

Responses (text in blue) to comments by Referee #2 (text in black)

We thank the referee for the valuable comments, which have greatly helped us to improve the manuscript. Please find below our point-by-point responses (in blue) after the referee comments (in black). The changes in the revised manuscript are written *in italic*.

Referee #2

The authors performed measurements of VOCs, NO_x and CO at two locations in New Delhi, India: an urban and a suburban location. For VOC measurements, two proton transfer reaction time of flight mass spectrometers (PTR-ToF-MS) were used. VOC data was interpreted using positive matrix factorization (PMF). The authors find six factors explaining observations for both sites reasonable well: Traffic1, Traffic2, Solid Fuel Combustion1, Solid Fuel Combustion2, Secondary1 and Secondary2. Overall, the manuscript is suited for publication in ACP after revisions.

Specific comments:

1) The authors explain that they excluded ions such as methanol, acetaldehyde, acetone, and acetic acid with extremely high mixing ratios. A comprehensive list would be useful; I assume it also includes Formaldehyde, (which is hard to quantify with PTR-MS, but it would be worth mentioning). It would be useful to quantify all ions not taken into account, and plotting a diurnal cycle of these compounds. Although I'm not an expert in PMF, I wonder if downscaling these signals before feeding it to the PMF algorithm would solve the issue that these signals dominate PMF factors. More discussion is needed on that.

Reply: We thank the referee for pointing out these interesting topics. The referee raises two issues here: (1) characteristics of excluded compounds and (2) application of downscaling technique. We discuss these issues separately below.

(1) This point was discussed in detail above (Line 143) of the reply to comments #1 by Referee 1 (Line 143), and our response is repeated here:

Reply: We agree with the referee that mass peaks below m/z 60 are important and interesting in terms of their reactivity, emission ratios and sources. These topics are being prepared for publication in a separate manuscript. (Tripathi et al., in preparation). In that paper the relative contributions from anthropogenic and biogenic sources of these ions are discussed. In addition, the discussion on mass contributions are combined in response to Specific comments, Line 243-245 #1 by Referee 1 below.

Line 393-401. In addition, several ions below m/z 60 that can be detected by the PTR-ToF-MS are excluded from PMF as discussed in Sec. 2.3, such as methanol, acetaldehyde, acetone and acetic acids. These ions are 3-4 times higher than the dominant ions in the PMF analysis, possibly owing to much higher emission rates and natural abundance. Besides, other excluded compounds such as C₁-C₄ alkanes and C₁-C₄ alkenes which are not detectable by the PTR-ToF-MS are substantial contributors to the total VOC mixing ratio as well. However, these ions are minor contributors to SOA formation and only substantially contribute to the formation of ozone, which is a major issue in summer. Although the mixing ratio of the sum of VOCs in the PMF only accounts for 39.6 % at IITD and 24.2 % at MRIU (Fig. S11), many of these compounds are the dominant precursors in terms of SOA formation (Wu and Xie, 2017, 2018).

(2) Although downscaling could in theory push the high concentration signals into other factors, in this study, we believe that applying this technique would bring more uncertainties. For instance, chosen of the downscaling parameter is critical. Therefore, without any reference/technical support, an unideal parameter could bring more uncertainties to both the source composition and contribution. Further, the VOC fingerprints might be rather different in different locations, for example, different types of rather local biomass burning are present. Therefore, locally adapted parameters might be needed for each dataset and each compound.

2) Diurnal patterns of Traffic1 and Traffic2 in Figures 3 and 4 are quite similar; Assigning Traffic2 to heavy-duty vehicles seems to be problematic, since the diurnal pattern of this factor is very close to zero (including its 90th percentile) from 10 am to 5 pm, which is exactly the time window where the ban of heavy-duty vehicles is lifted.

Reply: We apologize for the mistake; heavy-duty vehicles are banned from 7:00-21:00 LT. The discrimination of Traffic1 and Traffic2 are revised in response to comments #1 by Referee 1 (Line238-243), and our response is repeated here.

Line 261-270. As shown in Fig. S7, the ratio of Traffic 2 to Traffic 1 is very low during the day time and starts to increase slightly from 16:00 LT. Although both Traffic1 and Traffic2 are high during the night with their maximum concentrations around 21:00 LT, the Traffic2/Traffic1 ratio is as low as 0.6 at that time. The ratio increases overnight with a sharp increase during the early morning, reaching a maximum value of 1.4 at 07:00 LT, suggesting that Traffic1 is the dominant traffic source both day and night. This can be explained as cold start emissions from gasoline vehicles emit high amounts of VOCs while heavy-duty vehicles contribute much less to VOCs but more to BC and NO_x (Platt et al., 2017). Further, the spectrum of Traffic2 is characterized by high fractions of high mass aromatic compounds. For instance, the ratio of C8/C7 aromatics is tripled in Traffic2 compared to that in Traffic1, which is similar to the ratio of the emission factors from previous studies (3.5 times (Gentner et al., 2013)).

3) (Line 245+:) Are there numbers on how much traffic increased in New Delhi during the last two decades? Is traffic really the dominant VOC source when large VOC signals are not accounted for in PMF (acetone etc.)

Reply: We have added the discussion on traffic increase.

Line 271-272. the registered vehicular population has tripled since 1994 and has reached 7.6 million.

We added discussion regarding the concentration of excluded VOCs replying to comments #1 by Referee 1 (Line243-245), and our response is repeated here.

Line 393-401. In addition, several ions below m/z 60 that can be detected by the PTR-ToF-MS are excluded from PMF as discussed in Sec. 2.3, such as methanol, acetaldehyde, acetone and acetic acids. These ions are 3-4 times higher than the dominant ions in the PMF analysis, possibly owing to much higher emission rates and natural abundance. Besides, other excluded compounds such as C₁-C₄ alkanes and C₁-C₄ alkenes which are not detectable by the PTR-ToF-MS are substantial contributors to the total VOC mixing ratio as well. However, these ions are minor contributors to SOA formation and only substantially contribute to the formation of ozone, which is a major issue in summer. Although the mixing ratio of the sum of VOCs in the PMF only accounts for 39.6 % at IITD and 24.2 % at MRIU (Fig. S11), many of these compounds are the dominant precursors in terms of SOA formation (Wu and Xie, 2017, 2018).

4) Evaluation of biogenic VOCs: Line 359: please avoid "very low" and similar ill-defined expressions; I don't think that 0.46 ppbv is "very low"; Personal care products may be another possible source of Monoterpenes.

Reply: We agree 0.46 ppbv is not "very" low in terms of BVOCs. We modified the text and added the discussion on personal care products in response to comments #1 by Referee 1 (Line 264), and our response is repeated here.

Line 418-420. One recent paper showed that fragrances and personal care products may be an important emission source of urban monoterpenes and are correlated with traffic emissions (McDonald et al., 2018).

Technical comments:

Abstract: avoid abbreviations "IITD" and "MRIU"

Reply: We adjusted the abstract replacing the abbreviations of IITD with *the urban site* and MRIU with *the suburban site*.

Line 44: no need for "natural" when talking about BVOCs

Reply: Done. We removed "natural"

Line 54: "high atmospheric reactivity and higher SOA yield" - need reference

Reply: Done.

Line 64: "The critical air quality problems have left India with high death rates from ..." need reference or numbers

Reply: Done

Line 71: "..., a comprehensive investigation *of* VOC pollution levels..."

Reply: Done

Line 75: "...pointed out the lack of ..."

Reply: Done.

Line 93: "The study site is approximately 150 m north of a busy street and surrounded by several streets as well" - unclear

Reply: We revised the sentence.

Line 95-96. The study site is approximately 80 m north of a busy street and is surrounded by several streets inside the campus as well.

Line 97: "The site is located to the southeast of higher elevation terrain as shown in Figure 1" - unclear

Reply: We revised the sentence.

Line 101-102. Besides, the northeast territory of MRIU is of slightly higher elevation compared to the sampling site as shown in Fig. 1.

Line 116" use the term *reduced* electric field (E/N)

Reply: Done.

Line 124: *Volume* mixing ratios

Reply: Done.

Line 125: Please add a note of how and how often background measurements were performed

Reply: We have added the background performance.

Line 124-125. The background measurements were performed using a dry zero air cylinder every two weeks

Line 203: "... nor included in the PMF analysis ..." -> " ... or not included in this PMF analysis ..."

Reply: Done. We revised it.

Line 208: please define "very high"

Reply: We revised the sentence.

Line 225-226: At IITD, the concentrations of several aromatics were very high, being 10-20 times higher than those of the major phenols, and over 100 times higher than for the compounds with the lowest concentration.

Line 252: "These ions are tentatively attributed to phenolic compounds and furans" - reference needed

Reply: Done.

Line 279: "However, many of these ions can be formed rapidly during daytime and may have a short lifetime owing to partitioning to the condensed phase and/or heterogeneous processes" - please re-phrase: I think this is suggested by the data, not by the identity of the compounds.

Reply: We revised the sentence.

Line 309-313. The time series of SecVOC1 follows that of the solar radiation, which has a regular contribution cycle during daytime. The diurnal of SecVOC1 shows a rapid enhancement starting from around 7:00-8:00 LT and declines continuously after 13:00 LT. This indicates that while many of these ions can be formed rapidly during daytime, they may have a short lifetime owing to partitioning to the condensed phase and/or heterogeneous processes.

Line 287: "Major fractions of alkyl nitrates (RONO₂) are detected as (ROH⁺) fragment ions by the PTR-ToF-MS" - please cite Aoki et al: "Detection of C1–C5 alkyl nitrates by proton transfer reaction time-of-flight mass spectrometry" or similar

Reply: We thank the referee for the suggestion. We added the reference. (Now Line 319)

Line 350: "But more importantly, differences in SecVOC *is probably owing to that chemical ...*" - please rephrase; hard to follow

Reply: We revised the sentence.

Line 388-393. More importantly, the difference in SecVOC is probably due to different oxidation conditions at the two sites. Owing to the high mixing ratio of NO_x and the suppression of oxidants like OH radicals, the chemical oxidation of primary VOCs occurs to a greater extent downwind of urban emission sources. As shown in Fig. S8, high mixing ratios of SecVOC at MRIU originate from northwest directions, different from the origins of local primary factors (southeast). Besides, the longer oxidation time may be another reason of the higher SecVOC mixing ratios at MRIU.

Reference

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