

Interactive comment on “Composition of gaseous organic carbon during ECOCEM in Beirut, Lebanon: new observational constraints for VOC anthropogenic emission evaluation in the Middle East” by Thérèse 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 “Composition of gaseous organic carbon during ECOCEM in Beirut, Lebanon: new observational constraints for VOC anthropogenic emission evaluation in the Middle East” according to your comments. Kindly find below our response to the comments.

Sincerely yours,

Thérèse Salameh

Anonymous Referee #1

This paper provides a nice presentation of emission ratios (ER) calculated by two different methods, and then follows up with a comparison with regional to global emission inventories. This paper is especially relevant given the lack of measurement data from this region of the world. Overall, the paper is well organized, and quite relevant. I would however like to see a few revisions before it is accepted for publication. More general comments and specific edits/suggestions, including some language corrections, follow.

General comments:

1. In general, the paper cites a lot of work from authors, which is fine given the lack of work in this region on the topic, but it would be good if there could also be some more citations that are beyond self-citation. For example, on L238, that toluene and xylenes are related to traffic sources, there are references other than Salameh 2016 that are earlier and more authoritative on this, as this is something that is more broadly true and not limited to the Middle East. It would be good to integrate some of these as well.

We referred to Salameh et al. 2016 because it is a source apportionment study where these species are present in the road-transport profile. Nevertheless, we added two other references for other regions: Watson et al. 2001 and Badol et al. 2008.

2. L95: CO is not inert. It is much less reactive than many of the VOCs but it is definitely not inert.

At the time scale of air mass transport in Beirut (hour), CO can be considered as inert. The word “inert” is removed from the whole manuscript. Thank you.

3. P7: this text discusses where speciations in emission inventories come from, but it does not make clear which species/speciation information is used from which sources for the comparisons in the study. Please try to be more explicit/clearer about this, since a variety of inventories, etc are discussed.

We have indicated in line 191 that “we rely on the ACCMIP inventory from ECCAD database which provides a detailed speciation of VOCs including acetylene.” In line 201 we mentioned that the “speciation of NMVOC emissions is performed using the RETRO inventory” and in line 187 we mentioned that the same methodology for the NMVOCs speciation is used in MACCity and ACCMIP emission inventories. In line 207, we specified that “the emission fluxes of 11 individual NMVOCs as well as CO” were extracted from the ECCAD database. The list of target species is reported in Table 3.

4. L202-204: This sentence does not make sense. Why does what is said above make the approach for Beirut valid? Please explain this more clearly.

By this, we mean that the use of emission ratios from our measurement site is relevant because there is no significant spatial variability of the fluxes of the grids covering Lebanon and the site is representative of Beirut anthropogenic emissions.

The sentence is changed to: “Since the flux of the 8 grids is spatially homogeneous for all compounds, we calculated a mean flux for each NMVOC to derive the emission ratio from the inventory. Comparing emission ratios from the inventory to observations collected at one measurement site stays relevant. Indeed the sub-urban site is far enough from strong direct emissions (industrial, road transport) since they can hide the emissions from distant sources, and it receives air masses coming from Greater Beirut Area which includes the city of Beirut and close suburbs.”

5. L252: I find it very hard to believe that photochemical removal/photochemistry is truly ‘negligible’ in winter.

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. Please refer to Salameh et al. 2015 for more detailed information.

6. L270-274: Here the authors state that ER were derived using all the data ‘since there is no effect of photochemistry even during the day in summer’. That simply cannot be true. No photochemistry during summer mid-day? If the authors wanted to argue that the LRF were derived based on all data because the emissions were fresh and therefore had not undergone significant photochemistry I could follow the argument/logic, but to state no photochemistry seems very unreasonable. Also, in section 4 the degree of chemical removal is stated to be kOH dependent. Overall, the discussion in section 4 and section 5 should be made more consistent, but if ‘no photochemistry’ rather than e.g., ‘fresh emissions’ wants to be argued, the data to prove this will need to be much more substantial. That there is substantial influence from emissions is discussed and a relevant point.

Kindly refer to the previous comment regarding the impact of photochemistry during summer and winter. Additionally, this sentence from L. 285 to 289 concerns only the less reactive species as we have stated in the beginning of the sentence “for other species”. The more reactive species affected by photochemical removal during the midday in summer are treated in a different way (please see lines 277 – 282).

Furthermore, the impact of fresh emissions was addressed many times: in lines 239-240 “...compensation of chemical removal at midday by evaporative emission cannot be excluded for aromatics like toluene” and lines 250 – 252 “...strong enrichment of aromatics during the day originating from the traffic related source where toluene and m,p-xylenes are significantly present.” We added “fresh” to the line 239: “...at midday by fresh evaporative emission”.

7. Section 5.2: It would be helpful to bring Figure 4 into the discussion earlier. I think visualizing this and referring to the plot will help the explanation. It would also be helpful if a number of points could be more explicitly mentioned. The ER is determined by extrapolating the photochemical age to $t=0$, so that means the y-intercept is the ER, correct? State this explicitly. Photochemical age is being shown on the x-axis, but what does that correspond to in terms of the equation that is shown? It would be good to be explicit about this too.

The section 5.2 is changed according to the comments. We introduced figure 4 in the first paragraph: “...NMVOC species is dominated by a reaction with the OH radical. In this method, the ratio of NMVOC with acetylene is plotted versus the photochemical age as shown in Figure 4.” We added the explanation to line 329: “...The emission ratios of NMVOCs are estimated by extrapolating the photochemical age to zero which is the intercept on the y-axis of the linear fit (figure 4).” We added “ Δt ” in the caption of figure 4.

8. L319-322: the r^2 values and stdev values are listed, but nothing about their implications is mentioned or explained. It would be good to include one sentence as to what these values are telling the reader.

The sentence is changed to: “The calculated determination coefficients R^2 with acetylene and CO ranged from 0.3 for some species like ethane to 0.9 for the majority of the species in winter, and with acetylene in summer from 0.5 to 0.9 showing the importance of combustion related sources during both seasons. The standard deviation of the ER determined by the photochemical method was low and varied between zero and 0.04 for propane, the coefficient of variation was below 3% for the majority of the species indicating the robustness of the photochemical method.”

9. Section 6: it would help the reader follow the comparisons if the section were better organized, either by city or compound class. There is a lot of back and forth and it makes it rather confusing and more difficult than necessary to follow, as I think this is a very interesting and relevant part of the paper.

The section 6 is modified as follows: "...Usually ERs agree within a factor of 2 except for aromatics (benzene excepted) and some alkanes (C2 – C5). Those species are related to the unburned fuel fraction and natural gas or liquefied petrol usage.

Among C2-C5 alkanes and regardless of the season, ER of ethane is much lower in Beirut than Los Angeles, Beijing, and Strasbourg but similar to Saudi Arabia since the natural gas source is not widely used in Lebanon and Middle East countries (Salameh et al., 2015). Regardless of the season, ERs of aromatics are higher in Beirut compared to northern post-industrialized countries and even the Middle Eastern city Mecca. One should note that aromatic differences are quite significant between the two Middle Eastern cities, from a factor of 3 up to a factor of 6 for (m,p)-xylenes. The maximum difference is observed between Beirut and Strasbourg and reached a factor of 10 for m,p-xylenes in winter. Differences are greater in winter than in summer as a consequence of a marked seasonal variability of ER in other cities (Strasbourg and Beijing) in contrast to Beirut. In Beirut, the aromatics are emitted from combustion related sources and from gasoline evaporation which accounts for more than 40% in winter as well as in summer (Salameh et al., 2016). ERs of alkenes, which are combustion products, usually agree within a factor of two between Beirut, Los Angeles, Beijing, and Strasbourg in both seasons, except for C4 and C5 alkenes with LA and Beijing; whereas they are higher in Mecca due to their additional evaporative origin (Simpson et al., 2014)."

10. Section 7.1: can you clarify which method used to calculate the ERs was used in this comparison with EI? I realize the agreement between the methods was quite good, but it would still be helpful to mention if it was the LRF or PA method.

The method used is LRF method and it was added to the sentence line 419: "...ratios during summer and winter obtained by the LRF method."

11. L390-393/Figure 8: to state that more reactive VOCs are reasonably well represented is difficult to determine from this plot, as some of the compounds are labeled but others are not. I think I would try to be a bit more specific about this and avoid blanket statements. Also because looking at these figures I'm not sure that there is a clear pattern, and it seems that some are just better than others, and it would be much better if this were just discussed more explicitly in the text rather than trying to draw very general conclusions and then listing a bunch of exceptions. Maybe it would be worth considering different shapes for the different species, or more labeling, or possibly color coding based on reactivity?

The sentence is changed to: "Except benzene, xylenes to a less extent and long-lived alkanes, ER relative to acetylene agree within a factor of 2 between observations and inventory suggesting that the VOC speciation in ACCMIP is better represented for more reactive VOCs such as alkenes and some aromatics." The color coding is based on NMVOC groups but also gives information about the reactivity: Alkanes as less reactive; Alkenes as more reactive; aromatics as more reactive except benzene. When the ERs are < or > 2, the species are labeled.

12. L393/L402/L405/L467: in a number of cases the authors state that species are 'reasonably represented' or 'reasonably underestimated'. This seems rather subjective, also because

‘reasonably represented’ seems to be agreement by within a factor of 2. I would suggest either trying to avoid such subjective statements, or defining somewhere that ‘reasonable’ is somehow tied to this specific range. At the end of L406, I would suggest to not leave it with reasonably represented, but go further to state that these can still use improvement. (I leave that to the author’s discretion.)

Thank you for this comment. We replaced “reasonable” with “better” in lines 424-439-505 and in the abstract (line 21). We removed “reasonable” in line 435. We added a sentence in line 414: “We consider that the speciation is “reasonable” when there is an agreement within a factor of two between observations and emission inventory.”

We added in line 440: “...SOA precursors in ACCMIP is better represented than the others species but it is still need improvement.”

13. L402: the authors state that xylenes are reasonably underestimated, but it seems from the figure that some of the dots for xylenes are as far out as the benzene dots. Please explain what this means or ideally be more specific, as mentioned in the above comment.

We removed the word “reasonable” and changed the sentence to: “...xylenes are underestimated in the ACCMIP global emission inventory but not systematically.”

14. L397-406: it would help to explain this method a bit more clearly. Are the ratios always [beirut]/[accmip]? Include this.

An explanation was added: “In order to consolidate our conclusions regarding VOC speciation within ACCMIP, we performed the systematic calculation of the ratios of every NMVOC to each of the other NMVOCs (NMVOC_i) in the global emission inventory and in the observations (Coll et al., 2010) separately, and then we reported in figure 9, the ERs obtained from ACCMIP versus those obtained from the observations.”

15. L418-420: If this sentence is referring to Figure 10, it seems that a number of the EMEP dots are beyond the 2:1 line for overestimation and even one beyond for underestimation, which is not what the sentence states.

The description is modified to: “ERs of alkenes from the road transport sector are usually consistent within a factor of 2 for the regional emission inventory EMEP and the global inventory ACCMIP. In EMEP, benzene and ethane are overestimated whereas butanes are underestimated; while xylenes and toluene are underestimated over a factor of 2 by ACCMIP. At a more detailed level, by calculating the ratios for individual NMVOC, figure 11 confirms that xylenes and toluene are underestimated species by both inventories, and benzene is overestimated by EMEP.”

Furthermore, the species with ER < or > 2 are labeled in figure 10.

16. L416-422: generally this section seems to draw conclusions that are far too generalized and not really supported by the figures when one examines the details. A more explicit discussion is warranted to avoid blanket statements.

Please refer to the previous comment. Thank you!

17. Conclusions: given many of the above comments requesting more explicit discussion and less generalizations, please make sure that the conclusions text is updated to reflect the revised discussion.

We modified the conclusions according to above mentioned comments from line 503 – 510: “This comparison suggests that the overall speciation of anthropogenic sources for major hydrocarbons that act as ozone and SOA precursors in ACCMIP is better represented than other species but it is still need improvement.

The road transport ER relative to acetylene derived from near-field measurements are compared to ER from ACCMIP and EMEP regional emission inventory for the road transport sector. ERs of more reactive species (alkenes and aromatics except benzene) are usually consistent within a factor of 2 for the regional emission inventory EMEP while xylenes and toluene are underestimated over a factor of 2 by ACCMIP.”

18. L473-474/L476-477: yes! This is a very important point. Thank you for including it.

Thank you for all your valuable comments.

Specific edits:

1. L4: write out volatile organic compounds first followed by the VOCs abbreviation in parentheses.

Changed.

2. L36-39: This sentence, ‘Future projections...’ seems redundant with the previous sentence. Please correct.

The sentence is removed.

3. L60: ‘...the road transport sector by the Middle East...’ the ‘by’ should be ‘in’

The sentence is changed to: “They also found that the road transport sector in the Middle East region is a contributor to the global emissions of CO and NOx as significant as road transport in Western Europe and North America.”

4. L64: suggest to change this sentence for language to ‘The same picture is presented by emission inventories.’

The sentence is changed accordingly.

5. L71 & L73: no ‘s’ after RCP

The “s” is removed.

6. L71: Replace ‘On the opposite’ with ‘In contrast’

Changed.

7. L72: replace ‘reaching respectively’ with ‘with totals of’ and move ‘respectively’ to the end of the sentence.

The sentence is changed to: “In contrast, the NMVOC emissions have been strongly decreasing in USA and Europe, with totals of 7 and 10 Tg/year in 2010 respectively according to RCP 8.5 (Figure 1).”

8. L80: ‘...and even more so in cities..’ add the ‘so’

Added.

9. L111: change ‘..region at a whole...’ to ‘...region as a whole..’

Changed.

10. L112: change ‘strong’ to ‘significant’

Changed.

11. L136-137: suggest to change the sentence to read ‘...proposed by Salameh et al. (2014) by sampling close to emission sources in real-world operating conditions as far as possible.’

The sentence is changed accordingly.

12. L142: remove ‘ambient’

Removed.

13. L146-147: suggest to change the sentence to ‘...by a forested pine and high density residential area.’

The sentence is changed to: “The site is surrounded by a forested pine and high density residential area.”

14. L176: change ‘each sectoral layer’ to ‘each sector’

Changed.

15. L182: remove ‘only’

Removed.

16. L212: would be good to include/mention that the tracer was acetylene. (again, not inert, just less reactive)

The sentence is changed to: “...the average diurnal normalized profiles to the midnight value of some NMVOC relative to a tracer to examine the relative importance of these processes (Borbon et al., 2013). Acetylene was chosen as a less reactive combustion tracer and its normalized diurnal profile is reported in each panel (grey shaded).”

17. L224: change ‘neglected’ to ‘less’

Changed.

18. L235-236: aromatics and alkanes should be singular

The “s” is removed.

19. L250: ‘on’ should be replaced by ‘in’ before LRF

We replaced “on” by “in”.

20. L328-329: please be clearer whether the more than 80% of the species was true for both seasons or just one season was sufficient to be included.

One season was sufficient to be included, the sentence is changed to: “The ER derived from the observations (summer and winter) are comparable at $\pm 50\%$ to the ratios of road transport sector, during at least one season, for more than 80% of the species.”

21. L371-372: this sentence does not make sense. Differences compared to what? Mecca? Also, ‘opposite’ should be ‘in comparison’ or ‘in contrast’ to.

The sentence is changed to: “Differences are greater in winter than in summer as a consequence of a marked seasonal variability of ER in other cities (Strasbourg and Beijing) in contrast to Beirut.”

22. L394: replace ‘remarkable’ with ‘significant’ or something else more appropriate.

“Remarkable” is replaced with “significant”.

23. L403: replace ‘lay around’ with ‘are closer to’

“Lay around” is replaced with “are closer to”.

24. L429: replace ‘homogeneity’ with ‘agreement’

“Homogeneity” is replaced with “agreement”.

25. L436: I would suggest that ‘poorer in alkenes’ be ‘poorer in some alkenes’

“Some” is added.

26. L439: suggest to end the sentence after ‘MEA’, and then revising the next sentence to ‘This could be indicative for other MEA countries where emissions data and measurements are scarce.’

The sentence is changed accordingly.

27. Table 2: at the very end of the table caption, please add ‘..for the VOC/acetylene ERs’

The caption is changed to: “...Bold characters indicate the similarity at $\pm 50\%$ of the VOC/acetylene ER from the measurement campaigns to the one of near-field measurements.”

28. Table 2: at the end of the table, 'nd: not determined' is included but does not show up in the table.

"nd: not determined" is removed.

29. Table 3: in the table caption, the parentheses need to be fixed.

The parentheses are fixed.

30. Figure 2/3: having the middle thickness line as a dashed line would help readability

The figures 2 and 3 are changed.

31. Figure 7: swapping the summer Beijing plot with the summer Mecca plot would put the two Beijing plots next to each other, which is more logical for the reader.

We changed the position of the figures accordingly.

32. Figure 9: given that the plots seem to be organized by compound class, it would be good to include these compound class labels in the top left corner of the plots for orientation. I also assume that the 'all data' in grey dots is also just for those compound classes. But maybe this is not the case?

The figure is change accordingly. The grey dots are for all compound classes; this explanation is added to the caption of the figure.

Interactive comment on “Composition of gaseous organic carbon during ECOCEM in Beirut, Lebanon: new observational constraints for VOC anthropogenic emission evaluation in the Middle East” by Thérèse 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 “Composition of gaseous organic carbon during ECOCEM in Beirut, Lebanon: new observational constraints for VOC anthropogenic emission evaluation in the Middle East” according to your comments. Kindly find below our response to the comments.

Sincerely yours,

Thérèse Salameh

Anonymous Referee #2

This paper describes NMVOCs measurements conducted in summer and winter time in Beirut and the assessment of emission ratios using two different methods. Emission ratios derived from measurements conducted at a suburban site were compared with those performed near a road transport sector. This comparison suggested that for the majority of NMVOCs, road transport is the main source of emission in Beirut. Therefore, ERs derived from the observations at a suburban site were also compared with those extracted from emission inventories for all the anthropogenic sectors. The authors concluded that the overall speciation of anthropogenic sources is reasonably represented. Additionally, ERs derived from near-road measurements were compared with those from emission inventories only from the road transport, concluding that there is a consistency of ER from road transport within a factor of 2 with EMEP but a high underestimation was found for xylenes and toluene by ACCMIP.

General comments: This paper presents a rich data-set for a region where emission data and measurements are still scarce. The paper is well written and structured and the methodology adapted for deriving ERs and comparing them to emission inventories is rigorous. I recommend the manuscript for publication with minor corrections.

Some minor comments:

1. I would recommend to shorten the abstract

We tried to shorten the abstract but unfortunately we couldn't remove any important message, therefore the abstract is still relatively long:

“The relative importance of Eastern Mediterranean emissions is suspected to be largely underestimated compared to other regions worldwide. Here we use detailed speciated measurements of volatile organic compounds (VOCs) to evaluate the spatial heterogeneity of VOC urban emission composition and the consistency of regional and global emission inventories downscaled to Lebanon (EMEP, ACCMIP, and MACCity). The assessment was conducted through the comparison of the emission ratios extracted from the emission

inventories to the ones obtained from the hourly observations collected at a sub-urban site in Beirut, Lebanon during summertime and wintertime ECOCEM campaigns. The observed ERs were calculated by two independent methods. ER values from both methods agree very well and are comparable to the ones of the road transport sector from near-field measurements for more than 80% of the species. There is no significant seasonality in ER for more than 90% of the species unlike the seasonality usually observed in other cities worldwide. Regardless of the season, ERs agree within a factor of 2 between Beirut and other representative worldwide cities except for the unburned fuel fraction and ethane. ERs of aromatics (benzene excepted) are higher in Beirut compared to northern post-industrialized countries and even the Middle Eastern city Mecca. The comparison of the observed ER to the ones extracted from ACCMIP and MACCity global emission inventories suggests that the overall speciation of anthropogenic sources for major hydrocarbons that act as ozone and SOA precursors in ACCMIP is better represented than other species.

The comparison of the specific road transport ER relative to acetylene derived from near-field measurements to ER from ACCMIP and EMEP emission inventories for road transport sector showed that ER of more reactive species are usually consistent within a factor of 2 with EMEP while xylenes and toluene are underestimated over a factor of 2 by ACCMIP.

The observed heterogeneity of anthropogenic VOC emission composition between Middle Eastern cities can be significant for reactive VOC but is not depicted by global emission inventories. This suggests that systematic and detailed measurements are needed in the Eastern Mediterranean Basin in order to better constrain emission inventory.”

2. L170 Rephrase “Only the anthropogenic part of the emissions regarding road transport (SNAP 07) “. As formulated it seems that there is a biogenic part of the road transport

The sentence is changed to: “Only the emissions regarding road transport (SNAP 07) is included in this study.”

3. L283: Did you use the same value of OH concentration for both seasons? ($5 \cdot 10^6$ molecules.cm⁻³). Could you briefly discuss the impact on the results if this value is different between summer and wintertime?

The photochemical age method was only applied to summertime dataset as indicated in L.292. Additionally, previous studies (Borbon et al. 2013; Warneke et al. 2007) have shown that the emission ratios determined with this method are not affected when reducing or increasing the OH values by a factor of 2. This was mentioned in L.329 – 331.

4. L222: Please define kOH the first time it appears in the text. Specify that it’s a reaction rate coefficient.

The sentence is changed to: “The degree of chemical removal during the day is k_{OH}-dependent (k_{OH}: rate coefficient for the reaction with OH).”

5. L225-226: This sentence is not very clear and should be reformulated. What is this threshold value of $8.52 \cdot 10^{-12}$ cm³ molecule⁻¹ s⁻¹?

The sentence is changed to: “Then the importance of daytime maximum and minimum concentrations becomes modulated by chemical removal when k_{OH} is higher than $8.52 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (rate coefficient of ethylene with OH).”

6. L270-273: It is hard to believe that there is “no photochemistry during daytime in summer” especially in the Middle East region

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. Please refer to Salameh et al. 2015 for more detailed information.

7. L299: Please indicate that the value in the parenthesis is the assumed concentration of OH.

The sentence is changed to: “...the reaction of those compounds with OH radical ($[OH] = 5.10^6 \text{ molecules.cm}^{-3}$).”

8. L306 Replace “keeps” with “remains” or “is”

“Keeps” is replaced with “remains”.

9. L337: the sentence should be completed in order to specify that wintertime ER agree at +/- 30% . . . with the summertime ERs

The sentence becomes: “The wintertime emission ratios for most NMVOC species agree at $\pm 30\%$ (slope of 0.71) with the summertime ERs and within a factor of 2 and a high determination coefficient of 0.94.”

10. Figure 4: Please use different markers for the different compounds

Figure 4 is changed.

11. Figure 5. It should be added in the legend that the figure represents only ethane data.

The figure represents the ERs of all the compounds; each dot corresponds to a species. We just indicated the name of the compound with $ER < 2$ which is ethane.

Composition of gaseous organic carbon during ECOCEM in Beirut, Lebanon: new observational constraints for VOC anthropogenic emission evaluation in the Middle East

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1 **Abstract:**

2 The relative importance of Eastern Mediterranean emissions is suspected to be largely
3 underestimated compared to other regions worldwide. Here we use detailed speciated
4 measurements of [volatile organic compounds \(VOCs\)](#) to evaluate the spatial heterogeneity of
5 VOC urban emission composition and the consistency of regional and global emission
6 inventories downscaled to Lebanon (EMEP, ACCMIP, and MACCity). The assessment was
7 conducted through the comparison of the emission ratios extracted from the emission
8 inventories to the ones obtained from the hourly observations collected at a sub-urban site in
9 Beirut, Lebanon during summertime and wintertime ECOCEM campaigns. The observed ERs
10 were calculated by two independent methods. ER values from both methods agree very well
11 ~~(difference up to 10%)~~ and are comparable to the ones of the road transport sector from near-
12 field measurements for more than 80% of the species. There is no significant seasonality in
13 ER for more than 90% of the species unlike the seasonality usually observed in other cities
14 worldwide. Regardless of the season, ERs agree within a factor of 2 between Beirut and other
15 representative worldwide cities except for the unburned fuel fraction and ethane. ERs of
16 aromatics (benzene excepted) are higher in Beirut compared to northern post-industrialized

17 countries and even the Middle Eastern city Mecca. The comparison of the observed ER
18 ~~relative to CO and to acetylene as well as the ratios of every NMVOC to each of the other~~
19 ~~NMVOCs (NMVOC_i)~~ to the ones extracted from ACCMIP and MACCity global emission
20 inventories suggests that the overall speciation of anthropogenic sources for major
21 hydrocarbons that act as ozone and SOA precursors in ACCMIP is ~~reasonably better~~
22 represented than other species.

23 The comparison of the specific road transport ER relative to acetylene derived from near-field
24 measurements to ER from ACCMIP and EMEP emission inventories for road transport sector
25 showed that ER of more reactive species from the road transport sector are usually consistent
26 within a factor of 2 with ~~the regional emission inventory~~ EMEP while xylenes and toluene are
27 underestimated over a factor of 2 by ACCMIP.

28 The observed heterogeneity of anthropogenic VOC emission composition between Middle
29 Eastern cities can be significant for reactive VOC but is not depicted by global emission
30 inventories. This suggests that systematic and detailed measurements are needed in the
31 Eastern Mediterranean Basin in order to better constrain emission inventory.

Keywords: emission inventory; sources; emission ratios; photochemical age; VOC; transport;
East Mediterranean

Highlights:

- No significant seasonality in ER regardless of the species
- The transport sector is the major source of 80% of the species
- Reasonable discrepancies, within a factor of two, between ER from observations and global inventories for the main precursors of ozone and SOA
- Consistency of ER from the road transport sector within a factor of 2 with EMEP but underestimations of xylenes and toluene over a factor of 2 by ACCMIP
- Spatial heterogeneity of VOC emission composition in MEA region especially for reactive species

32 1. Introduction

33 In the context of global climate change and growing urbanization, the East Mediterranean
34 Basin (EMB) and the Middle East as a whole is a highly sensitive environment under
35 considerable anthropogenic and environmental pressures. Future decadal projections point to
36 the EMB as a possible hot spot of poor air quality and predict a continual and gradual

37 | warming in the region, much stronger than other regions ([Gurjar et al., 2008](#); Lelieveld et al.,
38 | 2012, 2014; Pozzer et al., 2012). ~~Future projections using the Multi-Pollutant Index defined~~
39 | ~~by Gurjar et al. (2008) recently identified North Africa and the Middle East as possible future~~
40 | ~~hot spot of poor air quality (Pozzer et al., 2012).~~ The increase and accumulation of
41 | anthropogenic emissions of gaseous and particulate pollutants from surrounding urban areas,
42 | and on-road transport emissions in particular, are suspected as one of the key compounding
43 | factors of those environmental impacts (Konovalov et al., 2010; von Schneidmesser et al.,
44 | 2011; Waked and Afif, 2012; Hillboll et al., 2013). The EMB area includes two megacities:
45 | Istanbul (>12 million inhabitants) and Cairo (>15 million inhabitants), which experience
46 | extremely high levels of pollutions (Kanakidou et al., 2011). Satellite images of NO₂ columns
47 | from SCIAMACHY also point to the coastal urban areas of the Middle East as an important
48 | hot spot of pollution in the region (Lelieveld et al., 2009).

49 | Trend analysis from satellite and ground-based observations found decreasing trend of
50 | primary pollutants in Western Europe and increasing trends from hydrocarbon ground-based
51 | observations and NO_x satellite retrievals in other regions (Konovalov et al., 2010; von
52 | Schneidmesser et al., 2011). Downward trends in pollutant emissions are a shared feature of
53 | northern mid-latitude urban areas. The mixing ratios of [volatile organic compounds \(VOCs\)](#)
54 | and CO have decreased by almost two orders of magnitude during the past five decades in
55 | Los Angeles (Warneke et al., 2012). In UK, long-term trends show significant decreases for
56 | VOCs reaching 26% per year as well as for CO up to 12% per year (von Schneidmesser et
57 | al., 2010). Indeed, vehicle exhaust emission control has successfully reduced emissions of
58 | nitrogen oxides, carbon monoxide, volatile organic compounds and particulate matter (Uherek
59 | et al., 2010). In developing countries however, pollutants emissions have been growing
60 | strongly. Waked and Afif (2012) have shown that the emissions of CO have rapidly increased
61 | by a factor of 2.8 in the countries of the Middle East between 2000 and 2005, as a result of the
62 | increase of fuel consumption. They also found that the road transport sector ~~in~~by the Middle
63 | East region is a contributor to the global emissions of CO and NO_x as significant as road
64 | transport ~~in~~by Western Europe and North America. These findings are consistent with results
65 | reported by Uherek et al. (2010) for a larger range of pollutants (CO₂, CO, NO_x, and
66 | NMVOCs).

67 | ~~The same picture is presented by emission inventories. Same picture can be drawn from~~
68 | ~~emission inventories.~~ Figure 1 compares the annual total anthropogenic emissions of non-
69 | methane volatile organic compounds (NMVOCs) from three reference emission inventories
70 | between the Middle East (MEA) region, Europe and North America: ACCMIP (Atmospheric

71 Chemistry and Climate Model Intercomparison Project), EDGARv4.2 (Emissions Database
72 for Global Atmospheric Research), and RCPs (Representative Concentrations Pathways)
73 (ECCAD database, 2015, <http://eccad.sedoo.fr>). NMVOC emissions have been constantly
74 increasing over the last thirty years reaching up to 18 Tg/year according to RCPs 8.5 in 2010.
75 ~~In contrast~~~~On the opposite~~, the NMVOC emissions have been strongly decreasing in USA and
76 Europe, ~~with totals of reaching respectively~~ 7 and 10 Tg/year in 2010 ~~respectively~~ according
77 to RCPs 8.5 (Figure 1). While differences up to a factor of 2 can be found between ACCMIP
78 and EDGARv4.2 for the MEA in 2000 (Figure 1), all inventories suggest that NMVOCs
79 emissions from the MEA region are as significant as the ones from post-industrialized regions
80 or even higher. Finally no source regions clearly dominate global anthropogenic emissions
81 and therefore an accurate representation of anthropogenic emissions in developing country
82 regions like the MEA is of importance where highest uncertainties are expected.

83 The quantification of emission distribution is a challenge, and even more ~~so~~ in cities of the
84 EMB and the Middle East as a whole where local emission data are sparse. Indeed, emission
85 inventories usually combine bottom-up and top-down calculations to estimate emissions.
86 Comprehensive bottom-up calculations aggregate multiple local statistics on different
87 emission source categories where possible. Top-down calculations use regional or national
88 activity data and re-allocate emissions to finer scale by using spatial surrogates (e.g.
89 population statistics at the local level). Therefore, the uncertainties of numerous data sources
90 are cumulated in the overall estimation of emission amounts and along increasing scales (local
91 to regional to global). Granier et al. (2011) had assessed the evolution of anthropogenic and
92 biomass burning emissions of CO, NO_x, SO₂ and BC at global and regional scales from
93 several inventories during the 1980–2010 period and had concluded that there is still no
94 consensus on the best estimates for surface emissions of atmospheric compounds (Granier et
95 al., 2011).

96 Several studies in the literature have reported evaluations of emission inventories in
97 developed countries by the use of ambient pollutant observations at ground level, on-board
98 aircraft and from satellite retrievals (Martin et al., 2003; Kim et al., 2011). For instance urban
99 emission ratios of various VOC relative to an ~~inert~~ tracer of incomplete combustion (CO,
100 acetylene) have been used as high-quality field constraints to evaluate regional emission
101 inventories in cities of post-industrialized countries (Warneke et al., 2007; Coll et al., 2010;
102 Borbon et al., 2013). The most recent diagnostic studies reveal large discrepancies between
103 observations and inventories as large as a factor 4 for VOC in Paris and Los Angeles for

104 instance (Borbon et al., 2013). In-situ observations are therefore necessary constraints for the
105 development of reliable emission inventories. Moreover, they also provide direct indications
106 on air pollution exposure. While some highly resolved inventories have been developed at the
107 regional scale in the EMB area for Beirut (Waked et al., 2012) and Istanbul (Im et al., 2011;
108 Markakis et al., 2012), their uncertainties are unknown and speciation of NMVOC is usually
109 disregarded. For solely Lebanon, the atmospheric emission inventory of anthropogenic and
110 biogenic sources was established by Waked et al. (2012) for a base year of 2010 for CO, NO_x,
111 SO₂, total NMVOCs, NH₃, PM₁₀ and PM_{2.5}, according to EEA/EMEP guidelines
112 (EMEP/EEA, 2009). The NMVOC total emissions in Lebanon were estimated to be 115 Gg
113 for the year 2010. According to this inventory, transport is the main source of NMVOC with a
114 relative contribution of 67% of total emissions of NMVOCs (Waked et al., 2012). In addition,
115 there is a strong need for developing better emission inventories in the Middle East region as
116 a whole (Waked et al., 2013a). The paucity of observations in this region, especially for
117 VOCs and PM composition, is a significant ~~strong~~ limitation to the achievement of evaluated
118 and accurate emission inventories. Finally, accurate modelling of individual NMVOCs and
119 better understanding of ozone precursors is also important for policy-makers and for the
120 improvement of air quality leading to better estimates of secondary organic aerosols (SOA)
121 ~~(Secondary Organic Aerosols)~~ formation and ozone levels.

122 The present paper aims at evaluating global VOC speciated emission inventories, in the
123 absence of regional emission inventories for MEA, by the use of detailed observations
124 recently collected in Beirut, Lebanon in the frame of ECOCEM project (Emissions and
125 Chemistry of Organic Carbon in the East Mediterranean) (Salameh et al., 2015). Those
126 observations include detailed near-source field measurements and ambient measurements at a
127 suburban site. We used regional (EMEP) and global (ACCMIP and MACCity) emission
128 inventories downscaled to Lebanon. Two independent methods already applied to Los
129 Angeles basin during the CalNex experiment (Borbon et al., 2013) that take into consideration
130 the effects of chemical removal were used to estimate the urban enhancement emission ratios
131 (ERs) of various NMVOC relative to CO and acetylene for winter and summer. First,
132 calculated ERs are compared to available ERs in other cities worldwide in order to assess the
133 spatial variability of emission composition. Second, calculated ERs are compared to the ones
134 derived from global emission inventories for all the anthropogenic sectors and for the road
135 transport sector. Finally perspectives for the whole Middle East region are discussed.

136

137 2. Experiment

138 The experimental strategy includes near field measurements close to major emission sources
139 and two intensive field campaigns conducted in summer 2011 and in winter 2012 in Beirut at
140 a suburban site, within the ECOCEM project. VOC have been measured by a combination of
141 on-line and off-line techniques (table 1). A set of eight speciated profiles of four major non-
142 methane hydrocarbons (NMHC) sources in Lebanon was proposed by Salameh et al. (2014)
143 by ~~performing~~ sampling ~~experiments~~ close to emission sources in real-world operating
144 conditions ~~real-condition operation~~ as far as possible. Field sampling has been carried out in
145 Beirut city and in the suburban area during March and April 2012. The sampling was
146 performed by canisters and the analyses were performed in the laboratory by thermal
147 desorption-gas chromatography (TD-GC) technique coupled to a flame ionisation detector
148 (FID) from Perkin-Elmer (Salameh et al., 2014; 2015).

149 The ~~ambient~~ field campaigns were conducted on the roof of the Faculty of Sciences building
150 of Saint Joseph University located in the eastern suburbs of the city of Beirut from 2 to 18
151 July 2011 in summer and from 28 January to 12 February 2012 in winter. The site is
152 appropriately located in order to receive air masses coming from Greater Beirut Area which
153 includes the city of Beirut and close suburbs. The site is surrounded by a forested pine ~~area~~
154 and ~~a~~ high density ~~of~~ residential premises ~~area~~. Beirut International Airport is located 8 km
155 southwest of the site and one fuel storage facility is located at 3.6 km North. More details are
156 reported in Salameh et al. (2015). During both measurement periods, NMHCs were
157 continuously analyzed on an hourly basis covering 30 min of ambient air sampling, by the
158 same system (TD-GC-FID) used for canister analysis. Additional measurements of trace gases
159 concentrations including CO, NO_x and O₃ were provided on a 1-min basis by specific
160 analyzers. Basic meteorological parameters (wind speed and direction, temperature, relative
161 humidity and atmospheric pressure) were measured on a 1-min basis for the duration of the
162 campaigns.

163 During the summer field campaign, the average temperature was around 25 °C ± 2 °C and the
164 average wind speed was low, 2 m s⁻¹, with maximum wind speeds (4-10 m s⁻¹) recorded
165 during the days under south-western wind regimes and under northern wind regimes. During
166 the winter measurement campaign, the temperature stayed mild with an average of 13 °C ± 2
167 °C. The average wind speed was still low at 2 m s⁻¹ and the wind direction was mostly south-
168 easterly and easterly.

169

170 3. Regional and global emission database

171 At the global and the regional scales, several emission inventories were developed during the
172 past few years in order to provide the distribution of surface emissions of different gaseous
173 and particulate compounds.

174 The EMEP regional emission inventory (European Monitoring and Evaluation Programme)
175 covers the period from 1980 to 2020, at a 0.5° resolution. It contains national total emissions
176 for Europe, sector data and gridded emission data for modelling purposes. The sectors follow
177 the SNAP categorization (Selected Nomenclature for reporting of Air Pollutants). Only the
178 ~~anthropogenic part of the~~ emissions regarding road transport (SNAP 07) is included in this
179 study.

180 Since there is no global emissions dataset available after 2000, the MACCity emissions have
181 been developed within two European Commission funded projects (MACC and CityZen) as
182 an extension of the ACCMIP and the RCP 8.5 emissions dataset. The emissions for each
183 compound were then linearly interpolated, for each sector and each year between 2000 and
184 2010. A seasonal cycle was applied for each sectoral ~~layer~~, and the NMVOC species
185 anthropogenic emissions have been lumped to 13 species (excluding acetylene) using the
186 same methodology for the NMVOCs speciation as used in the ACCMIP dataset.

187 A large number of emission inventories only provide the distribution of total NMVOC
188 emissions by lumping organic species (alkanes, alkenes, alkynes, alcohols, aldehydes, ketones
189 and aromatic compounds) for chemistry modelling purposes (EDGARv4.2, ECLIPSE-
190 GAINS-4a). We ~~only~~ rely on the ACCMIP inventory from ECCAD database which provides
191 a detailed speciation of VOCs including acetylene. ACCMIP global emission inventory
192 covers the historical period (1850–2000) in decadal increments at a horizontal resolution of
193 0.5° in latitude and longitude, based on the combination of the best global and regional
194 available datasets. ACCMIP was developed mainly to provide consistent gridded emissions of
195 reactive gases and aerosols for use in chemistry model simulations needed by climate models
196 for the Climate Model Intercomparison Program 5 (CMIP5) in support of the
197 Intergovernmental Panel on Climate Change (IPCC) Fifth Assessment report (AR5)
198 (Lamarque et al., 2010). 40 regions and 12 sectors were used to combine the various sources
199 within this inventory and a set of species including CO, NO_x, total and speciated NMVOCs is
200 provided. Speciation of NMVOC emissions is performed using the RETRO (REanalysis of
201 the TROpospheric chemical Composition) (Schultz et al., 2007) inventory and is kept

202 constant for the whole historical period because of the lack of additional information. For all
203 NMVOC species of the RETRO inventory, a factor was calculated only for the year 2000 by
204 dividing the emission of each individual species by the total NMVOC anthropogenic
205 emissions for each sector in each grid cell.

206 For comparison with observations, we extracted the emission fluxes ($\text{kg/m}^2/\text{s}$) of 11 individual
207 NMVOCs as well as CO of 8 grids covering Lebanon surface area (ECCAD database). Target
208 sectors cover all anthropogenic sectors and the transport sector for 2000. Since the flux of the
209 8 grids is spatially homogeneous for all compounds, we calculated a mean flux for each
210 NMVOC to derive the emission ratio from the inventory. Comparing emission ratios from the
211 inventory to observations collected at one measurement site stays relevant. Indeed the sub-
212 urban site is far enough from strong direct emissions (industrial, road transport) since they can
213 hide the emissions from distant sources, and it receives air masses coming from Greater
214 Beirut Area which includes the city of Beirut and close suburbs.

215

216 **4. Emission and chemistry of gaseous organic carbon in Beirut on a seasonal basis**

217 The intensity of the emissions, chemistry, and atmospheric dynamics varying throughout the
218 day can affect the diurnal profiles of NMVOC absolute mixing ratios and as a consequence
219 the values of urban enhancement emission ratios (ER) (see section 5). We report in figures 2
220 and 3 for summer and winter, respectively, the average diurnal normalized profiles to the
221 midnight value of some NMVOC relative to an ~~inert~~ tracer to examine the relative importance
222 of these processes (Borbon et al., 2013). Acetylene was chosen as a ~~relatively inertless~~
223 reactive combustion tracer and its normalized diurnal profile is reported in each panel (grey
224 shaded). The NMVOCs extremely high concentrations have been filtered by removing the
225 northern wind direction events, referring to the identified gasoline evaporation episodic PMF
226 (Positive Matrix Factorization) factor (Salameh et al. 2016), in order to minimize the impact
227 of the local industrial source located in the northern part of the site (Salameh et al., 2015,
228 2016).

229 In summer all NMHCs including acetylene show the same bi-modal pattern with one midday
230 and one midnight maximum as a result of primary emissions from Greater Beirut transported
231 at the background receptor site between 09:00 and 10:00 and accumulation of emissions at
232 night in a shallower boundary layer. The degree of chemical removal during the day is k_{OH} -
233 dependent (k_{OH} : rate coefficient for the reaction with OH) and increases with k_{OH} as

234 illustrated for alkenes and aromatics. At night alkenes and aromatics follows the pattern of
235 acetylene due to common sources, dilution and ~~less neglected~~ photochemistry. Then the
236 ~~magnitude~~ importance of daytime maximum and minimum concentrations becomes modulated
237 by chemical removal when k_{OH} is higher than $8.52 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (rate coefficient
238 of ethylene with OH). Compensation of chemical removal at midday by fresh evaporative
239 emission cannot be excluded for aromatics like toluene.

240 In winter the diurnal profiles of NMHCs including acetylene show a unimodal pattern
241 characterized by maximum concentrations in the morning typical of traffic rush hours and a
242 slight decrease until late evening. Contrary to summer, the absence of a midday minimum of
243 normalized concentrations indicates a strong accumulation of primary emissions during the
244 day which is favored by poor dilution and negligible photochemistry. However, the diurnal
245 profiles of alkenes illustrated in figure 3 are characterized by a most pronounced enhancement
246 in the evening which can be related to additional combustion sources like domestic heating
247 since the measurement site is surrounded by a residential area (Salameh et al., 2015).
248 Aromatics and alkanes diurnal profiles follow the shape of acetylene profile in general.
249 Nevertheless, one can see a strong enrichment of aromatics during the day originating from
250 the traffic related source where toluene and m,p-xylenes are significantly present (Watson et
251 al. 2001; Badol et al. 2008; Salameh et al., 2016).

252 In this section, we showed that some NMHC especially shorter-lived species like >C7-
253 aromatics, ethylene and propene could be affected by chemical removal in summer so that the
254 measured urban enhancement ratios can be different from the emission ratios. These results
255 are consistent with Salameh et al., 2015. The determination of ER in the next section will take
256 into account the potential effect of chemistry by applying temporal filters for the most
257 reactive species in summer. When NMHCs are not influenced by photochemistry, the
258 enhancement ratios will be estimated using all the data.

259 5. Determination of urban enhancement emission ratios

260 The emission ratio for NMVOC species is the ratio of a selected VOC to a reference
261 compound in fresh emissions without undergoing photochemical processing. We applied two
262 methods to determine emission ratios (ER) for each VOC species relative to CO and
263 acetylene. The first method consists in ~~non~~ linear regression fits (LRF) on data applied to
264 summer and winter datasets and the other method relies on extrapolating the photochemical

265 age to zero which was applied to the summer data, photochemical removal being negligible in
266 winter.

267 **5.1. Linear Regression Fit (LRF) method**

268 A commonly applied method to determine emission ratios is the linear regression fit (LRF) by
269 calculating the slope of the scatterplot between a particular NMVOC versus acetylene or CO
270 (Borbon et al., 2013). These reference compounds have been chosen due to their low
271 reactivity and since they are two tracers of incomplete combustion. Additionally, according to
272 the national emission inventory (Waked et al., 2012) and to PMF results (Salameh et al.,
273 2016), the road transport is the dominant source of NMVOCs in Lebanon and Greater Beirut;
274 in urban areas as well, emissions of CO are also dominated by vehicular emissions (von
275 Schneidemesser et al., 2010).

276 During both campaigns, as shown in the discussion in section 4, photochemical processing did
277 not play an important role in influencing NMVOC chemical compositions in ambient air of
278 Greater Beirut except for the most reactive species during the day in summer (alkenes and
279 aromatics). For the latter, emission ratios for NMVOC versus CO and for NMVOC versus
280 acetylene were derived from slopes of LRF for measurements made between 23:00 and 07:00
281 local time in summer when chemistry can be neglected. For isoprene, anthropogenic
282 emissions can be derived from nighttime data in the absence of its light-dependent biogenic
283 origin (Borbon et al., 2001). The LRF approach assumes that the composition of urban
284 emissions relative to CO and to acetylene does not change between day and night. For other
285 species, the emission ratios were derived from slopes of LRF for all the data in winter and
286 summer since there is no effect of photochemistry even during the day in summer, and in
287 order to cover the urban mixing of emissions from all the sources. The results are detailed in
288 section 5.4 and summarized in table 2.

289 **5.2. The Photochemical Age method**

290 The photochemical method takes into consideration the photochemical processing of
291 measured ratios of NMVOC with acetylene. We applied this method to all the summertime
292 dataset. Following de Gouw et al. (2005), Warneke et al. (2007), and Borbon et al. (2013), we
293 assume that the photochemical removal of NMVOC species is dominated by a reaction with
294 the OH radical. In this method, the ratio of NMVOC with acetylene is plotted versus the
295 photochemical age as shown in Figure 4.

296 | Firstly, tThe photochemical age of air masses, Δt , is estimated by using the NMVOC ratios
 297 following this equation:

$$298 \quad \Delta t = \frac{1}{[OH](k_{135TMB} - k_{benzene})} \times \left[\ln\left(\frac{[135TMB]}{[benzene]}\right)_{t=0} - \ln\left(\frac{[135TMB]}{[benzene]}\right) \right] \quad (1)$$

299 Where [OH] is the concentration of hydroxyl radical, fixed to $5 \times 10^6 \text{ molec.cm}^{-3}$; k_{135TMB}
 300 ($56.7 \times 10^{-12} \text{ cm}^3 \cdot \text{molec}^{-1} \cdot \text{s}^{-1}$) and $k_{benzene}$ ($1.22 \times 10^{-12} \text{ cm}^3 \cdot \text{molec}^{-1} \cdot \text{s}^{-1}$) are the reaction rate
 301 coefficients with OH radical of 1,3,5-trimethylbenzene and benzene, respectively; [135TMB]
 302 and [benzene] are the volume mixing ratios in ppb of benzene and 1,3,5-trimethylbenzene,
 303 respectively. The 1,3,5-trimethylbenzene/benzene ratio was chosen to investigate the
 304 photochemical age because these two compounds have similar sources but their lifetimes are
 305 significantly different and lower than air mass transport timescale. The ratio of [135TMB]
 306 over [benzene] at time zero ($t=0$) defines the emission ratio at a photochemical age of zero.
 307 This emission ratio was derived from a scatter plot of [135TMB] vs. [benzene], it corresponds
 308 to the emission enhancement ratio at nighttime data where photochemical processing can be
 309 neglected.

310 In figure 4, we report the ratios of measured benzene/acetylene, m,p-xylenes/acetylene, and
 311 ethylene/acetylene as a function of the photochemical age. Calculated photochemical age is
 312 usually lower than 1h. As expected, the benzene/acetylene ratio ~~keeps~~ remains constant with
 313 increasing photochemical age whereas a decrease of m,p-xylenes/acetylene and
 314 ethylene/acetylene ratios is observed because they are more reactive. Surprisingly the
 315 ethylene/acetylene ratio decreases faster than the (m,p)-xylenes/acetylene one while (m,p)-
 316 xylenes are two times more reactive than ethylene. The decrease of the (m,p)-
 317 xylenes/acetylene ratio might be modulated by additional evaporative emissions during the
 318 day that counterbalance its chemical removal.

319 Following de Gouw et al. (2005) and Warneke et al. (2007), the equation used for
 320 emission ratio determination illustrated in figure 4 is described as follows for primary
 321 NMHCs (equation 2):

$$322 \quad \frac{[NMVOC]}{[C_2H_2]} = ER_{NMVOC} \times \exp[-(k_{NMVOC} - k_{C_2H_2})[OH]\Delta t] \quad (2)$$

323 where [NMVOC] and [C₂H₂] are the volume mixing ratios in ppb of the NMVOC and
 324 acetylene respectively; ER_{NMVOC} is the emission ratio of the NMVOC relative to acetylene;

325 k_{NMVOC} and $k_{\text{C}_2\text{H}_2}$ are the OH rate coefficients for the reaction of those compounds with OH
326 radical ($[\text{OH}] = 5.10^6 \text{ molecules.cm}^{-3}$); and Δt is the photochemical age calculated by equation
327 1. The emission ratios of NMVOCs are estimated by extrapolating the photochemical age to
328 zero which is the intercept on the y-axis of the linear fit (figure 4).

329 Following Borbon et al. (2013) and Warneke et al. (2007), the emission ratios determined
330 with the photochemical age method are not affected when reducing or increasing the OH
331 values by a factor of 2.

332 **5.3. Performance of the different methods**

333 Figure 5 illustrates the performance of the ER determination methods for the summertime
334 data where ER from the photochemical age and LRF methods are compared. There is an
335 overall very good agreement between the two methods (slope of the linear fit in red = 0.90
336 and correlation coefficient of 0.99) showing the robustness of the methods and confirming
337 that the selection of all the data for less-reactive species and nighttime data for more reactive
338 species for summer in the LRF method does not bias the results. The calculated determination
339 coefficients R^2 with acetylene and CO ranged from 0.3 for some species like ethane to 0.9 for
340 the majority of the species in winter, and with acetylene in summer from 0.5 to 0.9 showing
341 the importance of combustion related sources during both seasons. The standard deviation of
342 the ER determined by the photochemical method was low and varied between zero and 0.04
343 for propane, the coefficient of variation was below 3% for the majority of the species
344 indicating the robustness of the photochemical method.

345 **5.4. Emission ratios and seasonal variability**

346 The ER derived from all wintertime and summertime (nighttime dataset for most reactive
347 species) datasets by the LRF method as well as the ER from the road transport established by
348 near-field measurements (Salameh et al., 2014) are summarized in Table 2. ERs relative to
349 CO were not calculated in summer because CO data were not available for the whole
350 campaign.

351 The ER derived from the observations (summer and winter) are comparable at $\pm 50\%$ to the
352 ratios of road transport sector, during at least one season, for more than 80% of the species.
353 This shows that urban emission fingerprint is mainly driven by traffic emissions including
354 ethane which does not have any urban natural gas usage contribution in Lebanon. For other
355 species like C4 to C6-alkenes, styrene, and a few alkanes in winter the differences stay within

356 a factor of 2, except for propane where they are 5 in summer and 3 in winter. These
357 differences can be partly explained by the contribution of additional sources.

358 In general, the ERs in winter are slightly lower than in summer (Table 2). Figure 6 compares
359 the derived emission ratios of NMVOC species relative to acetylene at the measurement site
360 during summer and winter. The wintertime emission ratios for most NMVOC species agree at
361 $\pm 30\%$ (slope of 0.71) with the summertime ERs and within a factor of 2 and a high
362 determination coefficient of 0.94. Finally, there is no significant seasonality in ER regardless
363 of the species except for 1-pentene, cyclohexane, styrene, 2,2-dimethylbutane, and 1,2,3-
364 trimethylbenzene. Those species are associated with ER lower than 0.1. These results indicate
365 that the urban emission composition contributing to the ambient concentrations is not
366 significantly different between summer and winter. The sources usually affected by
367 seasonality are in winter related to combustion and to fuel evaporation in summer. Our results
368 based on ER are consistent with previous PMF results (Salameh et al., 2016), showing that the
369 road transport sector (combustion and gasoline evaporation) is the dominating source in both
370 seasons in Beirut.

371 These findings are different from the results usually found in recent studies. For instance,
372 Boynard et al. (2014) found that the emission ratios relative to acetylene in French cities
373 (Paris and Strasbourg) are slightly affected by the seasonality of emissions for benzene and
374 alkenes whereas other NMVOC species (alkanes and higher aromatics) exhibit 3 to 7 higher
375 emission ratios in summer. Moreover, Wang et al. (2014) reported lower wintertime emission
376 ratios for most NMVOC species than the summertime values by a factor ≥ 2 in Beijing,
377 China. This seasonal difference in emission ratios for most NMVOC species is possibly due
378 to the seasonal variations in NMVOC sources and in particular the modulation between
379 wintertime combustion and summertime evaporation.

380 **6. Comparison to other cities worldwide**

381 The NMVOC emission ratios relative to acetylene determined in Beirut by the LRF method
382 are compared to those recently determined in contrasted cities of North America (Los
383 Angeles, USA), Europe (Strasbourg, France), Middle East (Mecca, Saudi Arabia), and Asia
384 (Beijing, China) on a seasonal basis in figure 7.

385 Usually ERs agree within a factor of 2 except for aromatics (benzene excepted) and some
386 alkanes (C2 – C5). Those species are related to the unburned fuel fraction and natural gas or
387 liquefied petrol usage.

388 Among C2-C5 alkanes and regardless of the season, ER of ethane is much lower in Beirut
389 than Los Angeles, Beijing, and Strasbourg but similar to Saudi Arabia since the natural gas
390 source is not widely used in Lebanon and Middle East countries (Salameh et al., 2015). ~~The~~
391 ~~maximum difference reached a factor of 10 for m,p-xylenes in winter.~~ Regardless of the
392 season, ERs of aromatics are higher in Beirut compared to northern post-industrialized
393 countries and even the Middle Eastern city Mecca. One should note that aromatic differences
394 are quite significant between the two Middle Eastern cities, from a factor of 3 up to a factor of
395 6 for (m,p)-xylenes. The maximum difference is observed between Beirut and Strasbourg and
396 reached a factor of 10 for m,p-xylenes in winter. ~~ERs of alkenes are higher in Mecca due to~~
397 ~~their additional evaporative origin (Simpson et al., 2014).~~ Differences are greater in winter
398 than in summer as a consequence of a marked seasonal variability of ER in other cities
399 (Strasbourg and Beijing) in opposite contrast to Beirut. In Beirut, the aromatics are emitted
400 from combustion related sources and from gasoline evaporation which accounts for more than
401 40% in winter as well as in summer (Salameh et al., 2016). ERs of alkenes, which are
402 combustion products, usually agree within a factor of two between Beirut, Los Angeles,
403 Beijing, and Strasbourg in both seasons, except for C4 and C5 alkenes with LA and Beijing;
404 whereas ~~ERs of alkenes they are higher in Mecca due to their additional evaporative origin~~
405 (Simpson et al., 2014).

406 **7. Evaluation of global emission inventories for anthropogenic speciated VOC emissions**

407 The emission fluxes ($\text{Kg/m}^2/\text{s}$) extracted from ECCAD database are converted to mole
408 emission fluxes, then the NMVOC ratios relative to CO and relative to acetylene are
409 determined.

410 The comparison held here will consider the common compounds present in the ACCMIP and
411 MACCity, when possible, global emission inventories and measured during ECOCEM
412 campaigns which are listed in table 3. Important NMVOC species are present within these
413 inventories as tracers of many anthropogenic sources, reactive species, and important
414 precursors of ozone and SOA (Table 3). We consider that the speciation is “reasonable” when
415 there is an agreement within a factor of two between observations and emission inventory.

416 **7.1. Emission inventory vs. observations: all anthropogenic sectors**

417 To analyze the consistency of the speciation of NMVOCs in the ACCMIP and MACCity
418 global emission inventories, we compared the individual NMVOC relative to CO as well as to
419 acetylene ratios during summer and winter obtained by the LRF method. Figure 8 displays the

420 ratios from the anthropogenic emissions data (ACCMIP and MACCcity) and the observations
421 in a logarithmic scale for 11 individual NMVOC species color coded by the NMVOC groups.
422 Except benzene, xylenes to a less extent and long-lived alkanes, ER relative to acetylene
423 agree within a factor of 2 between observations and inventory suggesting that the ~~overall~~
424 VOC speciation in ACCMIP is ~~reasonably better~~ represented for more reactive VOCs ~~such as~~
425 ~~alkenes and some aromatics~~. Regarding ER relative to CO, differences with ACCMIP are
426 ~~remarkable~~ significant. A global underestimation by the inventory by a shift towards lower ER
427 over an order of magnitude is observed suggesting an overestimation of CO emissions by
428 ACCMIP.

429 In order to consolidate our conclusions regarding VOC speciation within ACCMIP, we
430 performed the systematic calculation of the ratios of every NMVOC to each of the other
431 NMVOCs (NMVOC_i) in the global emission inventory and in the observations (Coll et al.,
432 2010) ~~separately, and then we reported in figure 9, the ERs obtained from ACCMIP versus~~
433 ~~those obtained from the observations~~. From figure 9, it appears that benzene is systematically
434 overestimated up to a factor of 5 in ACCMIP and to a lesser extent, pentanes and butanes by a
435 factor >2 whereas xylenes are ~~reasonably~~ underestimated in the ACCMIP global emission
436 inventory ~~but not systematically~~. The other compounds ~~lay around~~ are closer to the line of the
437 slope (= 1), below a factor of 2. Finally, comparisons between ACCMIP and observations
438 (figures 8 and 9) suggest that the overall speciation of anthropogenic sources for major
439 hydrocarbons that act as ozone and SOA precursors in ACCMIP is ~~reasonably better~~
440 represented ~~than the others species but it is still need improvement~~.

441 **7.2. Emission inventory vs. observations: road transport sector**

442 Our study has shown that calculated ER are comparable to the ones of road transport sector
443 for more than 80% of the species (table 2) which is consistent with PMF results (Salameh et
444 al., 2016). In Lebanon, PMF results showed that the major sources of NMHCs were traffic-
445 related emissions (combustion and gasoline evaporation) in winter and in summer accounting
446 for 51 and 74 wt% respectively. Moreover, according to Parrish et al. (2009), the largest
447 source of emissions in most urban areas is road traffic, which includes tailpipe and
448 evaporative emissions. Therefore, it is also crucial to assess the emission inventories
449 regarding the road transport sector namely ACCMIP and EMEP SNAP 07.

450 We proceeded as in the previous section by comparing the road transport ER relative to
451 acetylene for all VOCs and individual VOCs from ACCMIP and EMEP emission inventories

452 | to the ER from near-field measurements (figures 10 and 11) (Salameh et al., 2014). ERs of
453 | alkenes from the road transport sector are usually consistent within a factor of 2 for the
454 | regional emission inventory EMEP and the global inventory ACCMIP. In EMEP, benzene
455 | and ethane are overestimated whereas butanes are underestimated; while xylenes and toluene
456 | are underestimated over a factor of 2 by ACCMIP. At a more detailed level, by calculating the
457 | ratios for individual NMVOC, figure 11 confirms that xylenes and toluene are underestimated
458 | species by both inventories, and benzene is overestimated by EMEP.

459 | **7.3. Perspectives for Middle East region (MEA)**

460 | After a focus on Lebanon, the purpose of this last section is to provide some perspectives
461 | regarding the whole MEA region. Figure 12 shows the comparison of ER relative to acetylene
462 | from the ACCMIP emission inventory considering all the anthropogenic sectors of Lebanon
463 | compared to the ones of four other Middle Eastern countries that are expected to be high VOC
464 | emitters (Saudi Arabia, Egypt, Iran and Turkey). An overall homogeneity agreement within a
465 | factor of 2 of the ERs is observed between countries of the Mediterranean border (Lebanon,
466 | Turkey, and Egypt). However, when comparing Lebanon to other Middle East countries,
467 | some gaps are depicted: The emission inventory suggests that the ERs of benzene, toluene, as
468 | well as of C4-C5 alkanes are lower in Lebanon compared to Iran and Saudi Arabia. For the
469 | latter those observations are completely contradictory with the ones reported in figure 7. We
470 | have shown that the anthropogenic emissions in Beirut were more enriched in aromatics and
471 | propane and poorer in some alkenes than the ones of Mecca while benzene ER was consistent
472 | between both countries. While the comparison here is limited by the number of species
473 | compared to figure 7 this suggests that the global emission inventory does not reproduce the
474 | heterogeneity of VOC anthropogenic emission composition between countries of the MEA.
475 | This could be indicative for other and same results can be expected for all the MEA countries
476 | where emissions data and measurements are scarce. Systematic and additional observations
477 | are needed in order to test the importance of such spatial variability in anthropogenic VOC
478 | emission composition.

479 | **8. Conclusions**

480 | Detailed measurements of NMVOCs collected at a sub-urban site in Beirut, Lebanon, have
481 | been used to evaluate regional and global emission inventories (ACCMIP, MACCity and
482 | EMEP) downscaled to the studied domain. These data were collected during two intensive
483 | field campaigns in summer 2011 and in winter 2012 within the framework of the ECOCEM
484 | project.

485 The emission ratios (ER) of individual NMVOC species relative to CO and acetylene were
486 successfully derived from ambient measurements in summer and in winter as well as from
487 near-field measurements for the road transport sector by applying two independent methods:
488 the linear regression fit method and the photochemical age method. Emission ratios from both
489 methods show a very good agreement at $\pm 10\%$.

490 The ER derived from the observations (summer and winter) are comparable to the ratios of
491 the road transport sector for more than 80% of the species. There is generally no significant
492 seasonality in ER regardless of the species unlike the seasonality usually observed in other
493 cities. These results are consistent with the significant contribution of road transport sector
494 (combustion and gasoline evaporation) in winter and summer (Salameh et al., 2016).

495 Regardless of the season, ERs derived from observations agree within a factor of 2 between
496 Beirut and other representative worldwide cities except for the unburned fuel fraction and
497 ethane. Aromatics (benzene excepted) show the largest differences up to a factor of 10 for
498 m,p-xylenes compared to northern post-industrialized countries and even another middle
499 eastern city like Mecca in Saudi Arabia.

500 ER relative to CO and to acetylene as well as the ratios of every NMVOC to each of the other
501 NMVOCs ($NMVOC_i$), extracted from ACCMIP and MACCity global emission inventory
502 were compared with the corresponding observed ER during both seasons, for all
503 anthropogenic sectors. This comparison suggests that the overall speciation of anthropogenic
504 sources for major hydrocarbons that act as ozone and SOA precursors in ACCMIP is
505 reasonably better represented than other species but it is still need improvement.

506 The road transport ER relative to acetylene derived from near-field measurements are
507 compared to ER from ACCMIP and EMEP regional emission inventory for the road transport
508 sector. ERs of more reactive species (alkenes and aromatics except benzene) from the road
509 transport sector are usually consistent within a factor of 2 for the regional emission inventory
510 EMEP while xylenes and toluene are underestimated over a factor of 2 by ACCMIP.

511 It should be emphasized that when a consensus is met between observed and inventory ER
512 (the ER lay around the ratio of 1), this does not necessarily mean that the absolute emissions
513 are correct. Indeed, Salameh et al. (2016) have shown that global inventories (ACCMIP,
514 EDGAR, MACCity) could underestimate the NMVOC emissions up to a factor of 10 for the
515 transportation sector. Both speciation and absolute emissions have to be taken into
516 consideration.

517 Finally, we have shown that the emission inventory is in disagreement with the observations
518 when comparing Lebanon with Saudi Arabia. The observed heterogeneity of anthropogenic

519 VOC emission composition can be significant for reactive VOC (factor of 6 for m,p-xylenes)
520 but is not depicted by global emission inventories. This suggests that systematic and detailed
521 measurements are needed in the MEA region in order to better constrain emission inventory.
522 VOC emission inventory is the fundamental input of air quality modelling, therefore it plays a
523 major role in characterizing secondary pollution and control policy formulation. To improve
524 the quality of future VOC emission estimates, more efforts should be made toward refinement
525 of source classification, development of representative local emission factors, comprehensive
526 collection of activity data, and more accurate spatio temporal characterization. Additionally,
527 comparison of available datasets will allow a quantification of the uncertainties on emissions.

528 At a regional and global level, long term and continuous studies integrating more than one
529 measuring site and more specific tracers are of great interest in order to provide more reliable
530 information and the use of surface observations from monitoring stations could help defining
531 better speciations.

532

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543 **References:**

544 Amann, M., Bertok, I., Borken-Kleefeld, J., Cofala, J., Heyes, C., Höglund-Isaksson, L.,
545 Klimont, Z., Nguyen, B., Posch, M., Rafaj, P., Sandler, R., Schöpp, W., Wagner, F., and
546 Winiwarter, W.: Cost-effective control of air quality and greenhouse gases in Europe:
547 Modelling and policy applications, Environmental Modelling and Software, Vol. 26, pp. 1489-
548 1501, 2011.

549 Atkinson, R., and Arey, J.: Atmospheric degradation of volatile organic compounds. Chem.
550 Rev. 103, 4605. doi:10.1021/CR0206420, 2003.

551 Atkinson, R.: Gas-phase tropospheric chemistry of organic compounds: a review. *Atmos.*
552 *Environ.* 41, 200. doi:10.1016/J.ATMOSENV.2007.10.068, 2007.

553 [Badol, C, Locoge, N, Léonardis, T., and Gallo, J.-C.: using a source–receptor approach to](#)
554 [characterise VOC behaviour in a French urban area influenced by industrial emissions Part I:](#)
555 [Study area description, data set acquisition and qualitative data analysis of the data set.](#)
556 [Science of The Total Environment, 389, 441–452, 2008.](#)

557 Bechara, J., Borbon, A., Jambert, C., and Perros, P. E.: New off-line aircraft instrumentation for
558 non-methane hydrocarbon measurements, *Anal. Bioanal. Chem.*, 392, 865–876,
559 doi:10.1007/s00216-008-2330-3, 2008.

560 Borbon, A., Fontaine, H., Veillerot, M., Locoge, N., Galloo, J.C., and Guillermo, R.: An
561 investigation into the traffic related fraction of isoprene at an urban location, *Atmos. Environ.*,
562 35(22), 3749–3760, 2001.

563 Borbon, A., Gilman, J.B., Kuster, W.C., Grand, N., Chevaillier, S., Colomb, A., Dolgorouky,
564 C., Gros, V., Lopez, M., Sarda-Esteve, R., Holloway, J., Stutz, J., Perrussel, O., Petetin, H.,
565 McKeen, S., Beekmann, M., Warneke, C., Parrish D.D., and de Gouw, J.A.: Emission ratios
566 of anthropogenic VOC in northern mid-latitude megacities: observations vs. emission
567 inventories in Los Angeles and Paris, *J. Geophys. Res.*, vol. 118, 2041 - 2057,
568 doi:10.1002/jgrd.50059, 2013.

569 Boynard, A., Borbon, A., Leonardis, T., Barletta, B., Meinardi, S., Blake, D. R., and Locoge,
570 N.: Spatial and seasonal variability of measured anthropogenic non-methane hydrocarbons in
571 urban atmospheres: Implication on emission ratios, *Atmos. Environ.*, 82, 258–267,
572 doi:10.1016/j.atmosenv.2013.09.039, 2014.

573 Coll, I., Rousseau, C., Barletta, B., Meinardi, S., and Blake, D.R.: Evaluation of an urban
574 NMHC emission inventory by measurements and impact on CTM results, *Atmospheric*
575 *Environment*, 44, 3843-3855, 2010.

576 de Gouw, J. A., Middlebrook, A. M., Warneke, C., Goldan, P.D., Kuster, W. C., Roberts,
577 J.M., Fehsenfeld, F. C., Worsnop, D. R., Canagaratna, M. R., Pszenny, A. A. P., Keene, W.
578 C., Marchewka, M., Bertman, S. B., and Bates, T. S.: Budget of organic carbon in a
579 polluted atmosphere: Results from the New England Air Quality Study in 2002, *J. Geophys.*
580 *Res.-Atmos.*, 110, D16305, doi:10.1029/2004jd005623, 2005.

581 deGouw, J., and Warneke, C.: Measurements of volatile organic compounds in the Earth's
582 atmosphere using proton-transfer-reaction mass spectrometry, *Mass Spectrom. Rev.*, 26(2),
583 223–257, 2007.

584 Derwent, R.G., Jenkin, M.E., Utembe, S.R., Shallcross, D.E., Murrells, T.P., and Passant,
585 N.R.: Secondary organic aerosol formation from a large number of reactive man-made
586 organic compounds, *Science of the Total Environment*, 408, 3374–3381, 2010.

587 ECCAD database: http://eccad.sedoo.fr/eccad_extract_interface/JSF/page_products_em.jsf

588 EMEP/EEA, 2009. Air Pollutant Emission Inventory Guidebook. www.eea.europa.eu.

589 Granier, C., Bessagnet, B., Bond, T., D'Angiola, A., van der Gon, H.D., Frost, G.J., Heil, A.,
590 Kaiser, J.W., Kinne, S., Klimont, Z., Kloster, S., Lamarque, J-F., Liousse, C., Masui,
591 T., Meleux, F., Mieville, A., Ohara, T., Raut, J.-C., Riahi, K., Schultz, M.G., Smith, S.J.,
592 Thompson, A., van Aardenne, J., van der Werf, G.R., and van Vuuren, D.P.: Evolution of
593 anthropogenic and biomass burning emissions of air pollutants at global and regional
594 scales during the 1980–2010 period, *Climatic Change*, 109, 163 - 190, doi: 10.1007/s10584-
595 011-0154-1, 2011.

596 Gurjar, B., Butler, T., Lawrence, M., and Lelieveld, J.: Evaluation of emissions and air quality
597 in megacities, *Atmos. Environ.*, 42, 1593–1606, 2008.

598 Hillboll, A., Richter, A., and Burrows, J.P.: Long-term changes of tropospheric NO₂ over
599 megacities derived from multiple satellite instruments, *Atmos. Chem. Phys.*, 13, 4145–4169,
600 doi:10.5194/acp-13-4145-2013, 2013.

601 Im, U., Poupkou, A., Incecik, S., Markakis, K., Kindap, T., Unal, A., Melas, D., Yenigun, O.,
602 Topcu, S., Odman, M.T., Tayanc, M., and Guler, M.: The impact of anthropogenic and
603 biogenic emissions on surface ozone concentrations in Istanbul. *Science of the Total*
604 *Environment* 409, 1255-1265, 2011.

605 Janssens-Maenhout, G., Petrescu, A., Muntean, M., and Blujdea, V.: Verifying Greenhouse
606 Gas Emissions: Methods to Support International Climate Agreements, *Greenhouse Gas*
607 *Measurement and Management* vol. 1, no. 2, p. 132-133, JRC67524, 2011.

608 Kanakidou, M., Mihalopoulos, N., Kindap, T., Im, U., Vrekoussis, M., Gerasopoulos, E.,
609 Dermizaki, E., Unal, A., Koçak, M., Markakis, K., Melas, D., Kouvarakis, G., Youssef, A.F.,

610 Richter, A., Hatzianastassiou, N., Hilboll, A., Ebojie, F., Wittrock, F., von Savigny, C.,
611 Burrows, J.P., Ladstaetter-Weissenmayer, A., and Moubasher, H.: Megacities as hot spots of
612 air pollution in the East Mediterranean. *Atmospheric Environment* 45, 1223 – 1235,
613 doi:10.1016/j.atmosenv.2010.11.048,2011.

614 Kim, S. W., McKeen, S.A., Frost, G.J., Lee, S.H., Trainer, M., Richter, A., Angevine,
615 W. M., Atlas, E., Bianco, L., Boersma, K. F., Brioude, J., Burrows, J. P., de Gouw, J., Fried,
616 A., Gleason, J., Hilboll, A., Mellqvist, J., Peischl, J., Richter, D., Rivera, C., Ryerson,
617 T.,te Lintel Hekkert, S., Walega, J., Warneke, C.,Weibring, P., and Williams, E.: Evaluations
618 of NO_x and highly reactive VOC emission inventories in Texas and their implications for
619 ozone plume simulations during the Texas Air Quality Study 2006, *Atmos. Chem. Phys.*,
620 11(22), 11,361–11,386, 2011.

621 Klimont, Z., Smith, S.J., and Cofala, J.: The last decade of global anthropogenic sulfur
622 dioxide: 2000–2011 emissions, *Environmental Research Letters* 8 (1): 014003,
623 doi:10.1088/1748-9326/8/1/014003,2013.

624 Konovalov, I. B., Beekmann, M., Richter, A., Burrows, J. P., and Hilboll, A.: Multi-annual
625 changes of NO_x emissions in megacity regions: nonlinear trend analysis of satellite
626 measurement based estimates, *Atmos. Chem. Phys.*, 10, 8481–8498, doi:10.5194/acp-10-
627 8481-2010, 2010.

628 Lamarque, J.F., Bond, T.C., Eyring, V., Granier, C., Heil, A., Klimont, Z., Lee, D., Liousse,
629 C., Mieville, A., Owen, B.,Schultz, M.G., Shindell, D., Smith, S.J., Stehfest, E., Van
630 Aardenne, J., Cooper, O.R., Kainuma, M., Mahowald, N.,McConnell, J.R., Naik, V., Riahi,
631 K., and van Vuuren, D.P.: Historical (1850–2000) gridded anthropogenicand biomass burning
632 emissions of reactive gases and aerosols: methodology and application,*AtmosChemPhys* 10,
633 7017–7039, doi:10.5194/acp-10-7017-2010, 2010.

634 Lelieveld, J., Hoor, P., Jöckel, P., Pozzer, A., Hadjinicolaou, P., Cammas, J.P., and Beirle, S.:
635 Severe ozone air pollution in the Persian Gulf region, *AtmosChemPhys* 9, 1393–1406, 2009.

636 Lelieveld, J., Hadjinicolaou, P., Kostopoulou, E., Chenoweth, J., Giannakopoulos,C.,
637 Hannides, C., Lange, M. A., El Maayar, M.,Tanarhte, M., Tyrlis, E., and Xoplaki, E.: Climate
638 change andimpacts in the Eastern Mediterranean and the Middle East, *Clim.Chang.*, 114,
639 667–687, 2012.

640 Lindinger, W., Hansel, A., and Jordan, A.: On-line monitoring of volatile organic compounds
641 at pptv levels by means of proton transfer-reaction mass spectrometry (PTR-MS): Medical
642 applications, food control and environmental research, *Int. J. Mass Spectrom.*, 173(3), 191–
643 241, 1998.

644 Markakis, K., Im, U., Unal, A., Melas, D., Yenigun, O., Incecik, S.: Compilation of a GIS
645 based high spatially and temporally resolved emission inventory for the greater Istanbul area,
646 *Atmospheric Pollution Research* 3, 112-125, 2012.

647 Martin, R. V., Jacob, D. J., Chance, K., Kurosu, T.P., Palmer, P.I., and Evans, M.J.: Global
648 inventory of nitrogen oxides emissions constrained by space-based observations of NO₂
649 columns, *J. Geophys. Res.*, 108(D17), 4537, doi: 10.1029/2003JD003453, 2003.

650 Parrish, D. D., Kuster, W.C., Shao, M., Yokouchi, Y., Kondo, Y., Goldan, P.D., de Gouw,
651 J.A., Koike, M., and Shirai, T.: Comparison of air pollutant emissions among mega-cities,
652 *Atmospheric Environment* 43 6435 – 6441, doi:10.1016/j.atmosenv.2009.06.024, 2009.

653 Pozzer, A., Zimmermann, P., Doering, U.M., van Aardenne, J., Tost, H., Dentener, F.,
654 Janssens-Maenhout, G., and Lelieveld, J.: Effects of business-as-usual anthropogenic
655 emissions on air quality, *Atmos. Chem. Phys.*, 12, 6915–6937, doi:10.5194/acp-12-6915-
656 2012, 2012.

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

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

664 Salameh, T., Sauvage, S., Afif, C., Borbon, A., and Locoge, N.: Source apportionment
665 vs. emission inventories of non-methane hydrocarbons (NMHC) in an urban area of the
666 Middle East: local and global perspectives. *Atmos. Chem. Phys.*, 16, 3595–3607,
667 doi:10.5194/acp-16-3595-2016, 2016.

668 Sauvage, S., Plaisance, H., Locoge, N., Wroblewski A., Coddeville P., and Galloo, J.C.: Long
669 term measurement and source apportionment of non-methane hydrocarbons in three
670 French rural areas. *Atmos Environ* 43:2430–2441, 2009.

671 Schultz, M., Rast, S., van het Bolscher, M., Pulles, T., Pereira, J., Spessa, A., Dalsøren, S.,
672 van Noije, T., and Szopa, S.: REanalysis of the Tropospheric chemical composition over the
673 past 40 years, A long-term global modeling study of tropospheric chemistry funded under the
674 5th EU framework programme. Tech.rep., EU-Contract No. EVK2-CT-2002-00170, 2007.

675 Simpson, I.J., Aburizaiza, O.S., Siddique, A., Barletta, B., Blake, N.J., Gartner, A., Khwaja, H.,
676 Meinardi, S., Zeb, J., and Blake, D.R.: Air Quality in Mecca and Surrounding Holy Places in
677 Saudi Arabia During Hajj: Initial Survey. *Environ. Sci. Technol.* 48, 8529–8537,
678 [dx.doi.org/10.1021/es5017476](https://doi.org/10.1021/es5017476), 2014.

679 Uherek, E., Halenka, T., Borcken-Kleefeld, J., Balkanski, Y., Berntsen, T., Borrego, C., Gauss,
680 M., Hoor, P., Juda-Rezler, K., Lelieveld, J., Melas, D., Rypdal, K., Schmid, S.: Transport
681 impacts on atmosphere and climate: Land transport, *Atmospheric Environment* 44, 4772-
682 4816, 2010.

683 Van Vuuren, D.P., Edmonds, J., Kainuma, M., Riahi, K., Thomson, A., Hibbard, T., Hurtt,
684 G.C., Kram, T., Krey, V., Lamarque, J.F., Masui, T., Meinshausen, M., Nakicenovic, N., Smith,
685 S.J., and Rose, S.K.: The Representative Concentration Pathways: an overview, *Climatic*
686 *Change*, 109, 5-31, [doi:10.1007/s10584-011-0148-z](https://doi.org/10.1007/s10584-011-0148-z), 2011.

687 Von Schneidemesser, E., Monks, P.S., Gros, V., Gauduin, J., and Sanchez O.: How important
688 is biogenic isoprene in an urban environment? A study in London and Paris, *Geophysical*
689 *Research Letters*, Vol. 38, L19804, [doi: 10.1029/2011GL048647](https://doi.org/10.1029/2011GL048647), 2011.

690 Waked, A., and Afif, C.: Emissions of air pollutants from road transport in Lebanon and other
691 countries in the Middle East region, *Atmos Environ* 61, 446 – 452, 2012.

692 Waked, A., Afif, C., and Seigneur, C.: An atmospheric emission inventory of anthropogenic
693 and biogenic sources for Lebanon, *Atmospheric Environment* 50, 88-96, 2012.

694 Waked, A., Seigneur C., Couvidat F., Kim Y., Sartelet K., Afif C., Borbon A., Formenti P.,
695 and Sauvage, S.: Modeling air pollution in Lebanon: evaluation at a suburban site in Beirut
696 during summer, *Atmos Chem Phys* 13, 5873 – 5886, 2013a.

697 Wang, M., Shao, M., Chen, W., Yuan, B., Lu, S., Zhang, Q., Zeng, L., and Wang, Q.: A
698 temporally and spatially resolved validation of emission inventories by measurements of
699 ambient volatile organic compounds in Beijing, China, *Atmos. Chem. Phys.*, 14, 5871–5891,
700 doi:10.5194/acp-14-5871, 2014.

701 Warneke, C., McKeen, S. A. , de Gouw, J.A., Goldan, P.D., Kuster, W.C., Holloway, J.S.,
702 Williams, E.J., Lerner, B.M., Parrish, D.D., Trainer, M., Fehsenfeld, F.C., Kato, S., Atlas,
703 E.L., Baker, A., and Blake, D.R. :Determination of urban volatile organic compound emission
704 ratios and comparison with an emissions database, *J. Geophys. Res.*, 112, D10S47,
705 doi:10.1029/2006JD007930, 2007.

706 Warneke, C., de Gouw, J. A., Holloway, J. S., Peischl, J., Ryerson, T. B., Atlas, E., Blake, D.,
707 Trainer, M., and Parrish, D. D.: Multiyear trends in volatile organic compounds in Los
708 Angeles, California: Five decades of decreasing emissions, *J. Geophys. Res.*, 117,
709 D00V17, doi:10.1029/2012JD017899, 2012.

710 [Watson, J.G., Chow, J.C., Fujita, E.M.: Review of volatile organic compound source](#)
711 [apportionment by chemical mass balance. *Atmos Environ* 35, 567–1584, 2001.](#)

712 Zanis, P., Hadjinicolaou, P., Pozzer, A., Tyrllis, E., Dafka, S., Mihalopoulos, N., and
713 Lelieveld, J.: Summertime free-tropospheric ozone pool over the
714 easternMediterranean/Middle East, *Atmos. Chem. Phys.*, 14, 115–132, 10.5194/acp-14-115-
715 2014, 2014.

Table 1: Measurements during ECOCEM Campaigns.

Species	Instrument	Time resolution	Performances	References
On-line				
67 C2-C9 NMHC 29 alkanes 19 alkenes 2 alkynes 17 aromatics	TD-GC-FID	1 h	DL: 40 - 90 ppt, uncertainty: 4 - 35% for the majority of the NMHCs	Salameh et al., 2014, 2016
Off-line				
67 C2-C9 NMHC	Canister / TD-GC-FID	Sampling < 3 min / 1h analysis	DL: 40 - 90 ppt, uncertainty: 15%	Salameh et al., 2014, Sauvage et al., 2009

Table 2: Urban Emission Ratios of VOCs Relative to Acetylene and CO in Beirut in summer and in winter obtained by calculating a Linear Regression Fit to Data. The ERs from road transport by near-field measurements are also reported. Bold characters indicate the similarity at $\pm 50\%$ of the VOC/acetylene ER from the measurement campaigns to the one of near-field measurements.

NMVOC	$\Delta\text{VOC}/\Delta\text{C}_2\text{H}_2$ (ppb/ppb)			$\Delta\text{VOC}/\Delta\text{CO}$ (ppb/ppm)
	Beirut– summer 2011	Beirut– winter 2012	road transport-near field spring 2012 measurement (Salameh et al., 2014)	Beirut – winter 2012
ethane	0.23	0.18	0.21	1.50
propane	1.02	0.58	0.21	5.40
n-butane	1.14	0.95	1.87	6.70
i-butane	0.25	0.48	0.72	3.30
n-pentane	0.26	0.15	0.40	1.10
i-pentane	1.22	0.75	1.77	5.30
2-methyl-pentane	0.29	0.18	0.30	1.20
3-methyl-pentane	0.17	0.11	0.16	0.80
2,2-dimethylbutane	0.10	0.03	0.11	0.20
n-hexane	0.11	0.10	0.10	0.90
Methylcyclopentane	0.13	0.11	0.06	0.90
2-methyl-hexane	0.11	0.08	0.08	0.70
3-methyl-hexane	0.11	0.09	0.09	0.70
cyclohexane	0.04	0.01	0.01	0.10
n-heptane	0.07	0.05	0.06	0.40

2,3-dimethylpentane	0.04	0.03	0.03	0.20
Methylcyclohexane	0.04	0.03	0.03	0.20
3-methyl-heptane	0.03	0.02	0.02	0.20
n-octane	0.04	0.02	0.02	0.20
2,2,4-trimethylpentane	0.17	0.13	0.19	1.00
2,3,4-trimethylpentane	0.06	0.04	0.08	0.30
n-nonane	0.04	0.03	0.01	0.20
acetylene	-	-	-	8.20
propyne	0.05	0.04	0.04	0.40
ethene	1.59	1.02	0.97	9.30
propene	0.47	0.32	0.31	3.00
1-butene	0.10	0.09	0.20	0.70
cis-2-butene	0.13	0.08	0.15	0.60
trans-2-butene	0.16	0.11	0.19	0.90
isobutene	0.17	0.12	0.42	1.00
3-methyl-1-butene	0.03	0.02	0.05	0.10
2-methyl-1-butene	0.09	0.06	0.15	0.40
1-pentene	0.05	0.17	0.34	1.40
cis-2-pentene	0.05	0.05	0.11	0.40
trans-2-pentene	0.11	0.11	0.25	0.80
1,3-butadiene	0.08	0.05	0.07	0.50
isoprene	0.04	0.02	0.04	0.20
Cyclopentene	0.02	0.01	0.03	0.10
Methylcyclopentene	0.02	0.01	0.02	0.10
1-hexene	0.02	0.01	0.03	0.10
benzene	0.25	0.23	0.24	2.00
toluene	1.56	1.33	1.09	11.10
m,p-xylenes	0.81	0.57	0.61	4.80
o-xylene	0.27	0.19	0.19	1.70
Ethylbenzene	0.23	0.16	0.15	1.40
n-propylbenzene	0.03	0.02	0.02	0.20
Isopropylbenzene	0.01	0.01	0.01	0.04
m-ethyltoluene	0.14	0.09	0.09	0.80
p-ethyltoluene	0.06	0.04	0.04	0.30
o-ethyltoluene	0.04	0.03	0.04	0.30
styrene	0.05	0.02	0.02	0.20
1,3,5-trimethylbenzene	0.08	0.04	0.05	0.30
1,2,3-trimethylbenzene	0.05	0.01	0.04	0.08
1,2,4-trimethylbenzene&decane	0.24	0.16	0.19	1.40

nd: not determined

Table 3: List of target species and their K_{OH} (Atkinson and Arey 2003; Atkinson 2007) and Y_{SOA} (SOA formation potential) (Derwent et al., 2010)

ACCMIP nomenclature MACCity*	Compounds considered from ECOCEM database	K_{OH} ($10^{-12} \text{cm}^3 \cdot \text{molécule}^{-1} \cdot \text{s}^{-1}$)	Y_{SOA}
Ethane*	Ethane	0.25	0.1
Propane*	Propane	1.09	0
Butanes	Butane and isobutane	2.36 and 2.12	0.3 and 0
Pentanes	Pentane and isopentane	3.8 and 3.6	0.3 and 0.2
Ethene*	Ethene	8.52	1.3
Propene*	Propene	26.3	1.6
Acetylene	Acetylene	0.9	0.1
Benzene	Benzene	1.22	92.9
Trimethylbenzene	Sum of 1,2,3-1,2,4-,1,3,5-trimethylbenzene	32.7; 32.5; 56.7	43.9; 20.6; 13.5
Toluene	Toluene	5.63	100
Xylenes	Sum of m,p-xylenes and o-xylene	13.6; 23.1; 14.3	95.5; 84.5; 67.1
CO*	CO		

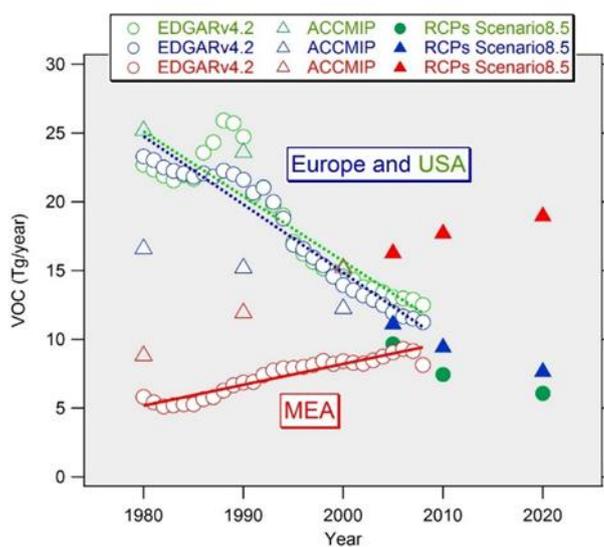


Figure 1: Evolution of the NMVOC anthropogenic total emissions (Tg/year) in the MEA, USA and Europe (OECD Europe and Eastern Europe) from 1980 to 2020 from reference global emission inventories (ECCAD database).

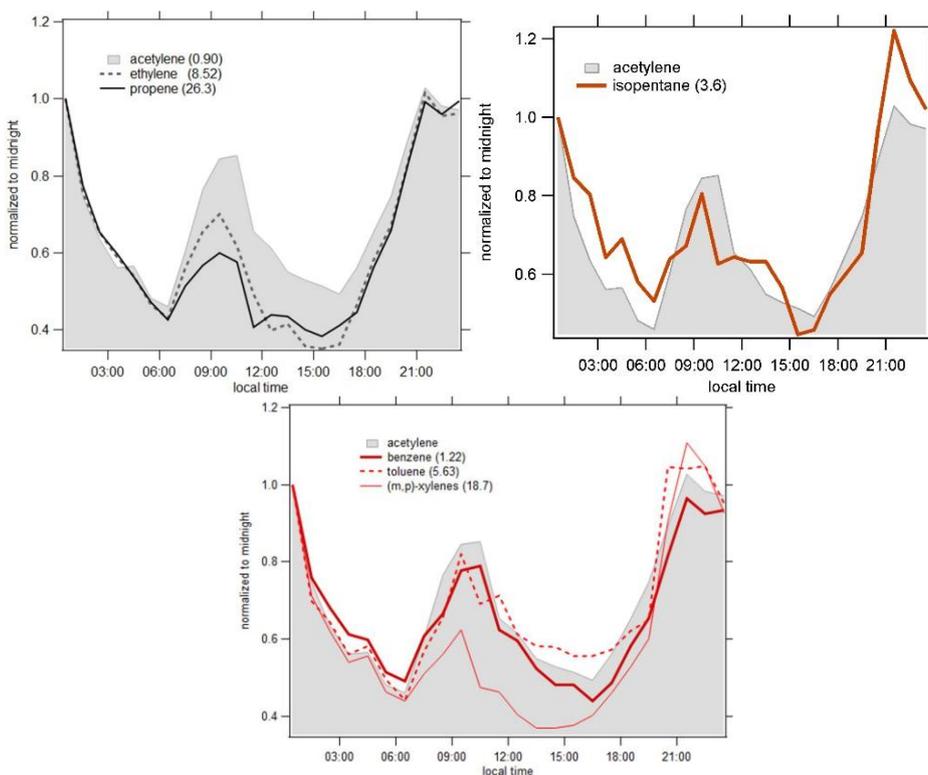


Figure 2: Normalized diurnal profiles of the mixing ratios of selected species to midnight values in summer. Numbers in parentheses are the rate coefficient with $\text{OH} \times 10^{-12} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ (Atkinson and Arey2003; Atkinson 2007).

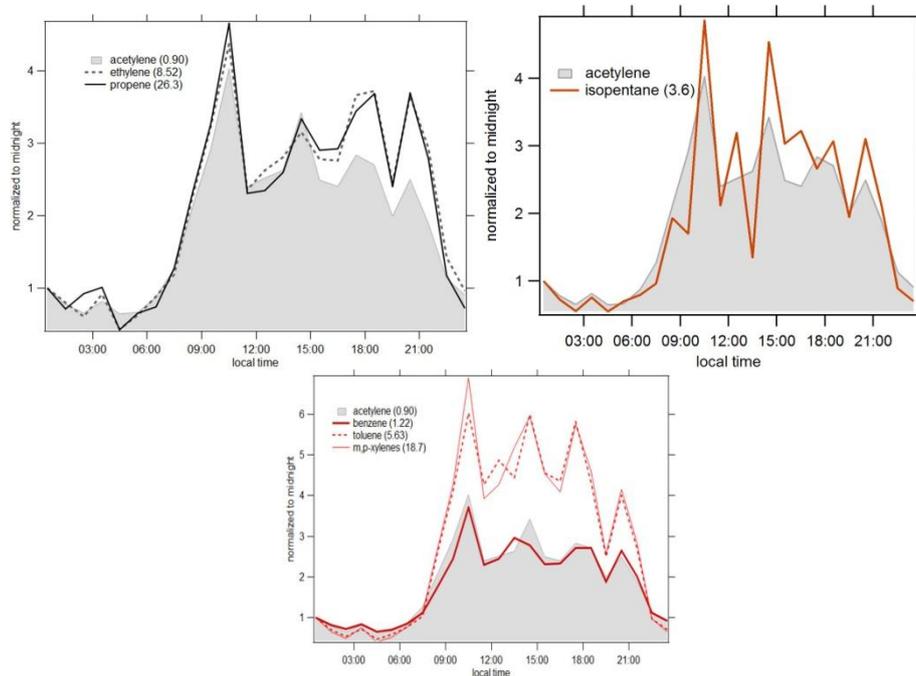


Figure 3: Normalized diurnal profiles of the mixing ratios of selected species to midnight values in winter. Numbers in parentheses are the rate coefficient with $\text{OH} \times 10^{-12} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ (Atkinson and Arey2003; Atkinson 2007).

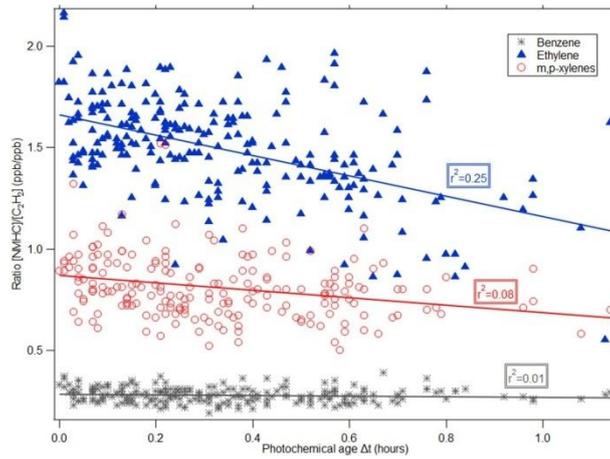


Figure 4: Measured ratios of benzene/acetylene, m,p-xylenes/acetylene, and ethylene/acetylene as a function of photochemical age (hours).

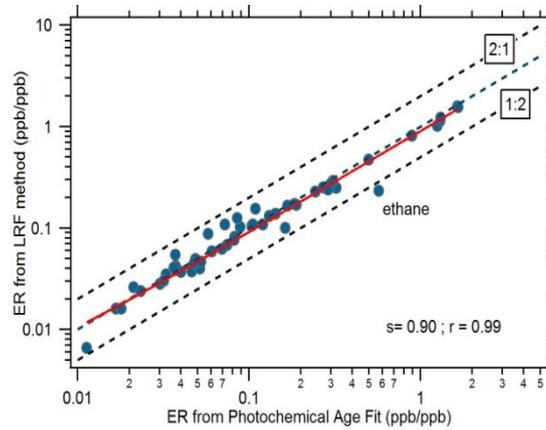


Figure 5: Comparison of the emission ratio (ER) estimated relative to acetylene by the nighttime linear regression fit and the photochemical age fit in summer.

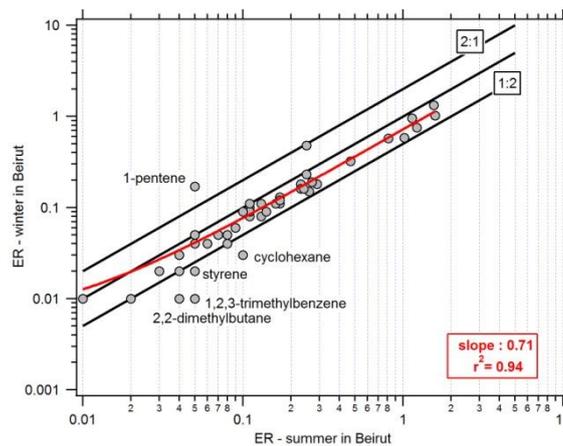


Figure 6: Comparison of summertime and wintertime emission ratios vs. acetylene in Beirut.

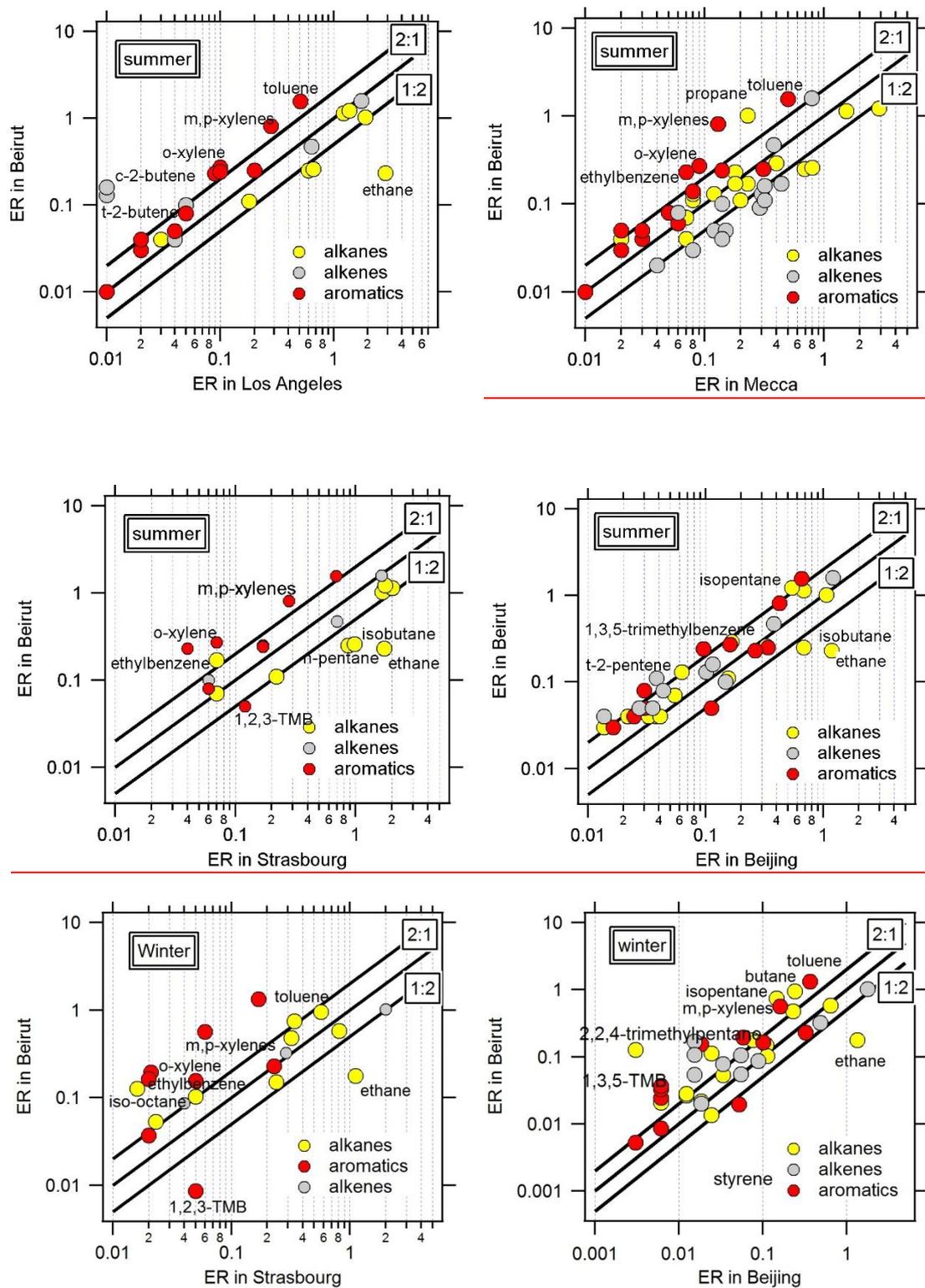


Figure 7: Comparisons of NMVOC emission ratios determined at the Beirut sub-urban site with those for Los Angeles, US (Borbon et al., 2013); Strasbourg, France (Boynard et al., 2014); Beijing, China (wang et al., 2014); and Mecca, Saudi Arabia (Simpson et al., 2014). (TMB: Trimethylbenzene)

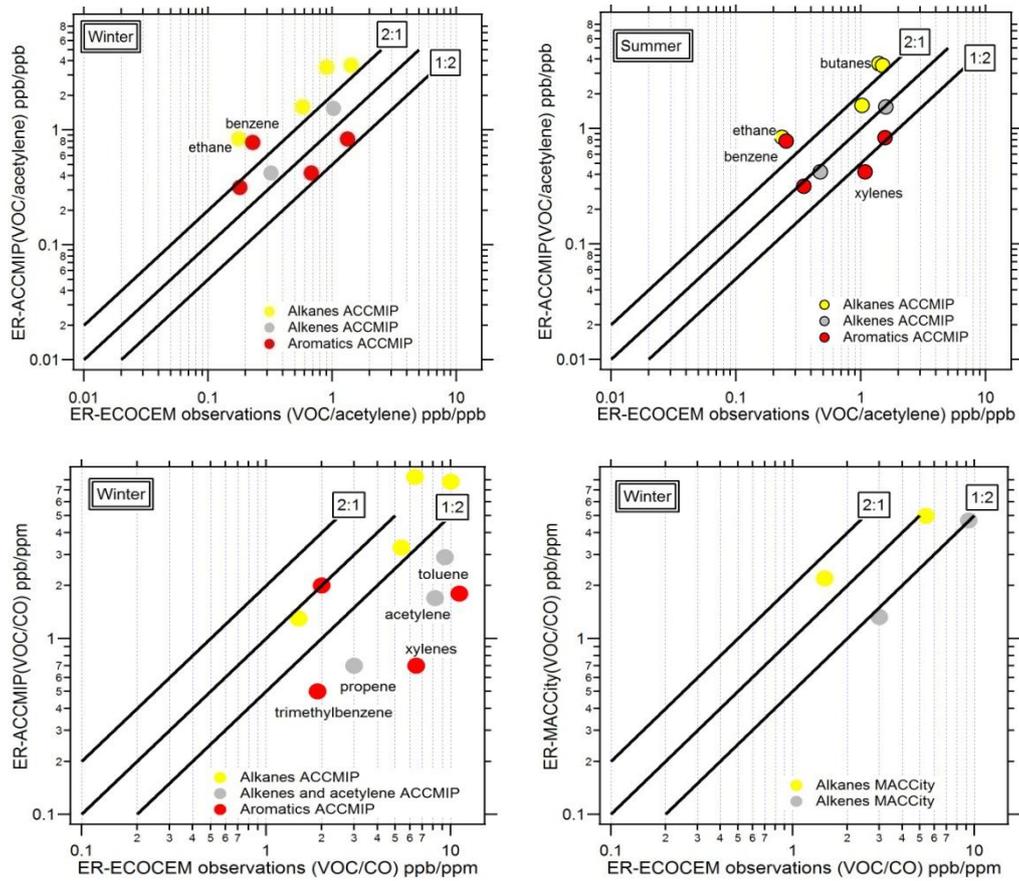


Figure 8: Comparison of the emission ratios from ACCMIP and MACCcity to the measured ones by LRF method, in summer and in winter, relative to CO and acetylene, for all the anthropogenic sectors.

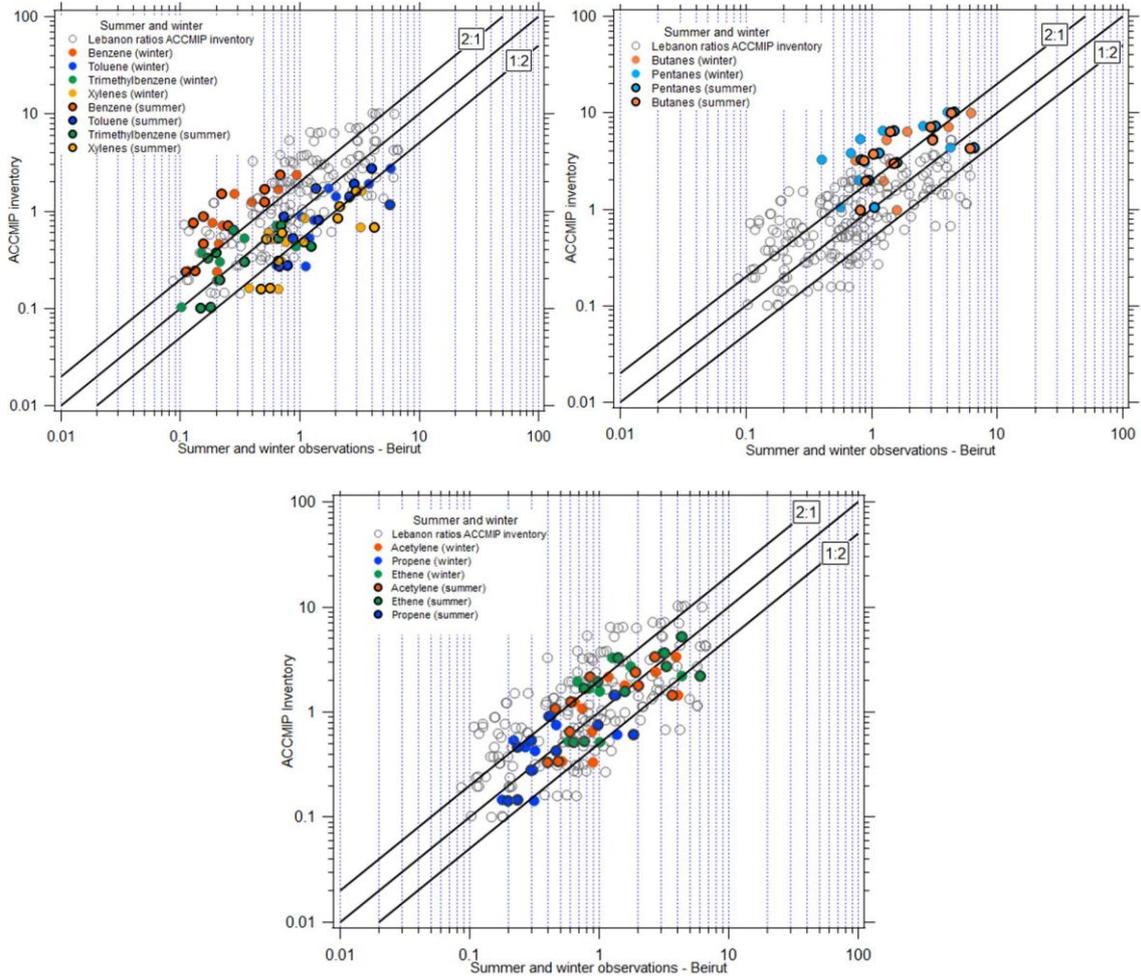


Figure 9: Comparison of the emission ratios of NMVOC vs. NMVOC_i from ACCMIP to the measured ones, in summer and in winter, for all the anthropogenic sectors, for all data of all compound classes (in grey dots) and for a given NMVOC (colored dots).

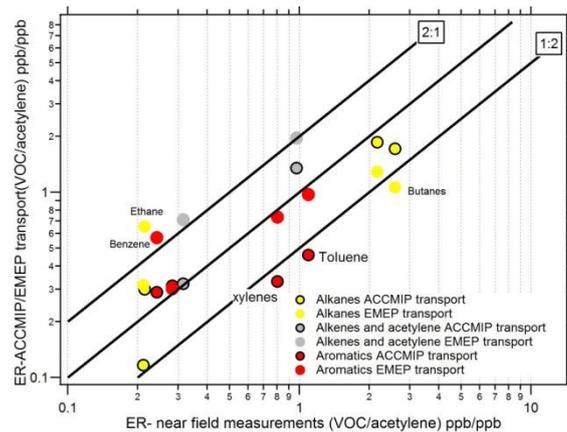


Figure 10: Comparison of the emission ratios relative to acetylene, from ACCMIP and EMEP emission inventories for road transport to the ER from road transport by near-field measurements.

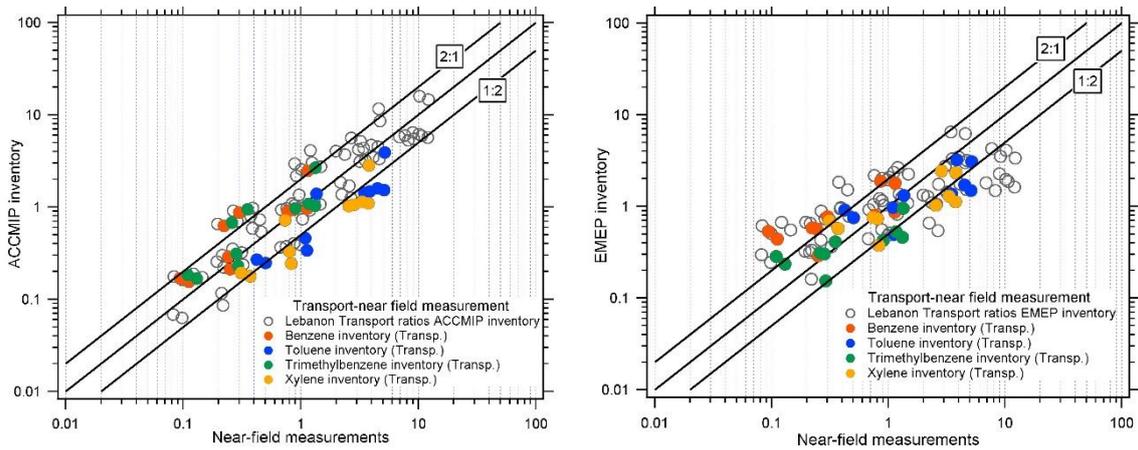


Figure 11: Comparison of the emission ratios of NMVOC vs. NMVOC_i from ACCMIP and EMEP to the ER from near-field measurements for the road transport sector, for all data (in grey dots) and for a given NMVOC (colored dots).

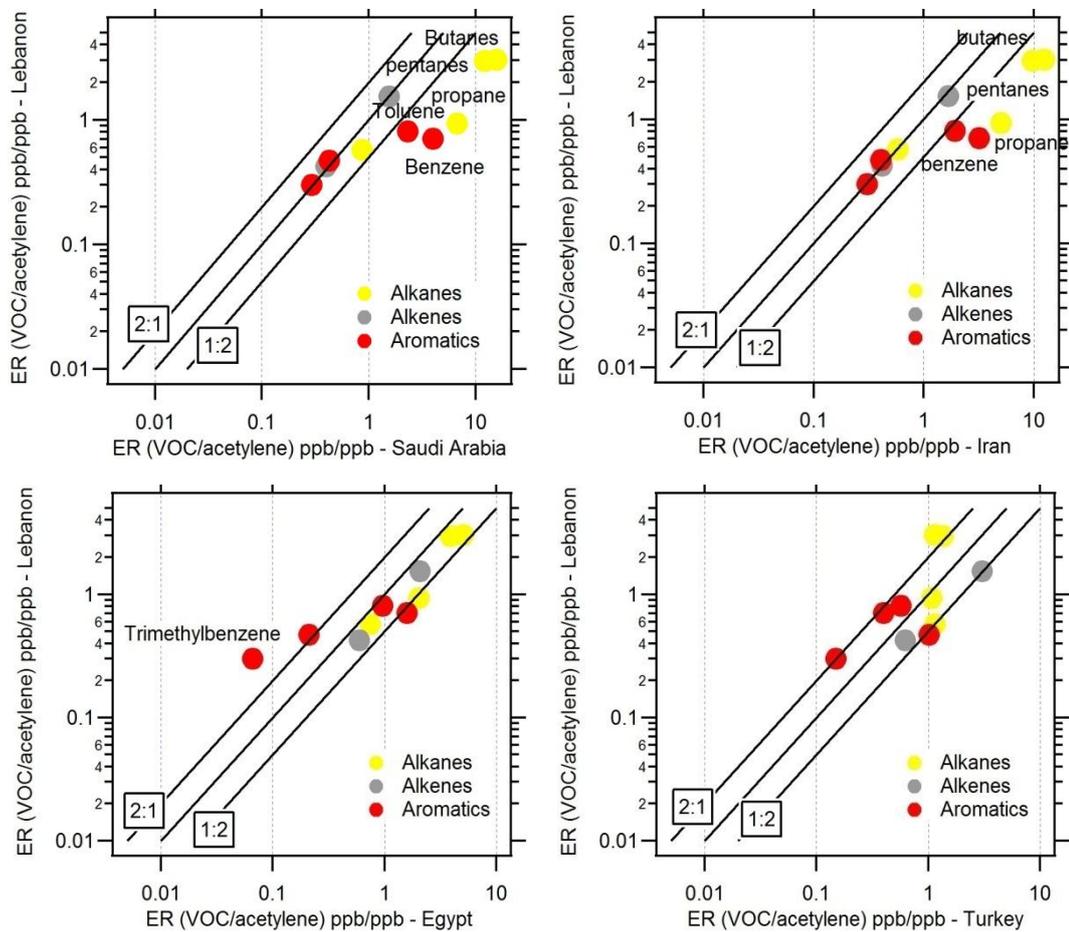


Figure 12: Comparison of the emission ratios from ACCMIP relative to acetylene for all the anthropogenic sectors for five Middle Eastern countries (Lebanon, Egypt, Turkey, Iran, and Saudi Arabia).