Source apportionment of NMVOCs in the Kathmandu Valley during the SusKat-ABC international field campaign using positive matrix factorization

by Chinmoy Sarkar et al., 2017 (ACPD)

REFEREE 2:

General comment: The manuscript shows results of a source apportionment study of NMVOCs measured by PTR-TOF-MS in the Kathmandu Valley in Nepal during winter 2013. Positive matrix factorization analysis was conducted to identify possible emission sources for 37 m/z measured by PTR-MS. The sources were identified from the chemical fingerprint of each PMF factor and their diurnal profiles. Conditional probability functions plots were used to determine the directions of the sources and attribute the chemical emissions to specific spatial areas in the region and specific activities. The sources found by the authors through PMF were compared with the results of current emission inventories used for Nepal, which, in contrast to the authors results, rely on sources emission factors measured in other regions of the world and are not supported by in-situ collected measurements. Sources and species contributions differ among the authors results and the current inventories as well as between different inventories. Finally, the atmospheric impact as daytime ozone production and SOA formation based on the measured compounds and PMF sources contributions is briefly discussed. I found the manuscript very interesting, of high quality and of high impact as it presents several new findings which can help mitigating the emissions in the region under study. The presented topic also follows in the scope of ACP. The article is overall well written, and results are presented clearly with figures and tables. I highly recommend the manuscript publication, once these specific comments have been addressed:

We thank the referee for the kind words appreciating the importance of the work and for highly recommending the manuscript for publication in ACP. We have found several of Referee 2'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).

Specific comments:

-It is a bit confusing how the methods section is presented. There should be a small section introducing the measurement site, the PTR-MS data used, and the grab samples, before any PMF discussion. This would be helpful to follow better section 2.2 and support the nudging tool. Could you list the m/z from PTR-MS you used for implementing the PMF and why? Could you also provide some references of the nudging procedure?

Done.

We have now reorganized the Materials and Methods section (section 2) as per the suggestion of both the referees.

We have now included a column to Table S1 of the supplementary information to show the m/z ratios corresponding to the NMVOCs used for PMF. The detailed description concerning selection of these NMVOCs for the PMF run has now been added to the revised Materials and Methods section (Section 2).

The nudging procedure described in this work was performed using the priori knowledge of the emission sources in the Kathmandu valley and the emission ratios (ERs) obtained from the analysis of the grab samples collected from the point sources. This is the first ever study to use such nudging procedure to obtain robust solution using PMF. An earlier work of Baudic et al., 2016 has mentioned the need of using the nudging procedure/constrains using priori knowledge of the emission sources and ERs obtained from point sources to obtain robust solution using PMF but did not implement the same.

-PTR-TOF-MS usually provides an unambiguous identification of chemical species, however, it would be interesting to know briefly, the operational settings of PTR-MS, which m/z were selected for running the PMF and how the m/z were attributed to the chemical compounds. Were the grab samples measured with the same PTR-MS? Could you provide some information about these data: m/z selected and how the compounds were identified. Line 331, could you provide the standard deviation for the signal stability?

We have now included a section on PTR-TOF-MS measurements in the revised manuscript (Section 2.2 of the revised manuscript) that briefly discusses about the operational settings of the PTR-TOF-MS, sampling of ambient air and the identification procedure of the NMVOCs. The m/z ratios to the corresponding NMVOCs used for the PMF run is now provided in Table S1 of the supplementary information.

No, the grab samples were measured with a PTR-QMS which is installed at IISER Mohali, India. The analytical details, calibration procedure and information regarding the identification of NMVOCs using this PTR-MS are available in Sinha et al., 2014.

For the grab samples we only reported 7 compounds which we have tested to be stable in glass flasks. These compounds are: acetonitrile, benzene, toluene, sum of C8 aromatics, sum of C9 aromatics, styrene and naphthalene.

The zero air background for the m/z reported was 0.04±0.05 ppb, 0.04±0.04 ppb, 0.04±0.06 ppb, 0.07±0.08 ppb, 0.10±0.11 ppb, 0.02±0.06 ppb and 0.02±0.05 ppb for acetonitrile, benzene, toluene, sum of C8 aromatics, sum of C9 aromatics, styrene and naphthalene, respectively. The concentration range in the grab samples was 4±0.3 to 323±8 ppb for acetonitrile, 27±4 to 339±19 ppb for benzene, 32±5 to 150±14 ppb for toluene, 40±6 to 113±8 ppb for C8 aromatics, 33±6 to 62±12 ppb for C9 aromatics, 11±1.3 to 95±17 ppb for styrene and 11±1.5 to 64±9 ppb for naphthalene.

We have now included this information in the Section describing the grab sampling and included a citation to the article that details the storage stability and validation of the glass flask sampling procedure and thank the referee for the excellent suggestion.

Citation:

Chandra, P., Sinha, V., Hakkim, H. Sinha, B.: Storage stability studies and field application of low cost glass flasks for analyses of thirteen ambient VOCs using proton transfer reaction mass spectrometry, International Journal of Mass Spectrometry, https://doi.org/10.1016/j.ijms.2017.05.008, 2017.

-It would be interesting to provide some details about the calculations for ozone and SOA formation, you could do this with a short section in the methods after section 2.4.

The ozone formation potential of individual NMVOCs was calculated as described by the following equation (Sinha et al., 2012):

$$Ozone\ production\ potential = (\Sigma k_{(VOC_i+OH)}\ [VOC_i]) \times OH \times n$$

For the ozone production potential calculation, the average hydroxyl radical concentration was assumed to be [OH] = 1×10^6 molecules cm^{-3} with n = 2 and only data pertaining to the mid-daytime period were considered (11:00 - 14:00 LT).

This information is now included in Section 2.7

"The ozone formation potential of individual NMVOCs was calculated as described by the following equation (Sinha et al., 2012):

$$Ozone\ production\ potential = (\Sigma k_{(VOC_i+OH)}\ [VOC_i]) \times OH \times n$$

For the ozone production potential calculation, the average hydroxyl radical concentration was assumed to be [OH] = 1×10^6 molecules cm^{-3} with n = 2 and only data pertaining to the mid-daytime period were considered (11:00 - 14:00 LT)."

Secondary organic aerosol (SOA) production was calculated using the concentrations and the known SOA yields for benzene, toluene, styrene, xylene, trimethylbenzenes, naphthalene and isoprene (Ng et al., 2007; Chan et al., 2009; Yuan et al., 2013; Kroll et al., 2006). SOA yield of a particular NMVOC depends on the NO$_x$ conditions and Pudasainee et al. (2006) previously reported NO$_x$-rich conditions in the Kathmandu valley. Therefore, SOA production was calculated by using reported SOA yield at high NO$_x$ conditions according to the following equation:

$$SOA\ production = [VOC_i] \times SOA\ yield\ of\ VOC_i$$

This information is now included in Section 2.7

"SOA yield of a particular NMVOC depends on the NO$_x$ conditions and Pudasainee et al. (2006) previously reported NO$_x$-rich conditions in the Kathmandu valley. Therefore, SOA production was calculated by using reported SOA yield at high NO$_x$ conditions according to the following equation:

$$SOA\ production = [VOC_i] \times SOA\ yield\ of\ VOC_i"$$

Pudasainee, D., Sapkota, B., Shrestha, M. L., Kaga, A., Kondo, A., and Inoue, Y.: Ground level ozone concentrations and its association with NO$_x$ and meteorological parameters in

Kathmandu Valley, Nepal, Atmos. Environ., 40, 8081–8087, doi:10.1016/j.atmosenv.2006.07.011, 2006
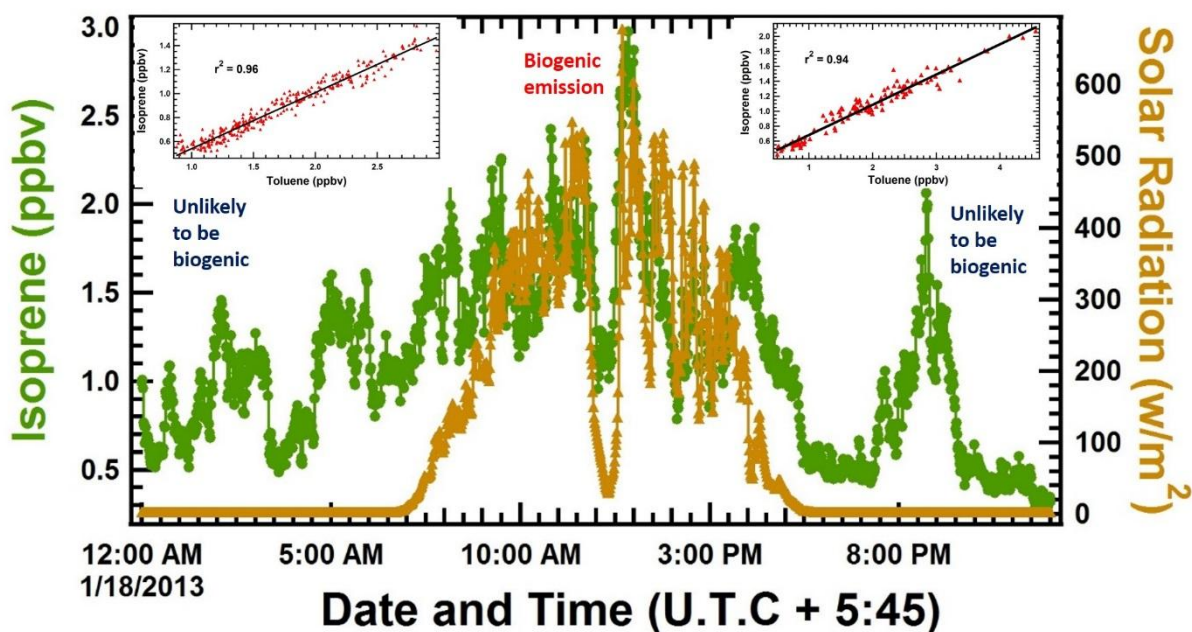
-Figure 2. The contribution of propyne compared to isoprene for the biogenic factor is quite high, can you comment it?

Since the source fingerprint of the primary source (traffic) is determined by night time emissions and the traffic factor profile during the daytime is different due to photochemical loss (between the source and the receptor downwind). As a consequence, some of the co-emitted compounds (in particular those on which we placed no specific constraint) remain in the biogenic source profile even after constraints are imposed to remove combustion derived isoprene and other associated primary emissions such as propyne.

-Figure 3. How do you explain the higher background and general higher peaks during the first part of the campaign? L. 370: Could you provide more information about isoprene emission from traffic? Could you have any interference on the PTR-MS m/z attributed to isoprene?

The higher peaks during the first part of the campaign are due to emissions from deciduous trees which shed their leaves during the latter part of the campaign. The highest peaks during this period occur during the daytime and not at night. We have provided additional references for isoprene emissions from traffic and have discussed them in more detail also in response to reviewer 1.

During the measurement period, significant isoprene concentrations ($\sim$ 0.5-2 ppb) were observed during evening and night time which are likely from biomass combustion and traffic emission sources (Sarkar et al., 2016) as the evening and night time isoprene has a strong correlation with vehicular emission tracer toluene. The following figure (Figure S9 of the supplementary material) shows an illustrative day's (18 January 2013) isoprene data against solar radiation. It can be observed from the figure that the daytime isoprene emission correlates very nicely with solar radiation which indicates biogenic emission while during evening hours and night time, isoprene showed high peaks that show good correlation (r>0.9) with toluene.

The issue of possible interferences to the isoprene signal has already been discussed above while addressing the comment of referee 1 and revisions have been made as outlined in the reply to reviewer 1's comment.

Could be there a connection between oxidation products of traffic emission and the unresolved industrial emissions, as for mixed daytime emissions as oxidation products from biogenic emissions?

The traffic factor is dominated by the contribution of toluene and higher aromatics (C8- and C9-aromatics). The oxidation of all these aromatics produces phenols and cresols. However, we did not observe phenols and cresols above 200 ppt in the Kathmandu valley. The unresolved industrial emissions factor is dominated by propene, propyne, methanol, acetone, acetic acid, formic acid and 1,3 butadiyne. Propene, propyne and 1,3 butadiyne cannot be formed due to oxidation of higher aromatics. Consequently the methanol, acetone, acetic acid and formic acid found in the same factor profile cannot be from photo-oxidation either. Furthermore, a bimodal diel profile as observed for the unresolved industrial emissions profile is not characteristic of photochemically emitted compounds.

The mixed daytime emissions profile is dominated by nitrogen containing compounds, most notably isocyanic acid, and its precursors formamide and acetamide. In addition, the profile contains photochemically formed methanol, acetone, acetaldehyde, formaldehyde, formic acid and acetic acid. One of its features is, that the mass loadings of the photo-oxidation products present in the mixed daytime increases after the brick kilns resume operation. The biogenic emissions, on the other hand, decrease in the second half of the campaign when the deciduous trees shed their leaves. As a consequence, the primary oxidation products of isoprene, MVK+MACR (methyl vinyl ketone + methacrolein) and MEK (methyl ethyl

ketone). MVK+MACR are associated with the biogenic emission factor itself and do not enter the photo-oxidation factor.

-Why biogenic emissions are higher during the first part of the campaign? Were temperature and solar radiation also higher for this part of the campaign?

Primarily because deciduous trees shed their leaves in early January (Sarkar et al., 2016) and no longer contribute to biogenic emissions during the second part of the campaign. We do not have measurements of temperature and solar radiation from the first part of the campaign due to a software glitch but in general conditions were warmer in the first part with reduced fog relative to the second part of the campaign.

-Section 3.2 would be easier to follow with a map of the measurement site and mentioned cities, industrial estates and forests.

Done.

We have now added a map of the measurement site to the revised manuscript (Figure 1).

-Section 3.3, The differences between the current inventories used in Nepal are briefly mentioned in the text, however, it would be interesting to write a few lines at the beginning of this section to introduce the inventories and on which data and assumptions they are based on. Is EDGAR v4.2 also considered for the winter season?

For EDGAR v4.2 spatially resolved seasonal data is not available. We have mentioned in the text and in the figure that the EDGAR v4.2 emission inventory are for the year 2008, while REAS 2.1 emissions are for December and January 2008. To make this clearer we have inserted "full" before "year" and added the following text in the paragraph on the EDGAR inventory: "EDGAR v4.2 inventory provides only spatially resolved data, not seasonally resolved data."

- Lines 786-808, Did you compare your NMVOCs data with the wind directions? How was the wind direction affecting the sources emissions captured at the measurements site?

The conditional probability function (CPF) plots shown in Figure 12 shows the wind directional dependency of different source categories reported in this study. The figure is discussed in Section 3.2.

Lines 786-808 describe the time series of the total VOC mass. The raw NMVOC data and its dependency on wind direction was analysed in Sarkar et al. (2016) already. As stressed in Sarkar et al. (2016) and in the materials and methods section of the current paper, during this time of the year, wind direction and speed in the Kathmandu valley usually followed predictable diurnal cycles. Such behaviour is typical for a site heavily influence by mountain meteorology. Hence the changes in the source strength of emission sources are not caused by

changes in the wind direction, between the first and the second part of the campaign. They are due to genuine changes in the activity/emission strength.

-Line 815 and 840, please give the equations used for O₃ and SOA formation with respective references. It is not easy to understand figure 18 without any specification on the compounds used for each pie chart. Were the measured data used for pie b) the same data sets used to run the PMF?

Done. We have now included the equations used to calculate the O_3 and SOA formation in the materials and methods section of the revised manuscript.

Yes. The measured data used in Figure 19.b) is the same data set used to run the PMF model. As suggested by reviewer 1 we have improved the discussion of this figure.

-Line 828-832, much information is provided, please rephrase the period. Conclusions: Please include a short summary of the main findings here.

Done.

Earlier the sentence was:

"Based on measured methane and 63 non methane hydrocarbon measurements in the city of Lahore which is much larger and by all indications more polluted than Kathmandu (Barletta et al. 2016)) the authors reported a maximum contribution of about 14% due to all alkanes including methane to the total measured OH reactivity."

We have now modified this as follows:

"For the city of Lahore, Barletta et al.2016 , reported the maximum contribution of methane and 63 non methane hydrocarbons to the total measured OH reactivity as 14%. Lahore, is much larger and by all indications more polluted city than Kathmandu."

Done. We have now included a short summary of the main findings in a paragraph in the conclusions as mentioned while addressing the comments of referee 1.

Technical comments: -Some acronyms are not explained, or only explained once in the whole manuscript. Could you also provide the extended form of all acronyms used for tables and figures in their captions?

Done.

The extended form of the acronyms are now provided in the figure and table captions/footnotes.

-L. 698, ca. 30%.

 Done