

Interactive comment on “Seasonal variability and source apportionment of volatile organic compounds (VOCs) in the Paris megacity (France)” by A. Baudic et al.

Anonymous Referee #1

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General comments

The presented manuscript presents data on NMHCs and OVOCs from two sampling sites in Paris covering about 10 months of quasi-continuous measurements as well as on-site measurements at three potential major source categories. Since long-term datasets covering more than several weeks (usually obtained from short campaigns) are quite rare, in particular for combined NMHCs and OVOCs, this dataset is very valuable. However, the presented paper needs some major improvement before it can be considered for publication in ACP.

The analysis of data was kept at a very descriptive level. Diurnal and annual variations are shown for single compounds and for the resolved factors from the PMF analysis. A

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detailed source apportionment has been performed and the conducted PMF seems to be solid. All applied methods are quite standard and widely used in the scientific community. But apart from the new data, none of the methods are original. The manuscript could profit a lot from deeper analysis of the very nice dataset. The authors mention that the originality of the work derives from using near-field speciation profiles to refine the identification of the profiles. It is a good approach to compare modeled profiles with real measurements and it definitely helps to apportion source profiles. Despite the fact that this is also not a new approach, since there is a lot of literature, where it has been done before, it is new for Paris, and thus it is very useful to have this additional information for the SA. The authors only mention the measured profiles in one half-sentence for motor vehicle sources and for the background factor and not at all in the apportionment section of the wood burning factor. For the latter factor, the agreement is only partially fulfilled, since a lot of ethane and propane is assigned to the factor by PMF but not detected in the fireplace experiment. The authors should discuss the discrepancy and make more use of the added value by the experiments.

The performed analysis of the wind fields and the usage of the simple wind roses for interpretation of air-mass origin are not sufficient. The authors should consider a more elaborate analysis of the air-mass history, e.g. by trajectory analysis/clusters or to take a look into general weather patterns to really draw conclusions.

The structure of the paper could be improved. Many parts of the results section, where interpretation and already discussion is performed, would better fit into the discussion section. Also some parts of the results could be a bit and more stringent and focused. The English throughout the manuscript is okay, however, some rephrasing could sharpen the expressions and bring the content a bit more to the point. Past tense should be used more consequently when methods and results etc. are described.

Specific and technical comments:

2-26: 12 million inhabitants, omit “of”

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3-16: some citations could be helpful

3-28: should be elaborated further in the source apportionment section.

4-3ff: some redundant information from the introduction

4-8: please state which background site

The authors should discuss and prove that it is valid to merge the two datasets from two locations. Emissions in urban areas can be quite heterogeneous upon receptor location, wind patterns etc. and some further explanation is needed.

6-8f: calibration once a month seems little; how was the stability of the systems within the months checked? How was the zeroing performed?

7-5: since it is only a very small selection of papers out of the many studies from urban areas, I would put in an "e.g.," before the citations.

7-6: not too many studies were performed in rural areas, but the ones could be mentioned, e.g. Lanz et al. 2009 ACP (doi:10.5194/acp-9-3445-2009) and Leuchner et al. 2015 ACP (doi:10.5194/acp-15-1221-2015)

7-20: "acetonitrile"

7-22: "except"

7-25: why was the proportion of missing values estimated? It should be known exactly.

7-27: "constraints"

It is quite problematic that isoprene had such a high amount of missing values thus it is not too surprising that the biogenic factor could not be resolved very clearly from some substances.

7-32: since most of PMF studies describe their results in ppb units, it might be nice to have some information how much ppb/ppt the units equal for comparison (throughout the manuscript)

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8-1: how were the uncertainties determined? Was there a standard procedure for each substance following guidelines from GAW or ACTRIS?

8-7: what other tests were performed? Might be interesting for other readers.

8-10: it is not entirely clear what exactly was done and what modeling parameters are meant here. Please specify.

8-14: For what reason was the total VOC mass included in the model? What is the benefit of it? In the results it basically looks like this parameter is just apportioned equally to all factors more or less.

9-5: omit "specially".

9-20: "omit" instead of "get out from".

9-22: what is meant by "w/w"?

10-23: Please re-phrase "weather indicators"

11-3ff: the analysis of air-mass origin need to be more profound; only wind direction does not explain the origin of the air masses. To determine if air masses were originating from the clean marine BL or from LRT or deriving from industrial areas from the PBL of central Europe a trajectory analysis (e.g. trajectory clusters) or at least an analysis of general weather patterns could bring further information and support to the assumptions in the manuscript. The wind rose plots could go to the supplement or replaced by a more profound analysis.

11-12: Omit "From this table, it was observed that"

11-23f: what is the reason for the difference? Meteorological conditions? Should be discussed in the discussion section.

11-29: "global studies"

11-34: Last sentence is quite generic.

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12-3: omit "time"

12-15: better to use a 24h time instead of am/pm, avoids confusion

12-17ff: the increase occurs until 21h. And after that the levels stay quite high. Is there another (meteorological) reason for this? Interpretation of the graphs should be done in the discussion section.

12-26: Format of citations should be "Gros et al. (2011)" etc.

12-32ff: the conclusions cannot be drawn from wind roses. As stated before a trajectory analysis or similar is needed for that.

12-4ff, entire section: parts of the whole section better fit into the discussion.

13-6: "peaks" rather than increases; values high for longer time (see CO)

13-8: "to" instead of "with"

13-10: it is a bit hard to read because the description jumps between the normal manuscript and the supplement. It might be worth to think about including important graphs that are discussed here into the main part and leave the supplement to really supplemental information.

13-10: "..., however,..."

13-18: in the plots no clear difference can be see between the two species

13-24: these substances are not "emissions" but secondary products of isoprene oxidation

13-27f: into methods section

13-30: "such as" instead of "like"

14-7: "fair" instead of "good"

14-9ff: link to respective figure should be inserted; a table or small figure of the absolute

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contributions could be useful

Chapter 3.4: In general, reactivity of the different factors could be investigated in addition to stating only mass contributions; the biogenic factor and the motor vehicle factor would potentially gain importance compared to the factors with more stable gases such as background/natural gas and gas evaporation

14-13: why are the values so high in the middle of the night? Meteorology?

14-19: No reference to the tunnel experiment is given here. Since it is the value added to have these kind of data it should be described here (and discussed later)

14-26: if part of the isoprene is from vehicles, it should show up in F1, since it would be a combustion product instead of an evaporative source.

14-31ff: link to figure 9 should be given.

15-1: correct citation: "Frachon (2009; pers. communication)"

15-30: a lot of acetonitrile was apportioned also to F4, why is that?

16-6: "on" instead of "with" Chapter 3.4.3: reference to experiment needs to be included; a lot of ethane and propane is allocated to this factor that should very likely not be in there

16-16: "includes isoprene's"

16-24: r-value of the PAR correlation missing

16-27: very high values at night, why? Stability of the atmosphere?

17-14: what does "panel 5" mean?

17-14: the PBL is higher in the afternoon, that contradicts the statement of the diurnal pattern. Emissions might be higher and also a temperature dependency.

17-18: not shown

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17-22: "except"

17-31: BLH not defined. Better to use only one abbreviation, e.g. PBL Chapter 3.4.6: the annual course of the background does not fit with similar observations; there should be a maximum in February and minimum in late summer due to the OH reactivity (delayed by 2 months to the annual solar cycle because of the long-lifetime of ethane)

18-7ff: cannot be concluded only from wind roses. Statements need to be supported that it really results from different air masses, since annual cycle does not fit.

Chapter 3.5: pure discussion, also better fits into discussion section.

18-21: background not really fresh emission, but aged air mass

18-21ff: additional information on the contribution of reactivity of each factor would be very useful

19-4: most of the conclusions are quite speculative and need to be supported by more profound analysis

20-9: this discussion would fit to the discussion of factors

20-13: "combination"

20-33: there are some other longer time series, but the dataset indeed is very useful

21-23: absolute values could also be interesting in addition for comparison to other studies

22-12: why were exactly these studies chosen? There are many other studies described in the literature from e.g., Houston, Santiago de Chile, etc. Graphics: some of the axis titles and labels (e.g., Figs. 8, 9 but also all others) are quite small and might be hard to read when formatted to the actual page size.

Fig. 5 could go to supplement or omitted if replaced with a more profound air mass investigation

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Fig. 8: logarithmic scale makes it hard to see the "real" profile for absolute contributions"

47-12: the factors could be shown in supplement, would be interesting to see

47-6ff: quite important information. Could be moved to methods section of main text.

Appendix A: here the calculation of uncertainties could be shown.

Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-185, 2016.

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