

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

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

We thank the anonymous referee 2 for his/her time and efforts.

Please find below the referee's comments in black and our point wise replies in blue for easy perusal.

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_x. 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 H₃O⁺ 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 ±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, O₃ 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 (H_3O^+ ; 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 ± 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 throughout 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_x 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_x 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.