

Anonymous Referee #2

General comments:

The paper presents a new record of flask sample observations of long-lived trace gases from two sites in mainland India and one site on the Andaman Islands. Data from the two mainland sites are presented from 2007 to 2011 and from the island site from 2009 to 2011. The target sampling frequency is weekly, though there are significant gaps in the record, sometimes weeks/months, due to bad weather and technical problems (see figure S2 in the supplement). The target compounds are CO₂, CH₄, N₂O, SF₆, CO and H₂. The paper describes in detail the sampling and analysis stages and the data processing techniques used to generate annual means, seasonal cycles and gradients between stations. The paper compares these new flask data with observations from stations in other countries such as Kazakhstan and China. An attempt is made to relate the seasonal cycles and gradients between stations to variations in natural GHG fluxes, anthropogenic emissions and monsoon circulations.

The Indian continent is currently experiencing rapid industrial development and as such is an important region globally for emissions of these long-lived trace gases. There appears to be a paucity of ground-based GHG measurements from this region and these observations go some way to filling the data gap. The authors should be encouraged to continue their observations and where possible improve future measurement frequency/reliability to avoid large data gaps. Have the authors considered analysing the flask samples for stable carbon isotope ratio which would be a big help in determining source apportionment especially for CH₄ and CO₂?

I recommend that this paper be published after consideration to the following minor specific comments and technical corrections.

An interactive comment indicated that a site in India at Sinhagad has been collecting samples for CO₂ and CH₄ analysis since 2009 (Y.K. Tiwari et al, 2014). The authors do refer to this paper in the conclusions (p 7204, line23) but could also refer to it earlier in the CO₂/CH₄ discussion section.

[Response] Thanks a lot for your careful review and comments. Until now flask sampling at the three stations and analyses of the flask samples are still on-going for the trace gases we investigated here. The analyses of ¹³CO₂ for HLE have been started but data are not available at the moment. The in-situ measurements of CO₂ and CH₄ have been deployed at HLE and PON as well. For PBL, the in-situ measurements have not been started yet due to logistical difficulties.

Following your suggestion, we referred to Tiwari et al., (2014) in *Section 3.1.1*. (Lines 432–434). We also referred to several other papers on Indian surface observations (Bhattacharya et al., 2009; Ganesan et al., 2013; Tiwari et al., 2011) and added more discussions in *Section 3.1* (Lines 429–434, 494–497, 534–536).

Specific comments (individual scientific questions/issues):

1 Introduction, page 7174, line 1: it would be useful to compare the estimated increase in GHG emissions from India (1.4 to 2.8 GtCO₂ eq) with the estimate from Europe or the USA.

[Response] Following your suggestion, we added this information in our manuscript (Lines 48–49). Between 1991 and 2010, anthropogenic GHG emissions in India increased by ~100% from 1.4 to 2.8 GtCO₂eq, much faster than rates of most developed countries and economies like the USA (9%) and EU (-14%) over the same period (EDGAR v4.2).

1 Introduction, page 7174, line 17: suggest to add a sentence defining what is meant by the top-down and bottom-up approaches.

[Response] Follow your suggestion, we revised this sentence to “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” (Lines 66–67).

1 Introduction, page 7174, line 24: suggest to extend the sentence starting ‘Notably, these ...’ to include a comparison of Indian bottom-up uncertainties with those from say Western Europe where inventories are more accurate.

[Response] Following your suggestion, we revised this sentence to “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” (Lines 72–75).

1 Introduction, page 7175, line 17: suggest add here an extra sentence describing key meteorological features of the NE winter monsoon.

[Response] During the winter monsoon period, little deep convection occurs over South Asia and the monsoon system carries less moisture than it does during the summer monsoon period (Lawrence and Lelieveld, 2010). Following your suggestion, we added a sentence describing key meteorological features of the NE winter monsoon to the manuscript (Lines 109–111).

2.1 Sampling stations, page 7176, line 15: I would like to see a map, possibly as an extra panel in Fig.1 centred and zoomed on India showing the three sampling stations and terrain.

[Response] Following your suggestion, we revised Fig. 1 and added an extra panel (Fig. 1b) zoomed over India to show locations of the three stations and terrain. Additionally, following other reviewers’ suggestions, we also modified the color scheme of Fig. 1, with back-trajectories colored by elevations of air masses instead of CO₂ levels.

2.1 Sampling stations, page 7177, line 8: suggest add sentence somewhere here describing the inlet location, height above the ground, type of inlet tubing used etc.

[Response] For HLE, the flask sampling inlet is installed on the top of a 3m 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". Following your suggestion, we added the sentence to the manuscript (Lines 159–161).

2.1 Sampling stations, page 7178, line 19: suggest add an extra sentence detailing the inlet location, inlet height above ground, type of tubing used etc.

[Response] For PBL, 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". Following your suggestion, we added the sentence to the manuscript (Lines 203–204).

2.2.1 Flask sampling, page 7179, lines 10-14: is the loss correction the same for both valve types used? If so please state in text.

[Response] No, this correction is only applied to the Teflon sealed flasks. We revised the manuscript accordingly for clarification (Lines 225–229).

2.2.1 Flask sampling, page 7179, lines 15-17: has the magnesium perchlorate drier been tested for loss of the target compounds?

[Response] Yes, we have performed tests and didn't find any influence of the magnesium perchlorate drier on the target gases.

2.2.2 Flask analyses, page 7180, lines 2-4: is the pressure inside each flask on arrival at LSCE the same as it was after filling in India? Some concern about loss/leakage during air-freight.

[Response] We cannot guarantee that the pressure inside each flask on arrival at LSCE is the same as it was after filling in India. If the flask pressure is too low, we will flag the sample during the flask analyses.

2.2.2 Flask analyses, page 7180, line 6: is this the Agilent micro-cell ECD? If so please state.

[Response] No, it is a standard ECD.

2.2.2 Flask analyses, page 7180, line 14: are samples flushed through the sample loop under the pressure inside the flask or is a pump used? If so, is the pump upstream or downstream of the sample loops?

[Response] No pump is used. We use the overpressure of the flasks. We revised the manuscript accordingly for clarification (Line 256).

2.2.2 Flask analyses, page 7180, lines 17-22: please also state column flow rates, oven temperature, isothermal or oven program etc.

[Response] Following your suggestion, we revised the manuscript (Lines 259– 268, also see Table S1).

2.2.2 Flask analyses, page 7180, line 25: please include more detail on the ECD detector temperature, make-up gas flow etc.

[Response] Following your suggestion, we added the temperature and flow rate in the manuscript (Lines 259– 268, also see Table S1). We don't use make-up gas here.

2.2.2 Flask analyses, page 7181, line 1: please include RGD detector temperature.

[Response] The oven temperature is kept at 105°C, and the catalytic chamber is heated to 265°C. Following your suggestion, we added this information to manuscript (Lines 268– 272, also see Table S1).

2.2.2 Flask analyses, page 7181, lines 2-7: are the working calibration cylinders filled with synthetic air or ambient air? Please state if they are filled by LSCE or purchased (then include supplier details). Also please state make and model of gas regulator used on the calibration cylinders.

[Response] The calibration and quality control cylinders are filled and spiked in a matrix of synthetic air containing N₂, O₂ and Ar prepared by Deutsche Steininger (Germany). Following your suggestion, we added this information to the manuscript (Lines 275– 276).

2.2.2 Flask analyses, page 7181, line 10: please name the international calibration scale used.

[Response] Following your suggestion, we added the international calibration scales used (Lines 282–285, also see Table S1).

2.3.2 Ratio of Species, page 7184, lines 2-7: please expand this section by adding a couple of sentences giving more detail of the procedure used.

[Response] Following your suggestion, we added a couple of sentences and references in *Section 2.3.2* to clarify the procedures we used to calculate the ratios of species and uncertainties (Lines 356–362).

3.1.2 CH₄, page 7187, line 1: the low observations of CH₄ at PBL in summer 2009 and 2011 are striking and should be mentioned here. Presumably the air arriving at PBL at this time of year has southern hemisphere origin, arriving on the SW monsoon flow.

[Response] As we mentioned in the paragraph describing the CH₄ mean seasonal cycles at PON and PBL (Lines 488–491), we attributed this summer minimum to influence of southern

hemispheric air transported at lower altitudes, the dilution effect by increased local planetary boundary layer height and higher rates of removal by OH.

3.1.3 N₂O, page 7188, lines 16-18: suggest compare the observed N₂O growth rate at HLE to say AGAGE northern hemisphere average growth rate.

[Response] Following your suggestion, here we compared the observed N₂O growth rate at HLE (0.8±0.0 ppb/yr) to that at MLO during the same period (1.0±0.0 ppb/yr). We revised the manuscript accordingly (Line 513).

3.1.4 SF₆, page 7192, lines 1-2: there is also a strong possibility that some of the episodic SF₆ pollution events originate in China.

[Response] Following your suggestion, we revised the manuscript (Lines 618, 640).

3.1.5 CO, page 7194, lines 26-28: China should also be considered as an influence on CO enriched air-masses arriving at PBL during NE monsoon.

[Response] Following your suggestion, we revised the manuscript (Line 715).

4 Conclusions, page 7203, lines 7-9: This sentence needs some qualification as it implies a five year history of observations at PBL when in fact only 2.5 years are available at that site with a long data break during 2010. The site at PBL is somewhat under-sampled in relation to HLE and PON.

[Response] Following your suggestion, we rephrased this sentence (Lines 955– 962).

4 Conclusions, page 7204, lines 17-26: In this paragraph the authors could mention any plans to continue flask sampling and if possible extend the measurement suite. Although in-situ continuous measurement techniques are hard to deploy reliably in these remote tropical locations this would add considerably to the value of the sites. The authors could also consider adding stable carbon isotope ratio analysis to the flask measurement process which help with source apportionment, especially for CO₂ and CH₄.

[Response] At present, analyses of δ¹³C-CO₂ have been started for HLE but data are not available yet. Isotopic measurements for CH₄ have not been started. Apart from the flask measurements of trace gases presented in this study for the three stations, in-situ measurements of CO₂ and CH₄ have also been deployed at HLE and PON in parallel, which would considerably contribute to the value of the stations through high-frequency air sampling. As you know, for PBL, the in-situ measurements have not been started yet due to logistical difficulties. Following your suggestion, we revised the conclusions accordingly (Lines 992–1001).

Figure 14, page 7235: I suggest also give in each panel the number of samples used to create each fitting line, there are noticeably fewer points available for PBL. Same also for Fig.15 and Fig. 16.

[Response] Following your suggestion, we revised Figs. 14–16 accordingly.

References

- King, A. W., Andres, R. J., Davis, K. J., Hafer, M., Hayes, D. J., Huntzinger, D. N., de Jong, B., Kurz, W. A., McGuire, A. D., Vargas, R., Wei, Y., West, T. O. and Woodall, C. W.: North America's net terrestrial CO₂ exchange with the atmosphere 1990–2009, *Biogeosciences*, 12(2), 399–414, doi:10.5194/bg-12-399-2015, 2015.
- Lawrence, M. G., and Lelieveld, J.: Atmospheric pollutant outflow from southern Asia: a review, *Atmos. Chem. Phys.*, 10, 11017–11096, 10.5194/acp-10-11017-2010, 2010.
- Luysaert, S., Abril, G., Andres, R., Bastviken, D., Bellassen, V., Bergamaschi, P., Bousquet, P., Chevallier, F., Ciais, P., Corazza, M., Dechow, R., Erb, K.-H., Etiope, G., Fortems-Cheiney, A., Grassi, G., Hartmann, J., Jung, M., Lathière, J., Lohila, A., Mayorga, E., Moosdorf, N., Njakou, D. S., Otto, J., Papale, D., Peters, W., Peylin, P., Raymond, P., Rödenbeck, C., Saarnio, S., Schulze, E.-D., Szopa, S., Thompson, R., Verkerk, P. J., Vuichard, N., Wang, R., Wattenbach, M. and Zaehle, S.: The European land and inland water CO₂, CO, CH₄ and N₂O balance between 2001 and 2005, *Biogeosciences*, 9(8), 3357–3380, doi:10.5194/bg-9-3357-2012, 2012.

Technical corrections (typing errors, etc.):

1 Introduction, page 7173, line 24: ‘... during the recent decades ...’

[Response] Following your suggestion, we revised it.

1 Introduction, page 7174, line 5 to 7: remove brackets from ‘... (in 2010, the per capita...)’ and make new sentence starting: ‘For comparison, in 2010, the per capita GHG emission rates ...’

[Response] Following your suggestion, we revised it.

1 Introduction, page 7174, line 8: ‘... agriculture-related ...’ replace with ‘... agricultural ...’

[Response] Following your suggestion, we revised it.

1 Introduction, page 7174, line 12: try to improve this sentence, e.g. ‘Reducing emissions of these two non-CO₂ greenhouse gases may offer a more cost-effective way to mitigate future climate change than by attempting to directly reduce CO₂ emissions (Montzka et al., 2011)’

[Response] Following your suggestion, we revised it.

1 Introduction, page 7176, line 8: suggest to re-arrange this sentence to remove brackets, for e.g. ‘We examine synoptic variations of CO₂, CH₄ and CO by analysing co-variances between species, using deviations from their smoothed fitting curves (Sect. 3.2).’

[Response] Following your suggestion, we revised it.

2.1 Sampling stations, page 7177, line 4: suggest to give HLE lat/lon co-ordinates to three decimal places. Same also for PON and PBL, with only two decimal places these two sites appear to be offshore.

[Response] Following your suggestion, we revised it.

2.1 Sampling stations, page 7177, line 15: suggest to re-arrange sentence for ease of reading, e.g. ‘... background free tropospheric air masses in the northern mid-latitudes.’

[Response] Following your suggestion, we revised it.

2.1 Sampling stations, page 7177, line 26: suggest to modify sentence, e.g. ‘The flask sampling inlet, was initially located on a 10m mast fixed on the roof of the University Guest House, was later moved to a 30 m high tower in June 2011.’ Also give the type of inlet tubing used.

[Response] For PON, the ambient air is pumped from the top of the tower through a Dekabon tubing with a diameter of 1/4". Following your suggestion, we revised it and added the sentence to the manuscript (Lines 180–182).

2.1 Sampling stations, page 7178, line 7: suggest to combine the sentences starting ‘Flask sampling ...’ and ‘Over the period ...’, how about: ‘Flask sampling began in September 2006 and over the period 2007–2011, a total of 185 flask sample pairs were collected at the site.’

[Response] Following your suggestion, we revised it.

2.2.2 Flask analyses, page 7180, line 4: ‘... HP86890 ...’

[Response] Following your suggestion, we revised it.

2.2.2 Flask analyses, page 7180, line 18: ‘... 3/16” ...’, is this the internal or external column diameter? Please state. Same on line 19 and 20. Use either “ or inches, both are used in text.

[Response] They all indicate external column diameters. We revised the manuscript accordingly.

3.1.2 CH₄, page 7188, line 7: ‘This These not only ...’

[Response] Following your suggestion, we revised it.

3.1.3 N₂O, page 7188, line 25: ‘We also analyze analyzed ...’

[Response] Following your suggestion, we revised it.

3.1.3 N₂O, page 7190, line 11-13: Improve sentence starting ‘One reason may be ...’, for example: ‘One reason may be that air arriving at the site during the SW monsoon period is relatively enriched in N₂O compared to CH₄, reflecting differences in their relative emissions along the air mass history.’

[Response] Following your suggestion, we revised it.

3.1.4 SF₆, page 7192, line 22: delete ‘southwesterly’ which would otherwise imply winds from the SW. Also consider China as well as Southeast Asia to explain some of the polluted air masses.

[Response] Following your suggestion, we revised it.

3.1.6 H₂, page 7195, line 27: ‘The mean H₂ seasonal cycle cycles ...’

[Response] Following your suggestion, we revised it.

3.2.1 $\Delta\text{CH}_4/\Delta\text{CO}$, page 7198, line 10: add ‘that’, so: ‘... estimates are 1.5 to 4 times that of the ...’

[Response] Following your suggestion, we revised it.

Table 1, page 7220: define RSD abbreviation in the caption, same for D_{max} and D_{min} . Consider also adding additional row after the trend row for each compound, giving northern hemisphere average trends say from the AGAGE network.

[Response] Following your suggestion, we revised the caption of Table 1. We also included in Table 1 the observed trends at MLO for CO_2 , CH_4 , N_2O , SF_6 and CO during the study period. The trend of H_2 is not presented because reliable data are not available yet at MLO for the study period.

Figure 2, page 7223: use “open circles” and “crosses” in the caption description rather than “o” and “x”. Same throughout the text, figure captions and in supplement.

[Response] Following your suggestion, we revised it.

Figure 3, page 7224: all three panels are too small.

[Response] Following your suggestion, we enlarge the three panels.

Figure 4, page 7225: Needs full caption, not just ‘same as Fig. 2 ...’

[Response] Following your suggestion, we revised it.

Figure 8, page 7229: Needs full caption, not just ‘same as Fig. 6 ...’

[Response] Following your suggestion, we revised it.

Figure 9, page 7230: Needs full caption, not just ‘same as Fig. 7 ...’. Also can the uncertainty shaded areas be made clearer?

[Response] Following your suggestion, we revised it. We also tried to make the uncertainty shaded areas of Fig. 7 clearer.

Figure 10, page 7231: Needs full caption, not just ‘same as Fig. 2 ...’

[Response] Following your suggestion, we revised it.

Figure 12, page 7233: Needs full caption, not just ‘same as Fig. 2 ...’

[Response] Following your suggestion, we revised it.

Figure 13, page 7233: Needs full caption, not just ‘same as Fig. 11 ...’

[Response] Following your suggestion, we revised it.

Figure 15, page 7236: Needs full caption, not just ‘same as Fig. 14 ...’

[Response] Following your suggestion, we revised it.

Figure 16, page 7237: Needs full caption, not just ‘same as Fig. 14 ...’

[Response] Following your suggestion, we revised it.

Supplement, Table S5: what is the reason for the grey shaded columns? Different instrument network? Same for Table S7 and Table S9.

[Response] Here the grey shaded columns indicate results for the reference stations. We did this for better display of the data. We revised the captions to clarify it.

Supplement, Figure S3: can the shaded uncertainty areas be made clearer?

[Response] The uncertainties of the mean CO₂ seasonal cycles for HLE, KZM and WLG are too small (relative to scales of the plot) to be visible. Following your suggestion, we tried to revised it and make the uncertainty shaded area in Fig. S3 clearer.

Supplement, Figure S7 caption: ‘ MHD, BGU, FIK, ~~FIK~~ and LPO ...’

[Response] Following your suggestion, we revised it.