
Acp-2016-185: "Seasonal variability and source apportionment of volatile organic compounds (VOC) in the Paris megacity (France)" -- Baudic et al.

Authors' Responses to Referee #2

We would like to thank the Referee #2 for her/his general feedback and each of her/his useful comments/questions for improving the quality of this manuscript. All of them have been taken into account when preparing the revised version of the manuscript. In the present document, authors' answers to the specific comments addressed by Referee #2 are mentioned in **blue**, while changes made to the revised manuscript are shown in *italic.*

General/scientific comments

This paper reports the results of a source apportionment by positive matrix factorization (PMF) of the concentrations of a suite of ambient VOCs measured in urban background air in Paris over a period of several months from January to November 2010. VOCs were measured both by on-line GC and by PTR-MS. In order to help in the assignment of some of the factors emanating from the application of PMF, the authors compared the speciated VOC profiles of the factors with speciated VOC profiles the authors separately measured at three locations where they assume that a single emission source will dominate the ambient VOC, specifically: (1) measurements during busy (and traffic jam) periods in a highway tunnel, to represent vehicle related VOC emissions; (2) measurements close to a domestic gas flue, to represent natural gas source; and (3) measurements at a fireplace facility, to represent residential wood-burning emissions (the authors acknowledge that their measured VOC profile from this source may be less quantitative than for other source profiles). To further assist in the assignment of PMF factors to particular VOC emission sources the authors also make use of additional co-located atmospheric compositional data available to them, such as NO, CO and black carbon (BC).

The authors present results in which the ambient urban background VOC has been apportioned into six sources, each of which has been assigned an identification, albeit that one factor is assigned to be a mixed natural gas/background source. The analysis presented includes speciated VOC profiles for each factor and monthly and average-hourly variation in the absolute contribution (ug/m3) of each of the six identified factors/sources. The largest contributions in total are from traffic-related activities (through two identified factors: motor-vehicle exhaust, and gasoline evaporation), although all six identified sources have not that dissimilar relative contributions, on average. A noteworthy observation is significant contributions to ambient VOC from wood burning, 18% on average but up to ~50% at times in winter. Biogenic emissions were also reported to be significant, 15% on average but more in summer.

The authors have a large dataset of time-resolved speciated VOC over an extended time period, almost a year. They have used standard, but appropriate, statistical methods to endeavour to decompose the ambient measurements into individual source contributions. These are statistical, rather than dispersion-/chemistry-based source apportionments. These methods have been widely employed to apportion ambient PM, but less so for VOC.

The presentation of results and their discussion are largely descriptive, in the sense that the authors present the details for their factor/source contributions and their monthly and hourly variations, which are rationalised with general text about anticipated behaviour of particular sets of pollutant mixtures in the urban background atmosphere. The authors also present a qualitative and quantitative comparison of their VOC source apportionment with previous literature.

Although in one sense the presentation of this work could be described as 'formulaic' – following previous data presentation and analysis styles – nonetheless the large dataset presented here for a large European city presents a valuable addition to the VOC apportionment literature. A particular feature is the presentation of VOC speciated profiles for three potential VOC sources, although the authors acknowledge some shortcomings in these. The paper is already lengthy and contains much new data, supported by detailed descriptions of the data collection and processing protocols and results. As an overall summary, the content of the paper is suitable for publication in ACP.

The authors thank Reviewer#2 very much for his/her attention to our manuscript. All comments addressed by both reviewers have been taken into account in the preparation of the revised version of the manuscript. In this respect, several figures and tables were notably added and modified (e.g. air masses trajectory analysis – Fig. 5; comparison between "highway tunnel" and "motor vehicle exhaust" profiles – Fig. 9; relative and absolute contributions of reactivity of each PMF factor – Fig. 11) and in the supplementary (e.g. PMF profiles issued from simulations using the FRANCIPOL dataset & comparison of speciated PMF profiles issued from our two different datasets – Section S1; representativeness of meteorological parameters in 2010 – S4; mean absolute contributions of factors per month in 2010). Please note that figures and tables numeration is now different in this new version.

Technical comments

1/ The tables and figures are generally clearly presented. The written text is largely unambiguous in conveying its meaning, but it is overly long in places. There are instances where introductory sentences to a section could be substantially abbreviated, or even deleted as repeating what the reader will have picked up from the methods section. The authors should be encouraged to edit text further for conciseness of expression.
Following reviewer's suggestions, the authors made efforts to write a revised version of the manuscript with conciseness. Some rephrasing also aimed at bringing the content a bit more to the point.

The following are more specific comments.

2/ P6, L-18: should read "Raw data were corrected using…."?
The initial sentence "Raw data were compensated using…" was substituted by the following one: *"Raw data were corrected using the algorithm described in Weingartner et al. (2003) and Sciare et al. (2011)".*

3/ P6, L-25: delete "is" before "analyzer"
Correction applied in the revised manuscript: *"Nitrogen monoxide and dioxide (NO, NO_2) were measured by chemiluminescence using an AC31M analyzer (Environment SA, Poissy, France) and ozone (O_3) was monitored with an automatic UltraViolet absorption analyzer (41M, Environment SA, Poissy, France)."*

4/ P6, L-32: delete "at"
Correction applied in the revised manuscript: *"Standard meteorological parameters […] were provided by the French national meteorological service "Météo-France" from continuous measurements recorded at the Paris-Montsouris monitoring station (14th district, 48°49'N, 02°20'E), located about 2 km away from the LHVP site."*

5/ P7, L-22: should read "except for"
Correction applied in the revised manuscript: *"This combination of hydrocarbon species and masses is similar to that from Gaimoz et al. (2011), except for iso-butene."*

6/ P8, L-9: I don't understand what is being described in the sentence beginning "Finally, these different processings…." Please rephrase this sentence to make clear to what "it" is referring in this sentence and to clarify what the procedure undertaken was.
In this study, only 59% of isoprene data are modeled by the PMF technique, what is not objectively considered as sufficient. To address this problem, input values of isoprene were modified when detecting missing data. We have investigated the possibility of replacing missing values with data more appropriate than the median. Indeed, a "virtual" averaged pattern was calculated from 1-h real samples observed in June and August (to keep the summer variability of isoprene). Another option was to preserve raw data of isoprene (no subsequent changes) and to increase the analytical uncertainty initially estimated at 15% (gradually from 15 % to 30%) – instead of categorizing isoprene as *weak* (as uncertainties are tripled implying a lower Signal to Noise). This was intended to better display this biogenic compound. PMF simulations were performed by considering these different options. As a consequence of these tests, no significant improvement on the quality of modeling isoprene was observed. Regular statistical parameters such as R^2, slope, slope/intercept SE (Standard Error) were used to draw such conclusions. As empirical tests have not helped, isoprene is still categorizing as *strong*.

In the previous version of the manuscript, "processings" referred to "empirical tests" and "it" to isoprene. To avoid any ambiguity in the meaning of this sentence, corresponding lines were rephrased.

Correction applied in the revised manuscript: *"To address this lack of isoprene data, several empirical tests (e.g. simulating an averaged seasonal/diurnal cycle of isoprene or increasing the analytical uncertainty of raw data from 15 % up to 30 %) were conducted within PMF simulations with the aim of better modeling the variability of this compound. As a consequence of these tests, no significant improvement on the quality of modeling isoprene was observed. Finally, isoprene is still categorizing as strong here".*

7/ P10, L-26: the phrase "fairly comparable" is not scientifically precise.
The corresponding sentence was rephrased.
More specific statements about weather conditions are given here.
Correction applied in the revised manuscript: *"Air temperatures observed during the campaign were comparable to standard values determined by the French national meteorological service "Météo-France" (available at: http://meteofrance.com), with however an uncommon cold wintertime (Bressi et al., 2013- Fig. S1a). Temperatures recorded in January and February 2010 were respectively between -2°C and -3.5°C below normal values (see. Section S2 in the Supplement). Extreme unusual cold-air outbreaks and a few snow flurries affected the Paris region, thus explaining higher temperature anomalies during that period. Levels of hours of sunshine and rainfall were globally consistent with standard values, with however some discrepancies in winter/autumn and spring, respectively (Fig. S3)."*

8/ P10, L-29: "a few flurries" of what? Please write specific statements about the nature of the weather.
Please refer to the previous comment n°7.

9/ P11, L-15: the phrase "contribute to the tune of" is too colloquial; please use more direct wording.
Correction applied in the revised manuscript: *"Both alkanes and OVOCs significantly contribute up to 75 % of the TVOC concentrations."*

10/ P11, L30-L35: there are several instances in these lines of text of negative values for VOC concentrations. These are surely some aberration (albeit repeated aberration) of typing error. Please correct.
A comparison between mean concentrations of aromatics and OVOCs measured in this study and ambient air levels reported in the literature for different urban atmospheres (see Table 2) was made. It aims at highlighting existing differences in VOC levels monitored for a given time period between our work (Paris) and another European or global studies (the selection is not exhaustive here). We note that VOC concentrations measured in European cities (Paris, Barcelona, and London) are in the same order of magnitude depending on the compounds. Instead, more significant differences in VOC levels were found between Paris and Houston, Beijing, Mohali or Mexico City.

The negative values were due to differences between VOC concentrations from our study compared to others. But to avoid confusion, differences are now only given with absolute values.

Correction applied in the revised manuscript: *"Average VOC concentrations were also calculated in line with sampling periods of the other European and global studies over different years (see Table 2). In this study, measured VOC levels were in the range of those found with some European cities (Barcelona, London – from 0.1 to 2.1 ppb concentration differences). However, average VOC levels observed in Paris were significantly lower than those measured in Houston (USA – from 0.1 to 6.9 ppb concentration differences) and more particularly in Beijing (China - from 2.5 to 8.9 ppb), in Mexico City (Mexico – from 0.1 to 27.4 ppb) and in Mohali (India – from 0.9 to 32.7 ppb)".*

It is important to note that Table 2 was modified and all reported values are given in ppb (see the comment n° 13 – Referee 1).

11/ P13, L-3: I do not understand the scientific sense of the sentence starting "With an atmospheric residence time…" How does the statement at the end of this sentence (about methanol emissions contributing to background levels) derive from, or otherwise relate to, the text at the start of the sentence about methanol residence time? Please reword to clarify.
We agree with this comment. There is no direct link between the beginning and the end of this sentence. This additional information did not bring an added value to the scientific approach. To avoid confusion, we opted to omit the start of this sentence.

Correction applied in the revised manuscript: *"Methanol is usually released into the atmosphere by vegetation and man-made activities contributing to a relatively high background levels during most of the year."*

12/ P14, L-24: I do not follow the scientific logic here. The text appears to state that iso-pentane is known to be a key tracer for gasoline evaporation, but also to say that iso-pentane was not present in the speciated profile the authors have assigned in their work to gasoline evaporation.
In this study, the "evaporative sources" factor is mainly characterized by the presence of propane and butanes (*iso-/n-*). The species composition of the F2 profile is consistent

with those obtained from other SA studies (Brown et al., 2007; Gaimoz et al., 2011; Waked et al., 2016). In addition to C_3-C_4 species, pentanes (*iso-/n-*) and toluene are also considered as key tracers for gasoline evaporation (Salameh et al., 2016 – in preparation). A small contribution of these species was identified in F2. However, their highest contributions were assigned to the "Motor Vehicle Exhaust" factor" (F1) in agreement with that observed during the tunnel experiment.

To avoid any misunderstanding, the corresponding sentence was removed.

13/ P14, L-32: please explain more clearly what about the monthly change "remains ambiguous".

The seasonal cycle of "Evaporative sources" profile is expected to be significant in spring and summer (when higher temperatures are observed). The minimum mean contribution of this source is observed in July when road-traffic emissions are usually significant (See Figure 10 – Panel 1).

This explanation is given with more details in the main text (P14, L-31 – P15, L-5).

14/ P20, L19: The phrasing that the mean temperature was "in the range +/- 20 degC" does not make sense. Either quote the range, or quote the mean and some recognized statistic of the variation about the mean. Likewise for later in this sentence in connection with "+/- 16 degC".

Correction applied in the revised manuscript: *"The mean temperature recorded in May-June 2007 and 2010 was 20°C and 16°C, respectively".*

15/ Caption of Table 1: It would be helpful for the caption to remind the reader with a statement of the time resolution of the raw data from which these statistical summaries are derived, and of the time duration/dates of the total dataset.

Caption of Table 1:

Statistical summaries (µg.m^{-3}) of selected VOC concentrations measured at urban background sites. Statistics were calculated based on hourly mean data, initially obtained every 30 min. (ethane > isoprene) and every 5 to 10 min. (for aromatics and OVOCs). These measurements were undertaken from 15 January to 22 November 2010 (~ 10 months. A conversion factor is provided here to convert VOC concentrations (µg.m^{-3}) into (ppb) mixing ratios.