

Interactive comment on “Source apportionment of NMVOCs in the Kathmandu Valley during the SusKat-ABC international field campaign using positive matrix factorization” by Chinmoy Sarkar et al.

Anonymous Referee #1

Received and published: 27 March 2017

Summary: The authors conducted VOC measurements using PTR-ToF in Kathmandu, Nepal. PMF was used to separate various source contributions to ambient VOC as a function of time. The authors then used a PMF “nudging” tool and some a priori knowledge of source profiles to move the PMF solution into a more physically realistic space. The various PMF factors are identified by comparing their VOC composition with known sources, and their diurnal behavior. The contribution of each PMF factor to total VOC mass is compared to comparable sources in several emissions inventories. The PMF-derived source contributions are quite different from the emissions inventories, which are also quite different from one another. Contributions of the different sources to VOC

Printer-friendly version

Discussion paper



mass, O3 formation potential, and SOA potential are discussed.

This is a thorough, detailed, well-written manuscript that provides valuable new information about an important, but underreported, region of the world. I highly recommend publication in ACP, if the following revisions are considered:

General comments: A general concern is that some important information about the data and PMF implementation are missing. I understand that many of the details of data collection and quality assurance have been published elsewhere (Sarkar et al., 2016). Nonetheless, this paper should be able to stand on its own. Several basic pieces of information should be included. For example: - a small map showing the geographical context of the measurement site - a brief description of the instrument & its measurement capability. - a list of the 37 ions used as PMF input, and the reasoning behind their selection. On a similar note, in many locations values for PMF input or assessment are given, but there is no explanation for why these particular values are chosen. (For example: bootstrapping factor assignment with $R > 0.6$; Line 219- Why this particular length of time?). Could you provide a reason for selecting these values, or a literature citation?

Specific comments: Section 2.1 This section needs some minor reorganization. A brief description of the PTR-ToF measurement should come first, then the description of the grab-sampling, then the PMF implementation. I suggest this because the PTR-ToF measurements, and the grab-samples, are referred to several times in the discussion of PMF; however, they had not yet been introduced.

Line 127 I found this sentence very hard to parse. Perhaps you can break this down to provide a clearer explanation of the information provided by bootstrapping.

Lines 127-139 This section could benefit from literature citations describing the use of bootstrapping. I'd also like to see a citation supporting your assertion that a fraction $< 20\%$ of unmapped factors indicates low random error.

[Printer-friendly version](#)[Discussion paper](#)

Lines 155-160 This explanation of rotational ambiguity is a little convoluted. Can you rephrase to make this easier to follow? See Ulbrich et al. (2009) as an example.

Line 192 What does it mean to be classified as a “weak” vs. a “strong” species?

Line 193 The conversion from mixing ratio to mass concentration introduces additional variability due to meteorology. Additionally, higher molecular weight species now have more “pull” in the PMF solution, because their signals are higher. Do you see evidence for meteorological influence in the PMF solution? Any evidence of a bias towards explaining variability of heavy species, at the expense of light VOCs? Why did you choose to run PMF on the mass concentration data rather than mixing ratio data?

Lines 200-220 On my first read-through, the presentation of the eight factors was very sudden and it wasn't at all clear to me how their identifications were derived, or that more information would be provided later in the text.

It would be very helpful to see a plot of Q/Q_{expected} as a function of number of factors, and an additional plot showing what happens to each of your identified factors as the number of factors is changed (perhaps in the supplemental information).

Eight factors is a quite large number compared to PMF solutions reported in many other studies. Without strong supporting evidence for each factor, I find it hard to believe that PMF can robustly separate this many distinct sources. It is especially hard to believe when each factor, on average, accounts for 12.5% of signal – but you have stated that the overall measurement uncertainty is 20% (line 190). Any additional information that you can provide to show that an 8 factor solution is physically plausible would be very helpful in convincing the reader of your solution. This could include additional PMF diagnostics (as suggested above) or other information. For example, it seems that prior to running PMF, you had some idea of what important emission sources to expect, perhaps from your previous paper or from an emissions inventory (I see four listed in the introduction). Can you make a stronger connection between the a priori knowledge and the PMF solution?

[Printer-friendly version](#)[Discussion paper](#)

Line 204 You discarded solutions with 7 or fewer factors because there appeared to be “mixing” of sources. But, this could also be due to rotational ambiguity. Did you attempt to unmix solutions with ≤ 7 factors by exploring FPEAK, for example?

Line 226 Can you provide a scatterplot showing R2 between each factor time series, vs R2 between each factor profile? It isn't clear to me if you are discussing correlation between time series or profile here, and it would help to see the “whole picture”.

Lines 237-240 Not sure I understand this. Is “mixed daytime” a photochemistry tracer? Why wouldn't solvent evaporation contain acetonitrile or aromatics? Both acetonitrile and aromatics are commonly found in solvents. Why use a ratio to acetic acid as the nudging control?

Figure 2 To which axis do the gray bars and red lines-and-markers belong, respectively?

Line 370 You are interpreting m/z 69 C5H8H+ as isoprene, correct? I suggest that this ion mass is actually a cycloalkane or alkane fragment, which seems far more plausible for vehicle exhaust. See Gueneron et al. (2015).

Line 477 Why would solvent evaporation correlate with the rate of change of temperature/sunlight, and not directly with temperature?

Lines 545-548 Can you state (or reiterate, possibly I missed this above) why it cannot be that the solvent evaporation and unresolved industrial factors are “split” from a single source by the PMF? This section also seems fairly complex and highly speculative. Can you cite an example where such a situation has been shown to occur?

Lines 600-610 This also seems to point to a “splitting” of a single source into the unresolved industrial and solvent evaporation factors.

Figure 17 Can you also include the time series of the total VOC mass loading?

Line 818 Many of the oxygenated VOCs are direct emissions from solvents, industry

[Printer-friendly version](#)[Discussion paper](#)

etc (Figure 16). So I do not think it is correct to say that photochemically produced VOCs are a dominant source of O₃ potential, especially when Figure 18a shows that the mixed daytime source contributed only about 5%.

Lines 847-848 Can you clarify how this is related to a result of your work.

Conclusion The conclusion is heavily weighted towards comparison with the emission inventories. While this is an important result, it is not the only finding discussed in the paper. The conclusion could be improved by an assessment of the major findings related to the source contributions to different categories of VOCs, specific VOCs, and O₃ and SOA formation potential.

Minor comments (typographical corrections):

Lines 140-145 Put all verbs in present tense for consistency (“will provide” → “provides”)

Line 203 “Fewer” than 7 factors

Line 235 “constraints”

Line 289 “FCBTBK”: what does this acronym stand for?

Figures 15, 16 Can you include the explanation for the different source acronyms (e.g. “MD, SE, UI”) in the caption.

References

Gueneron, M., Erickson, M. H., VanderSchelden, G. S., and Jobson, B. T.: PTR-MS fragmentation patterns of gasoline hydrocarbons, *Int. J. Mass Spectrom.*, 379, 97-109, <http://dx.doi.org/10.1016/j.ijms.2015.01.001>, 2015.

Sarkar, C., Sinha, V., Kumar, V., Rupakheti, M., Panday, A., Mahata, K. S., Rupakheti, D., Kathayat, B., and Lawrence, M. G.: Overview of VOC emissions and chemistry from PTR-TOF-MS measurements during the SusKat-ABC campaign: high acetaldehyde,

Printer-friendly version

Discussion paper



isoprene and isocyanic acid in wintertime air of the Kathmandu Valley, Atmos. Chem. Phys., 16, 3979-4003, 10.5194/acp-16-3979-2016, 2016.

Ulbrich, I. M., Canagaratna, M. R., Zhang, Q., Worsnop, D. R., and Jimenez, J. L.: Interpretation of organic components from Positive Matrix Factorization of aerosol mass spectrometric data, Atmos. Chem. Phys., 9, 2891-2918, 10.5194/acp-9-2891-2009, 2009.

Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-1139, 2017.

ACPD

Interactive
comment

Printer-friendly version

Discussion paper

