (GC) systems.” to “On average the flasks arrive at LSCE, France about 150 days after the sampling date. Leakage could occur during shipment, and any flask sample with too low pressure will be flagged in the analyses. Flask samples are analyzed for CO₂, CH₄, N₂O, SF₆, CO, and H₂ with two coupled gas chromatograph (GC) systems.”.

Page 12, Line 266: change “an electron capture detector” to “a standard electron capture detector”.

Page 16, Lines 365–372: add “Particularly, for PON where observations can be influenced by local emissions, we also tried to use CO as a tracer and filtered time series of other species by CO outliers. Results show that this additional filtering does not make significant difference to the trends, seasonal cycles and mean annual gradients (relative to HLE) for all the other species at PON (Table S5, Fig. S2). On the other hand, however, the approach may substantially decrease the number of samples used to fit the smooth curve (e.g. ~38% for CH₄) and result in larger data gaps (Table S5, Fig. S2), probably compromising reliability of the analyses. Therefore finally we didn’t use CO as a tracer of local emissions for additional filtering.” after “flagging (Table S3).”.

Page 16, Line 374: add “For each species at each station,” before “The annual means ...”, and start a new paragraph.

Page 17, Line 383: change “Table S5, Figs. S1 and S2” to “Table S6, Figs. S1 and S3”

Page 18, Line 427: change “Fig. S7” to “Fig. S8”.

Page 19, Line 433: change “Fig. S3” to “Fig. S4”.

Page 19, Line 441: change “Fig. S4” to “Fig. S5”.

Page 19, Line 445: change “Fig. S5a,d,e” to “Fig. S6a,d,e”.

Page 20, Line 475: change “Fig. S4” to “Fig. S5”.

Page 21, Lines 496–498: change “due to vertical mixing between the mid- and upper troposphere (Fig. 5a)” to “due to the rapid vertical mixing over the monsoon region and the strong anticyclone that develops in the upper troposphere (Fig. 5a; Schuck et al., 2010)”.

Page 21, Lines 499–501: change “due to the rapid uplift in regions of strong convection” to “, as a result of the rapid vertical transport of surface air masses by deep convection and subsequent accumulation and confinement of pollutants within the strong, closed circulation of the anticyclone (Li et al., 2005; Randel and Park, 2006)”.

Page 23, Lines 554: change “Table S5” to “Table S6”

Page 23, Lines 555: change “Fig. S9, Table S6” to “Fig. S10, Table S7”.

Page 24, Lines 560–561: change “Fig. S9, Table S6” to “Fig. S10, Table S7”.

Page 24, Line 563: change “Table S6” to “Table S7”.

Page 24, Line 578: change “Table S7” to “Table S8”.

Page 24, Line 580: change “Fig. S10, Table S6” to “Fig. S11, Table S7”.

Page 25, Lines 589–590: change “Like CH₄, the N₂O enhancement at HLE during the summer monsoon period (June-September) is consistent with” to “Like CH₄, the N₂O enhancement during the summer monsoon period (June-September) was also observed by”.

Page 26, Line 613: change “Table S7” to “Table S8”.

Page 27, Line 632: change “Figs. 8 and S11a, Table 1, Table S8” to “Figs. 8 and S12a, Table 1, Table S9”

Page 27, Line 642: change “Table S8” to “Table S9”.

Page 27, Line 649: change “Figs. 8b and S6d” to “Figs. 8b and S7d”.

Page 28, Line 655: change “Table S9” to “Table S10”.

Page 28, Lines 661–672: change “Although the CARIBIC aircraft flask measurements over the Indian region demonstrated SF₆ enhancements in the upper troposphere at ~30 °N (approximately where HLE is located) in August, 2008, back-trajectories from the CARIBIC flights showed that the summer enhancements in SF₆ were more related to the influences of westerly jet transport in the upper troposphere, rather than the SW monsoon and sources from India that contributed to the summer maxima in CH₄ and N₂O (Schuck et al., 2010, Fig. S8).” to “Although the CARIBIC aircraft flask measurements over the Indian region demonstrated SF₆ enhancements in the upper troposphere at ~30 °N (approximately where HLE is located) in August, 2008, they are not related to the deep convection and surface sources that contribute to the summer maxima in CH₄ and N₂O. Back-trajectories from the CARIBIC

flights showed that the summer enhancements in SF₆ were related to air samples collected north of 20°N along the flight routes, where air masses were more influenced by the westerly subtropical jet (and a smaller anticyclone embedded in it over the Arabian Peninsula) rather than the deep convection in the monsoon region (Krishnamurti et al. 2008; Schuck et al., 2010; Fig. S9). Since HLE is not influenced by the westerly subtropical jet in the upper troposphere (also clearly seen by the colors of back-trajectories in Fig. S9), the summer enhancements of SF₆ observed by the CARIBIC flights are not detected by the flask measurements at HLE.”.

Page 28, Line 674: change “Figs. 9b and S6d” to “Figs. 9b and S7d”

Page 28, Line 675: change “Table S9” to “Table S10”.

Page 28, Line 676: change “Fig. S6d” to “Fig. S7d”.

Page 29, Line 702: change “Fig. S4” to “Fig. S5”.

Page 31, Line 749: change “Fig. S6e” to “Fig. S7e”

Page 32, Line 775: change “Fig. S12c and d; Table S10” to “Fig. S13c and d; Table S11”

Page 33, Line 778: change “Fig. S6f” to “Fig. S7f”.

Page 33, Line 783: change “Fig. S6f” to “Fig. S7f”.

Page 33, Line 789: change “Figs. 13d and S13a, Tables 1 and S10” to “Figs. 13d and S14a, Tables 1 and S11”.

Page 34, Line 802: change “Tables 1 and S10, Figs. 13a and b and S13b” to “Tables 1 and S11, Figs. 13a and b and S14b”.

Page 36, Line 851: change “Table S11” to “Table S12”.

Page 36, Line 854: change “Table S11” to “Table S12”.

Page 36, Line 859: change “Fig. S4” to “Fig. S5”.

Page 36, Line 867: change “Table S11” to “Table S12”.

Page 38, Line 911: change “Fig. S14a” to “Fig. S15a”.

Page 38, Line 917: change “Fig. S14b” to “Fig. S15b”.

Page 38, Line 924: change “Fig. S2” to “Fig. S3”.

Page 40, Line 980: change “Fig. S15” to “Fig. S16”.

Page 42, Line 1001: remove “, whereas SF₆ emission sources are weak”.

Page 42, Lines 1007–1010: add at the end of this paragraph “On the other hand, despite of substantial anthropogenic GHG emissions in India (whether based on national inventories or atmospheric observations), unlike the USA and EU countries, its SF₆ emissions are rather weak.”.

Changes to the references

Page 49, Line 1306: add a reference: “Ministry of Environment and Forests, Government of India (MoEF): India Second National Communication to the United Nations Framework Convention on Climate Change, New Delhi. [online] Available from: <http://unfccc.int/resource/docs/natc/indnc2.pdf>, 2012.”

1 **Title: Flask measurements of long-lived trace gases at three ground stations in India**

2

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21

22 **Abstract**

23 With a rapid growth in population and economic development, emissions of greenhouse
24 gases (GHGs) from the Indian subcontinent have sharply increased during recent decades.
25 However, evaluation of regional fluxes of GHGs and characterization of their spatial and
26 temporal variations by atmospheric inversions remain uncertain due to a sparse regional
27 atmospheric observation network. As a result of an Indo-French collaboration, three new
28 atmospheric stations were established in India at Hanle (HLE), Pondicherry (PON) and Port
29 Blair (PBL), with the objective of monitoring the atmospheric concentrations of GHGs and
30 other trace gases. Here we present the results of the measurements of CO₂, CH₄, N₂O, SF₆,
31 CO, and H₂ from regular flask sampling at these three stations **over the period 2007–2011**.
32 For each species, annual means, seasonal cycles and gradients between stations were
33 calculated and related to variations in the natural GHG fluxes, anthropogenic emissions, and
34 the monsoon circulations. Covariances between species at the synoptic scale were analyzed to
35 investigate the likely source(s) of emissions. The flask measurements of various trace gases at
36 the three stations show potential to constrain the inversions of fluxes over Southern and
37 Northeastern India. However, this network of ground stations needs further extension to other
38 parts of India to better constrain the GHG budgets at regional and continental scales.

39

40 **1 Introduction**

41 Since the pre-industrial times, anthropogenic greenhouse gas (GHG) emissions have
42 progressively increased the radiative forcing of the atmosphere, leading to impacts on the
43 climate system and human society (IPCC, 2013, 2014a, b). With rapid socio-economic
44 development and urbanization during recent decades, a large and growing share of GHG
45 emissions is contributed by emerging economies like China and India. In 2010, India became
46 the world's third largest GHG emitter, next to China and the USA (EDGAR v4.2; Le Quéré
47 et al., 2014). Between 1991 and 2010, anthropogenic GHG emissions in India increased by
48 ~100% from 1.4 to 2.8 GtCO₂eq, much faster than rates of most developed countries and
49 economies like the USA (9%) and EU (-14%) over the same period (EDGAR v4.2). Without
50 a systematic effort at mitigation, this trend would continue in the coming decades, given that
51 the per capita emission rate in India is still much below that of the more developed countries.
52 For comparison, in 2010, the per capita GHG emission rates were 2.2, 10.9, 17.6, and 21.6
53 tonCO₂eq/capita for India, the UK, Russia, and the USA, respectively (EDGAR v4.2). In
54 particular, non-CO₂ GHG emissions are substantial in India, most of which are contributed by
55 agricultural activities over populous rural areas (Pathak et al., 2010). In 2010, anthropogenic
56 CH₄ and N₂O emissions in India amounted to 29.6 TgCH₄ (≈0.62 GtCO₂eq) and 0.8 TgN₂O
57 (≈0.23 GtCO₂eq), together accounting for 32% of the country's GHG emissions, of which
58 contributions of the agricultural sector were 60 and 73%, respectively (EDGAR v4.2).
59 Reducing emissions of these two non-CO₂ GHGs may offer a more cost-effective way to
60 mitigate future climate change than by attempting to directly reduce CO₂ emissions (Montzka
61 et al., 2011).

62

63 Effective climate mitigation strategies need accurate reporting of sources and sinks of GHGs.

64 This is also a requirement of the United Nations Framework Convention on Climate Change

65 (UNFCCC). Current estimates of GHG budgets in India, either from the top-down
66 approaches (based on atmospheric inversions) or bottom-up approaches (based on emission
67 inventories or biospheric models), have larger uncertainties than for other continents. For
68 instance, Patra et al. (2013) reported a net biospheric CO₂ sink of -104 ± 150 TgCyr⁻¹ over
69 South Asia during 2007–2008 based on global inversions from 10 TransCom-CO₂ models
70 (Peylin et al., 2013) and a regional inversion (Patra et al., 2011b), while the bottom-up
71 approach gave an estimate of -191 ± 193 TgCyr⁻¹ over the period of 2000–2009 (Patra et al.,
72 2013). Notably, these estimates have uncertainties as high as 100–150%, much larger
73 compared to those of Europe (~30%, see Luyssaert et al., 2012) and North America (~60%,
74 see King et al., 2015), where observational networks are denser and emission inventories are
75 more accurate. Evaluation of N₂O emissions from 5 TransCom-N₂O inversions also exhibited
76 the largest differences over South Asia (Thompson et al., 2014b). A main source of
77 uncertainty is the lack of atmospheric observation datasets with sufficient temporal and
78 spatial coverage (Patra et al., 2013; Thompson et al., 2014b). Networks of atmospheric
79 stations that were used to constrain estimates of global GHG fluxes show gaps over South
80 Asia (Patra et al., 2011a; Thompson et al., 2014b, c; Peylin et al., 2013), with Cape Rama
81 (CRI – 15.08°N, 73.83°E, 60m a.s.l.) on the southwest coast of India being the only Indian
82 station (Rayner et al., 2008; Patra et al., 2009; Tiwari et al., 2011; Bhattacharya et al., 2009;
83 Saikawa et al., 2014). Recently a few other ground stations have been established in Western
84 India and the Himalayas to monitor GHGs and atmospheric pollutants, which are located in
85 Sinhagad (SNG – 18.35°N, 73.75°E, 1600m a.s.l.; Tiwari and Kumar, 2012; Tiwari et al.,
86 2014), Mount Abu (24.60°N, 72.70°E, 1700m a.s.l.; S. Lal, personal communication),
87 Ahmedabad (23.00°N, 72.50°E, 55m a.s.l.; Lal et al., 2015), Nainital (29.37°N, 79.45°E,
88 1958m a.s.l.; Kumar et al., 2010) and Darjeeling (27.03°N, 88.15°E, 2194m a.s.l.; Ganesan
89 et al., 2013). Most of these stations started to measure atmospheric GHG concentrations very

90 recently (e.g. Sinhadgad – since 2009; Ahmedabad – since 2013; Mount Abu – since 2013;
91 Nainital – since 2006; Darjeeling – since 2011), and datasets are not always available. In
92 addition, aircraft and satellite observations have also been carried out and provided useful
93 constraints on estimates of GHG fluxes in this region (Park et al., 2007; Xiong et al., 2009;
94 Schuck et al., 2010; Patra et al., 2011b; Niwa et al., 2012; Zhang et al., 2014). Although
95 inclusion of measurements from South Asia significantly reduces uncertainties in top-down
96 estimates of regional GHG emissions (e.g., Huang et al., 2008; Niwa et al., 2012; Zhang et al.,
97 2014), a denser atmospheric observational network with sustained measurements is still
98 needed over this vast and fast-growing region for an improved, more detailed, and necessary
99 understanding of GHG budgets.

100

101 Besides the lack of a comprehensive observational network, the seasonally reversing Indian
102 monsoon circulations and orographic effects complicate simulation of regional atmospheric
103 transport, which contributes to uncertainty of the inverted GHG fluxes (e.g., Thompson et al.,
104 2014b). The Indian monsoon system is a prominent meteorological phenomenon in South
105 Asia, which, at lower altitudes, is characterized by strong southwesterlies from the Arabian
106 Sea to the Indian subcontinent during the boreal summer, and northeasterlies during the
107 boreal winter (Goswami, 2005). The summer monsoon is associated with deep convection,
108 which mixes the boundary layer air into the upper troposphere and lower stratosphere
109 (Schuck et al., 2010; Lawrence and Lelieveld, 2010). On the contrary, little deep convection
110 occurs over South Asia during the winter monsoon period, which carries less moisture
111 (Lawrence and Lelieveld, 2010). The Indian monsoon also impacts biogenic activities (e.g.,
112 vegetation growth, microbial activity) and GHG fluxes through its effects on rainfall
113 variations (Tiwari et al., 2013; Valsala et al., 2013; Gadgil, 2003). Given that accurate
114 atmospheric transport is critical for retrieving reliable inversion of GHG fluxes, an

115 observational network that comprises a range of altitudes including monitoring stations in
116 mountainous regions would be valuable for validating and improving atmospheric transport
117 models.

118

119 Since the 2000s, three new atmospheric ground stations have been established in India as part
120 of the Indo-French collaboration, with the objective of monitoring the atmospheric
121 concentrations of major GHGs and other trace gases in flask air samples. Of the three Indian
122 stations, Hanle (HLE) is a high-altitude station situated in the western Indian Himalayas,
123 while Pondicherry (PON) and Port Blair (PBL) are tropical surface stations located
124 respectively on the southeastern coast of South India and on an oceanic island in the
125 southeastern Bay of Bengal. In this study, we briefly describe the main features of these
126 stations and present time series of flask air sample measurements of multiple trace gases at
127 HLE, PON, and PBL over the period 2007–2011. Descriptions of the three stations as well as
128 methods used to analyze and calibrate the flask measurements are given in Sect. 2. For each
129 station, we measure the atmospheric concentrations of four major GHG species (CO_2 , CH_4 ,
130 N_2O and SF_6) and two additional trace gases (CO and H_2). Among these trace gases, CO_2 ,
131 CH_4 and N_2O are the three most abundant GHGs in the atmosphere, and the UNFCCC
132 requires each Non-Annex I Party to regularly report anthropogenic emissions of these gases
133 (MoEF, 2012). Sulfur hexafluoride (SF_6) is widely considered as a good tracer for
134 anthropogenic activities with a long atmospheric lifetime and almost purely anthropogenic
135 sources (Maiss et al., 1996), and the Non-Annex I Parties are also encouraged to provide
136 information on its anthropogenic emissions (MoEF, 2012). Although CO and H_2 are not
137 GHGs by themselves, both of them play critical roles in the CH_4 budgets through reaction
138 with the free OH radicals (Ehhalt and Rohrer, 2009). Besides, CO and H_2 are good tracers for
139 biomass/biofuel burning (Andreae and Merlet, 2001), an important source of GHG emissions

140 that is quite extensive in India (Streets et al., 2003; Yevich and Logan, 2003). Time series of
141 atmospheric concentrations of all these trace gases are analyzed for each station to
142 characterize the annual means and seasonal cycles, with results and discussions presented in
143 Sect. 3. Gradients between different stations are interpreted in the context of regional flux
144 patterns and monsoon circulations (Sect. 3.1). We examine synoptic variations of CO₂, CH₄
145 and CO by analyzing the co-variances between species, using deviations from their smoothed
146 fitting curves (Sect. 3.2). Finally, we investigate two abnormal CH₄ and CO events at PBL
147 and propose likely sources and origins (Sect. 3.3). A summary of the paper as well as
148 conclusions drawn from these results are given in Sect. 4.

149

150 **2 Sampling stations and methods**

151 **2.1 Sampling stations**

152 Figure 1 and S1 in the supplement show the locations of HLE, PON, and PBL. We also
153 present five-day back-trajectories from each station for all sampling dates in April–June
154 (AMJ; Fig. 1a), July–September (JAS; Fig. 1b), October–December (OND; Fig. 1c) and
155 January–March (JFM; Fig. 1d), respectively. Note that this four-period classification scheme
156 is slightly different from the climatological seasons defined by the India Meteorological
157 Department (IMD; Attri and Tyagi, 2010), in which months of a year are categorized into the
158 pre-monsoon season (March–May), SW monsoon season (June–September), post-monsoon
159 season (October–December) and the winter season (January and February). We adapted the
160 IMD classification to facilitate better display and further analyses (e.g., Sect. 3.2), making
161 sure that samples are fairly evenly distributed across all seasons. The back-trajectories were
162 generated using the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT4)
163 model (Draxler and Rolph, 2003), driven by wind fields from the Global Data Assimilation

164 System (GDAS) archive data based on National Centers for Environmental Prediction (NCEP)
165 model output (<https://ready.arl.noaa.gov/gdas1.php>).

166

167 The Hanle (HLE) station (32.780 °N, 78.960 °E, 4517 m a.s.l.) is located in the campus of the
168 Indian Astronomical Observatory (IAO) atop Mt. Saraswati, about 300 m above the
169 Nilamkhul Plain in the Hanle Valley of southeastern Ladakh in northwestern Himalayas. The
170 station was established in 2001 as a collaborative project between the Indian Institute of
171 Astrophysics and LSCE, France. The flask sampling inlet is installed on the top of a 3 m mast
172 fixed on the roof of a 2m high building, and the ambient air is pumped through a Dekabon
173 tubing with a diameter of 1/4". The area around the station is a cold mountain desert, with
174 sparse vegetation and a small population of ~1700 distributed over an area of ~20 km².
175 Anthropogenic activities are limited to small-scale crop production (e.g., barley and wheat)
176 and livestock farming (e.g., yaks, cows, goats, and sheep). The nearest populated city of Leh
177 (34.25 °N, 78.00 °E, 3480 m a.s.l.) with ~27 000 inhabitants, lies 270 km to the northwest of
178 this station. By virtue of its remoteness, high altitude, and negligible biotic and anthropogenic
179 influences, HLE is representative of the background free tropospheric air masses in the
180 northern mid-latitudes. Regular flask air sampling at this station has been operational since
181 February, 2004, and continuous in-situ CO₂ measurements started in September, 2005. Over
182 the period 2007–2011, a total of 188 flask sample pairs were collected at HLE. Back-
183 trajectories show that, HLE dominantly samples air masses that pass over northern Africa and
184 the Middle East throughout the year, and those coming from South and Southeast Asia during
185 the SW monsoon season (Fig. 1a). More detailed station information of HLE would be found
186 in several earlier publications (Babu et al., 2011; Moorthy et al., 2011).

187

188 The Pondicherry (PON) station (12.010 °N, 79.860 °E, 20 m a.s.l) is located on the southeast
189 coast of India, about 8 km north of the city of Pondicherry with a population of ~240,000
190 (Census India, 2011). The station was established in collaboration with Pondicherry
191 University in 2006. The flask sampling inlet, initially located on a 10 m mast fixed on the
192 roof of the University Guest House, was later moved to a 30 m high tower in June, 2011. The
193 ambient air is pumped from the top of the tower through a Dekabon tubing with a diameter of
194 1/4". The surrounding village Kalapet, has a population of ~9000 (Sivakumar and Anitha,
195 2012). A four-lane highway runs nearly 80 m to the west of the station with a low traffic flow
196 especially during the nighttime, while the Indian Ocean stands about 100 m to the east of the
197 station. Moreover, the two nearest megalopolises of Chennai and Bangalore, both with
198 populations of over 6 million (Census India, 2011), are approximately 143 km to the north
199 and 330 km to the west of the station. **Given its proximity to an urban area and a highway,**
200 **PON can be influenced by local emissions. Although the highway nearby has a low traffic**
201 **flow, in-situ measurements at PON (not presented in this paper) do show that this site is**
202 **heavily polluted by local emissions during nighttime.** In order to minimize the influences of
203 local GHG sources/sinks, flask air sampling at PON is performed between 12:00 and 18:00
204 local time (LT) **(actually 97% of flask samples taken between 12:00 and 14:00 LT),** when the
205 sea breeze moves clean air masses towards the land and the boundary layer air is well mixed.
206 **Further, we also remove outliers that are likely polluted by local emissions and not**
207 **representative of regional background concentrations (see Sect. 2.3.1 for details). We believe**
208 **that through these two approaches the local influences at PON should be sufficiently**
209 **minimized.** Flask sampling at PON began in September, 2006 and over the period 2007–2011,
210 a total of 185 flask sample pairs were collected at the site. As shown in Fig. 1a, the air masses
211 received at PON are strongly related to the monsoon circulations. During the boreal summer
212 when the southwest monsoon prevails, PON is influenced by air masses originating from the

213 Arabian Sea and South India, whereas during the boreal winter, it receives air masses from
214 the east and northeast parts of the Indian subcontinent, and the Bay of Bengal. During the
215 boreal spring and autumn when the monsoon changes its direction, air masses of both origins
216 are observed.

217

218 The Port Blair (PBL) station (11.650 °N, 92.760 °E, 20 m a.s.l.) is located on the small
219 Andaman Islands in the southeastern Bay of Bengal, ~1400 km east of Pondicherry, and
220 roughly 600 km west of Myanmar and Thailand. The station was established in collaboration
221 with the National Institute of Ocean Technology (NIOT), India, and flask air sampling was
222 initiated in July, 2009. The flask sampling inlet is located on the top of a 30 m high tower,
223 and the ambient air is pumped through a Dekabon tubing with a diameter of 1/4". The main
224 city on the Andaman Islands, Port Blair, is about 8 km to the north of the station, with a
225 population of ~100,000 (Census India, 2011). Due to its proximity to vegetation and a small
226 rural community, the station is not completely free from influences of local GHG fluxes.
227 Therefore, flask samples at PBL are obtained in the afternoon between 13:00 and 15:00 LT,
228 when the sea breeze moves towards the land, to minimize significant local influences. Over
229 the period 2009–2011, a total of 63 flask sample pairs were collected at PBL. Back-
230 trajectories show that the air masses sampled at PBL are also controlled by the seasonally
231 reversing monsoon circulations (Fig. 1a), with air masses from the Indian Ocean south of the
232 Equator during the southwest monsoon season, and from the northeast part of the Indian
233 subcontinent, the Bay of Bengal, and Southeast Asia during the northeast monsoon season.
234 As for PON, air masses of both origins are detected at PBL during the boreal spring and
235 autumn when the monsoon changes its direction.

236

237 2.2 Flask sampling and analysis

238 2.2.1 Flask sampling

239 In principle, flask samples are taken in pairs on a weekly basis at all three stations. However,
240 in practice air samples are collected less frequently (on average every 10-12 days) due to bad
241 meteorological conditions or technical problems. Whole air samples are filled into pre-
242 conditioned 1-L cylindrical borosilicate glass flasks (Normag Labor und Prozesstechnik
243 GmbH, Germany) with valves sealed by caps made from KEL-F (PTCFE) fitted at both ends.
244 Besides, a few flasks are equipped with valves sealed by the original Teflon PFA O-ring
245 (Glass Expansion, Australia), accounting for ~5.0, 1.2 and 1.1% of air samples respectively
246 for HLE, PON and PBL during the study period. For the air samples stored in flasks sealed
247 with the original Teflon PFA O-ring, corrections are made for the loss of CO₂ (+0.0027
248 ppm/day) and of N₂O (+0.0035 ppb/day) after analyses of the samples. The correction factors
249 are empirically determined based on laboratory storage tests using flasks filled with
250 calibrated gases. Drying of the air is performed using 10 g of magnesium perchlorate
251 (Mg(ClO₄)₂) confined at each end with a glass wool plug in a stainless steel cartridge, located
252 upstream of the pump unit. Tests have shown that use of the magnesium perchlorate drier
253 doesn't result in any loss of the target compound. To prevent entrainment of material inside
254 the sampling unit, a 7 µm filter is attached at the end of the cartridge. The flasks are flushed
255 prior to sampling for 10-20 min at a rate of 4–5 L min⁻¹, and the air is compressed in the
256 flasks to about 1 bar over the ambient pressure (pump: KNF Neuberger diaphragm pump
257 powered by a 12V DC motor, Germany, N86KNDC with EPDM membrane). The
258 pressurizing process lasts for less than a minute.

259

260 2.2.2 Flask analyses

261 On average the flasks arrive at LSCE, France about 150 days after the sampling date.
262 Leakage could occur during shipment, and any flask sample with too low pressure will be
263 flagged in the analyses. Flask samples are analyzed for CO₂, CH₄, N₂O, SF₆, CO, and H₂ with
264 two coupled gas chromatograph (GC) systems. The first gas chromatograph (HP6890,
265 Agilent) is equipped with a flame ionization detector (FID) for CO₂ and CH₄ detection, and a
266 standard electron capture detector (ECD) for N₂O and SF₆ detection. It is coupled with a
267 second GC equipped with a reduced gas detector (RGD, Peak Laboratories, Inc., California,
268 USA), for analyzing CO and H₂ via reduction of HgO and subsequent detection of Hg vapor
269 through UV absorption. In the following paragraph we summarize the major configurations
270 and parameters of the GC systems (also see Table S1). Further details on the analyzer
271 configuration are described in Lopez (2012) and Yver et al. (2009).

272

273 Both GC systems are composed of three complementary parts: the injection device, the
274 separation elements and the detection sensors. As flask samples are already dried during
275 sampling, they are only passed through a 5 mL glass trap maintained in an ethanol bath kept
276 at -55°C by a cryocooler (Thermo Neslab CC-65) to remove any remaining water vapor. The
277 air samples are flushed with flask overpressure through a 15 mL sample loop for CO₂ and
278 CH₄ analyses, a 15 mL sample loop for N₂O and SF₆ analyses, and a 1 mL sample loop for
279 CO and H₂, at a flow rate of 200 mL min⁻¹. After temperature and pressure equilibration, the
280 air sample is injected into the columns. The CO₂ and CH₄ separation is performed using a
281 Hayesep-Q (12' × 3/16"OD, mesh 80/100) analytical column placed in an oven at 80°C, with
282 a N₂ 5.0 carrier gas at a flow rate of 50 ml min⁻¹. Detection of CH₄ and CO₂ (after conversion
283 to CH₄ using a Ni catalyst and H₂ gas) is performed in the FID kept at 250°C. The flame is
284 fed with H₂ (provided by a NM-H₂ generator from F-DBS) at a flow rate of 100 ml min⁻¹ and
285 zero air (provided by a 75-82 zero air generator from Parker-Balston) at a flow rate of 300 ml

286 min⁻¹. For N₂O and SF₆ separation, a Hayesep-Q (4' × 3/16" OD, mesh 80/100) pre-column
287 and a Hayesep-Q (6' × 3/16" OD, mesh 80/100) analytical column, both placed in an oven at
288 80°C, are used together with an Ar/CH₄ carrier gas at a flow rate of 40 ml min⁻¹. Detection of
289 N₂O and SF₆ is performed in the ECD heated at 395°C. For CO and H₂, we use a Unibeads
290 1S pre-column (16.5" × 1/8" OD; mesh 60/80) to separate the two gases from the air matrix,
291 and use a Molecular Sieve 5Å analytical column (80" × 1/8" OD; mesh 60/80) to effectively
292 separate H₂ from CO. Both columns are placed in an oven kept at 105°C. CO and H₂ are
293 analyzed in the RGD detector heated to 265°C. A measurement takes ~5 min and calibration
294 gases are measured at least every 0.45 hour. For CO₂, CH₄, N₂O, and SF₆, we use two
295 calibration gases, one with a high concentration and the other with a low concentration. The
296 calibration and quality control cylinders are filled and spiked in a matrix of synthetic air
297 containing N₂, O₂ and Ar prepared by Deuste Steininger (Germany). The concentration of the
298 sample is calculated using a linear regression between the two calibration gases with a time
299 interpolation between the two measurements of the same calibration gas (Messenger, 2007;
300 Lopez, 2012). For CO and H₂, we use only one standard and apply a correction for the non-
301 linearity of the analyzer (Yver et al., 2009; Yver, 2010). The nonlinearity is verified regularly
302 with 5 calibration cylinders for CO and 8 calibration cylinders for H₂. All the calibration
303 gases themselves are determined against an international primary scale (CO₂: WMOX2007;
304 CH₄: NOAA2004; N₂O: NOAA2005A; SF₆: NOAA2005; CO: WMOX2004; H₂:
305 WMOX2009; Hall et al., 2007; Dlugokencky et al., 2005; Jordan and Steinberg, 2011; Zhao
306 and Tans, 2006). Finally, a "target" gas is measured every two hours after the calibration
307 gases as a quality control of the scales and of the analyzers. The repeatability of the GC
308 systems estimated from the target cylinder measurements over several days is 0.06 ppm for
309 CO₂, 1 ppb for CH₄, 0.3 ppb for N₂O, 0.1 ppt for SF₆, 1 ppb for CO and 2 ppb for H₂.

310 Additional quality control is made by checking the values of a flask target (a flask filled with
311 calibrated gases) placed on each measurement sequence.

312

313 For both of the GC systems, data acquisition, valve shunting, and temperature regulation are
314 entirely processed by the Chemstation software from Agilent. Concentrations are calculated
315 with a software developed at LSCE using peak height or area depending on the species.

316

317 **2.2.3 Uncertainty of flask measurements**

318 Uncertainties in the measured concentrations stemmed from both the sampling method and
319 the analysis. Collecting flask samples in pairs and measuring each flask twice allow us to
320 evaluate these uncertainties. A large discrepancy between two analyses of the same flask
321 reveals a problem in the analysis system, while a difference between a pair of flasks reflects
322 both analysis and sampling uncertainties. Flask pairs with differences in mole fractions
323 beyond a certain threshold are flagged and rejected (see Table S2 in the supplement for the
324 threshold for each species). The percentages of flask pairs retained for analyses are 65.9-88.3%
325 for CO₂, 88.6-94.1% for CH₄, 74.6-91.5% for N₂O, 92.0-96.8% for SF₆, 68.6-88.3% for CO,
326 and 76.2-95.2% for H₂ (Table S3). For each species, we evaluate the uncertainties by
327 averaging differences between the two injections of the same flask (analysis uncertainty) and
328 between the pair of flasks (analysis uncertainty + sampling uncertainty) across all retained
329 flask pairs from the three Indian stations (Table S4). For all species except SF₆, the sampling
330 uncertainty turns out to be the major uncertainty, while the analysis uncertainty is equivalent
331 to the reproducibility of the instrument. For SF₆, both uncertainties are extremely low due to
332 the small amplitudes and variations of the signals at the three stations.

333

334 At LSCE, there are regular comparison exercises in which flasks are measured by different
335 laboratories on the same primary scale (e.g., Inter-Comparison Project (ICP) loop, Integrated
336 non-CO₂ Greenhouse gas Observing System (InGOS) ‘Cucumber’ intercomparison project).
337 These comparisons allow us to estimate possible biases in our measurements. In Table S4, the
338 bias for each species is calculated over the sampling period using the ICP flask exercise that
339 circulates flasks of low, medium and high concentrations between different laboratories. For
340 CO₂, CH₄, SF₆ and CO, the biases are reported against NOAA (NOAA-LSCE) as it is the
341 laboratory responsible for the primary scales for these species. The bias of H₂ is calculated
342 against Max Planck Institute for Biogeochemistry (MPI-BGC) in Jena, Germany, which is
343 responsible for the primary scale of H₂. The bias of N₂O is reported against MPI-BGC instead
344 of NOAA. Although NOAA is responsible for the primary scale of N₂O, the instruments they
345 use for the N₂O flask analyses and cylinder calibration are not the same as ours. For CH₄,
346 N₂O, SF₆ and H₂, the estimated biases are within the noise level of the instrument and
347 negligible. For CO₂ and CO, we observe a bias of -0.15 ± 0.11 ppm and 3.5 ± 2.2 ppb,
348 respectively (Table S4), which could be due to the nonlinearity of the instrument and/or an
349 improper attribution of the secondary scale values.

350

351 **2.3 Data analyses**

352 **2.3.1 Curve-fitting procedures**

353 For each time series of flask measurements, we calculated annual means and seasonal cycles
354 using a curve-fitting routine (CCGvu) developed by NOAA/CMDL (Thoning et al., 1989). A
355 smoothed function was fitted to the retained data, consisting of a first-order polynomial for
356 the growth rate and two harmonics for the annual cycle (Levin et al., 2002; Ramonet et al.,
357 2002), as well as a low pass filter with 80 and 667 days as short-term and long-term cutoff

358 values, respectively (Bakwin et al., 1998). Residuals were then calculated as the differences
359 between the original data and the smoothed fitting curve. Any data lying outside three
360 standard deviations of the residuals were regarded as outliers and discarded from the time
361 series (Harris et al., 2000; Zhang et al., 2007). This procedure was repeated until no outliers
362 remained. These outliers were likely a result of pollution by local emissions and not
363 representative of regional background concentrations. The data discarded through this
364 filtering procedure accounts for less than 4% of the retained flask pairs after flagging (Table
365 S3). Particularly, for PON where observations can be influenced by local emissions, we also
366 tried to use CO as a tracer and filtered time series of other species by CO outliers. Results
367 show that this additional filtering does not make significant difference to the trends, seasonal
368 cycles and mean annual gradients (relative to HLE) for all the other species at PON (Table S5,
369 Fig. S2). On the other hand, however, the approach may substantially decrease the number of
370 samples used to fit the smooth curve (e.g. ~38% for CH₄) and result in larger data gaps
371 (Table S5, Fig. S2), probably compromising reliability of the analyses. Therefore finally we
372 didn't use CO as a tracer of local emissions for additional filtering.

373

374 For each species at each station, the annual means, as well as the amplitude and phases of
375 seasonal cycles, were determined from the smoothed fitting curve and its harmonic
376 component. We bootstrapped the curve-fitting procedures 1000 times by randomly sampling
377 the original data with replacement to further estimate uncertainties of annual means and
378 seasonal cycles. Since the observation records are relatively short, we used all flask
379 measurements between 2006 and 2011 to fit the smooth curve when available (Fig. S3). For
380 each species, we also compared results with measurements from stations outside India that
381 belong to networks of NOAA/ESRL (<http://www.esrl.noaa.gov/gmd/>) and Integrated Carbon

382 Observation System (ICOS, <https://www.icos-cp.eu/>). Locations and the fitting periods of
383 these stations are also given in Table S6, Figs. S1 and S3.

384

385 **2.3.2 Ratio of species**

386 We analyzed CH₄-CO, CH₄-CO₂, and CO-CO₂ correlations using the residuals from the
387 smoothed fitting curves that represent synoptic-scale variations (Harris et al., 2000; Ramonet
388 et al., 2002; Grant et al., 2010). To determine the ratio between each species pair, as in
389 previous studies, we used the slope calculated from the orthogonal distance regression (Press
390 et al., 2007) to equally account for variances of both species (Harris et al., 2000; Ramonet et
391 al., 2002; Schuck et al., 2010; Baker et al., 2012). We also bootstrapped the orthogonal
392 distance regression procedure 1000 times and estimated the 1- σ uncertainty for each ratio.
393 The analyses were performed with R3.1.0 (R Core Team, 2014) following the recipes
394 described in Teetor (2011).

395

396 **3 Results and discussions**

397 **3.1 Annual means and seasonal cycles**

398 **3.1.1 CO₂**

399 Figure 2 shows CO₂ flask measurements and the corresponding smooth curves fitted to the
400 data at HLE, PON and PBL, as well as two additional NOAA/ESRL stations, namely Plateau
401 Assy, Kazakhstan (KZM – 43.25 °N, 77.88 °E, 2519 m a.s.l.) and Waliguan, China (WLG –
402 36.29 °N, 100.90 °E, 3810 m a.s.l.) (Dlugokencky et al., 2014b). HLE observed an increase
403 in CO₂ mole fractions from 382.3±0.3 to 391.4±0.3 between 2007 and 2011, with annual
404 mean values being lower (by 0.2–1.9 ppm) than KZM and WLG (Fig. 2c and d, Table 1). At
405 PON, the annual mean CO₂ mole fractions were generally higher than at HLE, with

406 differences ranging 1.8–4.3 ppm (Fig. 2a, Table 1). The annual mean CO₂ gradient between
407 PON and HLE reflects the altitudinal difference of the two stations, and a larger influence of
408 CO₂ emissions at PON, mostly from South India (Fig. 1a, EDGAR v4.2). Besides this, as
409 shown in Fig. 2a and Table 1, the CO₂ observations at PON are influenced by synoptic scale
410 events, with a large variability of individual measurements relative to the fitting curve (see
411 the relative SDs (RSD) in Table 1). At PBL, the annual mean CO₂ mole fractions were on
412 average 1.2–1.8 ppm lower than that at HLE (Table 1). The negative gradient between PBL
413 and HLE is particularly large during summer, possibly due to clean air masses transported
414 from the ocean (Figs. 1a and 2b). Note that caution should be exercised in interpreting the
415 gradient at PBL because of the data gap and short duration of the time series.

416

417 The different CO₂ seasonal cycles observed at the five stations reflect the seasonality of
418 carbon exchange in the northern terrestrial biosphere as well as influences of long-range
419 transport and the monsoon circulations. At HLE, the peak-to-peak amplitude of the mean
420 seasonal cycle was 8.2 ± 0.4 ppm, with the maximum early May and the minimum mid-
421 September, respectively (Fig. 3, Table 1). The mean seasonal cycle estimated from flask
422 measurements at HLE is in good agreement with that derived from vertical profiles of in-situ
423 aircraft measurements over New Delhi (~500 km southwest of HLE) from the
424 Comprehensive Observation Network for Trace gases by Airliner (CONTRAIL,
425 <http://www.cger.nies.go.jp/contrail/>) project at similar altitudes ($R=0.98-0.99$, $p<0.001$, Fig.
426 3a; Machida et al., 2008), and back-trajectories show that they represent air masses with
427 similar origins as HLE (Fig. S8), confirming that HLE is representative of the regional free
428 mid-troposphere background concentrations. When comparing with the two other background
429 stations located further north in central and East Asia, a significant delay of the CO₂ phase is
430 seen at HLE compared to KZM and WLG (Fig. 3b, Table 1). We also note that the CO₂ mean

431 seasonal cycle at HLE is in phase with the composite zonal marine boundary layer (MBL)
432 reference at 32°N, while for KZM and WLG, an advance in the CO₂ phase by about 1 month
433 is observed compared to the zonal MBL reference (Fig. S4; Dlugokency et al., 2014b). The
434 phase shifts in the CO₂ seasonal cycles mainly result from differences in the air mass origins
435 between stations. HLE is influenced by the long-range transport of air masses from mid-
436 latitudes around 30 °N, as well as air masses passing over the Indian subcontinent in the
437 boreal summer (Fig. 1a), therefore its CO₂ seasonal cycle is related to the seasonality of
438 vegetation activity over the entire latitude band. KZM and WLG receive air masses passing
439 over the Middle East and western Asia as HLE does, but they are also influenced by air
440 masses of more northern origins with signals of strong CO₂ uptake over Siberia during JAS
441 (Fig. S5). At WLG, negative CO₂ synoptic events, indicative of large-scale transport of air
442 masses exposed to carbon sinks in Siberia in summer, were also detected by in-situ
443 measurements during 2009-2011 (Fang et al., 2014). Moreover, the back trajectories indicate
444 that WLG and KZM are more influenced than HLE by air masses that have exchanged with
445 the boundary layer air being affected by vegetation CO₂ uptake (Fig. S6a,d,e). This could
446 additionally account for the earlier CO₂ phase observed at KZM and WLG compared to HLE.

447

448 At PON and PBL, the peak-to-peak amplitudes of the CO₂ mean seasonal cycles were
449 7.6 ± 1.4 and 11.1 ± 1.3 ppm, with their maxima observed in April. The CO₂ mean seasonal
450 cycle is controlled by changes in the monsoon circulations, in combination with the
451 seasonality of CO₂ biotic exchange and anthropogenic emissions in India. During the boreal
452 winter when the NE monsoon prevails, PON and PBL receive air masses enriched in CO₂
453 from the East and Northeast Indian subcontinent as well as from Southeast Asia, with large
454 anthropogenic CO₂ emissions (EDGAR v4.2; Wang et al., 2013; Kurokawa et al., 2013).
455 During April when the SW monsoon begins to develop, the two stations record a decrease in

456 CO₂ because of the arrival of air masses depleted in CO₂ originating from the Indian Ocean
457 south of the Equator (Fig. 1a, Fig. 3c). Compared to PBL, the CO₂ decrease at PON is less
458 pronounced and longer, probably because of the influence of anthropogenic emissions in
459 South India. The CO₂ mean seasonal cycle at PON is also similar to that observed at CRI
460 (15.08°N, 73.83°E, 60m a.s.l.), another station on the southwest coast of India, yet the
461 seasonal maximum at CRI is reached slightly earlier than at PON in March (Bhattacharya et
462 al., 2009; Tiwari et al., 2011, 2014). The SNG station (18.35°N, 73.75°E, 1600m a.s.l.),
463 located over the Western Ghats, observes a larger CO₂ seasonal cycle with a peak-to-peak
464 amplitude of ~20 ppm (Tiwari et al., 2014).

465

466 **3.1.2 CH₄**

467 Figure 4 presents the time series of CH₄ flask measurements at the three Indian stations and
468 the two NOAA/ESRL stations (Dlugokencky et al., 2014a), with their corresponding
469 smoothed curves for 2007–2011. At HLE, the annual mean CH₄ concentration increased from
470 1814.8±2.9 to 1849.5±5.2 ppb between 2007 and 2011 (Fig. 4, Table 1). The multiyear mean
471 CH₄ value at HLE was lower than at KZM and WLG by on average 25.7±3.1 and 19.6±7.8
472 ppb (Fig. 4c and d, Table 1), respectively, reflecting the latitudinal and altitudinal CH₄
473 gradients. Indeed, KZM and WLG receive air masses transported from Siberia with large
474 wetland CH₄ emissions in summer, as well as those from regional sources closer to the
475 stations (Fang et al., 2013; Fig. S5), which may further contribute to the positive gradients
476 between these two stations and HLE. At PON and PBL, the annual mean CH₄ mole fractions
477 were higher than those at HLE by as much as 37.4±10.7 and 19.8±24.5 ppb respectively (Fig.
478 4a and b, Table 1). The positive gradients indicate significant regional CH₄ emissions,
479 especially during winter when the NE monsoon transports air masses from East and
480 Northeast India and Southeast Asia, where emissions from livestock, rice paddies and a

481 variety of waterlogged anaerobic sources and residential biofuel burning are high (EDGAR
482 v4.2; Baker et al., 2012; Kurokawa et al., 2013). The in-situ measurements at Darjeeling,
483 India (27.03°N, 88.25°E, 2194 m a.s.l.), another station located in the eastern Himalayas, also
484 showed large variability and frequent pollution events in CH₄ mole fractions, which largely
485 result from the transport of CH₄-polluted air masses from the densely populated Indo-
486 Gangetic Plains to the station (Ganesan et al., 2013).

487

488 The CH₄ seasonal cycles exhibit contrasting patterns across stations. As shown in Fig. 5, a
489 distinct characteristic of the mean seasonal cycle at HLE is a CH₄ maximum from June to
490 September. Even KZM and WLG do not show a minimum in summer that would be
491 characteristic for the enhanced CH₄ removal rate by reaction with OH. The pronounced HLE
492 feature is consistent with the result from the aircraft flask measurements over India at flight
493 altitudes of 8–12.5 km by the Civil Aircraft for the Regular Investigation of the atmosphere
494 Based on an Instrument Container (CARIBIC, <http://www.caribic-atmospheric.com/>) project
495 (Schuck et al., 2010, 2012; Baker et al., 2012), although a larger seasonal cycle amplitude is
496 found in the CARIBIC composite data due to **the rapid vertical mixing over the monsoon**
497 **region and the strong anticyclone that develops in the upper troposphere** (Fig. 5a; **Schuck et**
498 **al., 2010**). CARIBIC sampled the mid- to upper tropospheric air masses that were earlier and
499 more strongly enriched in CH₄, **as a result of the rapid vertical transport of surface air masses**
500 **by deep convection and subsequent accumulation and confinement of pollutants within the**
501 **strong, closed circulation of the anticyclone** (Li et al., 2005; Randel and Park, 2006). Xiong et
502 al. (2009) also reported enhancements of CH₄ during the summer monsoon season over South
503 Asia based on satellite retrievals of CH₄ using the Atmospheric Infrared Sounder (AIRS) on
504 the EOS/Aqua platform as well as model simulations. Moreover, the mean CH₄ seasonal
505 cycle at HLE agrees well with the seasonal variations of CH₄ emissions from wetlands and

506 rice paddies and convective precipitation over the Indian subcontinent (Fig. 5b), suggesting
507 that the summer maximum at HLE are likely related to the enhanced biogenic CH₄ emissions
508 from wetlands and rice paddies and deep convection that mixes surface emissions into the
509 mid-to-upper troposphere. During the SW monsoon period (June–September), convection
510 over the Indian subcontinent and the Bay of Bengal rapidly mixes surface polluted air with
511 the upper troposphere, therefore concentrations of trace gases would be enhanced at higher
512 altitudes rather than at the surface (Schuck et al., 2010; Lawrence and Lelieveld, 2010).
513 Further analyses of carbon isotopic measurements and/or chemical transport model are
514 needed to disentangle and quantify the contributions of meteorology and biogenic emissions
515 to the CH₄ summer maximum at HLE. As stated above, KZM and WLG also record CH₄
516 increases during summertime, but with smaller magnitudes (Fig. 5a), possibly because they
517 are not directly influenced by deep convection from the Indian monsoon system.

518

519 In contrast to HLE, the CH₄ mean seasonal cycles at PON and PBL have distinct phases and
520 much larger amplitudes, with minimum CH₄ values during July (Fig. 5c). These not only
521 reflect higher rates of removal by OH, but rather the influence of southern hemispheric air
522 transported at low altitudes from the southwest as well as the dilution effect by increased
523 local planetary boundary layer height. In boreal winter, the maxima at PON and PBL are
524 associated with CH₄-enriched air masses transported from East and Northeast India, and
525 Southeast Asia, mostly polluted by agricultural-related sources (e.g., livestock, rice paddies,
526 agricultural waste burning). As PON and PBL, the flask measurements at CRI also showed
527 the seasonal maximum CH₄ values during the NE monsoon season, reflecting influences of
528 air masses with elevated CH₄ from the Indian subcontinent (Bhattacharya et al., 2009; Tiwari
529 et al., 2013).

530

531 3.1.3 N₂O

532 Nitrous oxide (N₂O) is a potent greenhouse gas that has the third largest contribution to
533 anthropogenic radiative forcing after CO₂ and CH₄ (IPCC, 2013). It also becomes the
534 dominant ozone depleting substance (ODS) emitted in the 21st century with the decline of
535 chlorofluorocarbons (CFCs) under the Montreal Protocol (Ravishankara et al., 2009). Since
536 the pre-industrial era, the atmospheric N₂O increased rapidly from ~270 ppb to ~325 ppb in
537 2011 (IPCC, 2013), largely as the result of human activities. Of the several known N₂O
538 sources, agricultural activities (mainly through nitrogen fertilizer use) contribute to ~58% of
539 the global anthropogenic N₂O emissions, with a higher share in a predominantly agrarian
540 country like India (~75%; Garg et al., 2012).

541

542 The time series of N₂O flask measurements over the period of 2007–2011 and their smoothed
543 curves are presented in Fig. 6. At HLE, the annual mean N₂O concentration rose from
544 322.2±0.1 to 325.2±0.1 ppb during 2007–2011 (Table 1), with a mean annual growth rate of
545 0.8±0.0 ppb yr⁻¹ (r² = 0.97, p = 0.001), smaller than that at MLO (1.0±0.0 ppb yr⁻¹, Table 1).
546 At PON and PBL, the annual mean N₂O mole fractions are higher than at HLE by 3.1±0.3
547 and 3.8±1.7 ppb (Fig. 6, Table 1), respectively. The N₂O gradients between PON, PBL and
548 HLE are larger than typical N₂O gradients observed between stations scattered in Europe or
549 in North America. For example, Haszpra et al. (2008) presented N₂O flask measurements at a
550 continental station – Hegyhátsál, Hungary (HUN – 46.95 °N, 16.65 °W, 248 m a.s.l.) from
551 1997 to 2007. The annual mean N₂O mole fraction at HUN was higher than at Mace Head
552 (MHD) by only 1.3 ppb. We also analyzed N₂O time series of flask measurements during
553 2007–2011 at several European coastal stations – BGU in Spain, FIK in Greece, and LPO in
554 France (Table S6), and the N₂O gradients between these stations and MHD were 1.1±0.2,
555 0.4±0.1, and 2.1±0.6 ppb, respectively (Fig. S10, Table S7). In the United States, N₂O flask

556 measurements from the NOAA/ESRL stations at Park Falls, Wisconsin (LEF – 45.95 °N,
557 90.27 °W, 472 m a.s.l.), Harvard Forest, Massachusetts (HFM – 42.54 °N, 72.17 °W, 340 m
558 a.s.l.) and a continental, high-altitude station at Niwot Ridge, Colorado (NWR – 40.05 °N,
559 105.58 °W, 3523 m a.s.l.) also show that, the annual mean N₂O concentrations at HFM and
560 LEF were higher than that at NWR by only 0.5±0.1 and 0.3±0.1 ppb, respectively (Fig. S10,
561 Table S7). Besides, the N₂O concentrations measured at PON and PBL have a notably higher
562 variability (around the smoothed fitting curve) than that at European and US stations (see
563 relative SDs (RSD) in Table 1 and Table S7). The larger N₂O gradient between PON, PBL
564 and HLE, as well as higher variability at PON and PBL, demonstrate the presence of
565 substantial N₂O sources in South Asia and over the Indian Ocean during the observation
566 period. The in-situ measurements at Darjeeling also exhibited N₂O enhancements to be above
567 the background level, suggesting significant N₂O sources in this region (Ganesan et al., 2013).
568 These sources may be related to emissions from natural and cultivated soils probably
569 enhanced by extensive use of nitrogen fertilizers, as well as emissions from regions of coastal
570 upwelling in the Arabian Sea (Bange et al., 2001; Garg et al., 2012; Saikawa et al., 2014).

571

572 Compared to CO₂ and CH₄, the seasonal cycle of N₂O is very small due to the long lifetime
573 of ~120 years (Minschwaner et al., 1993; Volk et al., 1997), and has a larger uncertainty
574 probably because synoptic events are more likely to mask the seasonal signal. At HLE, PON
575 and PBL, the peak-to-peak amplitudes of the N₂O seasonal cycle are 0.6±0.1, 1.2±0.5, and
576 2.2±0.6 ppb, respectively (Table 1). HLE displays a N₂O maximum in mid-August (Student's
577 t-test, t=1.78, p=0.06), and a secondary maximum is in January/February but not significant
578 (Student's t-test, t=-0.84, p=0.79) (Table 1, Fig. 7, Table S8 for detailed t-test statistics). The
579 N₂O seasonal cycle at HLE is out of phase with that at other northern background stations
580 such as MHD (Fig. S11, Table S7), where an N₂O summer minimum is always observed,

581 likely due to the downward transport of N₂O-depleted air from the stratosphere to the
582 troposphere during spring and summer (Liao et al., 2004; Morgan et al., 2004; Jiang et al.,
583 2007b). The timing of the summer N₂O maximum at HLE is consistent with that of CH₄
584 (Table 1; Figs. 5 and 7), giving evidence that the N₂O seasonal cycle may probably be
585 influenced by the convective mixing of surface air, rather than by the influx of stratospheric
586 air into the troposphere. Given that the populous Indo-Gangetic plains have high N₂O
587 emission rates due to the intensive use of nitrogen fertilizers (Garg et al., 2012; Thompson et
588 al., 2014a), during summer, the surface air enriched in N₂O is vertically transported by deep
589 convection and enhances N₂O mole fractions in the mid-to-upper troposphere. Like CH₄, the
590 N₂O enhancement during the summer monsoon period (June–September) **was also observed**
591 by the aircraft flask measurements at flight altitudes 8–12.5 km from the CARIBIC project in
592 2008 (Schuck et al., 2010).

593

594 At PON, N₂O also decreases during February–April and reaches a minimum at the end of
595 May. However, the decrease of N₂O does not persist during June–September, which is in
596 contrast with CH₄ (Table 1, Fig. 7a). One reason may be that the air masses arriving at the
597 site during the southwest monsoon period is relatively enriched in N₂O compared to CH₄,
598 reflecting differences in their relative emissions along the air mass route. The increase of N₂O
599 at PON during June–August and the maximum during September–October are likely related
600 to N₂O emissions from coastal upwelling along the southern Indian continental shelf, which
601 peak during the SW monsoon season (Patra et al., 1999; Bange et al., 2001). According to
602 Bange et al. (2001), the annual N₂O emission for the Arabian Sea is 0.33–0.70 Tg/yr, of
603 which N₂O emissions during the SW monsoon account for about 64–70%. This coastal
604 upwelling N₂O flux is significantly larger than the annual anthropogenic N₂O emissions in
605 South India south of 15 °N, which is estimated to be on average 0.07–0.08 Tg/yr during

606 2000–2010 (EDGAR v4.2). At PBL, the maximum and minimum N₂O occur in November
607 and February/March, respectively (Table 1, Fig. 7b). The late N₂O peak at PBL in November
608 may be associated with the N₂O-enriched air masses transported from South and Southeast
609 Asia, which could be attributed to natural and agricultural N₂O emissions from this region
610 (Saikawa et al., 2014). It should be noted that, the mean seasonal cycles of N₂O at PON and
611 PBL are subject to high uncertainties because of the short observation periods and data gaps
612 (shaded area in Fig. 7). The N₂O maximum and/or minimum obtained from the mean
613 seasonal cycle are marginally significant for PON and PBL (Table S8 for detailed t-test
614 statistics). Therefore, caution should be exercised in interpreting mean seasonal cycles at
615 these stations. Sustained, long-term measurements are needed in order to generate more
616 reliable estimates of the seasonal cycles for the two stations.

617

618 **3.1.4 SF₆**

619 Sulfur hexafluoride (SF₆) is an extremely stable greenhouse gas, with an atmospheric lifetime
620 as long as 800–3200 year and a global warming potential (GWP) of ~23,900 over a 100-year
621 time horizon (Ravishankara et al., 1993; Morris et al., 1995; IPCC, 2013). The main sources
622 of atmospheric SF₆ emissions are electricity distribution systems, magnesium production, and
623 semi-conductor manufacturing (Olivier et al., 2005), while its natural sources are negligible
624 (Busenberg and Plummer, 2000). As its sources are almost purely anthropogenic (Maiss et al.,
625 1996), SF₆ is widely considered as a good tracer for population density, energy consumption
626 and anthropogenic GHG emissions (Haszpra et al., 2008).

627

628 Figure 8 presents the time series of SF₆ flask measurements and corresponding fitting curves
629 at HLE, PON, and PBL. At HLE, the annual mean SF₆ mole fractions increased from

630 6.26±0.03 to 7.38±0.01 ppt between 2007 and 2011, which is in good agreement with the SF₆
631 trend observed at MLO during the same period (HLE: 0.29±0.05 ppt/yr, r²=0.99, p<0.001;
632 MLO: 0.29±0.03 ppt/yr, r²=0.99, p<0.001; Figs. 8 and S12a, Table 1, Table S9). The annual
633 mean SF₆ gradient between PON and HLE is -0.060±0.030 ppt, whereas the gradient between
634 PBL and HLE is statistically insignificant (-0.002±0.097 ppt). The slight negative gradient
635 between PON and HLE is a reversed signal compared with the SF₆ observations at stations
636 influenced by continental emissions in Europe and United States. For example, the SF₆ mole
637 fractions at HUN over the years of 1997–2007 are higher than those at MHD by on average
638 0.19 ppt (Haszpra et al., 2008). We also analyzed the SF₆ gradients between two coastal
639 European stations – BGU (41.97 °N, 3.3 °E, 30 m a.s.l.) and LPO (48.80 °N, 3.57 °W, 30 m
640 a.s.l.) – and MHD, which are 0.10±0.03 and 0.05±0.02 ppt averaged over the period of 2007–
641 2011, respectively. At HFM, the SF₆ mole fractions are higher than those of the NWR on
642 average by 0.15±0.06 ppt during 2007–2011 (Table S9). Given the long atmospheric lifetime
643 of SF₆, the positive gradients between continental European and US stations and background
644 reference stations suggest significant sources in Europe and the US. On the contrary, the
645 slight negative gradient between PON and HLE implies weak SF₆ emissions over the Indian
646 subcontinent, which is also indicated by recent high-frequency in-situ SF₆ measurements at
647 Darjeeling (Ganesan et al., 2013). It is also worthwhile to note that high SF₆ values occur
648 repeatedly at HLE and PBL in winter, which is likely related to episodic SF₆ pollution events
649 from the Middle East, South/Southeast Asia and China (Figs. 8b and S7d).

650

651 The annual mean SF₆ seasonal cycles for HLE, PON, and PBL are presented in Fig. 9. The
652 peak-to-peak amplitudes at the three stations are 0.15±0.03, 0.24±0.02, and 0.48±0.07 ppt,
653 respectively (Table 1). At HLE, the SF₆ seasonal cycle is bimodal as for N₂O, with an
654 absolute maximum occurring in November (Student's t-test, t=2.425, p=0.014) and a

655 secondary maximum in May (Student's t-test, $t=2.443$, $p=0.016$) (Table S10 for detailed t-test
656 statistics). Given that SF₆ increases monotonously and that its sources are purely
657 anthropogenic and not subject to seasonally variations (Maiss et al., 1996), the seasonal cycle
658 of SF₆ should be driven by changes in atmospheric circulations, e.g., the SW monsoon
659 convection and stratosphere-atmosphere exchange (Levin et al., 2002). We note that, at HLE,
660 no enhancement of SF₆ during the SW monsoon season is recorded, unlike what is observed
661 for CH₄ and N₂O (Figs. 5 and 7). Although the CARIBIC aircraft flask measurements over
662 the Indian region demonstrated SF₆ enhancements in the upper troposphere at ~30 °N
663 (approximately where HLE is located) in August, 2008, they are not related to the deep
664 convection and surface sources that contribute to the summer maxima in CH₄ and N₂O. Back-
665 trajectories from the CARIBIC flights showed that the summer enhancements in SF₆ were
666 related to air samples collected north of 20°N along the flight routes, where air masses were
667 more influenced by the westerly subtropical jet (and a smaller anticyclone embedded in it
668 over the Arabian Peninsula) rather than the deep convection in the monsoon region
669 (Krishnamurti et al. 2008; Schuck et al., 2010; Fig. S9). Since HLE is not influenced by the
670 westerly subtropical jet in the upper troposphere (also clearly seen by the colors of back-
671 trajectories in Fig. S9), the summer enhancements of SF₆ observed by the CARIBIC flights
672 are not detected by the flask measurements at HLE. The absence of SF₆ enhancement in
673 summer at HLE confirms weak SF₆ emissions in India. At PBL, the SF₆ seasonal cycle is
674 related to the monsoon circulation and convection (Figs. 9b and S7d). The maximum during
675 November–December (Student's t-test, $t=5.138$, $p<0.001$; Table S10) is likely due to frequent
676 episodic SF₆ polluted air masses transported from Southeast Asia and China (Fig. S7d).

677

678 3.1.5 CO

679 Carbon monoxide (CO) plays important roles in atmospheric chemistry, as the dominant sink
680 for the hydroxyl radical (OH, the main tropospheric oxidant) and a precursor of tropospheric
681 ozone under high NO_x (NO+NO₂) concentrations (Logan et al., 1981; Novelli et al., 1998;
682 Seinfeld and Pandis, 2006). Although CO does not act as a greenhouse gas, it modulates the
683 atmospheric concentrations of CH₄ (the second anthropogenic greenhouse gas after CO₂)
684 through competition for the OH radicals. At the global scale, it contributes to an indirect
685 positive radiative forcing of $0.23 \pm 0.07 \text{ W m}^{-2}$ (IPCC, 2013). Besides, CO is an excellent tracer
686 for combustion processes, with emission sources mainly contributed by incomplete
687 combustion of fossil fuel and biofuels, and by biomass burning (Granier et al., 2011). In India,
688 biofuel and agricultural waste burning account for 70–80% of the total anthropogenic CO
689 emissions (EDGAR v4.2; Streets et al., 2003b; Yevich and Logan, 2003).

690

691 The time series of CO flask measurements and corresponding smoothed curves are shown in
692 Fig. 10. Over the period of 2007–2011, HLE recorded a slight decrease in CO mole fractions
693 from 104.7 ± 1.4 to 99.4 ± 2.2 ppb, with an annual rate of -2.2 ± 0.0 ppb yr⁻¹ ($r^2 = 0.65$, $p = 0.06$).
694 The CO mole fractions at HLE are lower than those at KZM and WLG (Novelli et al., 2014b),
695 by on average 18.8 ± 2.5 and 30.2 ± 7.4 ppb, respectively (Table 1, Fig. 10c and d). The
696 positive gradient between KZM, WLG and HLE does not only reflect decreasing CO with
697 altitude and the N-S global gradient, but also suggests differences in regional emission
698 sources. For example, compared to HLE, the CO signals at WLG are more influenced by
699 transport of polluted air, especially during summer when about 30% air masses pass over
700 industrialized and urbanized areas southeast of the station (Zhang et al., 2011). Besides, the
701 positive CO gradient between KZM, WLG and HLE may be further contributed by air
702 masses of northern Siberia origin in summer (Fig. S5), with higher CO emissions from
703 biomass burning and secondary CO from the oxidation of CH₄ and non-CH₄ hydrocarbons

704 (Konovalov et al., 2014). At PON and PBL, the annual mean CO mole fractions are higher
705 than that at HLE by on average 82.4 ± 10.7 and 52.5 ± 8.5 ppb, respectively (Table 1, Fig. 10a
706 and b). The PON and PBL stations are influenced by CO regional emissions, mainly due to
707 biofuel and agricultural burning over South and Southeast Asia (Lelieveld et al., 2001; Streets
708 et al., 2003a, b; Yevich and Logan, 2003). We also note that, for all the five stations, the CO
709 time series show larger variability with respect to their corresponding smoothed curves than
710 other species do (see the residual SD (RSD) in Table 1, Fig. 10), as a result of the unevenly
711 distributed CO sources and short atmospheric lifetime (Novelli et al., 1992).

712

713 As shown in Fig. 11, the CO seasonal cycle at HLE reaches a maximum in mid-March and a
714 minimum by the end of October, with a peak-to-peak amplitude of 28.4 ± 2.3 ppb (Table 1,
715 Fig. 11). The phase of the mean CO seasonal cycle at HLE generally agrees with the ones
716 observed at KZM and WLG, with a lag of up to 1 month in the timing of seasonal minimum
717 at the two stations (Table 1, Fig. 11c and d). In contrast with the three stations representative
718 of large-scale free tropospheric air masses, the stations at the maritime boundary layer in the
719 mid-to-high Northern Hemisphere observe the lowest CO values in July or August (Novelli et
720 al., 1992, 1998), when the concentration of OH – the major sink of CO – is highest (Logan et
721 al., 1981). The delay in timing of the seasonal CO minimum at the three free troposphere
722 stations in Central and South Asia compared to those boundary layer stations is probably due
723 to the mixing time of regional surface CO emissions and the relatively short lifetime of CO
724 (1-2 months on average). During summer, KZM and WLG sample air masses from Siberia
725 impacted by CO fire emissions (Duncan et al., 2003; Kasischke et al., 2005), as well as CO-
726 polluted air from urbanized and industrialized area (Zhang et al., 2011), while HLE is
727 influenced by convective mixing of CO emissions from India, either from anthropogenic
728 sources or oxidation of VOCs. It is interesting to note that the CO seasonal cycle at HLE does

729 not show an enhancement during JAS as CH₄ and N₂O do (Figs. 5 and 7), possibly as a result
730 of OH oxidation that reduces CO and acts oppositely to vertical transport, and/or differences
731 in seasonal emission patterns between CO and the other two species (Baker et al., 2012).
732 However, the CO enhancement during summer was observed in the upper troposphere over
733 South Asia from the CARIBIC aircraft measurements at flight altitudes 8-12.5 km and
734 Microwave Limb Sounder observations at 100–200 hPa (Li et al., 2005; Jiang et al., 2007a;
735 Schuck et al., 2010). The differences in the CO seasonal cycles at different altitudes suggest
736 faster transport (and younger air masses) at 10 km than at 5 km due to convection, controlling
737 the vertical profile of CO, which makes it difficult to directly compare aircraft measurements
738 in the upper troposphere and column remote sensing observations with surface data.

739

740 At PON and PBL, the mean CO seasonal cycles show maxima in the boreal winter and
741 minima in the boreal summer, with peak-to-peak amplitudes of 78.2 ± 11.6 and 144.1 ± 16.0
742 ppb, respectively (Fig. 11a and b). A strong and positive correlation is found between
743 detrended CO and CH₄ at PON ($r=0.70$, $p<0.001$) and PBL ($r=0.84$, $p<0.001$), suggesting that
744 the seasonal cycles of both species are dominated by the seasonally varying atmospheric
745 transport. During summer when the southwest monsoon prevails, the surface CO
746 concentrations at PON and PBL are low due to rapid convective uplifting and advection of
747 clean air masses from the ocean. During winter, the two stations are influenced by
748 northeasterly air masses enriched in CO from Northeast India, Southeast Asia and China
749 (back-trajectories in Fig. S7e), probably influenced by biofuel and agricultural waste burning
750 in these regions (Yevich and Logan, 2003; Lelieveld et al., 2001).

751

752 **3.1.6 H₂**

753 Hydrogen (H₂) is the second most abundant reduced trace gas in the troposphere after CH₄,
754 with an average mole fraction of ~530 ppb (Novelli et al., 1999). It plays important roles in
755 tropospheric and stratospheric chemistry and indirectly impacts budgets of CH₄, CO and non-
756 methane hydrocarbons (NMHCs) through reaction with the OH radicals (Novelli et al., 1999;
757 Ehhalt and Rohrer, 2009). Like CO, H₂ is also a good tracer for incomplete combustion
758 emissions from fossil fuel and biomass/biofuel burning, which is quite extensive in India
759 (Streets et al., 2003b; Yevich and Logan, 2003).

760

761 Figure 12 shows the time series of H₂ flask measurements with smoothed curves at HLE,
762 PON, and PBL, respectively. No significant trend was observed at any of the three stations
763 (Table 1, Fig. 12), consistent with the long-term H₂ measurements at other background
764 stations during the last three decades (Novelli et al., 1999; Ehhalt and Rohrer, 2009; Grant et
765 al., 2010). For the year 2008, comparing to KZM and WLG (Novelli et al., 2014a), HLE
766 recorded higher H₂ mole fractions by ~40 ppb, reflecting the latitudinal gradient of H₂ with
767 lower concentrations towards northern high latitudes, due to land uptake by soils (Novelli et
768 al., 1999; Price et al., 2007; Hauglustaine and Ehhalt, 2002; Ehhalt and Rohrer, 2009). Note
769 that these results based on only one-year comparison need to be confirmed by extended data
770 more up-to-date, which are not available yet. At PON and PBL, the annual mean H₂ mole
771 fractions were higher than at HLE by 29.8±4.1 and 21.8±4.6 ppb, respectively (Table 1; Fig.
772 12). Comparisons with H₂ measurements at Mariana Island, Guam (GMI – 13.39 °N,
773 144.66 °E, 0.00 m a.s.l.) (Novelli et al., 2014a), another maritime station in the western
774 Pacific at a similar latitude as PON and PBL, also showed positive gradients of ~40 ppb (Fig.
775 S13c and d; Table S11), suggesting substantial regional H₂ sources over the footprint area of
776 PBL and PON. During October–March when the NE monsoon prevails, both PON and PBL
777 receive H₂-enriched air masses from South and Southeast Asia, mainly influenced by fossil

778 fuel combustion and biomass burning (Fig. S7f; GFED v3.1; Hauglustaine and Ehhalt, 2002;
779 Price et al., 2007; Ehhalt and Rohrer, 2009; van der Werf et al., 2010). During April–
780 September, with the northward movement of Intertropical Convergence Zone (ITCZ), the two
781 stations are influenced by advection of air from south of the Equator. For PON, H₂-polluted
782 air masses are occasionally sampled during JAS when the SW monsoon moves over the
783 continent of South India with high population and heavy industry (Fig. S7f; Census India,
784 2011).

785

786 The mean H₂ seasonal cycles for HLE, PON, and PBL are presented in Fig. 13. At HLE, the
787 peak-to-peak H₂ seasonal amplitude is 15.8 ± 2.2 ppb, less than half of the seasonal amplitudes
788 at BMW (39.6 ± 2.6 ppb) and MID (38.0 ± 2.4 ppb) of similar latitudes (Novelli et al., 2014a),
789 and that at WLG (22.8 ± 3.0 ppb) (Figs. 13d and S14a, Tables 1 and S11). The maximum and
790 minimum of H₂ occur in April and September, respectively. The dampening of the H₂
791 seasonal amplitude with increasing altitude was previously found for another high-altitude
792 continental station at Jungfrauoch, Switzerland (JUN – 46.53 °N, 7.98 °E, 3580.00 m a.s.l.)
793 (Bond et al., 2011), and was also captured by the GEOS-Chem global chemical transport
794 model (Price et al., 2007). Since the soil sink dominates much of the surface H₂ seasonal
795 cycle in the mid-to-high Northern Hemisphere (Hauglustaine and Ehhalt, 2002; Price et al.,
796 2007; Bousquet et al., 2011; Yver et al., 2011; Yashiro et al., 2011), the smaller amplitude in
797 the H₂ seasonal cycle at HLE may be attributed to the weakened soil sink with increasing
798 altitude due to vertical mixing (Price et al., 2007; Bond et al., 2011).

799

800 At PON and PBL, the mean H₂ seasonal cycles are characterized by the peak-to-peak
801 amplitudes of 21.6 ± 3.4 and 21.3 ± 5.0 ppb respectively, comparable to that at GMI (21.5 ± 1.2

802 ppb) (Tables 1 and S11, Figs. 13a and b and S14b). At PBL, the H₂ maximum in March–
803 April and a secondary increase during September–October coincide with the double biomass
804 burning peaks in each hemisphere – in March for northern tropics, in August/September for
805 southern tropics (van der Werf et al., 2006; Price et al., 2007; Bousquet et al., 2011; Yver et
806 al., 2011). Given that the seasonal variation of soil H₂ uptake is probably small in the tropics
807 (Price et al., 2007; Bousquet et al., 2011; Yver et al., 2011; Yashiro et al., 2011), this bimodal
808 H₂ seasonal cycle at PBL could be related to biomass burning.

809

810 **3.2 Synoptic variations**

811 In this section we analyze synoptic variations of CO₂, CH₄, and CO by examining
812 correlations between species, after subtracting the smoothed curve from the original data.
813 Ratios of trace gas mole fractions or their enhancements have been widely used in previous
814 studies to partition contributions from different source types and origins (Langenfelds et al.,
815 2002; Paris et al., 2008, Lopez et al., 2012), to estimate emissions of one species given
816 emissions of another one that is better-known (Gamnitzer et al., 2006; Rivier et al., 2006;
817 Turnbull et al., 2006; Schuck et al., 2010), and to provide valuable constraints on inversion of
818 sources and sinks of trace gases (Xiao et al., 2004; Pison et al., 2009).

819

820 **3.2.1 $\Delta\text{CH}_4/\Delta\text{CO}$**

821 Figure 14 shows scatterplots of CH₄ and CO residuals with the orthogonal distance regression
822 lines at HLE, PON, and PBL for different seasons. A significant and positive correlation
823 between CH₄ and CO residuals (hereafter $\Delta\text{CH}_4/\Delta\text{CO}$, unit ppb ppb⁻¹) is found for all three
824 stations throughout the year. Furthermore, the $\Delta\text{CH}_4/\Delta\text{CO}$ ratio also shows seasonal variation
825 at each of the three stations. The most prominent feature is the occurrence of maximum

826 slopes in July–September (also October–December at PON), especially at HLE and the
827 generally higher ratios at this station. Wada et al. (2011) and Niwa et al. (2014) also reported
828 increased summer $\Delta\text{CH}_4/\Delta\text{CO}$ over the western North Pacific, according to the in-situ
829 measurements at several surface stations and aircraft flask measurements in the mid-
830 troposphere. The main process for this seasonal variation of $\Delta\text{CH}_4/\Delta\text{CO}$ might be the
831 enhanced emissions of biogenic CH_4 in summer (e.g., wetland and rice paddy emissions;
832 Streets et al., 2003a; Yan et al., 2003) combined with concurrent lower anthropogenic CO
833 emissions in summer than in winter (due to less residential fuel use for heating, see Streets et
834 al., 2003a). The faster photochemical destruction of CO by increased OH during summer
835 cannot explain such large changes (less than 15% according to Wada et al. (2011)).

836

837 At HLE, the $\Delta\text{CH}_4/\Delta\text{CO}$ ratio varies from 1.2 ± 0.3 to 4.0 ± 1.2 ppb ppb⁻¹ throughout the year,
838 with a maximum in JAS, corresponding to the summer monsoon season (Fig. 14a-d). Based
839 on the CARIBIC flights between 10 and 12 km from Frankfurt, Germany to Chennai, India,
840 Baker et al. (2012) derived a $\Delta\text{CH}_4/\Delta\text{CO}$ ratio in the range $1.88(\pm 0.22)$ to $4.43(\pm 0.56)$ in JAS
841 over South Asia. The maximum $\Delta\text{CH}_4/\Delta\text{CO}$ observed during summer in the mid-to-upper
842 troposphere may be the result of higher biogenic CH_4 emission over the Indian subcontinent,
843 lower CO emissions, combined with frequent widespread convective uplift of surface air
844 during the SW monsoon (Schuck et al., 2010; Baker et al., 2012). The CARIBIC flights
845 recorded similar $\Delta\text{CH}_4/\Delta\text{CO}$ values to HLE, confirming that convection plays a dominant
846 role compared to advection during the SW monsoon season. Outside the SW monsoon season,
847 both the CARIBIC flights and HLE do generally not record strong effects of surface
848 emissions due to the weakened vertical transport. With respect to the $\Delta\text{CH}_4/\Delta\text{CO}$ ratios for
849 January–March, April–June and October–December, our estimates are 1.5 to 4 times that of
850 the ratios determined for air masses with signatures of fossil fuel combustion, according to

851 several aircraft and ground observations in East and Southeast Asia (Table S12; Sawa et al.,
852 2004; Lai et al., 2010; Wada et al., 2011; Niwa et al., 2014), which rules out fossil fuel
853 combustion as an explanation for the higher ratios. Our ratios are comparable to the
854 $\Delta\text{CH}_4/\Delta\text{CO}$ values inferred for air masses of Siberian origin during winter (Table S12; Harris
855 et al., 2000; Chi et al., 2013), and we also obtain similar estimates of $\Delta\text{CH}_4/\Delta\text{CO}$ from the
856 flask measurements at KZM over the study period (The $\Delta\text{CH}_4/\Delta\text{CO}$ ratios for KZM are
857 0.8 ± 0.2 , 1.7 ± 0.2 and 1.5 ± 0.3 ppb ppb⁻¹ for AMJ, OND and JFM, respectively), which are
858 influenced by air masses originating from North Africa, the Middle East, and Central Asia as
859 seen at HLE (see back-trajectories in Fig. S5). Given that oil and gas production accounts for
860 50–70% of CH₄ emissions in these regions (EDGAR v4.2) and that over dry areas the
861 daytime boundary layer is higher which favors injection of surface emissions into the
862 troposphere, the preferential enrichment in CH₄ relative to CO at HLE may tentatively be
863 attributed to fossil CH₄ emissions over gas extraction regions and transported eastwards by
864 westerlies (Harris et al., 2000; Tohjima et al., 1996).

865

866 At PON and PBL, the $\Delta\text{CH}_4/\Delta\text{CO}$ ratios are in general considerably higher than 0.3 for all
867 seasons, putting them in the range of ratios indicative of urban/industrial sources (Table S12;
868 Harriss et al., 1994; Sawa et al., 2004; Xiao et al., 2004; Bakwin et al., 1995; Lai et al., 2010;
869 Wada et al., 2011; Niwa et al., 2014). However, this does not rule out contributions from
870 biomass/biofuel burning with emissions having a typical $\Delta\text{CH}_4/\Delta\text{CO}$ ratio less than 0.3
871 (Mauzerall et al., 1998; Andreae and Merlet, 2001; Mühle et al., 2002). Considering that
872 biofuel and agriculture waste burning are the primary energy sources in rural India (Streets et
873 al., 2003a; Yevich and Logan, 2003; Venkataraman et al., 2005), CO emissions from biofuel
874 burning must be substantial (Lelieveld et al., 2001). This is the case for NE India located
875 upwind of PON and PBL when the NE monsoon prevails during December–March.

876 Nevertheless, the relatively low $\Delta\text{CH}_4/\Delta\text{CO}$ derived from biomass/biofuel burning could be
877 increased by CH_4 emissions from livestock with similarly distributed sources (EDGAR v4.2).
878 Emissions of both trace gases from livestock and biomass/biofuel burning in the Indian
879 subcontinent compiled by EDGAR v4.2 also indicate a CH_4 to CO ratio of 0.64–0.69 over the
880 period of 2000–2008, close to the atmospheric measurements of $\Delta\text{CH}_4/\Delta\text{CO}$ at PON and PBL
881 during JFM (Fig. 14h and l).

882

883 **3.2.2 $\Delta\text{CH}_4/\Delta\text{CO}_2$**

884 The $\Delta\text{CH}_4/\Delta\text{CO}_2$ ratios are strongly influenced by the high variability of CO_2 and the
885 interpretation is complex. Unlike the positive correlation between CH_4 and CO consistently
886 observed at all three stations, the relationships between CH_4 and CO_2 residuals exhibit
887 scattered and differences in the residual slopes for different stations and seasons (Fig. 15). At
888 HLE, no significant correlations are found during AMJ, JAS, and OND (Fig. 15a–c), because
889 CH_4 and CO_2 have distinct biogenic and/or photochemical sources and sinks over the
890 northern mid-latitudes. During JFM when biogenic CO_2 fluxes and anthropogenic emissions
891 are positive to the atmosphere, there is a significant and positive relationship between CH_4
892 and CO_2 , with a $\Delta\text{CH}_4/\Delta\text{CO}_2$ ratio of 45.6 ± 1846.8 ppb ppm⁻¹ ($r=0.37$, $p=0.03$; Fig. 15d). This
893 value is close to the ratio of CH_4 and CO_2 anthropogenic emissions over North Africa (39.1–
894 46.2 mmol mol⁻¹), Central Asia (44.4–49.5 mmol mol⁻¹) and to a lesser degree the Middle
895 East (25.8–28.4 mmol mol⁻¹) during the period of 2000–2010 (EDGAR v4.2), corresponding
896 to the back-trajectories reaching HLE (Fig. 1a). It should be noted that this estimate of
897 $\Delta\text{CH}_4/\Delta\text{CO}_2$ is subject to large uncertainty according to the standard deviation calculated
898 with 1000 bootstrap replications (Fig. 15d), implying that CH_4 and CO_2 sources of various
899 types and origins influence the HLE records.

900

901 At PON, in contrast to HLE, positive correlations occur between CH₄ and CO₂ residuals for
902 all seasons except OND, with a $\Delta\text{CH}_4/\Delta\text{CO}_2$ ratio of 6.7 ± 2.4 ppb ppm⁻¹ ($r=0.72$, $p<0.001$) in
903 AMJ and 8.5 ± 0.9 ppb ppm⁻¹ in JAS ($r=0.74$, $p<0.001$), respectively (Fig. 15e and f). The
904 relatively narrow ranges of slopes compared to that for HLE and PBL likely suggest co-
905 located urban and industrial sources in South India upwind of PON during April–September
906 (see back-trajectories in Fig. 1a). Emissions from biofuel burning could be a common source
907 for both CH₄ and CO₂, given the substantial biofuel use in South India (Yevich and Logan,
908 2003) and the biofuel burning emission ratio of CH₄ and CO₂ derived from previous studies
909 ($5\text{--}10$ mmol mol⁻¹; Andreae and Merlet, 2001). Note that the CARIBIC flask measurements
910 over India south of 20°N indicate a negative correlation between CH₄ and CO₂ at the altitudes
911 of 10–12 km during July–September, 2008 ($r=-0.80$, $p=0.002$; Fig. S15a), interpreted as the
912 concurrent strong uptake of CO₂ with enhanced emissions of CH₄ during the SW monsoon.
913 During JFM when the NE monsoon predominates, CH₄ is positively correlated with CO₂ with
914 a $\Delta\text{CH}_4/\Delta\text{CO}_2$ ratio of 31.9 ± 1635.7 ppb ppm⁻¹ ($r=0.45$, $p=0.02$; Fig. 15h). Like at HLE, this
915 ratio is subject to large uncertainty due to variability in CH₄ and CO₂ sources. The ratio based
916 on the CARIBIC observations in the upper troposphere (10–12 km) is 23.5 ± 41.4 ppb ppm⁻¹
917 ($r=0.67$, $p=0.004$; Fig. S15b). The inconsistency of the $\Delta\text{CH}_4/\Delta\text{CO}_2$ ratios estimated from the
918 two datasets suggest that the flask measurements at the surface station PON do provide
919 information more specific for constraining estimates of regional CH₄ and CO₂ fluxes.

920

921 Finally, at PBL, the prominent feature of the CH₄–CO₂ relationship is the significant and
922 negative correlation observed during JAS, with a $\Delta\text{CH}_4/\Delta\text{CO}_2$ ratio of -14.6 ± 16.4 ppb ppm⁻¹
923 ($r=-0.73$, $p=0.007$; Fig. 15j). Since the time series of flask measurements at PBL is relatively
924 short and has large data gaps (Fig. S3), correlations between trace gases could be influenced

925 by abnormal pollution events. For example, excluding the event with CH₄ residuals > +20
926 ppb (corresponding to the observation at PBL on 16 September 2009, the point marked with
927 black circle in Fig. 15j) would substantially decrease the strength of negative correlation
928 between CH₄ and CO₂ (r=-0.54, p=0.09). We will investigate the CH₄ enriched event further
929 in Sect. 3.3.

930

931 **3.2.3 $\Delta\text{CO}/\Delta\text{CO}_2$**

932 As shown in Fig. 16, at HLE, CO is positively correlated with CO₂ during AMJ, with a
933 $\Delta\text{CO}/\Delta\text{CO}_2$ ratio of 35.8 ± 12.1 ppb ppm⁻¹ (r=0.53, p=0.001; Fig. 16a). During JFM, there is
934 no significant relationship between CO and CO₂ (r=0.15, p=0.39; Fig. 16d). However,
935 excluding an abnormal event with $\Delta\text{CO}_2 = -1.8$ ppm on 8 January 2007 (the point marked
936 with black circle in Fig. 16d) would give a significant and positive correlation between CO
937 and CO₂, with a $\Delta\text{CO}/\Delta\text{CO}_2$ ratio of 55.7 ± 259.1 ppb ppm⁻¹ (r=0.40, p=0.02; the red solid line
938 in Fig. 16d). This ratio is less than half the emission ratio of CO to CO₂ from forest/grassland
939 biomass burning (Mauzerall et al., 1998; Andreae and Merlet, 2001), but higher than ratios of
940 anthropogenic combustion sources in developed countries that are typically in the range of
941 10–15 ppb ppm⁻¹ (e.g., Suntharalingam et al., 2004; Wada et al., 2011; Takegawa et al., 2004).
942 This could be attributed not only to the lower combustion efficiency of fuels in North Africa,
943 the Middle East, and Central Asia where air masses at HLE originate from, but also to
944 additional contribution from biofuel burning with relatively high CO to CO₂ emission ratios
945 (e.g., fuelwood, charcoal, agricultural residuals; Andreae and Merlet, 2001). Besides, the
946 relatively high $\Delta\text{CO}/\Delta\text{CO}_2$ in JFM compared to AMJ may further indicate a contribution of
947 CO emissions from residential biofuel burning in winter (Wada et al., 2011), especially in
948 developing countries within the footprint area.

949

950 At PON, a positive and significant correlation between CO and CO₂ is found during AMJ,
951 with a $\Delta\text{CO}/\Delta\text{CO}_2$ ratio of 13.4 ± 76.8 ppb ppm⁻¹ ($r=0.46$, $p=0.03$; Fig. 16e). This ratio is
952 similar to the ratios determined for air masses influenced by both fossil fuel emissions and
953 biomass/biofuel burning during the same seasons. For example, based on the in-situ
954 measurements in the upper troposphere during the CARIBIC flights between South China
955 and Philippines in April 2007, Lai et al. (2010) reported the $\Delta\text{CO}/\Delta\text{CO}_2$ ratios of 15.6–29.3
956 ppb ppm⁻¹ during pollution events influenced by both biomass/biofuel burning and fossil fuel
957 combustion in Indochinese Peninsula. At PBL, CO is significantly and negatively correlated
958 with CO₂ during JAS ($r=-0.68$, $p=0.01$; Fig. 16j). However, we note that the CH₄ abnormal
959 event discussed in Sect. 3.2.2 is enriched in CO as well, and the negative relationship
960 between CO and CO₂ would no longer exist if we removed the event ($r=-0.45$, $p=0.16$). The
961 simultaneous enhancement of CO and CH₄ may suggest possible influences of biomass
962 burning episodes, which we will explore in detail in Sect. 3.3. During JFM, no significant
963 relationship is found between CO and CO₂ for PON or PBL (Fig. 16h and l).

964

965 **3.3 Elevated CH₄ and CO events at PBL**

966 In this section, we discuss two elevated CH₄ and CO events at PBL during the SW monsoon
967 season. Significant enhancements of CH₄ and CO were observed on September 16, 2009
968 (July 29, 2011), with residuals from smoothed curves as high as 34.2 (29.2) ppb and 36.2
969 (17.9) ppb for CH₄ and CO, respectively. We further analyzed CH₄ and CO measurements at
970 Bukit Kototabang (BKT – 0.20 °S, 100.32 °E, 845.00 m a.s.l.), Indonesia, located upwind of
971 PBL when the southwest monsoon prevails. The flask measurements at BKT detected
972 enhanced CH₄ and CO with a magnitude of 38.0 and 66.1 ppb on September 8, 2009, about

973 one week before the occurrence of the first CH₄ and CO event at PBL (Fig. 17a). The in-situ
974 measurements at BKT also showed CH₄ and CO enhancements about one week before the
975 second event at PBL, lasting over the period of 17 July–21 July 2011 (Fig. 17b). The
976 coincidence of the two abnormal CH₄ and CO events at PBL and BKT possibly suggests
977 influences of polluted air masses with common sources and origins. Moreover, the fire
978 radiative power (FRP, mWm⁻²) during the sampling dates implies that the two abnormal CH₄
979 and CO events could be related to fire emissions in Indonesia (GFAS product version 1.0;
980 Kaiser et al. 2012; Fig. S16). Note that the mechanisms we propose for the abnormal CH₄ and
981 CO events and the possible linkage between PBL and BKT during the SW monsoon season
982 are still speculative. Model experiments are needed to further confirm these hypotheses.

983

984 **4 Conclusions**

985 In this paper we present the results of flask measurements of CO₂, CH₄, N₂O, SF₆, CO, and
986 H₂ at three stations in India: Hanle (HLE), Pondicherry (PON) and Port-Blair (PBL), over the
987 period of 2007–2011. Of these three stations, HLE is located at a high altitude and regarded
988 as a continental background station in the mid-latitude of the Northern Hemisphere; PON is a
989 tropical surface station located on the southwest coast of India, while PBL is an oceanic
990 station located on the Andaman Islands, of similar latitude to PON. With a total of 188, 185,
991 and 63 flask pair samples collected respectively from HLE, PON and PBL between 2007 and
992 2011 (for PBL between 2009 and 2011), and analyzed at LSCE, the program represents an
993 important logistical and analytical effort to produce a unique dataset of atmospheric trace gas
994 observations over the Indian subcontinent. The observed records will serve as an important
995 source of information to infer regional patterns of trace gas fluxes and atmospheric transport
996 in this under-documented region. Several conclusions and implications are drawn from the
997 first analyses of the datasets.

999 The annual gradients of the atmospheric mole fractions observed at PON and PBL, with
1000 respect to HLE as a reference, suggest significant emission sources of CO₂, CH₄, N₂O, CO,
1001 and H₂ over the footprints of those stations. In particular, the annual mean N₂O mole
1002 fractions at PON and PBL are higher than at HLE by 3.1±0.3 and 3.8±1.7 ppb, notably larger
1003 than the typical N₂O gradients observed between stations in Europe or North America,
1004 indicating substantial N₂O emissions. The analyses of the atmospheric mole fractions with
1005 back-trajectories at the three stations further confirmed emission sources from South and NE
1006 India, and SE Asia, all of which are populous with high demand for food and energy, and
1007 thus high emissions from industrial, residential, and/or agricultural sectors. **On the other hand,**
1008 **despite of substantial anthropogenic GHG emissions in India (whether based on national**
1009 **inventories or atmospheric observations), unlike the USA and EU countries, its SF₆ emissions**
1010 **are rather weak.**

1011

1012 The seasonal cycles for each trace gas reflect not only the seasonal variations of natural
1013 sources/sinks and anthropogenic emissions over the Indian subcontinent, but also the
1014 seasonally varying atmospheric transport, especially the monsoon circulations (including
1015 convection). Strong influences of the monsoon circulations are well depicted by the
1016 contrasting phases of CH₄ seasonal cycles between HLE and PON/PBL. At HLE, the distinct
1017 CH₄ maximum during June-September is likely related to the enhanced biogenic CH₄
1018 emissions from wetlands and rice paddies in summer, combined with deep convection
1019 associated with the SW monsoon that mixes surface emissions into the mid-to-upper
1020 troposphere. By contrast, the CH₄ seasonal cycles at PON and PBL have seasonal minima
1021 during the SW monsoon season, reflecting influences of southern hemispheric air depleted in
1022 CH₄ transported at low altitudes, as well as high rates of OH oxidation. Covariance between

1023 species variations at the synoptic scale further helps identification and attribution of different
1024 sources and sinks, like fossil fuel combustion, biofuel burning and biogenic emissions.
1025 Besides, measurements of $\delta^{13}\text{C-CO}_2$ have been recently started for HLE, and the 4-D
1026 distributions of CO_2 and CH_4 have been realistically simulated using a chemical transport
1027 model (LMDz-OR-INCA, Hauglustaine et al., 2004; Folberth et al., 2006) with zoom over
1028 South and East Asia (manuscript in preparation). Both of them may serve as valuable tools to
1029 disentangle and quantify contributions of different sources and meteorology to trace gas
1030 signals.

1031

1032 Apart from the flask measurements of trace gases presented in this study for the three stations,
1033 in-situ continuous measurements of CO_2 and CH_4 have also been deployed at HLE, PON and
1034 PBL in parallel, which would considerably contribute to the value of the stations through
1035 high-frequency air sampling. While the three stations have the potential to provide useful
1036 constraints on estimates of trace gas fluxes over South and NE India (for example, Swathi et
1037 al. (2013) reported considerable reduction in the uncertainty of inverted CO_2 fluxes over
1038 temperate Eurasia by the inclusion of measurements at HLE), the monitoring network
1039 requires further expansion to sample air masses from other parts of the Indian subcontinent.
1040 Recently a few other atmospheric ground stations have been established in western India
1041 (Bhattacharya et al., 2009; Tiwari et al., 2011; Tiwari et al., 2014; Tiwari and Kumar, 2012)
1042 and the Himalayas (Kumar et al., 2010; Ganesan et al., 2013), with their concentration
1043 footprints covering Central India (e.g., the Sinhadgad station; Tiwari et al., 2014; Tiwari and
1044 Kumar, 2012), the Indo-Gangetic Plains and a large extent of the Himalayas (e.g., the
1045 Dajeeling station; Ganesan et al., 2013). More efforts are needed to develop a comprehensive
1046 observation network with adequate spatial and temporal coverage in this region.

1047

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1060

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1566

1567 **Table**

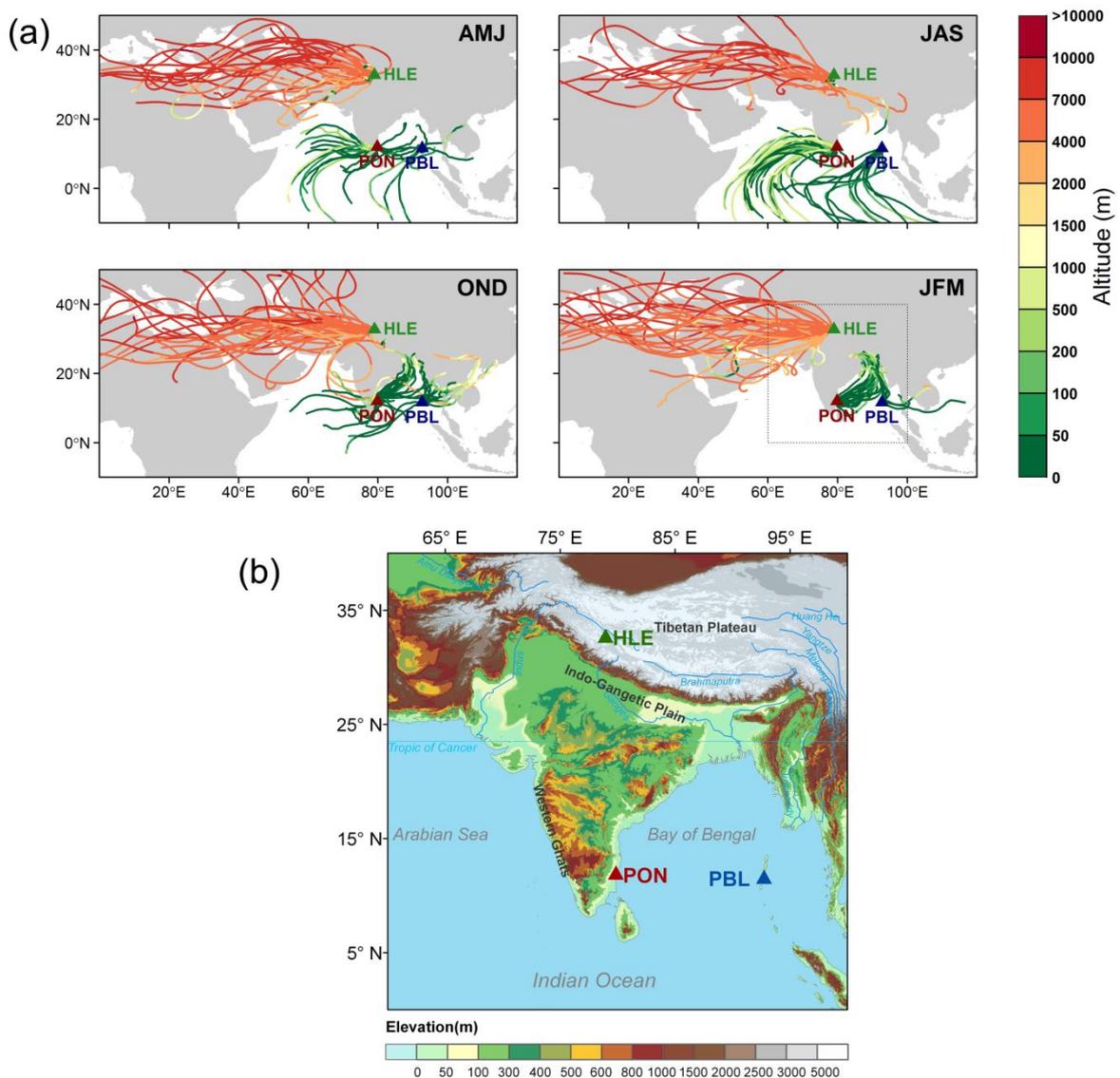
1568 **Table 1** Annual mean values, trend, and average peak-to-peak amplitudes of trace gases at
 1569 HLE, PON, PBL and the two additional NOAA/ESRL stations – KZM and WLG. For each
 1570 species at each station, the annual mean values and average peak-to-peak amplitude are
 1571 calculated from the smoothed curve and mean seasonal cycle, respectively. The residual
 1572 standard deviation (RSD) around the smoothed curve and the Julian days corresponding to
 1573 the maximum (D_{\max}) and minimum (D_{\min}) of the mean seasonal cycle are given as well.
 1574 Uncertainty of each estimate is calculated from 1 s.d. of 1000 bootstrap replicates.

	HLE	PON	PBL	KZM	WLG
CO₂ (ppm)					
Annual mean 2007	382.3±0.3	386.6±0.9	–	382.7±0.2	384.2±0.2
Annual mean 2008	384.6±0.5	388.1±0.9	–	385.7±0.2	386.0±0.2
Annual mean 2009	387.2±0.2	389.0±0.6	–	–	387.4±0.2
Annual mean 2010	389.4±0.1	391.3±1.5	387.6±0.7	–	390.1±0.2
Annual mean 2011	391.4±0.3	–	390.2±0.6	–	392.2±0.2
Trend (yr ⁻¹)	2.1±0.0	1.7±0.1	–	–	2.0±0.0
(Trend at MLO: 2.0±0.0)					
RSD	0.7	4.0	1.5	1.5	1.4
Amplitude	8.2±0.4	7.6±1.4	11.1±1.3	13.8±0.5	11.1±0.4
D_{\max}	122.0±2.9	111.0±13.4	97.0±26.0	75.0±2.6	100.0±1.5
D_{\min}	261.0±3.0	327.0±54.3	242.0±7.7	205.0±2.1	222.0±1.6
CH₄ (ppb)					
Annual mean 2007	1814.8±2.9	1859.2±6.7	–	1842.6±2.4	1841.0±1.8
Annual mean 2008	1833.1±5.4	1856.1±10.4	–	1856.6±2.3	1845.6±1.5
Annual mean 2009	1830.2±1.7	1865.7±5.1	–	–	1851.8±1.9
Annual mean 2010	1830.5±2.1	1876.9±9.1	1867.5±15.4	–	1857.6±1.4
Annual mean 2011	1849.5±5.2	–	1852.0±7.6	–	1859.9±1.2
Trend (yr ⁻¹)	4.9±0.0	9.4±0.1	–	–	5.3±0.0
(Trend at MLO: 6.2±0.0)					
RSD	9.1	34.4	22.4	14.6	12.3
Amplitude	28.9±4.2	124.1±10.2	143.9±12.4	22.7±4.7	17.5±2.2
D_{\max}	219.0±4.6	337.0±6.1	345.0±87.6	236.0±43.2	222.0±6.2
D_{\min}	97.0±58.9	189.0±10.7	193.0±13.5	338.0±39.0	340.0±96.6
N₂O (ppb)					
Annual mean 2007	322.2±0.1	324.8±0.3	–		
Annual mean 2008	322.9±0.1	326.3±0.3	–		
Annual mean 2009	323.5±0.1	326.7±0.3	–		
Annual mean 2010	324.0±0.1	327.1±0.5	329.0±0.5		
Annual mean 2011	325.2±0.1	–	327.9±0.3		

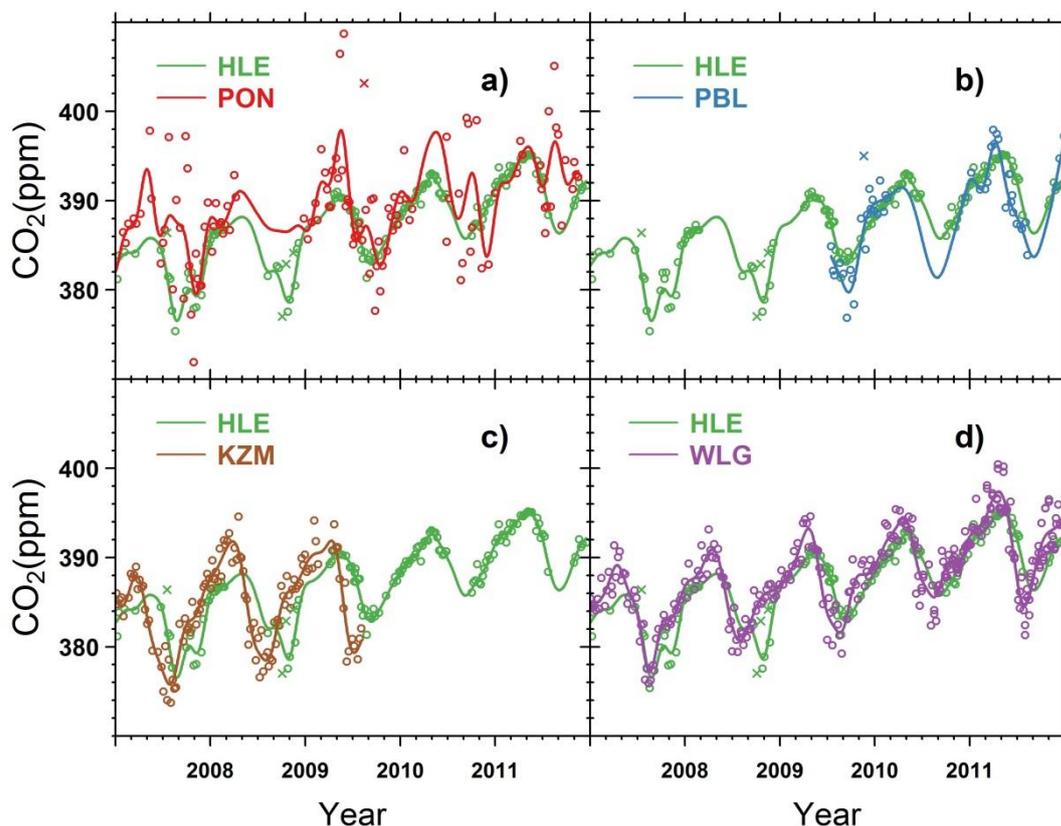
Trend (yr ⁻¹)	0.8±0.0	0.8±0.1	–		
(Trend at MLO: 1.0±0.0)					
RSD	0.3	1.4	1.1		
Amplitude	0.6±0.1	1.2±0.5	2.2±0.6		
D _{max}	227.0±11.8	262.0±83.2	313.0±42.6		
D _{min}	115.0±16.4	141.0±48.2	65.0±33.4		
SF₆ (ppt)					
Annual mean 2007	6.26±0.03	6.19±0.01	–		
Annual mean 2008	6.54±0.03	6.49±0.02	–		
Annual mean 2009	6.79±0.01	6.77±0.01	–		
Annual mean 2010	7.17±0.01	7.08±0.02	7.10±0.07		
Annual mean 2011	7.38±0.01	–	7.45±0.03		
Trend (yr ⁻¹)	0.29±0.05	0.31±0.05	–		
(Trend at MLO: 0.29±0.03)					
RSD	0.07	0.05	0.12		
Amplitude	0.15±0.03	0.24±0.02	0.48±0.07		
D _{max}	320.0±8.3	327.0±12.1	342.0±59.9		
D _{min}	211.0±65.1	204.0±3.3	210.0±18.1		
CO (ppb)					
Annual mean 2007	104.7±1.4	200.5±7.8	–	121.7±1.7	141.0±4.3
Annual mean 2008	103.1±2.1	175.3±13.1	–	123.7±1.7	129.0±2.9
Annual mean 2009	98.9±1.9	174.3±4.8	–	–	131.9±3.7
Annual mean 2010	99.0±1.2	185.1±8.7	157.6±20.4	–	130.2±3.9
Annual mean 2011	99.4±2.2	–	145.9±9.9	–	124.0±2.3
Trend (yr ⁻¹)	-2.2±0.0	0.4±0.1	–	–	-1.9±0.0
(Trend at MLO: -1.6±0.0)					
RSD	6.5	32.0	30.8	11.8	22.5
Amplitude	28.4±2.3	78.2±11.6	144.1±16.0	37.1±4.4	38.6±5.1
D _{max}	79.0±11.4	4.0±160.2	12.0±117.9	72.0±5.0	94.0±38.2
D _{min}	297.0±5.3	238.0±46.1	213.0±23.0	318.0±6.1	331.0±6.2
H₂ (ppb)					
Annual mean 2007	539.6±2.1	574.5±2.4	–	502.4±2.0	500.9±1.5
Annual mean 2008	533.2±3.2	558.2±5.3	–	–	–
Annual mean 2009	533.3±1.6	562.4±1.6	–	–	–
Annual mean 2010	533.5±1.8	563.9±2.3	558.6±2.4	–	–
Annual mean 2011	536.9±1.5	–	555.4±1.6	–	–
Trend (yr ⁻¹)	-0.5±0.0	-1.3±0.1	–	–	–
RSD	6.6	8.4	7.0	13.3	9.5
Amplitude	15.8±2.2	21.6±3.4	21.3±5.0	16.7±4.0	22.8±3.0
D _{max}	120.0±8.7	96.0±9.6	99.0±8.8	120.0±34.2	51.0±13.4
D _{min}	266.0±39.6	219.0±10.3	353.0±87.8	341.0±78.3	298.0±6.5

1576 **Figures**

1577 **Figure 1 (a)** Five-day back-trajectories calculated for all sampling dates over the period
 1578 2007–2011 at Hanle (HLE), Pondicherry (PON), and Port Blair (PBL) during April–June
 1579 (AMJ), July–September (JAS), October–December (OND) and January–March (JFM),
 1580 respectively. Back-trajectories are colored by the elevation of air masses at hourly time step.
 1581 **(b)** Map of terrain over the zoomed box in **(a)**, showing locations of HLE, PON and PBL.
 1582 The digital elevation data are obtained from NASA Shuttle Radar Topographic Mission
 1583 (SRTM) product at 1km resolution (<http://srtm.csi.cgiar.org>)

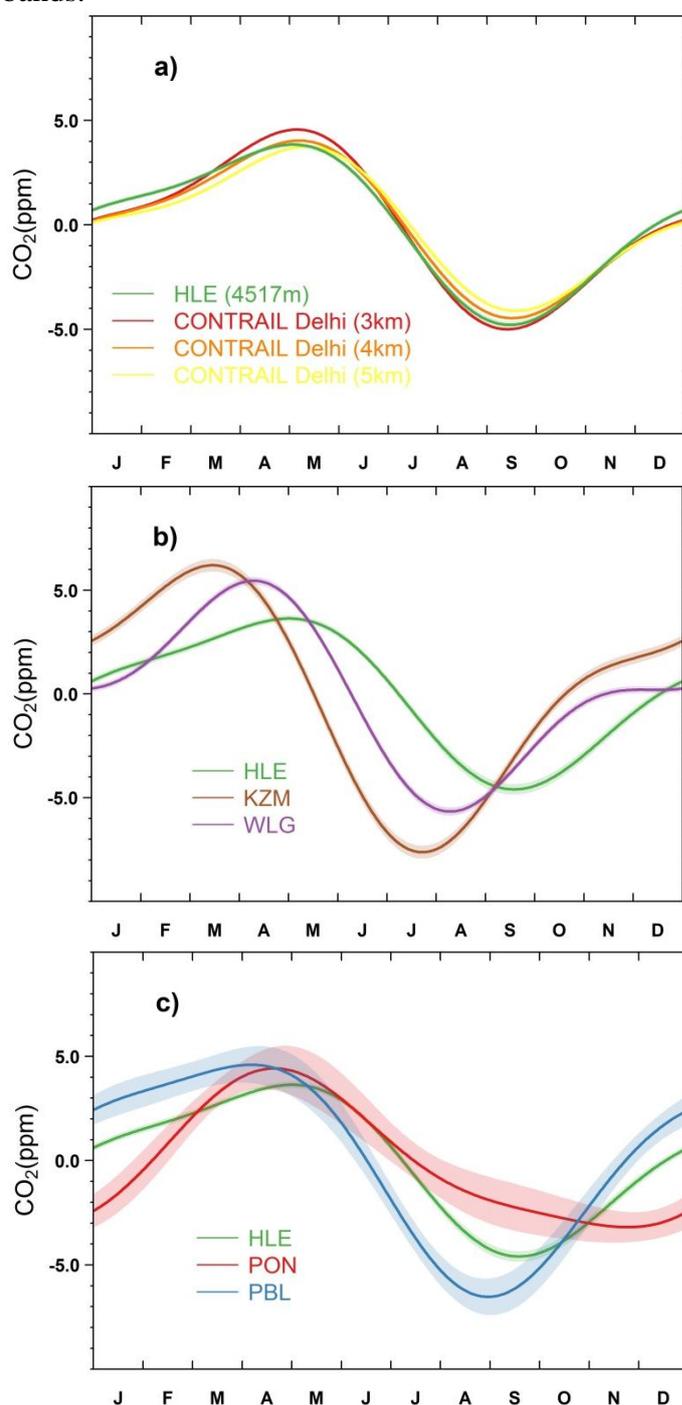


1585 **Figure 2** Time series of CO₂ flask measurements at **(a)** HLE and PON, **(b)** HLE and PBL, **(c)**
1586 HLE and KZM, and **(d)** HLE and WLG. The open circles denote flask data used to fit the
1587 smoothed curves, while the crosses denote discarded flask data lying outside 3 times the
1588 residual standard deviations from the smoothed curve fits. For each station, the smoothed
1589 curve is fitted using Thoning's method (Thoning et al., 1989) after removing outliers.

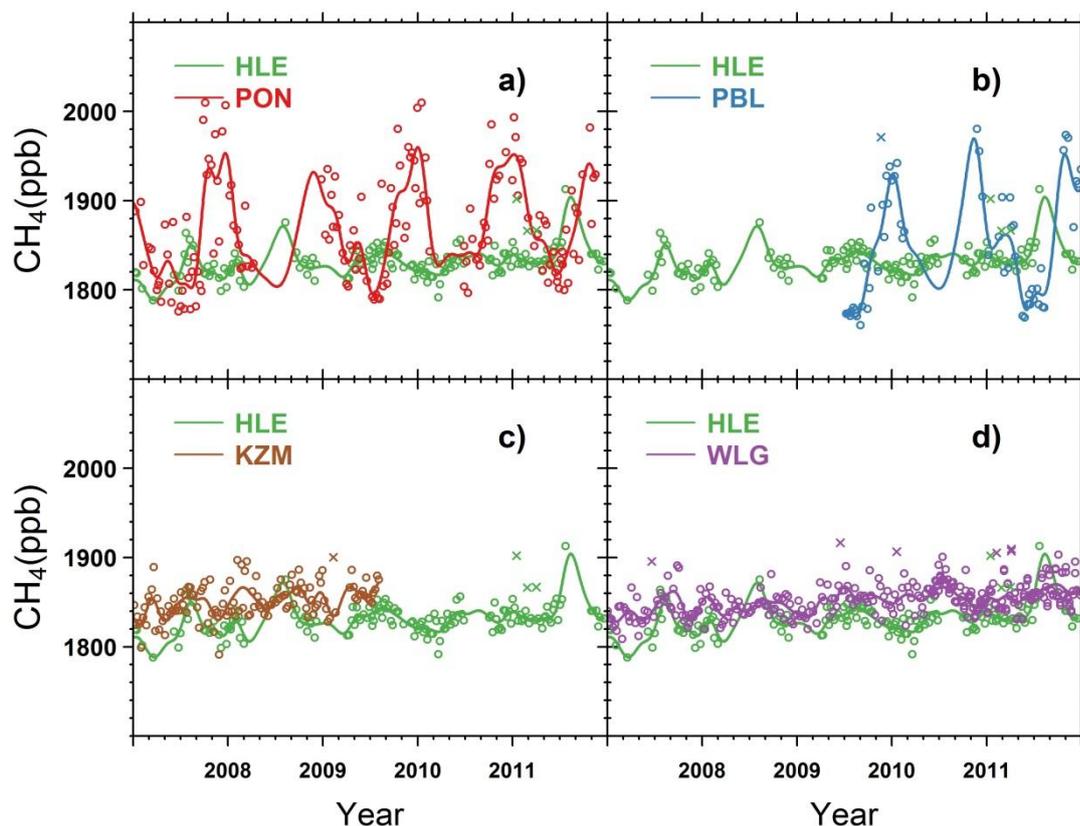


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1591 **Figure 3 (a)** The mean CO₂ seasonal cycle at HLE, in comparison with the mean seasonal
1592 cycles derived from the in-situ CO₂ measurements over New Delhi at different altitude bands
1593 (3–4 km, 4–5 km, and 5–6 km) by the CONTRAIL project (2006–2010). **(b)** The mean CO₂
1594 seasonal cycles at HLE, KZM and WLG. **(c)** The mean CO₂ seasonal cycles at HLE, PON
1595 and PBL. For each station, the mean seasonal cycle is derived from the harmonics of the
1596 smoothed fitting curve in Fig. 2. Shaded area indicates the uncertainty of the mean seasonal
1597 cycle calculated from 1 s.d. of 1000 bootstrap replicates. For the CONTRAIL datasets, CO₂
1598 measurements over New Delhi were first averaged by altitude bands. A fitting procedure was
1599 then applied to the aggregated CO₂ measurements to generate the mean season cycle for
1600 different altitude bands.



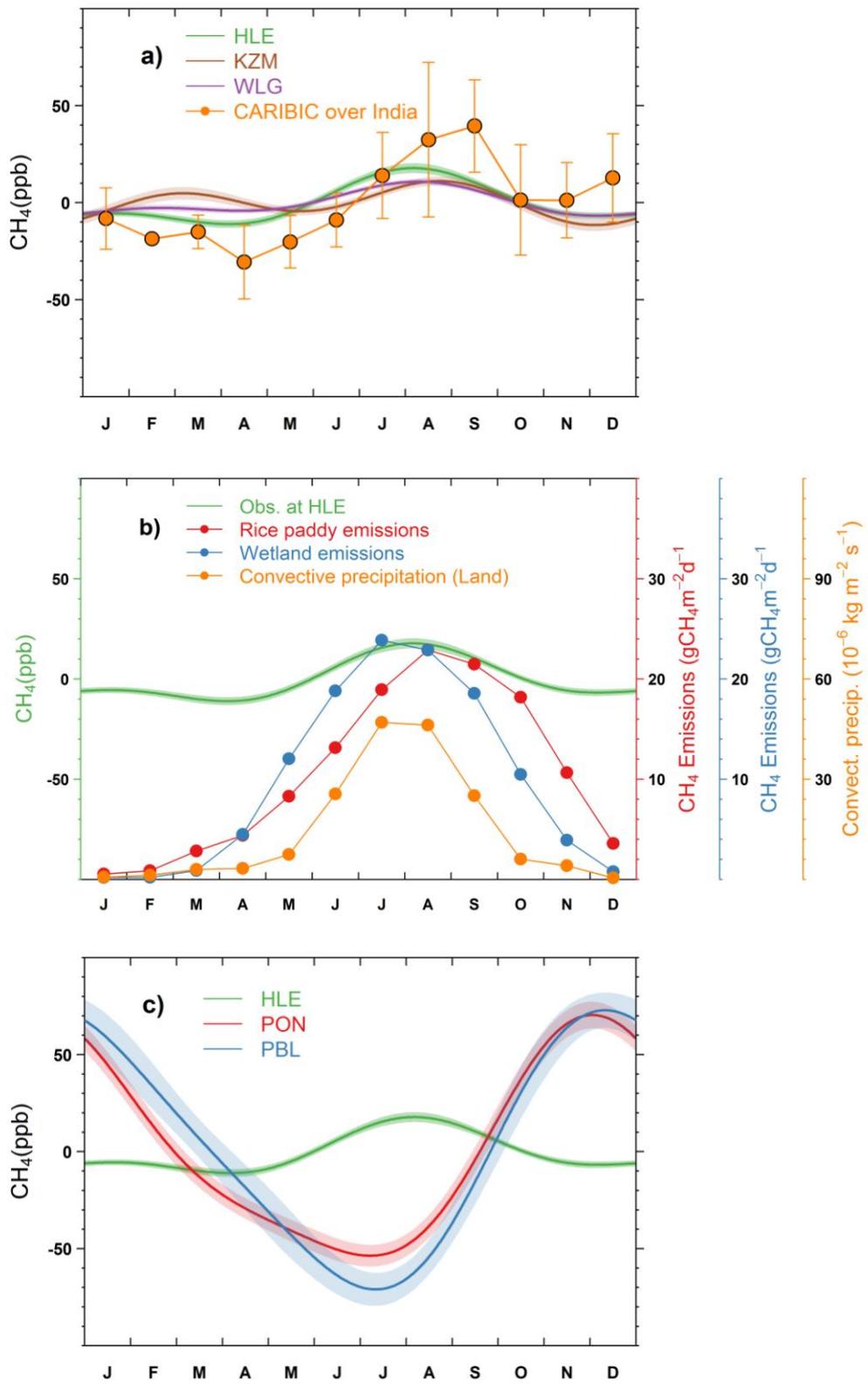
1601 **Figure 4** Time series of CH₄ flask measurements at (a) HLE and PON, (b) HLE and PBL, (c)
1602 HLE and KZM, and (d) HLE and WLG. The open circles denote flask data used to fit the
1603 smoothed curves, while the crosses denote discarded flask data lying outside 3 times the
1604 residual standard deviations from the smoothed curve fits. For each station, the smoothed
1605 curve is fitted using Thoning's method (Thoning et al., 1989) after removing outliers.



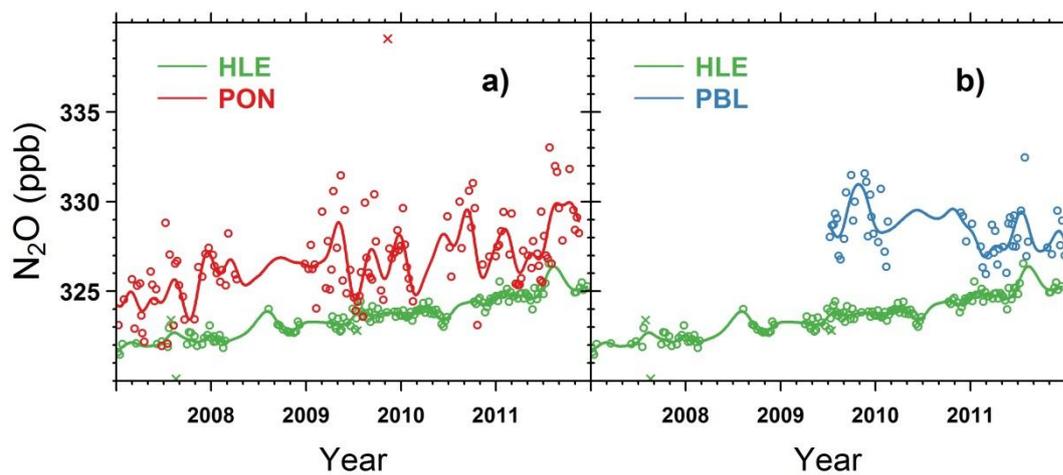
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1608 **Figure 5 (a)** The mean CH₄ seasonal cycles observed at HLE, KZM and WLG. The mean
1609 CH₄ seasonal cycle derived from aircraft flask measurements by the CARIBIC project is also
1610 presented. The CARIBIC flask measurements in the upper troposphere (200-300 hPa) during
1611 2005–2012 are averaged over the Indian subcontinent (10°N-35°N, 60°E-100°E) by month to
1612 generate the mean seasonal cycle. The error bars indicate 1 standard deviation of CH₄ flask
1613 measurements within the month. **(b)** The seasonal variations of CH₄ emissions from rice
1614 paddies and wetlands over the Indian subcontinent. The CH₄ emissions from rice paddies are
1615 extracted from a global emission map for the year 2010 (EDGAR v4.2), imposed by the
1616 seasonal variation on the basis of Matthews et al. (1991). The CH₄ emissions from wetlands
1617 are extracted from outputs of a global vegetation model (BIOME4-TG, Kaplan et al., 2006).
1618 The seasonal variation of deep convection over the Indian subcontinent is also presented,
1619 indicated by convective precipitation obtained from an LMDz simulation nudged with
1620 ECMWF reanalysis (Hauglustaine et al., 2004). The CH₄ emissions and convective
1621 precipitation are averaged over the domain 10–35 °N, 70°–90°E to give a regional mean
1622 estimate. **(c)** The mean CH₄ seasonal cycles observed at HLE, PON and PBL. For each
1623 station, the mean seasonal cycle is derived from the harmonics of the smoothed fitting curve
1624 in Fig. 4. Shaded area indicates the uncertainty of the mean seasonal cycle calculated from 1
1625 s.d. of 1000 bootstrap replicates.

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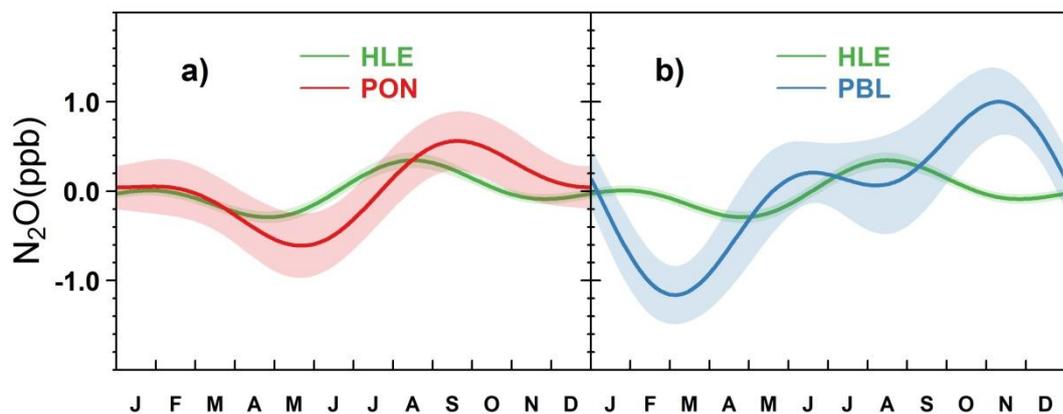


1628 **Figure 6** Time series of N₂O flask measurements at (a) HLE and PON, (b) HLE and PBL.
1629 The open circles denote flask data used to fit the smoothed curves, while crosses denote
1630 discarded flask data lying outside 3 times the residual standard deviations from the smoothed
1631 curve fits. For each station, the smoothed curve is fitted using Thoning's method (Thoning et
1632 al., 1989) after removing outliers.



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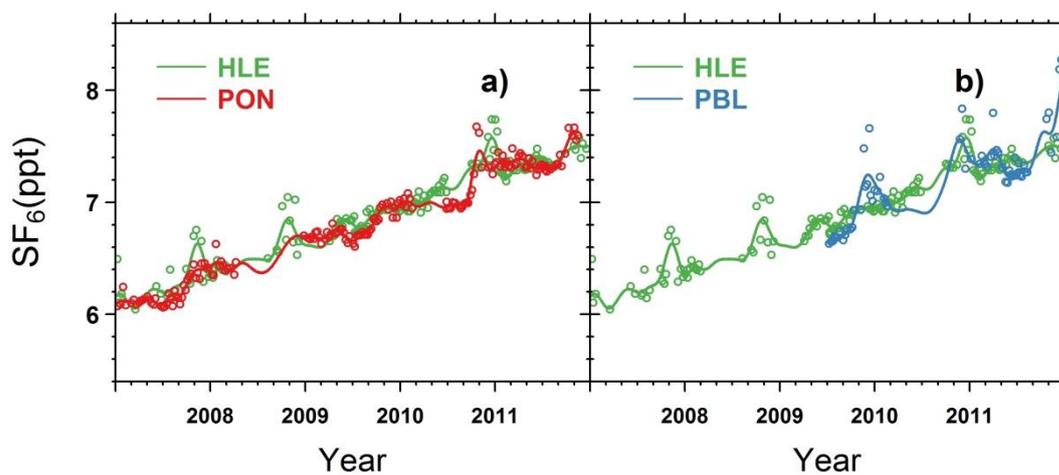
1635 **Figure 7** The mean N₂O seasonal cycles observed at **(a)** HLE and PON, **(b)** HLE and PBL.
1636 For each station, the mean seasonal cycle is derived from the harmonics of the smoothed
1637 fitting curve in Fig. 6. Shaded area indicates the uncertainty of the mean seasonal cycle
1638 calculated from 1 s.d. of 1000 bootstrap replicates.



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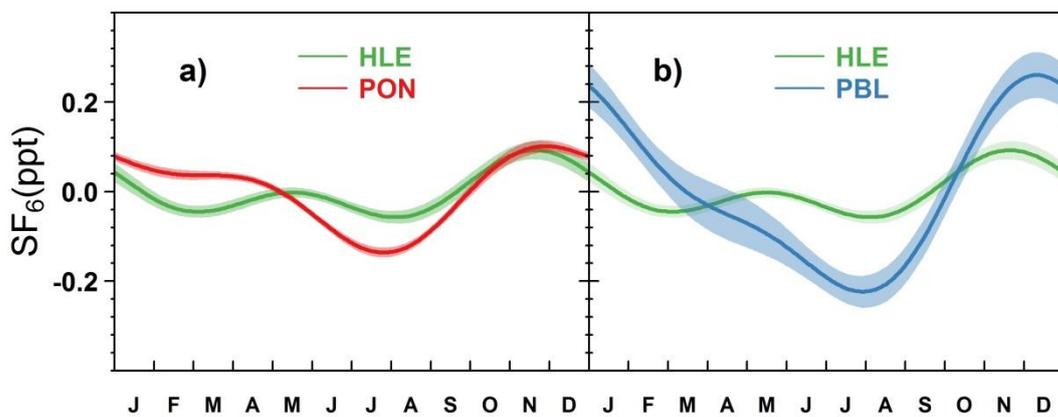
1641 **Figure 8** Time series of SF₆ flask measurements at (a) HLE and PON, (b) HLE and PBL, (c)
1642 HLE and KZM, and (d) HLE and WLG. The open circles denote flask data used to fit the
1643 smoothed curves. For each station, the smoothed curve is fitted using Thoning's method
1644 (Thoning et al., 1989) after removing outliers.



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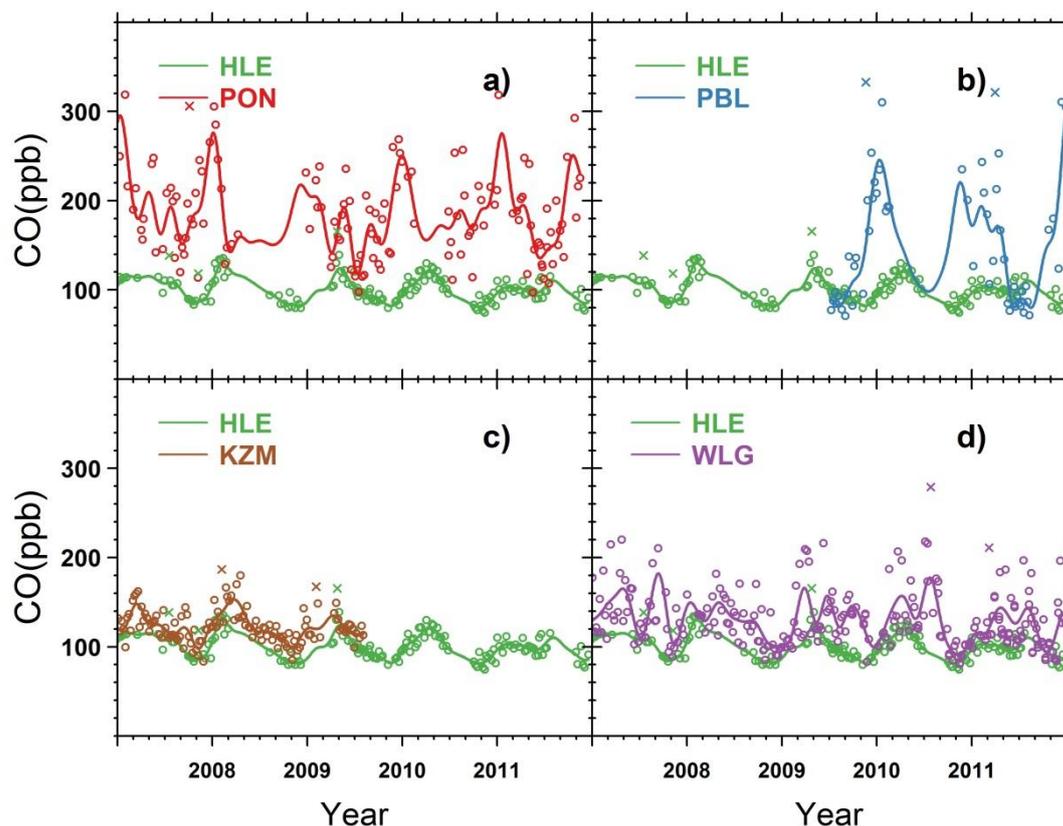
1647 **Figure 9** The mean SF₆ seasonal cycles observed at (a) HLE and PON, (b) HLE and PBL.
1648 For each station, the mean seasonal cycle is derived from the harmonics of the smoothed
1649 fitting curve in Fig. 8. Shaded area indicates the uncertainty of the mean seasonal cycle
1650 calculated from 1 s.d. of 1000 bootstrap replicates.



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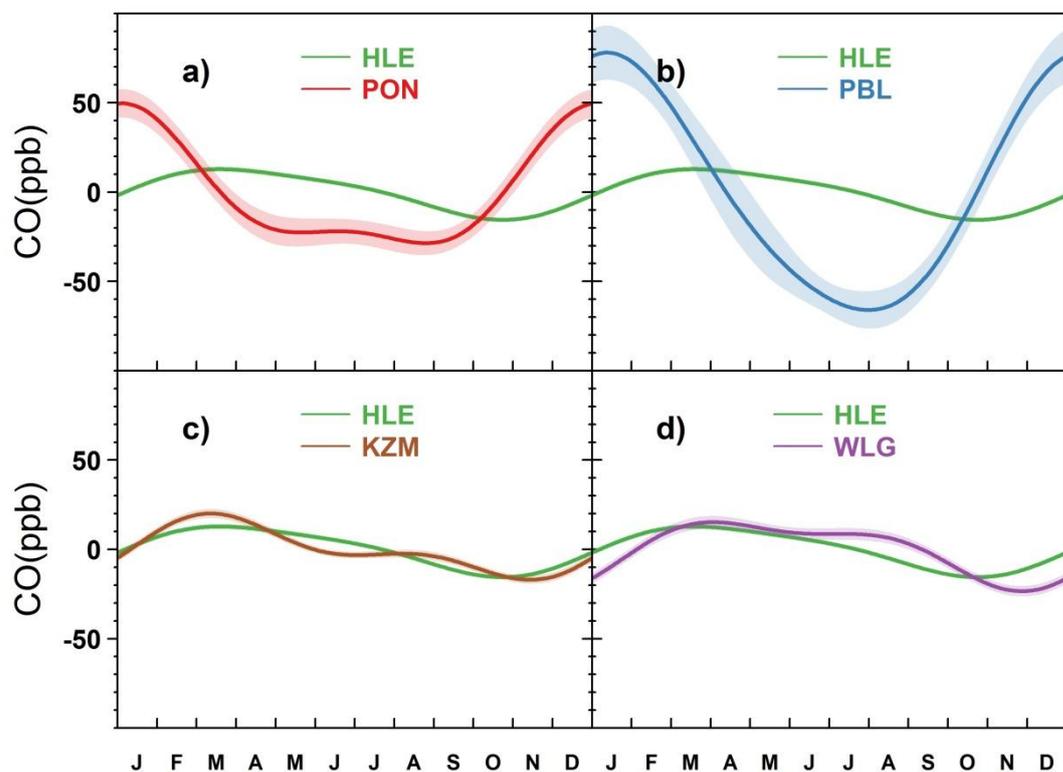
1653 **Figure 10** Time series of CO flask measurements at (a) HLE and PON, (b) HLE and PBL, (c)
1654 HLE and KZM, and (d) HLE and WLG. The open circles denote flask data used to fit the
1655 smoothed curves, while the crosses denote discarded flask data lying outside 3 times the
1656 residual standard deviations from the smoothed curve fits. For each station, the smoothed
1657 curve is fitted using Thoning's method (Thoning et al., 1989) after removing outliers.



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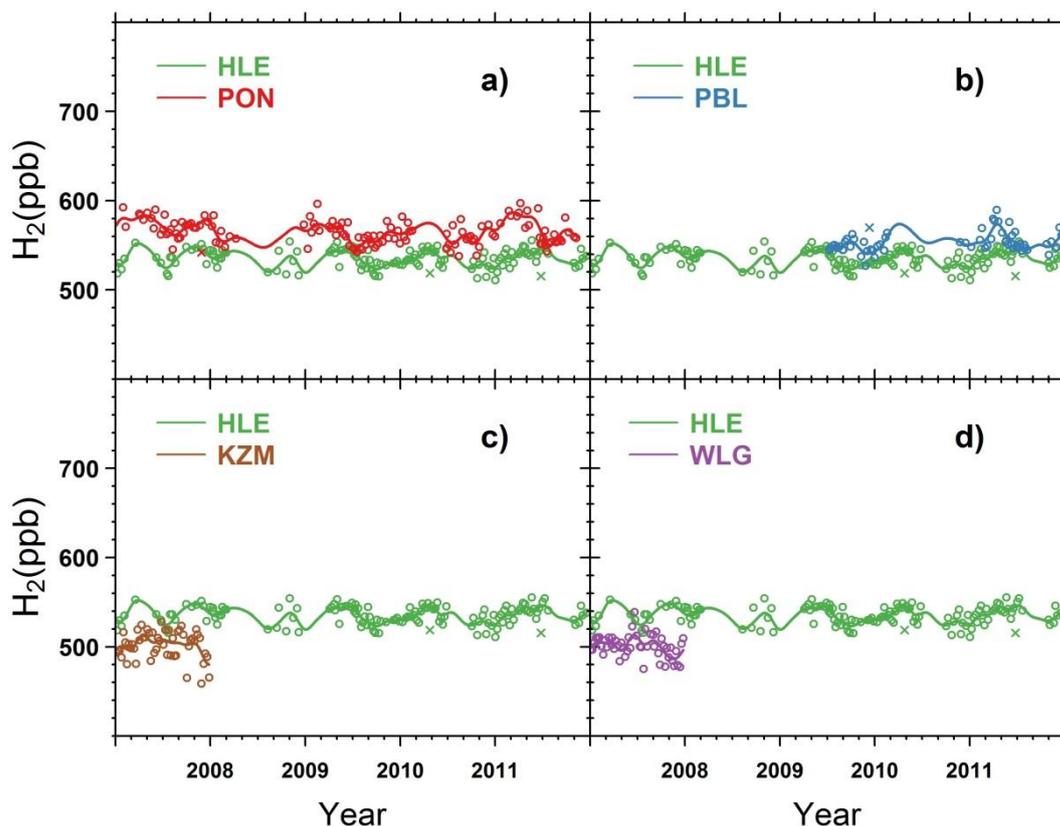
1660 **Figure 11** The mean CO seasonal cycles observed at (a) HLE and PON, (b) HLE and PBL,
1661 (c) HLE and KZM, and (d) HLE and WLG. For each station, the mean seasonal cycle is
1662 derived from the harmonics of the smoothed fitting curve in Fig. 10. Shaded area indicates
1663 the uncertainty of the mean seasonal cycle calculated from 1 s.d. of 1000 bootstrap replicates.



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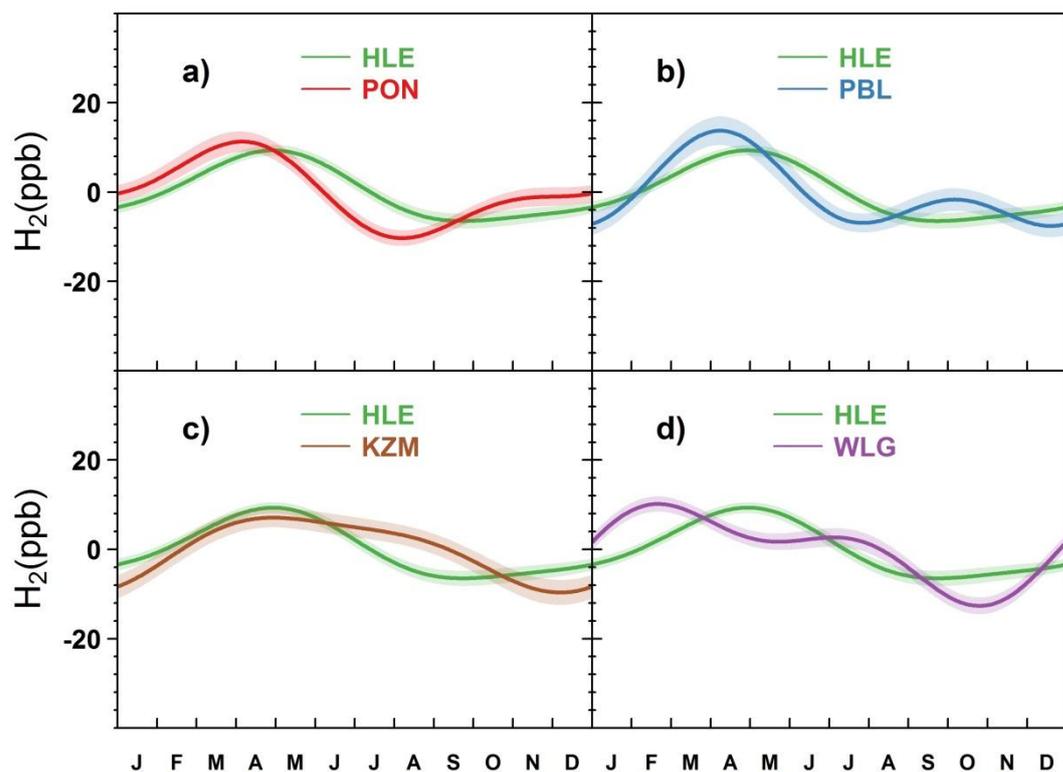
1666 **Figure 12** Time series of H₂ flask measurements at (a) HLE and PON, (b) HLE and PBL, (c)
1667 HLE and KZM, and (d) HLE and WLG. The open circles denote flask data used to fit the
1668 smoothed curves, while the crosses denote discarded flask data lying outside 3 times the
1669 residual standard deviations from the smoothed curve fits. For each station, the smoothed
1670 curve is fitted using Thoning's method (Thoning et al., 1989) after removing outliers.



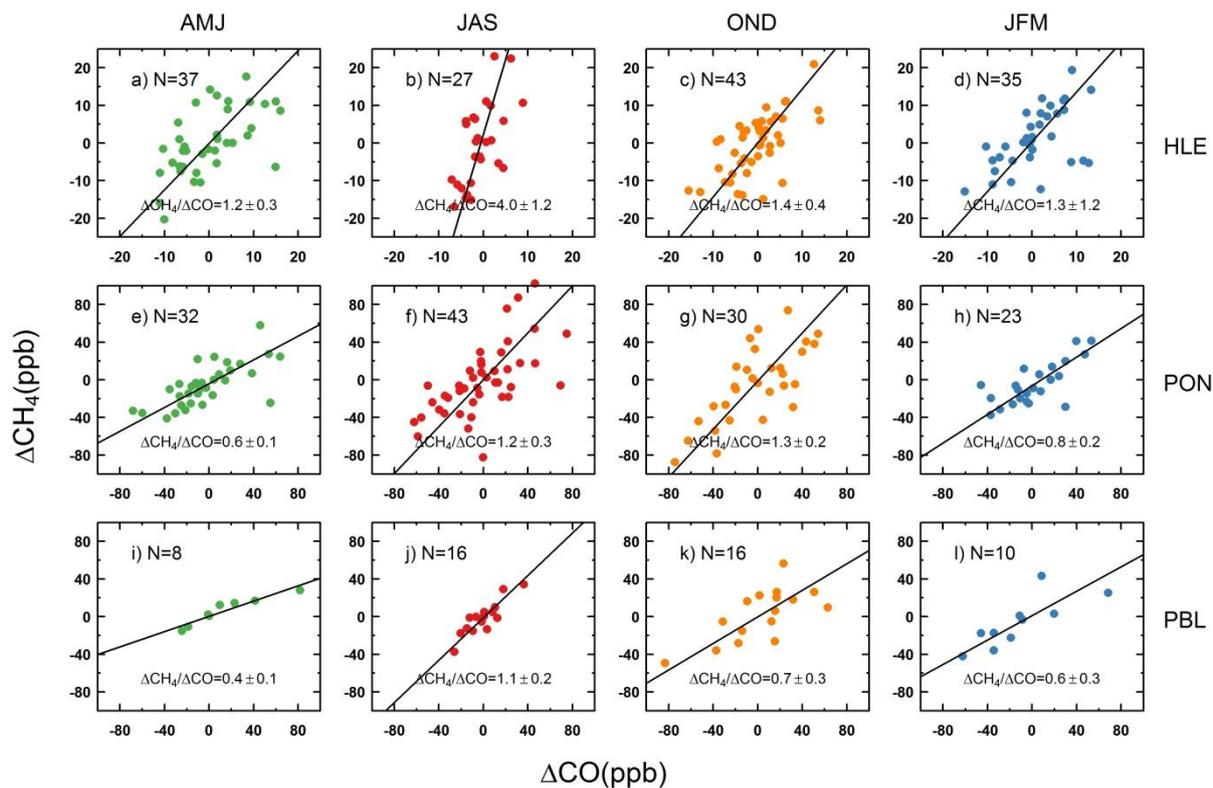
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1673 **Figure 13** The mean H_2 seasonal cycles observed at (a) HLE and PON, (b) HLE and PBL, (c)
1674 HLE and KZM, and (d) HLE and WLG. For each station, the mean seasonal cycle is derived
1675 from the harmonics of the smoothed fitting curve in Fig. 12. Shaded area indicates the
1676 uncertainty of the mean seasonal cycle calculated from 1 s.d. of 1000 bootstrap replicates.



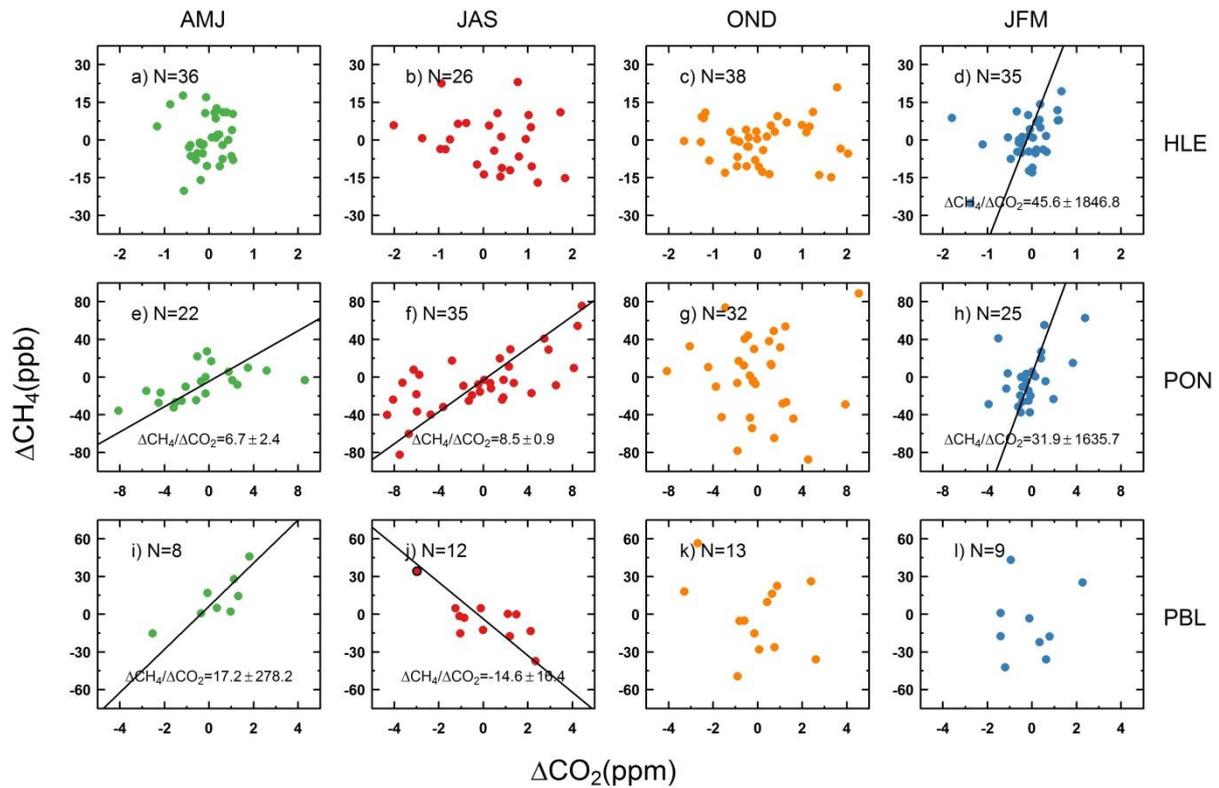
1678 **Figure 14** The relationships between ΔCH_4 and ΔCO at HLE (a–d), PON (e–h), and PBL (i–
 1679 l) for April–June (AMJ), July–September (JAS), October–December (OND), and January–
 1680 March (JFM). For each panel, ΔCH_4 and ΔCO are estimated as residuals from smoothed
 1681 curves. The $\Delta\text{CH}_4/\Delta\text{CO}$ ratio is the slope of the fitting line from the orthogonal distance
 1682 regression, with the SD calculated from 1000 bootstrap replications.



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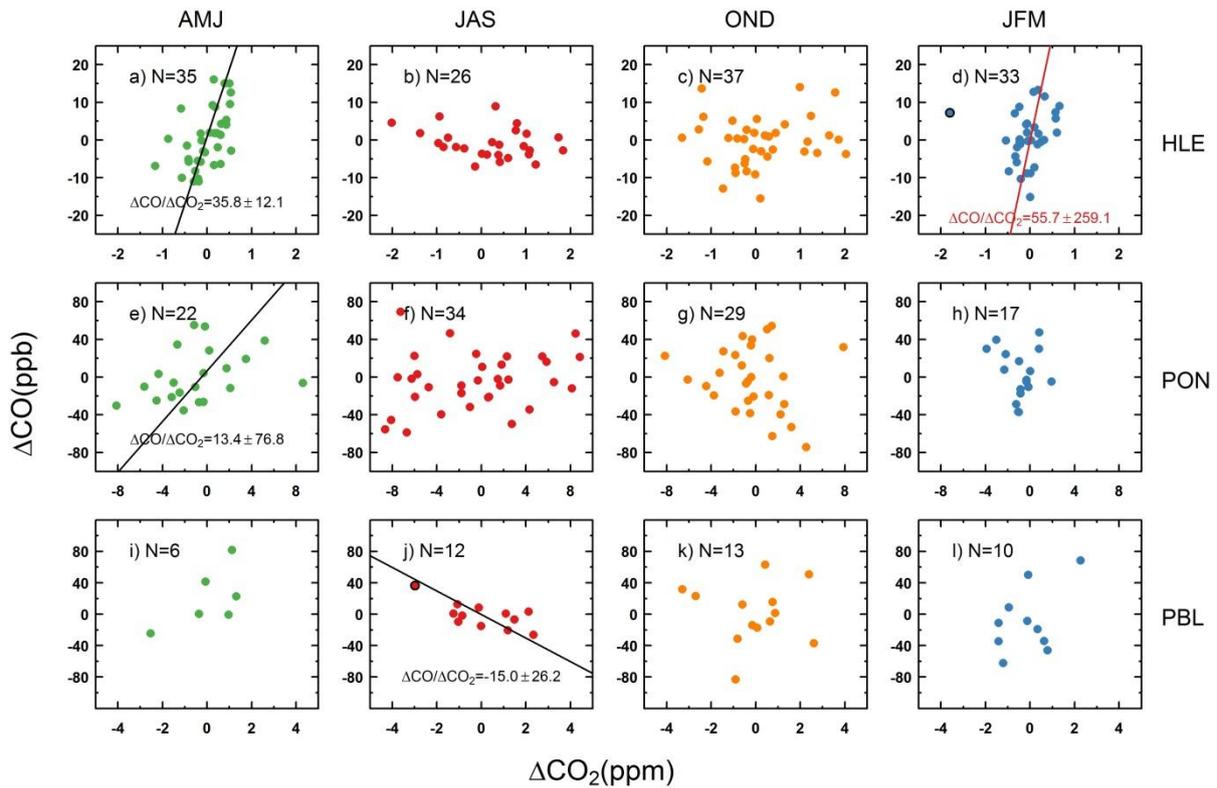
1685 **Figure 15** The relationships between ΔCH_4 and ΔCO_2 at HLE (a–d), PON (e–h), and PBL (i–l) for April–June (AMJ), July–September (JAS), October–December (OND), and January–
 1686 (i–l) for April–June (AMJ), July–September (JAS), October–December (OND), and January–
 1687 March (JFM). For each panel, ΔCH_4 and ΔCO_2 are estimated as residuals from smoothed
 1688 curves. The $\Delta\text{CH}_4/\Delta\text{CO}_2$ ratio is the slope of the fitting line from the orthogonal distance
 1689 regression, with the SD calculated from 1000 bootstrap replications. For ΔCH_4 and ΔCO_2 that
 1690 is not significantly correlated, the fitting line is not plotted.



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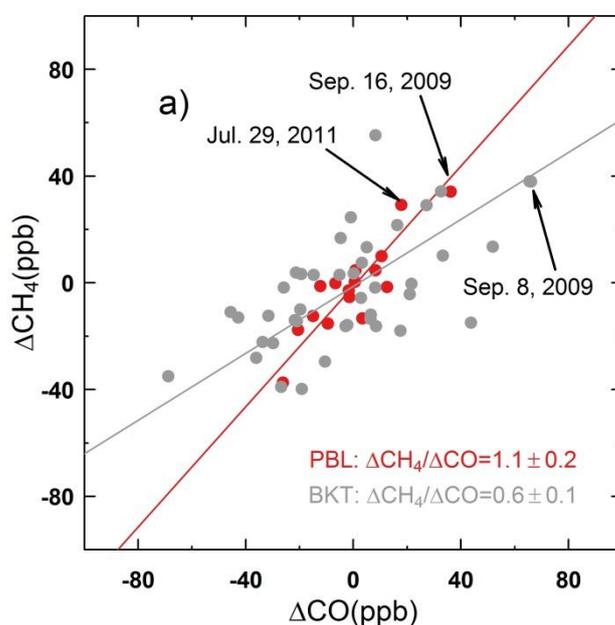
1693 **Figure 16** The relationships between ΔCO and ΔCO_2 at HLE (a–d), PON (e–h), and PBL (i–
 1694 l) for April–June (AMJ), July–September (JAS), October–December (OND), and January–
 1695 March (JFM). For each panel, ΔCO and ΔCO_2 are estimated as residuals from smoothed
 1696 curves. The $\Delta\text{CO}/\Delta\text{CO}_2$ ratio is the slope of the fitting line from the orthogonal distance
 1697 regression, with the SD calculated from 1000 bootstrap replications. For ΔCO and ΔCO_2 that
 1698 is not significantly correlated, the fitting line is usually not plotted.



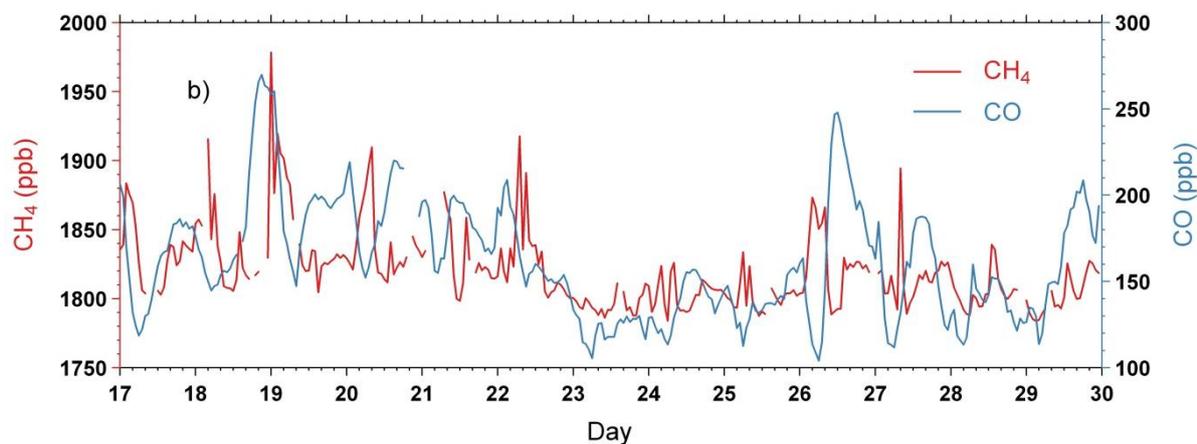
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1701 **Figure 17 (a)** The relationship between ΔCH_4 and ΔCO at PBL (colored by red) and BKT
 1702 (colored by grey) during July–September (JAS) over the period of 2007–2011. ΔCH_4 and
 1703 ΔCO are estimated as residuals from smoothed curves. The $\Delta\text{CH}_4/\Delta\text{CO}$ ratio is the slope of
 1704 the fitting line from orthogonal distance regression (ODR), with the SD calculated from 1000
 1705 bootstrap replications. Two abnormal events at PBL are labeled, with enhancements of CH_4
 1706 and CO on September 16, 2009 and July 29, 2011, respectively. Enhancements of CH_4 and
 1707 CO are also observed at BKT on Sep. 8, 2009. Enhancements of CH_4 and CO are observed during July 17–
 1708 21, 2011. (b) Hourly CH_4 and CO measurements at BKT in July, 2011 (BMKG & EMPA). Enhancements of CH_4 and CO
 1709 are observed during July 17–21, 2011.



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