Anonymous Referee #1

Received and published: 3 June 2015

Overall comments:

This study investigates the results of five-year sampling measurements of long-lived greenhouse gases (i.e. CO_2, CH_4, N_2O, and SF_6) and trace gases (i.e. CO and H_2) at three stations (Hanle, Pondicherry, and Port Blair) located in India. By the compounds in the collected air samples that measured by different analytical techniques, many approaches are made to investigate the regional features of the target compounds. The authors have characterized these trace gases with delta value ratios at these stations in different seasons. The data at numeric stations over Europe and the United States are also estimated and discussed.

My overall feeling to this manuscript is that all the target compounds are put together for discussion but little is mentioned regarding the relationship between them, especially for N_2O, SF_6, and H_2. What are the integrated findings that these compounds can together indicate? The authors are required to make more efforts to describe the scientific connections between these compounds. If the authors cannot adequately find major contribution of N_2O, SF_6, and H_2 that are relevant with other compounds, I would suggest remove them from this manuscript.

In addition, from the description and data presented in this manuscript, the PON site seemed to be easily influenced by local emissions, e.g. Pondicherry city with a population of ~240,00 at a distance of 8 km southward and a four-lane highway at ~80 m to the station. These can make the station not able to act as the regional background representative for the trace gases, especially for CO. I would suggest filter out the data that are possibly polluted significantly by local emissions at PON.

I suggest that this manuscript can get warranty for publication if these issues can be carefully revised or improved.

[Response] Thanks very much for your careful review and comments.

For the first general comment, in this study, we present the flask measurements of four GHG species (CO_2, CH_4, N_2O, SF_6) and two additional trace gases (CO, H_2) at three Indian stations. We put them together for several reasons. First, emissions of all the four GHG species contribute to global warming, and regularly reporting emissions and removals of these gases is required by the United Nations Framework Convention on Climate Change (UNFCCC). Although CO and H_2 are not greenhouse gas by themselves, both of them play critical roles in the CH_4 budget as products of CH_4 oxidation and as competitors 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).

Second, the importance of N_2O and SF_6 also rests in the fact that their emission patterns in India notably differ from those of the USA and Western Europe, where estimates of GHG budgets are better known and more accurate. As suggested by *Section 3.1.3*, there are substantial N_2O emission sources in the Indian subcontinent, most of which contributed by agricultural activities. SF_6 is widely considered as a good tracer for anthropogenic activities because it is extremely stable with purely anthropogenic sources (Maiss et al., 1996). While India ranked as the world's third largest GHG emitter in 2010 (EDGAR v4.2), unlike the USA and EU countries, its SF_6 emissions are rather weak as suggested by *Section 3.1.4*.

Last but not least, for all the trace gases, the variations of concentrations are influenced by atmospheric transport, including circulation of the monsoon system. For example, as shown in *Section 3.1.2* and *Section 3.1.3*, the summer maximum observed at HLE for both CH_4 and N_2O are likely related to the deep convection that is associated with the SW monsoon and mixes surface emissions of both species (and probably others) into the mid-to-upper troposphere. Following your suggestions, we revised the manuscript and clarify the importance of the trace gases we investigated in the study, especially for N_2O, SF_6, CO and H_2 (Lines 500–508, 588–595, 643–654, 720–726).

For the second general comment, we agree that 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. Therefore, we used two approaches to minimize the influences of local GHG sources/sinks. First, we took flask air samples at PON between 12:00 and 18:00 local time (actually 97% between 12:00 and 14:00 local time), when the sea breeze moves towards land and the boundary layer air is well mixed (see *Section 2.1* for details). The recirculation of continental air mass during the sea breeze period should average regional influences, even though the footprint of PON is less than those of HLE and PBL. Second, when we performed the CCGVU curve-fitting, any data lying outside 3 SD of the residuals were regarded as outliers and discarded from the time series, and this procedure was repeated until no outliers remained (Harris et al., 2000; Zhang et al., 2007) (see *Section 2.3.1* for details). These outliers were likely a result of pollution by local emissions and not representative of regional background concentrations (denoted by crosses in each panel of Fig. 2, 4, 6, 8, 10 and 12). We believe that through these two approaches the local influences at PON should be sufficiently minimized.

Further, following your suggestion, we also tried to use CO as a tracer for local emissions and filtered time series of other species by CO outliers. That means, for each species (other than CO), we removed the samples with abnormal CO values before the curve-fitting procedures. As shown in Table R1 and Fig. R1, filtering time series by CO outliers does not make significant difference to the trends, seasonal cycles and mean annual gradients (relative to

HLE) for other species at this station. On the other hand, however, this filtering approach may substantially decrease the number of samples used to fit the smooth curve (e.g. ~38% for CH_4) and result in larger data gaps (Table R1, Fig. R1), probably compromising reliability of the analyses. Therefore finally we didn’t use CO as a tracer of local emissions for additional filtering.

Specific comments:

Introduction: The authors have clearly indicated their research motivation on studying the GHGs in the introduction section. However, little is discussed about the additional trace gases (i.e. CO and H_2). What are the relationships between the GHGs and the additional trace gases scientifically? Please also address the importance of CO and H_2 for this study.

[Response] As we replied to your general comment #1, although CO and H_2 are not greenhouse gas by themselves, both of them play critical roles in the CH_4 budget as products of CH_4 oxidation and as competitors 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). Following your suggestions, we revised the manuscript and clarify the importance of CO and H_2 at the beginning of *Section 3.1.5* and *Section 3.1.6* (Lines 643–654, 720–726)

Section 2: Please provide the data availability. For example, the website of the data provided by LSCE, NOAA, aircraft measurements, etc.

[Response] Following your suggestion, we added in the manuscript the websites for the data from the NOAA and ICOS networks, as well as the CONTRAIL and CARIBIC projects. The dataset of flask measurements at Hanle, Pondicherry and Port Blair will be made available in the near future on the World Date Centre for Greenhouse Gases (WDCGG) website (http://ds.data.jma.go.jp/gmd/wdcgg/).

Figure 1: Not just CO_2 being discussed in this manuscript. Therefore I think the elevation of a trajectory is more important than its CO_2 level in this figure. By doing so, the 3-D traveling routes of air masses can be clearly viewed, which also can provide useful information for other trace gases. The authors can try to merge the vertical data of the trajectories in Figure S5 into Figure 1.

[Response] Follow your suggestion, we revised Fig. 1 and colored the back-trajectories by elevations of air masses instead of CO_2 levels. Additionally, following Reviewer #2's suggestion, we also added an extra panel (Fig. 1b) zoomed over India to show locations of the three stations and terrain.

Section 2.2.2: It seems that there were three channels for separating respective compound pairs (i.e. channel #1: CO_2 and CH_4, channel #2: N_2O and SF_6, channel #3: CO and H_2). However, the descriptions are given based on different part of a GC technique (e.g. sample loop, column, detector, etc.), which is quite easy to get readers confused. In order to improve the readability, the authors are encouraged to rephrase this paragraph based on different compound pairs.

[Response] Following your suggestion, we revised the second paragraph of *Section 2.2.2* to improve readability (Lines 259–272).

Page 7181 Line 24: stemmed

[Response] Follow your suggestion, we revised it.

Figure 2: The 4 subplots are recommended to be merged into 1 or 2 plots. This comment also applies to Figure 4, 6, 8, 10, and 12.

[Response] Thanks a lot for your suggestion. We did this previously as you suggested. However, in this way data points and smoothed curves from different stations overlap heavily. To better display contrasts between pairs of stations in trends, annual gradients and seasonal cycles, we didn't revise the plots.

Figure 3: The CO_2 levels are shown in relative scales. What are those "zeros" on the y-scale representing? Please clarify. Furthermore, the mean seasonal variations can contain some errors obtained from the increasing trends. In order to avoid this, the authors can estimate the detrended seasonal curves by subtracting the growth rates.

[Response] As we mentioned in *Section 2.3.1* (Lines 333–337), 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). The mean seasonal cycles we present at Fig. 3 (and many others) are already detrended by removing the growth rates. That's why we have "zeros" on the y-axes. We revised the caption to make it more clear and precise.

Figure 3(b): There are three lines in the figure, but only two are shown in the legend.

[Response] Following your suggestion, we revised it.

Page 7186 Line 11: How good is the agreement between the flask measurements at HLE and aircraft measurements over New Delhi? Please quantify.

[Response] The correlation coefficients between harmonics of the mean seasonal cycles derived from the flask measurements at HLE and the CONTRAIL measurements over Delhi are 0.98–0.99 ($p<0.001$). We also added this information in the text (Line 394).

Page 7186 Line 29: than those at HLE by . . .

[Response] Following your suggestion, we revised it.

Page 7188 Line 24 “The annual mean N_2O mole fraction at HUN was higher than at Mauna Loa (MLO) and Mace Head (MHD) by only 1.6 and 1.3 ppb, respectively.”: I think this sentence is referring the study at HUN and is irrelevant to this study.

[Response] The HUN (46.95 °N, 16.65 °W, 248 m a.s.l.) station is a rural monitoring station located in Hungary in Central Europe (Haszpra et al., 2008). Here we would like to compare the N_2O gradients observed between PON, PBL and HLE with the typical gradients observed in Europe and the US. As shown in *Section 3.1.3*, results showed that the N_2O gradients between PON, PBL and HLE are larger than typical N_2O gradients observed between stations scattered in Europe or in North America, suggesting substantial N_2O in the Indian subcontinent. Following your suggestion, we removed the N_2O gradient between HUN and MLO. The HUN observations and its gradients to MHD serve as an example to indicate the magnitude of N_2O sources in Central Europe, therefore we think it is relevant to the study and didn’t remove it from the manuscript.

Page 7188 Line 25: I do not think it is necessary to use the data observed at so many stations in this manuscript. It is better to choose just one background station at similar latitude or in nearby region to be compared with the Indian sites. For instance, the authors may choose GMI or MLO as the reference to be compared with PON and PBL. Or use NWR and JUN (Jungfraujoch) as the background reference station for United States and Europe, respectively. This comment is not only for N_2O, but also for other compounds such as SF_6 discussed in other sections.

[Response] Here we chose HLE as a background station simply because it is located in India and closest to PON and PBL. Any gradient in trace gas concentrations between PON, PBL and HLE would suggest regional sources/sinks easily. The principle is also applicable to stations in the USA and Europe used in this study.

Page 7189 Line 17 “more noisy due to regional sources and synoptic variability”: Why is N_2O the only compound influenced by the regional sources and synoptic variability? Why are other compounds like CO_2 and CH_4 not influenced due to the same reasons?

[Response] When we argue that the seasonal cycle of N_2O is noisier compared to CO_2 and CH_4 in the manuscript, it means the N_2O seasonal cycle has a larger uncertainty (i.e. lower signal-to-noise ratio and precision, also indicated by the wide shaded area in Fig. 7). Given that the N_2O seasonal cycle is very small, synoptic events are more likely to mask the seasonal signal. As shown in Table 1, if we take the ratio of the seasonal cycle amplitude to the residual standard deviation (RSD, an indicator of synoptic variability) as a surrogate of the signal-to-noise ratio, we find that this ratio is significantly lower for N_2O (2.0, 1.5 and 2.0 for HLE, PON and PBL) than CO_2 (11.1, 1.9 and 7.1 for HLE, PON and PBL) and CH_4 (3.2, 3.6, 6.3 for HLE, PON and PBL). Following your suggestion, we revised the statement in the manuscript for clarification (Lines 542–543).

Page 7191 Line 14 “the SF_6 mole fractions at HUN over the years of 1997-2007 are higher than those at MLO and MHD by ...” Line 19 “At HFM, the SF_6 mole fractions are higher than those of the NWR on average by 0.15...”: I think these sentences are irrelevant to this study.

[Response] Thanks a lot for your careful review comments. As we replied to your general comment #1, SF_6 is widely considered as a good tracer for anthropogenic activities because it is extremely stable with purely anthropogenic sources (Maiss et al., 1996). As shown in *Section 3.1.4*, the SF_6 gradients between PON, PBL and HLE are slightly negative, whereas the stations in Europe or in North America show positive SF_6 gradients above the background. While India ranked as the world’s third largest GHG emitter in 2010 (EDGAR v4.2), unlike the USA and EU countries, its SF_6 emissions are rather weak. We think the comparisons with stations in the USA and Europe are relevant to this study and didn’t remove it from the manuscript.

Page 7193 Line 13 “The PON and PBL stations are influenced by CO regional emissions, mainly due to biofuel and agricultural burning over South and Southeast Asia.": As mentioned above, I think PON station can be easier affected by local emissions from the Pondicherry city or the four-lane high way nearby.

[Response] As we replied to your general comment #2, we agree that 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. Therefore, we used two approaches to minimize the influences of local GHG sources/sinks. First, we took flask air samples at PON between 12:00 and 18:00 local time (actually 97% between 12:00 and 14:00 local time), when the sea breeze moves towards land and the boundary layer air is well mixed (see *Section 2.1* for details). The recirculation of continental air mass during the sea breeze period should average regional influences, even though the footprint of PON is less than those of HLE and PBL. Second, when we performed the CCGVU curve-fitting, any data lying outside 3SD of the residuals were regarded as outliers and discarded from the time series, and this procedure was repeated until no outliers were identified (Harris et al., 2000; Zhang et al., 2007) (see *Section 2.3.1* for details). These outliers were likely a result of pollution by local emissions and not representative of regional background concentrations (denoted by crosses in each panel of Fig. 2, 4, 6, 8, 10 and 12). We believe that through the two approaches the local influences at PON should be sufficiently minimized. Therefore the substantial and positive CO gradient between PON and HLE generally reflects regional sources rather than local influences.

Section 3.3: It seems that the PBL and PON site are at a similar location and elevation. Were CH_4 and CO elevated at PON due to the SW monsoon as well? How about the impacts of the monsoon prevails at PON? Please discuss that in this section.

[Response] Thanks a lot for your careful review and comments. We don’t know if PON also detected the two elevated CH_4 and CO events observed at PBL that could be related to biomass burning emissions in Indonesia. We don’t have enough data from flask measurements to test it. Besides, at PON this signal could be masked by influences of other CH_4 and CO sources (e.g. residential energy use, transportation, etc.) from South India. Note that the mechanisms we proposed for the abnormal CH_4 and CO events and the possible linkage between PBL and BKT during the SW monsoon season are speculative, and need further verification with model experiments.

References

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Maiss, M., Steele, L. P., Francey, R. J., Fraser, P. J., Langenfelds, R. L., Trivett, N. B. A., and Levin, I.: Sulfur hexafluoride—A powerful new atmospheric tracer, Atmos. Environ., 30, 1621-1629, http://dx.doi.org/10.1016/1352-2310(95)00425-4, 1996.

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Yevich, R., and Logan, J. A.: An assessment of biofuel use and burning of agricultural waste in the developing world, Global Biogeochem. Cy., 17, 1095, 10.1029/2002gb001952, 2003.

Tables

Table R1 Features of the smoothed fitting curves for flask measurements at PON (2007–2011). For each species, the smoothed curves are fitted to the data not filtered by CO outliers and the data filtered by CO outliers. The annual mean values and average peak-to-peak amplitude are calculated from the smoothed curve and mean season cycle, respectively. Uncertainty of each estimate is calculated from 1 s.d. of 1000 bootstrap replicates.

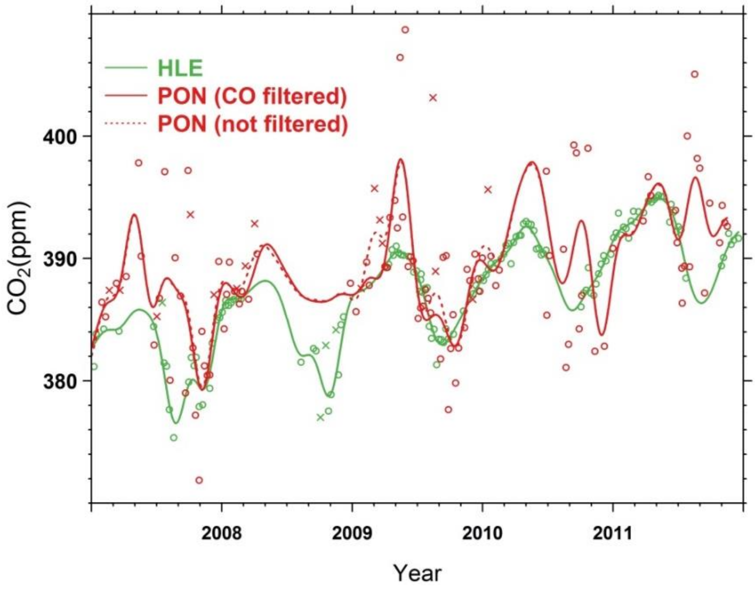
	Not CO filtered	CO filtered
CO_2 (ppm)		
N_{fit}	121	105
Annual mean 2007	386.6±0.9	386.5±1.1
Annual mean 2008	388.1±0.9	388.0±0.9
Annual mean 2009	389.0±0.6	388.4±0.8
Annual mean 2010	391.3±1.5	391.2±1.5
Annual gradient relative to HLE	2.9±1.2	2.6±1.4
Trend	1.7±0.1	1.7±0.1
RSD	4.0	4.1
Amplitude	7.6±1.4	7.8±1.6
D_{max}	111.0±13.4	116.0±14.1
D_{min}	327.0±54.3	327.0±55.8
CH_4 (ppb)		
N_{fit}	164	101
Annual mean 2007	1859.2±6.7	1854.2±5.9
Annual mean 2008	1856.1±10.4	1857.3±6.8
Annual mean 2009	1865.7±5.1	1855.5±6.2
Annual mean 2010	1876.9±9.1	1877.3±7.3
Annual gradient relative to HLE	37.4±10.7	34.0±11.0
Trend	9.4±0.1	9.0±0.1
RSD	34.4	19.8
Amplitude	124.1±10.2	127.8±11.4
D_{max}	337.0±6.1	331.0±5.4
D_{min}	189.0±10.7	192.0±9.8
N_2O (ppb)		
N_{fit}	137	110
Annual mean 2007	324.8±0.3	324.9±0.4
Annual mean 2008	326.3±0.3	326.3±0.3
Annual mean 2009	326.7±0.3	326.4±0.3
Annual mean 2010	327.1±0.5	327.0±0.5
Annual gradient relative to HLE	3.1±0.3	3.0±0.3
Trend	0.8±0.1	0.7±0.1
RSD	1.4	1.4
Amplitude	1.2±0.5	1.1±0.5

D_{max}	262.0±83.2	262.0±46.1
D_{min}	141.0±48.2	97.0±65.8
SF_6 (ppt)		
N_{fit}	174	139
Annual mean 2007	6.19±0.01	6.19±0.02
Annual mean 2008	6.49±0.02	6.49±0.02
Annual mean 2009	6.77±0.01	6.77±0.02
Annual mean 2010	7.08±0.02	7.08±0.02
Annual gradient relative to HLE	-0.06±0.03	-0.06±0.03
Trend	0.31±0.05	0.31±0.06
RSD	0.05	0.05
Amplitude	0.24±0.02	0.24±0.03
D_{max}	327.0±12.1	327.0±21.7
D_{min}	204.0±3.3	205.0±3.4
CO (ppb)		
N_{fit}	139	139
Annual mean 2007	200.5±7.8	200.5±7.8
Annual mean 2008	175.3±13.1	175.3±13.1
Annual mean 2009	174.3±4.8	174.3±4.8
Annual mean 2010	185.1±8.7	185.1±8.7
Annual gradient relative to HLE	82.4±10.7	82.4±10.7
Trend	0.4±0.1	0.4±0.1
RSD	32.0	32.0
Amplitude	78.2±11.6	78.2±11.6
D_{max}	4.0±160.2	4.0±160.2
D_{min}	238.0±46.1	238.0±46.1
H_2 (ppb)		
N_{fit}	140	120
Annual mean 2007	574.5±2.4	573.7±3.2
Annual mean 2008	558.2±5.3	558.3±5.1
Annual mean 2009	562.4±1.6	561.9±1.6
Annual mean 2010	563.9±2.3	563.0±2.5
Annual gradient relative to HLE	29.8±4.1	29.3±3.7
Trend	-1.3±0.1	-1.3±0.1
RSD	8.4	8.3
Amplitude	21.6±3.4	21.1±3.8
D_{max}	96.0±9.6	97.0±9.8
D_{min}	219.0±10.3	215.0±11.9

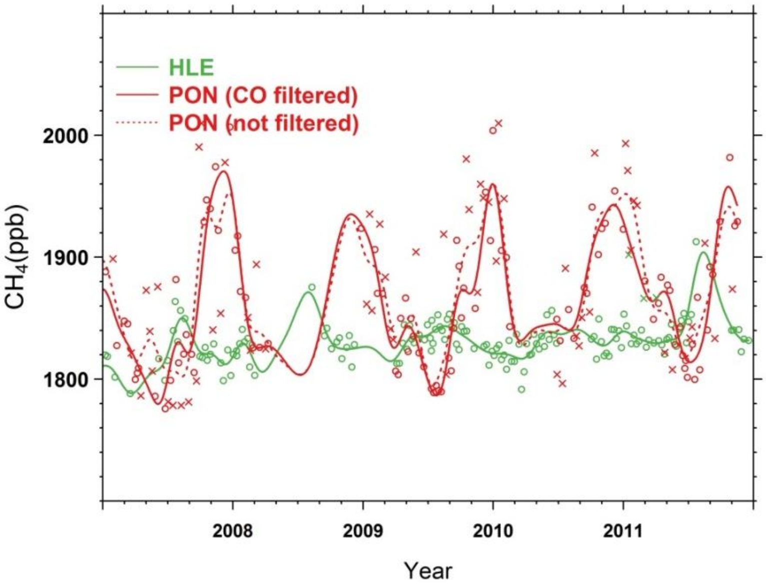
Figures

Figure R1 Time series of flask measurements at PON (2007–2011) with smoothed fitting curves for **(a)** CO_2, **(b)** CH_4, **(c)** N_2O, **(d)** SF_6 and **(e)** H_2. The open circles denote flask data used to fit the solid smoothed curves, while the crosses denote discarded flask data lying outside 3 times the residual standard deviations from the smoothed curve fits as well as those filtered by CO outliers. For PON, the solid (dotted) red line indicates the smoothed curve fitted to the data (not) filtered by CO outliers. The flask measurements at HLE and the corresponding smoothed fitting curve are also presented for comparison.

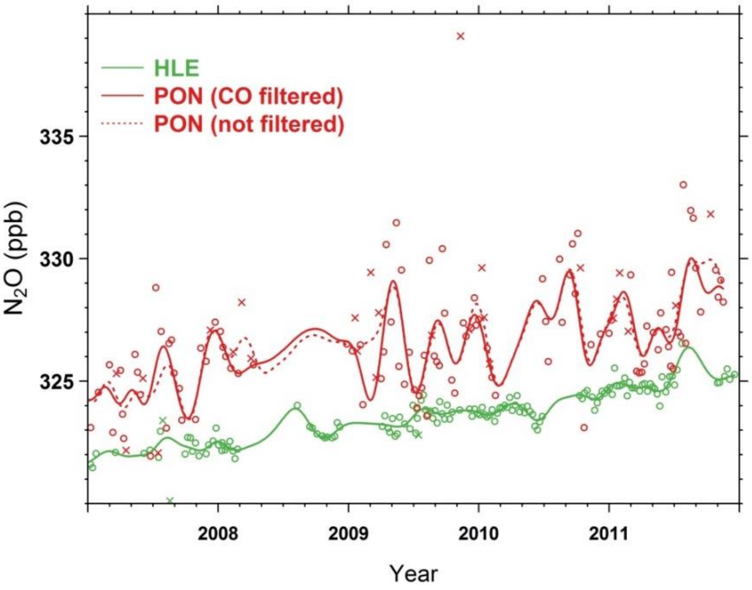
a)



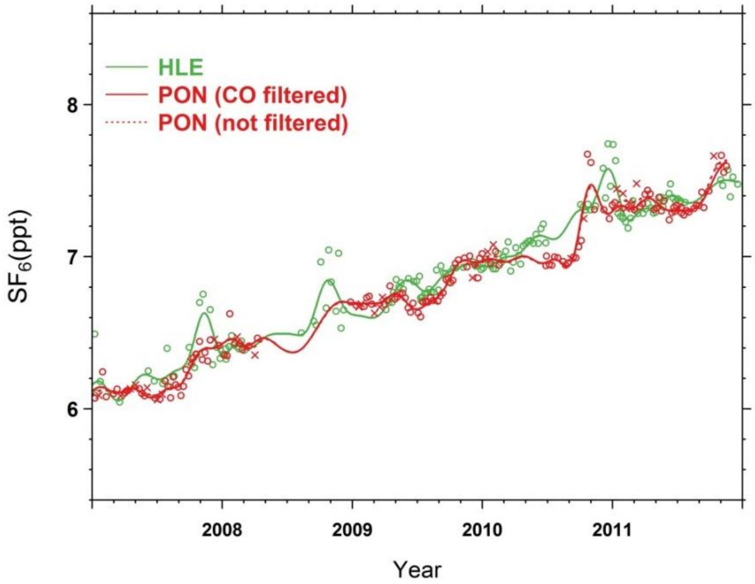
b)



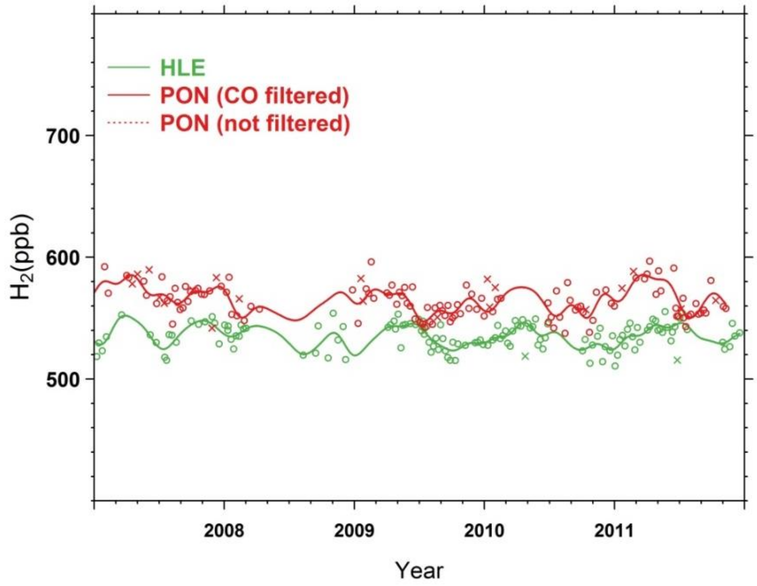
c)


HLE
PON (CO filtered)
PON (not filtered)
N_2O (ppb)
335
330
325
2008
2009
2010
2011
Year

d)


HLE
PON (CO filtered)
PON (not filtered)
SF_6(ppt)
8
7
6
2008
2009
2010
2011
Year

e)


HLE
PON (CO filtered)
PON (not filtered)
H_2(ppb)
700
600
500
2008
2009
2010
2011
Year