

Interactive comment on “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.

Anonymous Referee #2

Received and published: 9 December 2015

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

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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.

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Specific comments:

- Abstract: This part should be rewritten after revision of the MS if it is accepted.
- P.25050, L5-8: Add average concentration information of air pollutants for similar period when the experiment was conducted in winter.
- 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.
- P.25030, L18: Add the range of atmospheric pressure during the campaign.
- 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?
- 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.
- P.25032, L7-8: Shortly state how the RH was controlled? Moreover, as shown in

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the Figure 2, the RH went down below 40% during daytime, but the calibration did not covered below 60% of RH. Explain this.

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

- 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.

- 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.

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

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

- 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.

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

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- 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.
- P. 25041, L23-28: The descriptions in the parenthesis for two periods are not necessary since it is already mentioned previously.
- 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.
- 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.
- 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.
- 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.
- 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.
- P. 25050, L17-18: What is the correlation between acetonitrile and benzene through-

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out the whole period or different two periods?

- 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?

- 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.

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

Figures:

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

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

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

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