

Overview of VOC emissions and chemistry from PTR-TOF-MS measurements during the SusKat-ABC campaign: high acetaldehyde, isoprene and isocyanic acid in wintertime air of the Kathmandu Valley

by C. Sarkar et al., 2015 (ACPD)

We thank the anonymous referee 1 for his/her helpful comments and the generally positive remarks concerning the novelty of the work and its importance. Please find the referee's comments in black and our point wise replies in blue for easy perusal.

REFeree 1:

The study produced a lot of important, unique content of great interest to ACP readers. However, the presentation is not quite there. For example, the references have unwanted numbers appended throughout.

We thank the referee for appreciating the importance and content of the work and deeming it of great interest to ACP readers. Regarding improving the overall presentation and discussion, we found several of Referee 1's specific comments very helpful and these are now reflected in the revised submission (changes are specified in replies and manuscript version with "tracked changes" given at the end of the responses here).

Concerning the specific point of "references having unwanted numbers appended", we note that those "numbers" are actually page numbers at which the references have been cited in the ACPD manuscript and were inserted during the typesetting process by the editorial office as it seems to be a feature of their LATEX template for submissions to ACPD. As authors we only followed the journal's submission procedure.

More importantly, the length should be cut in half while both clarifying and focusing on the main points that are most strongly supported as discussed below.

For the revised version we have removed Figure 4 and Figure 9 completely and significantly shortened Sections 3.1, 3.6, 3.7, 3.8 and 3.9 by removing redundant points or discussion aspects that may have been speculative, obvious or repetitions. We have also removed/revised/clarified the text in other Sections of the MS in line with several relevant suggestions listed by the referee in his/her list of specific comments as detailed in this response.

SUMMARY LIST OF THE MAJOR CHANGES:

Figure 4 and Figure 9 have now been removed as the information conveyed by them was redundant, Figure 10 has been revised and the font size of Figures 2 and 12 (of ACPD version) have been improved for clarity.

Sections 3.1, 3.6, 3.7, 3.8 and 3.9 have been majorly re-written by removing redundant points or discussion aspects that were repetitive and speculative while clarifying certain points. We have also removed/revised/clarified the text in other Sections (including Abstract and Conclusions) of the manuscript (shown as track changes) in line with several relevant suggestions listed by the referees in their list of specific comments as detailed in this response. 18%, 32%, 20%, 50%, 60% reduction of the length relative to the ACPD version has been done for Sections 3.1, 3.6, 3.7, 3.8, 3.9, respectively.

Finally, we have re-numbered the Figures in the manuscript.

Some other summary thoughts about authors presumed key points in conclusions and abstract:

1. First deployment of PTR-TOF-MS in South Asia, This is very significant as are the high levels measured of certain species noted below.

Thank you for your positive remarks concerning the significance of the PTR-TOF-MS deployment and results.

2. 71 ion peaks detected, of which 37 had campaign average concentrations greater than 200 ppt, which highlights chemical complexity of the Kathmandu Valley's air. Great, but briefly, why the 200 ppt cut-off?

The 200 ppt cut off was chosen as one of the quality control measures so as to ensure attribution of ion peaks in the mass spectra only to the compounds present in the ambient air and not due to instrumental reasons. During the PTR-TOF-MS field deployment, the instrumental background checks revealed backgrounds as high as 170 ppt at certain m/z channels (e.g. m/z 125.958, m/z 90.947, m/z 108.957). This cut-off of > 200 ppt was applied only after the identification criteria used for the ion peaks mentioned in 25035, L1-13 of the original submission which were:

‘In order to minimize ambiguity arising due to multiple species or fragment ions contributing to ion peaks at a given m/z ratio, the following quality control measures were employed for attribution of mass identifications to the observed ion peaks: (1) Ion peaks for which the

observed mass spectra had competing/major shoulder peaks in a mass bin width of 0.005 amu centred at the relevant monoisotopic ion peak were excluded from exclusive mass assignments (2) Next, the ambient time series of the observed ion peak assigned after step 1, was carefully examined and cases where the concentration profile was completely flat/showed no ambient variability were also excluded from mass assignments (3) Thirdly, the concentration profiles of the ion peaks ascribed to rarely reported or new compounds after step 1 and step 2, were compared to the ambient time series and diel profiles of more frequently/regularly quantified VOCs, such as acetonitrile, isoprene, benzene, toluene, acetone and acetaldehyde as their diel profiles would likely indicate the driving processes and emission sources of the compounds.’

In the revised submission we have added the following lines in Section 3.1 after L13 on Page 25035 as follows:

“During the PTR-TOF-MS field deployment, instrumental background checks revealed backgrounds as high as 170 ppt at certain m/z channels (e.g. m/z 125.958, m/z 90.947, m/z 108.957). Therefore, the 200 ppt cut off was chosen as an additional quality control measure so as to ensure attribution of ion peaks in the mass spectra only to the compounds present in the ambient air and not due to instrumental reasons. The 37 compounds that were identified accounted for 86.7 % of the total mass due to all 71 ion peaks detected in the mass spectra.”

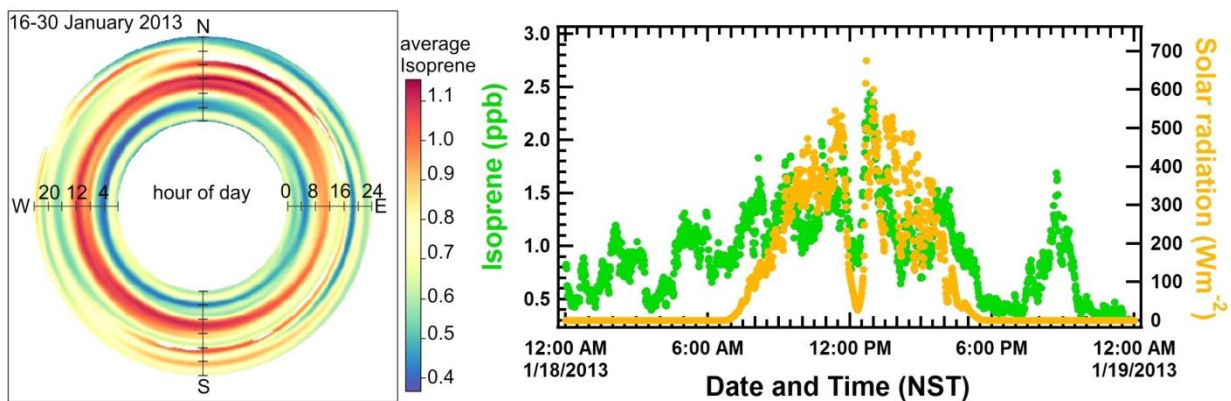
3. Acetaldehyde, acetonitrile, isoprene concentrations were among the highest recorded in the world. They are among the highest reported for urban ambient air. Urban area isoprene could be overestimated due to isomers from other sources. For instance, in smoke the “isoprene peak” is 20% pentenes.

Both the reviewers have raised the point about potential contribution from pentenes (M.W.: 70 g/mol) to isoprene (M.W.: 68 g/mol). We note that the molecular ion of pentenes would be detected using the PTR-MS technique at nominal m/z 71 and not m/z 69.07 (ion peak used for quantification of isoprene). Hence, their hypothesis of pentene isomers contributing to isoprene is not possible.

Perhaps the referees were referring to isomers of pentadiene and cyclopentene, which have been reported to occur in direct fire/smoke plumes from prescribed burns of select biomass fuels (Hatch et al., 2015). As noted in the work of Hatch et al. 2015, the assignment of the chromatographic peaks to these compounds was not even considered a positive identification by the authors themselves (e.g. Table A1 of Hatch et al., 2015). Stockwell et al. (2015) also

reported the presence of these compounds in smoke without elaborating as to how these were identified and quantified. None of these works or any other work to our knowledge has claimed or showed that 20% of the isoprene signal can be attributed to these compounds at urban sites.

On the other hand, several field studies and laboratory experiments reviewed by de Gouw and Warneke (2007) and other studies in the peer reviewed literature have shown good agreement between isoprene measured using the PTR-MS and GC techniques even in air influenced by urban emission sources. Our measurements were performed at a downwind site where smoke was not sampled continuously as there were no fires burning around the site all the time. The highest concentrations of isoprene measured in our study were during the daytime due to biogenic emissions (as stated in our submission). In our study we make the point that in the Kathmandu Valley, isoprene is emitted biogenically from vegetation and also from anthropogenic combustion sources. The latter assume significance in the evening, nighttime or early morning when combustion emissions are more widespread and can accumulate under shallow inversions. What is remarkable and a significant finding is that in contrast to wintertime measurements of isoprene from sites elsewhere in the world, the surprisingly strong contribution from biogenic sources in the Kathmandu valley results in average wintertime isoprene concentrations greater than 1 ppb (see Figure 6 of original submission and Figure 5 of revised submission). We highlighted this aspect using the polar annulus plot of isoprene (Figure 10 of the ACPD paper). To clarify these points further in the revised submission, we have merged the original Figure 10 with the following new Figure, where co-variation of daytime isoprene concentrations with solar radiation was clearly visible on January 18, 2013.



Also we have added the following new text to revised Section 3.6 (in P25051 after L22).

“The non-biogenic sources of isoprene acquire greater significance in the evening, nighttime or early morning when combustion emissions are more widespread and can accumulate under shallow inversions. What is remarkable is that in contrast to wintertime measurements of isoprene from sites elsewhere in the world due to the strong contribution from biogenic sources in the Kathmandu Valley, average wintertime concentrations of isoprene in Kathmandu were observed to be above 1 ppb (see Figure 5). To emphasize that the daytime isoprene concentrations were primarily controlled by biogenic emissions, we show real time data from a day (18 January 2013) where clear co-variation of the daytime isoprene concentrations occurred with changes in the solar radiation (Figure 8 b).”

It is known that 232-MBO (2-methyl-3-buten-2-ol) can contribute at m/z 69.070 (as an ion product resulted from ~75% fragmentation of the MBO parent ion) and it also has biogenic sources like isoprene (Goldan et al., 1993; Baker et al., 2001; Schade and Goldstein, 2001; Kim et al., 2010). However the tree species present in the forested regions upwind of our site in the Kathmandu Valley (e.g. tree species like oak and *Melia azedarach* , are known to be high isoprene emitters (with emission potentials of upto $350 \mu\text{g g}^{-1}$ dry leaf h^{-1} and $4.7 \mu\text{g g}^{-1}$ dry leaf h^{-1} respectively (Simon et al., 2005; Padhy and Varshney, 2005)). Therefore, interference from MBO is unlikely to be of any significance in the Kathmandu Valley as there were no significant MBO emitter tree species to the best of our knowledge but there definitely were known high isoprene emitters.

Hatch, L. E., Luo, W., Pankow, J. F., Yokelson, R. J., Stockwell, C. E., and Barsanti, K. C.: Identification and quantification of gaseous organic compounds emitted from biomass burning using two-dimensional gas chromatography–time-of-flight mass spectrometry, *Atmos. Chem. Phys.*, 15, 1865-1899, doi:10.5194/acp-15-1865-2015, 2015.

Stockwell, C. E., Veres, P. R., Williams, J., and Yokelson, R. J.: Characterization of biomass burning emissions from cooking fires, peat, crop residue, and other fuels with high-resolution proton-transfer-reaction time-of-flight mass spectrometry, *Atmos. Chem. Phys.*, 15, 845-865, doi:10.5194/acp-15-845-2015, 2015.

de Gouw, J., and Warneke, C.: Measurements of volatile organic compounds in the earth's atmosphere using proton-transfer-reaction mass spectrometry, *Mass Spectrometry Reviews*, 26, 223-257, 10.1002/mas.20119, 2007.

B. Baker, A. Guenther, J. Greenberg and R. Fall, Canopy Level Fluxes of 2-Methyl-3-buten-2-ol, Acetone, and Methanol by a Portable Relaxed Eddy Accumulation System, *Environmental Science & Technology* 2001 35 (9), 1701-1708, doi: 10.1021/es001007j.

Goldan, P., Kuster, W., Fehsenfeld, F., and Montzka, S. A.: The observation of a C5 alcohol emission in a north american pine forest, *Geophys. Res. Lett.*, 2, 1039–1042, 1993.

Kim, S., Karl, T., Guenther, A., Tyndall, G., Orlando, J., Harley, P., Rasmussen, R., and Apel, E.: Emissions and ambient distributions of Biogenic Volatile Organic Compounds (BVOC) in a ponderosa pine ecosystem: interpretation of PTR-MS mass spectra, *Atmos. Chem. Phys.*, 10, 1759–1771, doi:10.5194/acp-10-1759-2010, 2010.

Schade, G. W. and Goldstein, A. H.: Fluxes of oxygenated volatile organic compounds from a ponderosa pine plantation, *J. Geophys. Res.*, 106, 3111–3123, 2001.

4. Two new ambient compounds are reported: formamide and acetamide. I think the authors do remove interference from ^{13}C if applicable, but this should be clear.

For the calculation of VOC mixing ratios in this study, interference from ^{13}C were corrected wherever applicable. We have clarified this in the revised submission by adding the following text in Section 3.1, P25035 after L16 of the ACPD version:

“Potential interferences due to isotopic contributions (e.g. ^{13}C) were also corrected whenever applicable.”

5. Nitromethane (a tracer for diesel exhaust) is also reported. Nitromethane has been detected in ambient studies only recently. The authors mention that other sources also produce nitromethane and, incidentally, it is also used as accelerant in some engines (Wikipedia)

We thank the reviewer for drawing attention to the use of nitromethane in some engines. The engines being referred to are the ones used by racing enthusiasts in “drag races”. To our knowledge, “drag racing” is not common in the Kathmandu valley, hence we think such sources are not relevant for a discussion of nitromethane sources in the Kathmandu Valley.

6. First ambient measurements from any site in S. Asia of compounds with significant health effects- isocyanic acid, formamide, acetamide, naphthalene and nitromethane. This is significant that the HNCO, which may be a lower limit, is at exposure levels of documented concern. Can the authors compare their ambient levels with the recent

model-based estimates of HNCO model mixing ratios and address possible hydrolysis chemistry in PTR?

We thank the referee for these important comments, which will help clarify the isocyanic acid measurements in the revised submission.

We are aware that some loss of isocyanic acid can occur in the drift tube due to the following hydrolysis reaction:



Based on the available information in the peer reviewed literature, it is however difficult to quantify the magnitude of this gas phase reaction loss of HNCO for the typical conditions prevalent in the PTR-MS drift tube, involving a reaction time $< 100 \mu\text{s}$ and pressure of only 2.2 mbar. As appreciated by the referee in a later comment, even the potentially underestimated ambient isocyanic acid concentrations are close to concentrations of documented concern and therefore an important result of this work.

In the revised submission we now add the following clarification in Section 3.1 on Page 25035 after L27:

“Considering that some loss of isocyanic acid can occur due to hydrolysis in the drift tube, our measurements maybe a lower limit of the ambient concentrations of isocyanic acid.”

As noted in Section 3.4 on Page 25046, L7-L8 of the ACPD version, the modeling analysis by Young et al. (2012) did not consider any photochemical source for isocyanic acid in their model. Based on our results from Kathmandu and more recently published work from Mohali (Chandra and Sinha, 2016), there is clearly a strong photochemical source of isocyanic acid in South Asia. Nevertheless we think the referee’s suggestion to inter-compare with model is a good one and we have now added this information in Section 3.4 on Page 25046 of the ACPD paper after Line 8 and revised the existing text as follows:

“The recent model-based estimates of isocyanic acid (HNCO) by Young et al. (2012) showed annual mean concentrations of HNCO over the Indo Gangetic Plain and Nepal to be in the range of 0.2-0.5 ppb (values read from Figure 4 of Young et al. (2012)). The average concentrations measured during winter in Kathmandu and in the post monsoon season in Mohali were ~ 1 ppb (Chandra and Sinha, 2016) with clear daytime maxima. This suggests that inclusion of isocyanic acid’s photochemical sources are necessary for deriving better

estimates of the global isocyanic acid budget , as these are likely significant over South Asia where biomass burning and agricultural activities can also emit precursor compounds of isocyanic acid such as alkyl amines, formamide and acetamide (Roberts et al. 2011). ”

Chandra, B. P. and Sinha, V., Contribution of post-harvest agricultural paddy residue fires in the N.W. Indo-Gangetic Plain to ambient carcinogenic benzenoids, toxic isocyanic acid and carbon monoxide, Environment International, 88, 187-197 2016.

7. Oxygenated VOCs and isoprene contributed to more than 68% of total ozone production potential. Several quite similar approaches are taken to rank compounds by perceived importance, but I think this whole approach can be reduced and depicted as approximate since it ignores NO_x and other oxidants.

We have re-written and condensed the section significantly to focus only on the relative ranking of the measured VOC classes and individual compounds from the point of their ozone production potential, while removing discussion pertaining to ozone impacts and control strategies, as NO_x and O₃ data from Bode are not available for the time period of the PTR-TOF-MS deployment. Note also that oxidation of almost all VOCs with other atmospheric oxidants (e.g. Ozone) would not be as competitive as the reaction with hydroxyl radicals during afternoon hours. In particular, oxidation by NO₃ radicals is important only during the nighttime.

To strengthen the temporal context of the analyses performed using VOC data acquired during the afternoon (11:00-14:00 LT; period for which ozone production potentials were calculated), we have now included the recently published work of Putero et al. 2015 in the discussion, which highlighted that hourly average concentrations above 60 ppb O₃ are often observed during winter in the Kathmandu Valley (see Figure 9 of Putero et al., 2015). This shows that regional photochemistry is strong even during winter and formation of secondary pollutants contributes to hourly ozone concentrations in excess of 60 ppb.

The following clarification has been added in Section 3.7 on Page 25054 of the ACPD version after L3:

“The temporal context of the analyses performed using VOC data acquired during the afternoon (11:00-14:00 LT; period using which ozone production potentials were calculated) is quite relevant considering the recently published work of Putero et al. 2015, which highlighted that hourly average concentrations of > 60 ppb are often observed during winter

afternoons in the Kathmandu Valley (refer Figure 9 of Putero et al., 2015). This shows that regional photochemistry is strong even during winter and formation of secondary pollutants contributes to hourly ozone concentrations in excess of 60 ppb.”

Putero, D., Cristofanelli, P., Marinoni, A., Adhikary, B., Duchi, R., Shrestha, S. D., Verza, G. P., Landi, T. C., Calzolari, F., Busetto, M., Agrillo, G., Biancofiore, F., Di Carlo, P., Panday, A. K., Rupakheti, M., and Bonasoni, P.: Seasonal variation of ozone and black carbon observed at Paknajol, an urban site in the Kathmandu Valley, Nepal, *Atmos. Chem. Phys.*, 15, 13957-13971, doi:10.5194/acp-15-13957-2015, 2015.

8. Relative SOA (secondary organic aerosol) production potential of VOCs were in the order benzene > naphthalene > toluene > xylenes. . . .This doesn't consider compounds with unknown yield and/or unidentified peaks. How much unidentified mass is there relative to identified or total mass. This impacts several aspects of the study and would be a good addition.

We thank the referee for this good suggestion. While condensing the general information regarding SOA we have now also added the following relevant information at P25055, L8:

“The 71 detected ions collectively comprised total mass concentrations of $\sim 160.4 \mu\text{g}/\text{m}^3$, out of which the 37 identified ions reported in this work accounted for $\sim 139.1 \mu\text{g}/\text{m}^3$ (or 86.7%).”

9. Emissions from biomass burning and biomass co-fired brick kilns were found to be the dominant sources for compounds such as propyne, propene, benzene and propanenitrile and correlated strongly with acetonitrile, a chemical tracer for biomass burning. Some aspects of this finding need to be clarified as noted in detailed comments.

The clarifications have been provided in the reply to the detailed comments made by the referee.

10. Reduction of biomass burning and biomass co-fired brick kilns would be important to reduce emissions and formation of toxic VOCs and improve air quality in the Kathmandu Valley. At one point, the authors state that traffic is the main emission source in the valley – so why is it not targeted? Also, with regard to co firing - this statement needs to qualified and have caveats added. The authors have strong, but circumstantial evidence of an increase in pollutants associated with inefficient combustion in co-fired kilns. However, VOCs are not the whole air quality story and co-firing is a widely-accepted technology to reduce pollutants associated with higher

temperature combustion such as thermal NO_x. At least one highly touted recent study found significant climate and health benefits overall for co-firing biomass and coal such as reduction of black carbon and fossil CO₂.

(<http://www.sciencedaily.com/releases/2015/09/150925112110.htm>)

(<http://www.sciencedirect.com/science/article/pii/S0016236115008637>). **So reduction in certain pollutants while increasing others may not translate directly to improved AQ and good policy.**

We agree with the referee that toxic VOCs are not the “whole air quality story” as fine mode aerosol and black carbon are also important. However, while not being the “whole air quality story” they are certainly a critical component of the air quality story. While much attention has been focused on PM and black carbon (with good reason), the co-emission of toxic VOCs has received comparatively less attention, in part because of the difficulty in quantifying these VOCs routinely. Note that being gases, VOCs are not filtered by human nasal and airway passages as efficiently as PM. Thus, in the context of the Kathmandu Valley we think the finding of several health relevant VOCs (e.g. isocyanic acid, formamide, acetamide, nitromethane and naphthalene) being associated with emissions from inefficiently co-fired brick kilns is an important finding. We would also like to point out that the valuable and highly touted case study (Al-Naiema et al., 2015) reporting reduction in emissions (~40% reduction of fossil CO₂, particulate matter and heavy metal emissions) involved co-firing of oat hull biomass with coal for generation of electricity. The study did not examine co-emission of toxic VOCs but the most remarkable differences between that case study and the typical brick kilns that dot the Kathmandu Valley are in terms of the combustion efficiency, biomass fuel being co-fired and the end application. Thus though the same word “co-firing” is used colloquially, these are really different from an operational and environmental standpoint, with one being an efficient closed unit set up that employs good scrubbers whereas the other has numerous vents and combustion characteristics that are hardly comparable.

While we did not measure particulate matter emissions from the biomass co-fired brick kilns in the Kathmandu Valley during our deployment, previous studies by Pariyar et al. 2013 and Raut 2003 have reported and documented massive increases in PM₁₀ and TSP for periods marked by the operation of the brick kilns relative to periods when they were not operational. The study conducted by Clean Energy Nepal (Raut 2003) showed that 8 h averaged concentrations of air pollutants such as Total Suspended Particulate (TSP), PM₁₀, SO₂ and

NO_x were three times higher during the brick kiln operating period relative to the period they were not operational at the same location. The mass concentration of PM₁₀ increased from 218 µg m⁻³ to 603 µg m⁻³ while TSP increased from 265 µg m⁻³ to 634 µg m⁻³. Note that these were primarily Fixed Chimney Bull Trench Brick Kilns, similar to the ones that impacted our measurements. While brick kilns may be generic to developing countries as noted by the reviewer, the type of brick kilns in use in different developing countries is not the same. The Bull Trench kilns are an old and inefficient technology, which have been banned even in their place of origin, India, but continue to dominate the Kathmandu Valley landscape. A further point of consideration is that several brick kilns operate illegally in Kathmandu during the brick kiln seasons. All these facts have been documented in several works (Raut 2003, Tuladhar and Raut 2002, Pariyar et al. 2013).

Below we attach a picture of one of the typical brick kilns located near the measurement site Bode for a visual depiction of the emissions:



In our opinion, there is certainly more scope for improvement in the case of the brick kilns present in the Kathmandu valley. We clarify this in the following lines of the revised submission (Section 3.2; P25038 of ACPD version; after L23):

“A recent study by Al-Naiema et al. (2015) reported reduction in emissions (~40% reduction of fossil CO₂, particulate matter and heavy metal emissions) when co-firing of oat hull biomass with coal was carried out for generation of electricity in the United States. We note that the case study did not investigate co-emission of toxic VOCs such as isocyanic acid, formamide, acetamide, nitromethane and naphthalene which were associated with emissions from biomass co-fired brick kilns in the Kathmandu Valley. A study conducted by Clean Energy Nepal (Raut 2003) showed that 8 h averaged concentrations of air pollutants such as

Total Suspended Particulate (TSP) , PM₁₀, SO₂ and NO_x were three times higher during the brick kiln operating period relative to the period they were not operational at the same location. Notwithstanding this aspect, significant differences exist between the electricity generation unit studied by Al-Naiema et al. 2015 and the typical biomass co-fired brick kilns that dot the Kathmandu Valley in terms of design, combustion efficiency, biomass fuel being co-fired and the end application. Thus though the same word “co-firing” is used colloquially, these are really different from an operational and environmental standpoint, with one being an efficient closed unit set up that employs good scrubbers whereas the other has numerous vents and combustion characteristics that are hardly comparable.”

We did not wish to imply that “traffic” sources should not be targeted for improvements in air quality. Like all urban environments its contribution is significant. To make sure there is no confusion, in the Conclusion Section of the revised submission we have replaced Lines 7-9 on Page 25060 which were:

“A major conclusion of this study is that the wintertime air pollution in the Kathmandu Valley can be significantly reduced by replacing the existing brick kiln technology with cleaner and more efficient brick kiln technology.”

by

“Although like all urban environment, contribution of traffic sources to ambient VOCs is significant in the Kathmandu Valley, another anthropogenic source which occupies central importance in the Kathmandu Valley (due to inefficient combustion) is the biomass co-fired brick kilns.”

Ibrahim Al-Naiema, Armando D. Estillore, Imali A. Mudunkotuwa, Vicki H. Grassian, Elizabeth A. Stone, Impacts of co-firing biomass on emissions of particulate matter to the atmosphere, Fuel, Volume 162, 15 December 2015, Pages 111-120, ISSN 0016-2361, <http://dx.doi.org/10.1016/j.fuel.2015.08.054>.

11. Another summary comment: The OH reactivity could be better placed in context relative to oxidation by O₃ and NO₃.

We have added the following lines at the beginning of Section 3.7 (P25052) in the revised submission to put in context relative oxidation rates by ozone and the nitrate radical:

“The oxidation of VOCs (and consequently their removal rate) depends on the reactivity of VOCs with both ozone and hydroxyl radicals during daytime and the nitrate radical during nighttime. For the VOCs reported in this work and the typical maximum ozone concentrations observed during winter in the Kathmandu Valley (~ 60 -70 ppb; Putero et al. (2015)), the daytime oxidation with hydroxyl radicals is much faster relative to daytime oxidation with ozone and nighttime oxidation with nitrate radicals as $k_{VOC+OH} > k_{VOC+NO_3} > 10^3$ - 10^{10} times k_{VOC+O_3} (kinetics.nist.gov/kinetics).”

For easy perusal, we show the values below in tabular format:

Compound	k_{OH+VOC} in cm^3 $\text{molec}^{-1} \text{s}^{-1}$	k_{O_3+VOC} in cm^3 $\text{molec}^{-1} \text{s}^{-1}$	k_{NO_3+VOC} in cm^3 $\text{molec}^{-1} \text{s}^{-1}$
Hydrogen Cyanide	2.5×10^{-14}	-	-
Formaldehyde	8.5×10^{-12}	2.1×10^{-24}	5.6×10^{-16}
Methanol	8.6×10^{-13}	1.3×10^{-16}	1.3×10^{-16}
Propyne	2.8×10^{-12}	1.2×10^{-18}	2.3×10^{-16}
Acetonitrile	1.7×10^{-14}	-	5×10^{-19}
Propene	2.5×10^{-11}	1.0×10^{-17}	9.5×10^{-15}
Acetaldehyde	1.5×10^{-11}	3.4×10^{-20}	2.4×10^{-15}
Formamide	3.9×10^{-12}	-	-
Formic acid	4.0×10^{-13}	-	-
Ethanol	3.0×10^{-12}	-	2.0×10^{-15}
1,3-Butadiyne	1.4×10^{-11}	-	-
Propanenitrile	2.4×10^{-13}	-	-
Acrolein	1.9×10^{-11}	3.6×10^{-19}	1.1×10^{-15}
Acetone	1.5×10^{-13}	3.0×10^{-17}	8.5×10^{-18}
Acetamide	3.1×10^{-12}	-	-
Acetic acid	7.8×10^{-13}	2.8×10^{-18}	3.6×10^{-18}
Nitromethane	1.4×10^{-14}	1.2×10^{-20}	-
Dimethyl Sulfide	5.1×10^{-12}	1.0×10^{-18}	1.1×10^{-12}
1,3-Cyclopentadiene	8.2×10^{-11}	-	2.3×10^{-12}
Furan	3.8×10^{-11}	2.4×10^{-18}	1.4×10^{-12}

Isoprene	1.0×10^{-10}	1.2×10^{-17}	6.7×10^{-13}
MACR	3.0×10^{-11}	1.9×10^{-18}	3.3×10^{-15}
MVK	1.8×10^{-11}	4.4×10^{-18}	1.2×10^{-16}
Methylglyoxal	1.4×10^{-11}	5.9×10^{-21}	-
Methyl ethyl ketone	1.0×10^{-12}	2.0×10^{-16}	-
Hydroxyacetone	5.6×10^{-12}	-	-
Benzene	1.0×10^{-12}	1.7×10^{-22}	3.0×10^{-17}
2,3-Butanedione	2.0×10^{-13}	-	-
Toluene	5.8×10^{-12}	3.9×10^{-22}	6.7×10^{-17}
2-Furaldehyde	4.2×10^{-11}	-	-
Styrene	5.1×10^{-11}	1.6×10^{-17}	1.5×10^{-13}
Xylenes	1.3×10^{-11}	1.3×10^{-21}	4.5×10^{-16}
Trimethylbenzenes	2.9×10^{-11}	1.3×10^{-21}	1.8×10^{-15}
Naphthalene	2.3×10^{-11}	3.0×10^{-19}	-

12. As an example on length and clarity. After reading 29 pages, or the length of a typical paper; we get several important ideas. There are a lot of sources, but it's not clear if the kilns operate around the clock. Nor is it clear how much biomass-co-fired brick kilns are being singled out as opposed to considering a large variety of biomass burning sources. It is important that the kiln activity changes in January while cooking fires probably would not. What should be checked is if open burning also changes between Dec and Jan. We get the idea that pollution is diluted by boundary layer development during the day and possibly suspended above the valley by infill from downslope winds at night. What is not yet clear on meteorology is why would the downslope winds not just dilute the pollution (or bring in suburban pollution) and what happens to any suspended layer in AM? Does it blow out of valley or mix down into boundary layer, or both?

Finally we learn that various species correlate with known tracers suggesting a common source. My opinion is this can be clarified and conveyed succinctly in a few pages that actually better highlights the author's main points. This would also generate lots of space to bring in other helpful data like the CO and O3, which is one of the reasons why

people do large collaborative projects. That's especially important since the authors make policy recommendations without demonstrating how representative their site was of the Kathmandu Valley overall or including aerosol data. This despite the fact that SusKat deployed a network of aerosol monitoring sites across the valley.

We appreciate the feedback of the referee. In the revised version we have improved and shortened the existing text to address these points. The information is also summarized below:

All the brick kilns in the Kathmandu Valley are Fixed Chimney Bull Trench Brick Kilns (FCBTK), except for one Vertical Shaft Brick Kiln (VSBK) and two Hoffmann design brick kilns. FCBTKs are operated around the clock, from the first week of January to mid-April according to our survey. Thus, our deployment fortuitously was able to contrast the periods marked by the presence and almost complete absence of operational brick kilns in the fetch region of our measurement site. Most open burning and cooking activities remain similar in December and January. Due to reduced leaf fall in January (leaf fall of deciduous trees picks up in November and peaks in December) the open burning of leaf litter with other waste is generally less in January. With regard to increased open biomass burning from other sources in January, the first week of January was the coldest period of the deployment, so one could hypothesize that the higher emissions in this period were due to more open fires being lit to keep warm. However as can be seen in Figure 5 of ACPD version (Figure 4 of revised MS), the biomass burning emissions were much higher for most of January (including a rain event during 18 January 21:00 LT – 19 January 01:00 LT). Thus, the brick kiln activity is the singular feature that is prominently different between both the periods. This information has been added at Section 3.2, P25038 after L5.

To the best of our knowledge and survey, the fuel burnt in the brick kilns does not differ much between the brick kilns though the type of bio-fuel employed during different times in a year can vary depending on the availability and abundance of certain types of bio-fuel. One common biofuel used in the brick kilns is the seed of the lapsi fruit (*Choerospondias axillaris*). This information has been added at Section 3.2, P25038, L16.

The general meteorological conditions within the Kathmandu Valley remain fairly similar throughout the winter season (Panday et al., 2009; Regmi et al., 2003) and it is worth mentioning that the winter of 2012-2013 was not anomalous. Conditions were calm during the mornings with shallow boundary layer and therefore what we see in the morning hours

are emissions from the previous night and emissions from morning activities around the measurement site within a radius of few km, rather than regional emissions. Cold pooling of air at night resulting in dilution of pollution was observed in the diel profiles of VOCs for Period 1 when the 24/7 brick kilns were largely un-operational (for e.g. between midnight and 05:00 LT). Shortly after sunrise, the surface air mixes in with air that was aloft. Finally during the afternoon (10:00–15:00 LT), westerly winds sweep the valley from west to east at wind speeds of 3-4 m/s advecting the emissions, some of which may get transported across the mountain passes (Panday et al., 2009; Kitada and Regmi, 2003; Regmi et al, 2003). This information has been added at Section 2.1, P25029, L15.

Concerning the proposal to bring in more data, there are several reasons for absence of the other data for the period of PTR-TOF-MS deployment. Firstly, the logistics of transportation and installation of other gas phase instrumentation ran into several delays and in most cases data was available only from February 2013, by which time the PTR-TOF-MS was no longer available. There were no NO_y measurements during December 2012 –January 2013 (the period of the PTR-TOF-MS deployment) or even later from Bode (the measurement site). O₃ and CO measurements were available only towards the end of January 2013 and were performed by a PhD student from another research group and institute, whose thesis work will primarily involve interpretation of the ozone and CO datasets, using modeling analyses. As per the SusKat data sharing policy, data that is central to a PhD student's thesis cannot be used first by another research group. Data pertaining to ozone and CO will therefore be submitted to the SusKat-ABC campaign special issue in ACP and an overview paper summarizing the air quality and policy recommendations will be prepared by Rupakheti et al. (2016) and Panday et al. (2016).

The main objective of our work is investigation of the VOC speciation and their chemistry and emissions in the Kathmandu Valley. This has been clarified in the revised submission in relation to air quality/policy related statements.

Specific comments Page, Line:

25026, L2: Suggest changing lifetime range to “minutes to days”

Done.

25027, L18-19: Co-firing brick kilns is not the same as biomass burning (BB) in general.

We have removed “biomass burning” from the sentence and the revised sentence is as follows:

“By contrasting periods in the chemical dataset based on the dominance of biogenic emission sources and emissions from brick kilns co-fired with biomass, respectively, VOCs emitted from the brick kilns were constrained.”

25028: L7: Why single out wind speed in afternoon here?

We have deleted mention of the wind speed in this sentence. The revised sentence is as follows:

“It is encircled by a ring of mountains that range from 2000-2800 m (amsl), with about five mountain passes approximately 1500–1550 m amsl (Panday et al., 2009).”

25028: L11: Mention any presence of agriculture and distance to major roadways

We have added the following text in the revised submission on Page 25028 of ACPD version after L15:

“Most of the agricultural fields near the site have unpaved tracks and were sold as small plots, and are largely uncultivated. At some distance, there are agricultural fields on which rice is sown in the summer and either potatoes/vegetables or wheat is sown in winter. The major road (Bhaktapur road) is about 1 km south of the site.”

25028, L25 “a few”

Done.

25030, L2 due to

Done.

25030, L10-15: Some fog water analysis would be interesting.

We agree but unfortunately none was carried out during the SusKat study at Bode. Future research will focus on investigation of the winter fog characteristics and is being led by ICIMOD, Nepal (Arnico Panday, personal communication).

25030, L19: By now a brief description of the Bode site would be useful?

The detailed description of the Bode site was already provided and illustrated using Figure 1 in the same Section 2.1 on Pages 25028 and 25029, for which the referee also suggested some additions already.

25031, L Any test of filter effects on gases? No heating of sample line? Any temperature effects at e.g. night?

Teflon membrane particle filters similar to the ones used in the Kathmandu study have been used without issues in several previous PTR-MS VOC studies by some of the authors (e.g. Sinha et al., 2010), including at another South Asian site in Mohali, India (Sinha et al., 2014). Due precautions were taken for potential memory effects from filters when sampling high concentrations of certain gases or in the aftermath of nasty plumes (at ~ 100 ppb concentration of sticky gases). As noted in the original submission, the Teflon membrane particle filters were changed every 5-6 days or even sooner depending on the ambient conditions. The inlet lines used in Kathmandu were prepared prior to deployment by continuous purging at different flow rates in the laboratory at Mohali for more than three days and zero air was sampled through these lines. After purging, the background signals were always comparable to background signals observed during direct injection of zero air without a long inlet line for the m/z ion peaks reported in this work. Bearing in mind that the ambient air (range of ambient temperature: 5-15°C) was drawn in under 25 seconds (this is the sum of the residence + sampling time) into the mass spectrometer, the probability of inlet effects for sticky compounds is not high. In any case, the part of the inlet line that was indoors was well insulated and heated to 40°C all the time to ensure there were no condensation effects.

Finally, the clear difference in diel profiles (see Figure 7 of ACPD version; e.g. morning and evening concentrations of several sticky compounds such as methanol were higher than the daytime concentrations and thus not driven by ambient temperature variability) does not suggest inlet effects influenced the ambient concentration measurements and measured diel profiles.

We have clarified and added this in P25031, L12 and L13 (of the ACPD version):

“Teflon membrane particle filters similar to the ones used in the Kathmandu study have been used without issues in several previous PTR-MS VOC studies by some of the authors (e.g. Sinha et al. (2010)), including at another South Asian site in Mohali, India (Sinha et al., 2014).” and “The inlet lines used in Kathmandu were prepared prior to deployment by

continuous purging at different flow rates in the laboratory at Mohali for more than three days and zero air was sampled through these lines. After purging, the background signals were always comparable to background signals observed during direct injection of zero air without a long inlet line for the m/z ion peaks reported in this work. Bearing in mind that the ambient air (range of ambient temperature: 5-15°C) was drawn in under 25 seconds (residence + sampling time; determined by spiking the inlet with sesquiterpenes emitted from an orange peel) into the PTR-TOF-MS, the probability of inlet effects for sticky compounds is not high. In any case, the part of the inlet line that was indoors was well insulated and heated to 40°C all the time to ensure there were no condensation effects.”

Sinha, V., Williams, J., Lelieveld, J., Ruuskanen, T. M., Kajos, M. K., Patokoski, J., Hellen, H., Hakola, H., Mogensen, D., Boy, M., Rinne, J., and Kulmala, M.: OH Reactivity Measurements within a Boreal Forest: Evidence for Unknown Reactive Emissions, *Environmental Science & Technology*, 44, 6614-6620, 10.1021/es101780b, 2010.

Sinha, V., Kumar, V., and Sarkar, C.: 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, *Atmos. Chem. Phys.*, 14, 5921-5941, 10.5194/acp-14-5921-2014, 2014.

25031, L26-7: Are the last two species in this list continuously introduced mass standards?

No, they were not introduced continuously but only during the calibration experiments and when checking mass scale shifts.

25032, L22: Should be m37/m19

Thank you, has been corrected to m37/m19.

25032, L25-27: Regardless of calibration results, with the ambient RH varying between 35 and 100% it seems the laws of kinetics and known proton affinities guarantee RH effects on the HCHO data.

As reported in de Gouw and Warneke (2007) and Sinha et al. (2010), it is the absolute humidity content of the sampled air rather than the RH, which is responsible for changes in detection sensitivity of certain VOCs within the PTR-MS. The sensitivity dependence has been reported in numerous studies as function of RH because RH is more frequently used in meteorology and for no changes/small changes in temperature, RH is a good proxy of the

absolute humidity. We note that during the Kathmandu deployment, while the RH variability was large (35%-100% as noted by the reviewer) most of the RH change was on account of changes in the ambient temperature rather than changes in absolute humidity of sampled air. The variability in the absolute humidity was only in the range of 20% between Dec 19 2012 and Jan 30 2013.

Still as we could not get good instrumental background measurements for methanol and formaldehyde during the calibration experiments, we took care to point out that measurements of methanol and formaldehyde, despite being present in the calibration gas standard mixture, are associated with much larger uncertainty (circa 50%), in the same experimental section 2.1 (L 14- L19; Page 25033 of the ACPD version).

de Gouw, J., and Warneke, C.: Measurements of volatile organic compounds in the earth's atmosphere using proton-transfer-reaction mass spectrometry, *Mass Spectrometry Reviews*, 26, 223-257, 10.1002/mas.20119, 2007.

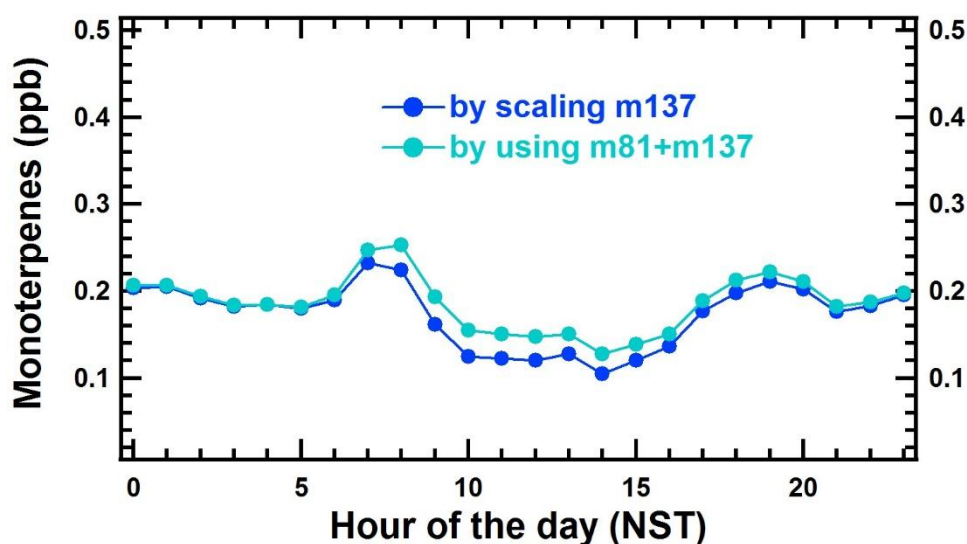
Sinha, V., Williams, J., Lelieveld, J., Ruuskanen, T. M., Kajos, M. K., Patokoski, J., Hellen, H., Hakola, H., Mogensen, D., Boy, M., Rinne, J., and Kulmala, M.: OH Reactivity Measurements within a Boreal Forest: Evidence for Unknown Reactive Emissions, *Environmental Science & Technology*, 44, 6614-6620, 10.1021/es101780b, 2010.

25033, L10-11: If only one monoterpene was tested for fragmentation, the fragmentation could be different for every monoterpene and the mix of monoterpenes could evolve. Why not use the sum of 137 and 81?

The referee has raised a valid concern. In our experience, m/z 81 can have major contributions from certain other compounds (e.g. contribution from the fragment ions of furfuryl alcohol (86%), 2-hexenal (13%), 3-hexenal (69%)), which is why we chose to scale the m/z 137 signal based on known fragmentation ratio of the molecular ion of the most abundant monoterpene (α -pinene). In any case, a comparison of the monoterpene concentrations (Figure also shown below) using both approaches show very little difference in the reported average values which are:

Using m81+m137 approach: 0.19 ± 0.06 ppb

Using scaling approach it was 0.17 ± 0.04 ppb



Hence no changes were deemed necessary for calculation of average monoterpene concentrations in the revised version, where only the average concentrations have been discussed to report the presence of monoterpenes in ambient Kathmandu air and their potential importance for SOA formation.

25035, L23: Acetamide was reported in biomass burning smoke by Stockwell et al., (2015) based on earlier observations cited there in by Barnes et al and Ge et al. Might be useful for interpretation.

The information obtained from Stockwell et al., (2015), Barnes et al., (2010) and Ge et al., (2011) has already been used for the interpretation of acetamide and all these papers are cited in the relevant sections of the manuscript. For example, 25048 L23-25 reads as, ‘Also it is reported that both formamide and acetamide could be emitted from tobacco smoke and hence likely from pyrolysis of biomass (Ge et al., 2011)’ and the rate coefficient of acetamide with OH was taken from Barnes et al. (2010) which was used for the calculation of OH reactivity of acetamide (section 3.7; 25052 L26-25053 L1-3).

25035, L26-27: There has been discussion in the PTR community about the possible hydrolysis of HNCO in the drift tube. Thus the peak attributed to HNCO is likely HNCO, but it may represent a lower limit.

We agree with the reviewer. This issue has already been addressed previously in the response while replying to major point 6 of the referee.

25036, L17: Is this sum accounting for the number of carbon atoms along with mixing ratio? I.e. would 5 ppb of ethene count as 10 ppbC?

Yes. See also reply to major point 8 of the referee above.

25036, L21-23: Why use those 3 one-hr periods here and in Fig 4 if they are evidently not representative?

25036, L23-24: Not sure why the O/C ratio of biomass burning aerosol enters the discussion of gases at this point?

We thank the referee for this comment. We agree and have removed the following text (Page 25036; L21-L24) from the original submission and removed the citation to Aiken et al. 2008:

“Although the average O/C ratios for morning (06:00-07:00 LT), afternoon (15:00-16:00 LT) and evening (18:00-19:00 LT) were 0.57, 0.68 and 0.60, the O/C ratio for the entire period of deployment was found to be 0.33 which is within the O/C ratio of 0.3-0.4 observed for laboratory produced primary biomass burning organic aerosol (Aiken et al., 2008). No significant change was noted for the N/C ratios on a diel basis which were always close to 0.08.”

25038, L5: Good place to start a new paragraph.

Done.

25038, L23: Does seem that the co-fired kilns are the cause of the enhancement in acetonitrile and benzene since kilns burning pure coal would likely have a different location and thus not correlate as well. But it should be checked if the hotspots or regional haze from open burning increased from Dec 2012 through Jan 2013. It may not be important but it's hard to say if the fuel contributing to the benzene is the biomass or an effect of co-firing on the coal combustion emissions. Also “periods” should not be capitalized.

Thank you for the comment.

The hotspot or regional haze imagery obtained using MODIS Terra satellite (at a spatial resolution of 500 m and time resolution of 5 minutes at 05:00-06:00 LT) between 19 December 2012 – 30 January 2013 (data accessed at NASA worldview; <https://worldview.earthdata.nasa.gov/>) were similar except for a 6 day period (12-17 January 2013), wherein the regional haze was stronger. We note that calmer meteorological conditions could be a potential contributory factor for stronger haze in this period. The MODIS satellite image do not show any active fire counts (at greater than 85% confidence

limit) over the Kathmandu Valley (latitude 27.7°N) during the whole campaign period (19 December 2012–30 January 2013). Thus, the higher chemical concentrations observed from 4–18 January and even later, appear to be linked to the re-start of the biomass co-fired brick kilns and cannot be explained by linkages with regional haze for increased open burning, considering the available evidence. As discussed previously in reply to major point 12, while there is ground evidence for major brick kiln activity from the first week of January 2013, there was no such evidence for occurrences of increased open biomass burning during period 2 relative to period 1. As noted in our original submission, a study by Stone et al., (2010) reported that the brick kilns in the Kathmandu Valley do burn biomass with coal. We add this important clarification in the revised manuscript in Page 25038 L23 (ACPD version) as follows:

“It is also worth mentioning that the hotspot and regional haze imagery obtained using MODIS Terra satellite (at a spatial resolution of 500 m and time resolution of 5 minutes at 05:00–06:00 Local Time) between 19 December 2012–30 January 2013 (data accessed at NASA worldview; <https://worldview.earthdata.nasa.gov/>) were similar except for a 6 day period (12–17 January 2013), wherein the regional haze was stronger. We note that calmer meteorological conditions could be a potential contributory factor for stronger haze in this period. The MODIS satellite image did not detect any active fire counts (at greater than 85% confidence limit) over the Kathmandu Valley (latitude 27.7°N) during the whole campaign period (19 December 2012–30 January 2013). Thus, the higher chemical concentrations observed from 4–18 January and even later, appear to be linked to the re-start of the biomass co-fired brick kilns and cannot be explained by linkages with regional haze or increased open burning of biomass, considering the available evidence.”

We do not have relevant data at this point to confirm if the fuel contributing to the benzene is the biomass or an effect of co-firing on the coal combustion emissions.

We have removed capitalization of “periods” throughout the paper now.

25038, L27: Sentence beginning with “For” does this refer to Jan 19 or campaign as a whole?

It refers to the whole campaign. We have rephrased the relevant line as follows:

“When considering the entire study period, high concentrations of OVOCs were typically observed in the early morning hours between 08:00–10:00 LT.....”

25039, L3-4: If you are referring to plume like episodes 3 and 8 days long that doesn't seem like appropriate terminology or appear to actually happen in the data in the time series figure.

We regret the inappropriate terminology. The text in L3-L6 has been re-written and reads as follows:

“Peak acetaldehyde concentrations of about 30-40 ppb were observed in the time series. These often correlated with peaks in the concentrations of acetonitrile and furan (chemical tracers for combustion) between 4 January 2013 and 30 January 2013 and occasionally with peaks in daytime isoprene concentrations before 2 January 2013.”

25040, L1-4: Why isn't propyne on this list of common emissions?

The list mentioned in 25040, L1-4 consists of only those VOCs for which the comparison with a number of previously reported wintertime VOC studies was possible and this comparison is shown in Figure 6 of ACPD version (Figure 5 of revised submission).

24040, L8-9: Since methanol is a major BB emission and BB is proposed as a major influence on Kathmandu air, why would London and Tokyo have higher methanol?

We note that methanol has several sources (Galbally and Kirstine, 2002).

The higher methanol in Tokyo (Yoshino et al., 2012) was attributed to the local use of methanol as a solvent. Whereas during the London study (Langford et al., 2010), advected emissions from non-traffic sources of methanol within the city including both biogenic (leaf wounding, microbial degradation of plant material.) and anthropogenic (solvents, adhesives, dyes, paints and varnishes etc.) sources were reported to be responsible for the high concentrations.

Galbally, I. E. and Kirstine, W.: The production of methanol by flowering plants and the global cycle of methanol, *J. Atmos. Chem.*, 43, 195–229, 2002.

25041, L12: “more industries”

Done.

25041, L18-20: Here the authors appear to have forgotten their earlier convincing argument that Kathmandu also has a topography problem compared to the megacities

discussed (even Mexico City is relatively unconfined in one direction) that causes concentrations to be higher across the board.

Thank you for this point.

We have removed L16-L20 on Page 25041 of ACPD version which was:

“While the studies in other cities were conducted in different years, it is unlikely that inter annual variability would be the sole reason for lower concentrations in the megacities. As a city located in a developing country it is more likely that even with a population that is less than one tenth of these megacities, Kathmandu air has higher concentrations of carcinogens like benzene due to inadequate access to efficient and clean technologies and limited controls on emissions from existing industries.”

and replaced it with the following summary:

“The combination of the topography of Kathmandu (which results in suppressed ventilation) and the anthropogenic and biogenic emissions within the Valley appear to cause high ambient wintertime concentrations for several VOCs (e.g. acetonitrile, acetaldehyde and benzene and isoprene).”

25042, L9: In addition to leaf burning, how can other forms of biomass burning (cooking, heating, agricultural waste, etc) or trash burning be ruled out? The high acetaldehyde suggests possible high PAN levels, which might be discussed to the extent possible. E.g. any evidence from other work in SusKat or other projects?

Other types of burning (e.g. garden waste, agro-residue burning and garbage burning) were not ruled out and were mentioned in the conclusions (25059, L7-11).

Nevertheless we make this clearer in the revised version (at Page 25042 after L6-9) as follows:

“We note that the concentrations of acetonitrile (a chemical tracer for biomass combustion), methanol, benzene and isocyanic acid are significantly higher in period 2 relative to period 1, indicating that for all of them, the biomass co-fired brick kilns that became operational in the first week of January and other forms of biomass burning (e.g. leaves and branches, garden waste and garbage) were major contributory sources.”

We agree with the reviewer. The high concentrations of acetaldehyde indicate high ambient PAN concentrations. We are unaware of any PAN measurements from previous works in the

region or the SusKat campaign. Our observation of high NO_2^+ (detected at m/z 45.990 as a fragment ion of C1-C5 alkyl nitrates (Aoki et al., 2007) with a campaign average concentration of 1.08 ppb) was reported in the original submission and is consistent with potentially high ambient concentrations of PAN.

We have added the following lines on Page 25042 after L11 to reflect this information as follows:

“The high acetaldehyde concentrations suggest the possibility of high levels of peroxy acetyl nitrate (PAN). The campaign average concentration of 1.08 ppb observed at m/z 45.990 and attributed to NO_2^+ (Table S1), which is a fragment ion of C1-C5 alkyl nitrates (Aoki et al., 2007), appears to be consistent with the presence of a large pool of gaseous organic nitrate species too.”

Aoki, N., Inomata, S., and Tanimoto, H.: Detection of C1–C5 alkyl nitrates by proton transfer reaction time-of-flight mass spectrometry, *International Journal of Mass Spectrometry*, 263, 12-21, <http://dx.doi.org/10.1016/j.ijms.2006.11.018>, 2007.

25042, L14: What does this mean? “. . . indicating the common influence of urban emission activities and biomass combustion sources for these compounds” ?

Bimodal profiles of VOCs are generally observed in the urban environment as mentioned on Page 25042, L15-19 due to common anthropogenic activities such as traffic and industrial emissions. This sentence means that these common urban emission activities along with biomass burning (including the biomass co-combusted in brick kilns) are the major sources for most of the VOCs (except those with biogenic and photochemical oxidation sources) in the Kathmandu Valley.

25042, L29 – 25043, L20 and beyond: what does “largely conserved” mean in the context of discussed profiles and more generally: is there a simple way to tie a bimodal acetonitrile profile to expected biomass burning diurnal activity? E.g. would kilns be continuous around the clock with open burning peaking in afternoon while cooking fires are mainly early AM (and evening?)? Or are the authors implying the kilns startup every day about the same time as rush hour? At present the discussion reads like a tour of the plots with “best-guess” explanations as one proceeds. Thus, the thread constantly switches between peaks, met, and activity. If possible, the discussion could be tweaked/reorganized logically to clarify in order what is known about: a) diurnal cycles

in activity for the various sources, b) the main ways these emissions are processed/modified by photochemistry, and c) how they are diluted and/or moved by the met resulting in observed profiles. I think there is good material here, but it's a bit confusing to digest at present.

Here by “largely conserved” we imply that the pattern in the diel profiles were similar for both periods.

We can tie the bimodal acetonitrile profile to expected biomass burning diurnal activity by applying source-receptor models such as Positive Matrix Factorization (PMF) which will be presented in the companion paper (Sarkar et al., 2016). In this companion paper, diurnal cycles of different sources and the effect of photochemistry and meteorology to the observed profiles for different sources will be explained. Generally, brick kilns operate continuously around the clock while domestic heating/cooking and open burning activities occur during morning and evening hours (08:00-09:00 LT; same time as the rush hour and 19:00-20:00 LT).

25043, L17: “mountain”

Thank you, corrected.

25045: L4-21: How could the dilution effect be turned off for selected species? Also benzene and toluene are emitted in comparable amounts by most forms of biomass burning so it's not clear why toluene could have a different profile if BB is main source of the benzene. The rationale is unclear at this point and if breaking down it might be best to dial back conclusions regarding sources?

We disagree with the referee's statement that benzene and toluene are emitted in comparable amounts by most forms of biomass burning. Below we have compiled a list which shows that for a wide variety of commonly used fuel types, the emission of benzene is almost twice as high as the emission of toluene.

Toluene/benzene ratio from different sources:

Type	T/B ratio	Reference
Waste burning	0.41 ± 0.20	Stockwell et al., 2015
Grasses	0.44 ± 0.26	Stockwell et al., 2015
Plastic bags	0.69	Stockwell et al., 2015

Tyres	0.06	Stockwell et al., 2015
3-stone cooking	0.09 ± 0.03	Stockwell et al., 2015
Wood burning	0.05	Tsai et al., 2003
Charcoal burning	0.59	Tsai et al., 2003
Household waste burning	0.45	Lemieux et al., 2004

Stockwell, C. E., Veres, P. R., Williams, J., and Yokelson, R. J.: Characterization of biomass burning emissions from cooking fires, peat, crop residue, and other fuels with high-resolution proton-transfer-reaction time-of-flight mass spectrometry, *Atmos. Chem. Phys.*, 15, 845–865, doi:10.5194/acp-15-845-2015, 2015.

Tsai, S. M., Zhang, J., Smith, K. R., Ma, Y., Rasmussen, R. A., and Khalil, M. A. K.: Characterization of Non-Methane Hydrocarbons emitted from various Cookstoves used in China, *Environmental Science & Technology*, 37, 2869-2877, doi: 10.1021/es026232a, 2003.

Lemieux, P. M., Lutes, C. C., and Santoianni, D. A.: Emissions of organic air toxics from open burning: a comprehensive review, *Progress in Energy and Combustion Science*, 30, 1-32, doi:10.1016/j.peccs.2003.08.001, 2004.

Dilution effect was not turned off for any species. In L14-17 it is mentioned ‘Despite the dilution effect of cold air descending from the mountain slopes, benzene concentrations increased during the night in period 2, whereas toluene concentrations did not show any increase during the night in both period 1 and period 2.’

This shows that despite the dilution effect during nighttime, increase in ambient benzene concentrations were observed (also observed in acetonitrile but not in toluene or higher aromatics), which is probably due to varied forms of biomass combustion, including the biomass co-fired brick kilns.

We clarify this point and have modified the text in the revised version as follows (P25045 after Lines 14-21 of the ACPD version):

“Despite the dilution effect of cold air descending from the mountain slopes, benzene concentrations increased during the night in period 2, whereas toluene concentrations did not show any increase during the night in both period 1 and period 2, suggesting that biofuel and biomass burning sources (including the brick kilns co-fired with biomass) and not traffic were the driving factors responsible for nighttime increase in benzene during period 2 probably due to varied forms of biomass combustion, including the biomass co-fired brick kilns. The emission ratios of benzene/toluene from previous studies show that, for a wide variety of commonly occurring fuels, the emission of benzene can be more than twice as high as the emission of toluene (Tsai et al., 2003; Lemieux et al., 2004; Stockwell et al., 2015).”

25045, L23: “quarters” – any info on when these scheduled power outages occur? This would be important in the emissions production section.

The power outages were scheduled at different timings on different days for each municipal zone. The following table shows the power outages at the measurement site which was under Bode zone 3:

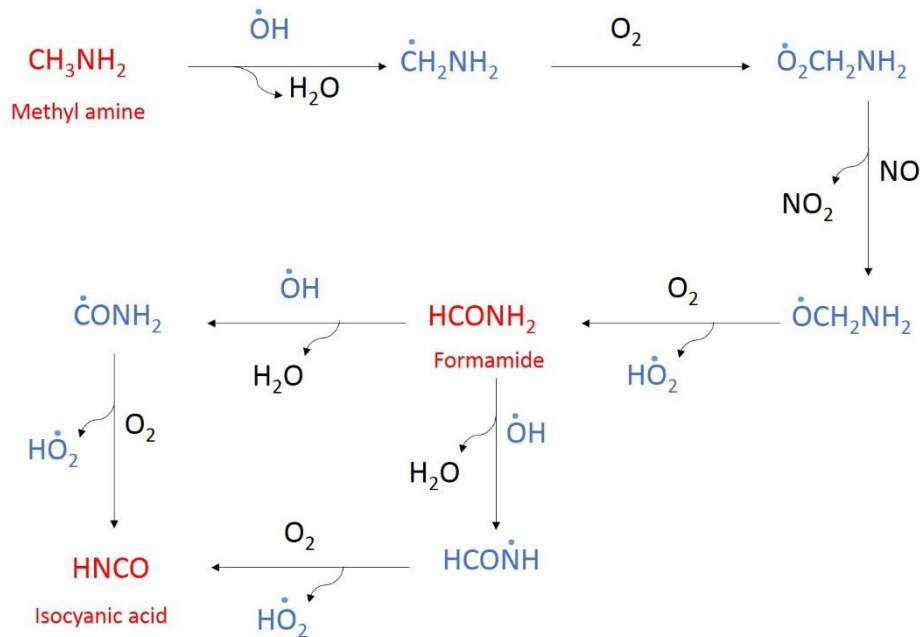
Day	Power outage timing (NST)
Sunday	11:00 - 14:00
Monday	19:30 - 21:30
Tuesday	20:00 - 22:00
Wednesday	10:00 - 14:00
Thursday	19:30 - 21:30
Friday	08:00 - 12:00
Saturday	20:00 - 22:00

So, from the power outage schedule it is very difficult to explain emission profile of any VOCs as there were alternate power outages in nearby areas and therefore no fixed timings can be associated with the operation of diesel generators.

25046, L9-12: “inclusion” . . . “is” - - - Also, in general, is enough known about the precursors of HNCO and the emissions of those precursors to model the photochemical source?

Done.

It is known from previous studies (Roberts et al., 2011, 2014; Zhao et al., 2014) that photooxidation of alkyl amines (which can be emitted as a result of incomplete combustion of biomass) leads to the formation of amides which then undergoes further photooxidation to produce isocyanic acid. This mechanism is the most likely pathway for the photochemical formation of isocyanic acid which was not included in the previous model based study by Young et al., 2012. The formation pathway for HNCO through photochemical oxidation reactions is represented in the following schematic:



25046, beginning section 3.5: What is the point here? The section starts off with widely known info that propene is emitted by fires and then mentions oil refineries in Texas? It's well known propene has multiple sources. The paper is very long so here and throughout you could condense considerably with sentences such as "Propene and possibly propyne have multiple sources (references), but the correlation with acetonitrile suggests that these compound were mostly from biomass burning."

Thanks for the suggestion.

We have deleted the following text from the original submission:

"This inference is consistent with previous studies (Hao et al., 1996; Akagi et al., 2011; Andreae and Merlet, 2001) that reported propyne and propene in plumes sampled from biomass burning. Average concentrations as high as 7.7 ppb propyne (maximum ~46 ppb) and 4 ppb propene (maximum ~34 ppb) were observed during the measurement period in the Kathmandu Valley. Previously, during the Texas Air Quality Study 2000, frequent propene concentrations of >100 ppb were measured using the PTR-MS technique (Karl et al., 2003). These were attributed to industrial sources related to oil refining."

The new lines now read as follows:

"These diel profiles correspond to data for the entire measurement period. Strong correlation ($r^2 \geq 0.7$ for the hourly averages) with acetonitrile clearly indicates that during our wintertime study in the Kathmandu Valley, all these compounds were primarily emitted from biomass

burning, despite having multiple sources (Hao et al., 1996; Akagi et al., 2011; Andreae and Merlet, 2001; Karl et al., 2003).”

25047, L11-12: How do long-lived N compounds contribute to reactive N budget?

Thank you for pointing out the incorrect choice of words. The corrected sentence now reads as follows:

“Propanenitrile reacts very slowly with hydroxyl radicals in the atmosphere ($k_{OH+propanenitrile}$ is of the order of $10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) but the oxidation of propanenitrile with OH radicals can produce nitrogen compounds in the troposphere and hence could contribute to the reactive nitrogen budget.”

25047, L25: Methanol is widely recognized as a biomass burning emission and biogenic emission, but its diurnal profile appears to resemble the acetonitrile profile in Figure 8, suggesting that it and nitromethane could be from biomass burning? Not sure why a diesel source of methanol is proposed? Biomass burning emits DMS also (Akagi et al., 2013 already cited) and forest vegetation can emit acetaldehyde and methanol each at 5-30 % of isoprene (see Table 1 in Karl et al., 2007, or Karl et al., 2004). The latter species are seen at much higher levels than isoprene, but taking lifetimes into account the biogenic source might be important. Most likely, given what we know about methanol and acetaldehyde ratios to acetonitrile from BB, the main methanol source could be BB and for acetaldehyde mostly photochemistry with some BB and biogenics. Not clear speculation about diesel for methanol is needed.

Karl, T.G., A. Guenther, R.J. Yokelson, J. Greenberg, M.J. Potosnak, D.R. Blake, and P. Artaxo, The tropical forest and fire emissions experiment: Emission, chemistry, and transport of biogenic volatile organic compounds in the lower atmosphere over Amazonia, J. Geophys. Res., 112, D18302, doi: 10.1029/2007JD008539, 2007.

Karl, T., Potosnak, M., Guenther, A., Clark, D., Walker, J., Herrick, J. D., and Geron, C.: Exchange processes of volatile organic compounds above a tropical rain forest: Implications for modeling tropospheric chemistry above dense vegetation, J. Geophys. Res., 109, D18306, doi: 10.1029/2004JD004738, 2004.

We thank the referee for this suggestion and have made appropriate corrections to the revised submission. Our main premise for thinking that methanol could be emitted from diesel

generators was the strong correlation with nitromethane (a tracer for diesel exhaust emissions as reported by Inomata et al., 2013, Sekimoto et al., 2013).

The referee's comment prompted us to check if methanol has been reported as a strong emission from diesel exhaust. We could not find any such result in the peer reviewed literature. We also compared the nitromethane/acetonitrile ratios (using nighttime data in the diel profiles of nitromethane and acetonitrile) with values reported by Akagi et al. (2013) from biomass fires.

We found that the Kathmandu nitromethane/acetonitrile ratios were 0.16 which is lower than the value of 0.27 reported by Akagi et al. (2013).

Hence we have removed the following line from the revised version:

“The correlation with methanol also suggests that diesel exhaust may be a contributory source for methanol.”

25049, L5-10: The authors state qualitatively that both BB and traffic dominate naphthalene emissions in KTM and then, by comparison to lower levels in Innsbruck, leap to a “profound” impact of BB in KTM that is not clear. There is actually substantial use of wood heat in Europe. “Profound” is not a quantitative term. Better to limit the paper to well-supported fractional contributions and insights and skip topics that are not clarified in this work.

For the revised version the following lines have been removed from the original submission to avoid the unintended confusion:

“Average morning (08:00-10:00 LT) ambient concentrations of ~0.6 ppb naphthalene observed during this study were much higher than the maximum concentrations of ~0.35 ppb reported by Jordan et al. (2009) in ambient air previously at Innsbruck, which is one more indicator of the profound influence on atmospheric composition exerted by biomass burning sources in the Kathmandu Valley during wintertime.”

25049, L14: It seems the designated so-called “prime emission times” are assuming a traffic source plus the authors already showed that ratios during these “prime emission times” are not representative of the whole day and they have referred often to a large BB impact. Maybe this concept of prime emission times is not that useful?

We agree that and have significantly revised and shortened Section 3.6. The major changes are:

Figure 9 of the original submission has been removed as per the referee's suggestion since the point about benzene from biomass burning sources has already been made.

Figure 10 of the ACPD version has been modified to highlight both the nighttime combustion source and daytime biogenic source of isoprene in the Kathmandu Valley.

25049, L25-6: Up to this point, it's as if the authors are arguing that biomass burning occurs mainly in early morning hours? Open burning is widely considered to peak in afternoon at lowest RH, cooking fires were stated to be bi-modal, brick kilns likely do not suspend firing during a multi-day production cycle. Thus maybe the early AM BB emissions are diverse local and regional/transported biomass burning (kilns, multiple types of open burning (garbage crop residue, etc), home heating fires) that accumulate overnight and stand out relative to traffic and biogenics that are less important at night? Or the wind direction is only right to see the BB in early AM? Also, is the location only 1 km from active kilns potentially more sensitive to kiln emissions than much of the rest of the valley?

Please see detailed reply to major comment 12 above for clarifications to some of the points being raised here which are repetitions of major comment 12 made by the referee.

We would like to point out that in South Asia, open burning does not peak in the afternoon at lowest RH. This is a misconception. The open burning peaks in the early morning or evening as a consequence of the traditional collective response of people who do not possess cleaner heating resources. This sizeable fraction of the populations copes with low temperatures (cold) by lighting small fires and huddling around the fires (this is a common sight in both rural and urban areas). In the context of the Kathmandu Valley and this work, the following points are worth re-iterating:

Outdoor fires for keeping people warm in winter normally take place in morning and evening, garden waste (leaves, grass and twigs) is also normally burnt in the evenings.

Burning of agricultural fields is not common in the valley. Also we note that there are either no winds or calm winds in the morning and very low mixing layer heights (~200 m) in the winter. Therefore what we see in the morning hours are emissions from the previous night

and emissions from morning activities around the measurement site, rather than regional emissions transported to the site.

Brick kilns operate 24 hours a day. Cooking with biofuel is not common among established households within the valley, but is done by construction crews in temporary camps/shelters.

Indoor heating with firewood is uncommon. Very few houses have fireplaces. If it is a very cold morning, people quite often light outdoor fires to gather around (similar to Northern India). Often they burn a combination of dry leaves, paper/cardboard/plastic etc.

Therefore, the early morning BB at the site is local in nature with contributions from the biomass co-fired brick kilns (as most of the time wind direction was south-east where brick kilns were located within 1 km) and domestic cooking activities.

25050. L8-22: Another lengthy section on a simple correlation that I believe was already mentioned. L18-22: the idea that “clean kilns” would reduce cancer, SOA, and winter fog is appealing, but it’s a bit complicated since (as mentioned in general comments) co-firing is used to reduce some pollutants.

As stated at the start of the response we have removed Figure 9 and have also deleted L8-22 on Page 25050 of the original submission. Regarding co-firing as a strategy for reducing emissions, please see reply to major comment 10 of the referee.

25050, L23 – 25051, L22: This could be clarified and shortened. It’s well known that traffic and BB make isoprene and that can rationalize nighttime isoprene and contribute to daytime isoprene. Isoprene can have on the order of 20% interferences though from other compounds even at high mass resolution (Yokelson et al. 2013 already cited) in fresh smoke. If the authors think the standard isoprene emissions inventories are too low can they: a) compare the inventory to observed emissions and b) estimate the fraction of observed isoprene from vegetation and combustion?

We have revised this section to clarify that both daytime biogenic sources of isoprene from vegetation, traffic sources as well as nighttime and morning biomass combustion contribute to the high concentrations of isoprene observed during winter in the Kathmandu Valley.

The contention of 20% interference has already been addressed in reply to major comment 3 of the referee.

The emission inventories REAS and EDGAR do not contain information regarding isoprene over Nepal. Using the MEGAN model, Guenther et al., 2012 reported isoprene emission factor of $< 2 \mu\text{mol m}^{-2} \text{h}^{-1}$ for January over Nepal.

The comparison and estimation of the fraction of isoprene from vegetation and combustion will be presented in the companion paper (Sarkar et al., 2016), in which source apportionment of VOCs has been performed using a positive matrix factorization (PMF) model. This is now mentioned in P25060, L27 as follows:

“The comparison and estimation of the fraction of isoprene from vegetation and combustion will also be presented in a companion paper (Sarkar et al., 2016) in which source apportionment of VOCs will be performed using a positive matrix factorization (PMF) model.”

25052, L1-6: Much higher isoprene mixing ratios (10-12 ppb) are often observed globally (Karl et al., 2007). Also “upto” not a word and a 2-orders of magnitude range of emissions get the same “very high” designation?

Karl et al., 2007 reported maximum 15 ppb of daytime isoprene in the Amazon rainforest during 14-29 September 2004 (not during winter) whereas our measurements were carried out during winter season. Moreover, Kathmandu Valley is an urban area while the Amazon is one of the world’s largest forested areas.

“upto” has been removed.

“very high” has been replaced by “significant”.

25052, L7-10: Mixing of biogenic and urban emissions has been a staple issue since at least the early 90s in SE US so 1-2 of hundreds of available citations could be enough. A general comment is that here and throughout, the analyses keep being pushed down the road and/or revisited. Suggest bringing up each topic where the authors can make a quantitative contribution just once and pursuing it at that point in full.

We have deleted it from here as it was redundant and a repetition from section 3.4.

25052, L17: For the OH reactivity estimate, it’s important to note what fraction of the total observed VOC mass is accounted for by the 33 species considered.

The 71 detected ions collectively comprised total mass concentrations of $\sim 160.4 \mu\text{g/m}^3$, out of which the 37 identified ions reported in this work accounted for $\sim 139.1 \mu\text{g/m}^3$ (or 86.7%).

This provides confidence that the major fraction has been accounted for in the subsequent analyses and discussion of the VOC speciation.

25053, L10: “four” should be “three”

Done.

25053, L23-27 and eqn 3: More sophisticated techniques are normally employed to determine AQ improvement strategies. It doesn't seem possible to rigorously rank/assess pollutants without considering O₃ and NO₃ as oxidants, NO₂ as a precursor to O₃ and PAN, etc. This is a job for a model.

The reason behind choosing OH as the primary oxidant has already been clarified and explained in the revised submission while addressing the previous comments (comments 7 and 11).

25054, L1-13: This is using a different part of the day, but just the same calculation as in equation 2, times a constant assumed OH and an undefined constant “n.” It doesn't seem like it could add a lot of insight? The discussions could be combined in summary form and both point to acetaldehyde as an important VOC. This is by the way a major emission of crop residue burning, in the cited reference by Stockwell et al. Piles of burning crop residue are notoriously common in Asia and this source may be worth more attention relative to brick kilns unless the authors can discount it?

This part showed the calculation for peak daytime hours (11:00-14:00 LT) when ozone photochemical production is maximum. The OH reactivity calculation represents the total reactive pollutant loading while ozone production potential calculation represents the peak daytime maximum ozone production potential due to VOCs. As mentioned while addressing the general comment 7:

The temporal context of the analyses performed using VOC data acquired during the afternoon (11:00-14:00 LT; period using which ozone production potentials were calculated) is quite relevant considering the recently published work of Putero et al. 2015, which highlighted that hourly average concentrations of > 60 ppb are often observed during winter afternoons in the Kathmandu Valley (refer Figure 9 of Putero et al., 2015). This shows that regional photochemistry is strong even during winter and formation of secondary pollutants contributes to hourly ozone concentrations in excess of 60 ppb.

The acetaldehyde peaks were observed in the morning (09:00-10:00 LT) and these peaks were sometimes as high as ~30 ppb and it did not have significant correlation with acetonitrile ($r^2 = 0.26$) which indicates acetaldehyde is unlikely to be from biomass/crop residue burning during 09:00-10:00 LT. Moreover, as explained previously trash burning activity occurred most strongly during the evening hours in the Kathmandu Valley.

25054, L14: “much lower” than what?

“much lower” than the ozone production potential of isoprene, oxygenated VOCs and other class of VOCs.

25054, L14-19: probably not necessary to put detailed minor results of approximate approach in text.

Ok, these lines have been removed from the revised manuscript.

25055, L1: Earlier the authors claim a significant fraction of the isoprene is from biomass burning, but appear to attribute it all to vegetation here.

We stated that nighttime isoprene had contributions from both traffic and biomass burning. Since in this section we have discussed about O₃ production potential and O₃ is formed only during daytime, we have chosen midday period (11:00-14:00 LT) when O₃ production is maximum. Since during midday hours isoprene concentrations are dominated by the biogenic source, O₃ production is mainly driven by biogenic isoprene.

In any case these lines have no longer been retained in the revised version as we have shortened the section by removing such discussion.

25055, L3-5: Again think the significance of this approximate approach may be exaggerated as noted above.

We have already addressed this concern and the relevance of such analyses in the replies to major comments 7 and 11.

25055, L19: Are the high-NO_x SOA yields known for most of the potentially significant precursors detected in this study? In a sentence, what are the gaps?

25055-6: Discussion of overall importance of SOA is general knowledge and can be condensed.

The high-NO_x SOA yields were known only for benzene, naphthalene, toluene, xylenes, monoterpenes, trimethylbenzenes, styrene and isoprene, which were detected in this study. For rest of the VOCs detected in this study, SOA yield at high NO_x are not known.

This section has been considerably shortened now in the revised manuscript. 50% reduction of the length relative to the ACPD version has been done for this section (Section 3.8).

Section 3.9. The discussion of health effects should be greatly reduced and referring to the average levels in table S1 is not that useful without also giving the recommended exposure limits. Synergistic effects are important and not well known. It should be noted that particulate matter typically dominates health effects and that PM is ignored here. Just present a brief list of gases of potential concern since the data to support conclusive statements is lacking.

This section has also been condensed in the revised manuscript and now we only mention the health relevant gases that were detected during this study and the context for putting in place a long term monitoring program for establishing exposure and assessing health risks due to these VOCs. 60% reduction of the length relative to the ACPD version has been done for this section (Section 3.9).

25057, L1-4: It's obvious that levels are higher closer to sources, but not that exposure lasts longer. This sort of statement is not needed in a scientific paper.

We have removed these lines for the revised manuscript.

25057, L5-14: Just summarize material given elsewhere.

Done, the revised summary on Page 25057 after Line 18 reads as follows:

“Atmospheric oxidation of amide compounds such as formamide and acetamide with hydroxyl radicals also contributes to the formation of isocyanic acid (Barnes et al., 2010). Ambient isocyanic acid was present at exposure levels of documented concern that can enhance human health risks for cataracts, cardiovascular diseases and rheumatoid arthritis via protein carbamylation (Wang et al. 2007 and Roberts et al., 2011).”

25057, L16-18: I don't think you can target the health impacts of a specific sector as a priority without aerosol data.

The concerned lines have been deleted and no longer appear in the revised submission.

25059, L14: delete repeated ppb

Done.

25059, L19-20: I thought methanol correlated with acetonitrile and I thought the authors said the acetaldehyde was largely photochemical, but DMS was a soil emission? Meanwhile, I think both the latter (and possibly all four) could be from crop residue burning.

As mentioned earlier, methanol has several sources in the Kathmandu Valley including the biomass co-fired brick kilns and burning of leaves and branches (mentioned in P25042, L8-9). Acetaldehyde also possibly had multiple sources such as biomass burning, photochemistry and solvent evaporation. Biogenic soil emissions and inefficient combustion of sulfur rich biofuel/biomass were suspected to be the major DMS sources (mentioned in P25048, L9-11). The possibility of crop residue burning as a source of methanol, acetaldehyde and DMS was insignificant as at the time of the year the VOC measurements were performed (December-January), no accumulation of crop residues were observed. The winter crops near the site were mainly vegetables. As the plot sizes were too small, nearby fields were mostly empty. Further away, some wheat was grown but since this was not the harvesting period, the crops were still growing on the fields. Stored crop residues used for co-firing the brick kilns (but not open crop residue burning at this time of the year) were investigated and confirmed and have also been reported previously by Stone et al. (2010).

As the text regarding the correlations of nitromethane with methanol and DMS with acetaldehyde on Page 25059 Lines19-20 does not add any new information and appears to create confusion, we have deleted those lines.

25060, L7-17: I think singling out co-fired kilns as opposed to traffic or other sources for mitigation would require aerosol data and an aerosol source apportionment as opposed to mainly circumstantial evidence regarding benzene emissions and peripheral discussions of “potential” for OH reactivity, O₃ formation, and SOA formation. I think the paper should focus on basic chemistry and a later SusKat paper could synthesize all the data and then hopefully make strongly supported recommendations. Also brick kilns are also “generic” in developing country cities and not just important in the Kathmandu Valley.

We appreciate the reviewer’s concerns.

Our study presents the first evidence of toxic VOCs such as benzene, isocyanic acid, nitromethane and naphthalene being associated with the biomass co-fired brick kilns emissions and biomass burning. While we did not measure particulate matter emissions from the biomass co-fired brick kilns in the Kathmandu Valley during our deployment, previous studies by Pariyar et al. 2013 and Raut 2003 have reported and documented massive increases in PM₁₀ and TSP for periods marked by the operation of the brick kilns relative to periods when they were not operational. The study conducted by Clean Energy Nepal (Raut 2003) showed that 8 h averaged concentrations of air pollutants such as Total Suspended Particulate (TSP), PM₁₀, SO₂ and NO_x were three times higher during the brick kiln operating period relative to the period they were not operational at the same location. The mass concentration of PM₁₀ increased from 218 µg m⁻³ to 603 µg m⁻³ while TSP increased from 265 µg m⁻³ to 634 µg m⁻³. Note that these were primarily Fixed Chimney Bull Trench Brick Kilns, similar to the ones that impacted our measurements. While brick kilns may be generic to developing countries as noted by the reviewer, the type of brick kilns in use in different developing countries is not the same. The Bull Trench kilns are an old and inefficient technology, which have been banned even in their place of origin, India, but continue to dominate the Kathmandu Valley landscape. A further point of consideration is that several brick kilns operate illegally in Kathmandu during the brick kiln seasons. All these facts have been documented in several works (Raut 2003, Tuladhar and Raut 2002, Pariyar et al. 2013).

We appreciate that these aspects would not be obvious and so to make things clearer in the revised submission have added these relevant references and following lines to the much shortened and re-written Conclusions Section (Page 25060, L7-17 of ACPD version) as follows:

“While we did not measure particulate matter emissions from the biomass co-fired brick kilns in the Kathmandu Valley during our deployment, previous studies by Pariyar et al. 2013 and Raut 2003 have reported and documented massive increases in PM₁₀ and TSP for periods marked by the operation of the brick kilns relative to periods when they were not operational. The study conducted by Clean Energy Nepal (Raut 2003) showed that 8 h averaged concentrations of air pollutants such as Total Suspended Particulate (TSP), PM₁₀, SO₂ and NO_x were three times higher during the brick kiln operating period relative to the period they were not operational at the same location. The mass concentration of PM₁₀ increased from 218 µg m⁻³ to 603 µg m⁻³ while TSP increased from 265 µg m⁻³ to 634 µg m⁻³. Note that

these were primarily Fixed Chimney Bull Trench Brick Kilns, similar to the ones that impacted our measurements. The Bull Trench kilns are an old and inefficient technology, which have been banned even in their place of origin, India, but continue to dominate the Kathmandu Valley landscape. Thus a major conclusion of this study is that the wintertime air pollution in the Kathmandu Valley can be significantly reduced by replacing the existing brick kiln technology with cleaner and more efficient brick kiln technology would aid air pollution mitigation efforts significantly.”

Pariyar, S. K., Das, T., and Ferdous, T.: Environment And Health Impact For Brick Kilns In Kathmandu Valley, INTERNATIONAL JOURNAL OF SCIENTIFIC & TECHNOLOGY RESEARCH, 2, 2013.

Raut, A. K.: Brick Kilns in Kathmandu Valley: Current status, environmental impacts and future options, Himalayan Journal of Sciences, 1, 10.3126/hjs.v1i1.189, 2003.

Tuladhar, B. and A. K. Raut, Environment & health impacts of Kathmandu’s brick kilns, Clean Energy Nepal, Kathmandu, 2002.

Regarding the other relevant manuscripts on SusKat, as mentioned in reply to general comment 12 , a companion paper on the source apportionment of VOCs in the Kathmandu Valley using the PMF model (Sarkar et al., 2016) and overview papers summarizing the air quality and policy recommendations are currently in preparation (Rupakheti et al. (2016) and Panday et al. (2016)).

This has been clarified by adding the following lines in the re-written Conclusion Section as follows:

“Comprehensive air quality and policy recommendations based on all the data acquired during the SusKat-ABC study and from other sites in the Kathmandu Valley will be summarized in future submissions to this Special Issue (Rupakheti et al. and Panday et al. (2016))”.