

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 #1

Received and published: 3 October 2015

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

C7547

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.
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?
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 % penetenes.
4. *Two new ambient compounds are reported: formamide and acetamide.* I think the authors do remove interference from ^{13}C if applicable, but this should be clear.
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)
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?
7. *Oxygenated VOCs and isoprene contributed to more than 68% of total ozone production potential.* Several quite similar approaches are taken to rank compounds by perceived importance, but I think this whole approach can be reduced and depicted as approximate since it ignores NO_x and other oxidants.

C7548

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.
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.
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_x. At least one highly touted recent study found significant climate and health benefits overall for co-firing biomass and coal such as reduction of black carbon and fossil CO₂. (<http://www.sciencedaily.com/releases/2015/09/150925112110.htm>) (<http://www.sciencedirect.com/science/article/pii/S0016236115008637>). So reduction in certain pollutants while increasing others may not translate directly to improved AQ and good policy.
11. Another summary comment: The OH reactivity could be better placed in context relative to oxidation by O₃ and NO₃.

C7549

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 inflow 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 highlight the author's main points. This would also generate lots of space to bring in other helpful data like the CO and O₃, which is one of the reasons why people do large collaborative projects. That's especially important since the authors make policy recommendations without demonstrating how representative their site was of the Kathmandu Valley overall or including aerosol data. This despite the fact that SusKat deployed a network of aerosol monitoring sites across the valley.

Specific comments Page, Line:

25026, L2: Suggest changing lifetime range to "minutes to days"

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

25028: L7: Why single out windspeed in afternoon here?

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

C7550

25028, L25 "a few"

25030, L2 due to

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

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

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

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

25032, L22: Should be 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.

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?

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.

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.

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?

25036, L21-23: Why use those 3 one-hr periods here and in Fig 4 if they are evidently

C7551

not representative?

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

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

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.

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

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.

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

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?

25041, L12: "more industries"

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.

25042, L9: In addition to leaf burning, how can other forms of biomass burning (cook-

C7552

ing, 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?

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

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.

25043, L17: "mountain"

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?

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

C7553

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?

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

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

C7554

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.

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.

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?

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?

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 com-

C7555

ments) co-firing is used to reduce some pollutants.

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?

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?

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.

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.

25053, L10: “four” should be “three”

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

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

C7556

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?

25054, L14: "much lower" than what?

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

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.

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

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

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

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.

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.

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

25057, L16-18: I don't think you can target the health impacts of a specific sector as a

C7557

priority without aerosol data.

25059, L14: delete repeated ppb

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.

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

C7558