

**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)

Dear Editor,

Thank you very much for your kind consideration in granting an extension for submission of the author replies and final response.

In this response file for completeness sake we have consolidated replies to all the comments received during the interactive discussion review stage followed by the manuscript version listing the changes made to the original submission (in track changes mode). We hope that the new revised submission has addressed all valid concerns and can be considered for final publication in ACP.

Thank you for your kind consideration,

On behalf of all authors,

Vinayak Sinha

### **Authors' response to review comments:**

We thank the referees and Dr. Pokhrel for their comments and the generally positive remarks concerning the novelty of the work and its importance. In accordance with the suggestions regarding the presentation, we have made several changes in the revised version which are outlined in the detailed replies to the referees' comments and shown at the end of the responses using the "track changes" feature for easy perusal.

### **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.

Below the referees' and Dr. Pokhrel's comments are listed in black and our replies are given in blue.

### **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.

**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.”

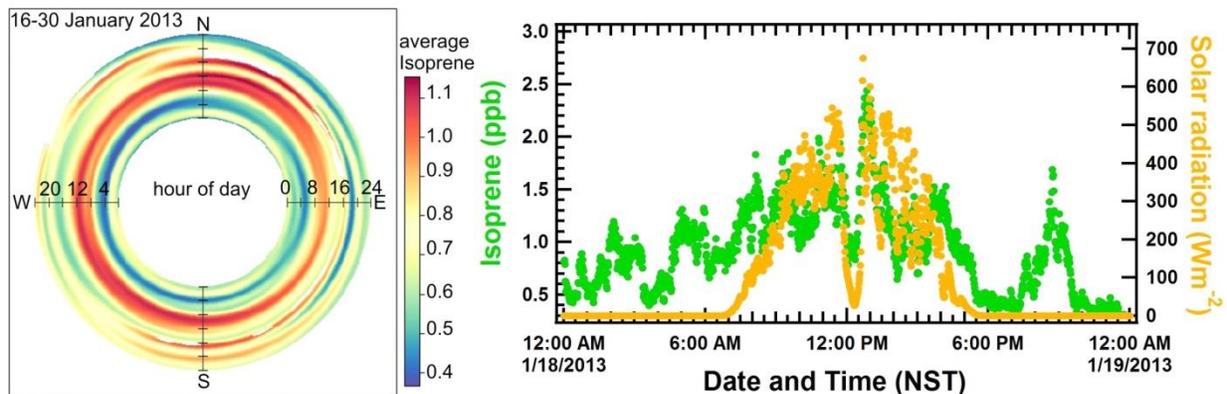
**3. Acetaldehyde, acetonitrile, isoprene concentrations were among the highest recorded in the world. They are among the highest reported for urban ambient air. Urban area isoprene could be overestimated due to isomers from other sources. For instance, in smoke the “isoprene peak” is 20% pentenes.**

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  $\text{h}^{-1}$  and  $4.7 \mu\text{g g}^{-1}$  dry leaf  $\text{h}^{-1}$  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  $^{13}\text{C}$  if applicable, but this should be clear.**

For the calculation of VOC mixing ratios in this study, interference from  $^{13}\text{C}$  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.  $^{13}\text{C}$ ) 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 μs 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<sub>x</sub> 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<sub>x</sub> and O<sub>3</sub> 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 NO<sub>3</sub> 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 O<sub>3</sub> 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 be 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<sub>x</sub>. 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 CO<sub>2</sub>.**

(<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 CO<sub>2</sub>, 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 PM<sub>10</sub> 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), PM<sub>10</sub>, SO<sub>2</sub> and NO<sub>x</sub> 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 PM<sub>10</sub> increased from 218 µg m<sup>-3</sup> to 603 µg m<sup>-3</sup> while TSP increased from 265 µg m<sup>-3</sup> to 634 µg m<sup>-3</sup>. 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 CO<sub>2</sub>, 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) , PM<sub>10</sub>, SO<sub>2</sub> and NO<sub>x</sub> 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 O<sub>3</sub> and NO<sub>3</sub>.**

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](http://kinetics.nist.gov/kinetics)).”

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

Compound	$k_{OH+VOC}$ in $\text{cm}^3$ $\text{molec}^{-1} \text{s}^{-1}$	$k_{O_3+VOC}$ in $\text{cm}^3$ $\text{molec}^{-1} \text{s}^{-1}$	$k_{NO_3+VOC}$ in $\text{cm}^3$ $\text{molec}^{-1} \text{s}^{-1}$
Hydrogen Cyanide	$2.5 \times 10^{-14}$	-	-
Formaldehyde	$8.5 \times 10^{-12}$	$2.1 \times 10^{-24}$	$5.6 \times 10^{-16}$
Methanol	$8.6 \times 10^{-13}$	$1.3 \times 10^{-16}$	$1.3 \times 10^{-16}$
Propyne	$2.8 \times 10^{-12}$	$1.2 \times 10^{-18}$	$2.3 \times 10^{-16}$
Acetonitrile	$1.7 \times 10^{-14}$	-	$5 \times 10^{-19}$
Propene	$2.5 \times 10^{-11}$	$1.0 \times 10^{-17}$	$9.5 \times 10^{-15}$
Acetaldehyde	$1.5 \times 10^{-11}$	$3.4 \times 10^{-20}$	$2.4 \times 10^{-15}$
Formamide	$3.9 \times 10^{-12}$	-	-
Formic acid	$4.0 \times 10^{-13}$	-	-
Ethanol	$3.0 \times 10^{-12}$	-	$2.0 \times 10^{-15}$
1,3-Butadiyne	$1.4 \times 10^{-11}$	-	-
Propanenitrile	$2.4 \times 10^{-13}$	-	-
Acrolein	$1.9 \times 10^{-11}$	$3.6 \times 10^{-19}$	$1.1 \times 10^{-15}$
Acetone	$1.5 \times 10^{-13}$	$3.0 \times 10^{-17}$	$8.5 \times 10^{-18}$
Acetamide	$3.1 \times 10^{-12}$	-	-
Acetic acid	$7.8 \times 10^{-13}$	$2.8 \times 10^{-18}$	$3.6 \times 10^{-18}$
Nitromethane	$1.4 \times 10^{-14}$	$1.2 \times 10^{-20}$	-
Dimethyl Sulfide	$5.1 \times 10^{-12}$	$1.0 \times 10^{-18}$	$1.1 \times 10^{-12}$
1,3-Cyclopentadiene	$8.2 \times 10^{-11}$	-	$2.3 \times 10^{-12}$
Furan	$3.8 \times 10^{-11}$	$2.4 \times 10^{-18}$	$1.4 \times 10^{-12}$
Isoprene	$1.0 \times 10^{-10}$	$1.2 \times 10^{-17}$	$6.7 \times 10^{-13}$
MACR	$3.0 \times 10^{-11}$	$1.9 \times 10^{-18}$	$3.3 \times 10^{-15}$
MVK	$1.8 \times 10^{-11}$	$4.4 \times 10^{-18}$	$1.2 \times 10^{-16}$
Methylglyoxal	$1.4 \times 10^{-11}$	$5.9 \times 10^{-21}$	-
Methyl ethyl ketone	$1.0 \times 10^{-12}$	$2.0 \times 10^{-16}$	-
Hydroxyacetone	$5.6 \times 10^{-12}$	-	-
Benzene	$1.0 \times 10^{-12}$	$1.7 \times 10^{-22}$	$3.0 \times 10^{-17}$
2,3-Butanedione	$2.0 \times 10^{-13}$	-	-
Toluene	$5.8 \times 10^{-12}$	$3.9 \times 10^{-22}$	$6.7 \times 10^{-17}$
2-Furaldehyde	$4.2 \times 10^{-11}$	-	-
Styrene	$5.1 \times 10^{-11}$	$1.6 \times 10^{-17}$	$1.5 \times 10^{-13}$
Xylenes	$1.3 \times 10^{-11}$	$1.3 \times 10^{-21}$	$4.5 \times 10^{-16}$
Trimethylbenzenes	$2.9 \times 10^{-11}$	$1.3 \times 10^{-21}$	$1.8 \times 10^{-15}$
Naphthalene	$2.3 \times 10^{-11}$	$3.0 \times 10^{-19}$	-

**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 O<sub>3</sub>, 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<sub>y</sub> measurements during December 2012 –January 2013 (the period of the PTR-TOF-MS deployment) or even later from Bode (the measurement site). O<sub>3</sub> 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.

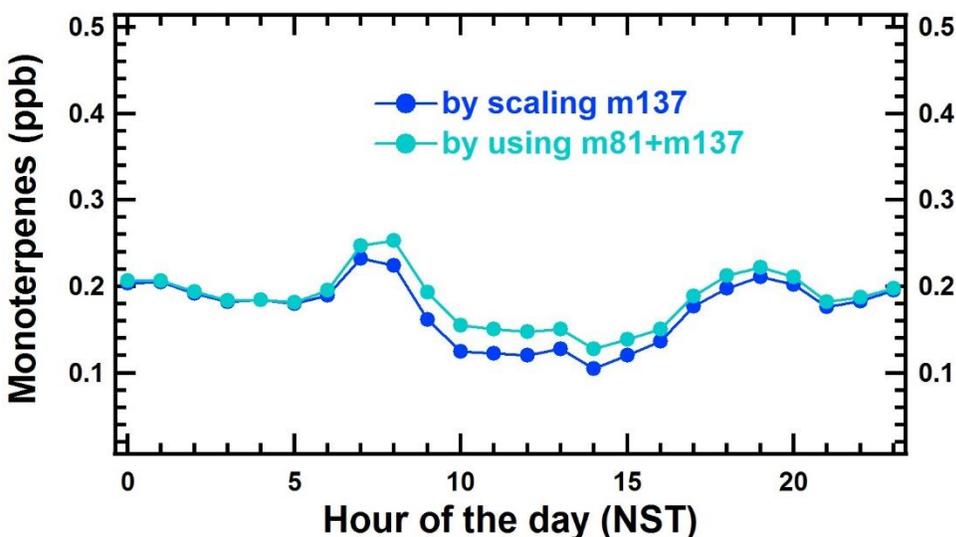
Sinha, V., Williams, J., Lelieveld, J., Ruuskanen, T. M., Kajos, M. K., Patokoski, J., Hellen, H., Hakola, H., Mogensen, D., Boy, M., Rinne, J., and Kulmala, M.: OH Reactivity Measurements within a Boreal Forest: Evidence for Unknown Reactive Emissions, *Environmental Science & Technology*, 44, 6614-6620, 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 ( $\alpha$ -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:  $0.19 \pm 0.06$  ppb

Using scaling approach it was  $0.17 \pm 0.04$  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  $\text{NO}_2^+$  (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  $\text{NO}_2^+$  (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.pecs.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

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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

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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:



“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 reiterating:

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  $\sim 160.4 \mu\text{g}/\text{m}^3$ , 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%). 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 O<sub>3</sub> and NO<sub>3</sub> as oxidants, NO<sub>2</sub> as a precursor to O<sub>3</sub> 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 O<sub>3</sub> production potential and O<sub>3</sub> is formed only during daytime, we have chosen midday period (11:00-14:00 LT) when O<sub>3</sub> production is maximum.

Since during midday hours isoprene concentrations are dominated by the biogenic source, O<sub>3</sub> 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<sub>x</sub> 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<sub>x</sub> 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<sub>x</sub> 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 Lines 19-20 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, O<sub>3</sub> 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 PM<sub>10</sub> 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), PM<sub>10</sub>, SO<sub>2</sub> and NO<sub>x</sub> 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 PM<sub>10</sub> increased from 218 μg m<sup>-3</sup> to 603 μg m<sup>-3</sup> while TSP increased from 265 μg m<sup>-3</sup> to 634 μg m<sup>-3</sup>. 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 PM<sub>10</sub> 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), PM<sub>10</sub>, SO<sub>2</sub> and NO<sub>x</sub> 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 PM<sub>10</sub> increased from 218 µg m<sup>-3</sup> to 603 µg m<sup>-3</sup> while TSP increased from 265 µg m<sup>-3</sup> to 634 µg m<sup>-3</sup>. 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))”.

Regarding the contents of this paper, please see list of major changes at the start of the response for details. Briefly, 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.

#### **REFEREE 2:**

**This manuscript by Sarkar et al. reports VOC composition in the Kathmandu Valley, Nepal and those were measured by high mass-resolution PTR-TOF-MS. In addition to quantifying and characterizing major VOCs in this area, they tried to calculate OH reactivity, ozone production potential, and SOA formation potential for understanding VOC's impacts on local air pollution. This study may be a noble measurement and unique analysis in South Asia. Using PTR-HR-TOF-MS, even though it provides a great data set with high time and mass resolution, there is a serious flaw when PTR-TOF-MS measurement data were solely used. Because either PTR-QMS or PTR-TOF-MS gives information of mass to charge ratios (m/z), it is necessary to do VOC speciation and inter-comparison by other techniques such as GC-MS/FID, thus VOC characterization at the site**

should be preceded or done at the same time. Otherwise, it is not easy to define each  $m/z$  as one or two specific compound(s) by PTR technique, though number of atoms like C, H, O, N and S in the molecule can be closely identified. For example, even though  $m/z$  69.07 is well known as protonated isoprene, it can also include some other compounds such as MBO fragment and pentenes as mentioned Referee #1. In this respect, the authors need to be very careful in defining and quantifying specific compounds with  $m/z$ . Even though the PTR-TOF-MS VOC data reported here are valuable and unique in this region, I think that the title starting with 'Overview: : ' is inappropriate since the data implies big uncertainties when PTR-MS data solely used as mentioned previously. In the discussion, it seems VOCs

In addition, the authors should more strengthen the reason why OH reactivity, ozone production potential, and SOA formation potential are crucial in this area. They just calculated them based on detected VOCs by PTR-TOF-MS, but I don't think this simple estimation is meaningful since there are no data shown related to photochemistry such as ozone and NO<sub>x</sub>. The authors did not even discuss about importance of photochemistry during winter in this area.

Overall, I agree most things which Referee #1 pointed out, and also the manuscript has to be considerably shortened. The manuscript is not logically written and not well organized. It was very hard to understand what the main points are in the result and discussion section. Although this manuscript may be worthy as a report for VOC concentration in where the data do not exist (but still highly uncertain due to instrumental limitation), it is not enough to be published in ACP in terms of scientific scope and findings for the readers. In my opinion, therefore, this manuscript cannot be accepted by current form. However, if it is accepted by any chance, all my comments and suggestions below should be reflected.

Although we appreciate the referee's efforts in considering and commenting the manuscript, it appears that the referee is not familiar with the interpretation and use of PTR-MS techniques and most of his/her remarks stem from this lack of familiarity and expertise with PTR-TOF-MS. He/she also does not realize that compounds measured using the PTR-MS technique are typically not even measured by GC-FID and GC-MS in field studies, and that both are rather complementary in terms of the species detected. Perhaps it is helpful to briefly state some points

regarding the advantages and disadvantages of analytical techniques such as PTR-MS (which is an example of positive chemical ionization mass spectrometry or CIMS), Negative ion-CIMS, GC-MS and FTIR for VOC speciation measurements as reported in the peer reviewed literature. We quote from the work of Yokelson et al. 2013 (Page 3) where all these techniques were deployed simultaneously for VOC speciation in biomass smoke and ambient air:

“CIMS is very sensitive (ppt detection limits), broadly sensitive when  $H_3O^+$  is the reagent ion (most NMOC, with the exception of alkanes, can be measured by PIT- or PTR-MS), and the sensitivity typically does not vary by more than about  $\pm 50\%$  between species. In contrast, FTIR, while sensitive to an even broader range of species (e.g. organics and inorganics), has higher detection limits and the sensitivity to individual NMOC can vary by several orders of magnitude (Sharpe et al., 2004). GC-MS sensitivity to individual NMOC can also vary by several orders of magnitude (Gilman et al., 2013). Thus, the amount of substance associated with an unknown peak in an IR spectrum, or a GC-MS chromatogram cannot usually be assigned with a level of certainty near that for CIMS. GC-MS and FTIR techniques can both detect some species not measured by CIMS and both can be useful for assigning at least some of the CIMS signal when more than one species has the same mass at unit mass resolution (Christian et al., 2003; Karl et al., 2007; Warneke et al., 2011; Gilman et al., 2013).”

We note that the PTR-TOF-MS deployed during our study had a mass resolution  $> 4200$  which was sufficient to yield the monoisotopic masses of detected VOCs. Considering the careful QA/QC measured followed for the attribution of ion peaks to ambient compounds, there is considerable confidence in the attribution of compounds to ions of specific  $m/z$  (please see Section 3.1 of the ACPD version, P25035, L1-13 and the reply to major comment 2 of referee 1). Further it is worth re-iterating here that for fifteen VOCs, the overall measurement uncertainties were less than 20% in all cases and for several even lower: (e.g. acetaldehyde 9.9%; acetone 9.6%; isoprene 15.4%; benzene 9.4% and toluene 8.9%). This has been clearly mentioned in Lines 7-8 on Page 25034 of the ACPD version. Validation studies involving attribution of ion peaks to specific compounds have been reviewed extensively by de Gouw and Warneke 2007 for unity resolution PTR-MS instruments during inter-comparison studies with other analytical techniques and for a variety of complex ambient air samples in varied ecosystems of the world. The analyses and results of the reviewed studies is that for several ambient compounds (notably

most of the fifteen compounds that were reported at uncertainties of less than 20%), one is fairly certain about the attribution. So in our opinion the sweeping remarks of referee 2 concerning the PTR-TOFMS technique are neither valid nor justified.

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.

Yokelson, R. J., Burling, I. R., Gilman, J. B., Warneke, C., Stockwell, C. E., de Gouw, J., Akagi, S. K., Urbanski, S. P., Veres, P., Roberts, J. M., Kuster, W. C., Reardon, J., Griffith, D. W. T., Johnson, T. J., Hosseini, S., Miller, J. W., Cocker Iii, D. R., Jung, H., and Weise, D. R.: Coupling field and laboratory measurements to estimate the emission factors of identified and unidentified trace gases for prescribed fires, *Atmos. Chem. Phys.*, 13, 89-116, 10.5194/acp-13-89-2013, 2013.

The possibility of interference in ambient measurements of isoprene from pentenes and MBO for our work is not significant and has already been discussed in detail while addressing general comment 3 of referee 1.

The title starting with 'Overview..' is appropriate as this paper reports the possible emission sources and the chemistry of a suite of reactive VOCs ( in all 37 compounds have been reported which is quite comprehensive considering most VOC speciation studies).

The importance of OH reactivity, O<sub>3</sub> and SOA production potential and the wintertime photochemistry has already been discussed and clarified where relevant in the replies to the comments of reviewer 1 (please see replies to general comments 7, 8 and 11 of referee 1 for details).

Christian, T. J., Kleiss, B., Yokelson, R. J., Holzinger, R., Crutzen, P. J., Hao, W. M., Shirai, T., and Blake, D. R.: Comprehensive laboratory measurements of biomass-burning emissions: 2. First intercomparison of open-path FTIR, PTR-MS, and GC-MS/FID/ECD, *J. Geophys. Res.*, 109, D02311, 10.1029/2003jd003874, 2004.

### **Specific comments:**

**- Abstract: This part should be rewritten after revision of the MS if it is accepted.**

Abstract has been suitably modified keeping in mind relevant changes.

**- P.25050, L5-8: Add average concentration information of air pollutants for similar period when the experiment was conducted in winter.**

This comment is no longer relevant. As mentioned while addressing the comments (short comment on 25049, L14 regarding selection of “prime emission hours”) of reviewer 1, these lines have been deleted for the revised submission.

**- P.25030, L4-8: The meteorological parameters obtained are limited for the last 15 days of the campaign period. Do you expect that the meteorological condition of this region is similar to the earlier period of the campaign and typical for winter time in this area? Please, add some more information on this issue.**

Yes, the meteorological conditions of this region during the winter season of December 2012 and January 2013 were quite similar and followed the typical diel pattern of westerly winds in the afternoon and shallow nocturnal boundary layer with similar wind direction changes (e.g. weak easterlies at night). This has also been reported in previous studies (Panday et al., 2009; Panday and Prinn, 2009; Regmi et al., 2003; Kitada and Regmi, 2003), so that the wintertime meteorology observed during our study is typical of the Kathmandu Valley. We have clarified this in the revised version as:

“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 and also been addressed in reply to the general comment 12 of reviewer 1.

**- P.25030, L18: Add the range of atmospheric pressure during the campaign.**

Done.

We have added this information in Section 2.1, P25030, after L18 which reads as:

“The range of atmospheric pressure during the campaign was 856-866 hPa.”

**- P.25031, L8-15: Indicate the size and length of Teflon tube, and the flow rate. Moreover, was the inlet heated or kept with a constant temperature? This is important for some sticky compounds such as methanol and acetic acid, because the wall loss for those kinds of compounds could be significant with low temperature in the long-line tube. Based on the data shown here, the ambient temperature fluctuation between day and night is almost more than 15 degree C. So, in the tube the wall loss and degassing for some OVOCs might be very significant. Have you conducted the wall loss test with the same inlet in the lab? This issue needs to be discussed in this section. In addition, as stated that the inlet was located on rooftop of the building, wasn't there any potential interference in sampling ambient air such as ventilation outputs of the building or air conditioning facilities?**

The queries regarding the use of Teflon tube, temperature effect and wall loss of VOCs have already been addressed in detail in reply to the comments of reviewer 1 (please see above).

The sampling flow was circa 500 sccm.

The inlet was located in a portion of the rooftop that was far away from the ventilation outputs of the building. There was no air conditioning facility in the building.

**- P.25032, L1-3: Twice of instrument calibration are not enough to confirm reliable concentration covering 40 days of the campaign. Even those calibrations were performed in the middle of the campaign. Justify these limited calibrations and reliability of data usage. Also, discuss if calibration factors for each standard compound between two calibrations were changed or not.**

It appears that the reviewer is not familiar with the sensitivity response of VOCs in a PTR-MS, which remain remarkably stable if instrumental operational conditions are not changed. This is borne by several previous studies (de Gouw et al., 2007) including our own group's recent studies in the South Asian environment which involved a three year study (Chandra and Sinha, 2016) and a month long study (Sinha et al., 2014). We have added this point and the references to clarify this aspect in the revised version. Once installed, optimized and deployed, the instrumental conditions employed in our work were not changed.

Note that the two calibration experiments made during the course of the field study did not shows changes in the VOC sensitivities (values were within the precision error; e.g. for acetonitrile the values were 20.9 and 21.4 ncps/ppb, respectively; for acetaldehyde the values were 20.0 and 20.4 ncps/ppb, respectively; for toluene the values were 15.8 and 15.6 ncps/ppb, respectively), as already reported in the original submission. We have now also clarified this in the revised text as follows (P25032, L16):

“The two calibration experiments made during the course of the campaign did not reveal changes for the VOC sensitivities (values were within the precision error) as instrumental operational conditions were not changed. Usually, the sensitivity response of VOCs in a PTR-MS remain remarkably stable if instrumental operational conditions are not changed. This is borne by several previous studies (de Gouw and Warneke, 2007) including our own group's recent studies in the South Asian environment which involved a three year study (Chandra and Sinha, 2016) and a month long study (Sinha et al., 2014).”

**- P.25032, L7-8: Shortly state how the RH was controlled? Moreover, as shown in the Figure 2, the RH went down below 40% during daytime, but the calibration did not covered below 60% of RH. Explain this.**

During the calibrations, the RH was controlled as per the details provided in Kumar and Sinha (2014). We have included this reference in the revised MS at the relevant sentence (P25032, L8).

“RH was controlled as per the details provided in Kumar and Sinha (2014).”

As reported in de Gouw and Warneke (2007) and Sinha et al. (2009), 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.

Kumar, V. and Sinha, V.: VOC–OHM: A new technique for rapid measurements of ambient total OH reactivity and volatile organic compounds using a single proton transfer reaction mass spectrometer, *Int. J. Mass Spectrom.*, 374, 55–63, doi:10.1016/j.ijms.2014.10.012, 2014.

Sinha, V., Custer, T. G., Kluepfel, T., and Williams, J.: The effect of relative humidity on the detection of pyrrole by PTR-MS for OH reactivity measurements, *International Journal of Mass Spectrometry*, 282, 108-111, 10.1016/j.ijms.2009.02.019, 2009.

**- P.25032, L8-12: How often was the zero air test performed in a day and during the campaign?**

Zero air tests were performed at intervals of 3-4 days during the campaign. This information has been added to Section 2.2, P25031 after L13 in the ACPD version.

**- P.25033, L7-14: Is alpha-pinene dominant at this area? Fragmentation patterns of monoterpenes are depends on not only instrumental condition but also different monoterpene species as shown Tani et al. (2004) paper. Thus, if this site is characterized as an alpha-pinene dominant area, the uncertainty in estimating MT concentration can be minimized. Otherwise, m81 and m137 which are calibrated and scaled in this study will imply a big uncertainty. Therefore, if this is the former case, please provide appropriate references or data. One idea which I can suggest is to compare the data you applied in the MS to the sum of major fragments' and parent ion's concentration (e.g. m81+m95+m137+...) obtained using the transmission curve.**

This has already been answered while addressing the comments of reviewer 1.

**- P.25033, L7-14: How did you get the transmission curve? Have you done any transmission test in the lab or at the site? Also, what do the black dots indicate in Figure**

**S1? Specify what gases and what concentrations of those gases were used to get the transmission curve.**

The sensitivity curve was obtained using the normalized response of calibration factors (ncps/ppb) versus mass (calibrated species labeled by name) which was overlaid with the linearly fitted mass-dependent transmission curve (black markers and dotted line). For example, in Figure S1, benzene has a mass-dependent transmission value of 3.31 (black dot) which was overlaid to its calibration factor of 13.43.

Transmission test was performed at the factory before the instrument was shipped to the field site with comparable results. The referee may kindly refer to Stockwell et al. 2015 for details of this approach as they were the first to outline this method for quantification of compounds in the absence of calibration standards the compounds. Black dots are the transmission values for primary ion ( $\text{H}_3\text{O}^+$ ; m21), benzene (m79), toluene (m93), trimethylbenzenes (m121), dichlorobenzenes (m147) and trichlorobenzenes (m181). These aromatic VOCs were present at ~1 ppm concentration in the VOC canister standard and the calibrations were performed in the concentration range of 2-10 ppb.

**- P.25033, L1-11: Did you also take account of the uncertainty by RH changes in the total uncertainty?**

No. These were not deemed necessary for reasons already mentioned while addressing the concern of RH effects on sensitivity of compounds during the deployment in Kathmandu.

**- P. 25036, L20-26: It is unclear how O/C and N/C ratios were estimated. Describe it or add references.**

It was calculated using the number of carbon/oxygen/nitrogen atoms present in a compound and their respective mixing ratios. In any case, this has been deleted from the revised version and therefore no longer has any relevance for the revised submission.

**- P. 25037, L15-20: How was the meteorological condition changed in two periods? Since the meteorological data shown in the manuscript only covered few days of period 2, it is not clear if the air mass also was changed or not.**

Meteorological conditions/air mass were similar during both the periods as mentioned while addressing the comments of reviewer 1 (general comment 12 and other short comments).

**- P. 25038, L8-9: When is daily operating time for the brick kilns? Were they closed during the weekend?**

The brick kilns were operational around the clock throughout the week as well as during the weekend during period 2.

**- P. 25040, L15-18: Are you sure that the evening isoprene peak is due to traffic from the cities? Based on the met data, the wind direction in the evening started to change from westerly to southerly.**

This has already been answered while addressing the comments of reviewer 1 (see reply to general comment 3 and other short comments).

**- P. 25041, L23-28: The descriptions in the parenthesis for two periods are not necessary since it is already mentioned previously.**

These lines have been removed from the revised manuscript.

**- P. 25042, L6-9: Based on figure 7, it seems morning time concentrations of methanol, acetonitrile, and benzene were relatively higher during period 2, but methanol and benzene in the afternoon (14:00 – 20:00) were lower than those in period 1. In addition, isocyanic acid was consistently higher during period 2. This indicates much more complexity to generalize contributing sources. For example, brick kilns are located to the east, but wind blew westerly during the daytime. So, I expect the daytime contribution by brick kilns is minimized. Moreover, if at night the brick kilns were not operated and no burning leaves, the source identification should be carefully discussed.**

Morning time concentrations of methanol, acetonitrile and benzene were relatively higher during period 2 due to contribution of different type of biomass combustion along with biomass co-fired brick kilns. For some of the oxygenated compounds such as methanol, acetone and benzene the afternoon high concentrations can be due to industrial solvent evaporation as some of them are widely used as solvents in the industries and period 1 had higher ambient temperature as compared to period 2.

Concentrations of isocyanic acid were consistently higher during period 2 likely due to contribution from biomass co-fired brick kiln emissions and biomass burning which emit the precursor compounds (alkyl amines, acetamide and formamide). These precursor compounds undergo photochemical oxidation to form amides such as formamide and acetamide which undergo further photochemical oxidation to produce isocyanic acid.

As mentioned while addressing the previous comments, the brick kilns in the Kathmandu Valley operated 24/7 after they commenced operations in the first week of January.

**- P. 25044, L12-19: Add a plot in figure 7 for m/z 71.049 (this is on the list in Table S1) which is major photo-oxidation products (MVK, MACR, : : :) from isoprene.**

We don't think adding the plot of m/z 71.049 (MVK + MACR..) is warranted as the objective of Figure 7 is to examine the variability in the major VOC emission tracers and isocyanic acid (a toxic VOC for which sources less well understood) between periods 1 and 2. Also, we do not expect MVK +MACR to only have a photochemical source from isoprene oxidation as happens within a forest, so in our opinion such analysis would not add much information in the context of the present work. We note that Figure 7 was appreciated by Referee 1.

**- P. 25044, L20- : What about sum of monoterpenes? In the experimental section, you mentioned about monoterpenes calibration, however no data were shown in the manuscript and supplementary.**

We note that the average ambient concentrations of the sum of monoterpenes ( $0.17 \pm 0.16$  ppb) were reported and discussed in Section 3.8, where SOA formation potentials were summarized.

**- P. 25045, L4-10: Again, the nighttime activity of brick factory has to be discussed since daytime concentration in the afternoon of acetonitrile and benzene did not differ from period 1 and even higher for benzene.**

As mentioned earlier while addressing the previous comments, brick kilns in the Kathmandu Valley were operational even during nighttime.

**- P. 25046, L16 - P 25049, L11 (Section 3.5): It is not necessary to overlap representative VOC diurnal cycle with rarely measured VOCs in figure 8. I would suggest re-making it**

the same way as figure 7 by dividing into period 1 & 2. By comparing them, discussion about sources will be clearer.

In Figure 8, comparison of rarely measured VOCs with major VOC tracers were useful to constrain sources of rarely measured VOCs as the major VOC tracers have known sources. Therefore, overlapping the diel profiles of rarely measured VOCs with the representative VOCs for which sources are better understood provides insights into the potential sources of the rarely measured VOCs (for which the sources are typically poorly understood).

**- P. 25050, L17-18: What is the correlation between acetonitrile and benzene through- out the whole period or different two periods?**

The  $r^2$  value between acetonitrile and benzene for the whole campaign was 0.72.

**- P. 25052, L11 - P 25055, L5 (Section 3.7): What is the motivation to calculate for OH reactivity and ozone production potential? Is the wintertime photochemistry important in this area? What were the ozone and NO<sub>x</sub> concentrations recorded during the campaign, and how much did detected VOCs contribute to produce actual ambient ozone? VOCs reported in this manuscript were only limited number of VOCs since those were detected by PTR-TOF-MS (i.e. PTR-MS detects VOCs having higher proton affinity than that of water), thus in the context ‘total VOC OH reactivity’ is not appropriate. Moreover, throughout the manuscript discussions on each VOC were more focused on direct emission from different sources without chemistry and also you discussed their diel profiles were mainly due to meteorological condition. So, what do OH reactivity and ozone production potential imply during wintertime?**

This has already been answered while replying and clarifying similar related concerns of referee 1 (general comments 7, 11 and other short comments).

**- P. 25055, L6 - P. 25056, L4 (Section 3.8): Along with Section 3.7, this section is not quite meaningful. How much did SOA formation by detected VOCs contribute to total aerosol in this area? Do you expect those were very significant? In addition, monoterpenes were suddenly discussed in this section because of their high reactivity. What do you expect about other VOCs which you excluded below 200 ppt.**

Both section 3.7 and 3.8 have now been shortened in the revised manuscript.

Among other VOCs below 200 ppt, SOA yield at high NO<sub>x</sub> concentrations were reported for monoterpenes only. That is why monoterpenes were mentioned in this section. In any case as the identified mass of VOCs is almost 88%, the unidentified mass is obviously less important.

**- P. 25057, L19 - P. 25056, L4 (Section 4): The conclusion should be re-written after reflecting all comments.**

Conclusions have been revised and shortened.

**Figures:**

**- Overall, the letters are too small to read, particularly Figures 2, 6, and 12.**

The font size of Figures 2, 6 and 12 (of ACPD version) have been increased in the revised manuscript.

**- Figure 2: Indicate site location in the valley if it was in the middle or towards to right or left.**

We don't think it is necessary as this Figure shows the wind pattern for the whole Valley.

**- Figure 8: Re-draw each compound as the same as Figure 7 by dividing into two periods.**

We don't think it is a good idea as in Figure 8 comparison of rarely measured VOCs with major VOC tracers were useful for constraining sources of the rarely measured VOCs. Therefore, we prefer to keep the original Figure as the new one proposed by the referee would be less useful.

**Short comments from A. Pokhrel:**

**Thanks for this new data set from new sampling site of Nepal. Data set are very interesting.**

**1. Author should improve explanation of Introduction, Discussion, and Conclusion. For instance, Page 25026 and lines 13-17 are unnecessary. Similar ways many speculations can be observed in discussion section.**

We have made significant revisions to the Discussion and Conclusion section. As Dr. Pokhrel has not been specific regarding why and what changes he would like in the Introduction, we do

not think any changes to the Introduction are required. We also note that none of the two referees had any such suggestions regarding the Introduction.

P25026 L13-17: We have removed the lines pertaining to health impacts of isocyanic acid but retain the lines pertaining to nitromethane and benzene as they have been recognized by WHO to be human carcinogens.

## **2. What is the duplicate and triplicate error of data set?**

It appears that Dr. A. Pokhrel is not familiar with online ambient air measurements.

Duplicate and triplicate error are not very relevant for high temporal resolution (online) ambient measurements which are even able to capture the short term variability (seconds to minutes) of chemical concentrations due to changing ambient conditions.

The measurement uncertainty for interpreting the VOC measurements reported using the PTR-TOF-MS technique has already been described on P25034, L1-11.

## **3. Author might read the following papers of VOCs and/or SOA tracers and isoprene SOA tracers for exact mechanism, and he can improve the discussion and conclusion.**

For example, Claeys et al., Surratt et al., Nozair et al., Faiola, et al., Guenther et al., Fu et al., Hallquist et al..

Specifically (at least),

Nozière et al., *Chem. Rev.*, **115**, 3919-3983, 2015.

Surratt et al., *Proc. Natl. Acad. Sci. U.S.A.*, **107**, 6640-6645, 2010.

Carlton et al., *Atmos. Chem. Phys.*, **9**, 4987-5005, 2009.

Surratt et al., *J. Phys. Chem. A*, **110**, 9665-9690, 2006.

Claeys et al., 2004 and 2007.

**4. Similar ways, author should read some specific literature of acetaldehyde and/or formaldehyde. For instance, Jacobi et al., JGR, 2012. Domine et al., JGR, 2011 and other papers from the same group. It gives another aspect to explain the acetaldehyde and related compounds.**

We note that the Domine group mentioned here works on snow chemistry and processes relevant to the Arctic environment ( [http://www.takuvik.ulaval.ca/team/florent\\_domine.php](http://www.takuvik.ulaval.ca/team/florent_domine.php)). The Kathmandu Valley is different from the Arctic and there was no snowfall or snow during our study period at the measurement site. Hence, we do not regard this suggestion to be at all relevant for interpreting our work.

The authors are aware of the excellent works being referred to and where relevant in the present work, had already included the works (e.g. Guenther et al and Claeys et al. were already cited). However, we do not think all the works listed by Dr. Pokhrel are of relevance in the context of the present work which is focused on VOC speciation in the Kathmandu Valley environment.

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

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## 1 Abstract

2 The Kathmandu Valley in Nepal suffers from severe wintertime air pollution. Volatile  
3 organic compounds (VOCs) are key constituents of air pollution, though their specific role in  
4 the Valley is poorly understood due to insufficient data. During the SusKat-ABC (Sustainable  
5 Atmosphere for the Kathmandu Valley-Atmospheric Brown Clouds) field campaign  
6 conducted in Nepal in the winter of 2012-2013, a comprehensive study was carried out to  
7 characterize the chemical composition of ambient Kathmandu air, including the  
8 determination of speciated VOCs by deploying a Proton Transfer Reaction Time of Flight  
9 Mass Spectrometer (PTR-TOF-MS) - the first such deployment in South Asia. 71 ion peaks  
10 (for which measured ambient concentrations exceeded the  $2\sigma$  detection limit) were detected  
11 in the PTR-TOF-MS mass scan data, highlighting the chemical complexity of ambient air in  
12 the Valley. Of the 71 species, 37 were found to have campaign average concentrations greater  
13 than 200 ppt and were identified based on their spectral characteristics, ambient diel profiles  
14 and correlation with specific emission tracers as a result of the high mass resolution ( $m/\Delta m >$   
15  $4200$ ) and temporal resolution (1 minute) of the PTR-TOF-MS. The concentration ranking in  
16 the average VOC mixing ratios during our wintertime deployment was acetaldehyde (8.8  
17 ppb) > methanol (7.4 ppb) > acetone + propanal (4.2 ppb) > benzene (2.7 ppb) > toluene (1.5  
18 ppb) > isoprene (1.1 ppb) > acetonitrile (1.1 ppb) > C8-aromatics (~1 ppb) > furan (~0.5 ppb)  
19 > C9-aromatics (0.4 ppb).~~The highest average VOC mixing ratios during the measurement~~  
20 ~~period were (in rank order): acetaldehyde (8.8 ppb), methanol (7.4 ppb), acetone (4.2 ppb),~~  
21 ~~benzene (2.7 ppb), toluene (1.5 ppb), isoprene (1.1 ppb), acetonitrile (1.1 ppb), C8-aromatics~~  
22 ~~(~1 ppb), furan (~0.5 ppb), and C9-aromatics (0.4 ppb).~~ Distinct diel profiles were observed  
23 for the nominal isobaric compounds isoprene ( $m/z = 69.070$ ) and furan ( $m/z = 69.033$ ).  
24 Comparison with wintertime measurements from several locations elsewhere in the world  
25 showed mixing ratios of acetaldehyde (~9 ppb), acetonitrile (~1 ppb) and isoprene (~1 ppb)  
26 to be among the highest reported till date. Two “new” ambient compounds namely,  
27 formamide ( $m/z = 46.029$ ) and acetamide ( $m/z = 60.051$ ), which can photochemically  
28 produce isocyanic acid in the atmosphere, are reported in this study along with nitromethane  
29 (a tracer for diesel exhaust), which has only recently been detected in ambient studies. Two  
30 distinct periods were selected during the campaign for detailed analysis: the first was  
31 associated with high wintertime emissions of biogenic isoprene, and the second with elevated  
32 levels of ambient acetonitrile, benzene and isocyanic acid, from biomass burning activities.  
33 Emissions from biomass burning and biomass co-fired brick kilns were found to be the

1 dominant sources for compounds such as propyne, propene, benzene and propanenitrile  
2 which correlated strongly with acetonitrile ( $r^2 > 0.7$ ), a chemical tracer for biomass burning.  
3 The calculated total VOC OH reactivity was dominated by acetaldehyde (24.0%), isoprene  
4 (20.2 %) and propene (18.7%), while oxygenated VOCs and isoprene collectively contributed  
5 to more than 68% of the total ozone production potential. Based on known SOA yields and  
6 measured ambient concentrations in the Kathmandu Valley, the relative SOA production  
7 potential of VOCs were: benzene > naphthalene > toluene > xylenes > monoterpenes >  
8 trimethylbenzenes > styrene > isoprene. The first ambient measurements from any site in  
9 South Asia of compounds with significant health effects such as isocyanic acid, formamide,  
10 acetamide, naphthalene and nitromethane have been reported in this study. Our results  
11 suggest that mitigation of intense wintertime biomass burning activities, in particular point  
12 sources such biomass co-fired brick kilns, would be important to reduce the emission and  
13 formation of toxic VOCs (such as benzene and isocyanic acid) in the Kathmandu Valley, ~~and~~  
14 ~~improve its air quality.~~

## 15 **1 Introduction**

16 The Kathmandu Valley is a bowl-shaped basin at an altitude of ~1300 m that is surrounded  
17 by the Shivapuri, Phulchowki, Nagarjun and Chandragiri mountains which have an altitude  
18 range of 2000-2800 m above mean sea level and is prone to poor air quality and air pollution  
19 episodes (Panday et al., 2009). In particular during the winter mornings, due to the  
20 combination of suppressed mixing, katabatic wind flows and the topography of the basin,  
21 pollutants remain trapped under an inversion layer close to the surface of the Valley (Kitada  
22 and Regmi, 2003;Regmi et al., 2003). Previous studies in similar Valley sites such as  
23 Santiago de Chile and Mexico City have investigated the coupling of topography,  
24 meteorology, atmospheric dynamics, emissions and chemical processes in exacerbating air  
25 pollution episodes and suggested ways to mitigate the air pollution and improve air quality  
26 (Molina et al., 2007;de Foy et al., 2006;Schmitz, 2005;Rappenglück et al., 2005). In contrast,  
27 only few such studies have been carried out within the Kathmandu Valley.

28 Previous studies in the Kathmandu Valley have examined pollution in relation to carbon  
29 monoxide (CO), nitrogen oxides (NO<sub>x</sub>), sulfur dioxide (SO<sub>2</sub>), ozone (O<sub>3</sub>) (Panday and Prinn,  
30 2009;Larssen et al., 1997;Yu et al., 2009;Ramana et al., 2004;Pudasainee et al., 2006) and  
31 particulate matter (Gurung and Bell, 2012;Sharma et al., 2012). An early study by Davidson  
32 et al. (1986) reported ambient average concentrations of 2 ppm CO during the winter season

1 of 1982-1983. Offline measurements of nitrogen dioxide (NO<sub>2</sub>) and sulphur dioxide (SO<sub>2</sub>)  
2 performed by Larssen et al. (1997) examined the average pollution exposure in different  
3 regions of the Valley and found that the brick kiln region south-east of the Valley and cities  
4 were most severely affected. With regard to quantification of volatile organic compounds in  
5 downtown Kathmandu and a rural site in Nagarkot, data pertaining to light C<sub>2</sub>-C<sub>6</sub>  
6 compounds was obtained in a study in November 1998 using thirty-eight whole air samples  
7 analyzed offline with a GC-FID (Sharma et al., 2000). Subsequently Yu et al. (2008)  
8 measured mixing ratios of seven monocyclic aromatic hydrocarbons, using long path  
9 differential optical absorption spectroscopy (DOAS) at a suburban site in Kathmandu during  
10 January–February, 2003. All these initial studies highlighted that traffic sources were major  
11 contributors to air pollution in the Kathmandu Valley (Yu et al., 2008). In the time since  
12 these studies, due to rapid urbanization and population growth over the last decade, the  
13 wintertime air quality has deteriorated severely. Yet very little information is currently  
14 available with regard to the emissions and chemistry of volatile organic compounds in the  
15 Kathmandu Valley. Except for a handful of species, most of which were measured only  
16 periodically using offline sampling methods, virtually no in-situ data is available from the  
17 region with regard to the concentration and speciation of several important volatile organic  
18 compounds.

19 Volatile organic compounds (VOCs), in particular the reactive ones, have atmospheric  
20 lifetimes ranging from ~~few hours to few minutes to~~ days (Atkinson, 2000) and exert a  
21 profound influence on regional air quality through their participation in chemical reactions  
22 leading to the formation of secondary pollutants such as tropospheric ozone and secondary  
23 organic aerosol (SOA). Both tropospheric ozone and secondary organic aerosol are important  
24 from the standpoint of air quality and climate due to their impact on health and the radiative  
25 forcing of the atmosphere (IPCC, 2013). Further, through reactions with the hydroxyl radicals  
26 (the detergent of the atmosphere (Lelieveld et al., 2004)), photodissociation reactions and  
27 radical recycling reactions, VOCs strongly influence ambient OH reactivity and the budget of  
28 HO<sub>x</sub> (OH, HO<sub>2</sub>) radicals which control the removal rates of gaseous pollutants, including  
29 most greenhouse gases from the atmosphere. Inhalation of certain VOCs present in air also  
30 produces direct adverse health effects. For example, benzene and nitromethane are reported  
31 to be human carcinogens by the World Health Organization (WHO, 2010). ~~and isocyanic~~  
32 ~~acid, which has only recently been quantified in ambient studies (Roberts et al., 2011) can~~

1 ~~cause cataracts, cardiovascular diseases and rheumatoid arthritis via protein carbamylation on~~  
2 ~~exposure to concentrations as low as 1 ppb (Roberts et al., 2011).~~

3 In order to address gaps in our scientific understanding of the air pollution in the Kathmandu  
4 Valley, a large scale scientific experiment called the Sustainable Atmosphere for the  
5 Kathmandu Valley-Atmospheric Brown Clouds (SusKat-ABC) campaign was carried out in  
6 the winter of 2012-2013 by an international team of scientists. An overview of the campaign  
7 objectives, measurement suite and sites will be presented in the overview paper (Rupakheti et  
8 al., 2016) while an overview of the meteorology and pollution transport processes will be  
9 presented in a second overview paper (Panday et al., 2016). We present here results derived  
10 from in-situ measurements of speciated VOCs using a proton transfer reaction time of flight  
11 mass spectrometer (PTR-TOF-MS), the first such deployment in South Asia. Another version  
12 of this type of instrument, which has lower mass resolution, namely a proton transfer reaction  
13 quadrupole mass spectrometer (PTR-Q-MS) has been previously deployed in the North-West  
14 Indo-Gangetic Plain in Mohali, India (Sarkar et al., 2013;Sinha et al., 2014).

15 With a mass resolving power ( $m/\Delta m$ ) of more than 4200, PTR-TOF-MS measurements  
16 enable identification of several compounds based on their exact monoisotopic mass  
17 (molecular formula) and have fast time response (~1 minute). These attributes were leveraged  
18 to quantify a suite of ambient VOCs at a suburban site (Bode; 27.689<sup>0</sup>N, 85.395<sup>0</sup>E, 1345  
19 amsl) in the Kathmandu Valley during December 2012-January 2013. Oxygenated VOCs  
20 such as methanol, acetaldehyde, sum of acetone and propanal, aromatic VOCs such as  
21 benzene, toluene, sum of C8-aromatics and sum of C9-aromatics, isoprene, furan and  
22 acetonitrile were quantified every minute and their diel emission profiles analyzed to  
23 constrain major sources. Careful analysis of the ambient mass spectra from 21-210 Th was  
24 undertaken to identify several “new” or rarely quantified VOCs based on their monoisotopic  
25 masses (and therefore molecular formula), spectral characteristics observed at a particular  
26  $m/z$  in a 0.005 amu bin relative to the ion peak, ambient diel profiles and correlation with  
27 specific emission tracer molecules such as acetonitrile (a tracer for biomass burning). By  
28 contrasting periods in the chemical dataset based on the dominance of biogenic emission  
29 sources and emissions from brick kilns co-fired with biomass, respectively, VOCs emitted  
30 from the brick kilns ~~and biomass burning sources~~ were ~~identified~~ constrained. The measured  
31 VOC concentrations in the Kathmandu Valley were compared with previous wintertime  
32 measurements from other urban/suburban sites and megacities. The diel profiles of rarely

1 detected and measured VOCs such as nitromethane and isocyanic acid were correlated with  
2 tracer VOCs. The major VOC contributors to the total measured reactive carbon, the VOC  
3 OH reactivity, ozone production potential and secondary organic aerosol formation potential  
4 were elucidated through detailed analyses. Finally, information pertaining to direct health  
5 impacts of some of the quantified VOCs detected in this complex chemical environment are  
6 discussed with conclusions and outlook for future VOC studies in the region.

## 7 **2 Experimental**

### 8 **2.1 Site Description and prevalent meteorology**

9 The Kathmandu Valley is a bowl-shaped basin in the Himalayan foothills. The average  
10 altitude of the Valley is 1300 m above mean sea level (amsl). It is encircled by a ring of  
11 mountains that range from 2000-2800 m (amsl), with about five mountain passes  
12 approximately 1500–1550 m amsl (Panday et al., 2009), ~~that enable winds to blow across the~~  
13 ~~Valley from west to east during the afternoon hours.~~ VOC measurements during this study  
14 were performed in the winter season from 19 December 2012 till 30 January 2013 at Bode  
15 (27.689<sup>0</sup>N, 85.395<sup>0</sup>E; 1345 amsl), which is a suburban site located in the westerly outflow of  
16 Kathmandu city.

17 Figure 1 shows a zoomed view of the land use in the vicinity of the measurement site (Bode;  
18 red circle; image derived using Google Earth on 22 May 2015 at 14:55 LT) in relation to the  
19 surrounding cities - Kathmandu (~10 km to the west; brown circle), Patan (~12 km south-  
20 west of the site; blue circle) and Bhaktapur (~5 km south-east of the site; pink circle), major  
21 point sources and forested areas. Most of the agricultural fields near the site have unpaved  
22 tracks and were sold as small plots, and are largely uncultivated. At some distance, there are  
23 agricultural fields on which rice is sown in the summer and either potatoes/vegetables or  
24 wheat is sown in winter. The major road (Bhaktapur road) is about 1 km south of the site. In  
25 2011, the total population of Kathmandu, Patan and Bhaktapur cities were: 1,003,285  
26 (population density: 20,289 km<sup>-2</sup>), 226,728 (population density: 14,966 km<sup>-2</sup>) and 83,658  
27 (population density: 12,753 km<sup>-2</sup>), respectively according to Central Bureau of Statistics,  
28 Nepal (2011). The region east of the site was usually downwind but it is important to note  
29 that several brick kilns (white marker in Figure 1; around 10 brick kilns) were located south-  
30 east of the site at about 1 km distance. Major industries (yellow triangles in Figure 1) were  
31 concentrated primarily in the cities of Kathmandu (Balaju industrial area) and Patan (Patan

1 industrial area), while Bhaktapur industrial area was located in the south-east direction within  
2 2 km of the measurement site. About 20 small industries, mainly pharmaceuticals, plastic, tin,  
3 electronics and fabrics were located in this industrial area. Also a few plastic, electronics,  
4 wood, aluminium and iron industries were located within 3 km from the Bode site in the  
5 south-east direction. The Tribhuvan international airport was located west of the site (~4 km  
6 from Bode).

7 The region north of the site has a small forested area (Nilbarahi Jungle in Figure 1; ~0.5 km<sup>2</sup>  
8 area) and a reserve forest (Gokarna Reserve Forest in Figure 1; ~1.8 km<sup>2</sup> area) at  
9 approximately 1.5 km and 7 km from the measurement site, respectively. Other nearby forest  
10 areas were located adjacent to the international airport (Mrigasthali and Bhandarkhal Jungle;  
11 8-10 km from the site). The forests in the Kathmandu Valley consist of broad-leaved  
12 evergreen mixed forest of *Schima Castanopsis* at the base (up to 1,800 m asl), *oak-laurel*  
13 forest in the middle (1,800 m to 2,400 m), and *oak* forest at the top, while the conifer tree  
14 species *Pinus roxiburghii* (Khote Salla) and *Pinus wallichiana* (Gobre Salla) are also found  
15 (Department of Plant Resources, Nepal, 2015). Other major tree species are *Melia azedarach*  
16 (Bakaino), *Schima wallichii* (Chilaune), *Castanopsis indica* (Dhale Katus), *Piptanthus*  
17 *nepalensis* (Suga Phul), *Persia bombycina* (Kaulo), *Madhuca longifolia* (Mauwa), *Celtis*  
18 *australis* (Khari), *Quercus semecarpifolia* (Khasru), and *Cryptomeria japonica* (Dhupi salla)  
19 (Department of Plant Resources, Nepal, 2015).

20 The general meteorological conditions within the Kathmandu Valley remain fairly similar  
21 throughout the winter season (Regmi et al., 2003; Panday and Prinn, 2009) and it is worth  
22 mentioning that the winter of 2012-2013 was not anomalous. Conditions were calm during  
23 the mornings with shallow boundary layer and therefore what we see in the morning hours  
24 are emissions from the previous night and emissions from morning activities around the  
25 measurement site within a radius of few km, rather than regional emissions. Cold pooling of  
26 air at night resulting in dilution of pollution was observed in the diel profiles of VOCs for  
27 period 1 when the 24/7 brick kilns were largely un-operational (for e.g. between midnight and  
28 05:00 LT). Shortly after sunrise, the surface air mixes in with air that was aloft. Finally  
29 during the afternoon (10:00–15:00 LT), westerly winds sweep the valley from west to east at  
30 wind speeds of 3-4 m/s advecting the emissions, some of which may get transported across  
31 the mountain passes (Kitada and Regmi, 2003; Regmi et al., 2003; Panday and Prinn, 2009).

1 ~~The wind flow pattern observed during our study was typical of wintertime meteorology in~~  
2 ~~the Kathmandu Valley and similar to meteorological observations reported in previous~~  
3 ~~studies carried out in the Kathmandu Valley during the winter season (Kitada and Regmi,~~  
4 ~~2003; Panday et al., 2009; Regmi et al., 2003). Figure 2 a presents a schematic of the wind~~  
5 ~~flow pattern observed during the study and its interaction with surface emissions. The~~  
6 ~~afternoon flow, as indicated by the local meteorological observations, was characterized by~~  
7 ~~westerly winds with moderate speed which aided ventilation of daytime emissions (typical~~  
8 ~~average speed at Bode:  $4 \text{ m s}^{-1}$ ). On the other hand, nighttime and early morning periods were~~  
9 ~~associated with weak easterlies (typical average speed:  $< 1 \text{ m s}^{-1}$ ). Thus, during afternoon~~  
10 ~~hours pollutants emitted in the Kathmandu Valley moved towards the eastern mountain~~  
11 ~~passes due to the strong westerlies whereas in the evening, the flow was mildly reversed and~~  
12 ~~a part of the pollutants transported to the eastern mountain passes moved back to the~~  
13 ~~Kathmandu Valley due to the development of downslope winds. At night, “pooling” of cold~~  
14 ~~air from the mountain slopes caused the warmer surface air to rise resulting in upward~~  
15 ~~transport of pollutants under the nocturnal inversion (Panday and Prinn, 2009). After sunrise,~~  
16 ~~the morning hours were characterized by convective mixing of the accumulated pollutants~~  
17 ~~due the nocturnal inversion, with surface emissions.~~

18 Figure 2-b shows the box and whisker plots for the meteorological parameters measured at  
19 Bode from 16-30 January 2013 derived from the one minute temporal resolution data  
20 acquired using meteorological sensors (Campbell Scientific Loughborough, UK) installed on  
21 the rooftop (~25 m above ground and ~5 m away from the instrument inlet). Daytime (08:00  
22 – 17:00 LT) average ambient temperature for the measurement period was observed to be  
23  $12.2 \pm 4.5 \text{ }^{\circ}\text{C}$ . It is worth mentioning that most mornings were associated with dense fog  
24 (average ambient RH  $> 90\%$  with visibility  $< 100 \text{ m}$ ) whereas the afternoons were associated  
25 with high speed westerly winds ( $> 4 \text{ m s}^{-1}$ ). Wind speeds from other wind sectors were  
26 generally lower (average wind speeds  $\sim 1 \text{ m s}^{-1}$ ). The early morning wind flow was normally  
27 from the south-east wind sector which comprised of several brick kilns and Bhaktapur city.  
28 Evening hours were also associated with dense fog and the relative humidity (RH) was  
29 generally greater than 90% throughout the night. Minimum RH levels ( $\sim 35\%$ ) were observed  
30 during midday. The sunrise typically occurred between 07:00 – 08:00 and sunset timings  
31 were around 17:00 Nepal Standard Time (NST), respectively. The range of atmospheric  
32 pressure during the campaign was 856-866 hPa.

## 1 2.2 VOC measurements using PTR-TOF-MS

2 Volatile organic compounds (VOCs) over the mass range (21-210 amu) were measured using  
3 a commercial high sensitivity proton transfer reaction time of flight mass spectrometer  
4 (Model PTR-TOF-MS 8000; Ionicon Analytic GmbH, Innsbruck, Austria). This instrument  
5 has been described in detail by Jordan et al. (2009) and is a more recent development of the  
6 PTR technique (Lindinger et al., 1998) that enables higher mass resolution at ppt level  
7 detection limit (Ruuskanen et al., 2011; Müller et al., 2010; Park et al., 2013; Stockwell et al.,  
8 2015). Briefly, the instrument consists of a hollow cathode ion source which produces a pure  
9 flow of the  $\text{H}_3\text{O}^+$  reagent ions, a drift tube where analyte VOCs undergo ionization and an  
10 orthogonal acceleration reflectron time of flight mass analyzer and multi-channel plate  
11 detector. The instrument was operated at a drift tube pressure of 2.2 mbar, drift tube  
12 temperature of  $60^\circ\text{C}$  and drift tube voltage of 600 V, resulting in an operating E/N ratio of  
13  $\sim 135 \text{ Td}$  ( $1 \text{ Td} = 10^{-17} \text{ V cm}^{-2}$  (de Gouw and Warneke, 2007)). The high mass resolution of  
14 the instrument ( $m/\Delta m > 4200$  at  $m/z 21.022$  and  $> 4800$  at  $m/z 205.195$ ) and detection limit  
15 of few tens of ppt permitted identification of several rarely measured or previously  
16 unmeasured compounds based on their monoisotopic masses.

17 The PTR-TOF-MS 8000 used in this work was installed in a room on the second floor of a  
18 building at the suburban measurement site in Bode, Kathmandu. Ambient air was sampled  
19 continuously from the rooftop ( $\sim 20$  m above ground) through a Teflon inlet line that was  
20 protected with a Teflon membrane particle filter to ensure that dust and debris did not enter  
21 the sampling inlet. Teflon membrane particle filters similar to the ones used in the  
22 Kathmandu study have been used without issues in several previous PTR-MS VOC studies  
23 by some of the authors (e.g. Sinha et al. (2010)), including at another South Asian site in  
24 Mohali, India (Sinha et al., 2014). The filters were changed on seven occasions during the 40  
25 day long deployment from 19 December 2012 to 30 January 2013. The inlet lines used in  
26 Kathmandu were prepared prior to deployment by continuous purging at different flow rates  
27 in the laboratory at Mohali for more than three days and zero air was sampled through these  
28 lines. After purging, the background signals were always comparable to background signals  
29 observed during direct injection of zero air without a long inlet line for the  $m/z$  ion peaks  
30 reported in this work. Bearing in mind that the ambient air (range of ambient temperature: 5-  
31  $15^\circ\text{C}$ ) was drawn in under 25 seconds (residence + sampling time; determined by spiking the  
32 inlet with sesquiterpenes emitted from an orange peel) into the PTR-TOF-MS, the probability  
33 of inlet effects for sticky compounds is not high. In any case, the part of the inlet line that was

1 indoors was well insulated and heated to 40°C all the time to ensure there were no  
2 condensation effects. Instrumental background checks using zero air were performed at  
3 intervals of 3-4 days during the campaign.

4 ~~The total inlet residence and sampling time was less than 25 s as determined by spiking the~~  
5 ~~inlet with sesquiterpenes emitted from an orange peel.~~

6 Data acquisition of mass spectra was accomplished using the TofDaq software (version 1.89;  
7 Tofwerk AG, Switzerland). This software controls the timing of the pulser (used to pulse the  
8 ions produced in the drift tube and channel them into the time-of-flight region) and stores the  
9 raw data as a series of mass spectra in HDF5 format along with relevant instrumental  
10 metadata. The raw mass spectral data was then analyzed using the PTRMS-viewer software  
11 (version 3.1; Ionicon Analytic GmbH, Innsbruck, Austria) enabling peak search, peak fits and  
12 mass assignments. Mass axis calibration was accomplished using the following intrinsic ions:  
13  $\text{H}_3^{18}\text{O}^+$  (monoisotopic mass 21.022) and  $\text{H}_3^{18}\text{O}^+(\text{H}_2\text{O})$  (monoisotopic mass 39.033). In  
14 addition the transmission values of benzene ( $m/z = 79.054$ ), toluene ( $m/z = 93.070$ ), xylenes  
15 ( $m/z = 107.086$ ), trimethylbenzenes ( $m/z = 121.101$ ), dichlorobenzene ( $m/z = 146.976$ ) and  
16 trichlorobenzene ( $m/z = 180.937$ ) were employed. Further analysis of the dataset was carried  
17 out using the IGOR Pro software (version 6.0; WaveMetrics, Inc.).

18 The instrument was calibrated twice (10 January 2013 and 15 January 2013) during the field  
19 deployment by dynamic dilution of VOCs using a 17-component VOC gas standard (Ionimed  
20 Analytik GmbH, Austria at ~1 ppm; stated accuracy better than 8%). Calibration for these  
21 seventeen VOCs namely formaldehyde, methanol, acetonitrile, acetaldehyde, ethanol,  
22 acrolein, acetone, isoprene, methacrolein, 2-butanone, benzene, toluene, o-xylene,  
23 chlorobenzene,  $\alpha$ -pinene, 1, 2-dichlorobenzene and 1, 2, 4-trichlorobenzene were carried out  
24 in the range of 2-10 ppb at various relative humidities (RH = 60%, 75% and 90%). RH was  
25 controlled as per the details provided in Kumar and Sinha (2014). In order to determine the  
26 instrumental background at all relevant  $m/z$  channels, VOC free zero air was produced by  
27 passing ambient air through an activated charcoal scrubber (Supelpure HC, Supelco,  
28 Bellefonte, USA) and a VOC scrubber catalyst maintained at 350°C (GCU-s 0703, Ionimed  
29 Analytik GmbH, Innsbruck, Austria). Following the procedure of Stockwell et al. (2015), the  
30 measured ion signals were normalized to  $\text{H}_3\text{O}^+$  ( $m/z = 19$ ) primary ions according to the  
31 following equation:

$$ncps = \frac{I(RH^+) \times 10^6}{I(H_3O^+)} \times \frac{2}{P_{drift}} \times \frac{T_{drift}}{298.15} \quad \dots (1)$$

2 The two calibration experiments made during the course of the campaign did not change the  
 3 VOC sensitivities (values were within the precision error) as instrumental operational  
 4 conditions were not changed. Usually, the sensitivity response of VOCs in a PTR-MS remain  
 5 remarkably stable if instrumental operational conditions are not changed. This is borne by  
 6 several previous studies (de Gouw and Warneke, 2007) including our own group's recent  
 7 studies in the South Asian environment which involved a three year study (Chandra and  
 8 Sinha, 2016) and a month long study (Sinha et al., 2014). Large changes in ambient humidity  
 9 are known to affect the sensitivity of some VOCs (e.g. benzene, methanol). This occurs due  
 10 to a change in the abundance and ratio of the primary reagent ions ( $H_3O^+$ ;  $m/z = 19$ ) and the  
 11 hydrated hydronium ions ( $H_3O^+ \cdot H_2O$ ;  $m/z = 37$ ) within the drift tube (de Gouw et al., 2003).  
 12 It assumes importance when ambient RH has large variability (e.g. very dry < 20% RH to  
 13 very humid > 80% RH) during the measurements (e.g. during airborne measurements) and  
 14 when the ratio of ~~m19/m37~~ m37/m19 in the drift tube is typically more than 10%. For the  
 15 measurements reported in this study, the ratio of the hydrated hydronium ions ( $H_3O^+ \cdot H_2O$ ;  
 16 nominal  $m/z = 37$ ) to the primary ions ( $H_3O^+$ ; nominal  $m/z = 19$ ) was lower than 10%, for  
 17 more than 92% of the dataset and the ratio never exceeded 16%. For the conditions during the  
 18 campaign, our calibration experiments did not reveal significant humidity dependence for the  
 19 VOC sensitivities (ncps  $ppb^{-1}$ ). Figure 3 shows the sensitivities (ncps  $ppb^{-1}$ ) for acetonitrile (a  
 20 biomass burning tracer), acetaldehyde (an oxygenated compound), isoprene (a biogenic  
 21 tracer) and benzene (an aromatic compound) at different RH regimes (60%, 75% and 90%)  
 22 during the calibration experiments. In all cases an excellent linearity ( $r^2 = 0.99$ ) was  
 23 observed. Hence the sensitivity (ncps  $ppb^{-1}$ ) derived at 90% RH was applied for converting  
 24 the measured normalized counts per second to ppb and no further humidity corrections were  
 25 deemed necessary.

26 In order to derive the sensitivity for the sum of monoterpenes, which have a molecular ion  
 27 peak at  $m/z = 137.132$  and for which fragmentation results in ion signals at  $m/z 81.070$  and  
 28  $m/z 137.132$ , the signal measured at  $m/z 137.132$  was scaled by 2.63, as calibrations at the  
 29 instrumental settings employed in the study clearly showed that 38% of the total molecular  
 30 ion signal for monoterpene was detected at  $m/z = 137.132$ , consistent with fragmentation  
 31 patterns reported previously by Tani et al. (2004) for similar reaction conditions in the drift  
 32 tube.

1 Variable background concentrations were observed for both formaldehyde and methanol  
2 while sampling zero air during the calibration experiments. Hence for these two compounds  
3 and all the other compounds not present in the 17 component VOC gas standard but reported  
4 in this work, sensitivity factors were determined following the example of Stockwell et al.  
5 (2015), wherein calculated mass-dependent calibration factors based on linearly  
6 approximated transmission curve fits for oxygenated VOCs and hydrocarbons were  
7 employed. Figure S1 a shows the linearly fitted mass-dependent transmission curve (black  
8 markers and dotted line) overlaid with the sensitivity factors of the calibrated compounds.  
9 Using linear approximations, mass-dependent calibration factors were determined separately  
10 for oxygenates (Figure S1 b) and hydrocarbons (Figure S1 c) in keeping with their different  
11 mass dependent behavior. For masses with heteroatoms other than oxygen, mass-dependent  
12 sensitivity factors were determined based on approximations used for the oxygenated  
13 compounds. For acetic acid, the sum of the signals at  $m/z$  61.207 (parent ion peak) and  $m/z$   
14 43.018 (fragment of the parent ion), were used to derive an upper limit for its ambient  
15 concentration.

16 The limit of detection was defined to be  $2\sigma$  of the measured normalized signal (ncps) while  
17 measuring VOC free zero air divided by the sensitivity expressed in ncps  $\text{ppb}^{-1}$  (Sinha et al.,  
18 2014). The total uncertainty for calibrated compounds was calculated using the root mean  
19 square propagation of the accuracy error of the VOC standard, the mass flow controller's  
20 flow fluctuations during the calibration and the instrumental precision error ( $2\sigma$  while  
21 measuring 2 ppb of the compound). Using this approach, all calibrated VOCs had a total  
22 uncertainty of  $< 20\%$  (e.g., acetaldehyde 9.9%, acetone 9.6%, isoprene 15.4%, benzene 9.4%  
23 and toluene 8.9%) whereas for the other compounds reported in this work that could not be  
24 calibrated, we estimate an overall uncertainty of  $\sim 50\%$  as also proposed by Stockwell et al.  
25 (2015) using a similar approach for quantification.

## 26 **3 Results and Discussions**

### 27 **3.1 Identification of VOCs present in ambient air using PTR-TOF-MS mass** 28 **scans**

29 The PTR-TOF-MS deployed in this study was operated over the range of 21-210 Th, with a  
30 mass resolution ( $m/\Delta m > 4200$  at  $m/z$  21.022 and  $> 4800$  at  $m/z$  205.195) sufficient to  
31 identify several compounds based on their monoisotopic masses. A maximum of 71 ion peaks

1 (m/z) were observed in the mass spectra during the measurement period for which the  
2 measured ambient concentrations exceeded the detection limit. Among these 71 species, 37  
3 compounds/species had an average concentration greater than or equal to 200 ppt during the  
4 study period. The molecular formula of compounds/species corresponding to these 37 ion  
5 peaks are listed in Table S1 of the supplement. Additionally Table S1 also provides: 1)  
6 identity of plausible organic/fragment ions (e.g.  $\text{NO}_2^+$  due to C1-C5 alkyl nitrates), 2)  
7 sensitivity, 3) limit of detection, and 4) average  $\pm 1 \sigma$  variability of ambient mixing ratios  
8 observed during the study period.

9 In order to minimize ambiguity arising due to multiple species or fragment ions contributing  
10 to ion peaks at a given m/z ratio, the following quality control measures were employed for  
11 attribution of mass identifications to the observed ion peaks: 1) Ion peaks for which the  
12 observed mass spectra had competing/major shoulder peaks in a mass bin width of 0.005 amu  
13 centred at the relevant monoisotopic ion peak were excluded from exclusive mass  
14 assignments 2) Next, the ambient time series of the observed ion peak assigned after step 1,  
15 was carefully examined and cases where the concentration profile was completely  
16 flat/showed no ambient variability were also excluded from mass assignments 3) Thirdly, the  
17 concentration profiles of the ion peaks ascribed to rarely reported or new compounds after  
18 step 1 and step 2, were compared to the ambient time series and diel profiles of more  
19 frequently/regularly quantified VOCs, such as acetonitrile, isoprene, benzene, toluene,  
20 acetone and acetaldehyde as their diel profiles would likely indicate the driving processes and  
21 emission sources of the compounds. During the PTR-TOF-MS field deployment,  
22 instrumental background checks revealed backgrounds as high as 170 ppt at certain m/z  
23 channels (e.g. m/z 125.958, m/z 90.947, m/z 108.957). Therefore, the 200 ppt cut off was  
24 chosen as an additional quality control measure so as to ensure attribution of ion peaks in the  
25 mass spectra only to the compounds present in the ambient air and not due to instrumental  
26 reasons. The 37 compounds that were identified accounted for 86.7 % of the total mass due to  
27 all 71 ion peaks detected in the mass spectra.

28 In cases, where the contributions of isotopologues were significant (e.g., acetic acid m/z =  
29 61.027 and nitromethane m/z = 62.026), the signal at the concerned m/z was duly corrected  
30 (Inomata et al., 2014). Potential interferences due to isotopic contributions (e.g.  $^{13}\text{C}$ ) were  
31 also corrected whenever applicable. -Out of these 37 ions which were identified with  
32 reasonable confidence, 8 contained nitrogen, 15 were oxygenated compounds, 13 were

1 hydrocarbons and one contained sulfur. Two ion peaks ( $m/z = 51.044$  and  $m/z = 56.060$ )  
2 could not be identified based on the exact protonated monoisotopic  $m/z$  and for these, the  
3 closest contenders namely 1,3-butadiyne ( $m/z = 51.023$ ) and propanenitrile ( $m/z = 56.050$ ),  
4 were tentatively assigned. Two “new” compounds, which to the best of our knowledge have  
5 not been reported in any previous study, namely- formamide ( $\text{CH}_3\text{NO}$ ; protonated  $m/z =$   
6  $46.029$ ) and acetamide ( $\text{C}_2\text{H}_5\text{NO}$ ; protonated  $m/z = 60.051$ ) were also detected. We discuss  
7 their diel variability and potential sources in Section 3.5 along with some of the other rarely  
8 reported compounds in ambient air. Figure S2 of the supplement shows an illustrative mass  
9 spectra for isocyanic acid which demonstrates that it is the major contributor in the relevant  
10 mass bins. Considering that some loss of isocyanic acid can occur due to hydrolysis in the  
11 drift tube, our measurements maybe a lower limit of the ambient concentrations of isocyanic  
12 acid.

13 ~~To highlight the complexity of ambient chemical composition on specific periods/activity~~  
14 ~~during the day, in Figure 4 we show the hourly averaged mass scan data for a selected day~~  
15 ~~(15 January 2013; not influenced by any anomalous events) during morning (06:00–07:00~~  
16 ~~LT), afternoon (15:00–16:00 LT) and evening (18:00–19:00 LT). It can be seen that the~~  
17 ~~maximum number of ion peaks were observed during evening hours (total 61 peaks) when~~  
18 ~~primary emissions from wintertime biomass combustion and evening traffic dominated the~~  
19 ~~ambient chemical composition. In contrast, fewer ion peaks were observed during morning~~  
20 ~~(52) and afternoon hours (51), respectively. 18 compounds had a mixing ratio  $\geq 1$  ppb either~~  
21 ~~in the morning, afternoon or in the evening. Distinct peaks were observed for the nominal~~  
22 ~~isobars: isoprene ( $m/z = 69.070$ ) and furan ( $m/z = 69.033$ ), which are shown in the inset of~~  
23 ~~Figure 4. The occurrence of high concentrations of isoprene in wintertime was surprising and~~  
24 ~~we investigate its major source in Section 3.6. To the best of our knowledge, formamide ( $m/z$~~   
25  ~~$= 46.029$ ) and acetamide ( $m/z = 60.051$ ) were identified for the first time in ambient air using~~  
26 ~~the PTRMS technique and both of these compounds were present at average ambient~~  
27 ~~concentrations greater than 200 ppt during the study period with clear daytime maxima~~  
28 ~~(details are described in Section 3.5).~~

29 The total reactive carbon calculated as the sum of the average mixing ratios of all the 37  
30 compounds reported in this study was 175.8 ppbC, of which fifteen compounds alone  
31 contributed 145.4 ppbC (83% of the total) and are listed in Table S2 of the supplement.  
32 Propyne, acetaldehyde, benzene, acetic acid, acetone, propene and toluene collectively

1 comprised more than 60 % of the measured reactive carbon. ~~Although the average O/C ratios~~  
2 ~~for morning (06:00–07:00 LT), afternoon (15:00–16:00 LT) and evening (18:00–19:00 LT)~~  
3 ~~were 0.57, 0.68 and 0.60, the O/C ratio for the entire period of deployment was found to be~~  
4 ~~0.33 which is within the O/C ratio of 0.3–0.4 observed for laboratory produced primary~~  
5 ~~biomass burning organic aerosol (Aiken et al., 2008). No significant change was noted for the~~  
6 ~~N/C ratios on a diel basis which were always close to 0.08.~~

7 In Section 3.2 and 3.4, we examine the general trends and diel concentration profiles of the  
8 most abundant VOCs to gain more detailed insights into the emission sources and chemistry  
9 of VOCs in wintertime air of the Kathmandu Valley.

### 10 **3.2 General trends in VOC concentrations during the SusKat-ABC campaign**

11 Figure 54 shows the general trends in VOC mixing ratios (as 1 minute temporal resolution  
12 data) during the period of study from 19 December 2012 – 30 January 2013. While the top  
13 panel represents the time series in mixing ratios of oxygenated VOCs namely methanol,  
14 acetaldehyde and the sum of acetone and propanal, the second and third panels show mixing  
15 ratios of isoprene, acetonitrile and furan, respectively. The bottom panel shows the mixing  
16 ratios of benzene, toluene, sum of C8-aromatics (xylenes and ethylbenzene), and sum of C9-  
17 aromatics (trimethylbenzenes and propylbenzenes). All these compounds collectively  
18 accounted for about 50% (total 85.4 ppbC) of the total reactive carbon and are amongst the  
19 most abundant VOCs known to be present in air influenced by urban emissions.

20 It can be seen that the time series was characterized by two contrasting periods in terms of  
21 chemical emission signatures: **p**Period 1 (shaded in pale yellow in Figure 45; 19 December  
22 2012 – 2 January 2013) and **p**Period 2 (shaded in grey in Figure 45; 4 – 18 January 2013).  
23 **p**Period 1 was characterized by high mixing ratios of isoprene (> 3 ppb) during the daytime  
24 and low acetonitrile mixing ratios relative to the remainder of the measurement period  
25 (generally < 2 ppb except for a plume on 28 December 2015 which was suspected to be due  
26 to garbage burning in the local vicinity), while **p**Period 2 was marked by a decrease in the  
27 amplitude of daytime isoprene and a significant increase in mixing ratios of acetonitrile  
28 (typically > 3 ppb) and benzene (typically > 10 ppb). The global budget of isoprene is  
29 dominated by emission from vegetation (500 Tg a<sup>-1</sup>; (Guenther et al., 2006)), in most cases as  
30 a function of photosynthetic active radiation (PAR) and temperature. Clearly, in the early part  
31 of this winter campaign, conditions were favourable for significant isoprene emissions from

1 vegetation. It is worth mentioning that *oak* and *Melia azedarach* were present in the forested  
2 regions upwind of the site and are high isoprene emitters ([www.es.lanacs.ac.uk/cnhgroup/iso-](http://www.es.lanacs.ac.uk/cnhgroup/iso-emissions.pdf)  
3 [emissions.pdf](http://www.es.lanacs.ac.uk/cnhgroup/iso-emissions.pdf)). As the ambient temperature and radiation decreased and early morning fog  
4 became frequent during the first half of January, biogenic emissions reduced in intensity (< 2  
5 ppb). Leaf fall in deciduous trees by the end of December and more frequent leaf litter  
6 burning were likely important contributors to reduced isoprene and increased acetonitrile  
7 emission in the second half of the campaign. While the highest isoprene concentrations were  
8 driven by biogenic sources, biomass burning sources also emitted isoprene, a finding  
9 consistent with reports from another South Asian site at Mohali, India (Sinha et al., 2014).

10 All the brick kilns in the Kathmandu Valley are Fixed Chimney Bull Trench Brick Kilns  
11 (FCBTK), except for one Vertical Shaft Brick Kiln (VSBK) and two Hoffmann design brick  
12 kilns. FCBTKs are operated around the clock, from the first week of January to mid-April  
13 according to our survey. Thus, our deployment fortuitously was able to contrast the periods  
14 marked by the presence and almost complete absence of operational brick kilns in the fetch  
15 region of our measurement site. Most open burning and cooking activities remain similar in  
16 December and January. Due to reduced leaf fall in January (leaf fall of deciduous trees picks  
17 up in November and peaks in December) the open burning of leaf litter with other waste is  
18 generally less in January. With regard to increased open biomass burning from other sources  
19 in January, the first week of January was the coldest period of the deployment, so one could  
20 hypothesize that the higher emissions in this period were due to more open fires being lit to  
21 keep warm. However as can be seen in Figure 4, the biomass burning emissions were much  
22 higher for most of January (including a rain event during 18 January 21:00 LT – 19 January  
23 01:00 LT). Thus, the brick kiln activity is the singular feature that is prominently different  
24 between both the periods. ~~The Federation of Nepalese Brick Industries (FNBI) provided~~  
25 ~~information on operation of brick factories in the Valley. According to the FNBI, most brick~~  
26 ~~kilns were closed for the season until the first week of January. Thereafter over the next 12–~~  
27 ~~14 days (4–20 January 2013) all 110 plus brick kilns in the Valley were restarted and became~~  
28 ~~fully operational. Thus, Period 2 represents the time when they were fired up again while the~~  
29 ~~last part of the January represents a period when they were up and running and emissions~~  
30 ~~from the brick kilns were no longer as high as during the firing up stage. The survey of 82~~  
31 ~~brick factories in the Valley showed that in addition to coal, a large amount of biomass such~~  
32 ~~as sawmill dust, wood and other biomass are co-combusted in the brick kilns, contributing,~~  
33 ~~on average, nearly 20% to the total energy used in firing bricks (Rupakheti et al., 2015).~~ To  
34 the best of our knowledge and survey, the fuel burnt in the brick kilns does not differ much

1 between the brick kilns though the type of bio-fuel employed during different times in a year  
2 can vary depending on the availability and abundance of certain types of bio-fuel. One  
3 common biofuel used in the brick kilns is the seed of the lapsi fruit (*Choerospondias*  
4 *axillaris*). This emission activity appears to have been captured quite well in the time series  
5 profile of acetonitrile, for which the major emission source is biomass burning (Holzinger et  
6 al., 1999;Sarkar et al., 2013;Sinha et al., 2014). It was also interesting to note the similarities  
7 in the time series of furan (~1 ppb), another combustion tracer, with acetonitrile. Biomass  
8 burning and biofuel use contribute to half of the global budget of benzene (Henze et al.,  
9 2008;Andreae and Merlet, 2001;Sarkar et al., 2013) and it appears that brick kilns in  
10 Kathmandu being co-fired with biomass as fuel were a major source of benzene. A recent  
11 study by Al-Naiema et al. (2015) reported reduction in emissions (~40% reduction of fossil  
12 CO<sub>2</sub>, particulate matter and heavy metal emissions) when co-firing of oat hull biomass with  
13 coal was carried out for generation of electricity in the United States. We note that the case  
14 study did not investigate co-emission of toxic VOCs such as isocyanic acid, formamide,  
15 acetamide, nitromethane and naphthalene which were associated with emissions from  
16 biomass co-fired brick kilns in the Kathmandu Valley. A study conducted by Clean Energy  
17 Nepal (Raut, 2003) showed that 8 h averaged concentrations of air pollutants such as Total  
18 Suspended Particulate (TSP) , PM<sub>10</sub>, SO<sub>2</sub> and NO<sub>x</sub> were three times higher during the brick  
19 kiln operating period relative to the period they were not operational at the same location.  
20 Significant differences exist between the electricity generation unit studied by Al-Naiema et  
21 al. (2015) and the typical biomass co-fired brick kilns that dot the Kathmandu Valley in terms  
22 of design, combustion efficiency, biomass fuel being co-fired and the end application. Thus  
23 though the same word “co-firing” is used colloquially, these are really different from an  
24 operational and environmental standpoint, with one being an efficient closed unit set up that  
25 employs good scrubbers whereas the other has numerous vents and combustion  
26 characteristics that are hardly comparable.

27 It is also worth mentioning- that the hotspot and regional haze imagery obtained using  
28 MODIS Terra satellite (at a spatial resolution of 500 m and time resolution of 5 minutes at  
29 05:00-06:00 Local Time) between 19 December 2012–30 January 2013 (data accessed at  
30 NASA worldview; <https://worldview.earthdata.nasa.gov/>) were similar except for a 6 day  
31 period (12-17 January 2013), wherein the regional haze was stronger. We note that calmer  
32 meteorological conditions could be a potential contributory factor for stronger haze in this  
33 period. The MODIS satellite image did not detect any active fire counts (at greater than 85%

1 confidence limit) over the Kathmandu Valley (latitude 27.7°N) during the whole campaign  
2 period (19 December 2012-30 January 2013). Thus, the higher chemical concentrations  
3 observed from 4-18 January and even later, appear to be linked to the re-start of the biomass  
4 co-fired brick kilns and cannot be explained by linkages with regional haze or increased open  
5 burning of biomass, considering the available evidence. We analyze the diel profiles for the  
6 two contrasting pPeriods and some of these aspects in detail in Sections 3.4 and 3.6.

7 In the time series it can also be seen that 19 January 2013 was characterized by the lowest  
8 VOC concentrations because of an intense rain event during the previous night. When  
9 considering the entire study period, high ~~For the oxygenated VOCs (OVOCs), high~~  
10 concentrations of OVOCs were typically observed in the early morning hours between 08:00-  
11 10:00 LT and surprisingly acetaldehyde, which is the most reactive VOC among the OVOCs,  
12 frequently reached concentrations as high as 40 ppb. In contrast methanol and the sum of  
13 acetone and propanal were generally below 20 ppb and 10 ppb, respectively. ~~Acetaldehyde~~  
14 ~~concentrations of about 30-40 ppb during several plume-like episodes (e.g. 24 December~~  
15 ~~2012-26 December 2012; 11 January 2013-18 January 2013), were characterized by co-~~  
16 ~~synchronous peaks in isoprene until 28 December 2012 and peaks in the combustion tracers~~  
17 ~~acetonitrile and furan from 4 January 2013 till 30 January 2013. Peak acetaldehyde~~  
18 concentrations of about 30-40 ppb were observed in the time series. These often correlated  
19 with peaks in the concentrations of acetonitrile and furan (chemical tracers for combustion)  
20 between 4 January 2013 and 30 January 2013 and occasionally with peaks in daytime  
21 isoprene concentrations before 2 January 2013. Biomass burning sources and photo oxidation  
22 of precursor compounds co-emitted from the biomass burning appear to contribute  
23 significantly to the high concentrations of oxygenated VOCs. This points to the fact that the  
24 major sources of oxygenated VOCs during the wintertime in Kathmandu are different from  
25 what are generally considered to be the most important sources based on studies conducted in  
26 several other regions of the world, where photo oxidation and industrial sources dominate and  
27 has large implications for wintertime oxidation chemistry in the Valley, as these species play  
28 a key role in radical chemistry (Singh et al., 1995). For example, the observed ranking in  
29 oxygenated VOCs is different from the ranking observed during wintertime in megacities like  
30 Paris and London (methanol > acetaldehyde > acetone) (Dolgorouky et al., 2012; Langford et  
31 al., 2010). Furthermore the ranking observed for aromatic VOCs during this study (benzene >  
32 toluene > C8-aromatics > C9-aromatics) was in contrast to the ranking (toluene > benzene >  
33 C8-aromatics > C9-aromatics) observed in several urban sites such as Paris, London and

1 Tokyo (Dolgorouky et al., 2012;Langford et al., 2010;Yoshino et al., 2012). This exemplifies  
2 that the nature and strength of emission sources for oxygenated and aromatic VOCs in the  
3 Kathmandu Valley differ from several urban areas in other parts of the world. Biomass  
4 burning sources and the manner in which regulation of benzene occurs, are likely the major  
5 causes for the observed differences.

### 6 **3.3 Comparison with wintertime VOC mixing ratios elsewhere**

7 Figure 56 provides a comparison of average VOC mixing ratios measured in the Kathmandu  
8 Valley with VOC mixing ratios reported at other urban or urban influenced environments  
9 including megacities, during the winter season. The concentration ranking in the average  
10 VOC mixing ratios during our wintertime deployment was acetaldehyde (8.8 ppb) >  
11 methanol (7.4 ppb) > acetone + propanal (4.2 ppb) > benzene (2.7 ppb) > toluene (1.5 ppb) >  
12 isoprene (1.1 ppb) > acetonitrile (1.1 ppb) > C8-aromatics (~1 ppb) > furan (~0.5 ppb) > C9-  
13 aromatics (0.4 ppb). As can be seen from Figure 45, when compared to average wintertime  
14 mixing ratios reported from several sites elsewhere in the world, the mixing ratios of  
15 acetaldehyde (~9 ppb), acetonitrile (~1 ppb) and isoprene (~1 ppb) in the Kathmandu Valley  
16 are among the highest measured anywhere in the world. In contrast, Kathmandu had lower  
17 methanol mixing ratios than measured in London and Tokyo (Langford et al., 2010;Yoshino  
18 et al., 2012) during winter 2006 and 2007 (19.4 ppb and 12.4 ppb, respectively) as well as  
19 lower acetone mixing ratios than what was measured in Barcelona (8 ppb) (Filella and  
20 Peñuelas, 2006) . Apart from the contribution of biogenic sources during daytime, which was  
21 major, isoprene was also emitted by biomass combustion sources in the Kathmandu Valley.  
22 Borbon et al. (2001) have previously reported that due to traffic emissions alone, isoprene  
23 mixing ratios can reach as high as 1.8 ppb in urban areas. The Bode site was located in the  
24 outflow of Kathmandu metropolitan city and Lalitpur sub-metropolitan city and therefore the  
25 evening time increase in isoprene can also be partially due to traffic emissions during the  
26 evening rush hour. The average benzene concentrations in Kathmandu (~3 ppb) were notably  
27 higher than those reported in other cities except for the city of Karachi (Barletta et al., 2002).  
28 The average toluene and sum of C8 – aromatics mixing ratios, however were lower than in  
29 other urban areas like Tokyo (Yoshino et al., 2012), Barcelona (Filella and Peñuelas, 2006),  
30 Karachi (Barletta et al., 2002), Hong Kong (Guo et al., 2007) and Guangzhou (Liu et al.,  
31 2008), where industrial and traffic sources are much larger than in Kathmandu. Whereas  
32 benzene is emitted in almost equal proportion from fossil fuel and biomass combustion

1 sources (Henze et al., 2008), fossil fuel combustion and industrial processes contribute a  
2 much larger fraction to the global budgets of toluene and sum of C-8 and C-9 aromatics. The  
3 observed trend in concentrations of some of the aromatic compounds made using the PTR-  
4 TOF-MS in this study differs from the trend reported in a previous study by Yu et al. (2008)  
5 who employed the long path differential optical absorption spectroscopy (DOAS) technique  
6 to make measurements of monocyclic VOCs in Kathmandu during winter 2003. In that study,  
7 xylene (a C-8 aromatic compound) concentrations were reported to be the highest followed  
8 by toluene and benzene respectively. We think two reasons are responsible for differences  
9 from that study. The first reason is that the measurements by Yu et al. (2008) were carried out  
10 near a fairly busy road (Chabahil-Bouddha-Jorpati road) and a traffic intersection (Chabahil-  
11 Ringroad intersection) and consequently the aromatic VOC concentrations were primarily  
12 influenced by traffic sources. Secondly, VOC measurements using the long path DOAS  
13 technique are reported to have potentially large interferences due to ambient ozone and  
14 suspended particles (Yu et al., 2008).

15 Despite much larger population and more industries compared to Kathmandu, wintertime  
16 measurements in the megacities of London (Langford et al., 2010) and Paris (Dolgorouky et  
17 al., 2012) suggest that the air is much cleaner for many of the VOCs shown in Figure 56. The  
18 combination of the topography of Kathmandu (which results in suppressed ventilation) and  
19 the anthropogenic and biogenic emissions within the Valley appear to cause high ambient  
20 wintertime concentrations for several VOCs (e.g. acetonitrile, acetaldehyde and benzene and  
21 isoprene). ~~While the studies in other cities were conducted in different years, it is unlikely~~  
22 ~~that inter annual variability would be the sole reason for lower concentrations in the~~  
23 ~~megacities. As a city located in a developing country it is more likely that even with a~~  
24 ~~population that is less than one tenth of these megacities, Kathmandu air has higher~~  
25 ~~concentrations of carcinogens like benzene due to inadequate access to efficient and clean~~  
26 ~~technologies and limited controls on emissions from existing industries.~~

27

### 28 **3.4 Diel profiles as a tool to constrain emission sources: VOCs emitted from** 29 **biomass burning activities in the Kathmandu Valley**

30 In order to contrast the role of diverse emission sources during ~~P~~period 1 ~~(19 December 2012~~  
31 ~~– 2 January 2013; shaded yellow in Figure 5; marked by high daytime emissions of isoprene~~

1 ~~and only a couple of operational brick kilns~~) and ~~pPeriod 2 (4 January 2013—18 January~~  
2 ~~2013; shaded in grey in Figure 5; coldest period of the year and marked by high acetonitrile~~  
3 ~~emissions and almost all brick kilns in the Valley becoming operational)~~, we analyzed the  
4 diel profiles of a number of VOCs. These are shown in Figure ~~67~~ as box and whisker plots  
5 for ~~pPeriod 1~~ (derived from total number of measurements > 20500) and ~~pPeriod 2~~ (derived  
6 from total number of measurements > 21500) for methanol, acetaldehyde, sum of acetone and  
7 propanal, isoprene, furan, isocyanic acid, acetonitrile, benzene and toluene. The time stamp is  
8 the start time of respective hourly data bin (e.g. 9 for data averaged between 9 and 10).  
9 We note that the concentrations of acetonitrile (a chemical tracer for biomass combustion),  
10 methanol, benzene and isocyanic acid are significantly higher in ~~pPeriod 2~~ relative to ~~Pperiod~~  
11 1, indicating that for all of them, the biomass co-fired brick kilns ~~that became operational in~~  
12 ~~the first week of January and other forms of biomass burning (e.g. leaves and branches,~~  
13 ~~garden waste and garbage) and burning of leaves and branches~~ were major contributory  
14 sources. In contrast, isoprene and toluene concentrations were markedly higher during  
15 ~~Pperiod 1~~ as compared to ~~pPeriod 2~~. Acetaldehyde and furan did not differ much between  
16 ~~pPeriod 1~~ and ~~pPeriod 2~~. ~~The high acetaldehyde concentrations suggest the possibility of high~~  
17 ~~levels of peroxy acetyl nitrate (PAN). The campaign average concentration of 1.08 ppb~~  
18 ~~observed at m/z 45.990 and attributed to NO<sub>2</sub><sup>+</sup> (Table S1), which is a fragment ion of C1-C5~~  
19 ~~alkyl nitrates (Aoki et al., 2007), appears to be consistent with the presence of a large pool of~~  
20 ~~gaseous organic nitrate species too.~~ Except for isoprene, isocyanic acid and acetaldehyde,  
21 which did not show a marked bimodal profile (morning and evening maxima), all the other  
22 VOCs shown in Figure ~~67~~ exhibited bimodal diel profiles to some degree, indicating the  
23 common influence of urban emission activities and biomass combustion sources for these  
24 compounds. Bimodal profiles for VOCs have previously been reported from several sites  
25 influenced by urban emissions (Staehelin et al., 1998; Stemmler et al., 2005), including our  
26 recent work in Mohali, India (Sinha et al., 2014), another site in South Asia that is somewhat  
27 closer to Kathmandu in terms of emission sources. Such bimodal profiles typically arise  
28 because morning and evening emissions get mixed into a shallow boundary layer, while the  
29 afternoon emissions are diluted under a rapidly growing boundary layer due to the surface  
30 heat flux, giving rise to a daytime minima in the diel profile. This holds for VOCs which are  
31 not formed photochemically or emitted anomalously during the daytime in large measure.  
32 Thus, bimodal diel profiles were not observed for isoprene which is emitted by terrestrial  
33 vegetation during daytime and acetaldehyde and isocyanic acid which are known to be  
34 emitted from biomass fires and produced photochemically from precursor compounds (Millet

1 et al., 2010;Roberts et al., 2014). In general, for both pPeriod 1 and pPeriod 2, the features of  
2 diel profiles in terms of rise and fall of concentrations are largely conserved for all the VOCs  
3 shown in Figure 67. The diel profiles of all VOCs also reveal at about 06:00 local time (LT),  
4 emission activities pertaining to cooking (use of biofuel and fossil fuel such as LPG), traffic  
5 and brick kilns pick up and the diel peaks for almost all VOCs occurs at around 08:00-09:00  
6 LT.

7 In addition to the typical boundary layer dynamics and emissions driving concentration  
8 profiles, the mountain meteorology appears to play a key role in the concentration peaks  
9 observed after sunrise around 08:00-09:00 LT. If one examines the diel pattern for wind  
10 speed, wind direction, temperature and solar radiation data (available for part of the study and  
11 shown in Figure 2 b, it is clear that the diel meteorological conditions (e.g. surface wind flow,  
12 direction, temperature, RH) were very consistent even on different days as there is a very  
13 narrow spread in the values for each hour and the average and median always converged. The  
14 wind speeds were typically lower than  $1 \text{ ms}^{-1}$  for almost all hours of the day except between  
15 10:00-16:00 LT, when westerly winds from the mountain passes lying west of the site swept  
16 across the Valley attaining wind speeds of upto  $3\text{-}4 \text{ ms}^{-1}$ , causing rapid venting and dilution.  
17 The wind direction was very consistent on daily timescales. During the evening and at night,  
18 the horizontal wind flow was mainly from the south-east direction, which changed to a  
19 westerly flow during the day. Down-slope ~~Mountain-mountain~~ winds during nighttime result  
20 in pooling of cleaner cold air. Then shortly after sunrise, convective mixing of surface air  
21 with residual air commences the growth of the well mixed daytime boundary layer (Panday  
22 and Prinn, 2009).

23 The highest mixing ratios for acetaldehyde (average value of  $\sim 25$  ppb for both pPeriod 1 and  
24 pPeriod 2) and acetone (average value of  $\sim 7$  ppb for both Pperiod 1 and pPeriod 2) and  
25 indeed for most of the other VOCs were observed during morning hours about one hour after  
26 sunrise (09:00 – 10:00 LT). The breaking of the nocturnal boundary layer and entrainment of  
27 air masses rich in accumulated oxygenated VOCs, which were displaced by cold air from the  
28 mountain slopes after midnight contribute towards the peaks observed in all VOCs between  
29 09:00-10:00 LT. In mountain basins such as the Kathmandu Valley, at nighttime, katabatic  
30 winds are generated due to radiative cooling of mountains that lead to pooling of cold air to  
31 the Valley bottom (Figure 2 a). Due to this katabatic flow, less cold and less dense air parcels  
32 in the Valley bottom containing the entire Valley's surface emissions rise upward during

1 nighttime, while relatively clean cold air parcels flow underneath. After sunrise, downward  
2 mixing of the uplifted accumulated VOCs occurs with new surface emissions, as a growing  
3 mixed layer entrains the elevated layers of the polluted air. Therefore during morning hours,  
4 mixing of oxygenated VOCs and their precursors that had accumulated during nighttime and  
5 a kick start to their photochemical production after sunrise, contributes to sharp peaks (e.g.  
6 for acetaldehyde and acetone). It should also be noted that the majority of the population in  
7 Kathmandu Valley cook their major meals in the morning and evening hours using fuel such  
8 as liquefied petroleum gas (LPG), kerosene and firewood (Panday et al., 2009).

9 Contributions from biogenic sources and oxidation of alkenes to acetaldehyde are also  
10 important. Reaction of oxygenated VOCs like ethanol and methyl ethyl ketone (MEK) with  
11 hydroxyl (OH) radicals and the reaction of tropospheric ozone (O<sub>3</sub>) with alkenes can  
12 significantly contribute to photochemical formation of acetaldehyde (Sommariva et al.,  
13 2011; Grosjean et al., 1994). After the morning peak (09:00 – 10:00 LT), a sharp decrease was  
14 observed in the average acetaldehyde mixing ratios (from ~25 ppb to ~8 ppb during 10:00 –  
15 13:00 LT) relative to methanol and acetone, which is not surprising considering its much  
16 higher OH reactivity.

17 The highest isoprene concentrations were observed during daytime for both pPeriod 1 and  
18 Pperiod 2 but the average concentrations were much higher during pPeriod 1 when ambient  
19 temperature and solar radiation were comparatively higher and deciduous trees had not shed  
20 much of their leaves. This clearly points to daytime biogenic emission sources of isoprene in  
21 the Kathmandu Valley. In Section 3.6 we investigate the spatial and temporal location of the  
22 biogenic sources. We note that while the isoprene emission profile was dominated by  
23 biogenic sources, biomass burning (Christian et al., 2003; Andreae and Merlet, 2001; Warneke  
24 et al., 2011) and traffic (Borbon et al., 2001) also contributed to the ambient isoprene as can  
25 be seen from the nighttime peaks and discussed in previous sections. Thus, the contribution  
26 of both biogenic and anthropogenic sources resulted in high isoprene even in winter in the  
27 Kathmandu Valley which is different from what has been observed at high latitude sites in  
28 winter (Seco et al., 2011).

29 Apart from the biomass burning practices typical of developing regions of the world, the  
30 brick kilns in the Kathmandu Valley do not only burn coal, but also burn large quantities of  
31 wood and crop residues, ca. 90 tons per month per brick factory (Stone et al., 2010; Rupakheti  
32 et al., 2016), which can emit acetonitrile and benzene (Sarkar et al., 2013). Both acetonitrile

1 and benzene levels were much higher during nighttime and morning hours in pPeriod 2 as  
2 compared to pPeriod 1 due to more intense biomass burning in pPeriod 2. During 08:00–  
3 09:00 LT (when highest ambient acetonitrile and benzene were observed) average mixing  
4 ratios were approximately 1 ppb and 2 ppb higher for acetonitrile and benzene, respectively  
5 during pPeriod 2 relative to pPeriod 1.

6 Unlike acetonitrile and benzene, toluene concentrations were higher during pPeriod 1 in  
7 comparison to pPeriod 2. Despite the dilution effect of cold air descending from the mountain  
8 slopes, benzene concentrations increased during the night in pPeriod 2, whereas toluene  
9 concentrations did not show any increase during the night in both pPeriod 1 and pPeriod 2,  
10 suggesting that biofuel and biomass burning sources (including the brick kilns co-fired with  
11 biomass) and not traffic were the driving factors responsible for nighttime increase in  
12 benzene during pPeriod 2 probably due to varied forms of biomass combustion, including the  
13 biomass co-fired brick kilns. The emission ratios of benzene/toluene from previous studies  
14 show that, for a wide variety of commonly occurring fuels, the emission of benzene can be  
15 more than twice as high as the emission of toluene (Tsai et al., 2003; Lemieux et al.,  
16 2004; Stockwell et al., 2015). ~~for key emission periods of the day are discussed further in~~  
17 ~~Section 3.6 to constrain source signatures.~~ The use of large number of diesel generators as an  
18 alternative power source in the Kathmandu Valley which suffers from scheduled daily power  
19 outages in some quarter of the city, could also have significant contributions to the observed  
20 high mixing ratios for aromatic VOCs.

21 To our knowledge, this paper reports the first measurements of isocyanic acid from any site  
22 in South Asia. Isocyanic acid has only recently been measured in ambient air using novel  
23 mass spectrometric methods (Roberts et al., 2011) and much remains to be understood  
24 regarding its sources and sinks in different environments. The high isocyanic acid  
25 concentrations observed during the daytime suggest a strong photochemical source from  
26 hydroxyl radical initiated oxidation of alkyl amines and amides with hydroxyl radicals  
27 (Roberts et al., 2014; Roberts et al., 2011; Zhao et al., 2014). Isocyanic acid has also been  
28 detected in diesel exhaust (Wentzell et al., 2013), tobacco smoke and wild fires and in  
29 emissions from low temperature combustion of coal (Nelson et al., 1996). From the diel  
30 profile, it is clear that around evening time there are primary emissions too but overall the  
31 secondary source dominates the ambient concentrations of isocyanic acid in this environment.  
32 Currently, global models of isocyanic acid (Young et al., 2012) do not incorporate a

1 photochemical source. The recent model-based estimates of isocyanic acid (HNCO) by  
2 Young et al. (2012) showed annual mean concentrations of HNCO over the Indo Gangetic  
3 Plain and Nepal to be in the range of 0.2-0.5 ppb (values read from Figure 4 of Young et al.  
4 (2012). The average concentrations measured during winter in Kathmandu and in the post  
5 monsoon season in Mohali were ~ 1 ppb (Chandra and Sinha, 2016) with clear daytime  
6 maxima. This suggests that inclusion of isocyanic acid's photochemical sources are necessary  
7 for deriving better estimates of the global isocyanic acid budget , as these are likely  
8 significant over South Asia where biomass burning and agricultural activities can also emit  
9 precursor compounds of isocyanic acid such as alkyl amines, formamide and acetamide  
10 Roberts et al. (2011). Our in-situ field data from the Kathmandu Valley suggests that  
11 inclusions of isocyanic acid's photochemical sources ~~is~~are necessary for deriving better  
12 estimates of the global isocyanic acid budget, as these are likely to be significant over South  
13 Asia where biomass burning and agricultural activities can emit alkyl amines. Serious health  
14 impairments can occur upon exposure to isocyanic acid at concentrations greater than 1 ppb,  
15 which occurred during our study for several hours during ~~p~~Period 2. These health impacts  
16 have been previously mentioned in Roberts et al. (2011) and are also discussed in Section 3.9.

### 17 **3.5 Diel profiles of rarely measured VOCs and correlation with emission tracer** 18 **VOC compounds for constraining their sources**

19 Figures ~~7~~8 a, b and c show the diel profiles of propyne (m/z = 41.039), propene (m/z =  
20 43.055) and propanenitrile (m/z = 56.060) alongside acetonitrile (an excellent tracer for  
21 biomass combustion), respectively. These diel profiles correspond to data for the entire  
22 measurement period. Strong correlation ( $r^2 \geq 0.7$  for the hourly averages) with acetonitrile  
23 clearly indicates that during our wintertime study in the Kathmandu Valley, all these  
24 compounds were primarily emitted from biomass burning, despite having multiple sources  
25 (Hao et al., 1996; Akagi et al., 2011; Andreae and Merlet, 2001; Karl et al., 2003). ~~This~~  
26 ~~inference is consistent with previous studies (Hao et al., 1996; Akagi et al., 2011; Andreae and~~  
27 ~~Merlet, 2001) that reported propyne and propene in plumes sampled from biomass burning.~~  
28 ~~Average concentrations as high as 7.7 ppb propyne (maximum ~46 ppb) and 4 ppb propene~~  
29 ~~(maximum ~34 ppb) were observed during the measurement period in the Kathmandu~~  
30 ~~Valley. Previously, during the Texas Air Quality Study 2000, frequent propene~~  
31 ~~concentrations of >100 ppb were measured using the PTR-MS technique (Karl et al., 2003).~~  
32 ~~These were attributed to industrial sources related to oil refining.~~ Both propene and propyne

1 participate in important chemical reactions in the troposphere. While propene is a source of  
2 OH radicals when it undergoes ozonolysis, propyne has been reported to produce  
3 methylglyoxal, formic acid and acetic acid in multistep reactions (Lockhart et al.,  
4 2013;Warneck and Williams, 2012). Propanenitrile has been previously detected in biomass  
5 smoke during laboratory studies (Akagi et al., 2013;Akagi et al., 2011;Yokelson et al.,  
6 2013;Karl et al., 2003;Karl et al., 2007). Average propanenitrile mixing ratios observed  
7 during the measurement period were ~0.21 ppb. Propanenitrile reacts very slowly with  
8 hydroxyl radicals in the atmosphere ( $k_{OH}$  is of the order of  $10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) but the  
9 oxidation of propanenitrile with OH radicals can produce ~~long-lived~~ nitrogen compounds in  
10 the troposphere and hence could contribute to the reactive nitrogen budget.

11 Figures 78 d, e and f show the diel profiles for nitromethane, dimethyl sulfide (DMS) and  
12 styrene alongside methanol, acetaldehyde and acetonitrile. Nitromethane (measured at m/z  
13 ratio 62.026) concentrations correlated strongly with the hourly average concentrations of  
14 methanol ( $r^2 = 0.81$ ). Nitromethane is known to be present in diesel exhaust (Inomata et al.,  
15 2014;Inomata et al., 2013;Sekimoto et al., 2013) and biomass burning plumes (Akagi et al.,  
16 2013). The maximum nitromethane mixing ratios observed in the Kathmandu Valley were  
17 ~1.2 ppb which falls within the range of ambient nitromethane mixing ratios (1-9 ppb)  
18 reported previously in urban environments (Grosjean et al., 1998;Yassaa et al., 2001;Inomata  
19 et al., 2014). In the Kathmandu Valley, a large number of diesel power generators are used to  
20 supplement the main power supply. Ambient nitromethane observed in the Kathmandu  
21 Valley is therefore also likely from a combination of biomass burning sources and diesel  
22 exhaust emissions. ~~The correlation with methanol also suggests that diesel exhaust may be a~~  
23 ~~contributory source for methanol.~~The major sink of nitromethane in the atmosphere is its  
24 photodissociation (photodissociation lifetime of ~10h), which produces methyl radicals and  
25 NO<sub>2</sub> (Taylor et al., 1980). Therefore nitromethane can act as a NO<sub>x</sub> source in the atmosphere  
26 and could contribute to surface ozone production.

27 Dimethyl sulfide measured (at m/z ratio 63.026) in the Kathmandu Valley showed good  
28 correlation with the diel profile of acetaldehyde (correlation of hourly averages:  $r^2 = 0.8$ ).  
29 Average concentrations in the morning (09:00-10:00 LT) reached 0.4 ppb. Although marine  
30 phytoplankton emissions are known to be the major source of DMS in the atmosphere  
31 (Andreae and Raemdonck, 1983;Sinha et al., 2007), ambient mixing ratios up to 160 ppt have  
32 been recently reported in the Amazon rainforest, which were attributed to biogenic soil

1 emissions (Jardine et al., 2015). Certain lichens, mosses, grasses and plant leaves can emit  
2 acetaldehyde (Kesselmeier et al., 1997;Kesselmeier and Staudt, 1999). Therefore the  
3 possibility of such vegetation on the mountain slopes and the soil acting as sources of DMS  
4 and acetaldehyde, respectively, is plausible. Inefficient combustion of sulfur rich  
5 biofuel/biomass are also potential sources of DMS (Jardine et al., 2015).

6 Figures 78 g and h show the diel profiles of formamide and acetamide alongside isoprene  
7 while Figure 78 i shows the diel profile of naphthalene and benzene. During the measurement  
8 period, daytime maximum average values of ~1 ppb and ~0.5 ppb were observed for  
9 formamide and acetamide, respectively. Although formamide and acetamide correlate  
10 strongly with isoprene (hourly average  $r^2 \geq 0.8$ ), to our knowledge, biogenic sources of  
11 formamide and acetamide have not been reported previously. On the other hand short chain  
12 amides such as formamide and acetamide can be produced as a result of photochemical  
13 oxidation of alkyl amines with hydroxyl radicals and nitrogen oxides (NO<sub>x</sub>) (Roberts et al.,  
14 2014). The presence of formamide in ambient air at concentrations as high as 1 ppb is  
15 consistent with the photochemical source of isocyanic acid discussed in the previous section.  
16 Also it is reported that both formamide and acetamide could be emitted from tobacco smoke  
17 and hence likely from pyrolysis of biomass (Ge et al., 2011). The good correlation of  
18 formamide and acetamide with isoprene's diel concentration profile suggests that the  
19 photochemical source arising from oxidation of amines dominates over any primary emission  
20 sources of amides.

21 The ion peak detected at m/z ratio of 129.070 in the PTR-TOF-MS spectra was attributed to  
22 naphthalene. Naphthalene is the most volatile and abundant polycyclic aromatic hydrocarbon  
23 (PAH) present in the atmosphere. Previously Martinez et al. (2004) have reported vehicle  
24 exhaust and residential heating in the urban environments as major sources of naphthalene.  
25 The similarity in diel profiles of naphthalene and benzene and their strong correlation with  
26 each other (hourly average  $r^2 = 0.79$ ), suggests that biomass burning and traffic sources  
27 dominated emissions of naphthalene in the Kathmandu Valley. ~~Average morning (08:00-~~  
28 ~~10:00 LT) ambient concentrations of ~0.6 ppb naphthalene observed during this study were~~  
29 ~~much higher than the maximum concentrations of ~0.35 ppb reported by Jordan et al. (2009)~~  
30 ~~in ambient air previously at Innsbruck, which is one more indicator of the profound influence~~  
31 ~~on atmospheric composition exerted by biomass burning sources in the Kathmandu Valley~~  
32 ~~during wintertime.~~

1  
2 **3.6 A detailed investigation of benzene from biomass co-fired brick kilns and**  
3 **isoprene from vegetation**High isoprene in the Kathmandu Valley: a daytime  
4 biogenic source and contributions from combustion sources  
5

6 ~~The observed benzene to toluene ratios for the prime emission hours in the morning (06:00–~~  
7 ~~08:00 LT) and in the evening (17:00–19:00 LT) were 1.08 and 0.44 for Period 1 (19~~  
8 ~~December 2012—2 January 2013) and 2.35 and 0.70 for Period 2 (4 January 2013—18~~  
9 ~~January 2013) respectively. The evening hour benzene to toluene ratio for both Period 1 and~~  
10 ~~Period 2 were comparable to the ratio for vehicle exhaust emissions (0.41—0.83) reported in~~  
11 ~~other cities (Langford et al., 2009). The morning period benzene to toluene ratio (06:00–08:00~~  
12 ~~LT) were somewhat high in Period 1 for traffic sources but in Period 2 considerably higher~~  
13 ~~than values reported for traffic sources which suggests strong contribution from sources other~~  
14 ~~than traffic to the ambient benzene levels. Stockwell et al. (2015) have reported~~  
15 ~~benzene/toluene ratios greater than 1 from a large number of diverse biomass burning sources~~  
16 ~~(e.g. crop residue, garbage fires), and the observed emission ratios in the morning clearly~~  
17 ~~indicate substantial biomass/biofuel emissions sources. As mentioned earlier, in Period 2~~  
18 ~~several biomass co-fired brick kilns were operational within a distance of 1 km from the site.~~  
19 ~~Brick kilns in the Kathmandu Valley burn coal, wood, crop residues, and municipal solid~~  
20 ~~waste (Stone et al., 2010) which can produce large amount of aromatic compounds (Tsai et~~  
21 ~~al., 2003;Sarkar et al., 2013). Therefore higher morning hour benzene to toluene ratios in~~  
22 ~~Period 2 likely had strong contribution from the biomass co-fired brick kilns along with other~~  
23 ~~typical biomass burning, domestic heating and cooking activities. While influence of the~~  
24 ~~morning traffic emissions at the site was still minimal, the evening hour peaks at the site were~~  
25 ~~dominated mainly by vehicular emissions and diesel exhaust advected from the cities.~~

26 ~~Along with benzene and acetonitrile, VOCs such as isocyanic acid, formamide, acetamide,~~  
27 ~~nitromethane and naphthalene were present at higher concentrations during Period 2, which~~  
28 ~~indicates biomass co-fired brick kiln emissions are also a potent source for these compounds~~  
29 ~~in the Kathmandu Valley. In order to highlight how dominant a role this source can have on~~  
30 ~~the ambient air quality, in Figure 9 we show a 24 h period on 18–19 January 2013 containing~~  
31 ~~high temporal resolution data (1 minute) of benzene and acetonitrile. The red markers~~

1 ~~represent ambient acetonitrile mixing ratios while the black markers represent ambient~~  
2 ~~benzene mixing ratios. Peak concentrations of ~6 ppb acetonitrile and ~12 ppb benzene were~~  
3 ~~observed during early morning hours (05:00–08:00 LT). The correlation of benzene with~~  
4 ~~acetonitrile for the data as shown in the inset of Figure 9 was excellent ( $r^2 = 0.97$ ). This~~  
5 ~~suggests that equipping the existing brick kilns with cleaner brick kiln technology and~~  
6 ~~scrubbers in the Kathmandu Valley would certainly help to lower concentrations of~~  
7 ~~carcinogenic compounds like benzene and a suite of co-emitted VOCs, which also fuel~~  
8 ~~formation of secondary organic aerosol in winter aggravating fog episodes.~~

9 Figure 810 shows a polar annulus plot of the hourly mean isoprene mixing ratio during the  
10 period 16-30 January 2013 (unfortunately, meteorological data for other periods of the study  
11 are unavailable). The polar annulus plot is a method of visualizing the temporal aspects of a  
12 specie's concentration with respect to wind direction. In the polar annulus plots, measured  
13 concentrations are averaged in separate wind speed and wind direction bins and then further  
14 interpolation using Kriging technique are applied for conversion to polar coordinates  
15 (Ropkins and Carslaw, 2012). Such plots reveal important spatio-temporal information  
16 regarding emission sources. In Figure 810 it can be seen that isoprene had highest ambient  
17 mixing ratios (~1 ppb isoprene) during the daytime (07:00-14:00 LT) which is an indication  
18 of biogenic sources. Significant isoprene concentrations (~0.5 ppb) could also be observed  
19 during evening and nighttime which are likely from biomass combustion and traffic emission  
20 sources. Furan contributed a maximum of only ~40% (during nighttime) to the sum of  
21 ambient isoprene and furan. This is a very important finding as previous studies using proton  
22 transfer reaction mass spectrometers equipped with quadrupole mass analyzers, which cannot  
23 distinguish between furan and isoprene peaks due to their lower mass resolution and detect  
24 the two compounds collectively at a nominal  $m/z = 69$ , tend to attribute the evening and  
25 nighttime concentrations to furan and not isoprene. Using a novel VOC-OHM chemical  
26 kinetics reactor (Kumar and Sinha, 2014), which constrained the rate coefficient of the  
27 isobaric contributor at nominal  $m/z = 69$ , it has been demonstrated at another South Asian  
28 site in the north-west Indo Gangetic Plain (Mohali), that isoprene is the major contributor to  
29  $m/z = 69$ . Thus it appears that isoprene has significant contributions from both vegetation and  
30 biomass/biofuel burning sources in South Asia, which has large implications for the  
31 atmospheric oxidation in this part of the world, as discussed also in Sinha et al. (2014). While  
32 several previous studies have reported significant contributions from anthropogenic sources  
33 to isoprene in urban areas elsewhere, especially in winter (Borbon et al., 2001; Barletta et al.,

1 2005;Hellén et al., 2012), the in-situ measurements from Mohali and Kathmandu suggest that  
2 the magnitude of the isoprene source from anthropogenic sources may be quite important  
3 regionally in South Asia. The non-biogenic sources of isoprene acquire greater significance  
4 in the evening, nighttime or early morning when combustion emissions are more widespread  
5 and can accumulate under shallow inversions. What is remarkable is that in contrast to  
6 wintertime measurements of isoprene from sites elsewhere in the world due to the strong  
7 contribution from biogenic sources in the Kathmandu Valley, average wintertime  
8 concentrations of isoprene in Kathmandu were observed to be above 1 ppb (see Figure 5). To  
9 emphasize that the daytime isoprene concentrations were primarily controlled by biogenic  
10 emissions, we show real time data from a day (18 January 2013) where clear co-variation of  
11 the daytime isoprene concentrations occurred with changes in the solar radiation (Figure 8 b).

12 High values of isoprene were generally observed from the west and northern sector (N.N.E  
13 where Nilbarahi Jungle and Gokarna Reserve Forest are located) and at appreciable wind  
14 speeds ( $> 3$  m/s). The advection of air across the Valley in the afternoon as they flow through  
15 the mountain passes from west to east due to the high speed westerly winds has been  
16 previously described by Panday and Prinn (2009). The forest areas on the mountain slopes  
17 appear to contribute to the high ambient isoprene concentrations measured during the  
18 afternoon hours. The average daytime (08:00 – 17:00 LT) isoprene concentrations observed  
19 during SusKat-ABC campaign (1.35 ppb) are comparable to the concentrations measured in  
20 south-east Asian tropical rainforest sites (Bryan et al., 2012; Jones et al., 2011). As mentioned  
21 in the site description section, the forested areas contained tree species like *oak* and *Melia*  
22 *azedarach*, which have ~~very high~~ significant isoprene emission potentials (~~upto~~  $350 \mu\text{g g}^{-1}$  dry  
23 leaf  $\text{h}^{-1}$  and  $4.7 \mu\text{g g}^{-1}$  dry leaf  $\text{h}^{-1}$  respectively (Simon et al., 2005; Padhy and Varshney,  
24 2005)). ~~The mixing of isoprene rich air with nitrogen oxides and anthropogenic emissions~~  
25 ~~likely plays a profound role on the regional ozone formation potential and oxidizing capacity.~~  
26 In the Section 3.7 we examine the importance of VOCs measured during this study in terms  
27 of their OH reactivity contributions and ozone formation potential.

### 28 **3.7 OH reactivity and Ozone Production Potential of VOCs**

29 The oxidation of VOCs (and consequently their removal rate) depends on the reactivity of  
30 VOCs with both ozone and hydroxyl radicals during daytime and the nitrate radical during  
31 nighttime. For the VOCs reported in this work and the typical maximum ozone  
32 concentrations observed during winter in the Kathmandu Valley (~ 60 -70 ppb; (Putero et al.,

1 2015)), the daytime oxidation with hydroxyl radicals is much faster relative to daytime  
2 oxidation with ozone and nighttime oxidation with nitrate radicals as  $k_{VOC+OH} \geq k_{VOC+NO_3} \geq$   
3  $10^3$ - $10^{10}$  times  $k_{VOC+O_3}$  (Atkinson et al., 2006; [kinetics.nist.gov/kinetics](http://kinetics.nist.gov/kinetics)). The hydroxyl  
4 radical reactivity of an air mass reflects the total reactive pollutant loading of the air mass and  
5 can be used to infer its ozone formation potential (Sinha et al., 2012). While direct total OH  
6 reactivity measurements were not performed during the SusKat-ABC campaign, it is still  
7 instructive to examine the diel profile of the OH reactivity due to the suite of measured VOCs  
8 and assess the relative contributions of individual VOCs. For this analysis, we considered  
9 thirty three out of the thirty seven species that were observed at average ambient  
10 concentrations greater than 200 ppt, for which the rate coefficients with the hydroxyl radical  
11 are known. Thus, out of the thirty seven species, four namely, the nitronium ion ( $m/z =$   
12 45.990), isocyanic acid, and assorted hydrocarbons detected at  $m/z$  ratios of 83.085 and  
13 97.102, respectively, were excluded from this analysis.

14 The total VOC OH Reactivity was calculated as follows (Sinha et al., 2012):

$$15 \quad \text{Total VOC OH reactivity} = \sum k_{(voci+OH)} [VOC_i] \quad \dots (2)$$

16 where  $k_{(voci+OH)}$  is the first order rate coefficient for the reaction of  $VOC_i$  with OH radicals  
17 and  $[VOC_i]$  is the measured concentration of  $VOC_i$ . The rate coefficients were taken from  
18 Atkinson et al. (2006), and from the NIST chemical kinetics database  
19 ([kinetics.nist.gov/kinetics](http://kinetics.nist.gov/kinetics)) and Barnes et al. (2010) when they were unavailable in Atkinson  
20 et al. (2006).

21 Figure ~~944~~ shows the diel profile of the average sum of VOC OH reactivity due to 33  
22 ambient VOCs, along with the diel profiles of the hourly averaged OH reactivity due to the  
23 top three contributors. The grey shaded region in Figure ~~944~~ represents the 10<sup>th</sup> and 90<sup>th</sup>  
24 percentiles of the sum of VOC OH reactivities due to the 33 ambient VOCs. The average diel  
25 profile is bimodal in nature with peaks of ca. 21 s<sup>-1</sup> at 09:00 LT and ca. 13 s<sup>-1</sup> at 18:00 LT.  
26 Interestingly, the nighttime value (22:00-06:00 LT) remains rather constant at ca. 12 s<sup>-1</sup>. The  
27 top ~~four~~three contributing compounds to the total calculated VOC OH reactivity due to all 33  
28 compounds were: acetaldehyde (24.0%) > isoprene (20.2%) > propene (18.7%). These three  
29 VOCs collectively accounted for ca. 63% of the campaign averaged total VOC OH reactivity  
30 of 12.3 s<sup>-1</sup>. Table S3 of the supplement lists the top ten VOC contributors to the total VOC  
31 OH reactivity, many of which are emitted strongly from biomass combustion sources. The

1 influence of south easterly winds advecting primary emissions from biomass co-fired brick  
2 kilns in the morning hours is clearly discernible on the ambient OH reactivity profile.

3 ~~VOCs significantly influence formation of tropospheric ozone in polluted environments.~~  
4 ~~Tropospheric ozone in turn has strong impacts on air quality (as a key ingredient of~~  
5 ~~photochemical smog), climate (due to its radiative forcing), human health (due to its ability to~~  
6 ~~act as a pulmonary irritant) and in causing crop yield losses. The crop effect is particularly~~  
7 ~~important for wintertime wheat crops grown in the Indo-Gangetic Plain (Jerrett et al.,~~  
8 ~~2009; Patton and Garraway, 1986; Sinha et al., 2015). In order to devise mitigation strategies~~  
9 ~~for the control of ozone, VOCs are typically ranked in terms of their ozone formation~~  
10 ~~potential. Here, The relative ozone formation potential of VOCs can be derived VOCs we~~  
11 ~~applied as described by the following equation (Sinha et al. (2012): for calculating ozone~~  
12 ~~production potential of VOCs~~

13 
$$\text{Ozone production potential} = (\sum k_{(voci+OH)}[VOC_i]) \times [OH] \times n \quad \dots (3)$$

14 For the ozone production potential calculation, the average hydroxyl radical concentration  
15 was assumed to be  $[OH] = 1 \times 10^6$  molecules  $\text{cm}^{-3}$  with  $n = 2$  and only data pertaining to the  
16 mid-daytime period was considered (11:00 – 14:00 LT). The temporal context of the analyses  
17 performed using VOC data acquired during the afternoon (11:00-14:00 LT; period using  
18 which ozone production potentials were calculated) is quite relevant considering the recently  
19 published work of Putero et al. (2015), which highlighted that hourly average concentrations  
20 of > 60 ppb are often observed during winter afternoons in the Kathmandu Valley (refer  
21 Figure 9 of (Putero et al., 2015)). This shows that regional photochemistry is strong even  
22 during winter and formation of secondary pollutants contributes to hourly ozone  
23 concentrations in excess of 60 ppb. Figures 10a and b summarize the results in the form of  
24 pie charts for pPeriod 1 (when most brick kilns were inactive but daytime biogenic emissions  
25 of isoprene dominated) and pPeriod 2 (when brick kilns became operational, isoprene  
26 emissions were lower and biomass burning was stronger in intensity). To ascertain the  
27 contribution of different chemical classes of compounds (e.g. OVOCs, benzenoids, isoprene)  
28 to total ozone formation potential, the 33 compounds were further divided into 5 chemical  
29 subgroups as shown. It was found that for both pPeriod 1 and pPeriod 2, oxygenated VOCs  
30 and isoprene collectively accounted for more than 68% (72% for pPeriod 1 and 68% for  
31 pPeriod 2) of the total ozone production potential. This is not surprising given that  
32 acetaldehyde and isoprene were among the highest contributors to the VOC OH reactivity.

1 Interestingly, the contribution of nitriles, furans and benzenoids was much lower (< 12% for  
2 both periods), whereas other VOCs (mainly alkenes) collectively contributed between 18%  
3 (for Period 1) to 21% (Period 2). Ozone production potential of xylenes, trimethylbenzenes,  
4 naphthalene and toluene were found to be highest among benzenoids. Nitriles did not have  
5 substantial contribution while some furan compounds such as 2-furaldehyde and furan made  
6 minor contributions to the total (< 3%). Some of the alkene compounds such as propene and  
7 1,3-cyclopentadiene along with propyne were found to be the major contributors for other  
8 class of compounds to total ozone production potential. The importance of alkenes in urban  
9 environments to ozone formation potentials is well established (Shao et al., 2009; Yoshino et  
10 al., 2012) but the stronger contribution of acetaldehyde and isoprene in the wintertime in  
11 Kathmandu in relation to the measured alkenes suggests differences in atmospheric chemical  
12 processes for this environment compared to the other environments. The calculated total  
13 ozone production potential due to the 33 VOCs considered was found to be 4.93 ppbh<sup>-1</sup> for  
14 Period 1 and 3.79 ppbh<sup>-1</sup> for Period 2. The difference was mainly due to the higher isoprene  
15 mixing ratios observed during Period 1 (ozone production potential for isoprene alone was  
16 1.68 ppbh<sup>-1</sup> for Period 1 and 0.81 ppbh<sup>-1</sup> for Period 2). Therefore biogenic isoprene emission  
17 is important for surface ozone formation even during the polluted conditions observed during  
18 the winter season in the Kathmandu Valley. This analysis puts in perspective the relative  
19 ranking of individual VOCs and classes of VOCs to the ozone production potential in the  
20 Kathmandu Valley for potential mitigation efforts.

### 21 3.8 SOA formation potential of VOCs in the Kathmandu Valley

22  
23 Apart from ground level ozone formation, secondary organic aerosols (SOA) can also be  
24 formed as a result of atmospheric oxidation of VOCs. These secondary organic aerosols  
25 significantly affect air quality, visibility, cloud properties and climate change (Rosenfeld et  
26 al., 2008). Previously isoprene was believed to be unimportant as a SOA precursor due to the  
27 high volatility of its reaction products (Kroll et al., 2006). However recent studies have  
28 highlighted that isoprene can also contribute to SOA formation along with aromatics and  
29 monoterpenes (Claeys et al., 2004; Capes et al., 2009; Lee et al., 2006; Ng et al., 2007). The  
30 SOA yield of individual VOCs depends on the ambient NO<sub>x</sub> concentrations. Under low NO<sub>x</sub>,  
31 the SOA yield is typically higher for aromatics, isoprene and monoterpenes whereas under  
32 high NO<sub>x</sub>, SOA yields of VOCs can get significantly reduced (Kroll et al., 2005; Henze et al.,

1 ~~2008;Presto et al., 2005~~). Apart from ground level ozone formation, secondary organic  
2 aerosols (SOA) can also be formed as a result of atmospheric oxidation of VOCs. ~~The 71~~  
3 ~~detected ions collectively summed up to a total mass concentration of ~160.4  $\mu\text{g}/\text{m}^3$ , out of~~  
4 ~~which the 37 identified ions and VOCs reported in this work, accounted for ~139.1  $\mu\text{g}/\text{m}^3$  (or~~  
5 ~~86.7%).~~ Pudasainee et al. (2006) ~~previously~~ reported  $\text{NO}_x$  rich conditions in ~~the~~ Kathmandu  
6 Valley and based on ~~the~~ SOA yields reported in the literature (e.g., 5%-10% for toluene and  
7 xylenes and ~28% for benzene; (Ng et al., 2007)) and the ambient concentrations of these  
8 VOCs measured during the period of study, we estimate the order of SOA production  
9 potential for these VOCs to be benzene > naphthalene > toluene > xylenes > monoterpenes >  
10 trimethylbenzenes > styrene > isoprene. Although the average ambient concentrations of the  
11 sum of monoterpenes ( $0.17 \pm 0.16$  ppb) were below 200 ppt, it contributed significantly to the  
12 total SOA formation due to its higher SOA yield under high  $\text{NO}_x$  conditions (Lee et al.,  
13 2006). ~~Apart from air quality and climate, SOA can substantially contribute to daily mortality~~  
14 ~~and morbidity (Nawrot et al., 2007). As the major source of aromatics appears to be~~  
15 ~~biofuel/biomass combustion and traffic and diesel exhaust, cleaner energy use practices in~~  
16 ~~these sectors will aid in reduction of secondary organic aerosol which is very important from~~  
17 ~~a health and climate perspective due to its contribution to fine mode aerosol mass~~  
18 ~~concentrations ( $\text{PM}_{10}$ ).~~

### 19 **3.9 VOCs with direct health implications for exposed population**

20 ~~Some of the VOCs in the Kathmandu were detected at concentrations (refer to column 7;~~  
21 ~~Table S1 of supplement) that can pose direct health risks to the exposed population. Benzene~~  
22 ~~which is a human carcinogen and mutagen was present at an average concentration of ca. 3~~  
23 ~~ppb during this wintertime study. It may be noted that no safe level of exposure for benzene~~  
24 ~~can be recommended (WHO, 2010). Formaldehyde (average observed concentration ~2 ppb~~  
25 ~~during this wintertime study) is regarded as a probable human carcinogen as exposure to it~~  
26 ~~can increase the possibility of lung and nasopharyngeal cancer (WHO, 2010). Other than its~~  
27 ~~possible carcinogenic effects, formaldehyde exposure can also cause eye, nose and throat~~  
28 ~~irritation and contribute to diseases like bronchitis ([www.epa.gov](http://www.epa.gov)).~~ Among the other rarely  
29 quantified ambient VOCs, nitromethane is reported to be a possible carcinogen to humans  
30 and is classified as a Group 2B carcinogen (Inomata et al., 2014). Nitromethane was present  
31 at an average concentration of 240 ppt during this study. Several other species can result in  
32 formation of toxic secondary VOCs. For example, naphthalene is not considered to be a

1 human carcinogen, but it can form mutagenic nitronaphthalenes by OH and NO<sub>3</sub>-initiated  
2 reactions (Sasaki et al., 1997;Zhang et al., 2012). Short chain amides, such as formamide and  
3 acetamide can have several health effects including irritation of eyes, skin, nose, throat and  
4 respiratory system, drowsiness and headache, dyspnea (breathing difficulty), conjunctivitis,  
5 corneal necrosis, abdominal pain, nausea, vomiting, diarrhea, and shock or collapse (Ge et al.,  
6 2011). Also cumulative liver, lung and kidney damage can occur due to exposure to  
7 formamide and acetamide. The exposure generally occurs through inhalation, ingestion and  
8 absorption through skin. Short chain amides, such as formamide and acetamide can have  
9 several health effects (Ge et al., 2011). Acetamide is also considered to be a Group 2B human  
10 carcinogen by International Agency for Research on Cancer (<http://www.iarc.fr/>). It is  
11 noteworthy that for some of these species the ambient concentrations measured at the  
12 measurement site may not be serious but exposure closer to the point sources (where  
13 concentrations are much higher) for longer time periods may pose a serious health risk.  
14 Atmospheric oxidation of amide compounds such as formamide and acetamide with OH  
15 radicals can also lead to the formation of isocyanic acid (Barnes et al., 2010)(HNCO) that has  
16 adverse impacts on human health (Barnes et al., 2010) exposure to >1 ppb of isocyanic acid  
17 can cause cataracts, cardiovascular diseases and rheumatoid arthritis via protein  
18 carbamylation (Roberts et al., 2011).. The average concentration of isocyanic acid measured  
19 during this study was ~1 ppb. It has been reported that The exposure concentration of 1 ppb is  
20 based on the study of Wang et al. (2007) who reported that at conjugate anion (NCO<sup>-</sup>)  
21 concentrations corresponding to 1 ppb of isocyanic acid, the conjugate anion NCO<sup>-</sup> can cause  
22 carbamylation of protein via post-translational protein modification initiating an  
23 inflammatory response that causes health effects similar to smoking., at NCO<sup>-</sup> concentrations  
24 corresponding to 1 ppb of isocyanic acid. Isocyanic acid had both photochemical and primary  
25 emission sources in Kathmandu Valley and its ambient concentrations were highest during  
26 the period when the biomass co-fired brick kilns were active. Thus, providing cleaner and  
27 more efficient brick kiln technology would help to reduce the manifold health risks posed to  
28 the population due to exposure to isocyanic acid.

29 Several VOCs detected in the Kathmandu Valley have consequences for human health, often  
30 at concentrations of documented concern. Benzene and formaldehyde are considered human  
31 carcinogens (Group A and B1, respectively) by WHO (2010). Among other rarely quantified  
32 ambient VOCs, short-chain amides, such as formamide and acetamide can have several  
33 health effects (Ge et al., 2011). While acetamide is considered a Group 2B human carcinogen

1 by the International Agency for Research on Cancer (<http://www.iarc.fr/>). nitromethane is  
2 also a Group 2B carcinogen and has been reported as a possible carcinogen to humans  
3 (Inomata et al., 2014). Some gases can result in formation of toxic secondary VOCs. For  
4 example, naphthalene is not considered to be a human carcinogen, but it can form mutagenic  
5 nitronaphthalenes by OH and NO<sub>3</sub> initiated reactions (Sasaki et al., 1997;Zhang et al., 2012).  
6 Atmospheric oxidation of amide compounds such as formamide and acetamide with hydroxyl  
7 radicals also contributes to the formation of isocyanic acid (Barnes et al., 2010). Ambient  
8 isocyanic acid was present at exposure levels of documented concern that can enhance human  
9 health risks for cataracts, cardiovascular diseases and rheumatoid arthritis via protein  
10 carbamylation (Wang et al., 2007;Roberts et al., 2011).Thus long term monitoring of these  
11 gases (isocyanic acid, formamide, acetamide, benzene, formaldehyde, nitromethane,  
12 naphthalene), which can cause adverse effects upon sustained exposure even at  
13 concentrations of few ppb is warranted for establishing exposure and assessing health risks  
14 due to these VOCs in the Kathmandu Valley.

#### 15 **4 Conclusions**

16 This study has comprehensively characterized the chemical composition of air in the  
17 Kathmandu Valley in terms of speciated volatile organic compounds during the SusKat-ABC  
18 wintertime campaign. The measurements performed at high time resolution (every minute)  
19 and high mass resolution ( $m/\Delta m > 4200$ ) enabled us to identify a multitude of compounds  
20 based on their monoisotopic masses and hence exact molecular formula. Novel insights could  
21 be acquired regarding chemical processes related to ozone and secondary organic aerosol  
22 formation in a complex chemical environment affected by mountain meteorology and both  
23 anthropogenic and biogenic sources (even in winter).

24 A total of 71 ion peaks were observed in the mass spectra of PTR-TOF-MS that were above  
25 the detection limit of the instrument. Out of these, 37 species that had average ambient  
26 concentrations greater than 200 ppt during the campaign could be identified with reasonable  
27 confidence based on 1) spectral characteristics observed at a particular  $m/z$  in a 0.005 amu  
28 bin relative to the ion peak, 2) ambient diel profiles and 3) correlation with specific emission  
29 tracer molecules such as acetonitrile (a biomass burning tracer). 200 ppt cut off was also  
30 chosen as an additional quality control measure so as to ensure attribution of ion peaks in the  
31 mass spectra only to the compounds present in the ambient air and not due to instrumental  
32 reasons. Among these 37 species, 8 contained nitrogen, 15 contained oxygen, 13 were

1 hydrocarbons and one contained sulfur. Based on chemical signatures of tracer compounds  
2 such as acetonitrile and isoprene, two periods with contrasting emission influences were  
3 identified during the campaign and investigated in detail. Period 1 (19 December 2012 – 2  
4 January 2013) was characterized by high daytime biogenic emissions of isoprene (average  
5 isoprene concentrations in pPeriod 1 and pPeriod 2 were 1.66 ppb and 0.97 ppb, respectively)  
6 and the absence of operational brick kilns (and hence their emissions); while Pperiod 2 (4  
7 January 2013 – 18 January 2013) was marked by high acetonitrile (average concentration  
8 during this pPeriod was 1.34 ppb), benzene (3.46 ppb) and isocyanic acid (1.03 ppb) due to  
9 emissions from the biomass co-fired brick kilns and other biofuel/biomass burning activities.  
10 A clear distinction of isoprene from furan, which had distinct emission profiles, highlighted  
11 the importance of deploying a PTR-TOF-MS for VOC measurements in the Kathmandu  
12 Valley.

13 Two “new” compounds which have not been reported in any previous ambient study namely,  
14 formamide ( $\text{CH}_3\text{NO}$ ; protonated  $m/z = 46.029$ ; campaign average 0.76 ppb) and acetamide  
15 ( $\text{C}_2\text{H}_5\text{NO}$ ; protonated  $m/z = 60.051$ ; campaign average 0.39 ppb) and are involved in  
16 photochemical formation of isocyanic acid were also detected. The average total reactive  
17 carbon (sum of the average mixing ratios of all the 378 species reported in this study) was  
18 175.8 ppbC to which propyne, acetaldehyde, benzene, acetic acid acetone, propene and  
19 toluene collectively contributed more than 60%. Isoprene concentrations as high as 3 ppb  
20 were observed frequently during the daytime, in the early part of the campaign (December  
21 2012) and could be traced to biogenic emissions from vegetation in fetch regions upwind of  
22 the site.

23 The concentration ranking in the average VOC mixing ratios during our wintertime  
24 deployment was acetaldehyde (8.8 ppb) > methanol (7.4 ppb) > acetone + propanal (4.2 ppb)  
25 > benzene (2.7 ppb) > toluene (1.5 ppb) > isoprene (1.1 ppb) > acetonitrile (1.1 ppb) > C8-  
26 aromatics (~1 ppb) > furan (~0.5 ppb) > C9-aromatics (0.4 ppb). The highest average VOC  
27 mixing ratios during our wintertime deployment were (in rank order): acetaldehyde (8.8 ppb),  
28 methanol (7.4 ppb), acetone (4.2 ppb), benzene (2.7 ppb), toluene (1.5 ppb), isoprene (1.1  
29 ppb), acetonitrile (1.1 ppb), C8-aromatics (~1 ppb), furan (~0.5 ppb), and C9-aromatics (0.4  
30 ppb). The results suggest that the emission sources of oxygenated and aromatic VOCs in the  
31 Kathmandu Valley are different compared to several cities such as Paris and London, likely  
32 due to the emissions from biomass co-fired brick kilns, open burning of biomass (e.g. garden

1 waste, agro-residue burning and garbage burning) and extensive use of diesel generators. In  
2 comparison to wintertime mixing ratios reported from several sites elsewhere in the world,  
3 the mixing ratios of acetaldehyde (~9 ppb), acetonitrile (~1 ppb) and isoprene (~1 ppb) in the  
4 Kathmandu Valley are among the highest measured anywhere in the world. The major  
5 sources of propyne, propene, benzene, and propanenitrile in the Valley appeared to be  
6 biomass burning as concentrations of all these compounds correlated well with the biomass  
7 burning tracer acetonitrile ( $r^2 > 0.7$ ) and had diel emission profiles similar to that of  
8 acetonitrile. ~~Nitromethane (a tracer for diesel exhaust) correlated with methanol while  
9 dimethyl sulfide (DMS) correlated strongly with acetaldehyde, indicating commonality of  
10 sources.~~

11 The top three contributing compounds to the total calculated VOC OH reactivity due to 33  
12 compounds were: acetaldehyde (24.0%), isoprene (20.2%), and propene (18.7%), which  
13 collectively accounted for ca. 63% of the campaign averaged total VOC OH reactivity of 12.3  
14  $s^{-1}$ . Oxygenated VOCs and isoprene collectively accounted for more than 68% (72% for  
15 pPeriod 1 and 68% for pPeriod 2) of the total ozone production potential. Based on known  
16 SOA yields of compounds and the ambient concentrations measured in the Kathmandu  
17 Valley, it was estimated that the relative SOA production potential of VOCs was in the  
18 following order: benzene > naphthalene > toluene > xylenes > monoterpenes >  
19 trimethylbenzenes > styrene > isoprene. Several VOCs known to enhance health risks for  
20 cancer, cataract and pulmonary diseases were detected in the ambient air. The synergistic  
21 effect of these VOCs on air toxicity is difficult to quantify but likely significant. The  
22 prominent ones were: isocyanic acid, formamide, acetamide, naphthalene and nitromethane  
23 for which this study presents the first measurements in ambient air from South Asia along  
24 with benzene, a human carcinogen.

25 Although like all urban environment, contribution of traffic sources to ambient VOCs is  
26 significant in the Kathmandu Valley, another anthropogenic source which occupies central  
27 importance in the Kathmandu Valley (due to inefficient combustion) are the biomass co-fired  
28 brick kilns. While we did not measure particulate matter emissions from the biomass co-fired  
29 brick kilns in the Kathmandu Valley during our deployment, previous studies by Pariyar et al.  
30 (2013) and Raut (2003) have reported and documented massive increases in PM<sub>10</sub> and TSP  
31 for periods marked by the operation of the brick kilns relative to periods when they were not  
32 operational . The study conducted by Clean Energy Nepal (Raut, 2003) showed that 8 h

1 averaged concentrations of air pollutants such as Total Suspended Particulate (TSP) , PM<sub>10</sub>,  
2 SO<sub>2</sub> and NO<sub>x</sub> were three times higher during the brick kiln operating period relative to the  
3 period they were not operational at the same location. The mass concentration of PM<sub>10</sub>  
4 increased from 218 µg m<sup>-3</sup> to 603 µg m<sup>-3</sup> while TSP increased from 265 µg m<sup>-3</sup> to 634 µg m<sup>-3</sup>.  
5 Note that these were primarily Fixed Chimney Bull Trench Brick Kilns, similar to the ones  
6 that impacted our measurements. The Bull Trench kilns are an old and inefficient  
7 technology, which have been banned even in their place of origin, India, but continue to  
8 dominate the Kathmandu Valley landscape. A-Thus a major conclusion of this study is that  
9 the wintertime air pollution in the Kathmandu Valley can be significantly reduced by  
10 replacing the existing brick kiln technology with cleaner and more efficient brick kiln  
11 technology would aid air pollution mitigation efforts significantly. While much has been  
12 learnt about wintertime VOC speciation in Kathmandu from this study, and the first  
13 comprehensive dataset has been acquired, long term measurements and further field  
14 intensives are required. To reduce the emission and formation of toxic VOCs (such as  
15 carcinogenic benzene and isocyanic acid) it is important to mitigate the intense biomass  
16 burning activities (agro-residue, garden waste, leaf litter burning) in the Kathmandu Valley,  
17 in particular biomass co-fired brick kilns, which appear to combust the fuel inefficiently (as  
18 evidenced by the reduced carbon compounds). While measures like introduction of better  
19 quality catalytic scrubbers in the traffic fleet and cleaner diesel generators are generic for  
20 urban sites in developing countries the world over, the inefficient biomass co-fired brick kilns  
21 seem to be specific point sources that are particularly important in the Kathmandu Valley.

22 ~~While this first study has quantified several important gaseous emission tracers and reactive~~  
23 ~~VOCs and revealed several new insights related to wintertime emissions and chemistry in the~~  
24 ~~Kathmandu Valley, Ffuture studies need to focus on what happens in the Valley on seasonal~~  
25 and inter-annual timescales. Of particular interest would be assessing the concentrations of  
26 isoprene and acetaldehyde in summer and their atmospheric chemistry. Assessment of source  
27 specific emission ratios (inter VOC ~~and VOC/CO~~) for the major sources (brick kilns, diesel  
28 generator exhaust, leaf litter fires etc.) and improvement of existing emission inventories  
29 using the in-situ data should be undertaken. The comparison and estimation of the fraction of  
30 isoprene from vegetation and combustion will also be presented in a companion paper  
31 (Sarkar et al., 2016) in which source apportionment of VOCs will be performed using a  
32 positive matrix factorization (PMF) model.- Comprehensive air quality and policy  
33 recommendations based on all the data acquired during the SusKat-ABC study and from

1 other sites in the Kathmandu Valley will be summarized in future submissions to this Special  
2 Issue ((Rupakheti et al., 2016) and (Panday et al., 2016). Some of these aspects will be  
3 presented in a companion paper (Sarkar et al., 2016) to this special issue. While much has  
4 been learnt about wintertime VOC speciation in this study, and the first comprehensive  
5 dataset has been acquired, the differences in emissions sources and chemical composition of  
6 the air call for long term measurements and further field intensives to unravel some of the  
7 new chemical processes identified in this part of the world.

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22 All the data reported in this article can be obtained from the corresponding author by sending  
23 an email to [ysinha@iisermohali.ac.in](mailto:ysinha@iisermohali.ac.in).

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10 **Table 1.** Principal operational settings for PTR-TOF-MS parameters

Parameter	Value
Overall drift voltage ( $U_{\text{drift}}$ )	600 V
Temperature at drift tube ( $T_{\text{drift}}$ )	60°C
Pressure at drift tube ( $P_{\text{drift}}$ )	2.2 mbar
Length of the drift tube ( $L_{\text{drift}}$ )	9.3 cm
Reaction time (t)	92 $\mu\text{s}$
Field strength of drift tube (E/N)*	135 Td

11 \* E is the electric field strength ( $\text{V cm}^{-1}$ ) and N is the gas number density ( $\text{molecule cm}^{-3}$ ).  $1\text{Td} = 10^{17} \text{ V}$   
12  $\text{cm}^2\text{molecule}^{-1}$

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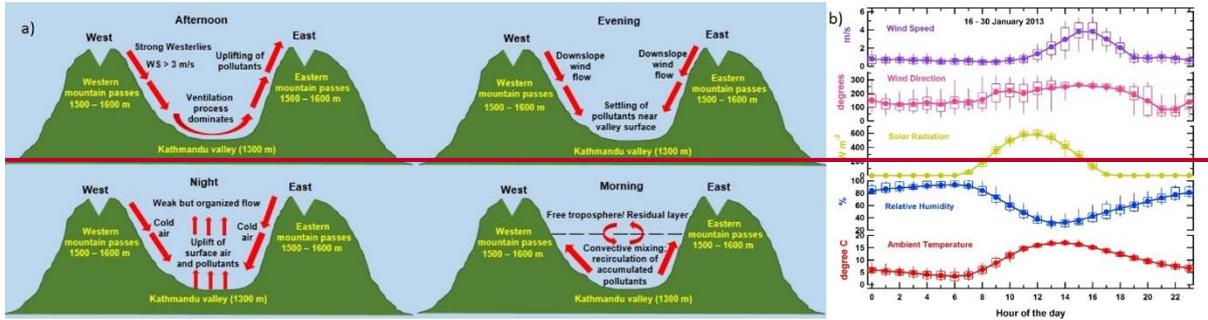


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2 **Figure 1.** Location of the measurement site (Bode; red circle) along with surrounding cities  
 3 (Kathmandu, brown circle; Patan, blue circle and Bhaktapur, pink circle), brick kilns (white  
 4 markers), major industries (yellow triangles), forest areas (green tree symbols), airport (blue  
 5 marker) and major river path (sky blue path) in the Google Earth image of the Kathmandu  
 6 Valley (obtained on 22 May 2015 at 14:55 LT)

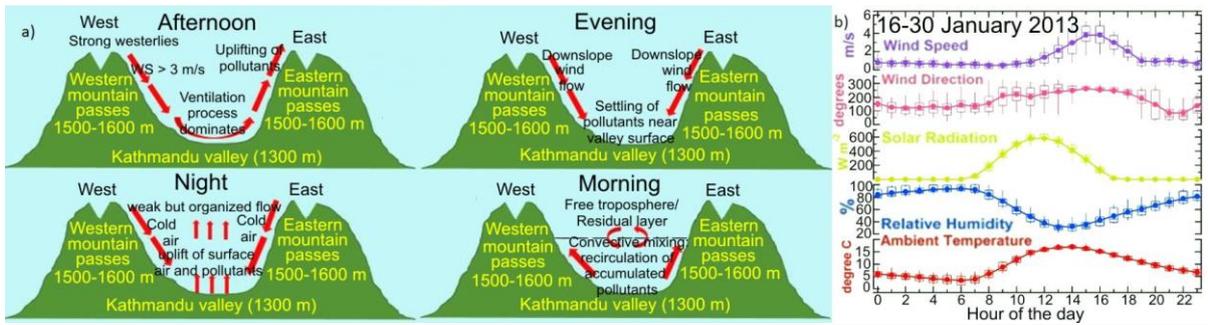
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2 **Figure 2.** a) Schematic of wind flow during different times of the day in the Kathmandu  
 3 Valley. b) Box and whisker plots of the measured meteorological parameters (wind speed,  
 4 wind direction, solar radiation, relative humidity and ambient temperature) at the Bode site  
 5 (16–30 January 2013)



6

7 **Figure 2.** a) Schematic of wind flow during different times of the day in the Kathmandu  
 8 Valley. b) Box and whisker plots of the measured meteorological parameters (wind speed,  
 9 wind direction, solar radiation, relative humidity and ambient temperature) at the Bode site  
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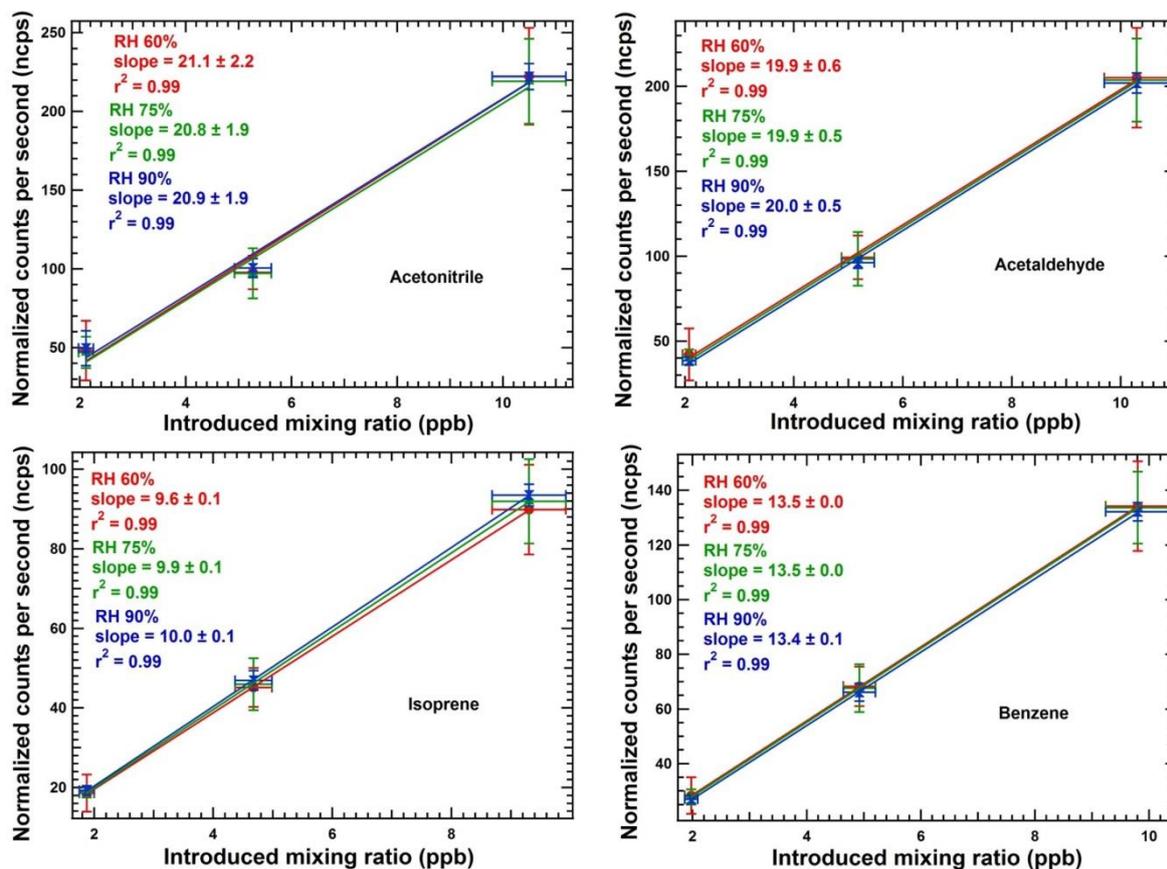
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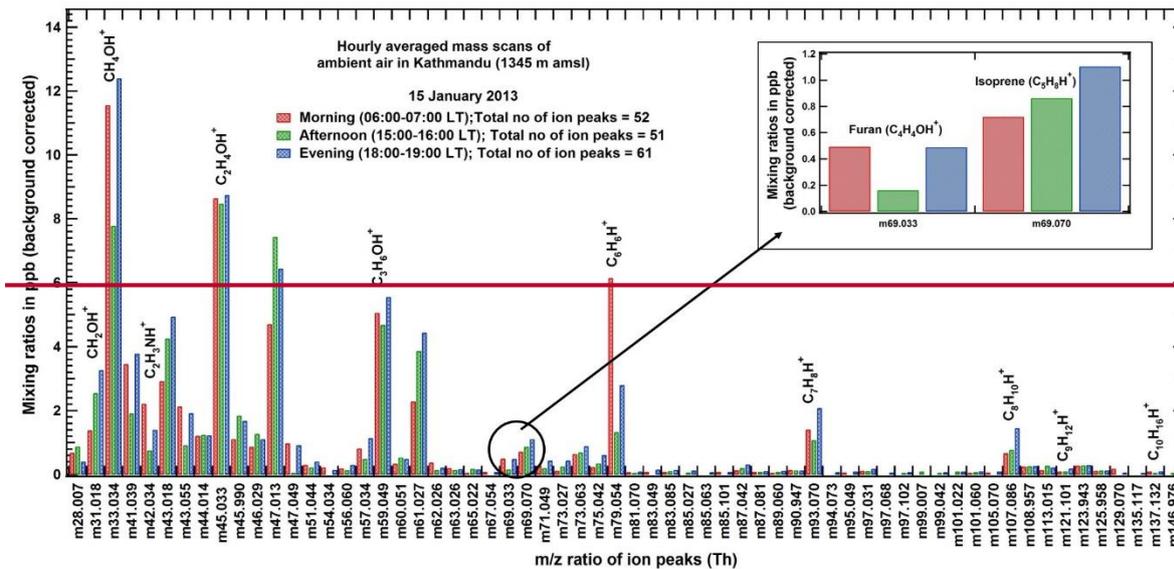


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2 **Figure 3.** Compound specific normalized sensitivities at different relative humidities (RH  
 3 60%, 75% and 90%) for acetonitrile, acetaldehyde, isoprene and benzene during the  
 4 calibration experiment performed on 10 January 2013. Horizontal bars reflect the error due to  
 5 the MFC flows and the accuracy of the VOC gas standard whereas vertical bars reflect the  
 6 precision error ( $2\sigma$ ) of the measurements.

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2 **Figure 4.** Ion peaks observed during ambient air mass scans (hourly averages) on 15 January  
3 2013. Zoom in of the isobaric species furan and isoprene is shown in the inset.

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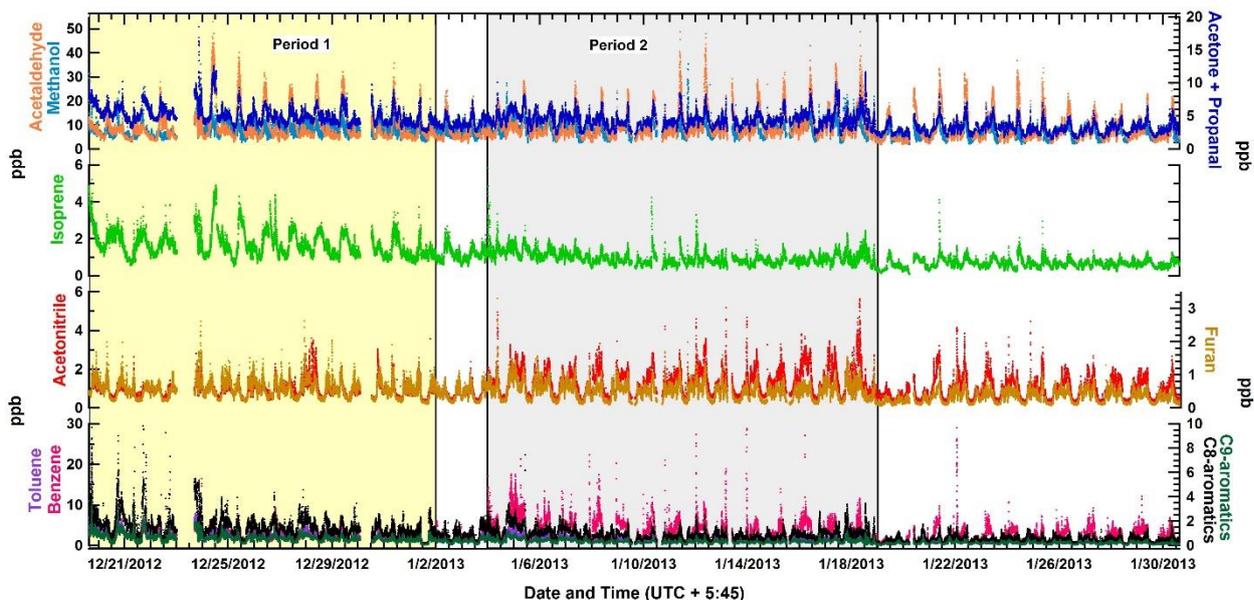
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2 **Figure 45.** Time series of one minute time resolution data for the mixing ratios of methanol,  
 3 acetaldehyde, and the sum of acetone and propanal (top panel); isoprene (second panel from  
 4 top); acetonitrile and furan (second panel from bottom); benzene, toluene, the sum of C8-  
 5 aromatics (xylene isomers and ethyl benzene) and the sum of C9-aromatics (isomers of  
 6 trimethyl benzenes and propyl benzenes) (bottom panel) during SusKat-ABC campaign

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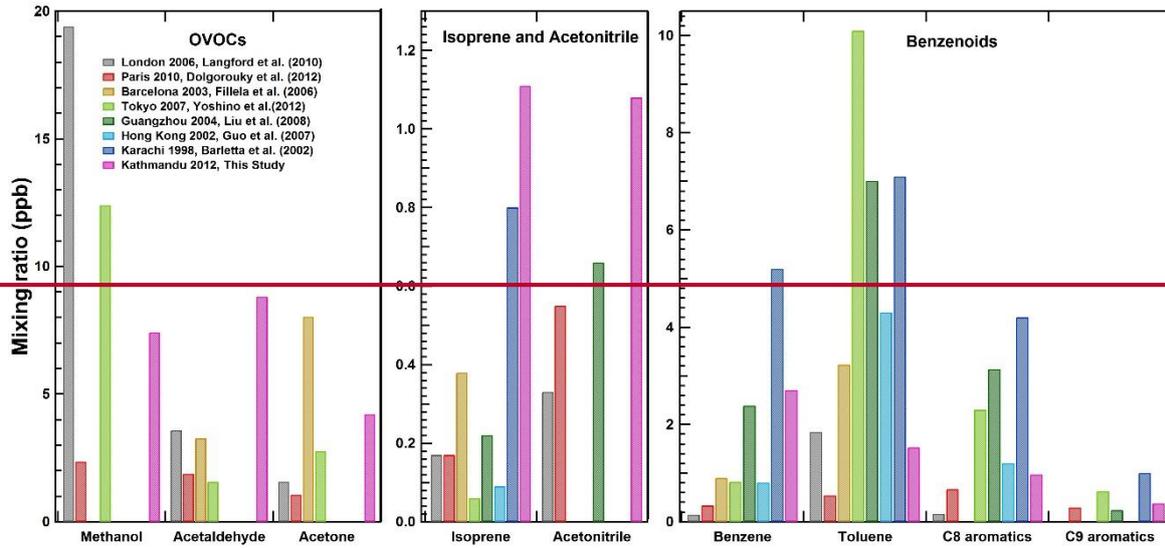
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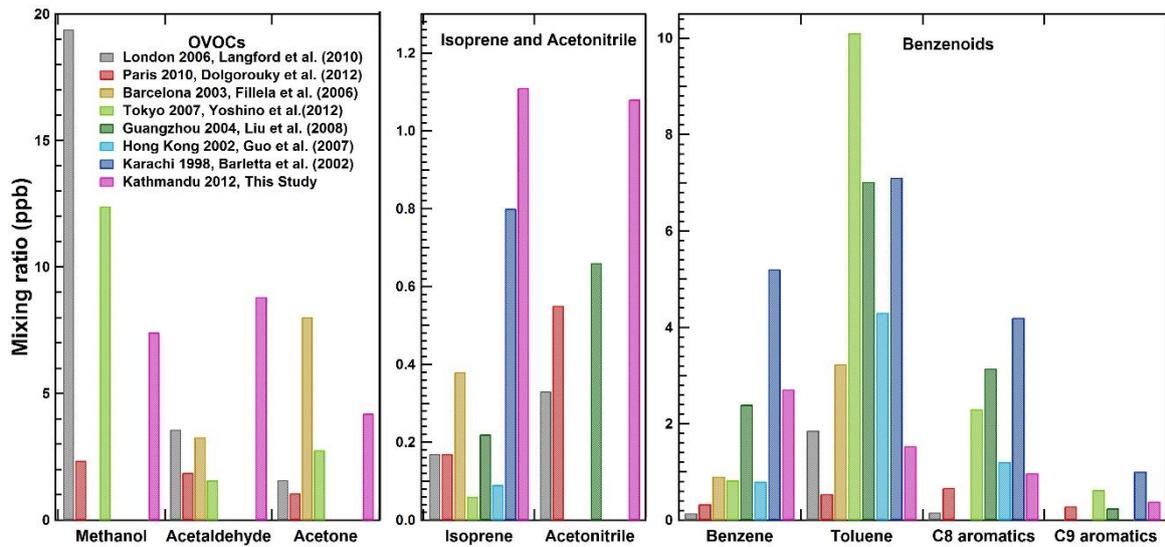
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2 **Figure 6.** Comparison of wintertime VOC mixing ratios measured in the Kathmandu Valley  
 3 with wintertime VOC mixing ratios at select urban sites elsewhere in the world



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5 **Figure 5.** Comparison of wintertime VOC mixing ratios measured in the Kathmandu Valley  
 6 with wintertime VOC mixing ratios at select urban sites elsewhere in the world

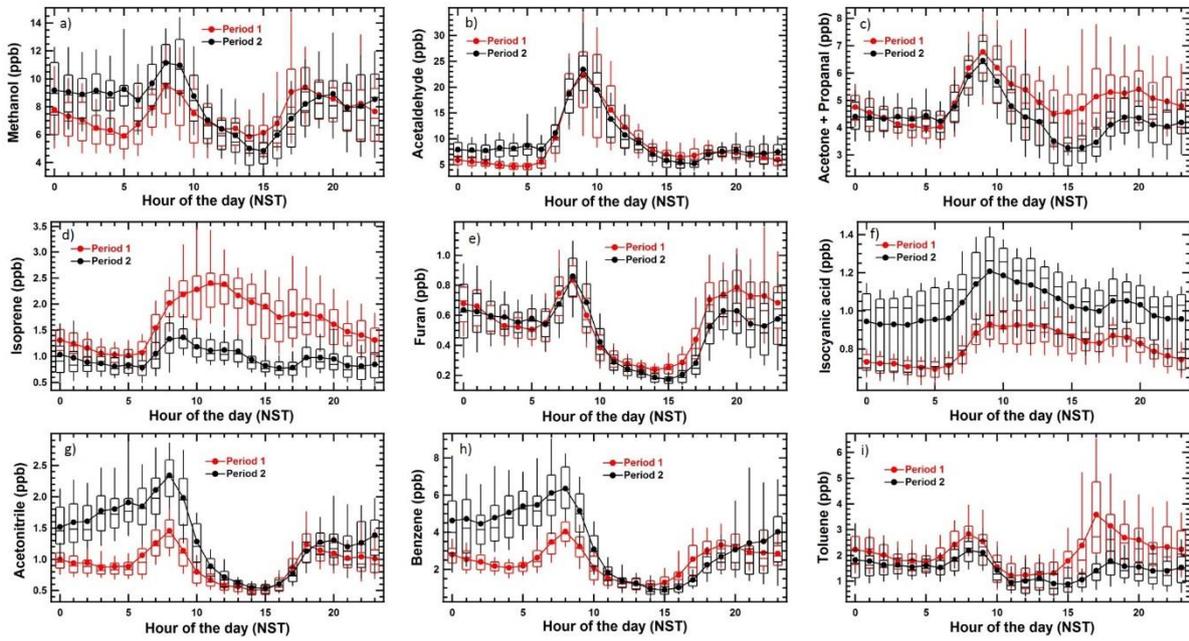
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4 **Figure 67.** Box and whisker plots showing average, median and variability (10<sup>th</sup>, 25<sup>th</sup>, 75<sup>th</sup>  
5 and 90<sup>th</sup> percentile) for some major VOCs in the Kathmandu Valley during pPeriod 1 and  
6 pPeriod 2

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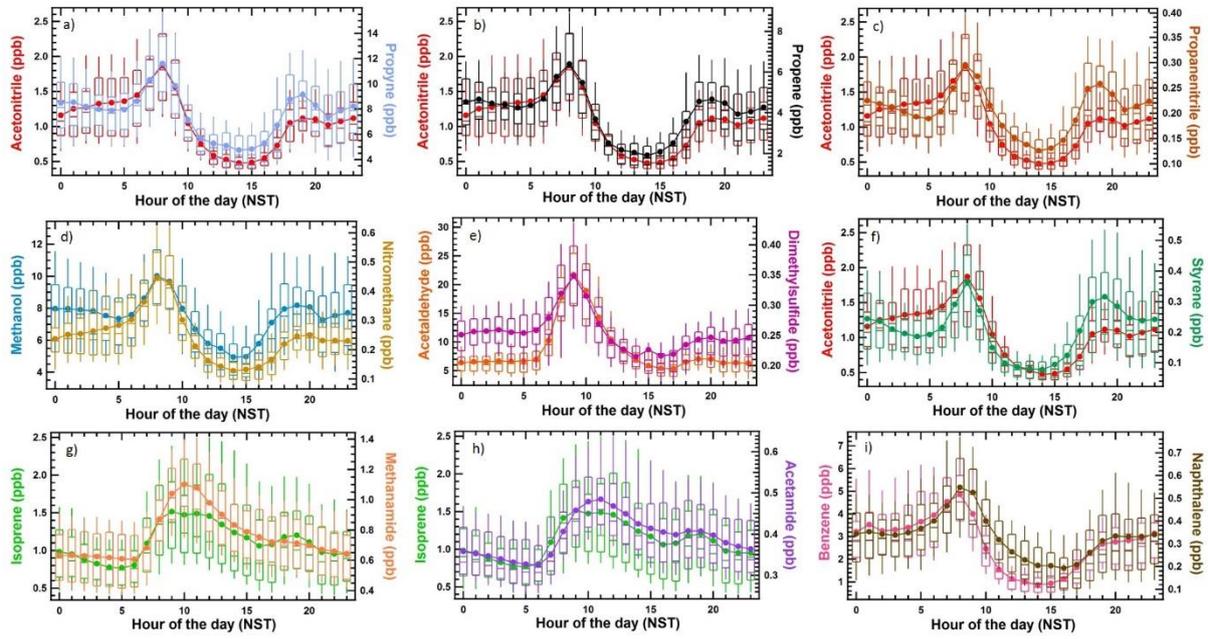
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4 **Figure 87.** Comparison of diel box and whisker profiles of several rarely measured or  
5 previously unreported ambient VOCs with more frequently measured VOCs/emission tracers

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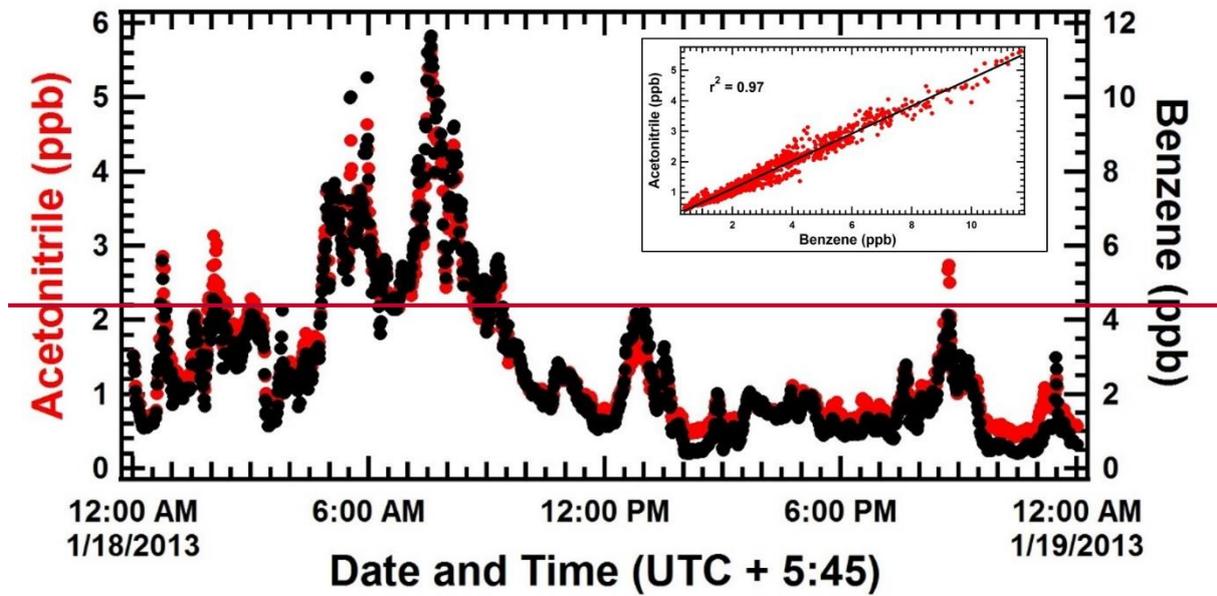
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2 **Figure 9.** Time series of benzene and acetonitrile for an illustrative day (18 January 2013)  
 3 that was influenced by biomass burning and biomass co-fired brick kiln emissions  
 4 (correlation of benzene with acetonitrile for same data is shown in the inset)

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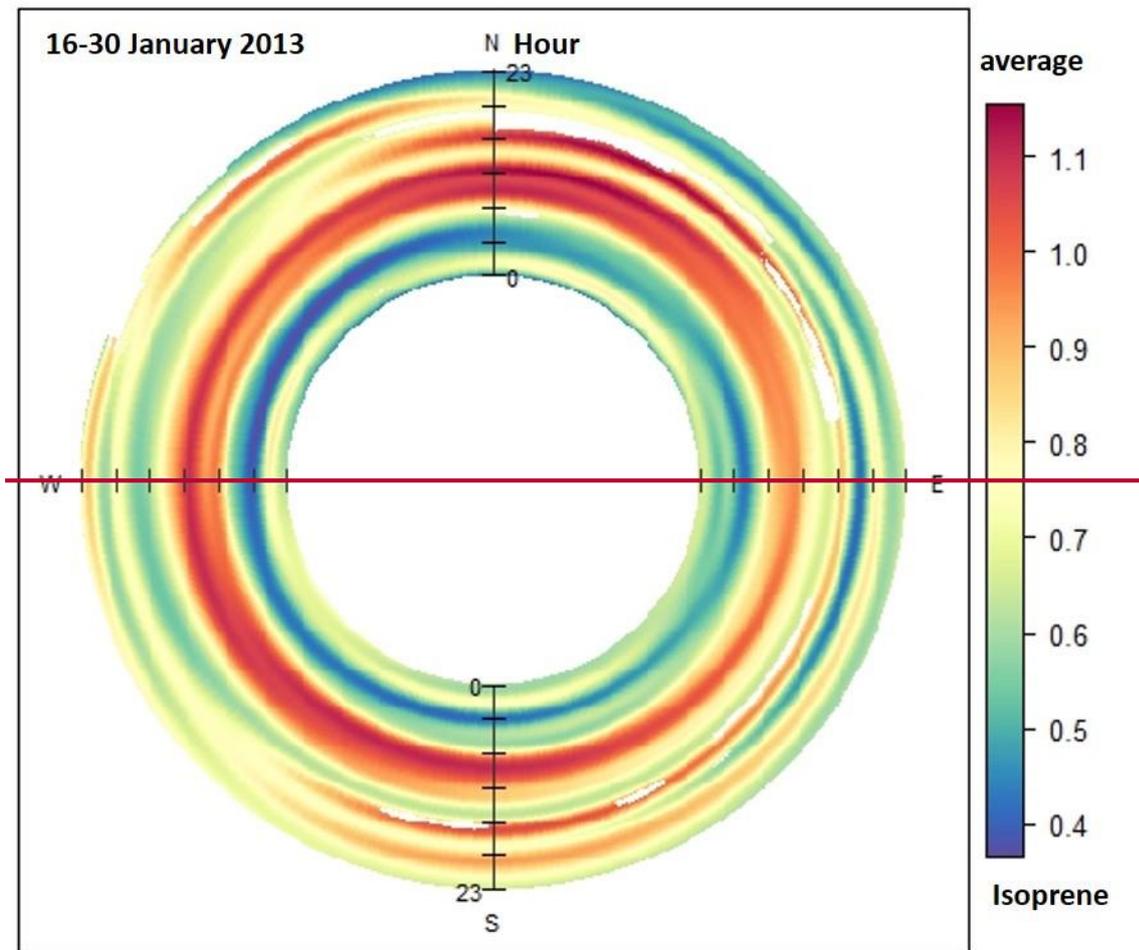
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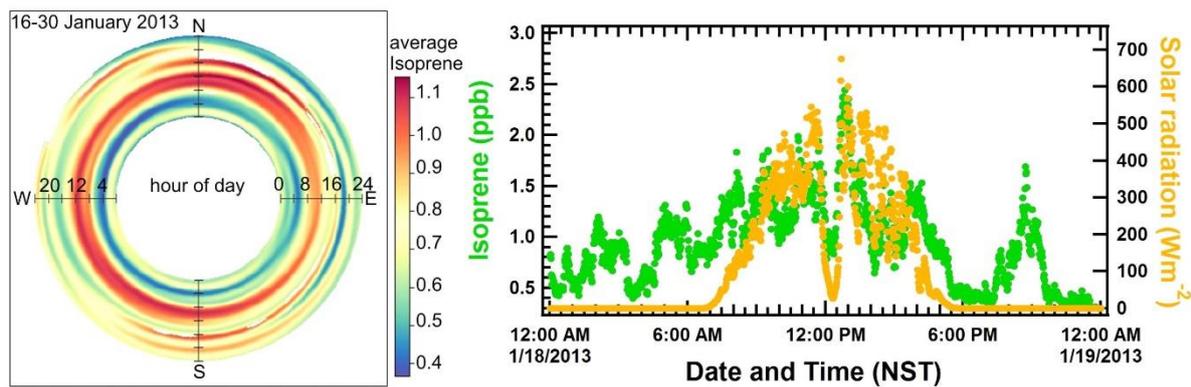
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2 **Figure 10.** Polar annulus plot of isoprene for the period 16–30 January 2013 highlighting the  
 3 spatio-temporal variation of isoprene and its biogenic sources.

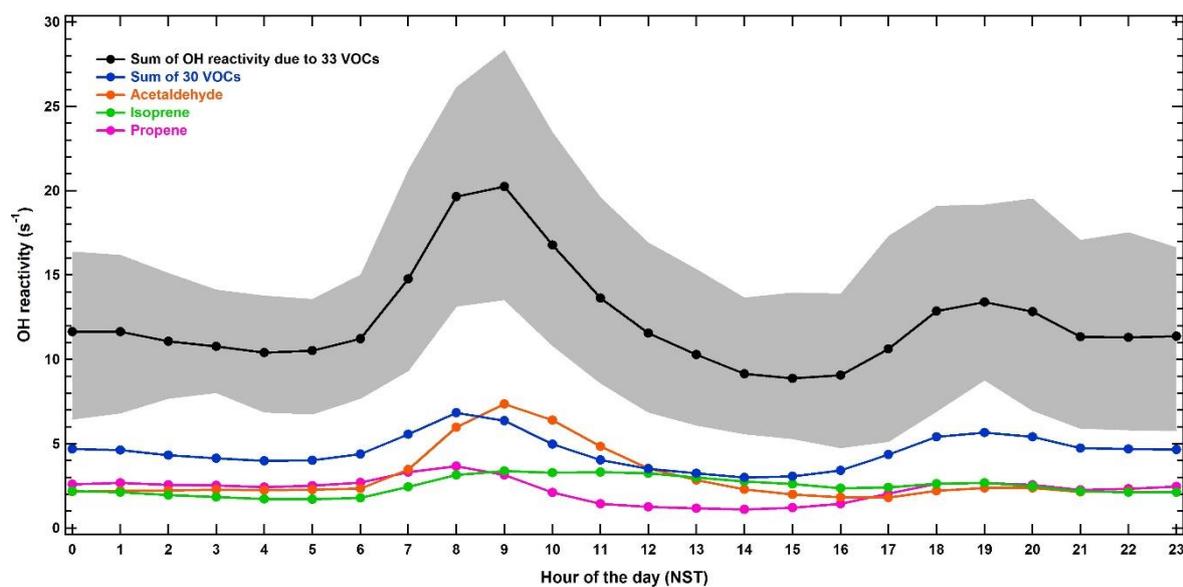


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5 **Figure 8.** a) Polar annulus plot of isoprene for the period 16–30 January 2013 highlighting the  
 6 spatio-temporal variation of isoprene and its biogenic sources; b) co-variation of daytime  
 7 isoprene concentrations with solar radiation on 18 January, 2013

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7 **Figure 911.** Diel profiles of the calculated total VOC OH reactivity (with 10<sup>th</sup> and 90<sup>th</sup>  
8 percentile contributions represented by the grey shaded region) and the major VOC  
9 contributors

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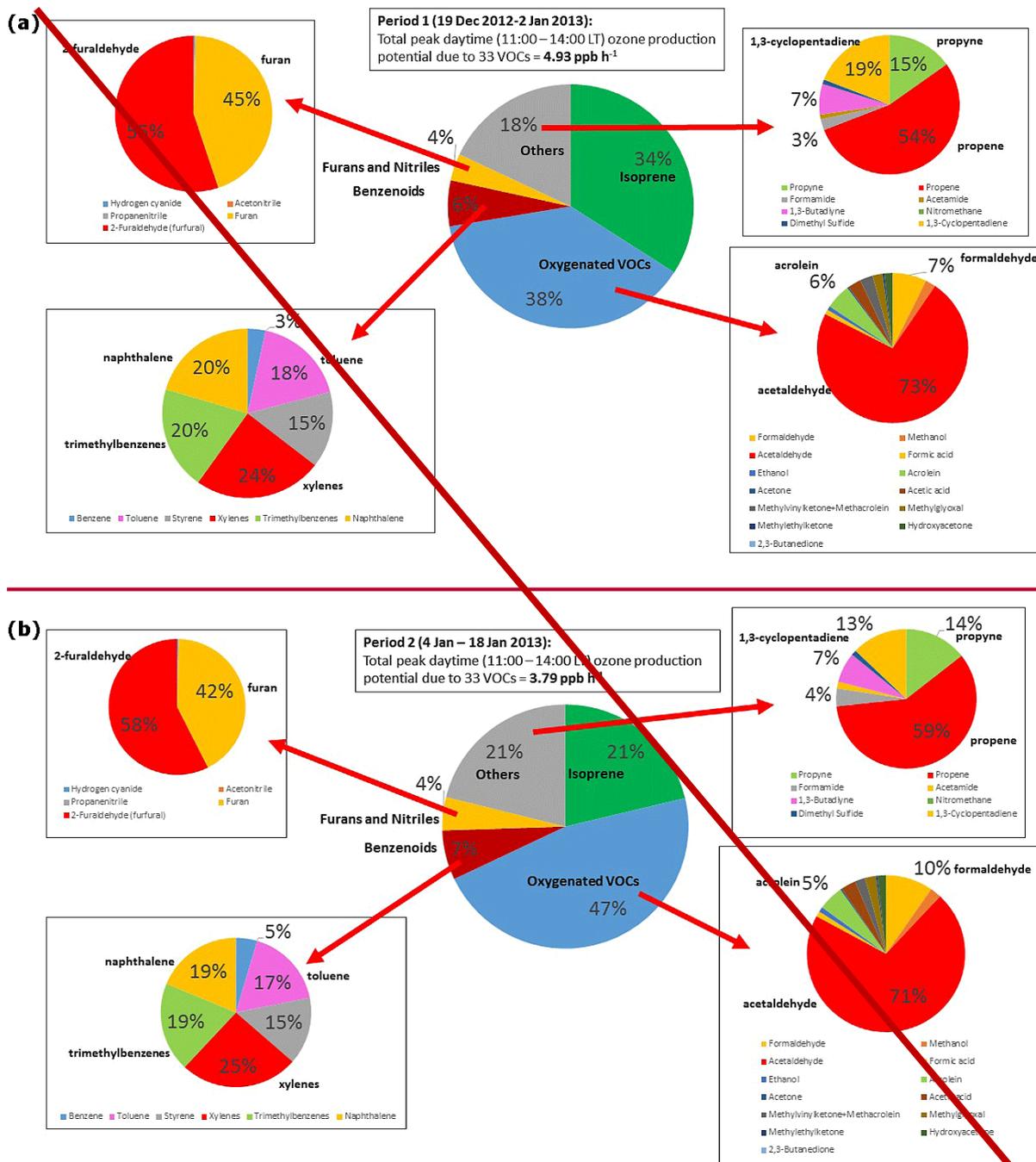
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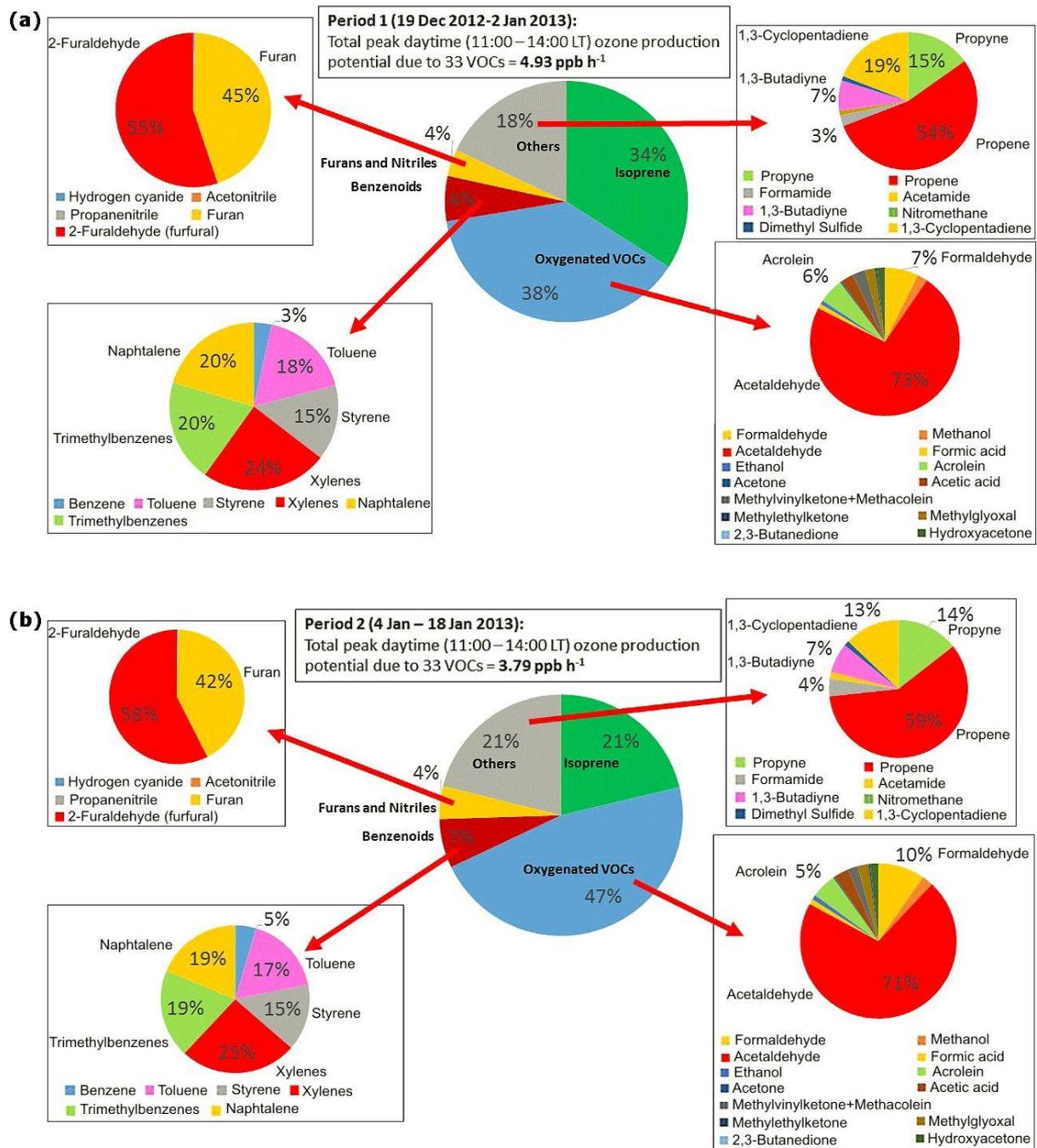
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Figure 12. (a) Pie-charts showing contribution of different class of compounds to total ozone formation potential for Period 1 (19 December 2012 – 2 January 2013). (b) Pie charts showing contribution of different class of compounds to total ozone formation potential for Period 2 (4 January 2013 – 18 January 2013)



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2 **Figure 10.** Pie charts showing contribution of different class of compounds to total ozone  
 3 formation potential for a) period 1 (19 December 2012 – 2 January 2013) and b) period 2 (4-  
 4 18 January 2013)

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