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-xylene) 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 r2 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 (NMVOCi) 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’
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 ±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 ±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? (5.10^6 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 8.52x10^{-12} cm^3 molecule^{-1} s^{-1}?
Then the importance of daytime maximum and minimum concentrations becomes modulated by chemical removal when $k_{OH}$ is higher than $8.52 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (rate coefficient of ethylene with OH).

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.

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

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.

Figure 4: Please use different markers for the different compounds

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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Abstract:
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 (difference up to 10\%) 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 relative to CO and to acetylene as well as the ratios of every NMVOC to each of the other NMVOCs \( (\text{NMVOC}_i) \) 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 reasonably 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 from the road transport sector are usually consistent within a factor of 2 with the regional emission inventory-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.

**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

**1. Introduction**

In the context of global climate change and growing urbanization, the East Mediterranean Basin (EMB) and the Middle East as a whole is a highly sensitive environment under considerable anthropogenic and environmental pressures. Future decadal projections point to the EMB as a possible hot spot of poor air quality and predict a continual and gradual
warming in the region, much stronger than other regions (Gurjar et al., 2008; Lelieveld et al., 2012, 2014; Pozzer et al., 2012). Future projections using the Multi Pollutant Index defined by Gurjar et al. (2008) recently identified North Africa and the Middle East as possible future hot spots of poor air quality (Pozzer et al., 2012). The increase and accumulation of anthropogenic emissions of gaseous and particulate pollutants from surrounding urban areas, and on-road transport emissions in particular, are suspected as one of the key compounding factors of those environmental impacts (Konovalov et al., 2010; von Schneidemesser et al., 2011; Waked and Afif, 2012; Hillboll et al., 2013). The EMB area includes two megacities: Istanbul (>12 million inhabitants) and Cairo (>15 million inhabitants), which experience extremely high levels of pollutions (Kanakidou et al., 2011). Satellite images of NO\textsubscript{2} columns from SCIAMACHY also point to the coastal urban areas of the Middle East as an important hot spot of pollution in the region (Lelieveld et al., 2009).

Trend analysis from satellite and ground-based observations found decreasing trend of primary pollutants in Western Europe and increasing trends from hydrocarbon ground–based observations and NO\textsubscript{x} satellite retrievals in other regions (Konovalov et al., 2010; von Schneidemesser et al., 2011). Downward trends in pollutant emissions are a shared feature of northern mid-latitude urban areas. The mixing ratios of volatile organic compounds (VOCs) and CO have decreased by almost two orders of magnitude during the past five decades in Los Angeles (Warneke et al., 2012). In UK, long-term trends show significant decreases for VOCs reaching 26% per year as well as for CO up to 12% per year (von Schneidemesser et al., 2010). Indeed, vehicle exhaust emission control has successfully reduced emissions of nitrogen oxides, carbon monoxide, volatile organic compounds and particulate matter (Uherek et al., 2010). In developing countries however, pollutants emissions have been growing strongly. Waked and Afif (2012) have shown that the emissions of CO have rapidly increased by a factor of 2.8 in the countries of the Middle East between 2000 and 2005, as a result of the increase of fuel consumption. They also found that the road transport sector in the Middle East region is a contributor to the global emissions of CO and NO\textsubscript{x} as significant as road transport in Western Europe and North America. These findings are consistent with results reported by Uherek et al. (2010) for a larger range of pollutants (CO\textsubscript{2}, CO, NO\textsubscript{x}, and NMVOCs).

The same picture is presented by emission inventories. Same picture can be drawn from emission inventories. Figure 1 compares the annual total anthropogenic emissions of non-methane volatile organic compounds (NMVOCs) from three reference emission inventories between the Middle East (MEA) region, Europe and North America: ACCMIP (Atmospheric
Chemistry and Climate Model Intercomparison Project), EDGARv4.2 (Emissions Database for Global Atmospheric Research), and RCPs (Representative Concentrations Pathways) (ECCAD database, 2015, http://eccad.sedoo.fr). NMVOC emissions have been constantly increasing over the last thirty years reaching up to 18 Tg/year according to RCPs 8.5 in 2010. In contrast, the NMVOC emissions have been strongly decreasing in USA and Europe, with totals of reaching respectively 7 and 10 Tg/year in 2010 respectively according to RCPs 8.5 (Figure 1). While differences up to a factor of 2 can be found between ACCMIP and EDGARv4.2 for the MEA in 2000 (Figure 1), all inventories suggest that NMVOCs emissions from the MEA region are as significant as the ones from post-industrialized regions or even higher. Finally no source regions clearly dominate global anthropogenic emissions and therefore an accurate representation of anthropogenic emissions in developing country regions like the MEA is of importance where highest uncertainties are expected.

The quantification of emission distribution is a challenge, and even more so in cities of the EMB and the Middle East as a whole where local emission data are sparse. Indeed, emission inventories usually combine bottom-up and top-down calculations to estimate emissions. Comprehensive bottom-up calculations aggregate multiple local statistics on different emission source categories where possible. Top-down calculations use regional or national activity data and re-allocate emissions to finer scale by using spatial surrogates (e.g. population statistics at the local level). Therefore, the uncertainties of numerous data sources are cumulated in the overall estimation of emission amounts and along increasing scales (local to regional to global). Granier et al. (2011) had assessed the evolution of anthropogenic and biomass burning emissions of CO, NO\textsubscript{x}, SO\textsubscript{2} and BC at global and regional scales from several inventories during the 1980–2010 period and had concluded that there is still no consensus on the best estimates for surface emissions of atmospheric compounds (Granier et al., 2011).

Several studies in the literature have reported evaluations of emission inventories in developed countries by the use of ambient pollutant observations at ground level, on-board aircraft and from satellite retrievals (Martin et al., 2003; Kim et al., 2011). For instance urban emission ratios of various VOC relative to an inert tracer of incomplete combustion (CO, acetylene) have been used as high-quality field constraints to evaluate regional emission inventories in cities of post-industrialized countries (Warneke et al., 2007; Coll et al., 2010; Borbon et al., 2013). The most recent diagnostic studies reveal large discrepancies between observations and inventories as large as a factor 4 for VOC in Paris and Los Angeles for...
instance (Borbon et al., 2013). In-situ observations are therefore necessary constraints for the
development of reliable emission inventories. Moreover, they also provide direct indications
on air pollution exposure. While some highly resolved inventories have been developed at the
regional scale in the EMB area for Beirut (Waked et al., 2012) and Istanbul (Im et al., 2011;
Markakis et al., 2012), their uncertainties are unknown and speciation of NMVOC is usually
disregarded. For solely Lebanon, the atmospheric emission inventory of anthropogenic and
biogenic sources was established by Waked et al. (2012) for a base year of 2010 for CO, NOx,
SO2, total NMVOCs, NH3, PM10 and PM2.5, according to EEA/EMEP guidelines
(EMEP/EEA, 2009). The NMVOC total emissions in Lebanon were estimated to be 115 Gg
for the year 2010. According to this inventory, transport is the main source of NMVOC with a
relative contribution of 67% of total emissions of NMVOCs (Waked et al., 2012). In addition,
there is a strong need for developing better emission inventories in the Middle East region as a whole (Waked et al., 2013a). The paucity of observations in this region, especially for VOCs and PM composition, is a significant limitation to the achievement of evaluated and accurate emission inventories. Finally, accurate modelling of individual NMVOCs and better understanding of ozone precursors is also important for policy-makers and for the improvement of air quality leading to better estimates of secondary organic aerosols (SOA) (Secondary Organic Aerosols) formation and ozone levels.

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

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

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

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

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

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

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

A large number of emission inventories only provide the distribution of total NMVOC emissions by lumping organic species (alkanes, alkenes, alkynes, alcohols, aldehydes, ketones and aromatic compounds) for chemistry modelling purposes (EDGARv4.2, ECLIPSE-GAINS-4a). We only rely on the ACCMIP inventory from ECCAD database which provides a detailed speciation of VOCs including acetylene. ACCMIP global emission inventory covers the historical period (1850–2000) in decadal increments at a horizontal resolution of 0.5° in latitude and longitude, based on the combination of the best global and regional available datasets. ACCMIP was developed mainly to provide consistent gridded emissions of reactive gases and aerosols for use in chemistry model simulations needed by climate models for the Climate Model Intercomparison Program 5 (CMIP5) in support of the Intergovernmental Panel on Climate Change (IPCC) Fifth Assessment report (AR5) (Lamarque et al., 2010). 40 regions and 12 sectors were used to combine the various sources within this inventory and a set of species including CO, NOx, total and speciated NMVOCs is provided. Speciation of NMVOC emissions is performed using the RETRO (REanalysis of the TROpospheric chemical Composition) (Schultz et al., 2007) inventory and is kept
constant for the whole historical period because of the lack of additional information. For all NMVOC species of the RETRO inventory, a factor was calculated only for the year 2000 by dividing the emission of each individual species by the total NMVOC anthropogenic emissions for each sector in each grid cell.

For comparison with observations, we extracted the emission fluxes (kg/m$^2$/s) of 11 individual NMVOCs as well as CO of 8 grids covering Lebanon surface area (ECCAD database). Target sectors cover all anthropogenic sectors and the transport sector for 2000. 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 suburban 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.

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

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

In summer all NMHCs including acetylene show the same bi-modal pattern with one midday and one midnight maximum as a result of primary emissions from Greater Beirut transported at the background receptor site between 09:00 and 10:00 and accumulation of emissions at night in a shallower boundary layer. The degree of chemical removal during the day is $k_{OH}$-dependent ($k_{OH}$ : rate coefficient for the reaction with OH) and increases with $k_{OH}$ as
illustrated for alkenes and aromatics. At night alkenes and aromatics follows the pattern of acetylene due to common sources, dilution and less neglected photochemistry. Then the magnitude of daytime maximum and minimum concentrations becomes modulated by chemical removal when $k_{\text{OH}}$ is higher than $8.52 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (rate coefficient of ethylene with OH). Compensation of chemical removal at midday by fresh evaporative emission cannot be excluded for aromatics like toluene.

In winter the diurnal profiles of NMHCs including acetylene show a unimodal pattern characterized by maximum concentrations in the morning typical of traffic rush hours and a slight decrease until late evening. Contrary to summer, the absence of a midday minimum of normalized concentrations indicates a strong accumulation of primary emissions during the day which is favored by poor dilution and negligible photochemistry. However, the diurnal profiles of alkenes illustrated in figure 3 are characterized by a most pronounced enhancement in the evening which can be related to additional combustion sources like domestic heating since the measurement site is surrounded by a residential area (Salameh et al., 2015).

Aromatics and alkanes diurnal profiles follow the shape of acetylene profile in general. Nevertheless, one can see a strong enrichment of aromatics during the day originating from the traffic related source where toluene and m,p-xylene are significantly present (Watson et al., 2001; Badol et al., 2008; Salameh et al., 2016).

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

5. Determination of urban enhancement emission ratios

The emission ratio for NMVOC species is the ratio of a selected VOC to a reference compound in fresh emissions without undergoing photochemical processing. We applied two methods to determine emission ratios (ER) for each VOC species relative to CO and acetylene. The first method consists in non-linear regression fits (LRF) on data applied to summer and winter datasets and the other method relies on extrapolating the photochemical
age to zero which was applied to the summer data, photochemical removal being negligible in winter.

5.1. Linear Regression Fit (LRF) method

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

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

5.2. The Photochemical Age method

The photochemical method takes into consideration the photochemical processing of measured ratios of NMVOC with acetylene. We applied this method to all the summertime dataset. Following de Gouw et al. (2005), Warneke et al. (2007), and Borbon et al. (2013), we assume that the photochemical removal of 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.
The photochemical age of air masses, $\Delta t$, is estimated by using the NMVOC ratios following this equation:

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

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

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

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

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

where $[NMVOC]$ and $[C_2H_2]$ are the volume mixing ratios in ppb of the NMVOC and acetylene respectively; $ER_{NMVOC}$ is the emission ratio of the NMVOC relative to acetylene;
\[ k_{\text{NMVOC}} \text{ and } k_{\text{C2H2}} \text{ are the OH rate coefficients for the reaction of those compounds with OH} \]
\[ (\text{[OH]} = 5.10^6 \text{ molecules.cm}^{-3}); \text{ and } \Delta t \text{ is the photochemical age calculated by equation} \]
\[ 1. \text{ The emission ratios of NMVOCs are estimated by extrapolating the photochemical age to zero which is the intercept on the y-axis of the linear fit (figure 4).} \]

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

### 5.3. Performance of the different methods

Figure 5 illustrates the performance of the ER determination methods for the summertime data where ER from the photochemical age and LRF methods are compared. There is an overall very good agreement between the two methods (slope of the linear fit in red = 0.90 and correlation coefficient of 0.99) showing the robustness of the methods and confirming that the selection of all the data for less-reactive species and nighttime data for more reactive species for summer in the LRF method does not bias the results. 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.

### 5.4. Emission ratios and seasonal variability

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

The ER derived from the observations (summer and winter) are comparable at ±50\% to the ratios of road transport sector, during at least one season, for more than 80\% of the species. This shows that urban emission fingerprint is mainly driven by traffic emissions including ethane which does not have any urban natural gas usage contribution in Lebanon. For other species like C4 to C6-alkenes, styrene, and a few alkanes in winter the differences stay within
a factor of 2, except for propane where they are 5 in summer and 3 in winter. These
differences can be partly explained by the contribution of additional sources.
In general, the ERs in winter are slightly lower than in summer (Table 2). Figure 6 compares
the derived emission ratios of NMVOC species relative to acetylene at the measurement site
during summer and winter. The wintertime emission ratios for most NMVOC species agree at
\[ \pm 30\% \text{ (slope of 0.71) with the summertime ERs} \] and within a factor of 2 and a high
determination coefficient of 0.94. Finally, there is no significant seasonality in ER regardless
of the species except for 1-pentene, cyclohexane, styrene, 2,2-dimethylbutane, and 1,2,3-
trimethylbenzene. Those species are associated with ER lower than 0.1. These results indicate
that the urban emission composition contributing to the ambient concentrations is not
significantly different between summer and winter. The sources usually affected by
seasonality are in winter related to combustion and to fuel evaporation in summer. Our results
based on ER are consistent with previous PMF results (Salameh et al., 2016), showing that the
road transport sector (combustion and gasoline evaporation) is the dominating source in both
seasons in Beirut.

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

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

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). The maximum difference reached a factor of 10 for m,p-xylene in winter. 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)-xylene. The maximum difference is observed between Beirut and Strasbourg and reached a factor of 10 for m,p-xylene in winter. ERs of alkenes are higher in Mecca due to their additional evaporative origin (Simpson et al., 2014). 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 opposite 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 ERs of alkenes in Mecca are higher due to their additional evaporative origin (Simpson et al., 2014).

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

The emission fluxes (Kg/m²/s) extracted from ECCAD database are converted to mole emission fluxes, then the NMVOC ratios relative to CO and relative to acetylene are determined. The comparison held here will consider the common compounds present in the ACCMIP and MACCity, when possible, global emission inventories and measured during ECOCEM campaigns which are listed in table 3. Important NMVOC species are present within these inventories as tracers of many anthropogenic sources, reactive species, and important precursors of ozone and SOA (Table 3). We consider that the speciation is “reasonable” when there is an agreement within a factor of two between observations and emission inventory.

7.1. Emission inventory vs. observations: all anthropogenic sectors

To analyze the consistency of the speciation of NMVOCs in the ACCMIP and MACCity global emission inventories, we compared the individual NMVOC relative to CO as well as to acetylene ratios during summer and winter obtained by the LRF method. Figure 8 displays the
ratios from the anthropogenic emissions data (ACCMIP and MACCity) and the observations in a logarithmic scale for 11 individual NMVOC species color coded by the NMVOC groups. 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 overall VOC speciation in ACCMIP is reasonably better represented for more reactive VOCs such as alkenes and some aromatics. Regarding ER relative to CO, differences with ACCMIP are remarkable significant. A global underestimation by the inventory by a shift towards lower ER over an order of magnitude is observed suggesting an overestimation of CO emissions by ACCMIP.

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,\textsubscript{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. From figure 9, it appears that benzene is systematically overestimated up to a factor of 5 in ACCMIP and to a lesser extent, pentanes and butanes by a factor \(>2\) whereas xylenes are reasonably underestimated in the ACCMIP global emission inventory but not systematically. The other compounds lay around closer to the line of the slope \((=1)\), below a factor of 2. Finally, comparisons between ACCMIP and observations (figures 8 and 9) suggest that the overall speciation of anthropogenic sources for major hydrocarbons that act as ozone and SOA precursors in ACCMIP is reasonably better represented than the others species but it is still need improvement.

### 7.2. Emission inventory vs. observations: road transport sector

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

We proceeded as in the previous section by comparing the road transport ER relative to acetylene for all VOCs and individual VOCs from ACCMIP and EMEP emission inventories
to the ER from near-field measurements (figures 10 and 11) (Salameh et al., 2014). 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.

7.3. Perspectives for Middle East region (MEA)

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

8. Conclusions

Detailed measurements of NMVOCs collected at a sub-urban site in Beirut, Lebanon, have been used to evaluate regional and global emission inventories (ACCMIP, MACCity and EMEP) downscaled to the studied domain. These data were collected during two intensive field campaigns in summer 2011 and in winter 2012 within the framework of the ECOCEM project.
The emission ratios (ER) of individual NMVOC species relative to CO and acetylene were successfully derived from ambient measurements in summer and in winter as well as from near-field measurements for the road transport sector by applying two independent methods: the linear regression fit method and the photochemical age method. Emission ratios from both methods show a very good agreement at ±10%.

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

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

ER relative to CO and to acetylene as well as the ratios of every NMVOC to each of the other NMVOCs (NMVOC_i), extracted from ACCMIP and MACCity global emission inventory were compared with the corresponding observed ER during both seasons, for all anthropogenic sectors. This comparison suggests that the overall speciation of anthropogenic sources for major hydrocarbons that act as ozone and SOA precursors in ACCMIP is reasonably 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) from the road transport sector 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.

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

Finally, we have shown that the emission inventory is in disagreement with the observations when comparing Lebanon with Saudi Arabia. The observed heterogeneity of anthropogenic
VOC emission composition can be significant for reactive VOC (factor of 6 for m,p-xylene) but is not depicted by global emission inventories. This suggests that systematic and detailed measurements are needed in the MEA region in order to better constrain emission inventory. VOC emission inventory is the fundamental input of air quality modelling, therefore it plays a major role in characterizing secondary pollution and control policy formulation. To improve the quality of future VOC emission estimates, more efforts should be made toward refinement of source classification, development of representative local emission factors, comprehensive collection of activity data, and more accurate spatio-temporal characterization. Additionally, comparison of available datasets will allow a quantification of the uncertainties on emissions.

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

Acknowledgments:
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References:


Kanakidou, M., Mihalopoulos, N., Kindap, T., Im, U., Vre foussis, M., Gerasopoulos, E., Dermitzaki, E., Unal, A., Koçak, M., Markakis, K., Melas, D.,Kouvarakis, G., Youssef, A.F.,


**Table 1**: Measurements during ECOCEM Campaigns.

<table>
<thead>
<tr>
<th>Species</th>
<th>Instrument</th>
<th>Time resolution</th>
<th>Performances</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>On-line</strong></td>
<td>67 C2-C9 NMHC</td>
<td>TD-GC-FID</td>
<td>1 h</td>
<td>DL: 40 - 90 ppt, uncertainty: 4 - 35% for the majority of the NMHCs</td>
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<tr>
<td>29 alkanes</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19 alkenes</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 alkynes</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17 aromatics</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Off-line</strong></td>
<td>67 C2-C9 NMHC</td>
<td>Canister / TD-GC-FID</td>
<td>Sampling &lt; 3 min / 1h analysis</td>
<td>DL: 40 - 90 ppt, uncertainty: 15%</td>
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</tbody>
</table>

**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 ±50% of the VOC/acetylene ER from the measurement campaigns to the one of the near-field measurements.

<table>
<thead>
<tr>
<th>NMVOC</th>
<th>ΔVOC/ΔC(_2)H(_2) (ppb/ppb)</th>
<th>ΔVOC/ΔCO (ppb/ppm)</th>
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<tbody>
<tr>
<td>ethane</td>
<td>0.23</td>
<td>1.50</td>
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<td>propane</td>
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<td>1.10</td>
</tr>
<tr>
<td>i-pentane</td>
<td>1.22</td>
<td>5.30</td>
</tr>
<tr>
<td>2-methyl-pentane</td>
<td>0.29</td>
<td>1.20</td>
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<tr>
<td>3-methyl-pentane</td>
<td>0.17</td>
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<tr>
<td>Methylcyclopentane</td>
<td>0.13</td>
<td>0.90</td>
</tr>
<tr>
<td>2-methyl-hexane</td>
<td>0.11</td>
<td>0.70</td>
</tr>
<tr>
<td>3-methyl-hexane</td>
<td>0.11</td>
<td>0.70</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>0.04</td>
<td>0.10</td>
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<td>n-heptane</td>
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<td>Compound</td>
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<td>Unit 2</td>
</tr>
<tr>
<td>--------------------------------</td>
<td>--------</td>
<td>--------</td>
</tr>
<tr>
<td>2,3-dimethylpentane</td>
<td>0.04</td>
<td>0.03</td>
</tr>
<tr>
<td>Methylcyclohexane</td>
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<td>0.03</td>
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<td>3-methyl-heptane</td>
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<td>n-nonane</td>
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<tr>
<td>acetylene</td>
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<td>-</td>
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<td>propyne</td>
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<tr>
<td>trans-2-butene</td>
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<td>isobutene</td>
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<td>3-methyl-1-butene</td>
<td>0.03</td>
<td>0.02</td>
</tr>
<tr>
<td>2-methyl-1-butene</td>
<td>0.09</td>
<td>0.06</td>
</tr>
<tr>
<td>1-pentene</td>
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<td>0.17</td>
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<tr>
<td>cis-2-pentene</td>
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<tr>
<td>trans-2-pentene</td>
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<td>0.11</td>
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<td>1,3-butadiene</td>
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<td>0.01</td>
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<td>0.01</td>
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<td>0.23</td>
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<tr>
<td>toluene</td>
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<td>m,p-xylene</td>
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<td>Ethylbenzene</td>
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<td>0.16</td>
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<td>n-propylbenzene</td>
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<td>0.02</td>
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<td>Isopropylbenzene</td>
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<td>0.01</td>
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<tr>
<td>p-ethyltoluene</td>
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<td>o-ethyltoluene</td>
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<tr>
<td>styrene</td>
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<td>1,2,3-trimethylbenzene</td>
<td>0.05</td>
<td>0.01</td>
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<tr>
<td>1,2,4-trimethylbenzene&amp;decane</td>
<td>0.24</td>
<td>0.16</td>
</tr>
</tbody>
</table>

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)

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

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 OH × 10⁻¹² cm³ molecule⁻¹ s⁻¹ (Atkinson and Arey 2003; 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 OH × 10⁻¹² cm³ molecule⁻¹ s⁻¹ (Atkinson and Arey 2003; 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 MACCity 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. NMVOCi 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. NMVOCi 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).