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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Chemical composition of pre-monsoon air in the Indo–Gangetic Plain measured using a new PTR-MS and air quality facility: high surface ozone and strong influence of biomass burning" *by* V. Sinha et al.

Anonymous Referee #2

Received and published: 28 January 2014

This paper describes a new high quality atmospheric chemistry observation station in a very important part of the world where very little data is available. The station is impacted by many types of globally important undersampled sources such as cooking fires, agricultural burning, and dust storms. It is also impacted by more conventionally sampled urban and biogenic sources, but in a new context. I don't see any major problems with the paper and fully support publishing these relevant results. I do have some suggestions that I think could strengthen the paper.

General.

1. One more thorough proofreading would help. I'll point out a few of the typos or sentences that could be shortened or reorganized in my specific comments, but not an exhaustive list.

2. The authors could insert a brief explanation somewhere why they show data for only May 2012 and what is status of the other data from the station. Maybe the station came on line on 1-May and then the monsoon arrived and those data may be presented separately? Then at least some of the data from the station during the next dry spell Oct-Nov 2012 is already published in the Sarkar et al paper cited in Current Science.

So a timeline for the station, the fate of the data, and possibility of access by modelers for model validation, would all be of interest in a few sentences.

3. The authors have done a good job of explaining the instrumental details. It does make the paper a bit long. It's OK as is, but they might want to move a few details to the supplement they already have or just cite a reference in a few cases if possible. This enables the reader to get to the interesting discussion faster. The one tricky subject is that the NOx analyzer sounds more like a NOy analyzer. The authors described the situation fairly in the text, but should probably footnote the "NO2" data in tables and specify in figure captions to see the text discussion.

4. Maybe Figures 1 and 2 can be improved with larger overall size, larger type, and possibly a different color scheme? Maybe a detailed, zoom, inset of few km around station – that is then located with slanted lines to a box on a larger more easily read map of the region?

5. A number of studies have observed furan/"isoprene" ratios on m/z 69 for various types of biomass burning and are summarized in Akagi et al., (2011). They range from 0.29 (for crop residue – similar to the authors value) to 8.5. This and/or the original studies should be acknowledged. Then a later study using FTIR and the NOAA GC-MS

presents actual furan/isoprene ratios and also shows there can be a significant amount of other C5H8 alkenes besides isoprene (Yokelson et al., (2013) and small amounts of carbon suboxide. The conclusions about high isoprene at night from biomass burning are still valid and interesting, but can be qualified a bit more.

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, 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, doi:10.5194/acp-13-89-2013, 2013.

Akagi, S. K., Yokelson, R. J., Wiedinmyer, C., Alvarado, M. J., Reid, J. S., Karl, T., Crounse, J. D., and Wennberg, P. O.: Emission factors for open and domestic biomass burning for use in atmospheric models, Atmos. Chem. Phys., 11, 4039-4072, doi:10.5194/acp-11-4039-2011, 2011.

6. In a few spots (mostly page 31777) I suggest potential additional brief analysis.

7. Adopting one consistent set of common units (ppb or ppbv?) throughout could make it easier to read and easier to compare values.

Detailed comments:

P31762, L11: “a” met station

P31762, L16: might read easier to use ppb throughout

P31762, L15-20: Maybe give the single values first and then give ranges?

P31762, L23: delete “activity”

P31762, L28: The abstract and text say the O3 exceeded 100 ug/m3, the figure shows nmol mol and it might be easiest to consistently use the common ppb term everywhere. I realize mass and mixing ratio are not exactly equivalent, but the mixing ratio equivalent

of the standard for typical May conditions at the station could be given in parentheses.

P31763, L27: should “equally” be “also”

P31764, L8-9: eliminate “but in contrast very little data on hydrocarbons has been acquired.” Since it is explained better and in more logical order just below.

P31764, L13: Define BTEX

P31764, L26: Of possible interest to the authors is that studies have shown that the combination of O3 and SO2 is more dangerous to crops than O3 alone. E.g. work of Joseph Hindawi: http://nepis.epa.gov/Adobe/PDF/9100E3K3.PDF page 25.

P31765, Paragraph one: this might be easier to read organized as follows “Comprehensively instrumented measurement sites in other regions of the world have yielded important data on the chemistry of ozone and aerosol formation. Examples include . . . ”

P31765, L14-21: This sentence also might work better as two sentences or leaving out some details.

P31766, L6: May not be necessary to give precise location a second time here.

P31766, L7: population of cities in parentheses?

P31766, L27: Ludhiana looks like it may be as big as Chandigarh though it is further away. Give population?

P31768, L8: Does the PTR-MS have higher sensitivity than average? If so, it might be good to specify that? If not maybe say something like: “A PTR-MS for sensitive VOC measurements”

P31768, L11: using mixing ratios here, which I like and think is most common, easiest to read, and shorter.

P31769, L16-23: Probably not necessary to describe the four main parts of PTR-MS

since several good review articles that do the same thing are already cited.

P31770, L28: Here or maybe later or both, a summary of published biomass burning measurements of the isoprene/furan emission ratio is in Akagi et al., 2011 as noted above, with some additional more recent values at Yokelson et al., 2013.

P31771-2: The calibration procedures are very sound! It could be moved to supplement though if authors preferred as well.

P31773, L23-29: The inner construction of the CO analyzer is probably covered in a citable paper and could be omitted here.

P31774, L13: re the "hydrocarbon kicker" – if it is described by Luke, 1997 move the citation closer; if it is known to remove all or most non-methane organic gases (NMOG) state that since hydrocarbons are a small fraction of total NMOG in smoke.

P31774, L26-7: no need to mention the 185 nm line.

P31775, L5-6: Minor point. It shouldn't matter if a single, split light source intensity decreases since the instrument uses a ratio of the two channels, however if there are two detectors and their sensitivity declines at unequal rates, then the zero checks are probably useful.

P31775, L11-25: The authors have done an excellent job of describing the limitations of the NO2 data. As is, it is somewhere between an NO2 and NOy measurement. There are a few more papers they may wish to cite (by Pollack, Fehsenfeld, Williams) that describe measurements of NOy with Mo or Au catalysts and NO2 with UV photolysis. Two more thoughts are:

1. In biomass burning smoke most of the NO2 is converted to PAN and nitrate within just 2-4 hours. See Akagi et al., (2012) and references there-in to Alvarado et al., etc. Probably important to mention/cite this.

2. Since many people may just glance at figures and tables and skip the experimental

section, the authors would ideally flag the word NO2 in figure captions and tables and direct the reader to Sect 2.2.3.

Akagi, S. K., Craven, J. S., Taylor, J. W., McMeeking, G. R., Yokelson, R. J., Burling, I. R., Urbanski, S. P., Wold, C. E., Seinfeld, J. H., Coe, H., Alvarado, M. J., and Weise, D. R.: Evolution of trace gases and particles emitted by a chaparral fire in California, Atmos. Chem. Phys., 12, 1397-1421, doi:10.5194/acp-12-1397-2012, 2012.

Apologies no time to type in these references, which should be easily located and useful.

Fehsenfeld, F. et al JGR, 103, 3579-3597, 1990

Pollack, I.B., et al.: J. Atmos. Chem. 2011

Williams, E. J., et al.: JGR, 103, 22261- 22280, 1998

P31777, L2: Fig. 6. I would put the PM species on a log scale or use a break in the scale to capture the peak of the dust event and still be able to see the rest of the data.

P31777, L16: Fig 3 in supplement is the third figure in supplement, but the figures are numbered wrong in the supplement.

P31777, L18-22: By comparing the peaks for other species "X" to the CO peak one comes up with "quick and dirty" X/CO ratios that are potentially due largely to wheat residue burning and can be compared to crop residue emission ratios (ER) to CO in the literature such as the collection in Akagi et al., (2011). The comparison of these rough ratios to Akagi et al is of course not exact, but not bad either for most species considering the inherent variability in biomass burning (BB) ER, the fact that it may be different crops, and the reactivity of some of the species. The two things that seem most different from usual BB ER are: (1) the high SO2/NO2 ratio, which is greater than 60% in this work, but usually lower than 10% in other work. That could indicate that more than one source contributes to the mix of pollutants observed, which would not be surprising. Perhaps industries such as brick kilns burning coal (or tires) which

have higher S content than biomass? See Maithel et al., (2012) and/or Christian et al., (2010), where the latter may also be a good reference for garbage burning the authors note later. The "quick and dirty" analysis above should be improved by subtracting background values before computing ER to CO. (2) the benzene and toluene ratios to CO are close to 1%, which is about 3 times higher than normal for BB. Again this could simply suggest other sources (traffic) are contributing to the mix as the authors themselves show in their Sect 3.3 (p31783. L8-12). None of this makes this work "wrong" or less important, it makes it more interesting.

Maithel, S., Lalchandani, D., Malhotra, G., Bhanware, P., Uma, R., Ragavan, S., Athalye, V., Bindiya, K. R, Reddy, S., Bond, T., Weyant, C., Baum, E., Thoa, V. T. K., Phuong, N. T., and Thanh, T. K.: Brick Kilns Performance Assessment, 164 pp, Greentech, New Delhi, 2012. http://www.unep.org/ccac/Portals/24183/docs/Brick_Kilns_Performance_Assessment.pdf

Christian, T. J., Yokelson, R. J., Cárdenas, B., Molina, L. T., Engling, G., and Hsu, S.-C.: Trace gas and particle emissions from domestic and industrial biofuel use and garbage burning in central Mexico, Atmos. Chem. Phys., 10, 565-584, 2010.

P31777, L22-23: Depending on how you define VOC or NMOG, etc. the authors could give themselves some credit for measuring a few organic trace gases (e.g. benzene, toluene, . . .) emitted by crop residue fires in India in the Sarkar et al paper.

P31777, L26: acetonitrile is misspelled

P31777, L27: How do the authors determine times that were "not impacted by wheat residue burning"? I agree that the industrial source of methanol is well described later and many other types of BB are extremely likely, but wondering how agricultural burning can be ruled out. If a lack of hotspots that might be mentioned, but also with the caveat that a lot of crop residue burning is missed by active fire detection as shown in Table 1 of Yokelson et al., (2011) and discussed there-in.

Yokelson, R. J., Burling, I. R., Urbanski, S. P., Atlas, E. L., Adachi, K., Buseck, P. R., Wiedinmyer, C., Akagi, S. K., Toohey, D. W., and Wold, C. E.: Trace gas and particle emissions from open biomass burning in Mexico, Atmos. Chem. Phys., 11, 6787-6808, doi:10.5194/acp-11-6787-2011, 2011.

P31778, L1-15: This is a great discussion of the probable complexity of the pollutant sources in the region. It's daunting, but also a major reason why this work is so important. Fortunately, the authors have an excellent start in this paper.

P31778, L16 - P31779, L15: Good discussion. An option is to add a few BB furan/isoprene references as noted above near P31779, L1. The author's estimate of $\sim$25% is remarkably close to the 29% for crop residue burning in Akagi et al., (2011).

P31779, L10-15: Are the author's measurements above the predictions of the MEGAN model? If not going to compare maybe omit this?

P31779, L13: "is not well not constrained" delete second "not" – also sentence kind of long.

P31779, L18: If the authors are saying their site is a few km downwind of urban centers then the following paper (and references there-in) showing enhanced O3 production when BB emissions mix with urban emissions may be of interest. Akagi et al., (2013) also contains information on BB emissions of isoprene and monoterpenes and their likely night-time chemistry. However, glancing at the figure it seems that large O3 peaks occur every day, which would include times the authors have identified as unaffected by wheat residue burning. Maybe there are statistically significant O3 increases on days affected by BB?

Akagi, S. K., Yokelson, R. J., Burling, I. R., Meinardi, S., Simpson, I., Blake, D. R., McMeeking, G. R., Sullivan, A., Lee, T., Kreidenweis, S., Urbanski, S., Reardon, J., Griffith, D. W. T., Johnson, T. J., and Weise, D. R.: Measurements of reactive trace gases and variable O_3 formation rates in some South Carolina biomass burning

plumes, Atmos. Chem. Phys., 13, 1141-1165, doi:10.5194/acp-13-1141-2013, 2013.

P31779, L23: in parentheses after standard ($\sim$50 ppb) might help?

P31780, L1-24: Long inconclusive discussion: maybe just state the conclusion that OH reactivity measurements would be useful in the future in 1-2 sentences.

P31780, L25: start a new paragraph.

P31781, L1: define “Loo winds”

P31781, L12-13: Mexico City “summertime” is the rainy season and MCMA was in the spring (March), which was the dry season. On the other hand Paris measurements were in the rainy, summer season. Maybe better title is “Comparison with selected other urban measurements”

P31782, L5 and Table 3: is “Texas” more precisely “Houston”?

P31782, L20 – P31783, L2: I’m not sure if night-time ambient levels (especially starting as soon as 6 pm) reflect just emissions since the emissions emitted during the day travel to Mohali. It might be interesting to see what correlations occur if starting the averaging period at midnight instead?

P31783: general q. Here at night when traffic is likely reduced compared to daytime, it is concluded that benzene and toluene are mainly from traffic and not so much from BB. Relevant to P31777, L20-21?

P31783, L27: Nightime BB emissions of isoprene and monoterpenes also a major theme of Akagi et al., (2013) referenced above.

P31791, L29: Is this reference correctly entered? Note - I did not check all the references.

Carslaw, D. C. and Ropkins, K.: openair – an R package for air quality data analysis, available

at: http://www.openair-project.org/, Environ. Modell. Softw., 27–28, 52–61, 2012. 31784

P31800, Table 1: good candidate to move to supplement so reader gets to discussion faster.

P31802, Table 3: The Tokyo values appear to sometimes be ranges. Also some of the values are huge, but not mentioned in the text.

P31803, Table 4: footnote NO2 and refer to experimental section.

P31784, L6-7: Table 3 has some huge values for Tokyo, but they may be ranges rather than averages?

Sect 3.4 general comment: excellent!

P31788, L5 and L26: “May” or “pre-monsoon” better than “summer” or “summertime” since the latter two may be taken as “Asian summer monsoon”?

P31790, L13-16: Comparison to existing emissions inventories and mobile lab measurements to characterize individual sources would also be very useful activities!

P31810, Fig 6: log scale on PM?