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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Composition and variability of gaseous organic pollution in the port megacity of Istanbul: source attribution, emission ratios and inventory evaluation" *by* Baye T. P. Thera et al.

Anonymous Referee #2

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The paper by Thera et al. presents a 2-weeks VOCs dataset obtained in Istanbul. On-line measurements have been performed at a main site (in the city centre) and has been completed by off-line measurements. Some additional off-line samples have been taken at other sites, in order to document chemical signatures from specific sources. In a first part, the daily and day-to-day variability has been examined, based on air mass back trajectories and meteorological parameters. In a second part, a PMF analysis has been performed and the 5 determined source profiles have been presented and discussed. Finally, a comparison with the emission inventory has been

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provided based on calculated emissions ratios VOCs/CO. Although quite limited in the number of measurements, the presented dataset is interesting as VOCs measurements are rather limited in this area and comparison of source contributions could bring important information to evaluate the emission inventory, which is a critical input of air quality models. Nevertheless, there is an important issue concerning the validity of this comparison, as explained below in the section “Main comment”. I would recommend publication of this manuscript in ACP if this issue is solved / explained along with some other requested clarifications /improvements described in the specific comments.

Main comment

The last two sections of the papers (3.3 and 3.4) are rather short but they are potentially important as they compare the results of this study with emission inventories data. Nevertheless, currently the way the emission ratio is calculated and compared is not convincing at all. The authors say that they can not use the “linear fit regression” method in order to derive emission ratio because there is a poor correlation between targets VOC and CO. They use then the median value of each VOC to CO during all the observation period to estimate an emission ratio (before to compare it to other cities and then to emission inventories). In absence of any correlation between VOC and CO, I do not see how a ratio of median VOC/CO could be used to estimate an emission ratio. . .from what is representative this emission ratio? From all sources for the whole city? Indeed, as the whole dataset is used, this means that all sources are mixed; and among them traffic contributes only 15%; so how can you compare your ratio to traffic emissions from inventories? As these 2 sections are based on this emission ratio calculation, so either this one is better justified and its representativity (and limitation) is discussed, or these sections have to be removed. We note also that there is no discussion about the fact that VOCs in the inventory stand for “all VOCs” whereas only a limited number of VOC were measured..

Specific comments

-L64: Is the given standard deviation calculated between both calibrations or does it include the 5- ppb control points? How were the calibration coefficients applied to the data? An average value was used or an interpolated one? How was the blank value substracted? An average value was used or an interpolated one? Please clarify all these points.

-L188: I agree with the author that the variability is highly consistent for aromatics between both techniques. Nevertheless, they claim that the difference in concentrations do not exceed 20%, although the slope for toluene is 22%. In addition, we note that for benzene, there is an underestimation of about 20% of the PTRMS compared to the GC; whereas for toluene, it is the contrary (overestimation by the PTRMS). How do you explain this feature? As ethyl benzene is known to fragment on the mass of benzene, I guess we would rather expect the contrary (i.e. an overestimation of benzene on the PTRMS). Moreover, there seems to exist an even higher difference between the sorbent tube and the GC. As the ratio toluene/benzene is later on used in the paper to comment on source origins, a more careful analysis on the uncertainty associated to this ratio, due to the differences which are pointed out by the intercomparison should be made (as the ratio could be over-estimated).

-L190: where is the graph showing the comparison for isoprene?

-L228: How was calculated the 30-min data? Did it take into account the sampling time of the GC? If not, could it have an impact on the results as there was a high degree of variability of the compounds?

-L244 : With missing values higher than 40% and the use of median values instead of missing data, one can wonder about the meaningfulness of using such compounds? The authors could refer to their sensitivity tests to justify this point

-L251: Even if all details are given in the SM, please give in the main text the values used as input for uncertainties (at least the range)

-L265 to 269 : I would suggest to move the part in the methodology section

-Fig. S4 could be in the main text as it is discussed in details here

-L301: “terpens”: does it include isoprene?

-L307: Give the references associate to the measurements in Paris, London and Beirut

-L308: one general comment which could be made here is that despite different years and seasons, Istanbul is quite similar to other cities, except for toluene and xylens (and this could be later on reminded when analysing the sources to discuss which of the source(s) would explain these high values in Istanbul)

-L312: what element suggests the traffic influence? (“This would suggest. . .”)

-L314/Table S6: Why presenting a table of mean concentration which have been measured in different sites (and date/time). It would be more interesting to present a value (or a mean +/-std value) for a given time for each site for some compounds, this would allow a comparison with the main site.

-L331 : The section 3.2.2. could be re-arranged, in order to directly introduce the discussion on diurnal variations. In the current version, the overall variability is discussed and then the diurnal variation is discussed but this leads to some confusions (for example, L338 diurnal cycles of NOx and CO are discussed, although the figures of the diurnal cycles of are not yet properly introduced) and several repetitions (for example, the vegetation type in Istanbul. . .).

-L338 and the corresponding paragraph: The discussion of this section is not clear and might be improved, once the discussion includes as well the diurnal cycles (see previous comment). In addition the discussion focusses mainly on local meteorological conditions (wind, dispersion..) but no discussion is made on the possible influence of long-range transport. If not discussed at all, why studying Flexpart back-trajectories over such long periods?

-L338: At midday, it is not a maximum. In addition, why a midday concentrations max is expected from traffic-related compounds? Usually, a morning and an evening peak are observed

-L341: Isoprene and its oxidation products co-variate most of the time. This is not true for period 2. Be more precise in your analysis and description.

-L384 and Figure 5 : there is a large peak of benzene, isopentane, isobutene, m71 during the night of event 2. How do you interpret it? Is it due to a single event or it was observed several times? It could be useful to show toluene on this figure (directly near to benzene)

-L406 to L418: I would suggest to move this part in the methodology section

-L422 : why naming a source after a compound and not only “solvent use”?

-L422: The recent study about VOCs from petrochemical sources in urban areas (Mac Donald et al;, Science, 2018) must be referenced somewhere when discussing about solvent use

-L432: The sentence “low T/B ratio indicates the influence of traffic emissions on measured VOCs. ....” could be mis-leading and should be checked /re-formulated (see for example Gaeggeler et al., 2008 which says the opposite: “Another indicator for traffic emissions is a low benzene/toluene ratio (Stemmler et al., 2002)”. In addition, the uncertainty of the T/B ratio should be reminded here (see comment L188). Therefore, this section should be either removed or discussed more thoroughly.

-L477: could this factor represents the “regional background”? If so, the discussion could be shortened, as there is no specific source associated and therefore no need to detail all biogenic/anthropogenic, primary/secondary source. That would avoid some vague statement. For example, L486 “these species are formed by the oxidation of primary biogenic hydrocarbons. However these oxygenated can have also primary both anthropogenic and biogenic sources”. And the mention of 1,3-butadiene and 1-

pentene being emitted by plants is not so convincing in such a highly populated city.

-L480: the sensitivity study should be mentioned here (otherwise the 70% missing value would lead to the comment that this compound should not be taken into account).

-L517: it is difficult to see on the figure that a strong increase in minimum concentrations is observed during period 2

-L549: This sentence is too vague; how has it been analysed? Either remove or give a bit more information on this point

-L551: This section on sensitivity tests is important and is convincing to show that the most appropriate run has been selected. As these results are needed before, I'm wondering if it would not be more appropriate to move it at the beginning of the PMF results section (or even in the methodology part). The second part of the section (starting from L560) does not really belong to a section called "sensitivity tests" and it is not clear what it brings to the discussion. Therefore, it is suggested either to remove it or to discuss it in more details (probably in another section then).

-L551: Before to start a new section, it would be useful to have a section which comments the PMF results as a whole (for example, the contribution of the different sources compared to the other cities where levels and variability were compared. . .)

Technical corrections

-L53 the sentence is incomplete

-L65: "include" instead of 'includes"

-L68: rephrase (the paper by Panopoulou does not present a receptor oriented approach")

-L103: correct the English of the sentence

-L111: precise that it is at one season

-L211: There is no PM on figure S1

-L238: There is a “%” alone (with no number)

-L270/L271: Once it is referred to three main periods„ another time to four types of periods, try to be consistent in the naming and numbering

-L278 “wind” instead of “win”

-L299: some oxygenated “compounds”

-L420: “in” figure 6

-L430: there is on “(“ too much

Table 1: m/z from acetone should be given as well

Figure 1 : it would be useful to have a figure zoomed on the main sites and the 2 side sites , if possible with wind roses, allowing to locate all local sources

Figure 2 and 3: it would help to harmonize the site locations names between both figures

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