

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 k_{OH} 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 $8.52 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$?

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.