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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Source apportionment vs. emission inventories of non-methane hydrocarbons (NMHC) in an urban area of the Middle East: local and global perspectives" *by* T. Salameh et al.

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Interactive comment on "Source apportionment vs. emission inventories of non-methane hydrocarbons (NMHC) in an urban area of the Middle East: local and global perspectives" by T. Salameh et al.

Dear referee,

We would like to thank you for your comments, which significantly improved the quality of this work. We have revised the manuscript entitled "Source apportionment vs. emis-

sion inventories of non-methane hydrocarbons (NMHC) in an urban area of the Middle East: local and global perspectives" according to your comments. Kindly find below our response to the comments.

Sincerely yours,

Thérèse Salameh

Answers to reviewer comments: Ms. A. Claude

General Comments: The paper "Source apportionment vs. emission inventories of NMHC in the middle East" by Salameh et al., presents emission factors derived from in-situ measured NMHC data in Beirut. Evaluation of emission inventories and numbers – also for NMHC - is a prevailing topic. In recent years several data sets have been assessed using PMF analysis (e.g. Sauvage et al, 2009; Leuchner et al. 2015, Yuan et al., 2012 and citations therein). Thus, this methodology is not new but was mostly applied to urban/rural sites in Europe, the US and the Far East. Here presented PMF results and derived emission factors are based on two 2-week measurement campaigns at a suburban site in Beirut, Lebanon. The respective data have been evaluated already in Salameh et al. (2015). This paper builds upon the therein presented results but unfortunately misses to wrap up and to discuss some of the previous results (from Salameh et al. 2015) with respect to the here presented work. Most prominent, it lacks a sufficient discussion of the range of uncertainty for the derived emission numbers. Nevertheless, it is a valuable data set from the Middle East, where data are usually very sparse, and it can thus add to our understanding and improvement of regional and global NMHC distributions and emissions. Therefore, I recommend this paper for publishing after some revision. As I am not a native speaker myself, please, review the technical corrections below critically.

Author's comment (AC): Thank you for your valuable comment. First, I would like to clarify that this paper does not present emission factors as mentioned in your comment. Here we present the emission sources of VOCs derived as factors from the PMF model.

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"Specific comments":

1-p.26798 l.22 Are 1.02% of the GPD much? How does it compare to other states? (I am afraid I have no idea. . .)

AC1: The World Bank also reported the cost of environmental degradation of air quality in other countries of the Middle East region. For instance, in Egypt it was ∼2% of the GDP in 1999; in Jordan (2006) as well as in Algeria (1999), it represented around 1% of the GDP. A joint study by the WHO Regional Office for Europe and the Organisation for Economic Cooperation and Development (OECD) published in April 2015 highlighted the economic cost of air pollution in 53 European countries. For instance, in France it was estimated at 2.3% of the GDP; in Sweden, Norway, and Finland, it was below 1% of the GDP; whereas in Ukraine, Serbia, and Moldova, it exceeded 20% of the GDP. In Lebanon, higher costs are expected in the current situation.

2-p.26799 l. 1 ". . .the particulate matter issue" – what issue? Rephrase or delete.

AC2: The phrase is deleted.

3-p. 26799 l.10 ". . .speciation profiles of the various emission sources" Do you mean the diversity in NMHC chemical composition of the emission profiles?

AC3: Yes, the chemical composition of the NMHC emission sources.

4-p.26801 l.18: Around 67 or exactly?

AC4: The word "around" is deleted.

5-p.26804 l.1: Why can the systematic integration error be neglected? This would only be the case if the chromatograms (characteristics of peak shapes, peak overlay) of the air sample and the calibration gas are very similar.

AC5: The systematic integration error can be neglected because the chromatograms of the air samples and the calibration gas for the considered species were quite similar, without any integration issues. This explanation is added to the manuscript.

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6-p.26804 l.7: Handling of data below the detection limit: If you replace the measured values below the detection by half the detection limit, do you not change the statistics?

AC6: This way of considering the data below the detection limit is rather common in literature and recommended in the PMF guidelines (Paatero and Hopke, 2003). Moreover, an uncertainty equal to 5/6*DL (Detection Limit) is then attributed to the measured values below the detection limit. The PMF model calculates the S/N (Signal to Noise) ratio which takes into consideration the concentration (x) and the uncertainty (s) of the species (i). Please refer to the figure below for the S/N formula.

A compound characterized by low concentrations or by a large number of observations (j) associated with relatively high uncertainties will have a low S / N ratio. Consequently, the data quality of a compound can be considered as strong if S/N $\geq$ 2, weak if 0.2<S/N<2, or bad if S/N $\leq$ 0. If the S/N ratio is less than 0.2, the species is excluded and if the ratio is greater than 0.2 but less than 2, the uncertainty is multiplied by four, reducing the importance of the species, marked as weak or bad, in the PMF analysis. Thus, concerning the detection limit and its impact on PMF results, this weighting principle makes this choice little influent.

7-p.26804 l.9-12: Sorry, I do not completely understand this paragraph: Which signal to noise ratios do mean? Peak area vs baseline noise? Please, help me here?

AC7: Kindly refer to my previous response (#6).

8-p.26804 l.13: You state that PMF requires a large sample. What does a large sample mean? Was the number of samples large enough? What do you mean with the data ". . .were lumped separately. . ."

AC8: According to the European guide on Air pollution source apportionment with receptor models (2014), the number of at least 100 samples is often mentioned although that depends on the degree of freedom and the number of variables. Therefore, the number of samples (time resolution of the measurement method) should be

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high enough to catch the variability of the sources and obtain stable and clear modeled factors. We applied the PMF model to the summer samples (298), and to the winter samples (179) separately.

9-p.26805 l.5: Section 4.1. It is a hillside location, correct? Therefore it might be effected by boundary layer changes. And in Salameh (2015), boundary layer effects were discussed to explain observed NMHC diurnal cycles. It would be nice to have a better overview/description of the meteorology. Was it a typical meteorological situation? Since you derive emissions for summer and winter from two weeks of measurements in each season, this would be an interesting fact to know.

AC9: This is a typical meteorological situation in summer season. The previous meteorological studies have shown the same wind regime controlled by the land-sea breeze circulation. Whereas, in winter there is no typical wind regime but the season is generally mild and the temperatures are not very low.

10-p. 26806 ff.: Numbering / names of Factors: eg. gasoline evaporation related to traffic is Factor 3 in winter but Factor 5 in summer. Though this numbering is probably a result of the analysis, I wonder if it might improve the understanding if you keep the same numbers for both seasons.

AC10: We changed the numbering of the factors according to their names in both seasons.

11-Fig.2: What is exactly shown? Do the weight percent reflect the relative abundance of the specific compound within a factor?

AC11: Yes, exactly. This explanation is added to the captions of figures 2 and 7: "Source composition profiles (relative abundance of specific compounds within each factor in weight %) . . ."

12-p.26806 l.25: "The average relative contribution of this factor is 19% in winter" – Just to be sure, you mean the Factor explains 19% of the observed variability of the

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NMHC data in winter?

AC12: Yes, it means the contribution of the factor to NMHC ambient levels.

13-p.26807-p.26808 Gasoline evaporation: In Salameh (2015), Fig. 2, you show that the wind was only on very few occasion coming from the North. And the few measurements with strongly elevated concentrations were measured at wind speed mostly below 2m/s (Fig. 6 this paper) indicating a very local source (highest concentration even at the lowest wind speed). Further, the diurnal cycle in winter (e.g. in Fig 3) how representative is this cycle for the whole period? The time series in Fig. 5 shows only two days with such a pronounced variability (and high concentrations at the same time) – is this really only traffic induced or might this be an effect of boundary layer changes during these days as well?

AC13: We have distinguished an episodic gasoline evaporation source located northern the measurement site (where the fuel storage facility is located at 3.6 km northern the site). When the wind blows from the north, the highest concentrations of the gasoline evaporation tracers are measured and it happens to be at noon when the temperatures are the highest contributing largely to the gasoline evaporation. That explains the diurnal cycle (fig. 3) as well as the time series (fig. 5) of the episodic gasoline evaporation source. The other gasoline evaporation is related to traffic because its diurnal profile (fig. 3) as well as the time series (fig. 5) display the same peaks as combustion related to traffic factor. Therefore, it is less likely to be an effect of boundary layer changes. Nevertheless, the apportionment of these two gasoline evaporation sources remains difficult when the wind blows from the North.

14-p. 26810: Why is there such intensive nighttime traffic? And why only in summer? Is this the effect of being outside the boundary layer in winter nights but still in the boundary layer during summer nights? This would modulate Factor 5, similarly. Summer PMF factors 5 and 3, could be a mixture of combustion and evaporation related sources which are in enriched after sunset due to a missing OH sink and the decreas-

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ing boundary layer height? Again, is this a typical situation for summer and winter time?

AC14: In summer at night, the highways networks are densely occupied. This is related to festivities and nightlife which increase during this touristic period in Lebanon and many Lebanese people living abroad come back during summer. At night, the wind direction is mostly from the North-East, the South, and South-West where are located these highways network. This situation is typical in summer. In winter, this situation could occur during December and January because of the festivities of Christmas and New Year's Eve.

15-Re-order sections 5 and 6– they seem not well structured. I suggest, to compare the summer and wintertime results in Section 5, only, and move the intercomparison with the emission inventories into Section 6, completely (e.g. starting from l. 19, p.26812)

AC15: We made the necessary modifications, thank you for your suggestion.

16-p.26812 l. 12: ". . .since the meteorological conditions are favorable." What exactly do you mean?

AC16: We mean high temperatures in summer which are favorable to biogenic VOC emissions.

17-p.26813 limitation of the study: This discussion is important and exhibits some interesting points but lacks some others, e.g. Uncertainties are hardly discussed though you derived them for the PMF analysis. With detection limits of up to 90ppt the uncertainty should influence the results of the PMF analysis essentially and thus uncertainty margins for the subsequently derived emission number would be interesting. You state in line 11, that the measurement site is located far from sources identified in the inventory. But the measurements clearly show very local sources (as you just mentioned on p. 26812, l.16). How does this affect the emission results? Really no effect of photochemical removal or long range transport? Or is it just covered by the strong local

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emissions? Did you observe a typical meteorological situation? These are essential questions if you estimate the emissions based on your measurements: Assuming that you measured very strong local sources, additionally enriched within the boundary layer it is plausible to assume further that the derived emissions are too high. It would be very interesting to have a more detailed discussion here. Especially, as I do think it is really likely that emission inventories underestimate the real emissions, substantially.

AC17: For the first part, please refer to my comment #6 above where I discussed the Signal to Noise ratio and the quality of data and how it is being handled by the PMF.

Effectively, the measurement site is far from some sources like the industries which are point sources and have a minor impact on VOC emissions according to the emission inventory (Waked et al. 2012), and from large forests.

The sources identified are from local origin. No effect of long range transport was observed during these measurements campaigns.

The impact of photochemistry was largely described in Salameh et al. 2015 as follows: It was assessed through the comparison of night-time and daytime scatterplots during summer and during winter. We assume that there is no photochemistry during night-time and the composition of emissions does not change. The advantage of using the mixing ratios of pairs of ambient NMHC species is that they are not sensitive to dilution and air-mass mixing compared with absolute concentrations themselves. Examining the ratios is useful in exploring the influence of photochemical depletion for compounds with different atmospheric lifetimes. The results show that the most reactive compounds are slightly affected by photochemistry (ethylene, m,p-xylenes) in summer and not affected at all in winter. As for less-reactive NMHC, there is no effect of photochemistry during both seasons. Therefore, the contribution of the most reactive species within the PMF factors is independent of their reactivity. Please refer to Salameh et al. 2015 for more detailed information.

18- p.26814ff: Emission numbers: Methodology: how does CO compare to NMHCs –

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would be interesting to see CO data? Is the observed ratio NMHC/CO stable? How good are the emission numbers for CO? Again, as mentioned above what are the uncertainties of the given emission numbers?

AC18: We added the mean concentration and the standard deviation of the measured CO during the measurements campaigns (P.26814 l.21). "The mean concentration of CO was equal to 470 $\pm$ 195 μg/m3 during summer, while it was equal to 388 $\pm$ 228 μg/m3 during winter campaign. The measured NMHC to CO ratio was estimated to 0.15 in summer and to 0.12 in winter." The time series and the diurnal cycle of CO concentrations present the same variation as the combustion related to traffic factors. The CO monthly emission numbers (in Gg) do not vary significantly, since CO is mainly emitted by the road transport which is dominant in winter and in summer (Waked et al. 2012).

19-p.26816: Methodologies of the inventories. Just to you information: maybe not thoroughly and really not easy to track but some information is available for EDGAR at the respective web site (http://edgar.jrc.ec.europa.eu/methodology.php and the EMEP/EEA air pollution inventory guidebooks). I agree, not easy to find and VOC are not listed in detail, however, the major "players" for the regarded NMHC emission factors are probably captured by your measurements as well as the emission inventories. For ACCMIP, Lamarque (2010) gives a speciation in Table 8 here in.

AC19: Thank you for the information. We have used these emission inventories covering Lebanon for their time resolution also: ACCMIP has a decadal time resolution; EDGAR has an annual time resolution, while MACCity has a monthly time resolution. Speciation of NMVOC emissions in all speciated emission inventory is performed using the RETRO (REanalysis of the TROpospheric chemical Composition) (Schultz et al., 2007) inventory and is kept constant because of the lack of additional information.

20-p.26816ff: Conclusions, first paragraph: ". . .Measurements of 67. . .performed . . .for the first time. . ." as you have published the data already in Salameh (2015) and

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included the same facts in the respective conclusion, I recommend to rephrase these sentences a bit. Last section: Absolutely true but would be even more convincing with a more detailed discussion in Sections 5 and 6.

AC20: We removed “for the first time”.

"Technical corrections":

1-Generally: Diel Cycle – diurnal cycle? Please stay with one term. (I usually use only diurnal cycle but do not claim that this is the correct wording...)

AC1: We replaced “diel” by “diurnal”.

2-p. 26797 l.13 – l.16: “. . .shows lower emissions than. . .” please rephrase this sentences. E.g. The PMF analysis finds 20-39% higher emission rates than the national road transport. . ..

AC2: We changed the sentence to: “The PMF analysis finds reasonable differences on emission rates, of 20 – 39 % higher than the national road transport inventory.”

3-p. 26798 l. 11 “. . .has been deteriorating. . .”

AC3: We mean “the air quality has been deteriorated” and not deteriorating.

4-p. 26798 l. 15: formulation not clear: is it 67ug/m3 higher than 40ug/m3, thus 107ug/m3?

AC4: No, we added “. . .67 μg/m3 which is higher than the WHO annual recommended value of 40 μg/m3”.

5-p.26798 l.20: please delete “Yet”

AC5: Deleted.

6-p.26798 l.24: “. . ., non-methane hydrocarbons. . .

AC6: Changed.

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7-p. 26799 l. 18-21 “Moreover, . . .the current emission inventory. . . overestimates. . . needs to be corrected” (not needed)

AC7: Changed.

8-p. 26799 l.25 “. . .emission uncertainties. . .”

AC8: Changed.

9-p. 26800 l.4: NMVOC? Do you mean NMHC? Further ozone (O3), nitrogen oxides (NOx) and so on, please check the manuscript for the proper first time introduction of molecular formulas.

AC9: NMVOC include also oxygenated compounds.

10-p.26800 l.10 – 19 better move into Section 3 (Source apportionment by Positive Matrix Factorization, between 3 and 3.1)

AC10: We prefer to leave it where it is because it justifies the choice of the PMF.

11-p.26800 l.10ff: “Several receptor. . .” please rephrase

AC11: We changed the phrase to: “The receptor modeling techniques are numerous; many of them have been previously used in NMHC source apportionment worldwide...”

12-p.26800 l.16: “. . .artificial dataset of VOCs” – please insert artificial.

AC12: We added “artificial”.

13-p.26800, l. 26-28: delete the dispensable sentences starting from “The experimental set-up...”

AC13: Deleted.

14-p.26801 l. 6ff: Change the order as usually should be location before time and thus “The measurements were conducted on the roof of the Faculty of Science. . ..from July 2 to 8, 2011, and again from January 28 to. . ..”

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AC14: The sentence is changed to: “The measurements were conducted on the roof of the Faculty of Sciences building of Saint Joseph University (33°87’ N, 35°56’ E) from 2 to 18 July 2011 in summer and again from 28 January to 12 February 2012 in winter.”

15-p.26801 l. 15/16: “. . .with an on-line thermal desorption gas chromatograph” or “. . .by on-line thermal desorption gas chromatography..”

AC15: We removed “an”: “NMHCs were continuously analyzed by on-line Thermal Desorption Gas Chromatography. . .”.

16-p. 26802 l.7-9: rephrase E.g. “NMHCs below the detection limit or not identified in both. . .”

AC16: We changed the phrase to: “NMHCs which are not identified during both seasons (like tetrachloroethylene) or their concentrations were frequently below the detection limits, were not considered in the PMF analysis.

17-p. 26803 l.16: “. . .obtained with Eq. (3)” please delete “the”

AC17: Deleted.

18-p. 26803 l.18: “. . . the working NPL standard gas”? Not clear, is it a “working standard” or a “standard gas”? No new line afterwards.

AC18: We removed “working”.

19-p. 26803 l.19:please rephrase a bit, e.g.: “Possible Systematic errors include the calibration gas uncertainty, systematic peak integration errors,. . .

AC19: The sentence is changed to: “Possible systematic errors include the calibration gas uncertainty, systematic peak integration errors, the sample volume determination, and potential blank value.”

20-p.26804 l.22 Section 3.3: Either, explain it more detailed or add it to the previous paragraph (3.2).

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AC20: We added an explanation: "...The diagnostic parameters include the value of Q, IM which is the maximum individual column mean and IS which is the maximum individual column standard deviation defined by Lee et al. (1999). Q, IM, and IS are then plotted against the number of factors (from 3 to 12). The number of factors chosen corresponds to a significant decrease of Q, IM, and IS. In order to control the rotation and to optimize the selected solution, the Fpeak parameter was used...".

21-p.26806 ff.: Please check the type setting for "ffi" in the word "traffic" or "ff" in "effect or different (e.g. p.26809 l. 4, l.14)

AC21: Checked within the whole word document.

22-p.26806 l.17 ff.: in my opinion it is enough to have the information UTC/GMT + 2h printed one time

AC22: "UTC/GMT + 2h" is mentioned one time.

23-p. 26807 l.12: ". . .of factor 3". Please, delete "the".

AC23: Deleted.

24-p.26807 l.14-16: ". . .including the larger contributors. . ." – please rephrase, as this is not clear. You mean, you regard only the larger contributors?

AC24: We changed the sentence: "Additionally, the profile of this factor, taking into account the larger NMHC contributors, is compared to three gasoline evaporation profiles..."

25-p.26807 l. 25: "Factor 5 is. . ." please, delete "The".

AC25: Deleted.

26-p.26807 l.26:please include "the" before isopentane and isobutene, thus "Nearly 42% of the isopentane. . ..of the isobutane. . .variability. . ."

AC26: We added "the" as requested.

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27-p.26809 l.9: ". . .related(. . .) to traffic. . .”; please include “to”

AC27: We added “to”.

28-p.26810 l.8: “the highway network”

AC28: We deleted the “S” in”highway”.

29-p.26810 l. 14: “Factor 5”, please delete “The”

AC29: Deleted.

30-p.26810 l.15: ". . .belongs to. . .” please, change the wording

AC30: “belongs to” was replaced by “related to”.

31-p.26811 l.2: ". . .close to the factor 5 composition. . .”, maybe better ". . .similar to the factor 5 compositon. . .”?

AC31: “Close” is replaced by similar”.

32-p.26814 l.10: ". . . for CO were 522 Gg. . .”

AC32: We added “Gg”.

33-p.26814 l.23: ". . .for Lebanon. . .” please, check comma placement!?

AC33: We removed the comma after before “for Lebanon”.

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$$\left(\frac{S}{N}\right)_j = \sqrt{\sum_{i=1}^{n}\left(x_{ij} - s_{ij}\right)^2 \Big/ \sum_{i=1}^{n} s_{ij}^2}$$

Figure 1 : S/N ratio formula

Fig. 1.

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