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 (CO$_2$, CH$_4$, N$_2$O, SF$_6$) and two additional trace gases (CO, H$_2$) 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 (CO$_2$, CH$_4$, N$_2$O and SF$_6$) and two additional trace gases (CO and H$_2$).”.

Page 6, Lines 130–143: add the following sentences before “Gradients between different stations”: “Among these trace gases, CO$_2$, CH$_4$ and N$_2$O 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 (SF$_6$) 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 H$_2$ are not GHGs by themselves, both of them play critical roles in the CH$_4$ budgets through reaction with the free OH radicals (Ehhalt and Rohrer, 2009). Besides, CO and H$_2$ 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 CH\textsubscript{4}, the N\textsubscript{2}O enhancement at HLE during the summer monsoon period (June-September) is consistent with” to “Like CH\textsubscript{4}, the N\textsubscript{2}O 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 SF\textsubscript{6} 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 SF\textsubscript{6} 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 CH\textsubscript{4} and N\textsubscript{2}O (Schuck et al., 2010, Fig. S8)” to “Although the CARIBIC aircraft flask measurements over the Indian region demonstrated SF\textsubscript{6} 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 CH\textsubscript{4} and N\textsubscript{2}O. Back-trajectories from the CARIBIC
flights showed that the summer enhancements in SF$_6$ 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 SF$_6$ 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 SF$_6$ 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 SF$_6$ emissions are rather weak.”.

Changes to the references

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

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Abstract

With a rapid growth in population and economic development, emissions of greenhouse gases (GHGs) from the Indian subcontinent have sharply increased during recent decades. However, evaluation of regional fluxes of GHGs and characterization of their spatial and temporal variations by atmospheric inversions remain uncertain due to a sparse regional atmospheric observation network. As a result of an Indo-French collaboration, three new atmospheric stations were established in India at Hanle (HLE), Pondicherry (PON) and Port Blair (PBL), with the objective of monitoring the atmospheric concentrations of GHGs and other trace gases. Here we present the results of the measurements of CO$_2$, CH$_4$, N$_2$O, SF$_6$, CO, and H$_2$ from regular flask sampling at these three stations over the period 2007–2011. For each species, annual means, seasonal cycles and gradients between stations were calculated and related to variations in the natural GHG fluxes, anthropogenic emissions, and the monsoon circulations. Covariances between species at the synoptic scale were analyzed to investigate the likely source(s) of emissions. The flask measurements of various trace gases at the three stations show potential to constrain the inversions of fluxes over Southern and Northeastern India. However, this network of ground stations needs further extension to other parts of India to better constrain the GHG budgets at regional and continental scales.
1 Introduction

Since the pre-industrial times, anthropogenic greenhouse gas (GHG) emissions have progressively increased the radiative forcing of the atmosphere, leading to impacts on the climate system and human society (IPCC, 2013, 2014a, b). With rapid socio-economic development and urbanization during recent decades, a large and growing share of GHG emissions is contributed by emerging economies like China and India. In 2010, India became the world’s third largest GHG emitter, next to China and the USA (EDGAR v4.2; Le Quéré et al., 2014). Between 1991 and 2010, anthropogenic GHG emissions in India increased by ~100% from 1.4 to 2.8 GtCO$_2$eq, much faster than rates of most developed countries and economies like the USA (9%) and EU (-14%) over the same period (EDGAR v4.2). Without a systematic effort at mitigation, this trend would continue in the coming decades, given that the per capita emission rate in India is still much below that of the more developed countries. For comparison, in 2010, the per capita GHG emission rates were 2.2, 10.9, 17.6, and 21.6 tonCO$_2$eq/capita for India, the UK, Russia, and the USA, respectively (EDGAR v4.2). In particular, non-CO$_2$ GHG emissions are substantial in India, most of which are contributed by agricultural activities over populous rural areas (Pathak et al., 2010). In 2010, anthropogenic CH$_4$ and N$_2$O emissions in India amounted to 29.6 TgCH$_4$ (~0.62 GtCO$_2$eq) and 0.8 TgN$_2$O (~0.23 GtCO$_2$eq), together accounting for 32% of the country’s GHG emissions, of which contributions of the agricultural sector were 60 and 73%, respectively (EDGAR v4.2). Reducing emissions of these two non-CO$_2$ GHGs may offer a more cost-effective way to mitigate future climate change than by attempting to directly reduce CO$_2$ emissions (Montzka et al., 2011).

Effective climate mitigation strategies need accurate reporting of sources and sinks of GHGs. This is also a requirement of the United Nations Framework Convention on Climate Change.
UNFCCC). Current estimates of GHG budgets in India, either from the top-down approaches (based on atmospheric inversions) or bottom-up approaches (based on emission inventories or biospheric models), have larger uncertainties than for other continents. For instance, Patra et al. (2013) reported a net biospheric CO$_2$ sink of -104±150 TgCyr$^{-1}$ over South Asia during 2007–2008 based on global inversions from 10 TransCom-CO$_2$ models (Peylin et al., 2013) and a regional inversion (Patra et al., 2011b), while the bottom-up approach gave an estimate of -191±193 TgCyr$^{-1}$ over the period of 2000–2009 (Patra et al., 2013). Notably, these estimates have uncertainties as high as 100–150%, much larger compared to those of Europe (~30%, see Luyssaert et al., 2012) and North America (~60%, see King et al., 2015), where observational networks are denser and emission inventories are more accurate. Evaluation of N$_2$O emissions from 5 TransCom-N$_2$O inversions also exhibited the largest differences over South Asia (Thompson et al., 2014b). A main source of uncertainty is the lack of atmospheric observation datasets with sufficient temporal and spatial coverage (Patra et al., 2013; Thompson et al., 2014b). Networks of atmospheric stations that were used to constrain estimates of global GHG fluxes show gaps over South Asia (Patra et al., 2011a; Thompson et al., 2014b, c; Peylin et al., 2013), with Cape Rama (CRI – 15.08°N, 73.83°E, 60m a.s.l.) on the southwest coast of India being the only Indian station (Rayner et al., 2008; Patra et al., 2009; Tiwari et al., 2011; Bhattacharya et al., 2009; Saikawa et al., 2014). Recently a few other ground stations have been established in Western India and the Himalayas to monitor GHGs and atmospheric pollutants, which are located in Sinhagad (SNG – 18.35°N, 73.75°E, 1600m a.s.l.; Tiwari and Kumar, 2012; Tiwari et al., 2014), Mount Abu (24.60°N, 72.70°E, 1700m a.s.l.; S. Lal, personal communication), Ahmedabad (23.00°N, 72.50°E, 55m a.s.l.; Lal et al., 2015), Nainital (29.37°N, 79.45°E, 1958m a.s.l.; Kumar et al., 2010) and Darjeeling (27.03°N, 88.15°E, 2194m a.s.l.; Ganesan et al., 2013). Most of these stations started to measure atmospheric GHG concentrations very
recently (e.g. Sinhagad – since 2009; Ahmedabad – since 2013; Mount Abu – since 2013; Nainital – since 2006; Darjeeling – since 2011), and datasets are not always available. In addition, aircraft and satellite observations have also been carried out and provided useful constraints on estimates of GHG fluxes in this region (Park et al., 2007; Xiong et al., 2009; Schuck et al., 2010; Patra et al., 2011b; Niwa et al., 2012; Zhang et al., 2014). Although inclusion of measurements from South Asia significantly reduces uncertainties in top-down estimates of regional GHG emissions (e.g., Huang et al., 2008; Niwa et al., 2012; Zhang et al., 2014), a denser atmospheric observational network with sustained measurements is still needed over this vast and fast-growing region for an improved, more detailed, and necessary understanding of GHG budgets.

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

Since the 2000s, three new atmospheric ground stations have been established in India as part of the Indo-French collaboration, with the objective of monitoring the atmospheric concentrations of major GHGs and other trace gases in flask air samples. Of the three Indian stations, Hanle (HLE) is a high-altitude station situated in the western Indian Himalayas, while Pondicherry (PON) and Port Blair (PBL) are tropical surface stations located respectively on the southeastern coast of South India and on an oceanic island in the southeastern Bay of Bengal. In this study, we briefly describe the main features of these stations and present time series of flask air sample measurements of multiple trace gases at HLE, PON, and PBL over the period 2007–2011. Descriptions of the three stations as well as methods used to analyze and calibrate the flask measurements are given in Sect. 2. 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). 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. Gradients between different stations are interpreted in the context of regional flux patterns and monsoon circulations (Sect. 3.1). We examine synoptic variations of CO$_2$, CH$_4$ and CO by analyzing the co-variances between species, using deviations from their smoothed fitting curves (Sect. 3.2). Finally, we investigate two abnormal CH$_4$ and CO events at PBL and propose likely sources and origins (Sect. 3.3). A summary of the paper as well as conclusions drawn from these results are given in Sect. 4.

2 Sampling stations and methods

2.1 Sampling stations

Figure 1 and S1 in the supplement show the locations of HLE, PON, and PBL. We also present five-day back-trajectories from each station for all sampling dates in April–June (AMJ; Fig. 1a), July–September (JAS; Fig. 1b), October–December (OND; Fig. 1c) and January–March (JFM; Fig. 1d), respectively. Note that this four-period classification scheme is slightly different from the climatological seasons defined by the India Meteorological Department (IMD; Attri and Tyagi, 2010), in which months of a year are categorized into the pre-monsoon season (March–May), SW monsoon season (June–September), post-monsoon season (October–December) and the winter season (January and February). We adapted the IMD classification to facilitate better display and further analyses (e.g., Sect. 3.2), making sure that samples are fairly evenly distributed across all seasons. The back-trajectories were generated using the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT4) model (Draxler and Rolph, 2003), driven by wind fields from the Global Data Assimilation
System (GDAS) archive data based on National Centers for Environmental Prediction (NCEP) model output (https://ready.arl.noaa.gov/gdas1.php).

The Hanle (HLE) station (32.780 °N, 78.960 °E, 4517 m a.s.l.) is located in the campus of the Indian Astronomical Observatory (IAO) atop Mt. Saraswati, about 300 m above the Nilamkhul Plain in the Hanle Valley of southeastern Ladakh in northwestern Himalayas. The station was established in 2001 as a collaborative project between the Indian Institute of Astrophysics and LSCE, France. The flask sampling inlet is installed on the top of a 3 m mast fixed on the roof of a 2m high building, and the ambient air is pumped through a Dekabon tubing with a diameter of 1/4”. The area around the station is a cold mountain desert, with sparse vegetation and a small population of ~1700 distributed over an area of ~20 km². Anthropogenic activities are limited to small-scale crop production (e.g., barley and wheat) and livestock farming (e.g., yaks, cows, goats, and sheep). The nearest populated city of Leh (34.25 °N, 78.00 °E, 3480 m a.s.l.) with ~27 000 inhabitants, lies 270 km to the northwest of this station. By virtue of its remoteness, high altitude, and negligible biotic and anthropogenic influences, HLE is representative of the background free tropospheric air masses in the northern mid-latitudes. Regular flask air sampling at this station has been operational since February, 2004, and continuous in-situ CO₂ measurements started in September, 2005. Over the period 2007–2011, a total of 188 flask sample pairs were collected at HLE. Back-trajectories show that, HLE dominantly samples air masses that pass over northern Africa and the Middle East throughout the year, and those coming from South and Southeast Asia during the SW monsoon season (Fig. 1a). More detailed station information of HLE would be found in several earlier publications (Babu et al., 2011; Moorthy et al., 2011).
The Pondicherry (PON) station (12.010 °N, 79.860 °E, 20 m a.s.l) is located on the southeast coast of India, about 8 km north of the city of Pondicherry with a population of ~240,000 (Census India, 2011). The station was established in collaboration with Pondicherry University in 2006. The flask sampling inlet, initially located on a 10 m mast fixed on the roof of the University Guest House, was later moved to a 30 m high tower in June, 2011. The ambient air is pumped from the top of the tower through a Dekabon tubing with a diameter of 1/4”. The surrounding village Kalapet, has a population of ~9000 (Sivakumar and Anitha, 2012). A four-lane highway runs nearly 80 m to the west of the station with a low traffic flow especially during the nighttime, while the Indian Ocean stands about 100 m to the east of the station. Moreover, the two nearest megalopolises of Chennai and Bangalore, both with populations of over 6 million (Census India, 2011), are approximately 143 km to the north and 330 km to the west of the station. 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. In order to minimize the influences of local GHG sources/sinks, flask air sampling at PON is performed between 12:00 and 18:00 local time (LT) (actually 97% of flask samples taken between 12:00 and 14:00 LT), when the sea breeze moves clean air masses towards the land and the boundary layer air is well mixed. 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. Flask sampling at PON began in September, 2006 and over the period 2007–2011, a total of 185 flask sample pairs were collected at the site. As shown in Fig. 1a, the air masses received at PON are strongly related to the monsoon circulations. During the boreal summer when the southwest monsoon prevails, PON is influenced by air masses originating from the
Arabian Sea and South India, whereas during the boreal winter, it receives air masses from the east and northeast parts of the Indian subcontinent, and the Bay of Bengal. During the boreal spring and autumn when the monsoon changes its direction, air masses of both origins are observed.

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

2.2.1 Flask sampling

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

2.2.2 Flask analyses
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. The first gas chromatograph (HP6890, Agilent) is equipped with a flame ionization detector (FID) for CO₂ and CH₄ detection, and a standard electron capture detector (ECD) for N₂O and SF₆ detection. It is coupled with a second GC equipped with a reduced gas detector (RGD, Peak Laboratories, Inc., California, USA), for analyzing CO and H₂ via reduction of HgO and subsequent detection of Hg vapor through UV absorption. In the following paragraph we summarize the major configurations and parameters of the GC systems (also see Table S1). Further details on the analyzer configuration are described in Lopez (2012) and Yver et al. (2009).

Both GC systems are composed of three complementary parts: the injection device, the separation elements and the detection sensors. As flask samples are already dried during sampling, they are only passed through a 5 mL glass trap maintained in an ethanol bath kept at -55°C by a cryocooler (Thermo Neslab CC-65) to remove any remaining water vapor. The air samples are flushed with flask overpressure through a 15 mL sample loop for CO₂ and CH₄ analyses, a 15 mL sample loop for N₂O and SF₆ analyses, and a 1 mL sample loop for CO and H₂, at a flow rate of 200 mL min⁻¹. After temperature and pressure equilibration, the air sample is injected into the columns. The CO₂ and CH₄ separation is performed using a Hayesep-Q (12’ × 3/16”OD, mesh 80/100) analytical column placed in an oven at 80°C, with a N₂ 5.0 carrier gas at a flow rate of 50 ml min⁻¹. Detection of CH₄ and CO₂ (after conversion to CH₄ using a Ni catalyst and H₂ gas) is performed in the FID kept at 250°C. The flame is fed with H₂ (provided by a NM-H₂ generator from F-DBS) at a flow rate of 100 ml min⁻¹ and zero air (provided by a 75-82 zero air generator from Parker-Balston) at a flow rate of 300 ml
For $\text{N}_2\text{O}$ and $\text{SF}_6$ separation, a Hayesep-Q (4’ × 3/16” OD, mesh 80/100) pre-column and a Hayesep-Q (6’ × 3/16” OD, mesh 80/100) analytical column, both placed in an oven at 80°C, are used together with an Ar/CH$_4$ carrier gas at a flow rate of 40 ml min$^{-1}$. Detection of $\text{N}_2\text{O}$ and $\text{SF}_6$ is performed in the ECD heated at 395°C. For CO and H$_2$, we use a Unibeads 1S pre-column (16.5” × 1/8” OD; mesh 60/80) to separate the two gases from the air matrix, and use a Molecular Sieve 5Å analytical column (80” × 1/8” OD; mesh 60/80) to effectively separate H$_2$ from CO. Both columns are placed in an oven kept at 105°C. CO and H$_2$ are analyzed in the RGD detector heated to 265°C. A measurement takes ~5 min and calibration gases are measured at least every 0.45 hour. For CO$_2$, CH$_4$, $\text{N}_2\text{O}$, and $\text{SF}_6$, we use two calibration gases, one with a high concentration and the other with a low concentration. The calibration and quality control cylinders are filled and spiked in a matrix of synthetic air containing N$_2$, O$_2$ and Ar prepared by Deuste Steininger (Germany). The concentration of the sample is calculated using a linear regression between the two calibration gases with a time interpolation between the two measurements of the same calibration gas (Messager, 2007; Lopez, 2012). For CO and H$_2$, we use only one standard and apply a correction for the non-linearity of the analyzer (Yver et al., 2009; Yver, 2010). The nonlinearity is verified regularly with 5 calibration cylinders for CO and 8 calibration cylinders for H$_2$. All the calibration gases themselves are determined against an international primary scale (CO$_2$: WMOX2007; CH$_4$: NOAA2004; $\text{N}_2\text{O}$: NOAA2005A; $\text{SF}_6$: NOAA2005; CO: WMOX2004; H$_2$: WMOX2009; Hall et al., 2007; Dlugokencky et al., 2005; Jordan and Steinberg, 2011; Zhao and Tans, 2006). Finally, a “target” gas is measured every two hours after the calibration gases as a quality control of the scales and of the analyzers. The repeatability of the GC systems estimated from the target cylinder measurements over several days is 0.06 ppm for CO$_2$, 1 ppb for CH$_4$, 0.3 ppb for $\text{N}_2\text{O}$, 0.1 ppt for $\text{SF}_6$, 1 ppb for CO and 2 ppb for H$_2$. 
Additional quality control is made by checking the values of a flask target (a flask filled with calibrated gases) placed on each measurement sequence.

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

2.2.3 Uncertainty of flask measurements

Uncertainties in the measured concentrations stemmed from both the sampling method and the analysis. Collecting flask samples in pairs and measuring each flask twice allow us to evaluate these uncertainties. A large discrepancy between two analyses of the same flask reveals a problem in the analysis system, while a difference between a pair of flasks reflects both analysis and sampling uncertainties. Flask pairs with differences in mole fractions beyond a certain threshold are flagged and rejected (see Table S2 in the supplement for the threshold for each species). The percentages of flask pairs retained for analyses are 65.9-88.3% 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, and 76.2-95.2% for H₂ (Table S3). For each species, we evaluate the uncertainties by averaging differences between the two injections of the same flask (analysis uncertainty) and between the pair of flasks (analysis uncertainty + sampling uncertainty) across all retained flask pairs from the three Indian stations (Table S4). For all species except SF₆, the sampling uncertainty turns out to be the major uncertainty, while the analysis uncertainty is equivalent to the reproducibility of the instrument. For SF₆, both uncertainties are extremely low due to the small amplitudes and variations of the signals at the three stations.
At LSCE, there are regular comparison exercises in which flasks are measured by different laboratories on the same primary scale (e.g., Inter-Comparison Project (ICP) loop, Integrated non-CO2 Greenhouse gas Observing System (InGOS) ‘Cucumber’ intercomparison project). These comparisons allow us to estimate possible biases in our measurements. In Table S4, the bias for each species is calculated over the sampling period using the ICP flask exercise that circulates flasks of low, medium and high concentrations between different laboratories. For CO₂, CH₄, SF₆ and CO, the biases are reported against NOAA (NOAA-LSCE) as it is the laboratory responsible for the primary scales for these species. The bias of H₂ is calculated against Max Planck Institute for Biogeochemistry (MPI-BGC) in Jena, Germany, which is responsible for the primary scale of H₂. The bias of N₂O is reported against MPI-BGC instead of NOAA. Although NOAA is responsible for the primary scale of N₂O, the instruments they use for the N₂O flask analyses and cylinder calibration are not the same as ours. For CH₄, N₂O, SF₆ and H₂, the estimated biases are within the noise level of the instrument and negligible. For CO₂ and CO, we observe a bias of -0.15±0.11 ppm and 3.5±2.2 ppb, respectively (Table S4), which could be due to the nonlinearity of the instrument and/or an improper attribution of the secondary scale values.

2.3 Data analyses

2.3.1 Curve-fitting procedures

For each time series of flask measurements, we calculated annual means and seasonal cycles using a curve-fitting routine (CCGvu) developed by NOAA/CMDL (Thoning et al., 1989). A smoothed function was fitted to the retained data, consisting of a first-order polynomial for the growth rate and two harmonics for the annual cycle (Levin et al., 2002; Ramonet et al., 2002), as well as a low pass filter with 80 and 667 days as short-term and long-term cutoff
values, respectively (Bakwin et al., 1998). Residuals were then calculated as the differences between the original data and the smoothed fitting curve. Any data lying outside three standard deviations of the residuals were regarded as outliers and discarded from the time series (Harris et al., 2000; Zhang et al., 2007). This procedure was repeated until no outliers remained. These outliers were likely a result of pollution by local emissions and not representative of regional background concentrations. The data discarded through this filtering procedure accounts for less than 4% of the retained flask pairs after flagging (Table S3). 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.

For each species at each station, the annual means, as well as the amplitude and phases of seasonal cycles, were determined from the smoothed fitting curve and its harmonic component. We bootstrapped the curve-fitting procedures 1000 times by randomly sampling the original data with replacement to further estimate uncertainties of annual means and seasonal cycles. Since the observation records are relatively short, we used all flask measurements between 2006 and 2011 to fit the smooth curve when available (Fig. S3). For each species, we also compared results with measurements from stations outside India that belong to networks of NOAA/ESRL (http://www.esrl.noaa.gov/gmd/) and Integrated Carbon
Observation System (ICOS, https://www.icos-cp.eu/). Locations and the fitting periods of these stations are also given in Table S6, Figs. S1 and S3.

2.3.2 Ratio of species

We analyzed CH$_4$-CO, CH$_4$-CO$_2$, and CO-CO$_2$ correlations using the residuals from the smoothed fitting curves that represent synoptic-scale variations (Harris et al., 2000; Ramonet et al., 2002; Grant et al., 2010). To determine the ratio between each species pair, as in previous studies, we used the slope calculated from the orthogonal distance regression (Press et al., 2007) to equally account for variances of both species (Harris et al., 2000; Ramonet et al., 2002; Schuck et al., 2010; Baker et al., 2012). We also bootstrapped the orthogonal distance regression procedure 1000 times and estimated the 1-σ uncertainty for each ratio. The analyses were performed with R3.1.0 (R Core Team, 2014) following the recipes described in Teetor (2011).

3 Results and discussions

3.1 Annual means and seasonal cycles

3.1.1 CO$_2$

Figure 2 shows CO$_2$ flask measurements and the corresponding smooth curves fitted to the data at HLE, PON and PBL, as well as two additional NOAA/ESRL stations, namely Plateau Assy, Kazakhstan (KZM – 43.25 °N, 77.88 °E, 2519 m a.s.l.) and Waliguan, China (WLG – 36.29 °N, 100.90 °E, 3810 m a.s.l.) (Dlugokencky et al., 2014b). HLE observed an increase in CO$_2$ mole fractions from 382.3±0.3 to 391.4±0.3 between 2007 and 2011, with annual mean values being lower (by 0.2–1.9 ppm) than KZM and WLG (Fig. 2c and d, Table 1). At PON, the annual mean CO$_2$ mole fractions were generally higher than at HLE, with
differences ranging 1.8–4.3 ppm (Fig. 2a, Table 1). The annual mean CO$_2$ gradient between
PON and HLE reflects the altitudinal difference of the two stations, and a larger influence of
CO$_2$ emissions at PON, mostly from South India (Fig. 1a, EDGAR v4.2). Besides this, as
shown in Fig. 2a and Table 1, the CO$_2$ observations at PON are influenced by synoptic scale
events, with a large variability of individual measurements relative to the fitting curve (see
the relative SDs (RSD) in Table 1). At PBL, the annual mean CO$_2$ mole fractions were on
average 1.2–1.8 ppm lower than that at HLE (Table 1). The negative gradient between PBL
and HLE is particularly large during summer, possibly due to clean air masses transported
from the ocean (Figs. 1a and 2b). Note that caution should be exercised in interpreting the
gradient at PBL because of the data gap and short duration of the time series.

The different CO$_2$ seasonal cycles observed at the five stations reflect the seasonality of
carbon exchange in the northern terrestrial biosphere as well as influences of long-range
transport and the monsoon circulations. At HLE, the peak-to-peak amplitude of the mean
seasonal cycle was 8.2±0.4 ppm, with the maximum early May and the minimum mid-
September, respectively (Fig. 3, Table 1). The mean seasonal cycle estimated from flask
measurements at HLE is in good agreement with that derived from vertical profiles of in-situ
aircraft measurements over New Delhi (~500 km southwest of HLE) from the
Comprehensive Observation Network for Trace gases by Airliner (CONTRAIL,
http://www.cger.nies.go.jp/contrail/) project at similar altitudes (R=0.98–0.99, p<0.001, Fig.
3a; Machida et al., 2008), and back-trajectories show that they represent air masses with
similar origins as HLE (Fig. S8), confirming that HLE is representative of the regional free
mid-troposphere background concentrations. When comparing with the two other background
stations located further north in central and East Asia, a significant delay of the CO$_2$ phase is
seen at HLE compared to KZM and WLG (Fig. 3b, Table 1). We also note that the CO$_2$ mean
seasonal cycle at HLE is in phase with the composite zonal marine boundary layer (MBL) reference at 32°N, while for KZM and WLG, an advance in the CO₂ phase by about 1 month is observed compared to the zonal MBL reference (Fig. S4; Dlugokency et al., 2014b). The phase shifts in the CO₂ seasonal cycles mainly result from differences in the air mass origins between stations. HLE is influenced by the long-range transport of air masses from mid-latitudes around 30 °N, as well as air masses passing over the Indian subcontinent in the boreal summer (Fig. 1a), therefore its CO₂ seasonal cycle is related to the seasonality of vegetation activity over the entire latitude band. KZM and WLG receive air masses passing over the Middle East and western Asia as HLE does, but they are also influenced by air masses of more northern origins with signals of strong CO₂ uptake over Siberia during JAS (Fig. S5). At WLG, negative CO₂ synoptic events, indicative of large-scale transport of air masses exposed to carbon sinks in Siberia in summer, were also detected by in-situ measurements during 2009-2011 (Fang et al., 2014). Moreover, the back trajectories indicate that WLG and KZM are more influenced than HLE by air masses that have exchanged with the boundary layer air being affected by vegetation CO₂ uptake (Fig. S6a,d,e). This could additionally account for the earlier CO₂ phase observed at KZM and WLG compared to HLE.

At PON and PBL, the peak-to-peak amplitudes of the CO₂ mean seasonal cycles were 7.6±1.4 and 11.1±1.3 ppm, with their maxima observed in April. The CO₂ mean seasonal cycle is controlled by changes in the monsoon circulations, in combination with the seasonality of CO₂ biotic exchange and anthropogenic emissions in India. During the boreal winter when the NE monsoon prevails, PON and PBL receive air masses enriched in CO₂ from the East and Northeast Indian subcontinent as well as from Southeast Asia, with large anthropogenic CO₂ emissions (EDGAR v4.2; Wang et al., 2013; Kurokawa et al., 2013). During April when the SW monsoon begins to develop, the two stations record a decrease in
CO₂ because of the arrival of air masses depleted in CO₂ originating from the Indian Ocean south of the Equator (Fig. 1a, Fig. 3c). Compared to PBL, the CO₂ decrease at PON is less pronounced and longer, probably because of the influence of anthropogenic emissions in South India. The CO₂ mean seasonal cycle at PON is also similar to that observed at CRI (15.08°N, 73.83°E, 60m a.s.l.), another station on the southwest coast of India, yet the seasonal maximum at CRI is reached slightly earlier than at PON in March (Bhattacharya et al., 2009; Tiwari et al., 2011, 2014). The SNG station (18.35°N, 73.75°E, 1600m a.s.l.), located over the Western Ghats, observes a larger CO₂ seasonal cycle with a peak-to-peak amplitude of ~20 ppm (Tiwari et al., 2014).

### 3.1.2 CH₄

Figure 4 presents the time series of CH₄ flask measurements at the three Indian stations and the two NOAA/ESRL stations (Dlugokencky et al., 2014a), with their corresponding smoothed curves for 2007–2011. At HLE, the annual mean CH₄ concentration increased from 1814.8±2.9 to 1849.5±5.2 ppb between 2007 and 2011 (Fig. 4, Table 1). The multiyear mean CH₄ value at HLE was lower than at KZM and WLG by on average 25.7±3.1 and 19.6±7.8 ppb (Fig. 4c and d, Table 1), respectively, reflecting the latitudinal and altitudinal CH₄ gradients. Indeed, KZM and WLG receive air masses transported from Siberia with large wetland CH₄ emissions in summer, as well as those from regional sources closer to the stations (Fang et al., 2013; Fig. S5), which may further contribute to the positive gradients between these two stations and HLE. At PON and PBL, the annual mean CH₄ mole fractions were higher than those at HLE by as much as 37.4±10.7 and 19.8±24.5 ppb respectively (Fig. 4a and b, Table 1). The positive gradients indicate significant regional CH₄ emissions, especially during winter when the NE monsoon transports air masses from East and Northeast India and Southeast Asia, where emissions from livestock, rice paddies and a
variety of waterlogged anaerobic sources and residential biofuel burning are high (EDGAR v4.2; Baker et al., 2012; Kurokawa et al., 2013). The in-situ measurements at Darjeeling, India (27.03°N, 88.25°E, 2194 m a.s.l.), another station located in the eastern Himalayas, also showed large variability and frequent pollution events in CH$_4$ mole fractions, which largely result from the transport of CH$_4$-polluted air masses from the densely populated Indo-Gangetic Plains to the station (Ganesan et al., 2013).

The CH$_4$ seasonal cycles exhibit contrasting patterns across stations. As shown in Fig. 5, a distinct characteristic of the mean seasonal cycle at HLE is a CH$_4$ maximum from June to September. Even KZM and WLG do not show a minimum in summer that would be characteristic for the enhanced CH$_4$ removal rate by reaction with OH. The pronounced HLE feature is consistent with the result from the aircraft flask measurements over India at flight altitudes of 8–12.5 km by the Civil Aircraft for the Regular Investigation of the atmosphere Based on an Instrument Container (CARIBIC, http://www.caribic-atmospheric.com/) project (Schuck et al., 2010, 2012; Baker et al., 2012), although a larger seasonal cycle amplitude is found in the CARIBIC composite data 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). CARIBIC sampled the mid- to upper tropospheric air masses that were earlier and more strongly enriched in CH$_4$, 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). Xiong et al. (2009) also reported enhancements of CH$_4$ during the summer monsoon season over South Asia based on satellite retrievals of CH$_4$ using the Atmospheric Infrared Sounder (AIRS) on the EOS/Aqua platform as well as model simulations. Moreover, the mean CH$_4$ seasonal cycle at HLE agrees well with the seasonal variations of CH$_4$ emissions from wetlands and
rice paddies and convective precipitation over the Indian subcontinent (Fig. 5b), suggesting that the summer maximum at HLE are likely related to the enhanced biogenic CH$_4$ emissions from wetlands and rice paddies and deep convection that mixes surface emissions into the mid-to-upper troposphere. During the SW monsoon period (June–September), convection over the Indian subcontinent and the Bay of Bengal rapidly mixes surface polluted air with the upper troposphere, therefore concentrations of trace gases would be enhanced at higher altitudes rather than at the surface (Schuck et al., 2010; Lawrence and Lelieveld, 2010).

Further analyses of carbon isotopic measurements and/or chemical transport model are needed to disentangle and quantify the contributions of meteorology and biogenic emissions to the CH$_4$ summer maximum at HLE. As stated above, KZM and WLG also record CH$_4$ increases during summertime, but with smaller magnitudes (Fig. 5a), possibly because they are not directly influenced by deep convection from the Indian monsoon system.

In contrast to HLE, the CH$_4$ mean seasonal cycles at PON and PBL have distinct phases and much larger amplitudes, with minimum CH$_4$ values during July (Fig. 5c). These not only reflect higher rates of removal by OH, but rather the influence of southern hemispheric air transported at low altitudes from the southwest as well as the dilution effect by increased local planetary boundary layer height. In boreal winter, the maxima at PON and PBL are associated with CH$_4$-enriched air masses transported from East and Northeast India, and Southeast Asia, mostly polluted by agricultural-related sources (e.g., livestock, rice paddies, agricultural waste burning). As PON and PBL, the flask measurements at CRI also showed the seasonal maximum CH$_4$ values during the NE monsoon season, reflecting influences of air masses with elevated CH$_4$ from the Indian subcontinent (Bhattacharya et al., 2009; Tiwari et al., 2013).
3.1.3 N₂O

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

The time series of N₂O flask measurements over the period of 2007–2011 and their smoothed curves are presented in Fig. 6. At HLE, the annual mean N₂O concentration rose from 322.2±0.1 to 325.2±0.1 ppb during 2007–2011 (Table 1), with a mean annual growth rate of 0.8±0.0 ppb yr⁻¹ ($r^2 = 0.97$, $p = 0.001$), smaller than that at MLO (1.0±0.0 ppb yr⁻¹, Table 1). At PON and PBL, the annual mean N₂O mole fractions are higher than at HLE by 3.1±0.3 and 3.8±1.7 ppb (Fig. 6, Table 1), respectively. The N₂O gradients between PON, PBL and HLE are larger than typical N₂O gradients observed between stations scattered in Europe or in North America. For example, Haszpra et al. (2008) presented N₂O flask measurements at a continental station – Hegyhátsálat, Hungary (HUN – 46.95 °N, 16.65 °W, 248 m a.s.l.) from 1997 to 2007. The annual mean N₂O mole fraction at HUN was higher than at Mace Head (MHD) by only 1.3 ppb. We also analyzed N₂O time series of flask measurements during 2007–2011 at several European coastal stations – BGU in Spain, FIK in Greece, and LPO in France (Table S6), and the N₂O gradients between these stations and MHD were 1.1±0.2, 0.4±0.1, and 2.1±0.6 ppb, respectively (Fig. S10, Table S7). In the United States, N₂O flask
measurements from the NOAA/ESRL stations at Park Falls, Wisconsin (LEF – 45.95 °N, 90.27 °W, 472 m a.s.l.), Harvard Forest, Massachusetts (HFM – 42.54 °N, 72.17 °W, 340 m a.s.l.) and a continental, high-altitude station at Niwot Ridge, Colorado (NWR – 40.05 °N, 105.58 °W, 3523 m a.s.l.) also show that, the annual mean N$_2$O concentrations at HFM and LEF were higher than that at NWR by only 0.5±0.1 and 0.3±0.1 ppb, respectively (Fig. S10, Table S7). Besides, the N$_2$O concentrations measured at PON and PBL have a notably higher variability (around the smoothed fitting curve) than that at European and US stations (see relative SDs (RSD) in Table 1 and Table S7). The larger N$_2$O gradient between PON, PBL and HLE, as well as higher variability at PON and PBL, demonstrate the presence of substantial N$_2$O sources in South Asia and over the Indian Ocean during the observation period. The in-situ measurements at Darjeeling also exhibited N$_2$O enhancements to be above the background level, suggesting significant N$_2$O sources in this region (Ganesan et al., 2013). These sources may be related to emissions from natural and cultivated soils probably enhanced by extensive use of nitrogen fertilizers, as well as emissions from regions of coastal upwelling in the Arabian Sea (Bange et al., 2001; Garg et al., 2012; Saikawa et al., 2014).

Compared to CO$_2$ and CH$_4$, the seasonal cycle of N$_2$O is very small due to the long lifetime of ~120 years (Minschwaner et al., 1993; Volk et al., 1997), and has a larger uncertainty probably because synoptic events are more likely to mask the seasonal signal. At HLE, PON and PBL, the peak-to-peak amplitudes of the N$_2$O seasonal cycle are 0.6±0.1, 1.2±0.5, and 2.2±0.6 ppb, respectively (Table 1). HLE displays a N$_2$O maximum in mid-August (Student’s t-test, t=1.78, p=0.06), and a secondary maximum is in January/February but not significant (Student’s t-test, t=−0.84, p=0.79) (Table 1, Fig. 7, Table S8 for detailed t-test statistics). The N$_2$O seasonal cycle at HLE is out of phase with that at other northern background stations such as MHD (Fig. S11, Table S7), where an N$_2$O summer minimum is always observed,
likely due to the downward transport of N₂O-depleted air from the stratosphere to the troposphere during spring and summer (Liao et al., 2004; Morgan et al., 2004; Jiang et al., 2007b). The timing of the summer N₂O maximum at HLE is consistent with that of CH₄ (Table 1; Figs. 5 and 7), giving evidence that the N₂O seasonal cycle may probably be influenced by the convective mixing of surface air, rather than by the influx of stratospheric air into the troposphere. Given that the populous Indo-Gangetic plains have high N₂O emission rates due to the intensive use of nitrogen fertilizers (Garg et al., 2012; Thompson et al., 2014a), during summer, the surface air enriched in N₂O is vertically transported by deep convection and enhances N₂O mole fractions in the mid-to-upper troposphere. Like CH₄, the N₂O enhancement during the summer monsoon period (June-September) was also observed by the aircraft flask measurements at flight altitudes 8–12.5 km from the CARIBIC project in 2008 (Schuck et al., 2010).

At PON, N₂O also decreases during February–April and reaches a minimum at the end of May. However, the decrease of N₂O does not persist during June–September, which is in contrast with CH₄ (Table 1, Fig. 7a). One reason may be that the air masses arriving at the site during the southwest monsoon period is relatively enriched in N₂O compared to CH₄, reflecting differences in their relative emissions along the air mass route. The increase of N₂O at PON during June–August and the maximum during September–October are likely related to N₂O emissions from coastal upwelling along the southern Indian continental shelf, which peak during the SW monsoon season (Patra et al., 1999; Bange et al., 2001). According to Bange et al. (2001), the annual N₂O emission for the Arabian Sea is 0.33–0.70 Tg/yr, of which N₂O emissions during the SW monsoon account for about 64–70%. This coastal upwelling N₂O flux is significantly larger than the annual anthropogenic N₂O emissions in South India south of 15 °N, which is estimated to be on average 0.07–0.08 Tg/yr during
2000–2010 (EDGAR v4.2). At PBL, the maximum and minimum N₂O occur in November and February/March, respectively (Table 1, Fig. 7b). The late N₂O peak at PBL in November may be associated with the N₂O-enriched air masses transported from South and Southeast Asia, which could be attributed to natural and agricultural N₂O emissions from this region (Saikawa et al., 2014). It should be noted that, the mean seasonal cycles of N₂O at PON and PBL are subject to high uncertainties because of the short observation periods and data gaps (shaded area in Fig. 7). The N₂O maximum and/or minimum obtained from the mean seasonal cycle are marginally significant for PON and PBL (Table S8 for detailed t-test statistics). Therefore, caution should be exercised in interpreting mean seasonal cycles at these stations. Sustained, long-term measurements are needed in order to generate more reliable estimates of the seasonal cycles for the two stations.

3.1.4 SF₆

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

Figure 8 presents the time series of SF₆ flask measurements and corresponding fitting curves at HLE, PON, and PBL. At HLE, the annual mean SF₆ mole fractions increased from
6.26±0.03 to 7.38±0.01 ppt between 2007 and 2011, which is in good agreement with the SF$_6$ trend observed at MLO during the same period (HLE: 0.29±0.05 ppt/yr, $r^2$=0.99, p<0.001; MLO: 0.29±0.03 ppt/yr, $r^2$=0.99, p<0.001; Figs. 8 and S12a, Table 1, Table S9). The annual mean SF$_6$ gradient between PON and HLE is -0.060±0.030 ppt, whereas the gradient between PBL and HLE is statistically insignificant (-0.002±0.097 ppt). The slight negative gradient between PON and HLE is a reversed signal compared with the SF$_6$ observations at stations influenced by continental emissions in Europe and United States. For example, the SF$_6$ mole fractions at HUN over the years of 1997–2007 are higher than those at MHD by on average 0.19 ppt (Haszpra et al., 2008). We also analyzed the SF$_6$ gradients between two coastal European stations – BGU (41.97 °N, 3.3 °E, 30 m a.s.l.) and LPO (48.80 °N, 3.57 °W, 30 m a.s.l.) – and MHD, which are 0.10±0.03 and 0.05±0.02 ppt averaged over the period of 2007–2011, respectively. At HFM, the SF$_6$ mole fractions are higher than those of the NWR on average by 0.15±0.06 ppt during 2007–2011 (Table S9). Given the long atmospheric lifetime of SF$_6$, the positive gradients between continental European and US stations and background reference stations suggest significant sources in Europe and the US. On the contrary, the slight negative gradient between PON and HLE implies weak SF$_6$ emissions over the Indian subcontinent, which is also indicated by recent high-frequency in-situ SF$_6$ measurements at Darjeeling (Ganesan et al., 2013). It is also worthwhile to note that high SF$_6$ values occur repeatedly at HLE and PBL in winter, which is likely related to episodic SF$_6$ pollution events from the Middle East, South/Southeast Asia and China (Figs. 8b and S7d).

The annual mean SF$_6$ seasonal cycles for HLE, PON, and PBL are presented in Fig. 9. The peak-to-peak amplitudes at the three stations are 0.15±0.03, 0.24±0.02, and 0.48±0.07 ppt, respectively (Table 1). At HLE, the SF$_6$ seasonal cycle is bimodal as for N$_2$O, with an absolute maximum occurring in November (Student’s t-test, t=2.425, p=0.014) and a
secondary maximum in May (Student’s t-test, t=2.443, p=0.016) (Table S10 for detailed t-test statistics). Given that SF₆ increases monotonously and that its sources are purely anthropogenic and not subject to seasonally variations (Maiss et al., 1996), the seasonal cycle of SF₆ should be driven by changes in atmospheric circulations, e.g., the SW monsoon convection and stratosphere-atmosphere exchange (Levin et al., 2002). We note that, at HLE, no enhancement of SF₆ during the SW monsoon season is recorded, unlike what is observed for CH₄ and N₂O (Figs. 5 and 7). 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. Backtrajectories 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. The absence of SF₆ enhancement in summer at HLE confirms weak SF₆ emissions in India. At PBL, the SF₆ seasonal cycle is related to the monsoon circulation and convection (Figs. 9b and S7d). The maximum during November–December (Student’s t-test, t=5.138, p<0.001; Table S10) is likely due to frequent episodic SF₆ polluted air masses transported from Southeast Asia and China (Fig. S7d).

### 3.1.5 CO
Carbon monoxide (CO) plays important roles in atmospheric chemistry, as the dominant sink for the hydroxyl radical (OH, the main tropospheric oxidant) and a precursor of tropospheric ozone under high NO\textsubscript{x} (NO+NO\textsubscript{2}) concentrations (Logan et al., 1981; Novelli et al., 1998; Seinfeld and Pandis, 2006). Although CO does not act as a greenhouse gas, it modulates the atmospheric concentrations of CH\textsubscript{4} (the second anthropogenic greenhouse gas after CO\textsubscript{2}) through competition for the OH radicals. At the global scale, it contributes to an indirect positive radiative forcing of 0.23±0.07Wm\textsuperscript{-2} (IPCC, 2013). Besides, CO is an excellent tracer for combustion processes, with emission sources mainly contributed by incomplete combustion of fossil fuel and biofuels, and by biomass burning (Granier et al., 2011). In India, biofuel and agricultural waste burning account for 70–80% of the total anthropogenic CO emissions (EDGAR v4.2; Streets et al., 2003b; Yevich and Logan, 2003).

The time series of CO flask measurements and corresponding smoothed curves are shown in Fig. 10. Over the period of 2007–2011, HLE recorded a slight decrease in CO mole fractions from 104.7±1.4 to 99.4±2.2 ppb, with an annual rate of -2.2±0.0 ppb yr\textsuperscript{-1} (r\textsuperscript{2} = 0.65, p = 0.06). The CO mole fractions at HLE are lower than those at KZM and WLG (Novelli et al., 2014b), by on average 18.8±2.5 and 30.2±7.4 ppb, respectively (Table 1, Fig. 10c and d). The positive gradient between KZM, WLG and HLE does not only reflect decreasing CO with altitude and the N-S global gradient, but also suggests differences in regional emission sources. For example, compared to HLE, the CO signals at WLG are more influenced by transport of polluted air, especially during summer when about 30% air masses pass over industrialized and urbanized areas southeast of the station (Zhang et al., 2011). Besides, the positive CO gradient between KZM, WLG and HLE may be further contributed by air masses of northern Siberia origin in summer (Fig. S5), with higher CO emissions from biomass burning and secondary CO from the oxidation of CH\textsubscript{4} and non-CH\textsubscript{4} hydrocarbons.
(Konovalov et al., 2014). At PON and PBL, the annual mean CO mole fractions are higher than that at HLE by on average 82.4±10.7 and 52.5±8.5 ppb, respectively (Table 1, Fig. 10a and b). The PON and PBL stations are influenced by CO regional emissions, mainly due to biofuel and agricultural burning over South and Southeast Asia (Lelieveld et al., 2001; Streets et al., 2003a, b; Yevich and Logan, 2003). We also note that, for all the five stations, the CO time series show larger variability with respect to their corresponding smoothed curves than other species do (see the residual SD (RSD) in Table 1, Fig. 10), as a result of the unevenly distributed CO sources and short atmospheric lifetime (Novelli et al., 1992).

As shown in Fig. 11, the CO seasonal cycle at HLE reaches a maximum in mid-March and a minimum by the end of October, with a peak-to-peak amplitude of 28.4±2.3 ppb (Table 1, Fig. 11). The phase of the mean CO seasonal cycle at HLE generally agrees with the ones observed at KZM and WLG, with a lag of up to 1 month in the timing of seasonal minimum at the two stations (Table 1, Fig. 11c and d). In contrast with the three stations representative of large-scale free tropospheric air masses, the stations at the maritime boundary layer in the mid-to-high Northern Hemisphere observe the lowest CO values in July or August (Novelli et al., 1992, 1998), when the concentration of OH – the major sink of CO – is highest (Logan et al., 1981). The delay in timing of the seasonal CO minimum at the three free troposphere stations in Central and South Asia compared to those boundary layer stations is probably due to the mixing time of regional surface CO emissions and the relatively short lifetime of CO (1-2 months on average). During summer, KZM and WLG sample air masses from Siberia impacted by CO fire emissions (Duncan et al., 2003; Kasischke et al., 2005), as well as CO-polluted air from urbanized and industrialized area (Zhang et al., 2011), while HLE is influenced by convective mixing of CO emissions from India, either from anthropogenic sources or oxidation of VOCs. It is interesting to note that the CO seasonal cycle at HLE does
not show an enhancement during JAS as CH$_4$ and N$_2$O do (Figs. 5 and 7), possibly as a result of OH oxidation that reduces CO and acts oppositely to vertical transport, and/or differences in seasonal emission patterns between CO and the other two species (Baker et al., 2012). However, the CO enhancement during summer was observed in the upper troposphere over South Asia from the CARIBIC aircraft measurements at flight altitudes 8-12.5 km and Microwave Limb Sounder observations at 100–200 hPa (Li et al., 2005; Jiang et al., 2007a; Schuck et al., 2010). The differences in the CO seasonal cycles at different altitudes suggest faster transport (and younger air masses) at 10 km than at 5 km due to convection, controlling the vertical profile of CO, which makes it difficult to directly compare aircraft measurements in the upper troposphere and column remote sensing observations with surface data.

At PON and PBL, the mean CO seasonal cycles show maxima in the boreal winter and minima in the boreal summer, with peak-to-peak amplitudes of 78.2±11.6 and 144.1±16.0 ppb, respectively (Fig. 11a and b). A strong and positive correlation is found between detrended CO and CH$_4$ at PON (r=0.70, p<0.001) and PBL (r=0.84, p<0.001), suggesting that the seasonal cycles of both species are dominated by the seasonally varying atmospheric transport. During summer when the southwest monsoon prevails, the surface CO concentrations at PON and PBL are low due to rapid convective uplifting and advection of clean air masses from the ocean. During winter, the two stations are influenced by northeasterly air masses enriched in CO from Northeast India, Southeast Asia and China (back-trajectories in Fig. S7e), probably influenced by biofuel and agricultural waste burning in these regions (Yevich and Logan, 2003; Lelieveld et al., 2001).

3.1.6 H$_2$
Hydrogen (H$_2$) is the second most abundant reduced trace gas in the troposphere after CH$_4$, with an average mole fraction of ~530 ppb (Novelli et al., 1999). It plays important roles in tropospheric and stratospheric chemistry and indirectly impacts budgets of CH$_4$, CO and non-methane hydrocarbons (NMHCs) through reaction with the OH radicals (Novelli et al., 1999; Ehhalt and Rohrer, 2009). Like CO, H$_2$ is also a good tracer for incomplete combustion emissions from fossil fuel and biomass/biofuel burning, which is quite extensive in India (Streets et al., 2003b; Yevich and Logan, 2003).

Figure 12 shows the time series of H$_2$ flask measurements with smoothed curves at HLE, PON, and PBL, respectively. No significant trend was observed at any of the three stations (Table 1, Fig. 12), consistent with the long-term H$_2$ measurements at other background stations during the last three decades (Novelli et al., 1999; Ehhalt and Rohrer, 2009; Grant et al., 2010). For the year 2008, comparing to KZM and WLG (Novelli et al., 2014a), HLE recorded higher H$_2$ mole fractions by ~40 ppb, reflecting the latitudinal gradient of H$_2$ with lower concentrations towards northern high latitudes, due to land uptake by soils (Novelli et al., 1999; Price et al., 2007; Hauglustaine and Ehhalt, 2002; Ehhalt and Rohrer, 2009). Note that these results based on only one-year comparison need to be confirmed by extended data more up-to-date, which are not available yet. At PON and PBL, the annual mean H$_2$ mole fractions were higher than at HLE by 29.8±4.1 and 21.8±4.6 ppb, respectively (Table 1; Fig. 12). Comparisons with H$_2$ measurements at Mariana Island, Guam (GMI – 13.39 °N, 144.66 °E, 0.00 m a.s.l.) (Novelli et al., 2014a), another maritime station in the western Pacific at a similar latitude as PON and PBL, also showed positive gradients of ~40 ppb (Fig. S13c and d; Table S11), suggesting substantial regional H$_2$ sources over the footprint area of PBL and PON. During October–March when the NE monsoon prevails, both PON and PBL receive H$_2$-enriched air masses from South and Southeast Asia, mainly influenced by fossil
fuel combustion and biomass burning (Fig. S7f; GFED v3.1; Hauglustaine and Ehhalt, 2002; Price et al., 2007; Ehhalt and Rohrer, 2009; van der Werf et al., 2010). During April–September, with the northward movement of Intertropical Convergence Zone (ITCZ), the two stations are influenced by advection of air from south of the Equator. For PON, H$_2$-polluted air masses are occasionally sampled during JAS when the SW monsoon moves over the continent of South India with high population and heavy industry (Fig. S7f; Census India, 2011).

The mean H$_2$ seasonal cycles for HLE, PON, and PBL are presented in Fig. 13. At HLE, the peak-to-peak H$_2$ seasonal amplitude is 15.8±2.2 ppb, less than half of the seasonal amplitudes at BMW (39.6±2.6 ppb) and MID (38.0±2.4 ppb) of similar latitudes (Novelli et al., 2014a), and that at WLG (22.8±3.0 ppb) (Figs. 13d and S14a, Tables 1 and S11). The maximum and minimum of H$_2$ occur in April and September, respectively. The dampening of the H$_2$ seasonal amplitude with increasing altitude was previously found for another high-altitude continental station at Jungfraujoch, Switzerland (JUN – 46.53 °N, 7.98 °E, 3580.00 m a.s.l.) (Bond et al., 2011), and was also captured by the GEOS-Chem global chemical transport model (Price et al., 2007). Since the soil sink dominates much of the surface H$_2$ seasonal cycle in the mid-to-high Northern Hemisphere (Hauglustaine and Ehhalt, 2002; Price et al., 2007; Bousquet et al., 2011; Yver et al., 2011; Yashiro et al., 2011), the smaller amplitude in the H$_2$ seasonal cycle at HLE may be attributed to the weakened soil sink with increasing altitude due to vertical mixing (Price et al., 2007; Bond et al., 2011).

At PON and PBL, the mean H$_2$ seasonal cycles are characterized by the peak-to-peak amplitudes of 21.6±3.4 and 21.3±5.0 ppb respectively, comparable to that at GMI (21.5±1.2
ppb) (Tables 1 and S11, Figs. 13a and b and S14b). At PBL, the H₂ maximum in March–April and a secondary increase during September–October coincide with the double biomass burning peaks in each hemisphere – in March for northern tropics, in August/September for southern tropics (van der Werf et al., 2006; Price et al., 2007; Bousquet et al., 2011; Yver et al., 2011). Given that the seasonal variation of soil H₂ uptake is probably small in the tropics (Price et al., 2007; Bousquet et al., 2011; Yver et al., 2011; Yashiro et al., 2011), this bimodal H₂ seasonal cycle at PBL could be related to biomass burning.

3.2 Synoptic variations

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

3.2.1 ΔCH₄/ΔCO

Figure 14 shows scatterplots of CH₄ and CO residuals with the orthogonal distance regression lines at HLE, PON, and PBL for different seasons. A significant and positive correlation between CH₄ and CO residuals (hereafter ΔCH₄/ΔCO, unit ppb ppb⁻¹) is found for all three stations throughout the year. Furthermore, the ΔCH₄/ΔCO ratio also shows seasonal variation at each of the three stations. The most prominent feature is the occurrence of maximum
slopes in July–September (also October–December at PON), especially at HLE and the generally higher ratios at this station. Wada et al. (2011) and Niwa et al. (2014) also reported increased summer ΔCH₄/ΔCO over the western North Pacific, according to the in-situ measurements at several surface stations and aircraft flask measurements in the mid-troposphere. The main process for this seasonal variation of ΔCH₄/ΔCO might be the enhanced emissions of biogenic CH₄ in summer (e.g., wetland and rice paddy emissions; Streets et al., 2003a; Yan et al., 2003) combined with concurrent lower anthropogenic CO emissions in summer than in winter (due to less residential fuel use for heating, see Streets et al., 2003a). The faster photochemical destruction of CO by increased OH during summer cannot explain such large changes (less than 15% according to Wada et al. (2011)).

At HLE, the ΔCH₄/ΔCO ratio varies from 1.2±0.3 to 4.0±1.2 ppb ppb⁻¹ throughout the year, with a maximum in JAS, corresponding to the summer monsoon season (Fig. 14a–d). Based on the CARIBIC flights between 10 and 12 km from Frankfurt, Germany to Chennai, India, Baker et al. (2012) derived a ΔCH₄/ΔCO ratio in the range 1.88(±0.22) to 4.43(±0.56) in JAS over South Asia. The maximum ΔCH₄/ΔCO observed during summer in the mid-to-upper troposphere may be the result of higher biogenic CH₄ emission over the Indian subcontinent, lower CO emissions, combined with frequent widespread convective uplift of surface air during the SW monsoon (Schuck et al., 2010; Baker et al., 2012). The CARIBIC flights recorded similar ΔCH₄/ΔCO values to HLE, confirming that convection plays a dominant role compared to advection during the SW monsoon season. Outside the SW monsoon season, both the CARIBIC flights and HLE do generally not record strong effects of surface emissions due to the weakened vertical transport. With respect to the ΔCH₄/ΔCO ratios for January–March, April–June and October–December, our estimates are 1.5 to 4 times that of the ratios determined for air masses with signatures of fossil fuel combustion, according to
several aircraft and ground observations in East and Southeast Asia (Table S12; Sawa et al., 2004; Lai et al., 2010; Wada et al., 2011; Niwa et al., 2014), which rules out fossil fuel combustion as an explanation for the higher ratios. Our ratios are comparable to the $\Delta$CH$_4$/ΔCO values inferred for air masses of Siberian origin during winter (Table S12; Harris et al., 2000; Chi et al., 2013), and we also obtain similar estimates of $\Delta$CH$_4$/ΔCO from the flask measurements at KZM over the study period (The $\Delta$CH$_4$/ΔCO ratios for KZM are 0.8±0.2, 1.7±0.2 and 1.5±0.3 ppb ppb$^{-1}$ for AMJ, OND and JFM, respectively), which are influenced by air masses originating from North Africa, the Middle East, and Central Asia as seen at HLE (see back-trajectories in Fig. S5). Given that oil and gas production accounts for 50–70% of CH$_4$ emissions in these regions (EDGAR v4.2) and that over dry areas the daytime boundary layer is higher which favors injection of surface emissions into the troposphere, the preferential enrichment in CH$_4$ relative to CO at HLE may tentatively be attributed to fossil CH$_4$ emissions over gas extraction regions and transported eastwards by westerlies (Harris et al., 2000; Tohjima et al., 1996).

At PON and PBL, the $\Delta$CH$_4$/ΔCO ratios are in general considerably higher than 0.3 for all seasons, putting them in the range of ratios indicative of urban/industrial sources (Table S12; Harriss et al., 1994; Sawa et al., 2004; Xiao et al., 2004; Bakwin et al., 1995; Lai et al., 2010; Wada et al., 2011; Niwa et al., 2014). However, this does not rule out contributions from biomass/biofuel burning with emissions having a typical $\Delta$CH$_4$/ΔCO ratio less than 0.3 (Mauzerall et al., 1998; Andreae and Merlet, 2001; Mühle et al., 2002). Considering that biofuel and agriculture waste burning are the primary energy sources in rural India (Streets et al., 2003a; Yevich and Logan, 2003; Venkataraman et al., 2005), CO emissions from biofuel burning must be substantial (Lelieveld et al., 2001). This is the case for NE India located upwind of PON and PBL when the NE monsoon prevails during December–March.
Nevertheless, the relatively low $\Delta \text{CH}_4/\Delta \text{CO}$ derived from biomass/biofuel burning could be increased by $\text{CH}_4$ emissions from livestock with similarly distributed sources (EDGAR v4.2). Emissions of both trace gases from livestock and biomass/biofuel burning in the Indian subcontinent compiled by EDGAR v4.2 also indicate a $\text{CH}_4$ to CO ratio of 0.64–0.69 over the period of 2000–2008, close to the atmospheric measurements of $\Delta \text{CH}_4/\Delta \text{CO}$ at PON and PBL during JFM (Fig. 14h and l).

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

The $\Delta \text{CH}_4/\Delta \text{CO}_2$ ratios are strongly influenced by the high variability of $\text{CO}_2$ and the interpretation is complex. Unlike the positive correlation between $\text{CH}_4$ and CO consistently observed at all three stations, the relationships between $\text{CH}_4$ and $\text{CO}_2$ residuals exhibit scattered and differences in the residual slopes for different stations and seasons (Fig. 15). At HLE, no significant correlations are found during AMJ, JAS, and OND (Fig. 15a–c), because $\text{CH}_4$ and $\text{CO}_2$ have distinct biogenic and/or photochemical sources and sinks over the northern mid-latitudes. During JFM when biogenic $\text{CO}_2$ fluxes and anthropogenic emissions are positive to the atmosphere, there is a significant and positive relationship between $\text{CH}_4$ and $\text{CO}_2$, 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 value is close to the ratio of $\text{CH}_4$ and $\text{CO}_2$ anthropogenic emissions over North Africa (39.1–46.2 mmol mol$^{-1}$), Central Asia (44.4–49.5 mmol mol$^{-1}$) and to a lesser degree the Middle East (25.8–28.4 mmol mol$^{-1}$) during the period of 2000–2010 (EDGAR v4.2), corresponding to the back-trajectories reaching HLE (Fig. 1a). It should be noted that this estimate of $\Delta \text{CH}_4/\Delta \text{CO}_2$ is subject to large uncertainty according to the standard deviation calculated with 1000 bootstrap replications (Fig. 15d), implying that $\text{CH}_4$ and $\text{CO}_2$ sources of various types and origins influence the HLE records.
At PON, in contrast to HLE, positive correlations occur between CH\textsubscript{4} and CO\textsubscript{2} residuals for all seasons except OND, with a $\Delta$CH\textsubscript{4}/$\Delta$CO\textsubscript{2} ratio of 6.7±2.4 ppb ppm\textsuperscript{-1} (r=0.72, p<0.001) in AMJ and 8.5±0.9 ppb ppm\textsuperscript{-1} in JAS (r=0.74, p<0.001), respectively (Fig. 15e and f). The relatively narrow ranges of slopes compared to that for HLE and PBL likely suggest co-located urban and industrial sources in South India upwind of PON during April–September (see back-trajectories in Fig. 1a). Emissions from biofuel burning could be a common source for both CH\textsubscript{4} and CO\textsubscript{2}, given the substantial biofuel use in South India (Yevich and Logan, 2003) and the biofuel burning emission ratio of CH\textsubscript{4} and CO\textsubscript{2} derived from previous studies (5–10 mmol mol\textsuperscript{-1}; Andreae and Merlet, 2001). Note that the CARIBIC flask measurements over India south of 20°N indicate a negative correlation between CH\textsubscript{4} and CO\textsubscript{2} at the altitudes of 10-12 km during July–September, 2008 (r=-0.80, p=0.002; Fig. S15a), interpreted as the concurrent strong uptake of CO\textsubscript{2} with enhanced emissions of CH\textsubscript{4} during the SW monsoon. During JFM when the NE monsoon predominates, CH\textsubscript{4} is positively correlated with CO\textsubscript{2} with a $\Delta$CH\textsubscript{4}/$\Delta$CO\textsubscript{2} ratio of 31.9±1635.7 ppb ppm\textsuperscript{-1} (r=0.45, p=0.02; Fig. 15h). Like at HLE, this ratio is subject to large uncertainty due to variability in CH\textsubscript{4} and CO\textsubscript{2} sources. The ratio based on the CARIBIC observations in the upper troposphere (10-12 km) is 23.5±41.4 ppb ppm\textsuperscript{-1} (r=0.67, p=0.004; Fig. S15b). The inconsistency of the $\Delta$CH\textsubscript{4}/$\Delta$CO\textsubscript{2} ratios estimated from the two datasets suggest that the flask measurements at the surface station PON do provide information more specific for constraining estimates of regional CH\textsubscript{4} and CO\textsubscript{2} fluxes.

Finally, at PBL, the prominent feature of the CH\textsubscript{4}–CO\textsubscript{2} relationship is the significant and negative correlation observed during JAS, with a $\Delta$CH\textsubscript{4}/$\Delta$CO\textsubscript{2} ratio of -14.6±16.4 ppb ppm\textsuperscript{-1} (r=-0.73, p=0.007; Fig. 15j). Since the time series of flask measurements at PBL is relatively short and has large data gaps (Fig. S3), correlations between trace gases could be influenced...
by abnormal pollution events. For example, excluding the event with CH$_4$ residuals $> +20$ ppb (corresponding to the observation at PBL on 16 September 2009, the point marked with black circle in Fig. 15j) would substantially decrease the strength of negative correlation between CH$_4$ and CO$_2$ ($r=-0.54$, $p=0.09$). We will investigate the CH$_4$ enriched event further in Sect. 3.3.

### 3.2.3 $\Delta$CO/$\Delta$CO$_2$

As shown in Fig. 16, at HLE, CO is positively correlated with CO$_2$ during AMJ, with a $\Delta$CO/$\Delta$CO$_2$ ratio of $35.8\pm12.1$ ppb ppm$^{-1}$ ($r=0.53$, $p=0.001$; Fig. 16a). During JFM, there is no significant relationship between CO and CO$_2$ ($r=0.15$, $p=0.39$; Fig. 16d). However, excluding an abnormal event with $\Delta$CO$_2$ = -1.8 ppm on 8 January 2007 (the point marked with black circle in Fig. 16d) would give a significant and positive correlation between CO and CO$_2$, with a $\Delta$CO/$\Delta$CO$_2$ ratio of $55.7\pm259.1$ ppb ppm$^{-1}$ ($r=0.40$, $p=0.02$; the red solid line in Fig. 16d). This ratio is less than half the emission ratio of CO to CO$_2$ from forest/grassland biomass burning (Mauzerall et al., 1998; Andreae and Merlet, 2001), but higher than ratios of anthropogenic combustion sources in developed countries that are typically in the range of 10–15 ppb ppm$^{-1}$ (e.g., Suntharalingam et al., 2004; Wada et al., 2011; Takegawa et al., 2004). This could be attributed not only to the lower combustion efficiency of fuels in North Africa, the Middle East, and Central Asia where air masses at HLE originate from, but also to additional contribution from biofuel burning with relatively high CO to CO$_2$ emission ratios (e.g., fuelwood, charcoal, agricultural residuals; Andreae and Merlet, 2001). Besides, the relatively high $\Delta$CO/$\Delta$CO$_2$ in JFM compared to AMJ may further indicate a contribution of CO emissions from residential biofuel burning in winter (Wada et al., 2011), especially in developing countries within the footprint area.
At PON, a positive and significant correlation between CO and CO\textsubscript{2} is found during AMJ, with a ΔCO/ΔCO\textsubscript{2} ratio of 13.4±76.8 ppb ppm\textsuperscript{-1} (r=0.46, p=0.03; Fig. 16e). This ratio is similar to the ratios determined for air masses influenced by both fossil fuel emissions and biomass/biofuel burning during the same seasons. For example, based on the in-situ measurements in the upper troposphere during the CARIBIC flights between South China and Philippines in April 2007, Lai et al. (2010) reported the ΔCO/ΔCO\textsubscript{2} ratios of 15.6–29.3 ppb ppm\textsuperscript{-1} during pollution events influenced by both biomass/biofuel burning and fossil fuel combustion in Indochinese Peninsula. At PBL, CO is significantly and negatively correlated with CO\textsubscript{2} during JAS (r=-0.68, p=0.01; Fig. 16j). However, we note that the CH\textsubscript{4} abnormal event discussed in Sect. 3.2.2 is enriched in CO as well, and the negative relationship between CO and CO\textsubscript{2} would no longer exist if we removed the event (r=-0.45, p=0.16). The simultaneous enhancement of CO and CH\textsubscript{4} may suggest possible influences of biomass burning episodes, which we will explore in detail in Sect. 3.3. During JFM, no significant relationship is found between CO and CO\textsubscript{2} for PON or PBL (Fig. 16h and l).

3.3 Elevated CH\textsubscript{4} and CO events at PBL

In this section, we discuss two elevated CH\textsubscript{4} and CO events at PBL during the SW monsoon season. Significant enhancements of CH\textsubscript{4} and CO were observed on September 16, 2009 (July 29, 2011), with residuals from smoothed curves as high as 34.2 (29.2) ppb and 36.2 (17.9) ppb for CH\textsubscript{4} and CO, respectively. We further analyzed CH\textsubscript{4} and CO measurements at Bukit Kototabang (BKT – 0.20 °S, 100.32 °E, 845.00 m a.s.l.), Indonesia, located upwind of PBL when the southwest monsoon prevails. The flask measurements at BKT detected enhanced CH\textsubscript{4} and CO with a magnitude of 38.0 and 66.1 ppb on September 8, 2009, about
one week before the occurrence of the first CH\textsubscript{4} and CO event at PBL (Fig. 17a). The in-situ measurements at BKT also showed CH\textsubscript{4} and CO enhancements about one week before the second event at PBL, lasting over the period of 17 July–21 July 2011 (Fig. 17b). The coincidence of the two abnormal CH\textsubscript{4} and CO events at PBL and BKT possibly suggests influences of polluted air masses with common sources and origins. Moreover, the fire radiative power (FRP, mWm\textsuperscript{-2}) during the sampling dates implies that the two abnormal CH\textsubscript{4} and CO events could be related to fire emissions in Indonesia (GFAS product version 1.0; Kaiser et al. 2012; Fig. S16). Note that the mechanisms we propose for the abnormal CH\textsubscript{4} and CO events and the possible linkage between PBL and BKT during the SW monsoon season are still speculative. Model experiments are needed to further confirm these hypotheses.

4 Conclusions

In this paper we present the results of flask measurements of CO\textsubscript{2}, CH\textsubscript{4}, N\textsubscript{2}O, SF\textsubscript{6}, CO, and H\textsubscript{2} at three stations in India: Hanle (HLE), Pondicherry (PON) and Port-Blair (PBL), over the period of 2007–2011. Of these three stations, HLE is located at a high altitude and regarded as a continental background station in the mid-latitude of the Northern Hemisphere; PON is a tropical surface station located on the southwest coast of India, while PBL is an oceanic station located on the Andaman Islands, of similar latitude to PON. With a total of 188, 185, and 63 flask pair samples collected respectively from HLE, PON and PBL between 2007 and 2011 (for PBL between 2009 and 2011), and analyzed at LSCE, the program represents an important logistical and analytical effort to produce a unique dataset of atmospheric trace gas observations over the Indian subcontinent. The observed records will serve as an important source of information to infer regional patterns of trace gas fluxes and atmospheric transport in this under-documented region. Several conclusions and implications are drawn from the first analyses of the datasets.
The annual gradients of the atmospheric mole fractions observed at PON and PBL, with respect to HLE as a reference, suggest significant emission sources of CO$_2$, CH$_4$, N$_2$O, CO, and H$_2$ over the footprints of those stations. In particular, the annual mean N$_2$O mole fractions at PON and PBL are higher than at HLE by 3.1±0.3 and 3.8±1.7 ppb, notably larger than the typical N$_2$O gradients observed between stations in Europe or North America, indicating substantial N$_2$O emissions. The analyses of the atmospheric mole fractions with back-trajectories at the three stations further confirmed emission sources from South and NE India, and SE Asia, all of which are populous with high demand for food and energy, and thus high emissions from industrial, residential, and/or agricultural sectors. 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 SF$_6$ emissions are rather weak.

The seasonal cycles for each trace gas reflect not only the seasonal variations of natural sources/sinks and anthropogenic emissions over the Indian subcontinent, but also the seasonally varying atmospheric transport, especially the monsoon circulations (including convection). Strong influences of the monsoon circulations are well depicted by the contrasting phases of CH$_4$ seasonal cycles between HLE and PON/PBL. At HLE, the distinct CH$_4$ maximum during June-September is likely related to the enhanced biogenic CH$_4$ emissions from wetlands and rice paddies in summer, combined with deep convection associated with the SW monsoon that mixes surface emissions into the mid-to-upper troposphere. By contrast, the CH$_4$ seasonal cycles at PON and PBL have seasonal minima during the SW monsoon season, reflecting influences of southern hemispheric air depleted in CH$_4$ transported at low altitudes, as well as high rates of OH oxidation. Covariance between
species variations at the synoptic scale further helps identification and attribution of different sources and sinks, like fossil fuel combustion, biofuel burning and biogenic emissions. Besides, measurements of $\delta^{13}$C-CO$_2$ have been recently started for HLE, and the 4-D distributions of CO$_2$ and CH$_4$ have been realistically simulated using a chemical transport model (LMDz-OR-INCA, Hauglustaine et al., 2004; Folberth et al., 2006) with zoom over South and East Asia (manuscript in preparation). Both of them may serve as valuable tools to disentangle and quantify contributions of different sources and meteorology to trace gas signals.

Apart from the flask measurements of trace gases presented in this study for the three stations, in-situ continuous measurements of CO$_2$ and CH$_4$ have also been deployed at HLE, PON and PBL in parallel, which would considerably contribute to the value of the stations through high-frequency air sampling. While the three stations have the potential to provide useful constraints on estimates of trace gas fluxes over South and NE India (for example, Swathi et al. (2013) reported considerable reduction in the uncertainty of inverted CO$_2$ fluxes over temperate Eurasia by the inclusion of measurements at HLE), the monitoring network requires further expansion to sample air masses from other parts of the Indian subcontinent. Recently a few other atmospheric ground stations have been established in western India (Bhattacharya et al., 2009; Tiwari et al., 2011; Tiwari et al., 2014; Tiwari and Kumar, 2012) and the Himalayas (Kumar et al., 2010; Ganesan et al., 2013), with their concentration footprints covering Central India (e.g., the Sinhagad station; Tiwari et al., 2014; Tiwari and Kumar, 2012), the Indo-Gangetic Plains and a large extent of the Himalayas (e.g., the Dajeeling station; Ganesan et al., 2013). More efforts are needed to develop a comprehensive observation network with adequate spatial and temporal coverage in this region.
Acknowledgement

This study has been initiated within the framework of CaFICA-CEFIPRA project (2809-1). X. Lin acknowledges PhD funding support from AIRBUS D&S and ESF T Torch Short Visiting Grant for the 1st ICOS Science Conference (No. 6849). P. Ciais acknowledges support of the Synergy grant ERC-2013-SyG-610028 IMBALANCE-P of the European Research Council. The authors thank the engineers and staff from Indian Astronomical Observatory, Hanle, who have been helpful at the station in Hanle, and Mr. Manil Kumar, Mr. Shambhulinga and Mr. Prabhath Prabhu, who helped in flask sampling at Pondicherry University, Mr. B. Parmeshwar from National Institute of Ocean Technology for operating and maintaining the facilities in the stations. We also acknowledge the LSCE staff (L. Klenov, A. Crevier, B. Gal, C. Peureux, M. Grand, L. Hogrel, V. Bazantay and A. Orgun) taking in charge the RAMCES network logistics, measurements, and data processing.
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Table 1 Annual mean values, trend, and average peak-to-peak amplitudes of trace gases at HLE, PON, PBL and the two additional NOAA/ESRL stations – KZM and WLG. For each species at each station, the annual mean values and average peak-to-peak amplitude are calculated from the smoothed curve and mean seasonal cycle, respectively. The residual standard deviation (RSD) around the smoothed curve and the Julian days corresponding to the maximum (Dmax) and minimum (Dmin) of the mean seasonal cycle are given as well. Uncertainty of each estimate is calculated from 1 s.d. of 1000 bootstrap replicates.

<table>
<thead>
<tr>
<th></th>
<th>HLE</th>
<th>PON</th>
<th>PBL</th>
<th>KZM</th>
<th>WLG</th>
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<tbody>
<tr>
<td>CO₂ (ppm)</td>
<td></td>
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<tr>
<td>Annual mean 2007</td>
<td>382.3±0.3</td>
<td>386.6±0.9</td>
<td>–</td>
<td>382.7±0.2</td>
<td>384.2±0.2</td>
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<tr>
<td>Annual mean 2008</td>
<td>384.6±0.5</td>
<td>388.1±0.9</td>
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<td>385.7±0.2</td>
<td>386.0±0.2</td>
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<tr>
<td>Annual mean 2009</td>
<td>387.2±0.2</td>
<td>389.0±0.6</td>
<td>–</td>
<td>–</td>
<td>387.4±0.2</td>
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<tr>
<td>Annual mean 2010</td>
<td>389.4±0.1</td>
<td>391.3±1.5</td>
<td>387.6±0.7</td>
<td>–</td>
<td>390.1±0.2</td>
</tr>
<tr>
<td>Annual mean 2011</td>
<td>391.4±0.3</td>
<td>–</td>
<td>390.2±0.6</td>
<td>–</td>
<td>392.2±0.2</td>
</tr>
<tr>
<td>Trend (yr⁻¹)</td>
<td>2.1±0.0</td>
<td>1.7±0.1</td>
<td>–</td>
<td>–</td>
<td>2.0±0.0</td>
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<tr>
<td>(Trend at MLO: 2.0±0.0)</td>
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<td>353.0±87.8</td>
<td>341.0±78.3</td>
<td>298.0±6.5</td>
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Figures

**Figure 1 (a)** Five-day back-trajectories calculated for all sampling dates over the period 2007–2011 at Hanle (HLE), Pondicherry (PON), and Port Blair (PBL) during April–June (AMJ), July–September (JAS), October–December (OND) and January–March (JFM), respectively. Back-trajectories are colored by the elevation of air masses at hourly time step.

**Figure 1 (b)** Map of terrain over the zoomed box in (a), showing locations of HLE, PON and PBL. The digital elevation data are obtained from NASA Shuttle Radar Topographic Mission (SRTM) product at 1km resolution (http://srtm.csi.cgiar.org)
Figure 2 Time series of CO$_2$ flask measurements at (a) HLE and PON, (b) HLE and PBL, (c) HLE and KZM, and (d) HLE and WLG. The open circles denote flask data used to fit the smoothed curves, while the crosses denote discarded flask data lying outside 3 times the residual standard deviations from the smoothed curve fits. For each station, the smoothed curve is fitted using Thoning’s method (Thoning et al., 1989) after removing outliers.
Figure 3 (a) The mean CO$_2$ seasonal cycle at HLE, in comparison with the mean seasonal cycles derived from the in-situ CO$_2$ measurements over New Delhi at different altitude bands (3–4 km, 4–5 km, and 5–6 km) by the CONTRAIL project (2006–2010). (b) The mean CO$_2$ seasonal cycles at HLE, KZM, and WLG. (c) The mean CO$_2$ seasonal cycles at HLE, PON and PBL. For each station, the mean seasonal cycle is derived from the harmonics of the smoothed fitting curve in Fig. 2. Shaded area indicates the uncertainty of the mean seasonal cycle calculated from 1 s.d. of 1000 bootstrap replicates. For the CONTRAIL datasets, CO$_2$ measurements over New Delhi were first averaged by altitude bands. A fitting procedure was then applied to the aggregated CO$_2$ measurements to generate the mean season cycle for different altitude bands.
Figure 4 Time series of CH$_4$ flask measurements at (a) HLE and PON, (b) HLE and PBL, (c) HLE and KZM, and (d) HLE and WLG. The open circles denote flask data used to fit the smoothed curves, while the crosses denote discarded flask data lying outside 3 times the residual standard deviations from the smoothed curve fits. For each station, the smoothed curve is fitted using Thoning’s method (Thoning et al., 1989) after removing outliers.
Figure 5 (a) The mean CH$_4$ seasonal cycles observed at HLE, KZM and WLG. The mean CH$_4$ seasonal cycle derived from aircraft flask measurements by the CARIBIC project is also presented. The CARIBIC flask measurements in the upper troposphere (200-300 hPa) during 2005–2012 are averaged over the Indian subcontinent (10°N-35°N, 60°E-100°E) by month to generate the mean seasonal cycle. The error bars indicate 1 standard deviation of CH$_4$ flask measurements within the month. (b) The seasonal variations of CH$_4$ emissions from rice paddies and wetlands over the Indian subcontinent. The CH$_4$ emissions from rice paddies are extracted from a global emission map for the year 2010 (EDGAR v4.2), imposed by the seasonal variation on the basis of Matthews et al. (1991). The CH$_4$ emissions from wetlands are extracted from outputs of a global vegetation model (BIOME4-TG, Kaplan et al., 2006). The seasonal variation of deep convection over the Indian subcontinent is also presented, indicated by convective precipitation obtained from an LMDz simulation nudged with ECMWF reanalysis (Hauglustaine et al., 2004). The CH$_4$ emissions and convective precipitation are averaged over the domain 10–35 °N, 70–90°E to give a regional mean estimate. (c) The mean CH$_4$ seasonal cycles observed at HLE, PON and PBL. For each station, the mean seasonal cycle is derived from the harmonics of the smoothed fitting curve in Fig. 4. Shaded area indicates the uncertainty of the mean seasonal cycle calculated from 1 s.d. of 1000 bootstrap replicates.
Figure 6 Time series of N$_2$O flask measurements at (a) HLE and PON, (b) HLE and PBL. The open circles denote flask data used to fit the smoothed curves, while crosses denote discarded flask data lying outside 3 times the residual standard deviations from the smoothed curve fits. For each station, the smoothed curve is fitted using Thoning’s method (Thoning et al., 1989) after removing outliers.
Figure 7 The mean N$_2$O seasonal cycles observed at (a) HLE and PON, (b) HLE and PBL. For each station, the mean seasonal cycle is derived from the harmonics of the smoothed fitting curve in Fig. 6. Shaded area indicates the uncertainty of the mean seasonal cycle calculated from 1 s.d. of 1000 bootstrap replicates.
Figure 8 Time series of SF$_6$ flask measurements at (a) HLE and PON, (b) HLE and PBL, (c) HLE and KZM, and (d) HLE and WLG. The open circles denote flask data used to fit the smoothed curves. For each station, the smoothed curve is fitted using Thoning’s method (Thoning et al., 1989) after removing outliers.
Figure 9 The mean SF$_6$ seasonal cycles observed at (a) HLE and PON, (b) HLE and PBL. For each station, the mean seasonal cycle is derived from the harmonics of the smoothed fitting curve in Fig. 8. Shaded area indicates the uncertainty of the mean seasonal cycle calculated from 1 s.d. of 1000 bootstrap replicates.
Figure 10 Time series of CO flask measurements at (a) HLE and PON, (b) HLE and PBL, (c) HLE and KZM, and (d) HLE and WLG. The open circles denote flask data used to fit the smoothed curves, while the crosses denote discarded flask data lying outside 3 times the residual standard deviations from the smoothed curve fits. For each station, the smoothed curve is fitted using Thoning’s method (Thoning et al., 1989) after removing outliers.
Figure 11 The mean CO seasonal cycles observed at (a) HLE and PON, (b) HLE and PBL, (c) HLE and KZM, and (d) HLE and WLG. For each station, the mean seasonal cycle is derived from the harmonics of the smoothed fitting curve in Fig. 10. Shaded area indicates the uncertainty of the mean seasonal cycle calculated from 1 s.d. of 1000 bootstrap replicates.
Figure 12 Time series of H₂ flask measurements at (a) HLE and PON, (b) HLE and PBL, (c) HLE and KZM, and (d) HLE and WLG. The open circles denote flask data used to fit the smoothed curves, while the crosses denote discarded flask data lying outside 3 times the residual standard deviations from the smoothed curve fits. For each station, the smoothed curve is fitted using Thoning’s method (Thoning et al., 1989) after removing outliers.
Figure 13 The mean $H_2$ seasonal cycles observed at (a) HLE and PON, (b) HLE and PBL, (c) HLE and KZM, and (d) HLE and WLG. For each station, the mean seasonal cycle is derived from the harmonics of the smoothed fitting curve in Fig. 12. Shaded area indicates the uncertainty of the mean seasonal cycle calculated from 1 s.d. of 1000 bootstrap replicates.
Figure 14 The relationships between $\Delta CH_4$ and $\Delta CO$ at HLE (a–d), PON (e–h), and PBL (i–l) for April–June (AMJ), July–September (JAS), October–December (OND), and January–March (JFM). For each panel, $\Delta CH_4$ and $\Delta CO$ are estimated as residuals from smoothed curves. The $\Delta CH_4/\Delta CO$ ratio is the slope of the fitting line from the orthogonal distance regression, with the SD calculated from 1000 bootstrap replications.
Figure 15 The relationships between ΔCH₄ and ΔCO₂ at HLE (a–d), PON (e–h), and PBL (i–l) for April–June (AMJ), July–September (JAS), October–December (OND), and January–March (JFM). For each panel, ΔCH₄ and ΔCO₂ are estimated as residuals from smoothed curves. The ΔCH₄/ΔCO₂ ratio is the slope of the fitting line from the orthogonal distance regression, with the SD calculated from 1000 bootstrap replications. For ΔCH₄ and ΔCO₂ that is not significantly correlated, the fitting line is not plotted.
Figure 16 The relationships between ΔCO 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–March (JFM). For each panel, ΔCO and ΔCO$_2$ are estimated as residuals from smoothed curves. The ΔCO/ΔCO$_2$ ratio is the slope of the fitting line from the orthogonal distance regression, with the SD calculated from 1000 bootstrap replications. For ΔCO and ΔCO$_2$ that is not significantly correlated, the fitting line is usually not plotted.
**Figure 17** (a) The relationship between $\Delta$CH$_4$ and $\Delta$CO at PBL (colored by red) and BKT (colored by grey) during July–September (JAS) over the period of 2007–2011. $\Delta$CH$_4$ and $\Delta$CO are estimated as residuals from smoothed curves. The $\Delta$CH$_4$/ΔCO ratio is the slope of the fitting line from orthogonal distance regression (ODR), with the SD calculated from 1000 bootstrap replications. Two abnormal events at PBL are labeled, with enhancements of CH$_4$ and CO on September 16, 2009 and July 29, 2011, respectively. Enhancements of CH$_4$ and CO are also observed at BKT on Sep. 8, 2009. (b) Hourly CH$_4$ and CO measurements at BKT in July, 2011 (BMKG & EMPA). Enhancements of CH$_4$ and CO are observed during July 17-21, 2011.