

Chemical composition of pre-monsoon air in the Indo–Gangetic Plain measured using a new PTR-MS and air quality facility: high surface ozone and strong influence of biomass burning

V. Sinha et al., 2013 (ACPD)

Reply to reviewers

We thank both the reviewers for their very encouraging comments regarding the relevance of the submitted work, the quality of measurements and their positive recommendation to publish the work in ACP. The authors greatly appreciate the careful reading and comments of the reviewers which has resulted in some excellent suggestions for the final version.

Accordingly, please find below our point–wise replies to the same, listing also the specific changes made for the revised submission to ACP. The reviewer’s comments are marked in bold.

REFEREE 1

This paper describes in-situ measurements of several volatile organic compounds (VOCs) at the Indo-Gangetic Plain (IGP) in the pre-monsoon season, using proton transfer reaction mass spectrometry (PTR-MS) deployed by the authors within India for the first time, along with air pollutants such as CO, NO_x, O₃, SO₂, and aerosols. Ambient levels and diurnal variations of the VOCs in the IGP region are summarized. The reported data will be worth understanding the chemical processes controlling the formation of surface ozone and secondary organic compounds in the IGP region where one seventh of the world population lives. The paper is generally well-written. In particular, the instrumentation is fully described and I have trust in the quality of the data obtained in the present study. I recommend this paper to be published in Atmospheric Chemistry and Physics after the authors’ consideration of my specific and technical comments detailed below.

Specific comments:

(1) At Page 31786, Lines 6-7, the authors mentioned “the time periods affected by wheat residue burning were filtered out”. Please denote the time periods affected by wheat residue burning in Experimental section.

Done.

The following text has been added to the Experimental section after line 13, Page 31766 of the discussion paper:

“The most intense pollution occurred when plumes affected by wheat residue burning emissions impacted the site during the following periods: 3rd May 19:23 - 23:33 ; 7th May 08:10 - 09:37; 10th May 07:15 - 08:00; 11th May 19:39 - 20:39; 16th May 05:38 - 06:34 and 31st May 21:00 - 23:59.”

(2) Sec. 3.3: Did the authors remove the data of the time periods affected by wheat residue burning for the correlation analysis? I recommend for the authors to show examples of scatterplots. And how about the correlation between VOCs and CO. Is there any difference in the slopes from the data during the time periods affected by wheat residue burning and the data during the time periods affected by residential biofuel cooking, garbage burning and leaf litter. The slope of VOC versus CO indicates

the emission ratio of the VOC to CO if the air mass is fresh. I believe that it is very informative.

As noted in Section 3.3 (Page 31782, lines 23-26 of the discussion paper), the data for time periods affected by wheat residue burning was removed from the correlation analysis in order to investigate the typical night-time emission sources.

We agree with the reviewer's suggestion that showing examples of the scatter plots would be helpful. We have now added a new Figure to the supplementary material (as Figure 4) for the important pairs: methanol and acetonitrile, acetaldehyde and acetonitrile, acetone + propanal and acetonitrile, isoprene and acetonitrile, acetonitrile and NO_x, C8- aromatics and NO_x.

In the revised manuscript, the following text has also been added on page 31782 after line 26: "Examples of the scatter plots using the 1 minute temporal resolution nighttime data for correlations with acetonitrile and NO_x for methanol, acetone + propanal, acetaldehyde, isoprene and C-8 aromatics can be found in Figure 4 of the supplementary material."

We agree with the reviewer that the VOC to CO correlation plots could be informative, so much so that we feel this topic is worthy of a separate publication. The focus of the present study is on providing the technical details of the new measurement facility, detailed site description and typical summertime levels of VOCs and air pollutants on diel and temporal scale along with explanations of the observed features. As noted in the discussion paper, emission signatures of different sources often over-layed, and as CO has stronger and more diverse emission sources than VOCs and NO_x, hence the VOC to CO emission ratios will require more extensive analysis. In the planned study on VOC to CO emission ratios, we also wish to combine the analysis of the VOC to CO emission ratios for both wheat residue (April-May) and paddy residue (October-November) combustion activity in addition to data from other seasons.

This is now conveyed in Section 4 (Conclusion) of the revised manuscript (after Line 11 on Page 31789 of discussion paper) as follows:

"Analysis of the VOC to CO emission ratios wherein the wheat residue combustion periods (occurring in April-May every year) and paddy residue combustion periods (occurring in October-November every year) are analyzed together with data from other seasons (e.g. winter and monsoon), would be helpful in constraining the regional source profiles and emission strengths. This work is already underway and the results will be communicated in a separate study (Chandra et al., in prep.)."

(3) Page 31813, Fig. 9: How about diurnal variations of acetone(+propanal), C8-aromatics, C9-aromatics, PM10, and PM2.5? I recommend for the authors to add the figures, at least to supplement.

We thank the reviewer for this pertinent suggestion.

We have added a new figure to the supplementary material (Figure 5) showing the diurnal variations of PM₁₀, PM_{2.5}, C-8 aromatics, C-9 aromatics and acetone + propanal.

In the revised manuscript, we describe the new Figure and highlight the bimodal nature of the diel profiles observed for all these species after Line 12, Page 31787 of the discussion paper as follows:

"Figure 5 of the supplementary material shows the box and whisker plots for PM₁₀, PM_{2.5}, C-8 aromatics, C-9 aromatics and acetone + propanal, which also exhibit the same bimodal nature observed in Figure 9."

Technical corrections:

(1) Title: Although the authors may say that the PTR-MS instrument was deployed for the first time within India and the IGP, the PTR-MS instrument used in the present work is not new but typical. The words “a new PTR-MS” make readers misunderstood.

We thank the reviewer for drawing attention to this alternative interpretation. Our intention in using the adjective “new” was to highlight the new facility that was set up in the Indo-Gangetic Plain and used in this study. Taking into account the possibility for misinterpretation highlighted by the reviewer, we have now changed the title of the revised manuscript to “Chemical composition of pre-monsoon air in the Indo–Gangetic Plain measured using a new air quality facility and PTR-MS: high surface ozone and strong influence of biomass burning”

(2) Page 31762, Line 13: N. W. IGP -> the North West IGP

Done

(3) Page 31765, Line 5: Dolgorouky et al., 2010 -> Dolgorouky et al., 2012

Done

(4) Page 31766, Line 7: I cannot find the cities of Chandigarh and Panchkula in Fig. 2.

We note that the city of Chandigarh is shown in Figure 2 of the discussion paper (both legend and the dot in the red urban land use are shown). Panchkula is not shown separately from Chandigarh as it is less than 11 km from Chandigarh and on the land use map which has a scale of 100 km x 200 km, it would not come out distinctly.

To clarify this we have added the following text to Section 2.1 of the revised manuscript: (after Line 30 on Page 31767 of discussion paper):

“Panchkula (not shown in Figure 2) is less than 11 km from Chandigarh (labelled in Figure 2 and shown as dot) and lies to its south east.”

(5) Page 31770, Line 17: What is “5.0 grade”? Please show the purity, for example >99.999%.

Done.

Now the purity has been mentioned in the text and the new line in the revised manuscript reads as follows:

“The instrumental background was determined at all the relevant m/z channels at frequent intervals by sampling cylinder zero air (5.0 grade or > 99.999 % purity synthetic air; Sigma Gases, New Delhi) that had been passed through an activated charcoal scrubber (Supelpure HC, Supelco, Bellefonte) and a heated VOC scrubber catalyst (Ionimed Analytik) maintained at 350⁰ C in series to ensure good background measurements.”

(6) Page 31781, Line 1: “Loo-winds” may be not familiar to many readers. I suggest for the authors to add some explanations or show some references.

Done; we thank the reviewer for this kind suggestion.

The following text and reference has been added to the revised manuscript. “Loo winds are very hot and dry westerly winds which blow in the plains of northern India and Pakistan in the months of May and June typically in the afternoon (Rana 2007).”

(7) Page 31787, Line 23: The unit of the rate constants is missing.

Done, we thank the reviewer for pointing out this omission.

The units of rate constants are now added. The line now reads “If there was no day time emission of isoprene between 07:00–10:00 LT, considering that isoprene is oxidized 100 times faster than benzene by ambient hydroxyl radicals ($k_{\text{isoprene}+\text{OH}} = 1.1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K; $k_{\text{benzene}+\text{OH}} = 1.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K; Atkinson et al., 2003), a sharper decrease would have been expected for isoprene relative to benzene between 07:00–10:00 LT.”

(8) Page 31800, Table 1: The units of “ppbv” and “nmol/mol” coexist. It should be noted that “ppbv” is the same as “nmol/mol”.

Done.

A footnote has been added to Table 1 mentioning that ppbv is the same as nmol mol^{-1}

(9) Supplement, Page 3: Figure caption of “actual” Fig. 2 is wrong; Figure 1 -> Figure 2.

Done

The numbering of Figures in the supplement has been corrected

(10) Supplement, Page 4: Figure caption of “actual” Fig. 3 is wrong; Figure 2 -> Figure 3. in addition, “may” used in the figure caption should be “May” (3 places).

Done

The numbering of Figures in the supplement has been corrected

REFEREE 2

This paper describes a new high quality atmospheric chemistry observation station in a very important part of the world where very little data is available. The station is impacted by many types of globally important undersampled sources such as cooking fires, agricultural burning, and dust storms. It is also impacted by more conventionally sampled urban and biogenic sources, but in a new context. I don't see any major problems with the paper and fully support publishing these relevant results. I do have some suggestions that I think could strengthen the paper.

General

1. One more thorough proofreading would help. I'll point out a few of the typos or sentences that could be shortened or reorganized in my specific comments, but not an exhaustive list.

We greatly appreciate the reviewer for her/his time and effort in pointing out such instances. Several of the typos and omissions actually crept into the paper during the typesetting process and eluded us during the proof reading. For the revised manuscript we will be more careful with the proof reading and typos.

2. The authors could insert a brief explanation somewhere why they show data for only May 2012 and what is status of the other data from the station. Maybe the station came on line on 1-May and then the monsoon arrived and those data may be presented separately? Then at least some of the data from the station during the next dry spell Oct-Nov 2012 is already published in the Sarkar et al paper cited in Current Science. So a timeline for the station, the fate of the data, and possibility of access by modellers for model validation, would all be of interest in a few sentences.

We thank the reviewer for this excellent suggestion and plead guilty to not acknowledging the tremendous coverage of quality measurements that has been accomplished by us! Accordingly we have now inserted a new Figure in the revised manuscript (which appears as the new Figure 1) to show the timeline for when different measurements came online. Our choice for analyzing the data from May 2012 was primarily due to the simultaneous availability of all instrumental data measured at the facility. Moreover, several interesting features typical of the North West Indo-Gangetic Plain in summer such as wheat residue burning, large scale dust storms characterize the month of May. The trace gas and VOC measurements commenced on 16th August, 2011 and have been running till date (13.03.2014). It required an additional 4 months to install the meteorological station and PM inlets and for the facility to attain full functionality. The only major gap in the PTR-MS data till date, occurred due to failure of a pump inside the instrument resulting in downtime from 14.12.2011- 22.02.2012. This information is clearly shown in the new Figure. The possibility to access the measurement data by the modellers has been communicated at various international fora in several conferences by the authors (e.g. IGAC Open Science conference 2012, EGU General Assembly 2012, and the AGU Fall Meeting 2013) as well as in national workshops/symposia. In addition a link to the facility is available at <http://www.iisermohali.ac.in/facilities/AtmosChemfacility/index.html>, where a data request form will soon be uploaded for external users.

In the revised manuscript, we have also added the following new paragraph to accompany the new Figure as per the reviewer's excellent suggestion (after line 14 Page 31765 of the discussion paper):

“Figure 1 shows the timeline of the data coverage until 13.03.2014 for different instrumental measurements ever since the facility became operational on 16.08.2011. The trace gas and VOC measurements were the first to become available and it took an additional 4 months to install the meteorological station and PM analyzers to attain full functionality for the facility. The only major break in the PTR-MS data as shown in Figure 1 occurred due to the failure of a pump inside the instrument resulting in downtime from 14.12.2011- 22.02.2012. In this work we focus on data acquired in May 2012, a period where all instrumental measurements were available (see Figure 1), and which is characterized by several typical regional summertime events occurring in the North West Indo-Gangetic Plain such as wheat residue burning, large scale dust storms and intense photochemistry.”

3. The authors have done a good job of explaining the instrumental details. It does make the paper a bit long. It's OK as is, but they might want to move a few details to the supplement they already have or just cite a reference in a few cases if possible. This enables the reader to get to the interesting discussion faster. The one tricky subject is that the NO_x analyzer sounds more like a NO_y analyzer. The authors described the

situation fairly in the text, but should probably footnote the “NO₂” data in tables and specify in figure captions to see the text discussion.

We thank the reviewer for the compliment.

As this is the first comprehensive paper from our site that reports all the measurements performed using the new facility in the N.W. IGP, we wanted to detail the important technical aspects and quality assurance procedures employed at the facility. We feel this is very important for the readers as it would enable them to have confidence in the scientific analyses derived from the dataset. Hence we prefer to keep the text as it is.

However we agree that the reviewer’s suggestion to highlight the limitation of the NO_x measurements more prominently is a good one. Hence in the revised manuscript we now footnote Table 2, Table 4, Figure 7 (Figure 6 of discussion paper) and Figure 9 (Figure 8 of discussion paper), wherever the NO_x/ NO₂ measurements are mentioned as follows:

“refer Section 2.2.3 for details of the NO_x measurements”

4. Maybe Figures 1 and 2 can be improved with larger overall size, larger type, and possibly a different color scheme? Maybe a detailed, zoom, inset of few km around station – that is then located with slanted lines to a box on a larger more easily read map of the region?

We prefer to retain Figure 1 and 2 of the discussion paper as they are for the following reasons:

- 1) Figure 1 b nicely shows the relevant fetch region for the measurements reported in this work.
- 2) Figure 2 is already a zoomed inset of Figure 1 b showing important urban agglomerates.
- 3) The colour scheme used in Figure 1b and Figure 2 is helpful as it is consistent with the land classification map colour scheme used by the European Space Agency (ESA) GlobCover 2009 Project

5. A number of studies have observed furan/“isoprene” ratios on m/z 69 for various types of biomass burning and are summarized in Akagi et al., (2011). They range from 0.29 (for crop residue – similar to the authors value) to 8.5. This and/or the original studies should be acknowledged. Then a later study using FTIR and the NOAA GC-MS presents actual furan/isoprene ratios and also shows there can be a significant amount of other C₅H₈ alkenes besides isoprene (Yokelson et al., (2013) and small amounts of carbon suboxide. The conclusions about high isoprene at night from biomass burning are still valid and interesting, but can be qualified a bit more.

We thank the reviewer for drawing our attention to the very relevant reference of Akagi et al. (2011).

This is now discussed in the revised manuscript (after line 2, Page 31779 of the discussion paper) as follows:

“Akagi et. al. (2011) have previously reported emission factors (in g/kg) due to combustion of different types of biomass. An emission ratio of 0.11 and 0.38 was observed from crop residue for furan and isoprene, respectively implying a furan/isoprene emission ratio of 0.29, which is close to the ratio of 0.25 suggested in this work.”

6. In a few spots (mostly page 31777) I suggest potential additional brief analysis.

Done

Please see replies to the detailed comments regarding text on Page 31777. Several significant changes have now made in the revised manuscript (listed in replies to specific comments below) and in our opinion, we have now provided sufficient detail of the general trends in the time series of gas phase species and aerosol mass concentrations, with a discussion of the influence of varied biomass burning and a massive dust event.

7. Adopting one consistent set of common units (ppb or ppbv?) throughout could make it easier to read and easier to compare values.

Done.

In the revised manuscript we use ppbv everywhere instead of ppb.

Detailed comments:

P31762, L11: “a” met station

Done.

The new sentence is as follows:

“A new atmospheric chemistry facility that combines India’s first high sensitivity proton transfer reaction mass spectrometer, an ambient air quality station and a meteorological station, was used to quantify in-situ levels of several VOCs and air pollutants in May 2012 at a suburban site in Mohali (N.W. IGP).”

P31762, L16: might read easier to use ppb throughout

Done.

nmol mol^{-1} is same as ppbv. Now we also mention the same in the footnote of Table 1.

P31762, L15-20: Maybe give the single values first and then give ranges?

We note that this is the abstract where average levels for different groups of VOCs (e.g. oxygenated and aromatic) and individual VOCs (acetonitrile and isoprene) are listed. Thus, where VOC groups are referred to, the range of the average mixing ratios of the VOCs that comprise the group are given and where individual VOCs are referred to, single values for the average levels of the compound have been given.

P31762, L23: delete “activity”

Done.

The new sentence reads “Wheat residue burning caused massive increases (> 3 times of baseline values) for all the measured VOCs and primary pollutants.”

P31762, L28: The abstract and text say the O3 exceeded 100 ug/m3, the figure shows nmol mol^{-1} and it might be easiest to consistently use the common ppb term everywhere.

I realize mass and mixing ratio are not exactly equivalent, but the mixing ratio equivalent of the standard for typical May conditions at the station could be given in parentheses.

Done.

The revised text is as follows:

“Surface ozone exceeded the 8 h national ambient air quality limit of $100 \mu\text{g}/\text{m}^{-3}$ (~ 50 ppbv) on a daily basis, except for 17 May 2012, when a severe dust storm event ($\text{PM}_{2.5} > 800 \mu\text{g}/\text{m}^{-3}$; $\text{PM}_{10} > 2700 \mu\text{g}/\text{m}^{-3}$) characterized by long range transport from the west impacted the site.”

P31763, L27: should “equally” be “also”

Done

We agree “also” is a better choice here.

P31764, L8-9: eliminate “but in contrast very little data on hydrocarbons has been acquired.” Since it is explained better and in more logical order just below.

Done

P31764, L13: Define BTEX

Done

The BTEX compounds are now specified in parenthesis. BTEX (Benzene, Toluene, Ethylbenzene, Xylenes).

P31764, L26: Of possible interest to the authors is that studies have shown that the combination of O3 and SO2 is more dangerous to crops than O3 alone. E.g. work of Joseph Hindawi: <http://nepis.epa.gov/Adobe/PDF/9100E3K3.PDF> page 25.

Done

We thank the reviewer for the suggestion and have included the reference with the following additional text:

“The synergistic effect of multiple pollutant exposure, for example for crops due to ozone and sulphur dioxide exposure simultaneously has been shown to be even more dangerous (Hindawi, 1970).”

P31765, Paragraph one: this might be easier to read organized as follows

“Comprehensively instrumented measurement sites in other regions of the world have yielded important data on the chemistry of ozone and aerosol formation. Examples include . . . ”

Done

We thank the reviewer for this suggestion and have rephrased the entire paragraph as follows:

“Comprehensively instrumented measurement sites in other regions of the world have yielded important data on the chemistry of ozone and aerosol formation. Examples include the ”Station for Measuring Forest Ecosystem-Atmosphere Relations” (SMEAR II) at Hyytiala in

Finland (e.g., Hari and Kulmala, 2005), and short term but comprehensively instrumented field experiment sites such as CALNEX over Los Angeles (Holzinger et al., 2013) in California, MEGAPOLI (Dolgorouky et al., 2012) in Paris, MCMA (Molina et al., 2007) and MILAGRO (Molina et al., 2010) in Mexico city.”

P31765, L14-21: This sentence also might work better as two sentences or leaving out some details.

Done

We agree with the reviewer that the sentence construction was too lengthy and tardy. As noted in reply to the reviewer’s general comment 2, we have added the following new paragraph (after line 14 Page 31765 of the discussion paper):

“Figure 1 shows the timeline of the data coverage until 13.03.2014 for different instrumental measurements ever since the facility became operational on 16.08.2011. The trace gas and VOC measurements were the first to become available and it took an additional 4 months to install the meteorological station and PM analyzers to attain full functionality of the facility. The only major break in the PTR-MS data as shown in Figure 1 occurred due to the failure of a pump inside the instrument resulting in downtime from 14.12.2011- 22.02.2012. In this work we focus on data acquired in May 2012, a period where all instrumental measurements were available (see Figure 1), and which is characterized by several typical regional summertime events occurring in the North West Indo-Gangetic Plain such as wheat residue burning, large scale dust storms and intense photochemistry.”

We have also deleted lines 14-21 on Page 31765 of the discussion paper, and now added the following lines only after the above paragraph as follows:

“The impact of regional emission activities such as open wheat residue burning, other types of biomass burning and a severe dust event on the ambient chemical composition of pre-monsoon air in the IGP was quantified using the unique dataset.”

P31766, L6: May not be necessary to give precise location a second time here.

As this is the start of the site description in the Experimental section, we prefer to repeat the precise location.

P31766, L7: population of cities in parentheses?

Done

Population of the cities as per census report 2011 (censusindia.gov.in) have now been added in parentheses. The new sentence is as follows:

“The measurement facility is housed inside the campus of the Indian Institute of Science Education and Research (IISER), a suburban site (30.667 °N–76.729 °E, 310 ma.s.l.) several kilometres away from the city centres of Mohali (Population 146,104), Chandigarh (Population 960,787) and Panchkula (Population 210,175).”

P31766, L27: Ludhiana looks like it may be as big as Chandigarh though it is further away. Give population?

Done

Ludhiana is much bigger as compared to Chandigarh both in terms of population and area. Population of both Ludhiana and Patiala have now been added in the revised manuscript. The new sentence is as follows:

“The land use in the wind sector spanning south to north-north-west (180–315⁰) is mainly rural and agricultural land for several hundred kilometres except for two wind directions: Patiala (~60 km from site at wind direction of ~215⁰, Population- 405,164) and Ludhiana (~100 km from site at wind direction of ~285⁰ Population- 1,613,878).

P31768, L8: Does the PTR-MS have higher sensitivity than average? If so, it might be good to specify that? If not maybe say something like: “A PTR-MS for sensitive VOC measurements”

We have used the phrase “high sensitivity proton transfer reaction mass spectrometer (PTR-MS)” to distinguish it from the other PTR-MS instrument models manufactured by the company Ionicon analytik which have lower sensitivity (e.g. the PTR-QMS 300 model; detection sensitivity < 300 pptv).

P31768, L11: using mixing ratios here, which I like and think is most common, easiest to read, and shorter.

Thank you

P31769, L16-23: Probably not necessary to describe the four main parts of PTR-MS since several good review articles that do the same thing are already cited.

We prefer to keep the description for ease of readers who are not PTR-MS experts. Note the review articles of de Gouw et al., 2007 and Blake et al., 2009 are included.

P31770, L28: Here or maybe later or both, a summary of published biomass burning measurements of the isoprene/furan emission ratio is in Akagi et al., 2011 as noted above, with some additional more recent values at Yokelson et al., 2013.

Done

We have added the references of Akagi et al., 2001 and Yokelson et al., 2013 (after Line 28 on Page 31770 of the discussion paper).

Note that in reply to point 5 raised by the reviewer we also discussed the relevant work of Akagi et al. 2011 in the Results and Discussion section as follows:

“Akagi et. al. (2011) have previously reported emission factors (in g/kg) due to combustion of different types of biomass. An emission ratio of 0.11 and 0.38 was observed from crop residue for furan and isoprene, respectively implying a furan/isoprene emission ratio of 0.29, which is close to the ratio of 0.25 suggested in this work.”

P31771-2: The calibration procedures are very sound! It could be moved to supplement though if authors preferred as well.

Thank you for the appreciation. See reply to point 3 above for reasons to retain it where it is currently.

P31773, L23-29: The inner construction of the CO analyzer is probably covered in a citable paper and could be omitted here.

Agreed

We have now removed the aforementioned text (Lines 23-29 on Page 31773 of the discussion paper) from the revised manuscript, as several works have already been cited in this paragraph where the said description can be found.

P31774, L13: re the “hydrocarbon kicker” – if it is described by Luke, 1997 move the citation closer; if it is known to remove all or most non-methane organic gases (NMOG) state that since hydrocarbons are a small fraction of total NMOG in smoke.

Done

Luke 1997 described both the aspects (i.e. the interference caused by highly fluorescent aromatic hydrocarbons e.g. benzene, toluene, o-xylene, m-xylene, p-xylene, m-ethyl toluene, ethylbenzene and 1,2,4-trimethylbenzene and the role of hydrocarbon kicker in the analyzer) We have moved the citation closer as follows:

“ The hydrocarbons (e.g toluene, o-xylene, m-xylene, p-xylene, m-ethyltoluene, ethylbenzene and 1,2,4-trimethylbenzene) present in ambient air are removed by passing the sample through a hydrocarbon kicker (Luke, 1997), as they can cause interference by also fluorescing at 350 nm.”

P31774, L26-7: no need to mention the 185 nm line.

Done

Line 25, Page 31774 has been removed

P31775, L5-6: Minor point. It shouldn't matter if a single, split light source intensity decreases since the instrument uses a ratio of the two channels, however if there are two detectors and their sensitivity declines at unequal rates, then the zero checks are probably useful.

There are two separate detectors at the end of each of the cell in the O₃ analyzer and their sensitivity might decrease at unequal rates. Hence zero checks are useful.

P31775, L11-25: The authors have done an excellent job of describing the limitations of the NO₂ data. As is, it is somewhere between an NO₂ and NO_y measurement. There are a few more papers they may wish to cite (by Pollack, Fehsenfeld, Williams) that describe measurements of NO_y with Mo or Au catalysts and NO₂ with UV photolysis.

Two more thoughts are:

1. In biomass burning smoke most of the NO₂ is converted to PAN and nitrate within just 2-4 hours. See Akagi et al., (2012) and references there-in to Alvarado et al., etc. Probably important to mention/cite this.

2. Since many people may just glance at figures and tables and skip the experimental section, the authors would ideally flag the word NO₂ in figure captions and tables and direct the reader to Sect 2.2.3.

We thank the reviewer for his/her kind words. We have already addressed point 2 in the reply to his/her general comment 3 as follows:

Hence in the revised manuscript we now footnote Table 2, Table 4, Figure 7 (Figure 6 of discussion paper) and Figure 9 (Figure 8 of discussion paper), wherever the NO_x/NO_2 measurements are mentioned as follows:

“refer Section 2.2.3 for details of the NO_x measurements”

With regard to point 1 mentioned here, we believe that adequate care has already been taken in describing the NO_x measurement principle used in this work and its implications. The other works mentioned by the reviewer, while very important, are not critical to the description in Lines 11-25, Page 31775 of our discussion paper.

P31777, L2: Fig. 6. I would put the PM species on a log scale or use a break in the scale to capture the peak of the dust event and still be able to see the rest of the data.

Done

We thank the reviewer for this good suggestion.

PM species have now been plotted on a log scale in Fig. 6 (Figure 7 of revised version).

P31777, L16: Fig 3 in supplement is the third figure in supplement, but the figures are numbered wrong in the supplement.

The numbering of the Figures in the supplement has been corrected.

P31777, L18-22: By comparing the peaks for other species “X” to the CO peak one comes up with “quick and dirty” X/CO ratios that are potentially due largely to wheat residue burning and can be compared to crop residue emission ratios (ER) to CO in the literature such as the collection in Akagi et al., (2011). The comparison of these rough ratios to Akagi et al is of course not exact, but not bad either for most species considering the inherent variability in biomass burning (BB) ER, the fact that it may be different crops, and the reactivity of some of the species. The two things that seem most different from usual BB ER are: (1) the high SO_2/NO_2 ratio, which is greater than 60% in this work, but usually lower than 10% in other work. That could indicate that more than one source contributes to the mix of pollutants observed, which would not be surprising. Perhaps industries such as brick kilns burning coal (or tires) which have higher S content than biomass? See Maithel et al., (2012) and/or Christian et al., (2010), where the latter may also be a good reference for garbage burning the authors note later. The “quick and dirty” analysis above should be improved by subtracting background values before computing ER to CO. (2) the benzene and toluene ratios to CO are close to 1%, which is about 3 times higher than normal for BB. Again this could simply suggest other sources (traffic) are contributing to the mix as the authors themselves show in their Sect 3.3 (p31783. L8-12). None of this makes this work “wrong” or less important, it makes it more interesting.

As noted in a related reply to Reviewer 1, we agree that the X/CO ratios would be informative, so much so that we feel this topic is worthy of a separate publication. The focus of the present study is on providing the technical details of the new measurement facility,

detailed site description and typical summertime levels of VOCs and air pollutants on diel and temporal scale along with explanations of the observed features. As noted in the discussion paper, emission signatures of different sources often over-layed, and as CO has stronger and more diverse emission sources than VOCs and NO_x, hence the VOC or X to CO emission ratios will require more extensive analysis. In the planned study on VOC or X to CO emission ratios, we also wish to combine the analysis of the VOC to CO emission ratios for both wheat residue (April-May) and paddy residue (October-November) combustion activity with data from different seasons. This will make the entire X/CO emission ratio analyses more meaningful and robust.

This is now conveyed in Section 4 (Conclusion) of the revised manuscript (after Line 11 on Page 31789 of discussion paper) as follows:

“Analysis of the VOC to CO emission ratios wherein the wheat residue combustion periods (occurring in April-May every year) and paddy residue combustion periods (occurring in October-November every year) are analyzed together with data from other seasons (e.g. winter and monsoon), would be helpful in constraining the regional source profiles and emission strengths. This work is already underway and the results will be communicated in a separate study (Chandra et al., in prep.)”

P31777, L22-23: Depending on how you define VOC or NMOG, etc. the authors could give themselves some credit for measuring a few organic trace gases (e.g. benzene, toluene, . . .) emitted by crop residue fires in India in the Sarkar et al paper.

Done

The text in the revised manuscript (replacing Lines 22-23 on Page 31777 of the revised manuscript) reads as follows:

“Except for the recent study by Sarkar et al. (2013), no in-situ data on the release of volatile organic compounds from crop residue burning in India has been reported till date.”

P31777, L26: acetonitrile is misspelled

The spelling of acetonitrile has been corrected

P31777, L27: How do the authors determine times that were “not impacted by wheat residue burning”? I agree that the industrial source of methanol is well described later and many other types of BB are extremely likely, but wondering how agricultural burning can be ruled out. If a lack of hotspots that might be mentioned, but also with the caveat that a lot of crop residue burning is missed by active fire detection as shown in Table 1 of Yokelson et al., (2011) and discussed there-in.

The reviewer is correct in her/his surmise. These timings were regarded as non wheat residue burning events on the basis of the preceding 96 h MODIS fire counts (at 80% confidence interval) and 72 h back trajectory of the air masses characterized by the peaks. We agree that by using this stringent approach, some lower intensity wheat residue burning fires could have been excluded but preferred this approach nevertheless, so that attribution to wheat residue burning events was beyond doubt.

We now mention this clearly by additions to the text (shown in bold below for Line 2-3; Page 31778 of discussion paper) as follows:

“During these other ‘non–wheat residue burning’ biomass burning peaks (**classified to be “non wheat residue burning” peaks because of the absence of MODIS fire counts in the preceding 96 h period over the fetch region ascribed by the 72 h back trajectory for the air masses that showed the peaks**), aromatics and isoprene also appear to have been co–emitted.”

P31778, L1-15: This is a great discussion of the probable complexity of the pollutant sources in the region. It’s daunting, but also a major reason why this work is so important. Fortunately, the authors have an excellent start in this paper.

Thank you

P31778, L16 - P31779, L15: Good discussion. An option is to add a few BB furan/ isoprene references as noted above near P31779, L1. The author’s estimate of ~25% is remarkably close to the 29% for crop residue burning in Akagi et al., (2011).

Done

Please see previous replies.

P31779, L10-15: Are the author’s measurements above the predictions of the MEGAN model? If not going to compare maybe omit this?

Done

We have removed the aforementioned lines from the revised manuscript.

P31779, L13: “is not well not constrained” delete second “not” – also sentence kind of long.

See reply to previous comment. All lines from L13-L15 have been removed.

P31779, L18: If the authors are saying their site is a few km downwind of urban centers then the following paper (and references there-in) showing enhanced O3 production when BB emissions mix with urban emissions may be of interest. Akagi et al., (2013) also contains information on BB emissions of isoprene and monoterpenes and their likely night-time chemistry. However, glancing at the figure it seems that large O3 peaks occur every day, which would include times the authors have identified as unaffected by wheat residue burning. Maybe there are statistically significant O3 increases on days affected by BB?

The scenarios and works referred to by the reviewer do not appear to be relevant to the conditions experienced in our study. Firstly the intense wheat residue burning periods (or BB as per the reviewer) that impacted our site occurred almost always at night and never in the afternoon when solar radiation availability is most conducive for ozone formation. Secondly, the large amount of fresh NO emitted in the plumes arising from the nighttime wheat residue

burning or BB burning in fact tended to suppress ozone levels at our site (can be seen in Figure 6 of discussion paper) due to the NO + O₃ titration.

P31779, L23: in parentheses after standard (~50 ppb) might help?

Done

P31780, L1-24: Long inconclusive discussion: maybe just state the conclusion that OH reactivity measurements would be useful in the future in 1-2 sentences.

We respectfully disagree with the reviewer. One of the major results of the paper are the high surface ozone levels and hence it is worth examining if the peak ozone production is sensitive to:

(i) only VOCs or (ii) both VOCs and NO_x or (iii) only NO_x.

The discussion presented in L1-L24 on Page 31780 narrows down the peak ozone production to either case (ii) or (iii), which is an important deduction and points to the potentially worrisome impact of increasing NO_x point sources (power plants, more cars etc..) on future ozone levels.

P31780, L25: start a new paragraph.

Done

P31781, L1: define “Loo winds”

Done; we thank the reviewer for this kind suggestion.

The following text and reference has been added to the revised manuscript (after L1, Page 31781 of discussion paper):

“Loo winds are very hot and dry westerly winds which blow in the plains of northern India and Pakistan in the months of May and June typically in the afternoon (Rana 2007).”

P31781, L12-13: Mexico City “summertime” is the rainy season and MCMA was in the spring (March), which was the dry season. On the other hand Paris measurements were in the rainy, summer season. Maybe better title is “Comparison with selected other urban measurements”

Agree.

We have rephrased Section 3.2 as : “Comparison of ambient levels with selected urban sites”

P31782, L5 and Table 3: is “Texas” more precisely “Houston”?

We thank the reviewer for this detail. The site was indeed closer to Houston and we have now made changes to reflect this in the text (Line5; Page 31782) and Table 3 of Discussion paper.

P31782, L20 – P31783, L2: I’m not sure if night-time ambient levels (especially starting as soon as 6 pm) reflect just emissions since the emissions emitted during the day travel

to Mohali. It might be interesting to see what correlations occur if starting the averaging period at midnight instead?

We have checked out the reviewer’s suggestion and examined the change in the correlations considering a midnight start for the averaging period. There is no significant difference in the values obtained for all the inter VOC correlations (please also see reply to next comment). This implies that the nighttime primary emission sources exert a much stronger control on the ambient levels of the VOCs, in comparison to the daytime upwind emissions that get transported to the site. The present and new correlation coefficients (shown in parentheses) are given below for completeness sake:

Table 5: Inter VOC correlation analysis of nighttime data

	Methanol	Acetonitrile	Acetaldehyde	Acetone	Isoprene	Benzene	Toluene	C8 aromatics	C9 aromatics
Methanol	1	0.6(0.7)	0.5(0.6)	0.6(0.7)	0.4(0.5)	0.5(0.6)	0.3(0.4)	0.3(0.3)	0.2(0.2)
Acetonitrile	-	1	0.8(0.8)	0.5(0.5)	0.5(0.6)	0.4(0.4)	0.2(0.3)	0.2(0.2)	0.2(0.1)
Acetaldehyde	-	-	1	0.4(0.3)	0.6(0.7)	0.4(0.4)	0.2(0.2)	0.2(0.2)	0.2(0.1)
Acetone	-	-	-	1	0.3(0.4)	0.4(0.4)	0.2(0.2)	0.2(0.2)	0.2(0.1)
Isoprene	-	-	-	-	1	0.5(0.5)	0.4(0.5)	0.4(0.4)	0.3(0.3)
Benzene	-	-	-	-	-	1	0.6(0.6)	0.8(0.7)	0.6(0.5)
Toluene	-	-	-	-	-	-	1	0.7(0.7)	0.4(0.4)
C8 aromatics	-	-	-	-	-	-	-	1	0.7(0.7)
C9 aromatics	-	-	-	-	-	-	-	-	1

P31783: general q. Here at night when traffic is likely reduced compared to daytime, it is concluded that benzene and toluene are mainly from traffic and not so much from BB. Relevant to P31777, L20-21?

No.

As noted at the start of Section 3.3, the periods influenced by wheat residue BB mentioned in L20-21, Page 31777 were excluded from the correlation analysis. We also note that the traffic does not really reduce at night compared to the day time due to active nightlife in Chandigarh and more importantly, local traffic regulations which permit convoys of goods transporting diesel trucks to enter the city precincts only late at night. This additional nighttime traffic more than compensates for the reduction due to absence of the daytime rush hour traffic at night.

We have added this important clarification to the text in Section 3.3 (after Line 8 on Page 31783 of the Discussion paper) as follows:

“It is important to note the traffic intensity does not really reduce at night compared to the day time traffic owing due to local traffic regulations and the active nightlife in Chandigarh city. As per traffic regulations, convoys of diesel trucks transporting goods are permitted to enter the city precincts without restriction only late at night and this more than compensates for the traffic reduction due to absence of the daytime rush hour traffic.”

P31783, L27: Nighttime BB emissions of isoprene and monoterpenes also a major theme of Akagi et al., (2013) referenced above.

We have already addressed this comment and line of thought proposed by the reviewer in previous replies above.

P31791, L29: Is this reference correctly entered? Note - I did not check all the references.

Carslaw, D. C. and Ropkins, K.: openair – an R package for air quality data analysis, available at: <http://www.openair-project.org/>, Environ. Modell. Softw., 27–28, 52–61, 2012.

31784

Thanks

We have cross checked this and the proper citations as advised by the authors of the work are now referenced as under:

Carslaw, D.C., and Ropkins, K.: openair - an R package for air quality data analysis, Environ. Model. Software, 27-28, 52-61, doi:10.1016/j.envsoft.2011.09.008, 2012.

Carslaw, D.C., and Ropkins, K.: openair - open source tool for analysis of air pollution data. R package version 3.0.3.

Other references have also been checked.

P31800, Table 1: good candidate to move to supplement so reader gets to discussion faster.

We prefer to retain it in the manuscript. See reply to point 3 for reasons.

P31802, Table 3: The Tokyo values appear to sometimes be ranges. Also some of the values are huge, but not mentioned in the text.

Where ranges have been used the values are hyphenated in Table 3. The high values for oxygenated VOCs in Tokyo are now mentioned in the text (after Line 6; Page 31782 of the discussion paper) as follows:

“High levels of circa 37 ppbv methanol and 4-12 ppbv of acetaldehyde have been previously measured in Tokyo city as shown in Table 3.”

P31803, Table 4: footnote NO2 and refer to experimental section.

Done

P31784, L6-7: Table 3 has some huge values for Tokyo, but they may be ranges rather than averages?

Where ranges have been used the values are hyphenated in Table 3.

Sect 3.4 general comment: excellent!

Thank you very much!

P31788, L5 and L26: “May” or “pre-monsoon” better than “summer” or “summertime” since the latter two may be taken as “Asian summer monsoon”?

Have replaced “summer” with “May” in both places

P31790, L13-16: Comparison to existing emissions inventories and mobile lab measurements to characterize individual sources would also be very useful activities!

We agree and have added the following text to the Conclusion (after Line 13; Page 31790) as follows:

Future studies should include source profiling of the varied emission sources using mobile platforms and comparison of in-situ emission ratios with those derived from the existing emission inventories.”

P31810, Fig 6: log scale on PM?

Done