

**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. emission 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:***

*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.*

**“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. . .)

*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.  
*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?

*Yes, the chemical composition of the NMHC emission sources.*

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

*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.

*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.*

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?

*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).*

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

*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 1.9-12: Sorry, I do not completely understand this paragraph: Which signal to noise ratios do mean? Peak area vs baseline noise? Please, help me here?

*Kindly refer to my previous response (#6).*

8-p.26804 1.13: 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. . .”

*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 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 1.5: 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.

*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.

*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?

*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 1.25: “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 NMHC data in winter?

*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?

*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 enriched after sunset due to a missing OH sink and the decreasing boundary layer height? Again, is this a typical situation for summer and winter time?

*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)

*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?

*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 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.

*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 – 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?

*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  $470 \pm 195 \mu\text{g}/\text{m}^3$  during summer, while it was equal to  $388 \pm 228 \mu\text{g}/\text{m}^3$  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.

*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 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.

*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...)

*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. . .

*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. . .”

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

4-p. 26798 l. 15: formulation not clear: is it 67ug/m<sup>3</sup> higher than 40ug/m<sup>3</sup>, thus 107ug/m<sup>3</sup>?

*No, we added “...67 μg/m<sup>3</sup> which is higher than the WHO annual recommended value of 40 μg/m<sup>3</sup>”.*

5-p.26798 l.20: please delete “Yet”

*Deleted.*

6-p.26798 1.24: “. . . , non-methane hydrocarbons. . .

*Changed.*

7-p. 26799 1. 18-21 “Moreover, . . . the current emission inventory. . . overestimates. . . needs to be corrected” (not needed)

*Changed.*

8-p. 26799 1.25 “. . . emission uncertainties. . .”

*Changed.*

9-p. 26800 1.4: NMVOC? Do you mean NMHC? Further ozone (O<sub>3</sub>), nitrogen oxides (NO<sub>x</sub>) and so on, please check the manuscript for the proper first time introduction of molecular formulas.

*NMVOC include also oxygenated compounds.*

10-p.26800 1.10 – 19 better move into Section 3 (Source apportionment by Positive Matrix Factorization, between 3 and 3.1)

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

11-p.26800 1.10ff: “Several receptor. . .” please rephrase

*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 1.16: “. . . artificial dataset of VOCs” – please insert artificial.

*We added “artificial”.*

13-p.26800, 1. 26-28: delete the dispensable sentences starting from “The experimental set-up. . .”

*Deleted.*

14-p.26801 1. 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. . .”

*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 1. 15/16: “. . .with an on-line thermal desorption gas chromatograph” or “. . .by on-line thermal desorption gas chromatography..”

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

16-p. 26802 1.7-9: rephrase E.g. “NMHCs below the detection limit or not identified in both. . .”

*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 1.16: “. . .obtained with Eq. (3)” please delete “the”

*Deleted.*

18-p. 26803 1.18: “. . . the working NPL standard gas”? Not clear, is it a “working standard” or a “standard gas”? No new line afterwards.

*We removed “working”.*

19-p. 26803 1.19: please rephrase a bit, e.g.: “Possible Systematic errors include the calibration gas uncertainty, systematic peak integration errors,. . .

*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 1.22 Section 3.3: Either, explain it more detailed or add it to the previous paragraph (3.2).

*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  $F_{peak}$  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, 1.14)

*Checked within the whole word document.*

22-p.26806 1.17 ff.: in my opinion it is enough to have the information UTC/GMT + 2h printed one time

*“UTC/GMT + 2h” is mentioned one time.*

23-p. 26807 1.12: “. . .of factor 3”. Please, delete “the”.

*Deleted.*

24-p.26807 1.14-16: “. . .including the larger contributors. . .” – please rephrase, as this is not clear. You mean, you regard only the larger contributors?

*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”.

*Deleted.*

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

*We added “the” as requested.*

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

*We added “to”.*

28-p.26810 l.8: “the highway network”

*We deleted the “S” in “highway”.*

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

*Deleted.*

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

*“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. . .”?

*“Close” is replaced by similar”.*

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

*We added “Gg”.*

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

*We removed the comma after before “for Lebanon”.*

### **References:**

Lamarque, J.-F., Bond, T. C., Eyring, V., Granier, C., Heil, A., Klimont, Z., Lee, D., Liousse, C., Mieville, A., Owen, B., Schultz, M. G., Shindell, D., Smith, S. J., Stehfest, E., Van Aardenne, J., Cooper, O. R., Kainuma, M., Mahowald, N., McConnell, J. R., Naik, V., Riahi, K., and van Vuuren, D. P.: Historical (1850–2000) gridded anthropogenic and biomass burning emissions of reactive gases and aerosols: methodology and application, *Atmos. Chem. Phys.*, 10, 7017–7039, doi:10.5194/acp-10-7017-2010, 2010.

Leuchner, M. et al.: Can positive matrix factorization help to understand patterns of organic trace gases at the continental Global Atmosphere Watch site Hohenpeissenberg?, *ACP*, 15, 1221-1236, 2015

Salameh, T., Sauvage, S., Afif, C., Borbon, A., Leonardis, T., Brioude, J., Waked, A., and Locoge, N.: Exploring the seasonal NMHC distribution in an urban area of the Middle East 15

during ECOCEM campaigns: very high loadings dominated by local emissions and dynamics, *Environ. Chem.*, 12, 316–328, doi:10.1071/EN14154, 2015.

Yuan, B., Shao, M., de Gouw, J., Parrish, D. D., Lu, S., Wang, M., Zeng, L., Zhang, Q., Song, Y., Zhang, J., and Hu, M.: Volatile organic compounds (VOCs) in urban air: how chemistry affects the interpretation of positive matrix factorization (PMF) analysis, *J. Geophys. Res.-Atmos.*, 117, D24302, doi:10.1029/2012JD018236, 2012.

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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. emission 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

**Anonymous Referee #1**

The authors use two datasets comprised of 56 non-methane hydrocarbons, CO, and NO<sub>x</sub> measured in winter 2011 and summer 2012 at a suburban site near Lebanon in order to investigate the relative contributions of various NMHC sources in the region using positive matrix factorization. The output of the source-receptor model is used to identify the major NMHC sources by comparison to measured sources and literature values, quantify the relative contributions of each modeled source, compare seasonal differences in sources and source strengths, and compare the source factors to local and global emission inventories. Gasoline and traffic-related sources are the largest contributors to observed NMHC levels in both seasons. The observed NMHC to CO ratios are used to compare the PMF-derived source profiles associated with on-road transportation to emission inventories. The authors have determined that the relative contribution of the on-road transportation sector to total NMHC emissions agree with the inventory; however, the overall magnitude of NMHC emissions in the inventory may be underestimated by a factor of 1.3-1.6 in the Lebanon NEI and a factor of 2.7-3.4 in global emission inventories for the road transport sector.

I recommend publication with major revisions as detailed below:

Major comments:

1. The NMHC measurements are not presented in the manuscript, only the PMF outputs are presented. In the introduction, the authors state that data in this region of the world is particularly scarce and is only limited to a few pollutants. I'm curious why the authors would not publish their measurements here, even if it appears in the supplemental material. If the NMHC measurements are published elsewhere (or will be), then it should be made more clear within the manuscript. It looks to be a very valuable dataset that would be very useful to the larger scientific community.

*Thank you for your comment. The data have been already published and described in details in two papers Salameh et al. 2014 and Salameh et al. 2015 that we cited within the manuscript. For more details, please find below are the two references.*

Salameh, T., Afif, C., Sauvage, S., Borbon, A., and Locoge, N.: *Speciation of Non-Methane Hydrocarbons (NMHC) from anthropogenic sources in Beirut, Lebanon, Environ. Sci. Pollut. R., 21, 10867–10877, doi:10.1007/s11356-014-2978-5, 2014.*

Salameh, T., Sauvage, S., Afif, C., Borbon, A., Leonardis, T., Brioude, J., Waked, A., and Locoge, N.: *Exploring the seasonal NMHC distribution in an urban area of the Middle East during ECOCEM campaigns: very high loadings dominated by local emissions and dynamics, Environ. Chem., 12, 316–328, doi:10.1071/EN14154, 2015.*

2. The author's state that photochemistry was negligible, but do not provide any basis for this conclusion. This is particularly important topic since the PMF results show 2 different traffic related sources in which the author's identify by day and nighttime traffic patterns. Please provide a brief description of how the author's came to this conclusion as is very important for the interpretation of the PMF results.

*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.*

3. The uncertainties (i.e., the actual numbers) of each NMHC should be clearly stated in Section 2. Why did the author's not include CO and NO<sub>x</sub> (especially as NO or NO<sub>2</sub>) in the PMF analysis? It's not clear which species were excluded from the PMF analysis. For example, P26802 L10 says that species below detection limit were excluded, but P26804 L7 says they were replaced by 1/2 the detection limit, while P26813 L17 states that terpenes and OVOCs were not included in the PMF analysis. Does this mean they were measured, but excluded? If so, why? P26804 L5: What constitutes "missing data"? Were whole samples replaced by median values or only a few individual points within a sample. What percentage of the data was missing or replaced?

*The uncertainties are added in section 3.2 after the description of the estimation of the uncertainty: "The relative expanded uncertainty ranged between 4 and 27% in summer for all the compounds excepting for octane which was 38%. In winter, the relative expanded uncertainty was between 5 and 35% for most of the compounds excepting for trimethylbenzenes, isoprene, octane and heptane which had an uncertainty between 40 and 60 %."*

*We did not include the CO and NO<sub>x</sub> in the PMF analysis because we preferred to use them as ancillary data to help in the identification of the PMF factors. Some OVOCs were measured and will be the subject of an upcoming study.*

*We changed the sentence P26802 L10 : “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.”*

*In Salameh et al. 2015, table 1 shows the mean, median, percentage of values below the detection limit (DL), maximum, and standard deviation of each species. The concentrations below detection limit of the species used in the PMF were replaced by 1/2 the detection limit.*

*The percentage of missing data ranged from 0 to 6%. Therefore, only a few individual points were replaced by median values.*

4. There is very little discussion on solvent use as a potential NMHC source as the PMF analysis did not resolve a factor for this potential source. Does this mean that solvent use is a negligible source in the region, as least in comparison to traffic related sources? If so, how does this compare to the emission inventory?

*Effectively, according to the national emission inventory, the anthropogenic sources including NMHC product source (like solvent use) is a negligible source of NMHC with a relative contribution of 6 % of total emissions.*

5. Figures 2 and 7 are extremely hard to decipher and yet they are the subject of the majority of the discussion section. In the current format, the species names are unreadable and it is very difficult to compare the contributions of the various sources to a particular compound (e.g., propane). Suggested changes include stacking the various Factor outputs (panels) vertically so that the width of the graphs can be expanded and the names of the individual species can more easily read on the bottom of the figure. Also, it would make more sense to arrange the species by chemical family (alkanes, alkenes, aromatics, etc.) rather than by retention time which has nothing to do with the source profiles or interpretation of the PMF results.

*We changed figures 2 and 7 following your suggestion, and we arranged the species by chemical family. We changed also the numbering of the factors according to their names in both seasons.*

**Minor comments and technical corrections in order of appearance:**

1-P26797 L13-16: I'm not sure what the following means: “The national road inventory shows lowest (lower?) emissions than the ones from PMF but with reasonable difference (?) lower than 50%. Global inventories show higher discrepancies with lower emissions up to a factor of 10 for the transportation sector.” Please rephrase.

*The text is changed to: “The PMF analysis finds reasonable differences on emission rates, of 20 – 39 % higher than the national road transport inventory. However, global inventories (ACCMIP, EDGAR, MACCity) underestimate the emissions up to a factor of 10 for the transportation sector.”*

2-P26798 L5: urbanization → urban

*We kept “urbanization” because it describes better what we want to say.*

3-P26798 L11: deteriorated → deteriorating?

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

4-P26798 L24: Non-Methane Hydrocarbons does not need to be capitalized.

*We changed it.*

5-P26798 L24-P26800 L5: This is one massive paragraph that can easily be split into multiple smaller paragraphs that will be easier to read and digest.

*We separated the paragraph into 5 smaller paragraphs.*

6-P26799 L4: exhausts → exhaust

*Changed.*

7-P26800 L14: “and” in China

*Added.*

8-P26804 L1-4: Why can the integration error be neglected? What is a “coverage factor”?

*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.*

*The coverage factor “k” is chosen on the basis of the desired level of confidence to be associated with the interval defined by  $U = k \cdot u_c$  (where “U” is the expanded uncertainty, “ $u_c$ ” is the total calculated uncertainty).  $k = 2$  defines an interval having a level of confidence of approximately 95 %, when the normal distribution applies.*

9-Move Section 4.1 to Section 2

*We find that it is more convenient to keep it within the results section since it describes the meteorological conditions during these measurements campaigns.*

10-P26804 L23-25: Is domestic heating source included in Factor 1 (regional traffic)? This is confusing.

*Factor 1 represents a combustion source mainly related to regional traffic. Nevertheless, the small peaks observed in the evening at 20:00 - 21:00 can be also due to domestic heating because the measurement site is surrounded by a residential area. We could not separate the combustion related to domestic heating because we do not have specific tracers.*

11-P26807 L14: Please describe what “hot soak” refers to.

*Hot soak is a type of evaporative emissions which occurs when a warmed-up vehicle is stationary and the engine is stopped.*

12-P26807 L18: Remove “In fact,” and “the” before light-duty

*Removed.*

13-P26808 L1” “The fingerprint is consistent with the one of other gasoline evaporation profiles.” Please rephrase for clarity.

*The sentence is changed to: “The fingerprint of the chemical composition is consistent with the ones of typical gasoline evaporation profiles established by near field measurements.”*

14-P26810 L7: North-East → northeast; South-West → southwest

*Changed in the text.*

15-P26810 L11: It says that the emission increase, but does the composition change? The composition is most critical to the PMF analysis.

*According to the French study of Fontaine (2000), less significant changes impact the composition when the vehicles speed is low in the case of vehicles running on gasoline without a functioning catalytic converter. Even though, the contribution of alkynes, alkenes and alkanes is more pronounced at low vehicles speed.*

*Vehicle engine, vehicle age and maintenance, environmental conditions especially ambient temperature, as well as emission controls, and fuel composition are important factors to consider because they may change from a place to another.*

16-P26810 L24: change “suggesting the gas leakage” to “suggesting natural gas (or liquefied petroleum) gas leakage”

*Changed.*

17-P26812 L30: “. . .but always maintained as the main contributor to NMHC emissions.” This needs rephrasing or removal.

*Removed.*

18-P26813 L8: “. . .and is associated with levels of uncertainties. . .” I’m not sure what this means.

*Removed.*

19-P26813 L27: somehow → somewhat

*Changed.*

20-P26815 L1: “reasonably underestimates” Remove “reasonably” or rephrase.

*We removed “reasonably”, the sentence is changed to: “These results suggest that the inventory underestimates the road transport emissions in a reasonable way.”*

21-P26815 L3: “estimated to be 29 Gg”

*We added “be”.*

22-P26815 L22: “estimate to be 8 Gg, which is a factor of 6 to 10 lower than the annual emissions. . .”

*The sentence is changed to: “The total annual NMVOCs transportation emissions from the ACCMIP are estimated to be 8 Gg, which is a factor of 6 to 10 lower than the annual emissions...”*

23-P26815 L25: “factor of 2 to 3” . . .what?

*We changed the sentence to: “...the annual transportation emissions are estimated to be 23 Gg, which is a factor of 2 to 3 lower than the road transport national inventory emissions and the annual emissions obtained via the PMF results.*

24-P26815 L28-P26816 L3: This is an incomplete sentence and the meaning is unclear.

*The sentence is changed to: “This comparison reveals that global inventories are not consistent between each other. Additionally, The global inventories do not describe the methodologies applied neither the data used (emission factors, NMVOC species considered...)”*



## Source apportionment vs. emission inventories of non-methane hydrocarbons (NMHC) in an urban area of the Middle East: local and global perspectives

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### **Abstract:**

1 We applied the Positive Matrix Factorization model to two large datasets collected  
2 during two intensive measurement campaigns (summer 2011 and winter 2012) at a  
3 sub-urban site in Beirut, Lebanon, in order to identify NMHC sources and quantify  
4 their contribution to ambient levels. Six factors were identified in winter and five  
5 factors in summer. PMF-resolved source profiles were consistent with source profiles  
6 established by near-field measurements. The major sources were traffic-related  
7 emissions (combustion and gasoline evaporation) in winter and in summer  
8 accounting for 51 wt. % and 74 wt. % respectively in agreement with the national  
9 emission inventory. The gasoline evaporation related to traffic source had a  
10 significant contribution regardless of the season (22 wt. % in winter and 30 wt.% in  
11 summer). The NMHC emissions from road transport are estimated from observations  
12 and PMF results, and compared to local and global emission inventories. The PMF  
13 analysis finds reasonable differences on emission rates, of 20 – 39 % higher than  
14 the national road transport inventory. The national road transport inventory shows  
15 lowest emissions than the ones from PMF but with a reasonable difference lower  
16 than 50%. However, Global inventories (ACCMIP, EDGAR, MACCity)  
17 underestimate the emissions show higher discrepancies with lower emissions up to a  
18 factor of 10 for the transportation sector. When combining emission inventory to our  
19 results, there is a strong evidence that control measures in Lebanon should be  
20 targeted on mitigating the NMHC emissions from the traffic-related sources. From a  
21 global perspective, an assessment of VOC anthropogenic emission inventories for  
22 the Middle East region as a whole seems necessary as these emissions could be  
23 much higher than expected at least from the road transport sector.

**Keywords:** VOC; Positive Matrix Factorization (PMF); urban area; emissions; traffic; emission inventories

**Highlights:**

- PMF model was applied to identify major NMHC sources and their seasonal variation.
- Gasoline evaporation accounts for more than 40% both in winter and in summer.
- NMHC urban emissions are dominated by traffic related sources in both seasons.
- Agreement with the national emission inventory regarding the relative contribution of the on-road mobile source.
- ~~but a~~Disagreement in terms of emission quantities suggesting an underestimation of the global inventories.

24 **1. Introduction**

25 Fast urbanization expansion, high population density, industrialization,  
26 intensive transport networks, and negligent pollution control have led to a substantial  
27 degradation of air quality in the Middle East (MEA) region (UNEP, 2006). Nowadays,  
28 air quality is taken as a major aspect of the quality of life leading to sustainable  
29 development in many areas of the world.

30 In Lebanon, a developing country in the MEA, which is located in Western Asia on  
31 the eastern shore of the Mediterranean Sea, air quality has been continuously  
32 deteriorated leading to high pollutant levels exceeding the World Health Organization  
33 (WHO) recommended values (WHO, 2005); for instance, Afif et al. (2009) reported  
34 an annual average concentration of nitrogen dioxide (NO<sub>2</sub>) in Beirut from December  
35 2004 to June 2006, of 67 µg/m<sup>3</sup> which is higher than the WHO annual recommended  
36 value of 40 µg/m<sup>3</sup> (WHO, 2005). In addition, high levels of particulate matter, PM<sub>10</sub>  
37 and PM<sub>2.5</sub>, were obtained with annual concentrations of 64 and 20 µg/m<sup>3</sup>  
38 respectively (Massoud et al., 2011) exceeding WHO guideline values of 20 and 10  
39 µg/m<sup>3</sup>. Although these measurements provide valuable information on air pollution,  
40 they are scarce and limited to a few pollutants. ~~Yet, in~~ the absence of adequate  
41 environmental policy and action, Lebanon is facing today significant urban air

42 pollution problems; the cost of environmental degradation of air quality was last  
43 estimated in 2001 at 1.02% of the annual gross domestic product (GDP) (Sarraf et  
44 al., 2004).

45 Among air pollutants, non-methane hydrocarbons (NMHCs) play an important  
46 role in urban areas since they contribute to the formation of photochemical oxidants  
47 such as ozone and peroxyacetyl nitrate (PAN) and they are also involved in the  
48 formation of secondary organic aerosols (SOA) (Seinfeld and Pandis, 2006)  
49 [significantly contributing to the particulate matter issue](#). Moreover, some species are  
50 associated with adverse health impact or even are carcinogenic (e.g. benzene, 1,3-  
51 butadiene, etc.) (WHO, 2000).

52 NMHCs are emitted mainly from anthropogenic sources in urban areas. Major  
53 anthropogenic sources include vehicle exhausts, fuel evaporation, solvent use,  
54 emissions of natural gas and industrial processes (Friedrich and Obermeier, 1999,  
55 Sauvage et al., 2009). While urban emission sources of NMHC are usually well  
56 identified, their relative importance is still under debate and can be region-dependent  
57 (Yuan et al., 2013).

58 Considering the diversity in chemical reactivity among NMHCs, their different  
59 ozone and SOA formation potentials (Carter 1994, Derwent et al., 2010) and the  
60 speciation profiles of the various emission sources, there is a clear need to identify  
61 and quantify NMHC emission sources, and their associated speciation by the  
62 development of regional emission inventories in order to apply efficient control  
63 strategies and air pollution management.

64 Moreover, emission inventories are used as input data for air quality models;  
65 therefore, their accuracy is also important for air quality impact assessment.  
66 However, recent in-situ observations have revealed persistent and high uncertainties  
67 in emission inventories in urban areas of post-industrialized countries. Borbon et al.  
68 (2013) found large discrepancies between observed emissions ratios and those  
69 calculated from the inventories in Los Angeles and Paris. Moreover, Gaimoz et al.  
70 (2011) showed that the current emission inventory for Paris strongly overestimates  
71 the volatile organic compounds (VOCs) emitted from solvent use and need [see](#) to be  
72 corrected. Niedojadlo et al. (2007) also revealed some inconsistency between  
73 emission inventory in Germany and source apportionment results, especially

74 regarding emissions related to solvent use. Those studies have revealed that  
75 source-receptor approaches could be a relevant alternative to emission inventories  
76 where provided observations are available.

77 For the MEA region, ~~uncertainties on~~ emissions uncertainties could be even  
78 higher. At present, local inventory/emission data and observations for their  
79 evaluation are sparse and not speciated, potentially resulting in higher uncertainty in  
80 modeling approaches (Waked and Afif, 2012, Waked et al., 2013). In particular, there  
81 is a paucity of data on NMHC levels and their emission sources in the Middle East  
82 region. At the global scale, several emission inventories exist but very few of them  
83 are speciated or exhibit fine temporal resolution (ECCAD database). For Lebanon, a  
84 recent work has led to the development of an atmospheric emission inventory of  
85 anthropogenic and biogenic sources considering CO, NO<sub>x</sub>, SO<sub>2</sub>, NMVOC, NH<sub>3</sub>,  
86 PM<sub>10</sub>, and PM<sub>2.5</sub>, for a base year of 2010 according to the 2009 EMEP/EEA  
87 guidelines (Waked et al., 2012).

88 The aim of this work is to identify major NMHC sources and quantify their  
89 contribution to NMHC concentrations on a seasonal basis by applying the source-  
90 receptor Positive Matrix Factorization model (PMF) to the observations collected at a  
91 suburban site in the urban area of Beirut, Lebanon, and evaluate its consistency with  
92 existing emission inventories. ~~Several~~ The receptor modeling techniques are  
93 numerous: many of them have been previously used in NMHC source apportionment  
94 worldwide including Principal Component Analysis (PCA), Positive Matrix  
95 Factorization (PMF), Chemical Mass Balance (CMB) and UNMIX like in Europe  
96 (Badol et al. 2008, Sauvage et al. 2009), the USA (Leuchner and Rappenglück  
97 2010), and in China (Guo et al. 2007, Yuan et al. 2013). The performance of four  
98 receptor models (PCA, PMF, CMB and UNMIX) was evaluated by Miller et al. (2002)  
99 by applying them to the same artificial dataset of VOCs. They found that PMF  
100 extracted factor profiles that most closely represented the major sources used to  
101 generate the simulated data, and concluded that PMF is the most appropriate model  
102 to explain the results (Miller et al., 2002).

103 A large set of speciated NMHC have been continuously measured during two-  
104 week periods in summer 2011 and winter 2012 in the frame of the Emission and  
105 Chemistry of Organic Carbon in the East Mediterranean (ECOCEM) experiment. The

106 consistency of the source composition obtained by the PMF on a seasonal basis is  
107 evaluated with regards to NMHC source profiles established by canister sampling in  
108 the vicinity of emission sources (Salameh et al., 2014). Finally, PMF results are used  
109 to evaluate local and global emission inventories. ~~The experimental set-up is  
110 described in section 2. The PMF implementation is discussed in section 3. PMF  
111 results are reported in section 4 and discussed in section 5. The evaluation of  
112 emission inventories is discussed on section 6.~~

## 113 2. Experimental procedures

### 114 2.1. Sampling site: location and surroundings

115 The site was chosen in a way to be far enough from strong direct emissions  
116 (industrial, road transport) since they can hide the emissions from distant sources. At  
117 the same time, the site is appropriately located in order to receive the air masses  
118 coming from Greater Beirut Area (Figure 1). The measurements were conducted on  
119 the roof of the Faculty of Sciences building of Saint Joseph University (33°87' N,  
120 35°56' E) from 2 to 18 July 2011 in summer and again from 28 January to 12  
121 February 2012 in winter ~~on the roof of the Faculty of Sciences building of Saint~~  
122 ~~Joseph University (33°87' N, 35°56' E)~~. The site is located in the eastern suburb of  
123 the city of Beirut (6 km South-East of Beirut downtown) at an altitude of 230 m ASL  
124 (Above Sea Level). The site is surrounded by a forested pine area and a high density  
125 of residential premises. Beirut International Airport is located 8 km southwest of the  
126 site and one fuel storage facility is located at 3.6 km north (Salameh et al., 2014).

### 127 2.2. Material and methods

128 NMHCs were continuously analyzed by ~~an~~ on-line Thermal Desorption Gas  
129 Chromatography with a Flame Ionization Detector (TD-GC-FID) provided by Perkin  
130 Elmer described elsewhere (Salameh et al., 2014). The on-line measurement was  
131 performed hourly, covering 30 minutes of ambient air sampling. ~~Around 67~~ NMHCs  
132 from C2 to C9 belonging to alkanes (29), alkenes (19), alkynes (2) and aromatics  
133 (17) were identified and quantified. The detection limits were around 40 pptv for the  
134 targeted compounds except for ethane and ethylene (90 pptv). A certified NPL  
135 (National Physical Laboratory) standard of NMHC mixture (~4 ppbv) was used to  
136 determine and check the stability of the GC carbon response during both  
137 measurement periods.

138 Additional trace gases including carbon monoxide (CO), NO<sub>x</sub> and O<sub>3</sub> were  
 139 measured on-line on a 1 min basis using trace gas analyzers. Basic meteorological  
 140 parameters (wind speed and direction, temperature, relative humidity and  
 141 atmospheric pressure) were measured on a 1 min basis during both campaigns.

### 142 3. Source apportionment by Positive Matrix Factorization (PMF)

#### 143 3.1. PMF model description:

144 The USEPA PMF v3.0 was applied for NMHC source apportionment analysis.  
 145 This method is described in details elsewhere (Paatero and Tapper, 1994, Paatero,  
 146 1997). NMHCs which are not identified during both seasons (like  
 147 tetrachloroethylene) or their concentrations were frequently below the detection  
 148 limits. Some NMHCs were not considered in the PMF analysis. since they were not  
 149 identified during both seasons (like tetrachloroethylene) or their concentrations were  
 150 below the detection limits.

151 According to the PMF, an observed concentration at a receptor site can be viewed  
 152 as a data matrix  $X$  of  $i$  by  $j$  dimensions in which  $i$  number of samples and  $j$  chemical  
 153 species were measured.

$$154 \quad x_{ij} = \sum_{k=1}^p g_{ik} f_{kj} + e_{ij} \quad (1)$$

Code de champ modifié

155 where  $g_{ik}$  is the mass contribution of the  $k$ <sup>th</sup> source to the  $i$ <sup>th</sup> sample,  $f_{kj}$  is the  $j$ <sup>th</sup>  
 156 species mass fraction from the  $k$ <sup>th</sup> source,  $p$  is the number of independent sources,  
 157 and  $e_{ij}$  is the residual associated with the concentration of the  $j$ <sup>th</sup> species in the  $i$ <sup>th</sup>  
 158 sample. The solution of the equation is obtained by minimizing the residual sum of  
 159 squares  $Q$  given by:

$$161 \quad Q = \sum_{i=1}^n \sum_{j=1}^m \frac{e_{ij}^2}{s_{ij}^2} = \sum_{i=1}^n \sum_{j=1}^m \left( \frac{x_{ij} - \sum_{k=1}^p g_{ik} f_{kj}}{s_{ij}} \right)^2 \quad (2)$$

162 where  $f_{kj} \geq 0$  and  $g_{ik} \geq 0$  and where  $n$  is the number of samples,  $m$  the number of  
163 considered species, and  $s_{ij}$  an uncertainty estimate for the  $j^{\text{th}}$  species measured in  
164 the  $i^{\text{th}}$  sample.

165 The results are constrained so that no sample can have significantly negative source  
166 contributions. The goal is to identify the number of factors  $p$ , the species profile  $f$  of  
167 each source, and the amount of mass  $g$  contributed by each factor to each individual  
168 sample by using measured source profile information, meteorological parameters  
169 analysis, and additional species.

### 170 3.2. PMF model implementation:

171 One of the advantages of the PMF is to consider the uncertainty of each individual  
172 concentration. Special attention was paid to the estimation of the uncertainty. For  
173 each measured concentration, an uncertainty was calculated following the method  
174 developed within the ACTRIS (Aerosols, Clouds, and Trace gases Research  
175 InfraStructure) network (Hoerger et al., 2015, see supplemental material). It includes  
176 the systematic errors in the measurement and the precision which reflects the  
177 random errors. Thus, the total uncertainty of a measurement is obtained with ~~the~~  
178 equation 3:

$$179 \Delta x^2_{\text{unc}} = \Delta x^2_{\text{precision}} + \Delta x^2_{\text{systematic}} \quad (3)$$

180 The precision is derived from a series of measurements of the ~~working~~-NPL standard  
181 gas. It covers the random errors of the sampling and analytical system.

182 ~~The p~~Possible systematic errors ~~can be due to include~~ the calibration gas uncertainty,  
183 ~~to the systematic~~ peak integration errors, ~~to the~~ sample volume determination, and ~~to~~  
184 ~~the~~ potential blank value (Hoerger et al., 2015, see supplemental material).

185 Therefore, the overall systematic error is described as follows:

$$186 \Delta x^2_{\text{systematic}} = \Delta x^2_{\text{calibration}} + \Delta x^2_{\text{integration}} + \Delta x^2_{\text{volume}} + \Delta x^2_{\text{blank}} \quad (4)$$

187 The systematic integration error can be neglected because the chromatograms of  
188 the air samples and the calibration gas for the considered species were quite similar,  
189 without any integration issues.

190 The systematic volume error is neglected since  $\delta V_{\text{sample}} = \delta V_{\text{calibration}}$ .

191 For the expanded uncertainty, the total uncertainty calculated is multiplied by the  
192 coverage factor  $k=2$ .

193 The relative expanded uncertainty ranged between 4 and 27% in summer for all the  
194 compounds excepting for octane which was 38%. In winter, the relative expanded  
195 uncertainty was between 5 and 35% for most of the compounds excepting for  
196 trimethylbenzenes, isoprene, octane and heptane which had an uncertainty between  
197 40 and 60 %.

198 The missing data were replaced by the median of the concentrations measured the  
199 other days at the same hour; and in these cases, the uncertainty was set as four  
200 times the concentration. Values reported as below DL were replaced by half of the  
201 DL and the corresponding uncertainty was set as 5/6 of the DL value.

202 Paatero and Hopke (2003) have introduced the signal-to-noise ratio (S/N) which  
203 indicates whether the variability in the measurements is real or within the noise of the  
204 data. If the S/N ratio is less than 0.2, the species is excluded and if the ratio is  
205 greater than 0.2 but less than 2, the uncertainty is multiplied by four.

206 For a reliable identification of the sources, the PMF requires a large number of  
207 samples. The large datasets collected during the two campaigns were lumped  
208 separately for PMF source apportionment seasonal analysis. By taking into  
209 consideration the different existing reactivities, mainly with OH radical within the  
210 NMHC species, the profile of each source may change temporally during transport of  
211 emission plumes. Nevertheless, we have examined the factors influencing the  
212 distribution of NMHCs (Salameh et al., 2015) and we concluded that NMHCs were  
213 freshly emitted from local sources in winter but also in summer, and the chemical  
214 losses of NMHC species, even for the most reactive species, were likely not  
215 significant.

### 216 **3.3. Determination of the optimal solution:**

217 Several base runs were performed with different number of factors from 3 to  
218 12. The diagnostic parameters include the value of Q, IM which is the maximum  
219 individual column mean and IS which is the maximum individual column standard  
220 deviation defined by Lee et al. (1999). Q, IM, and IS are then plotted against the  
221 number of factors (from 3 to 12). The number of factors chosen corresponds to a



222 [significant decrease of Q, IM, and IS](#). In order to control the rotation and to optimize  
223 the [selected](#) solution, the  $F_{\text{peak}}$  parameter was used. Six factors were extracted from  
224 winter dataset and five from summer dataset. Quality indicators from the PMF  
225 application are summarized in Table 1.

## 226 **4. Results and discussion**

### 227 **4.1. Meteorological conditions**

228 Lebanon is characterized by a narrow coastal strip located on his western part  
229 and by the Bekaa valley located between the Western and Eastern Lebanese  
230 mountain chains. The coastal region has a Mediterranean climate with land–sea  
231 breeze circulation. During the summer measurement campaign, the temperature at  
232 the Saint Joseph University site ranged from 20 to 29°C with an average of 25°C.  
233 The average wind speed was 2 m.s<sup>-1</sup> with a maximum wind speed of 10 m.s<sup>-1</sup> during  
234 the day coming mostly from the South-West and from the North on July 7, 8 and 9.  
235 The wind direction was mostly from the North-East and slightly from South, South-  
236 West at night. During the winter measurement campaign, the temperature ranged  
237 from 7 to 22°C with an average of 13°C. The average wind speed was 2 m.s<sup>-1</sup> and  
238 the wind direction was mostly coming South-Easterly and Easterly (Salameh et al.,  
239 2015).

### 240 **4.2. Identification of PMF profiles**

241 In order to attribute PMF factors to emission sources, a comparison between  
242 extracted PMF profiles and speciated profiles established in the vicinity of emission  
243 sources by Salameh et al. (2014) was carried out, when possible. In addition, the  
244 [diel diurnal](#) cycle and time series of the contributions of modeled sources were  
245 analyzed with independent parameters like meteorological data and specific tracers  
246 like CO and NO<sub>x</sub>.

#### 247 **4.2.1. Winter PMF factor identification and contribution**

248 In winter, six sources were identified corresponding to combustion mainly  
249 related to regional traffic, combustion related to local traffic, gas leakage, gasoline  
250 evaporation related to traffic, gasoline evaporation as an episodic point source and a  
251 source characterizing the urban background. The composition of the source profiles

252 and the [diel](#)diurnal variations of the source contribution are reported respectively in  
253 Figures 2 and 3.

254 *Combustion mainly related to regional traffic*

255 **Factor 1** has significant amounts of toluene, m,p-xylenes, ethylbenzene,  
256 ethylene, acetylene, 1,2,4-trimethylbenzene & decane (co-eluted), and benzene  
257 which are typical combustion products. Almost 30% of the variances of ethylene,  
258 propene, acetylene and benzene are explained by this factor. This profile is very  
259 similar to the profile determined in the vicinity of the emission sources in Beirut which  
260 consists of exhaust and evaporative running losses from vehicles (Salameh et al.,  
261 2014). The factor contribution is well correlated with the concentrations of CO and  
262 NO<sub>x</sub> which are combustion tracers (R=0.8 and 0.7 respectively). The daily time  
263 series of the contribution of this source are characterized by a first significant  
264 increase of concentrations at around 07:00-08:00 LT (UTC/GMT+2 h), the second  
265 one at 14:00-15:00 LT, another increase at 17:00-18:00 LT and a small peak is  
266 observed at 20:00-21:00 LT in the evening. According to Waked et al. (2012), the  
267 diurnal variation profile for on-road mobile source in urban areas in Lebanon shows  
268 two significant increases in weekdays, a morning peak at around 07:00-10:00 LT and  
269 an evening peak from 16:00 to 18:00 LT consistent with the important peaks  
270 observed for factor 1. In addition, in winter, additional sources related to domestic  
271 heating should be considered since the measurement site is surrounded by  
272 residential area. The average relative contribution of this factor is 19 % in winter.

273 **Factor 26** is also characterized by some combustion tracers (ethylene,  
274 acetylene, toluene, benzene, propene, and m,p-xylenes). Nearly 50% of the  
275 variances of ethylene as well as propene are explained by this factor. The factor  
276 contribution strongly correlates with CO and NO<sub>x</sub> (R=0.8 and 0.7 respectively). This  
277 factor is associated to “combustion related to local traffic” since it doesn’t show a  
278 significant contribution during the weekend which is due to the limited local activity  
279 nearby the measurement site (schools, universities, residential area). The daily  
280 variation of this factor is characterized by an initial increase at 07:00-08:00 LT, a  
281 peak at 18:00-19:00 LT and the last peak in the evening at 20:00-21:00 LT. These  
282 enhancements are far less than those of factor 1. The average relative contribution  
283 of this factor is 10% in winter.

284 *Gasoline evaporation related to traffic*

285 Isopentane, butane, isobutane, toluene and 2-methylpentane are the main  
286 compounds of ~~the~~ **factor 3**. Most of isopentane (53%) and around 36% of butane  
287 and isobutane are explained by this factor. This strongly suggests that this profile is  
288 related to fuel evaporation. Additionally, the profile of this factor, taking into account  
289 including the larger NMHC contributors, is compared to three gasoline evaporation  
290 profiles established by near field measurements including the fuel storage facilities,  
291 hot soak (a type of evaporative emissions which occurs when a warmed-up vehicle  
292 is stationary and the engine is stopped) and refueling cars (Salameh et al., 2014) in  
293 figure 4. The fingerprint is consistent within all the gasoline evaporation source  
294 profiles confirming the nature of this source. In ~~fact, in~~ Lebanon, ~~the~~ light-duty  
295 vehicles operate on gasoline while only heavy duty vehicles are allowed to run on  
296 diesel (4 % of fleet in Beirut) (Waked and Afif, 2012). The diurnal profile as well as  
297 the time series in figure 5 display the same aforementioned peaks in factors 1 and  
298 6 especially in the morning and in the evening assuming that the gasoline  
299 evaporation is linked to traffic. The average relative contribution of this factor is 22 %  
300 in winter.

301 *Gasoline evaporation*

302 ~~The~~ **Factor 5** is also characterized by the C4-C5 alkanes, toluene and 2-  
303 methylpentane. Nearly 42% of the isopentane and pentane variability and 48% of the  
304 isobutane and butane variability are explained by this factor. The fingerprint of the  
305 chemical composition is consistent with the ones of ~~other~~ typical gasoline  
306 evaporation profiles established by near field measurements (fig. 4). The diurnal  
307 profile of this source contribution is marked by a night minimum and an increase in  
308 the midday. The time series presented in figure 5 shows that this factor (F5) is  
309 primarily episodic with high contribution originating from the North wind sector as  
310 demonstrated in the pollution rose in figure 6. The extremely high levels of the  
311 source contribution come from the North sector where the fuel storage facilities are  
312 located (fig. 6). A collinearity between both gasoline evaporation factors (F3 and F5)  
313 is observed around noon when the wind blows from the North sector since the  
314 highest contributions are detected in this sector making the apportionment difficult.  
315 The average relative contribution of this factor is 21 % in winter.

316 *Gas leakage*

317 58% of propane variability is explained by **factor 26**. The composition of this  
318 source is mainly impacted by high loadings of propane, butane and isobutane which  
319 are the signatures of LPG (Liquified Petroleum Gas) (Blake and Rowland 1995).  
320 Hence, this source is attributed to gas leakage mainly LPG from residential use. LPG  
321 is the main fuel for cooking in households in Lebanon and it is used, among others,  
322 for domestic heating. The diurnal profile of this factor does not show significant  
323 peaks, only some small peaks are observed in the morning, at noon and in the late  
324 evening (fig. 3). The average relative contribution of this factor is 10 % in winter.

325 *Background*

326 Long-lived species are dominant in **factor 4**. The ethane and propane  
327 variability explained by this factor is 76% and 42% respectively, even though,  
328 toluene, butane and acetylene are also present in this profile. This factor is,  
329 therefore, categorized as urban background (Lanz et al. 2008, Sauvage et al. 2009).  
330 The diurnal profile of this factor does not show any significant peak and instead  
331 maintains the same contribution independently of the hour of the day (fig. 3). The  
332 average relative contribution of this factor is 18 % in winter.

333

#### 334 **4.2.2. Summer PMF profile identification and contribution**

335 One of the limitations of PMF application for summer data could be the effect  
336 of the photochemistry (Yuan et al., 2012). The effect of photochemistry has been  
337 assessed in Salameh et al. (2015), and the results showed a limited influence of the  
338 photochemistry in summer.

339 The five sources identified by the PMF analysis in summer correspond to  
340 combustion related (so-called nocturnal and diurnal) to traffic, gasoline evaporation  
341 related to traffic, gasoline evaporation as an episodic point source and a source  
342 characterizing the local background. The composition of the source profiles and the  
343 diel/diurnal variation of the source contribution are reported respectively in Figures 7  
344 and 8.

345 *Traffic related sources*

346 Two profiles (factor 1 and factor 3) related to traffic have been extracted with  
347 different contributions between day and night.

348 The profile of **factor 1** is essentially composed of aromatic compounds  
349 toluene, m,p-xylenes, o-xylene, ethylbenzene, 1,2,4-trimethylbenzene & decane (co-  
350 eluted), ethylene, acetylene and isopentane which are included in the traffic related  
351 sources (gasoline evaporation and combustion, fig. 9) and are present in the  
352 composition of factor F1 in winter (especially the aromatics). The diurnal variation  
353 shows high loadings during the day (fig. 8). A significant first increase is observed at  
354 07:00-08:00 LT (UTC/GMT+3 h), two other small peaks are observed during the  
355 afternoon (14:00-15:00 LT) and in evening (20:00-21:00 LT) comparable to the  
356 peaks observed in the combustion related to traffic during winter (winter F1). This  
357 factor is linked to traffic emissions occurring during the day and coming mainly from  
358 the dominating daytime the sSouth-Wwest sector. The average relative contribution  
359 of this factor, combustion related to diurnal traffic, is 17 % in summer.

360 Typical combustion tracers are the major contributors to the profile of the  
361 **factor 32**. The variability of acetylene (34%), ethylene (43%), propene (45%) and  
362 benzene (30%) is mostly explained by this factor. The daily variability of this factor  
363 displays high contributions during nighttime characterizing the combustion related  
364 mainly to nocturnal traffic. At night, the wind direction is mostly from the Nnorth-  
365 Eeast, the South, and Ssouth-Wwest where the highways network is densely  
366 occupied at night in summer and the vehicles run slowly. When the vehicles speed is  
367 low, especially in the case of vehicles running on gasoline without a functioning  
368 catalytic converter (Waked and Afif 2012), the NMVOC emissions increase (Fontaine  
369 2000). The average relative contribution of this factor is 27 % in summer.

#### 370 *Gasoline evaporation related to traffic*

371 ~~The f~~**Factor 53** encloses a high percentage of butane, toluene, propane, m,p-  
372 xylenes and isopentane which strongly suggests that this factor ~~belongs-is related~~  
373 to the gasoline evaporation. This factor exhibits also high loadings during nighttime  
374 alike the combustion related to nocturnal traffic factor ~~32~~ confirming the traffic as the  
375 origin of these two factors (F~~23~~ and F~~53~~).

376

377 By comparing both combustion (F1 and F23) and gasoline evaporation (F53) factors  
378 related to traffic profiles with the road transport profile established in near-field  
379 measurements (Salameh et al., 2014), which consists of exhaust and evaporative  
380 running losses from vehicles (figure 9), we notice the same overall fingerprint for the  
381 majority of the species, nevertheless, propane exhibits a high percentage in the  
382 gasoline evaporation profile and 75% of its variability is explained by this factor (F53)  
383 suggesting the liquefied petroleum gas leakage as an additional source to the  
384 gasoline evaporation. The average relative contribution of this factor is 30 % in  
385 summer.

386 *Gasoline evaporation (episodic point source)*

387 **Factor 25** is characterized by C4-C5 alkanes, toluene and 2-methylpentane  
388 ~~else~~ similar to the factor 5 composition in winter. This factor is gasoline evaporation  
389 showing a high contribution in the middle of the day. The pollution rose, as in winter,  
390 shows high contributions coming from the North sector, where the fuel storage  
391 facilities are located, as shown in figure 10 which corresponds to episodic events  
392 having occurred on July 7, 8 and 9. The average relative contribution of this factor is  
393 16 % in summer.

394 *Local background*

395 64% of the variability of isoprene, commonly used as the tracer of biogenic  
396 emissions, is explained by the **factor 4**. The profile of this factor consists largely of  
397 toluene, ethane, isopentane, m,p-xylenes, acetylene, butane and propene which are  
398 related to combustion. Therefore, “local background” is attributed to this factor  
399 including the regional background, the combustion from the surrounding sources, as  
400 well as the biogenic emissions from the forest nearby the measurement site. It is not  
401 possible to separate this type of source even by increasing the number of PMF  
402 factors. The diurnal profile shows higher contributions during the day starting 07:00 –  
403 08:00 LT and lower contributions during the night. The average relative contribution  
404 of this factor is 10 % in summer.

405

## 406 5. Similarities and differences between summer and winter results compared 407 to the National Emission Inventory for Lebanon -NEI-

408 Figure 11 summarizes the average relative contribution in weight % of each  
409 factor in winter and in summer. We found several common factors in winter and  
410 summer but their relative contribution was slightly different. For instance, the  
411 contribution of traffic related sources including the combustion and the gasoline  
412 evaporation from traffic accounted for 51% in winter and 74% in summer.  
413 Nevertheless, the episodic gasoline evaporation source contributed to 21% in winter  
414 and 16% in summer. This source was a major contributor to winter's NMHC  
415 concentrations reflecting the importance of gasoline evaporation in winter. If we  
416 consider the gasoline evaporation sources (episodic and related to traffic), we obtain  
417 a significant contribution of 43% in winter and 46% in summer.

418 Additional factors were found in winter but absent in summer. For instance, gas  
419 leakage due to the use of LPG in residential heating. Another factor characterizing  
420 the urban background highly contributed to winter's NMHC concentrations (18 %)  
421 mainly because of the meteorological conditions and the absence of photochemistry  
422 in winter (Salameh et al., 2015). A source characterizing the "local background"  
423 including the biogenic emissions was exclusively found in summer since the  
424 meteorological conditions are favorable. Nevertheless, this "local background" also  
425 includes regional background and combustion emissions.

426 Based on the PMF analysis, we conclude that the main contributors to the NMHCs  
427 are the combustion and gasoline evaporation sources in summer as well as in  
428 winter. These sources are of local origin confirming what has been demonstrated  
429 previously (Salameh et al., 2015) that there is no significant influence of long range  
430 transport of air masses on the NMHC concentrations.

## 431 6. Intercomparison with the National Emission Inventory for Lebanon -NEI-

432 The contribution of the factors discussed above is dependent ~~of~~ on the seasons and  
433 associated the meteorological conditions ~~in each season~~, therefore, care must be  
434 taken when comparing these results to the annual national emission inventory (NEI)  
435 for Lebanon.

436 The NEI is not specified, and was established for a base year of 2010 within the  
437 EEA/EMEP guidelines, by Waked et al. (2012), covering major anthropogenic and  
438 biogenic sources in the region with 5 km spatial resolution for Lebanon and 1 km  
439 spatial resolution for its capital city Beirut and its suburbs. The total VOC emissions

440 in Lebanon were estimated to be 115 Gg for the year 2010. According to this  
441 inventory, transport is the main source of NMVOCs with a relative contribution of  
442 67% of total emissions of VOCs in Beirut and its suburbs as well as in all over  
443 Lebanon. PMF results give nearly the same contribution of this sector in winter 51%  
444 and 74% in summer, ~~but always maintained as the main contributor to NMHCs~~  
445 ~~emissions~~. According to Waked and Afif (2012), the gasoline evaporation  
446 contribution was evaluated to be responsible for 8% of total NMVOC emissions in  
447 Beirut and its suburbs and 17 % of total NMVOC emissions at the national level  
448 based on gasoline consumption whereas the PMF gasoline evaporation (related to  
449 traffic) sources contributed to 22% in winter and 30% in summer.

450 The comparison held here is subject to several limitations. On one hand, the national  
451 emission inventory is not speciated, ~~and is associated with levels of uncertainties~~  
452 and it needs further improvements regarding the input data and the Lebanon-specific  
453 emission factors need to be established (Waked et al., 2012). On the other hand, the  
454 measurement site is qualified as sub-urban and is located far from some sources  
455 identified in the inventory, like for instance large forests representing biogenic  
456 sources, and industrial plants. These sources have not been identified in the PMF-  
457 resolved profiles since they weren't major sources during this study and some of  
458 them are located in the North and South of Lebanon far away from the measurement  
459 site. Additionally, it was hard to discern the biogenic source since the key tracers of  
460 this source such as terpenes and oxygenated volatile organic compounds (methanol,  
461 acetone...) were not included in the PMF analysis. Furthermore, the emission  
462 inventory data used for comparison are provided on annual statistical data, on a  
463 national scale whereas the data here is obtained from a single measurement site  
464 during a shorter time regarding a non-exhaustive list of species. Therefore, long term  
465 and continuous studies integrating more than one measuring site and more specific  
466 tracers are of great interest in order to provide more reliable information.

#### 467 **6.7. Comparison of PMF results and emission inventories for road transport**

468 Our study provides the first comprehensive observational constraints for a  
469 quantitative evaluation of anthropogenic emission inventories at local, national  
470 (Waked et al., 2012) and global levels for a Middle Eastern area. While such  
471 comparison is ~~somewhat~~~~somehow~~ limited as the basis for comparison is different



472 (NMHC speciation, number of NMHCs, temporal and spatial resolution), it still  
473 provides relevant insights on uncertainties and perspectives of improvement. The  
474 objective of this last section is to estimate NMHC emissions from the road transport  
475 sector from PMF results and carbon monoxide observations and to compare these  
476 values to the ones derived from various emission inventories.

#### 477 **6.4.7.1. Comparison to the National Emission Inventory for Lebanon -NEI-**

478 The annual emissions of air pollutants originating from on-road mobile sources in  
479 2010 in Beirut specifically and in Lebanon were investigated by Waked and Afif  
480 (2012). At a national level, the estimated annual emissions for CO were 522 Gg and  
481 48 Gg for NMVOCs by using the EMEP methodology (Waked and Afif, 2012). In  
482 parallel, we calculated separately, for each season, the ratio of the sum of the 59  
483 NMHC contributions (in  $\mu\text{g}/\text{m}^3$ ) coming from the PMF factors related to road  
484 transport (combustion and gasoline evaporation) and of the mean of the CO  
485 measured (in  $\mu\text{g}/\text{m}^3$ ) during each measurement campaign according to equation (5).  
486 Then, we used the estimated annual emissions for CO (Q) in Gg to generate the  
487 emissions of the 59 NMHCs based on the winter ratio on one hand, and on the  
488 summer ratio on the other hand, in order to give a range of annual emissions levels.

$$489 \quad \text{NMHC} = \text{ratio (NMHC/CO)}_{\text{ECOCEM}} \times Q_{\text{CO inventory}} \quad (5)$$

490 With NMHC = Sum of 59 measured species during ECOCEM (in Gg).

491 The mean concentration of CO was equal to  $470 \pm 195 \mu\text{g}/\text{m}^3$  during summer  
492 campaign, while it was equal to  $388 \pm 228 \mu\text{g}/\text{m}^3$  during winter campaign. The  
493 measured NMHC to CO ratio ~~for summer~~ was estimated to 0.15 in summer, whereas  
494 in winter it was equal and to 0.12 in winter.

495 By this method, the annual emissions, for Lebanon, ~~based on the summer ratio~~ are  
496 estimated to 78 Gg from the summer ratio and to 62 Gg by the winter ratio, which  
497 is are higher than the annual emissions of 48 Gg. ~~The same method using the winter~~  
498 ~~ratio estimates the annual emissions to 62 Gg.~~ In both cases, the emissions from the  
499 national road transport inventory are lower with a difference ranging from 22% for  
500 winter based emissions to 39% for summer based emissions (figure 12). These  
501 results suggest that the inventory ~~reasonably~~ underestimates the road transport  
502 emissions in a reasonable way. By applying the same calculation method for Beirut

Mis en forme : Exposant

503 and its suburbs, the annual emissions obtained using the summer ratio are  
504 estimated to ~~be~~ 29 Gg higher than the annual emissions calculated based on winter  
505 ratio (23 Gg) (figure 12).

506 The measurements we conducted are more representative of Beirut and its suburbs  
507 (Greater Beirut Area). The emissions from the inventory regarding the road transport  
508 for Greater Beirut Area are also lower with a difference ranging from 20% for winter  
509 based emissions to 37% for summer based emissions.

510 The discrepancies for Lebanon as well as for Beirut and its suburbs using winter and  
511 summer ratios are comparable since the road transport is the dominating sector in  
512 the whole country and especially in the capital.

#### 513 **6-2-7.2. Comparison to global emission inventories (for the road transport** 514 **sector)**

515 The objective here is to assess the PMF estimated emissions ~~modeled~~ to the  
516 global emission inventories for the road transport sector for 59 NMHCs and, where  
517 possible, for a common combustion tracer “ethylene” which is also an ozone  
518 precursor due to its reactivity towards the OH radical (Atkinson and Arey, 2003).

519 We estimated the annual total NMVOCs emissions for Lebanon by using a mean  
520 flux of total NMVOCs of 8 grids covering Lebanon surface area (ECCAD database)  
521 from the transportation sector ~~from evaluated by~~ the global historical emission  
522 inventory ACCMIP (Atmospheric Chemistry and Climate Model Intercomparison  
523 Project) (Lamarque et al., 2010) for 2000 at a spatial resolution of 0.5°. The total  
524 annual NMVOCs transportation emissions from the ACCMIP are estimated to ~~be~~ 8  
525 Gg, ~~which is a factor of 6 to 10 lower~~ than the annual  
526 emissions obtained via the PMF results (62 to 78 Gg) and the road transport national  
527 inventory emissions (48 Gg). This gap is expected to be a lower limit regarding the  
528 fact that PMF only consider 59 NMHCs. Nevertheless, when we apply the same  
529 method to another global inventory EDGARv4.2 (Emissions Database for Global  
530 Atmospheric Research) at a spatial resolution of 0.5°, the annual transportation  
531 emissions are estimated to ~~be~~ 23 Gg, ~~which is a factor of 2 to 3 lower than the road~~  
532 ~~transport national inventory emissions and the annual emissions obtained via the~~  
533 ~~PMF results~~. This comparison also reveals that global inventories are not consistent

534 between each other. ~~Additionally, the global inventories do not describe as a result of~~  
535 ~~different the~~ methodologies applied ~~and which were not presented in none of the~~  
536 ~~global inventories, and neither~~ the data used (emission factors, NMVOC species  
537 considered...).

538 For a more detailed evaluation of speciation accuracy, we compared the emissions  
539 of an individual NMHC, ethylene, obtained by the PMF results according to equation  
540 (5), where “NMHC” represents ethylene, to the emissions from a speciated inventory  
541 having a monthly temporal resolution, over the same period, called MACCity. The  
542 MACCity global emission inventory has been developed within two European  
543 Commission funded projects (MACC and CityZen) as an extension of the ACCMIP  
544 and RCP8.5 (Representative Concentrations Pathways) emission inventories  
545 (Granier et al., 2011) at a spatial resolution of 0.5°. Based on the PMF results, the  
546 emissions of ethylene during July 2011 are estimated to 0.30 Gg and 0.25 Gg during  
547 January 2012 for Lebanon. The MACCity global emission inventory displays very low  
548 ethylene emissions from the transportation sector (ECCAD database) during July  
549 2011 (0.05 Gg) and during January 2012 (0.04 Gg) for Lebanon (figure 12). The  
550 difference ~~with the PMF results~~ is ~~by therefore~~ a factor of 6 ~~with the PMF results~~.

## 551 **7.8. Conclusion**

552 Measurements of 67 gaseous organic carbon have been performed at a sub-  
553 urban site in Beirut ~~for the first time~~ during two intensive field campaigns in summer  
554 2011 and in winter 2012 within the framework of the ECOCEM project, resulting in a  
555 large and unique database, in order to improve our understanding of their major  
556 emission sources in the area.

557 The USEPA PMF v3.0 was applied to the winter and summer datasets in order to  
558 identify and quantify the source contribution. Six factors were then extracted in winter  
559 and five factors in summer. Source profiles established close to the main potential  
560 emitters by near field measurements (Salameh et al., 2014) were used to identify the  
561 PMF factors.

562 In winter, the six NMHC emission factors consist of traffic related sources including  
563 combustion mainly related to regional traffic, combustion related to local traffic and  
564 gasoline evaporation from vehicles accounting for 51%. In summer, the combustion  
565 and gasoline evaporation related to regional traffic contributed to 74% of which 57%

566 are nocturnal. Additionally, an episodic gasoline evaporation source originating  
567 principally from the fuel storage facilities was identified in winter and in summer  
568 contributing to 21% and 16% respectively. The gas leakage mainly LPG contributes  
569 to 10% and the urban background to 18% of the ambient NMHC levels during winter.  
570 A factor characterizing local background was identified in summer contributing to  
571 10%. Having similar species composition profiles, we found a difficulty in discerning  
572 the combustion related to power generators, running on diesel oil, within the  
573 combustion sources, hence, additional species (e.g. PM2.5 species measured with  
574 high temporal resolution) may have helped to extract this source.

575 Overall, the gasoline evaporation contribution (related to traffic and the episodic point  
576 source) was found to be a large contributor to the NMHC ambient concentrations:  
577 43% in winter and 46% in summer.

578 Control measures should be developed to mitigate the NMHC emissions resulting  
579 from traffic-related sources (combustion and gasoline evaporation).

580 Verification of the reported emission inventory for Lebanon and Greater Beirut Area  
581 can assist in the evaluation of future control strategy effectiveness. The comparison  
582 of the modeled results to the emission inventory shows an agreement regarding the  
583 load of the on-road mobile source, by considering the vehicle exhaust and gasoline  
584 evaporation linked to traffic, in both seasons. Nevertheless, the gasoline evaporation  
585 related to traffic is lower in the inventory (17%) by considering PMF summer results  
586 (30%) suggesting an underestimation of the inventory. We assessed also the  
587 accuracy of several global inventories for the transportation sector and high  
588 discrepancies [up to a factor of 10](#) still remain between the emission inventories.

589 To maximize current resources, continuous measurement of NMHC species and the  
590 implementation of ground based monitoring networks for ambient air quality  
591 monitoring and assessment are essential in order to conduct source apportionment  
592 which would be of less uncertainty and of greater help in establishing effective  
593 NMHC, ozone and PM abatement strategies in Lebanon.

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Table 1: Mathematical diagnostic for the PMF results.

|  | Summer | Winter |
|--|--------|--------|
| n (samples)  | 298    | 179    |
| m (species)  | 59     | 59     |
| k (factors)  | 5      | 6      |
| Q (model)  | 5670   | 1728   |
| NMHC <sub>modelled</sub> vs NMHC <sub>measured</sub> (R)             | 0.97   | 0.99   |
| F <sub>peak</sub>  | -0.5   | 0      |
| Mean ratio (modelled vs. measured)                                   | 1.05   | 0.99   |
| Number of species with R <sup>2</sup> >0.75 for modelled vs measured | 39     | 29     |

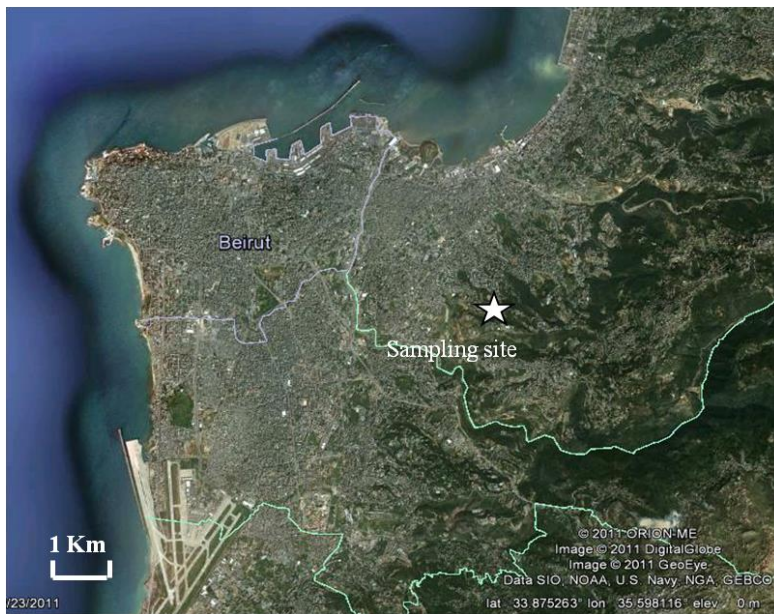
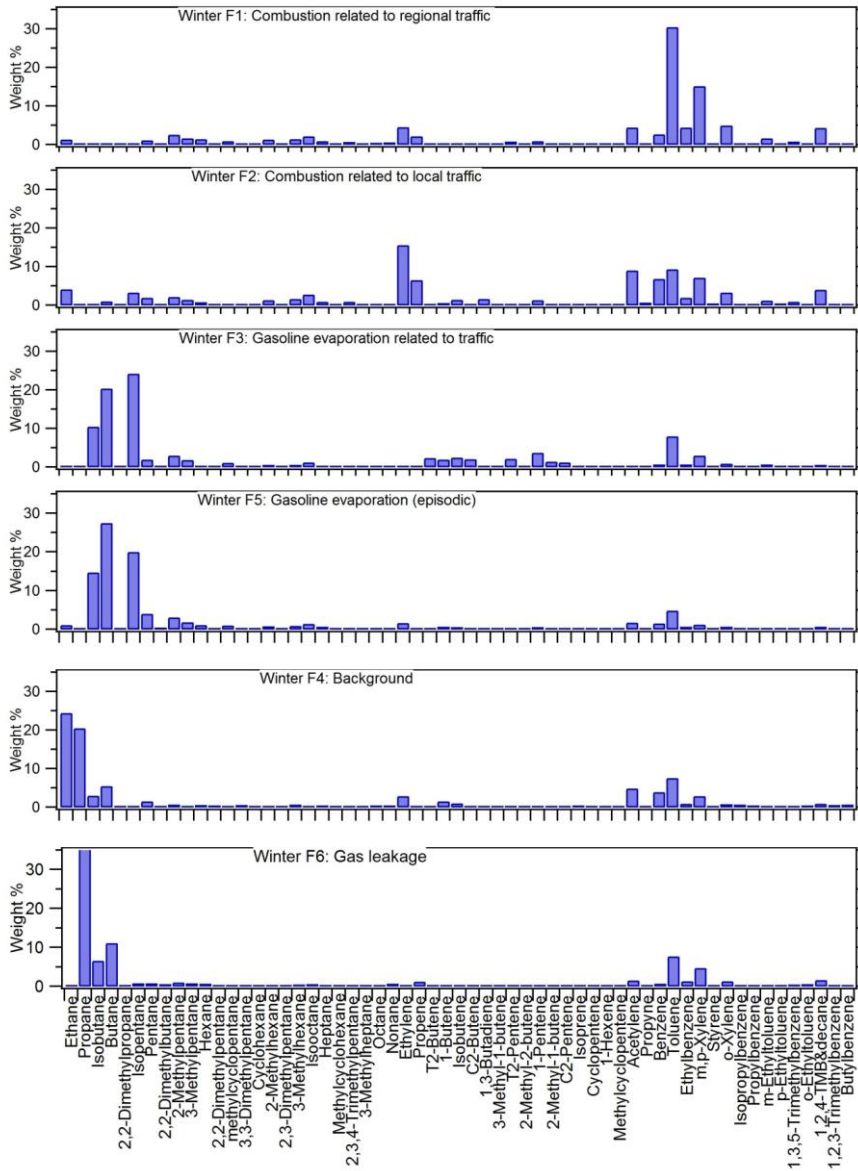


Figure 1: Sampling site in the eastern suburb of the city of Beirut.



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Figure 2: Source composition profiles (relative abundance of specific compounds within each factor in weight %) in winter 2012.

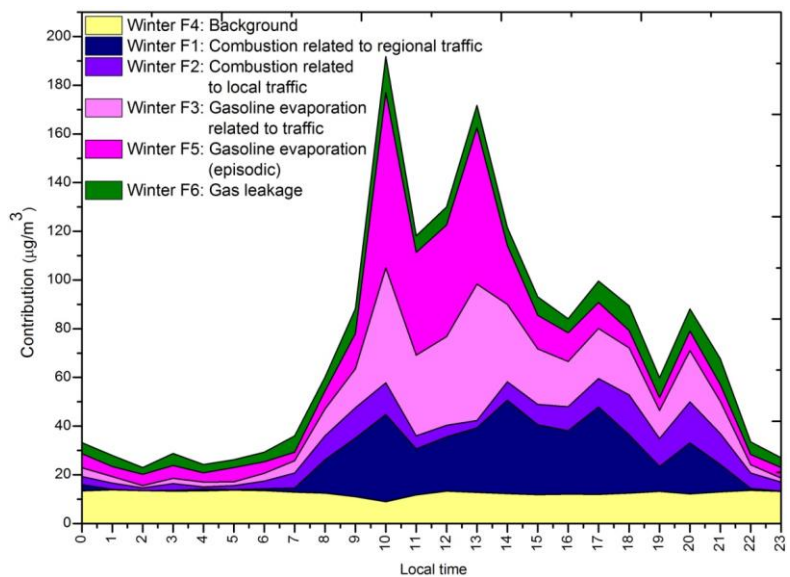


Figure 3: Diurnal variation of source contribution ( $\mu\text{g}/\text{m}^3$ ) to NMHC concentrations in winter 2012.

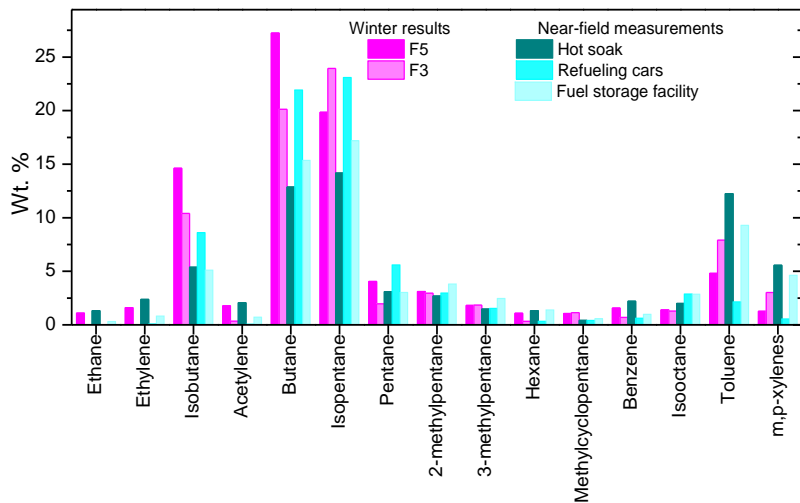


Figure 4: Composition profiles (weight %) of two gasoline evaporation factors (F5 and F3) in winter compared to typical gasoline evaporation profiles established by near field measurements (Salameh et al., 2014).

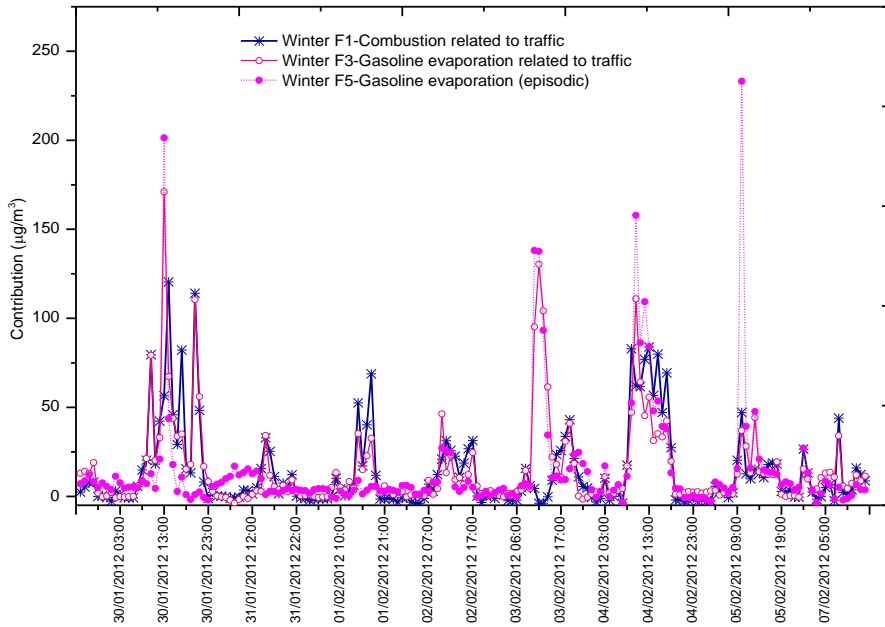


Figure 5: Time series of winter gasoline evaporation (F3 and F5) and combustion related to traffic factor contribution (F1) in  $\mu\text{g}/\text{m}^3$ .

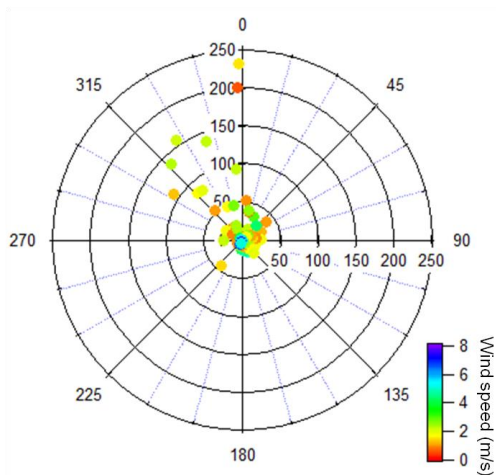


Figure 6: Pollution rose of factor 5 contribution ( $\mu\text{g}/\text{m}^3$ ) in winter.

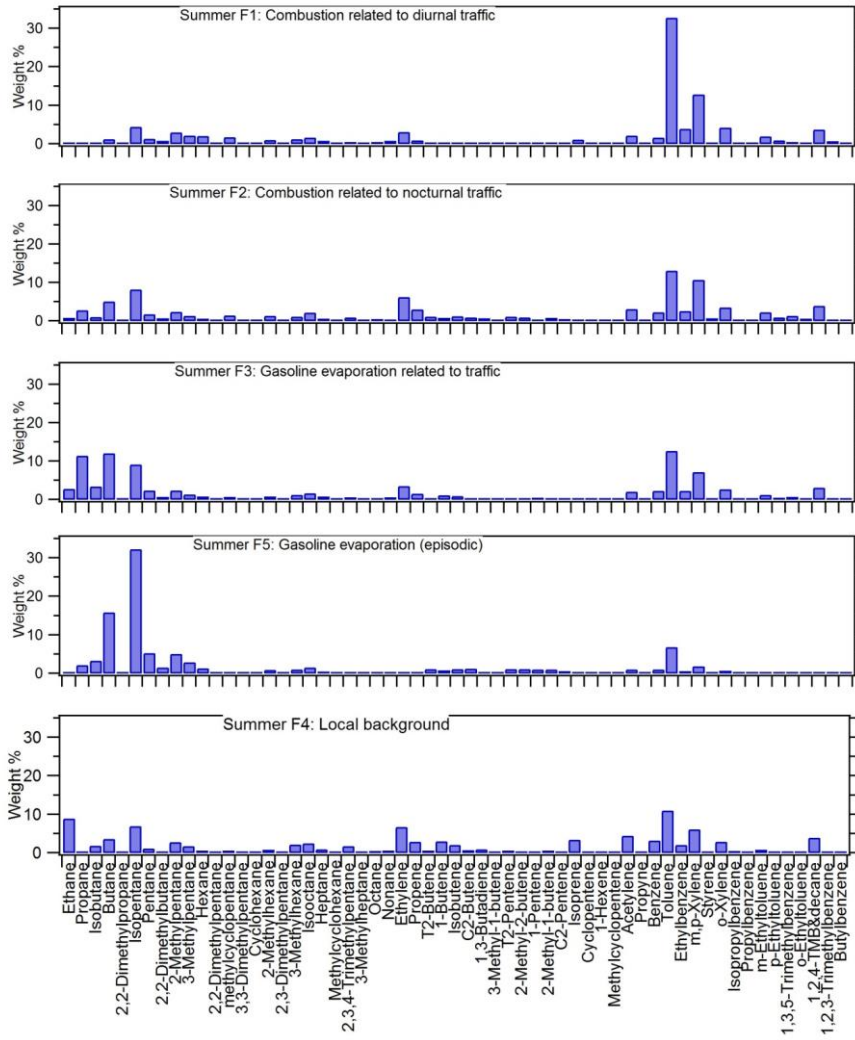


Figure 7 : Source composition profiles (relative abundance of specific compounds within each factor in weight %) in summer 2011.

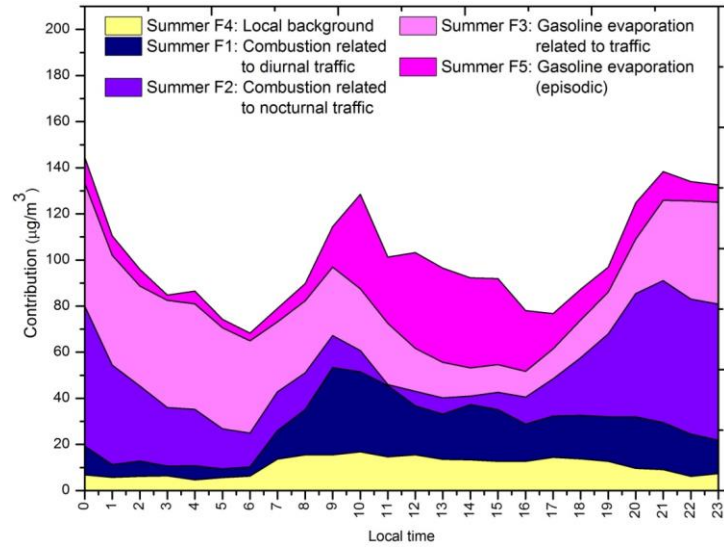


Figure 8 : Diurnal variation of sources contribution ( $\mu\text{g}/\text{m}^3$ ) in summer 2011 (local time).

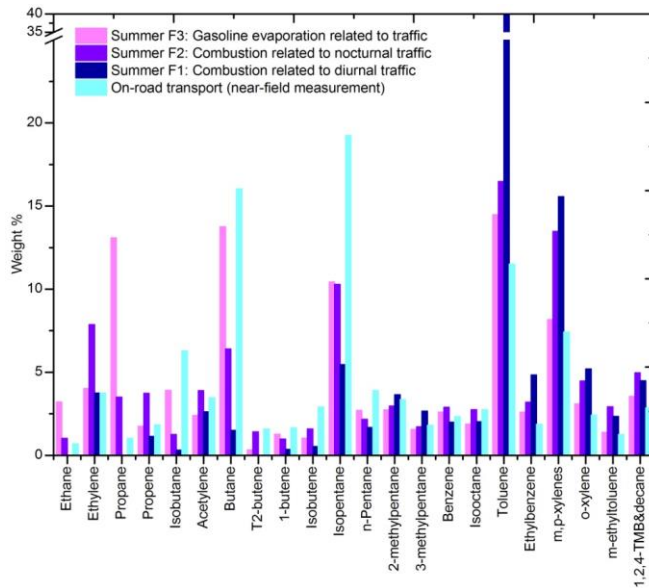


Figure 9: Source composition profiles (weight %) of gasoline evaporation (F3) and combustion related to diurnal and nocturnal traffic (F1 and F2) in summer compared to the on-road transport profile established by near field measurements (Salameh et al., 2014).

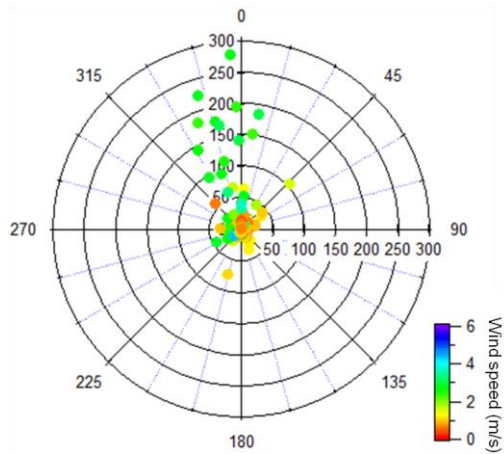


Figure 10: Pollution rose of factor 5 contribution ( $\mu\text{g}/\text{m}^3$ ) in summer.

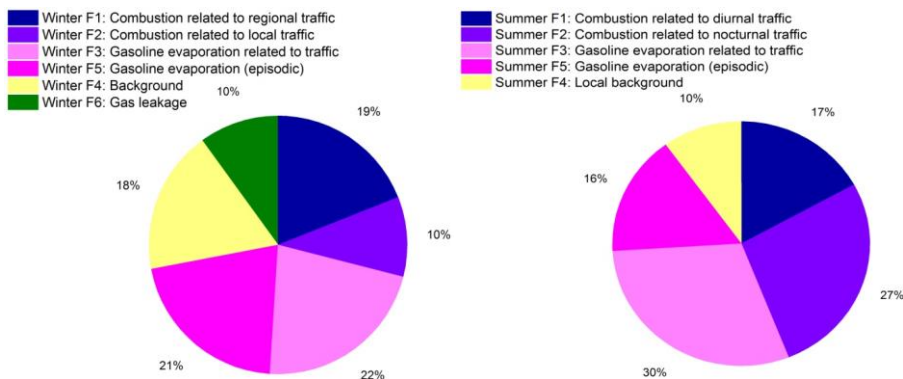


Figure 11: Sources contribution (weight %) in winter and in summer.

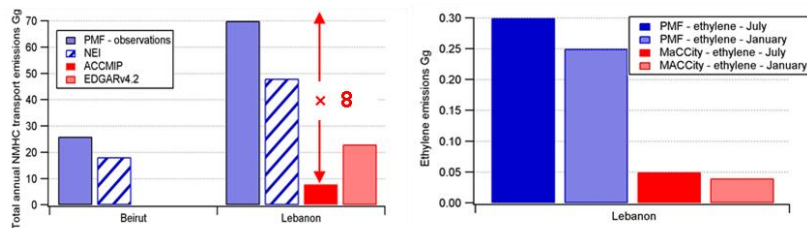


Figure 12: Comparison of the PMF results and emission inventories (national and global) for the transport sector emissions.