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

Thérèse Salameh[1], Agnès Borbon[1,a], Charbel Afif[2], Stéphane Sauvage[3,4], Thierry Leonardis[3,4], Cécile Gaimoz[1], and Nadine Locoge[3,4]

[1] Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), IPSL, CNRS – UMR7583, University of Paris Est Créteil (UPEC) and Paris Diderot (UPD), Créteil, France

[2] Emissions, Measurements, and Modeling of the Atmosphere (EMMA) Laboratory, Unité Environnement, Génomique Fonctionnelle et Études Mathématiques, Centre d'Analyses et de Recherche, Faculty of Sciences, Saint Joseph University, Beirut, Lebanon

[3] Mines Douai, Sciences de l'Atmosphère et Génie de l'Environnement (SAGE), F-59508 Douai CEDEX, France

[4] Université de Lille, 59655 Villeneuve d'Ascq, France

[a] Now at : Laboratoire de Météorologie Physique (LaMP), CNRS - UMR 6016, University of Blaise Pascal, Clermont-Ferrand, France

1   **Abstract:**

2   The relative importance of Eastern Mediterranean emissions is suspected to be largely

3   underestimated compared to other regions worldwide. Here we use detailed speciated

4   measurements of VOCs (volatile organic compounds) to evaluate the spatial heterogeneity of

5   VOC urban emission composition and the consistency of regional and global emission

6   inventories downscaled to Lebanon (EMEP, ACCMIP, and MACCity). The assessment was

7   conducted through the comparison of the emission ratios extracted from the emission

8   inventories to the ones obtained from the hourly observations collected at a sub-urban site in

9   Beirut, Lebanon during summertime and wintertime ECOCEM campaigns. The observed ERs

10   were calculated by two independent methods. ER values from both methods agree very well

11   (difference up to 10%) and are comparable to the ones of the road transport sector from near-

12   field measurements for more than 80% of the species. There is no significant seasonality in ER

13   for more than 90% of the species unlike the seasonality usually observed in other cities

14   worldwide. Regardless of the season, ERs agree within a factor of 2 between Beirut and other

15   representative worldwide cities except for the unburned fuel fraction and ethane. ERs of

16   aromatics (benzene excepted) are higher in Beirut compared to northern post-industrialized

17   countries and even the Middle Eastern city Mecca. The comparison of the observed ER relative

18   to CO and to acetylene as well as the ratios of every NMVOC to each of the other NMVOCs

19   (NMVOC$_i$) to the ones extracted from ACCMIP and MACCity global emission inventories

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20   suggests that the overall speciation of anthropogenic sources for major hydrocarbons that act

21   as ozone and SOA precursors in ACCMIP is reasonably represented.

22   The comparison of the specific road transport ER relative to acetylene derived from near-field

23   measurements to ER from ACCMIP and EMEP emission inventories for road transport sector

24   showed that ER from the road transport sector are usually consistent within a factor of 2 with

25   the regional emission inventory EMEP while xylenes and toluene are underestimated over a

26   factor of 2 by ACCMIP.

27   The observed heterogeneity of anthropogenic VOC emission composition between Middle

28   Eastern cities can be significant for reactive VOC but is not depicted by global emission

29   inventories. This suggests that systematic and detailed measurements are needed in the Eastern

30   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 between ER from observations and global inventories
➢ 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

31   **1. Introduction**

32   In the context of global climate change and growing urbanization, the East Mediterranean Basin

33   (EMB) and the Middle East as a whole is a highly sensitive environment under considerable

34   anthropogenic and environmental pressures. Future decadal projections point to the EMB as a

35   possible hot spot of poor air quality and predict a continual and gradual warming in the region,

36   much stronger than other regions (Lelieveld et al., 2012, 2014; Pozzer et al., 2012). Future

37   projections using the Multi Pollutant Index defined by Gurjar et al. (2008) recently identified

38   North Africa and the Middle East as possible future hot spot of poor air quality (Pozzer al.,

39   2012). The increase and accumulation of anthropogenic emissions of gaseous and particulate

40   pollutants from surrounding urban areas, and on-road transport emissions in particular, are

41 suspected as one of the key compounding factors of those environmental impacts (Konovalov

42 et al., 2010; von Schneidemesser et al., 2011; Waked and Afif, 2012; Hillboll et al., 2013). The

43 EMB area includes two megacities: Istanbul (>12 million inhabitants) and Cairo (>15 million

44 inhabitants), which experience extremely high levels of pollutions (Kanakidou et al., 2011).

45 Satellite images of NO_2 columns from SCIAMACHY also point to the coastal urban areas of

46 the Middle East as an important hot spot of pollution in the region (Lelieveld et al., 2009).

47 Trend analysis from satellite and ground-based observations found decreasing trend of primary

48 pollutants in Western Europe and increasing trends from hydrocarbon ground–based

49 observations and NO_x satellite retrievals in other regions (Konovalov et al., 2010; von

50 Schneidemesser et al., 2011). Downward trends in pollutant emissions are a shared feature of

51 northern mid-latitude urban areas. The mixing ratios of VOCs (volatile organic compounds)

52 and CO have decreased by almost two orders of magnitude during the past five decades in Los

53 Angeles (Warneke et al., 2012). In UK, long-term trends show significant decreases for VOCs

54 reaching 26% per year as well as for CO up to 12% per year (von Schneidemesser et al., 2010).

55 Indeed, vehicle exhaust emission control has successfully reduced emissions of nitrogen oxides,

56 carbon monoxide, volatile organic compounds and particulate matter (Uherek et al., 2010). In

57 developing countries however, pollutants emissions have been growing strongly. Waked and

58 Afif (2012) have shown that the emissions of CO have rapidly increased by a factor of 2.8 in

59 the countries of the Middle East between 2000 and 2005, as a result of the increase of fuel

60 consumption. They also found that the road transport sector by the Middle East region is a

61 contributor to the global emissions of CO and NO_x as significant as road transport by Western

62 Europe and North America. These findings are consistent with results reported by Uherek et al.

63 (2010) for a larger range of pollutants (CO_2, CO, NO_x, and NMVOCs).

64 Same picture can be drawn from emission inventories. Figure 1 compares the annual total

65 anthropogenic emissions of non-methane volatile organic compounds (NMVOCs) from three

66 reference emission inventories between the Middle East (MEA) region, Europe and North

67 America: ACCMIP (Atmospheric Chemistry and Climate Model Intercomparison Project),

68 EDGARv4.2 (Emissions Database for Global Atmospheric Research), and RCPs

69 (Representative Concentrations Pathways) (ECCAD database, 2015, http://eccad.sedoo.fr).

70 NMVOC emissions have been constantly increasing over the last thirty years reaching up to18

71 Tg/year according to RCPs 8.5 in 2010. On the opposite, the NMVOC emissions have been

72 strongly decreasing in USA and Europe, reaching respectively 7 and 10 Tg/year in 2010

73 according to RCPs 8.5 (Figure 1). While differences up to a factor of 2 can be found between

74 ACCMIP and EDGARv4.2 for the MEA in 2000 (Figure 1), all inventories suggest that

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75 NMVOCs emissions from the MEA region are as significant as the ones from post-

76 industrialized regions or even higher. Finally no source regions clearly dominate global

77 anthropogenic emissions and therefore an accurate representation of anthropogenic emissions

78 in developing country regions like the MEA is of importance where highest uncertainties are

79 expected.

80 The quantification of emission distribution is a challenge, and even more in cities of the EMB

81 and the Middle East as a whole where local emission data are sparse. Indeed, emission

82 inventories usually combine bottom-up and top-down calculations to estimate emissions.

83 Comprehensive bottom-up calculations aggregate multiple local statistics on different emission

84 source categories where possible. Top-down calculations use regional or national activity data

85 and re-allocate emissions to finer scale by using spatial surrogates (e.g. population statistics at

86 the local level). Therefore, the uncertainties of numerous data sources are cumulated in the

87 overall estimation of emission amounts and along increasing scales (local to regional to global).

88 Granier et al. (2011) had assessed the evolution of anthropogenic and biomass burning

89 emissions of CO, NO_x, SO_2 and BC at global and regional scales from several inventories

90 during the 1980–2010 period and had concluded that there is still no consensus on the best

91 estimates for surface emissions of atmospheric compounds (Granier et al., 2011).

92 Several studies in the literature have reported evaluations of emission inventories in developed

93 countries by the use of ambient pollutant observations at ground level, on-board aircraft and

94 from satellite retrievals (Martin et al., 2003; Kim et al., 2011). For instance urban emission

95 ratios of various VOC relative to an inert tracer of incomplete combustion (CO, acetylene) have

96 been used as high-quality field constraints to evaluate regional emission inventories in cities of

97 post-industrialized countries (Warneke et al., 2007; Coll et al., 2010; Borbon et al., 2013). The

98 most recent diagnostic studies reveal large discrepancies between observations and inventories

99 as large as a factor 4 for VOC in Paris and Los Angeles for instance (Borbon et al., 2013). In-

100 situ observations are therefore necessary constraints for the development of reliable emission

101 inventories. Moreover, they also provide direct indications on air pollution exposure. While

102 some highly resolved inventories have been developed at the regional scale in the EMB area

103 for Beirut (Waked et al., 2012) and Istanbul (Im at al., 2011; Markakis et al., 2012), their

104 uncertainties are unknown and speciation of NMVOC is usually disregarded. For solely

105 Lebanon, the atmospheric emission inventory of anthropogenic and biogenic sources was

106 established by Waked et al. (2012) for a base year of 2010 for CO, NO_x, SO_2, total NMVOCs,

107 NH_3, PM_{10} and $PM_{2.5}$, according to EEA/EMEP guidelines (EMEP/EEA, 2009). The NMVOC

108   total emissions in Lebanon were estimated to be 115 Gg for the year 2010. According to this

109   inventory, transport is the main source of NMVOC with a relative contribution of 67% of total

110   emissions of NMVOCs (Waked et al., 2012). In addition, there is a strong need for developing

111   better emission inventories in the Middle East region at a whole (Waked et al., 2013a). The

112   paucity of observations in this region, especially for VOCs and PM composition, is a strong

113   limitation to the achievement of evaluated and accurate emission inventories. Finally, accurate

114   modelling of individual NMVOCs and better understanding of ozone precursors is also

115   important for policy-makers and for the improvement of air quality leading to better estimates

116   of SOA (Secondary Organic Aerosols) formation and ozone levels.

117   The present paper aims at evaluating global VOC speciated emission inventories, in the absence

118   of regional emission inventories for MEA, by the use of detailed observations recently collected

119   in Beirut, Lebanon in the frame of ECOCEM project (Salameh et al., 2015). Those observations

120   include detailed near-source field measurements and ambient measurements at a suburban site.

121   We used regional (EMEP) and global (ACCMIP and MACCity) emission inventories

122   downscaled to Lebanon. Two independent methods already applied to Los Angeles basin during

123   the CalNex experiment (Borbon et al., 2013) that take into consideration the effects of chemical

124   removal were used to estimate the urban enhancement emission ratios (ERs) of various

125   NMVOC relative to CO and acetylene for winter and summer. First, calculated ERs are

126   compared to available ERs in other cities worldwide in order to assess the spatial variability of

127   emission composition. Second, calculated ERs are compared to the ones derived from global

128   emission inventories for all the anthropogenic sectors and for the road transport sector. Finally

129   perspectives for the whole Middle East region are discussed.

2. Experiment

131   The experimental strategy includes near field measurements close to major emission sources

132   and two intensive field campaigns conducted in summer 2011 and in winter 2012 in Beirut at a

133   suburban site, within the ECOCEM project (Emissions and Chemistry of Organic Carbon in

134   the East Mediterranean). VOC have been measured by a combination of on-line and off-line

135   techniques (table 1). A set of eight speciated profiles of four major non-methane hydrocarbons

136   (NMHC) sources in Lebanon was proposed by Salameh et al. (2014) by performing sampling

137   experiments close to emission sources in real-condition operation as far as possible. Field

138   sampling has been carried out in Beirut city and in the suburban area during March and April

139   2012. The sampling was performed by canisters and the analyses were performed in the

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140   laboratory by thermal desorption-gas chromatography (TD-GC) technique coupled to a flame

141   ionisation detector (FID) from Perkin–Elmer (Salameh et al., 2014; 2015).

142   The ambient field campaigns were conducted on the roof of the Faculty of Sciences building of

143   Saint Joseph University located in the eastern suburbs of the city of Beirut from 2 to 18 July

144   2011 in summer and from 28 January to 12 February 2012 in winter. The site is appropriately

145   located in order to receive air masses coming from Greater Beirut Area which includes the city

146   of Beirut and close suburbs. The site is surrounded by a forested pine area and a high density

147   of residential premises. Beirut International Airport is located 8 km southwest of the site and

148   one fuel storage facility is located at 3.6 km North. More details are reported in Salameh et al.

149   (2015). During both measurement periods, NMHCs were continuously analyzed on an hourly

150   basis covering 30 min of ambient air sampling, by the same system (TD-GC-FID) used for

151   canister analysis. Additional measurements of trace gases concentrations including CO, NO_x

152   and O_3 were provided on a 1-min basis by specific analyzers. Basic meteorological parameters

153   (wind speed and direction, temperature, relative humidity and atmospheric pressure) were

154   measured on a 1-min basis for the duration of the campaigns.

155   During the summer field campaign, the average temperature was around 25 °C ± 2 °C and the

156   average wind speed was low, 2 m s^{-1}, with maximum wind speeds (4-10 m s^{-1}) recorded during

157   the days under south-western wind regimes and under northern wind regimes. During the winter

158   measurement campaign, the temperature stayed mild with an average of 13 °C ± 2 °C. The

159   average wind speed was still low at 2 m s^{-1} and the wind direction was mostly south-easterly

160   and easterly.

161

162   **3. Regional and global emission database**

163   At the global and the regional scales, several emission inventories were developed during the

164   past few years in order to provide the distribution of surface emissions of different gaseous and

165   particulate compounds.

166   The EMEP regional emission inventory (European Monitoring and Evaluation Programme)

167   covers the period from 1980 to 2020, at a 0.5° resolution. It contains national total emissions

168   for Europe, sector data and gridded emission data for modelling purposes. The sectors follow

169   the SNAP categorization (Selected Nomenclature for reporting of Air Pollutants). Only the

170   anthropogenic part of the emissions regarding road transport (SNAP 07) is included in this

171   study.

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172   Since there is no global emissions dataset available after 2000, the MACCity emissions have

173   been developed within two European Commission funded projects (MACC and CityZen) as an

174   extension of the ACCMIP and the RCP 8.5 emissions dataset. The emissions for each

175   compound were then linearly interpolated, for each sector and each year between 2000 and

176   2010. A seasonal cycle was applied for each sectoral layer, and the NMVOC species

177   anthropogenic emissions have been lumped to 13 species (excluding acetylene) using the same

178   methodology for the NMVOCs speciation as used in the ACCMIP dataset.

179   While a large number of emission inventories only provide the distribution of total NMVOC

180   emissions by lumping organic species (alkanes, alkenes, alkynes, alcohols, aldehydes, ketones

181   and aromatic compounds) for chemistry modelling purposes (EDGARv4.2, ECLIPSE-GAINS-

182   4a). We only rely on the ACCMIP inventory from ECCAD database which provides a detailed

183   speciation of VOCs including acetylene. ACCMIP global emission inventory covers the

184   historical period (1850–2000) in decadal increments at a horizontal resolution of 0.5° in latitude

185   and longitude, based on the combination of the best global and regional available datasets.

186   ACCMIP was developed mainly to provide consistent gridded emissions of reactive gases and

187   aerosols for use in chemistry model simulations needed by climate models for the Climate

188   Model Intercomparison Program 5 (CMIP5) in support of the Intergovernmental Panel on

189   Climate Change (IPCC) Fifth Assessment report (AR5) (Lamarque et al., 2010). 40 regions and

190   12 sectors were used to combine the various sources within this inventory and a set of species

191   including CO, NOx, total and speciated NMVOCs is provided. Speciation of NMVOC

192   emissions is performed using the RETRO (REanalysis of the TROpospheric chemical

193   Composition) (Schultz et al., 2007) inventory and is kept constant for the whole historical

194   period because of the lack of additional information. For all NMVOC species of the RETRO

195   inventory, a factor was calculated only for the year 2000 by dividing the emission of each

196   individual species by the total NMVOC anthropogenic emissions for each sector in each grid

197   cell.

198   For comparison with observations, we extracted the emission fluxes (kg/m²/s) of 11 individual

199   NMVOCs as well as CO of 8 grids covering Lebanon surface area (ECCAD database). Target

200   sectors cover all anthropogenic sectors and the transport sector for 2000. Since the flux of the

201   8 grids is homogeneous and doesn't show large discrepancies in the spatial variability for each

202   considered compound, we used a mean flux for each NMVOC. This being said, the approach

203   we adopted by using the emission ratios collected at the measurement site in sub-urban Beirut

204   is valid. In addition, the site is far enough from strong direct emissions (industrial, road

205   transport) since they can hide the emissions from distant sources, and it receives air masses

206   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

208   The intensity of the emissions, chemistry, and atmospheric dynamics varying throughout the

209   day can affect the diurnal profiles of NMVOC absolute mixing ratios and as a consequence the

210   values of urban enhancement emission ratios (ER) (see section 5). We report in figures 2 and 3

211   for summer and winter, respectively, the average diurnal normalized profiles to the midnight

212   value of some NMVOC relative to an inert tracer to examine the relative importance of these

213   processes (Borbon et al., 2013). Acetylene was chosen as a relatively inert tracer and its

214   normalized diurnal profile is reported in each panel (grey shaded). The NMVOCs extremely

215   high concentrations have been filtered by removing the northern wind direction events,

216   referring to the identified gasoline evaporation episodic PMF (Positive Matrix Factorization)

217   factor (Salameh et al. 2016), in order to minimize the impact of the local industrial source

218   located in the northern part of the site (Salameh et al., 2015, 2016).

219   In summer all NMHCs including acetylene show the same bi-modal pattern with one midday

220   and one midnight maximum as a result of primary emissions from Greater Beirut transported

221   at the background receptor site between 09:00 and 10:00 and accumulation of emissions at night

222   in a shallower boundary layer. The degree of chemical removal during the day is k_{OH}-dependent

223   and increases with k_{OH} as illustrated for alkenes and aromatics. At night alkenes and aromatics

224   follows the pattern of acetylene due to common sources, dilution and neglected photochemistry.

225   Then the magnitude of daytime maximum and minimum becomes modulated by chemical

226   removal when k_{OH} is higher than 8.52×10^{-12} cm^3 molecule^{-1} s^{-1}. Compensation of chemical

227   removal at midday by evaporative emission cannot be excluded for aromatics like toluene.

228   In winter the diurnal profiles of NMHCs including acetylene show a unimodal pattern

229   characterized by maximum concentrations in the morning typical of traffic rush hours and a

230   slight decrease until late evening. Contrary to summer, the absence of a midday minimum of

231   normalized concentrations indicates a strong accumulation of primary emissions during the day

232   which is favored by poor dilution and negligible photochemistry. However, the diurnal profiles

233   of alkenes illustrated in figure 3 are characterized by a most pronounced enhancement in the

234   evening which can be related to additional combustion sources like domestic heating since the

235   measurement site is surrounded by a residential area (Salameh et al., 2015). Aromatics and

236   alkanes diurnal profiles follow the shape of acetylene profile in general. Nevertheless, one can

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237   see a strong enrichment of aromatics during the day originating from the traffic related source

238   where toluene and m,p-xylenes are significantly present (Salameh et al., 2016).

239   In this section, we showed that some NMHC especially shorter-lived species like >C7-

240   aromatics, ethylene and propene could be affected by chemical removal in summer so that the

241   measured urban enhancement ratios can be different from the emission ratios. These results are

242   consistent with Salameh et al., 2015. The determination of ER in the next section will take into

243   account the potential effect of chemistry by applying temporal filters for the most reactive

244   species in summer. When NMHCs are not influenced by photochemistry, the enhancement

245   ratios will be estimated using all the data.

246   **5. Determination of urban enhancement emission ratios**

247   The emission ratio for NMVOC species is the ratio of a selected VOC to a reference compound

248   in fresh emissions without undergoing photochemical processing. We applied two methods to

249   determine emission ratios (ER) for each VOC species relative to CO and acetylene. The first

250   method consists on linear regression fits (LRF) on data applied to summer and winter datasets

251   and the other method relies on extrapolating the photochemical age to zero which was applied

252   to the summer data, photochemical removal being negligible in winter.

253   **5.1. Linear Regression Fit (LRF) method**

254   A commonly applied method to determine emission ratios is the linear regression fit (LRF) by

255   calculating the slope of the scatterplot between a particular NMVOC versus acetylene or CO

256   (Borbon et al., 2013). These reference compounds have been chosen due to their low reactivity

257   and since they are two tracers of incomplete combustion. Additionally, according to the national

258   emission inventory (Waked et al., 2012) and to PMF results (Salameh et al., 2016), the road

259   transport is the dominant source of NMVOCs in Lebanon and Greater Beirut; in urban areas as

260   well, emissions of CO are also dominated by vehicular emissions (von Schneidemesser et al.,

261   2010).

262   During both campaigns, as shown in the discussion in section 4, photochemical processing did

263   not play an important role in influencing NMVOC chemical compositions in ambient air of

264   Greater Beirut except for the most reactive species during the day in summer (alkenes and

265   aromatics). For the latter, emission ratios for NMVOC versus CO and for NMVOC versus

266   acetylene were derived from slopes of LRF for measurements made between 23:00 and 07:00

267   local time in summer when chemistry can be neglected . For isoprene, anthropogenic emissions

268   can be derived from nighttime data in the absence of its light-dependent biogenic origin (Borbon

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269   et al., 2001). The LRF approach assumes that the composition of urban emissions relative to

270   CO and to acetylene does not change between day and night. For other species, the emission

271   ratios were derived from slopes of LRF for all the data in winter and summer since there is no

272   effect of photochemistry even during the day in summer, and in order to cover the urban mixing

273   of emissions from all the sources. The results are detailed in section 5.4 and summarized in

274   table 2.

275   **5.2. The Photochemical Age method**

276   The photochemical method takes into consideration the photochemical processing of measured

277   ratios of NMVOC with acetylene. We applied this method to all the summertime dataset.

278   Following de Gouw et al. (2005), Warneke et al. (2007), and Borbon et al. (2013), we assume

279   that the photochemical removal of NMVOC species is dominated by a reaction with the OH

280   radical. Firstly, the photochemical age of air masses, Δt, is estimated by using the NMVOC

281   ratios following this equation:

282
$$\Delta t = \frac{1}{[OH](k_{135TMB} - k_{benzene})} \times \left[\ln\left(\frac{[135TMB]}{[benzene]} \right)_{t=0} - \ln\left(\frac{[135TMB]}{[benzene]} \right) \right] \qquad (1)$$

283   Where [OH] is the concentration of hydroxyl radical, fixed to 5×10^6 molec.cm^{-3}; k_{135TMB}

284   (56.7×10^{-12} cm^3.molec^{-1}.s^{-1}) and $k_{benzene}$ (1.22×10^{-12} cm^3.molec^{-1}.s^{-1}) are the reaction rate

285   coefficients with OH radical of 1,3,5-trimethylbenzene and benzene, respectively; [135TMB]

286   and [benzene] are the volume mixing ratios in ppb of benzene and 1,3,5-trimethylbenzene,

287   respectively. The 1,3,5-trimethylbenzene/benzene ratio was chosen to investigate the

288   photochemical age because these two compounds have similar sources but their lifetimes are

289   significantly different and lower than air mass transport timescale. The ratio of [135TMB] over

290   [benzene] at time zero (t=0) defines the emission ratio at a photochemical age of zero. This

291   emission ratio was derived from a scatter plot of [135TMB] vs. [benzene], it corresponds to the

292   emission enhancement ratio at nighttime data where photochemical processing can be

293   neglected.

294   Following de Gouw et al. (2005) and Warneke et al. (2007), the equations used for

295   emission ratio determination are described as follows for primary NMHCs (equation 2):

296
$$\frac{[NMVOC]}{[C_2H_2]} = ER_{NMVOC} \times \exp[-(k_{NMVOC} - k_{C_2H_2})[OH]\Delta t] \qquad (2)$$

297   where [NMVOC] and [C_2H_2] are the volume mixing ratios in ppb of the NMVOC and acetylene

298   respectively; ER_{NMVOC} is the emission ratio of the NMVOC relative to acetylene; k_{NMVOC} and

299   k_{C2H2} are the OH rate coefficients for the reaction of those compounds with OH radical (5.10^6

300   molecules.cm^{-3}); and Δt is the photochemical age calculated by equation 1. The emission ratios

301   of NMVOCs are estimated by extrapolating the photochemical age to zero. Following Borbon

302   et al. (2013) and Warneke et al. (2007), the emission ratios determined with the photochemical

303   age method are not affected when reducing or increasing the OH values by a factor of 2.

304   As an illustration, we report the ratios of measured benzene/acetylene, m,p-xylenes/acetylene,

305   and ethylene/acetylene as a function of the photochemical age in figure 4. Calculated

306   photochemical age is usually lower than 1h. As expected, the benzene/acetylene ratio keeps

307   constant with increasing photochemical age whereas a decrease of m,p-xylenes/acetylene and

308   ethylene/acetylene ratios is observed because they are more reactive. Surprisingly the

309   ethylene/acetylene ratio decreases faster than the (m,p)-xylenes/acetylene one while (m,p)-

310   xylenes are two times more reactive than ethylene. The decrease of the (m,p)-xylenes/acetylene

311   ratio might be modulated by additional evaporative emissions during the day that

312   counterbalance its chemical removal.

5.3. Performance of the different methods

314   Figure 5 illustrates the performance of the ER determination methods for the summertime data

315   where ER from the photochemical age and LRF methods are compared. There is an overall very

316   good agreement between the two methods (slope of the linear fit in red = 0.90 and correlation

317   coefficient of 0.99) showing the robustness of the methods and confirming that the selection of

318   all the data for less-reactive species and nighttime data for more reactive species for summer in

319   the LRF method does not bias the results. The calculated determination coefficients R^2 with

320   acetylene and CO ranged from 0.3 for some species like ethane to 0.9 for the majority of the

321   species in winter, and with acetylene in summer from 0.5 to 0.9. The standard deviation of the

322   ER determined by the photochemical method varied between zero and 0.04 for propane.

5.4. Emission ratios and seasonal variability

324   The ER derived from all wintertime and summertime (nighttime dataset for most reactive

325   species) datasets by the LRF method as well as the ER from the road transport established by

326   near-field measurements (Salameh et al., 2014) are summarized in Table 2. ER relative to CO

327   were not calculated in summer because CO data were not available for the whole campaign.

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328   The ER derived from the observations (summer and winter) are comparable at ±50% to the

329   ratios of road transport sector for more than 80% of the species. This shows that urban emission

330   fingerprint is mainly driven by traffic emissions including ethane which does not have any

331   urban natural gas usage contribution in Lebanon. For other species like C4 to C6-alkenes,

332   styrene, and a few alkanes in winter the differences stay within a factor of 2, except for propane

333   where they are 5 in summer and 3 in winter. These differences can be partly explained by the

334   contribution of additional sources.

335   In general, the ERs in winter are slightly lower than in summer (Table 2). Figure 6 compares

336   the derived emission ratios of NMVOC species relative to acetylene at the measurement site

337   during summer and winter. The wintertime emission ratios for most NMVOC species agree at

338   ±30% (slope of 0.71) and within a factor of 2 and a high determination coefficient of 0.94.

339   Finally, there is no significant seasonality in ER regardless of the species except for 1-pentene,

340   cyclohexane, styrene, 2,2-dimethylbutane, and 1,2,3-trimethylbenzene. Those species are

341   associated with ER lower than 0.1. These results indicate that the urban emission composition

342   contributing to the ambient concentrations is not significantly different between summer and

343   winter. The sources usually affected by seasonality are in winter related to combustion and to

344   fuel evaporation in summer. Our results based on ER are consistent with previous PMF results

345   (Salameh et al., 2016), showing that the road transport sector (combustion and gasoline

346   evaporation) is the dominating source in both seasons in Beirut.

347   These findings are different from the results usually found in recent studies. For instance,

348   Boynard et al. (2014) found that the emission ratios relative to acetylene in French cities (Paris

349   and Strasbourg) are slightly affected by the seasonality of emissions for benzene and alkenes

350   whereas other NMVOC species (alkanes and higher aromatics) exhibit 3 to 7 higher emission

351   ratios in summer. Moreover, Wang et al. (2014) reported lower wintertime emission ratios for

352   most NMVOC species than the summertime values by a factor ≥ 2 in Beijing, China. This

353   seasonal difference in emission ratios for most NMVOC species is possibly due to the seasonal

354   variations in NMVOC sources and in particular the modulation between wintertime combustion

355   and summertime evaporation.

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

357   The NMVOC emission ratios relative to acetylene determined in Beirut by the LRF method are

358   compared to those recently determined in contrasted cities of North America (Los Angeles,

359   USA), Europe (Strasbourg, France), Middle East (Mecca, Saudi Arabia), and Asia (Beijing,

360   China,) on a seasonal basis in figure 7.

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361   Usually ER agree within a factor of 2 except for aromatics (benzene excepted) and some alkanes

362   (C2 – C5). Those species are related to the unburned fuel fraction and natural gas or liquefied

363   petrol usage. Among C2-C5 alkanes and regardless of the season, ER of ethane is much lower

364   in Beirut than Los Angeles, Beijing, and Strasbourg but similar to Saudi Arabia since the natural

365   gas source is not widely used in Lebanon and Middle East countries (Salameh et al., 2015). The

366   maximum difference reached a factor of 10 for m,p-xylenes in winter. Regardless of the season,

367   ER of aromatics are higher in Beirut compared to northern post-industrialized countries and

368   even the Middle Eastern city Mecca. One should note that aromatic differences are quite

369   significant between the two Middle Eastern cities, from a factor of 3 up to a factor of 6 for

370   (m,p)-xylenes. ER of alkenes are higher in Mecca due to their additional evaporative origin

371   (Simpson et al., 2014). Differences are greater in winter than in summer as a consequence of a

372   marked seasonal variability of ER in opposite to Beirut. In Beirut, the aromatics are emitted

373   from combustion related sources and from gasoline evaporation which accounts for more than

374   40% in winter as well as in summer (Salameh et al., 2016). ER for alkenes, which are

375   combustion products, usually agree within a factor of two between Beirut, Los Angeles,

376   Beijing, and Strasbourg in both seasons, except for C4 and C5 alkenes with LA and Beijing.

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

378   The emission fluxes ($Kg/m^2/s$) extracted from ECCAD database are converted to mole emission

379   fluxes, then the NMVOC ratios relative to CO and relative to acetylene are determined.

380   The comparison held here will consider the common compounds present in the ACCMIP and

381   MACCity, when possible, global emission inventories and measured during ECOCEM

382   campaigns which are listed in table 3. Important NMVOC species are present within these

383   inventories as tracers of many anthropogenic sources, reactive species, and important

384   precursors of ozone and SOA (Table 3).

385   **7.1. Emission inventory vs. observations: all anthropogenic sectors**

386   To analyze the consistency of the speciation of NMVOCs in the ACCMIP and MACCity global

387   emission inventories, we compared the individual NMVOC relative to CO as well as to

388   acetylene ratios during summer and winter. Figure 8 displays the ratios from the anthropogenic

389   emissions data (ACCMIP and MACCity) and the observations in a logarithmic scale for 11

390   individual NMVOC species color coded by the NMVOC groups. Except benzene, xylenes to a

391   less extent and long-lived alkanes, ER relative to acetylene agree within a factor of 2 between

392   observations and inventory suggesting that the overall VOC speciation in ACCMIP is

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393 reasonably represented for more reactive VOCs. Regarding ER relative to CO, differences with
394 ACCMIP are remarkable. A global underestimation by the inventory by a shift towards lower
395 ER over an order of magnitude suggesting an overestimation of CO emissions by ACCMIP.

396

397 In order to consolidate our conclusions regarding VOC speciation within ACCMIP, we
398 performed the systematic calculation of the ratios of every NMVOC to each of the other
399 NMVOCs ($NMVOC_i$) in the global emission inventory and in the observations (Coll et al.,
400 2010). From figure 9, it appears that benzene is systematically overestimated up to a factor of
401 5 in ACCMIP and to a lesser extent, pentanes and butanes by a factor >2 whereas xylenes are
402 reasonably underestimated in the ACCMIP global emission inventory. The other compounds
403 lay around the line of the slope (= 1), below a factor of 2. Finally comparisons between
404 ACCMIP and observations (figures 8 and 9) suggest that the overall speciation of anthropogenic
405 sources for major hydrocarbons that act as ozone and SOA precursors in ACCMIP is reasonably
406 represented.

407 **7.2. Emission inventory vs. observations: road transport sector**

408 Our study has shown that calculated ER are comparable to the ones of road transport sector for
409 more than 80% of the species (table 2) which is consistent with PMF results (Salameh et al.,
410 2016). In Lebanon, PMF results showed that the major sources of NMHCs were traffic-related
411 emissions (combustion and gasoline evaporation) in winter and in summer accounting for 51
412 and 74 wt% respectively. Moreover, according to Parrish et al. (2009), the largest source of
413 emissions in most urban areas is road traffic, which includes tailpipe and evaporative emissions.
414 Therefore, it is also crucial to assess the emission inventories regarding the road transport sector
415 namely ACCMIP and EMEP SNAP 07.

416 We proceeded as in the previous section by comparing the road transport ER relative to
417 acetylene for all VOCs and individual VOCs from ACCMIP and EMEP emission inventories
418 to the ER from near-field measurements (figures 10 and 11) (Salameh et al., 2014). ER from
419 the road transport sector are usually consistent within a factor of 2 for the regional emission
420 inventory EMEP while xylenes and toluene are underestimated over a factor of 2 by ACCMIP.
421 At a more detailed level, by calculating the ratios for individual NMVOC, figure 11 confirms
422 that xylenes and toluene are underestimated species by both inventories.

423

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7.3. Perspectives for Middle East region (MEA)

424

425   After a focus on Lebanon, the purpose of this last section is to provide some perspectives

426   regarding the whole MEA region. Figure 12 shows the comparison of ER relative to acetylene

427   from the ACCMIP emission inventory considering all the anthropogenic sectors of Lebanon

428   compared to the ones of four other Middle Eastern countries that are expected to be high VOC

429   emitters (Saudi Arabia, Egypt, Iran and Turkey). An overall homogeneity within a factor of 2

430   of the ERs is observed between countries of the Mediterranean border (Lebanon, Turkey, and

431   Egypt). However, when comparing Lebanon to other Middle East countries, some gaps are

432   depicted: The emission inventory suggests that the ERs of benzene, toluene, as well as of C4-

433   C5 alkanes are lower in Lebanon compared to Iran and Saudi Arabia. For the latter those

434   observations are completely contradictory with the ones reported in figure 7. We have shown

435   that the anthropogenic emissions in Beirut were more enriched in aromatics and propane and

436   poorer in alkenes than the ones of Mecca while benzene ER was consistent between both

437   countries. While the comparison here is limited by the number of species compared to figure 7

438   this suggests that the global emission inventory does not reproduce the heterogeneity of VOC

439   anthropogenic emission composition between countries of the MEA and same results can be

440   expected for all the MEA countries where emissions data and measurements are scarce.

441   Systematic and additional observations are needed in order to test the importance of such spatial

442   variability in anthropogenic VOC emission composition.

8. Conclusions

443

444   Detailed measurements of NMVOCs collected at a sub-urban site in Beirut, Lebanon, have been

445   used to evaluate regional and global emission inventories (ACCMIP, MACCity and EMEP)

446   downscaled to the studied domain. These data were collected during two intensive field

447   campaigns in summer 2011 and in winter 2012 within the framework of the ECOCEM project.

448   The emission ratios (ER) of individual NMVOC species relative to CO and acetylene were

449   successfully derived from ambient measurements in summer and in winter as well as from near-

450   field measurements for the road transport sector by applying two independent methods: the

451   linear regression fit method and the photochemical age method. Emission ratios from both

452   methods show a very good agreement at ±10%.

453   The ER derived from the observations (summer and winter) are comparable to the ratios of the

454   road transport sector for more than 80% of the species. There is generally no significant

455   seasonality in ER regardless of the species unlike the seasonality usually observed in other

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456 cities. These results are consistent with the significant contribution of road transport sector

457 (combustion and gasoline evaporation) in winter and summer (Salameh et al., 2016).

458 Regardless of the season, ER derived from observations agree within a factor of 2 between

459 Beirut and other representative worldwide cities except for the unburned fuel fraction and

460 ethane. Aromatics (benzene excepted) show the largest differences up to a factor of 10 for m,p-

461 xylenes compared to northern post-industrialized countries and even another middle eastern

462 city like Mecca in Saudi Arabia.

463 ER relative to CO and to acetylene as well as the ratios of every NMVOC to each of the other

464 NMVOCs (NMVOC$_i$), extracted from ACCMIP and MACCity global emission inventory were

465 compared with the corresponding observed ER during both seasons, for all anthropogenic

466 sectors. This comparison suggests that the overall speciation of anthropogenic sources for major

467 hydrocarbons that act as ozone and SOA precursors in ACCMIP is reasonably represented.

468 The road transport ER relative to acetylene derived from near-field measurements are compared

469 to ER from ACCMIP and EMEP regional emission inventory for road transport sector. ER from

470 the road transport sector are usually consistent within a factor of 2 for the regional emission

471 inventory EMEP while xylenes and toluene are underestimated over a factor of 2 by ACCMIP.

472 It should be emphasized that when a consensus is met between observed and inventory ER (the

473 ER lay around the ratio of 1), this does not necessarily mean that the absolute emissions are

474 correct. Indeed, Salameh et al. (2016) have shown that global inventories (ACCMIP, EDGAR,

475 MACCity) could underestimate the NMVOC emissions up to a factor of 10 for the

476 transportation sector. Both speciation and absolute emissions have to be taken into

477 consideration.

478 Finally, we have shown that the emission inventory is in disagreement with the observations

479 when comparing Lebanon with Saudi Arabia. The observed heterogeneity of anthropogenic

480 VOC emission composition can be significant for reactive VOC (factor of 6 for m,p-xylenes)

481 but is not depicted by global emission inventories. This suggests that systematic and detailed

482 measurements are needed in the MEA region in order to better constrain emission inventory.

483 VOC emission inventory is the fundamental input of air quality modelling, therefore it plays a

484 major role in characterizing secondary pollution and control policy formulation. To improve

485 the quality of future VOC emission estimates, more efforts should be made toward refinement

486 of source classification, development of representative local emission factors, comprehensive

487 collection of activity data, and more accurate spatiotemporal characterization. Additionally,

488 comparison of available datasets will allow a quantification of the uncertainties on emissions.

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489 At a regional and global level, long term and continuous studies integrating more than one

490 measuring site and more specific tracers are of great interest in order to provide more reliable

491 information and the use of surface observations from monitoring stations could help defining

492 better speciations.

493

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Table 1: Measurements during ECOCEM Campaigns.

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

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

NMVOC	$\Delta VOC/\Delta C_2H_2$ (ppb/ppb)			$\Delta VOC/\Delta CO$ (ppb/ppm)
	Beirut – summer 2011	Beirut – winter 2012	road transport-near field spring 2012 measurement (Salameh et al., 2014)	Beirut – winter 2012
ethane	**0.23**	**0.18**	**0.21**	1.50
propane	1.02	0.58	0.21	5.40
n-butane	**1.14**	**0.95**	1.87	6.70
i-butane	0.25	0.48	0.72	3.30
n-pentane	0.26	0.15	0.40	1.10
i-pentane	**1.22**	0.75	**1.77**	5.30
2-methyl-pentane	**0.29**	0.18	**0.30**	1.20
3-methyl-pentane	**0.17**	0.11	**0.16**	0.80
2,2-dimethylbutane	**0.10**	0.03	**0.11**	0.20
n-hexane	**0.11**	**0.10**	**0.10**	0.90
Methylcyclopentane	0.13	0.11	0.06	0.90
2-methyl-hexane	**0.11**	**0.08**	**0.08**	0.70
3-methyl-hexane	**0.11**	**0.09**	**0.09**	0.70
cyclohexane	0.04	**0.01**	**0.01**	0.10
n-heptane	**0.07**	**0.05**	**0.06**	0.40

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

nd: not determined

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

ACCMIP nomenclature MACCity*	Compounds considered from ECOCEM database	K_{OH} $(10^{-12}cm^3.molécule^{-1}.s^{-1})$	Y_{SOA}
Ethane*	Ethane	0.25	0.1
Propane*	Propane	1.09	0
Butanes	Butane and isobutane	2.36 and 2.12	0.3 and 0
Pentanes	Pentane and isopentane	3.8 and 3.6	0.3 and 0.2
Ethene*	Ethene	8.52	1.3
Propene*	Propene	26.3	1.6
Acetylene	Acetylene	0.9	0.1
Benzene	Benzene	1.22	92.9
Trimethylbenzene	Sum of 1,2,3-1,2,4-,1,3,5-trimethylbenzene	32.7; 32.5; 56.7	43.9; 20.6; 13.5
Toluene	Toluene	5.63	100
Xylenes	Sum of m,p-xylenes and o-xylene	13.6; 23.1; 14.3	95.5; 84.5; 67.1
CO*	CO		
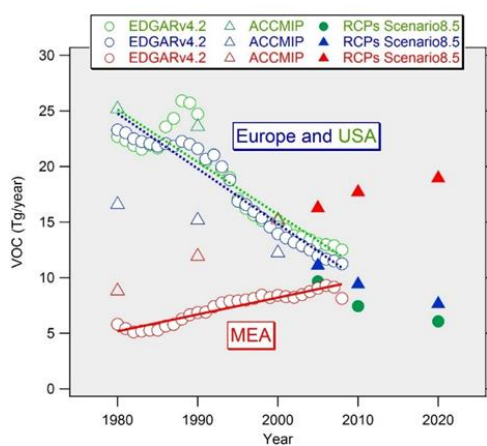
Figure 1: Evolution of the NMVOC anthropogenic total emissions (Tg/year) in the MEA, USA and Europe (OECD Europe and Eastern Europe) from 1980 to 2020 from reference global emission inventories (ECCAD database).

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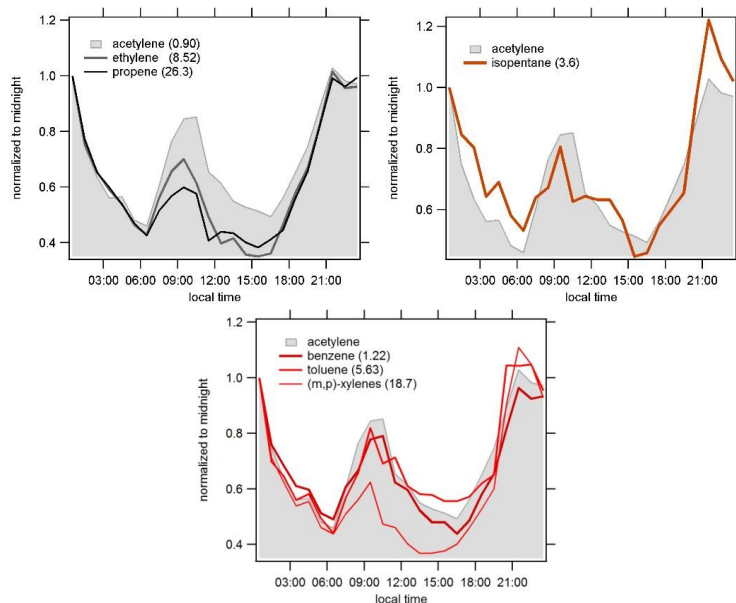
Figure 2: Normalized diurnal profiles of the mixing ratios of selected species to midnight values in summer. Numbers in parentheses are the rate coefficient with OH $\times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (Atkinson and Arey 2003; Atkinson 2007).
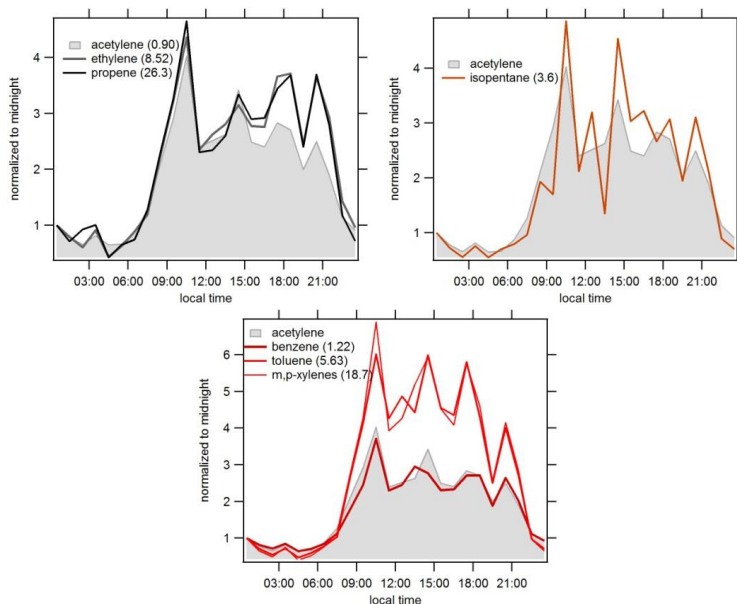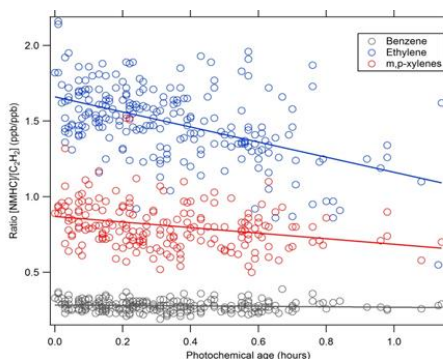

Figure 3: Normalized diurnal profiles of the mixing ratios of selected species to midnight values in winter. Numbers in parentheses are the rate coefficient with OH $\times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (Atkinson and Arey 2003; Atkinson 2007).

Figure 4: Measured ratios of benzene/acetylene, m,p- xylenes/acetylene, and ethylene/acetylene as a function of photochemical age (hours).
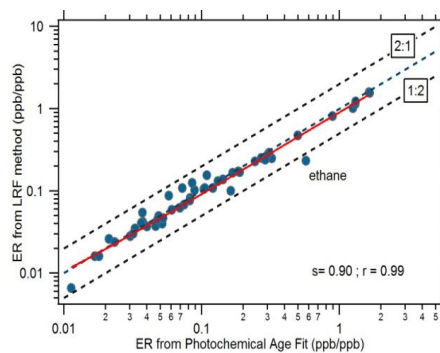
Figure 5: Comparison of the emission ratio (ER) estimated relative to acetylene by the nighttime linear regression fit and the photochemical age fit in summer.
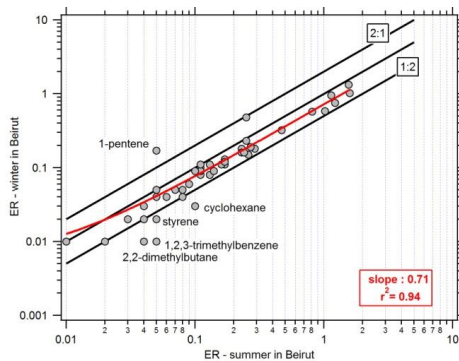
Figure 6: Comparison of summertime and wintertime emission ratios vs. acetylene in Beirut.
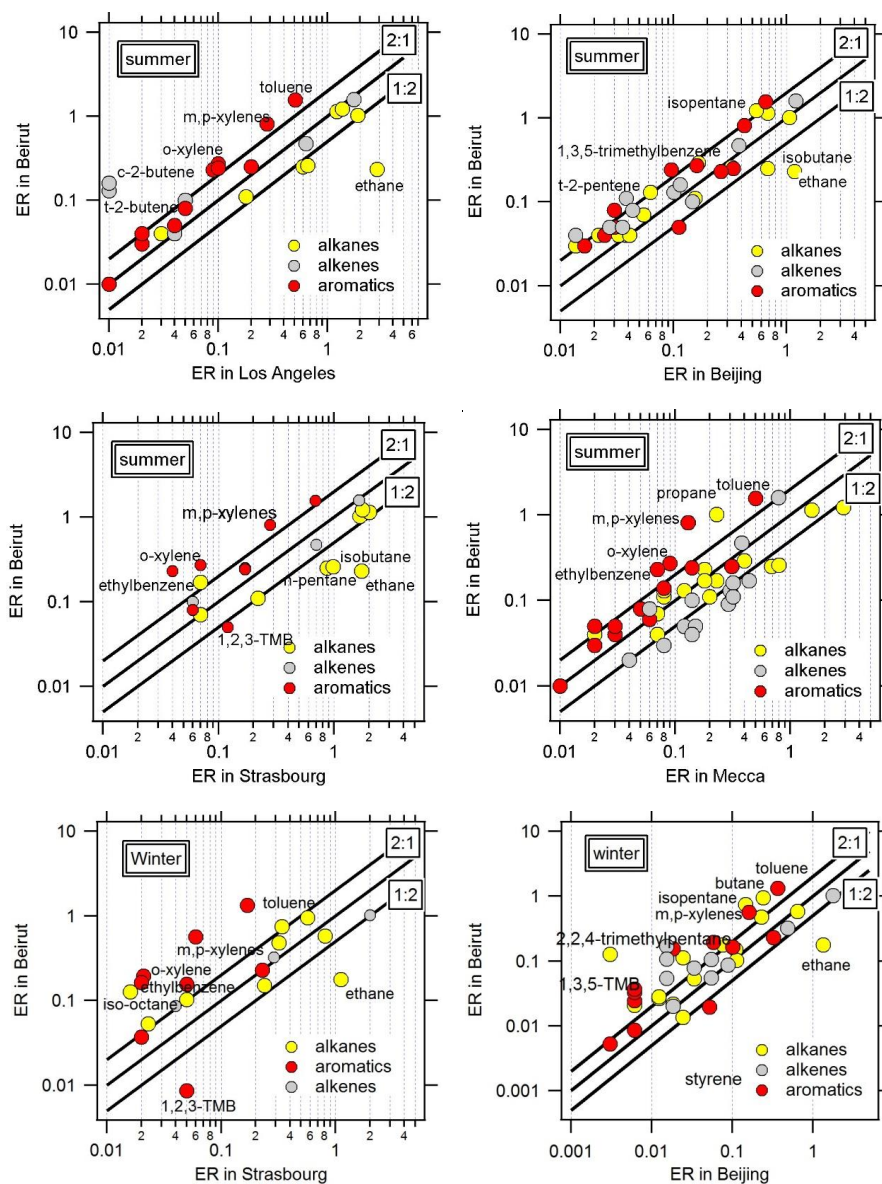
Figure 7: Comparisons of NMVOC emission ratios determined at the Beirut sub-urban site with those for Los Angeles, US (Borbon et al., 2013); Strasbourg, France (Boynard et al., 2014); Beijing, China (wang et al., 2014): and Mecca, Saudi Arabia (Simpson et al., 2014). (TMB: Trimethylbenzene)

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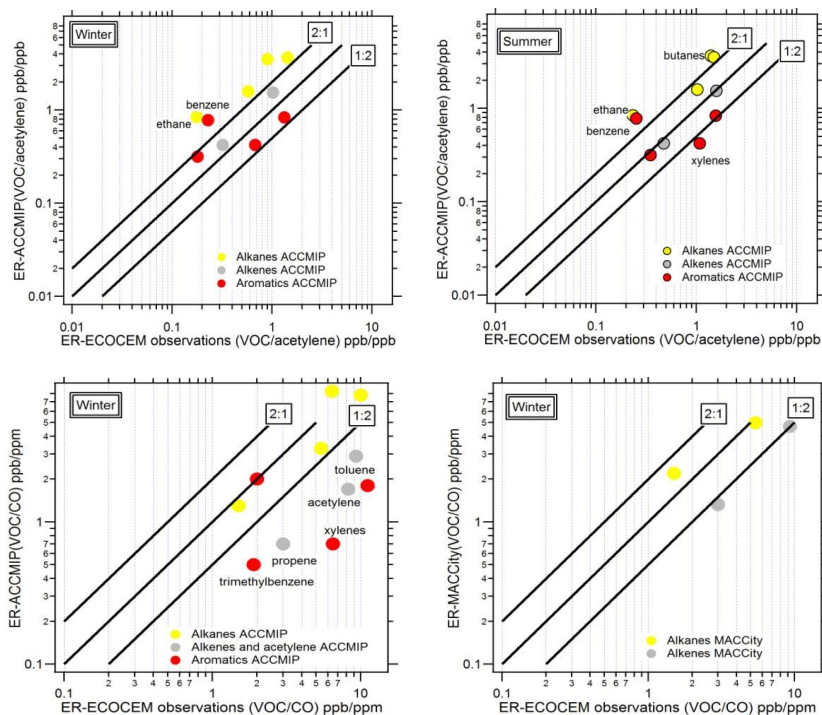
Figure 8: Comparison of the emission ratios from ACCMIP and MACCity to the measured ones by LRF method, in summer and in winter, relative to CO and acetylene, for all the anthropogenic sectors.

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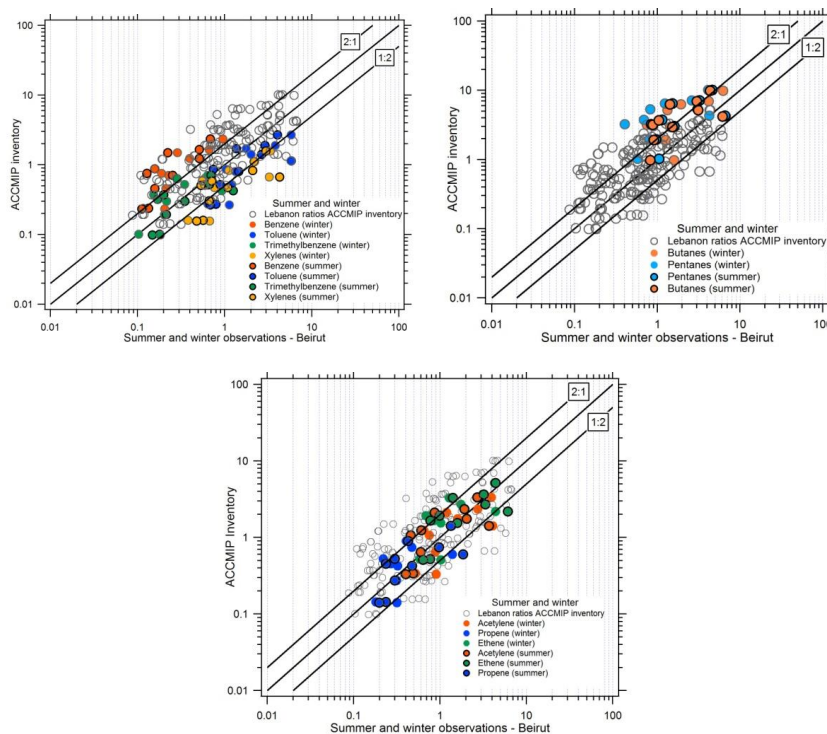
Figure 9: Comparison of the emission ratios of NMVOC vs. NMVOCi from ACCMIP to the measured ones, in summer and in winter, for all the anthropogenic sectors, for all data (in grey dots) and for a given NMVOC (colored dots).
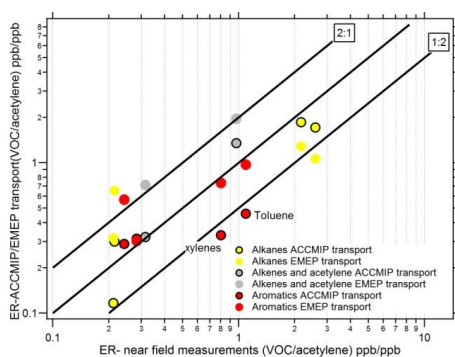

Figure 10: Comparison of the emission ratios relative to acetylene, from ACCMIP and EMEP emission inventories for road transport to the ER from road transport by near-field measurements.
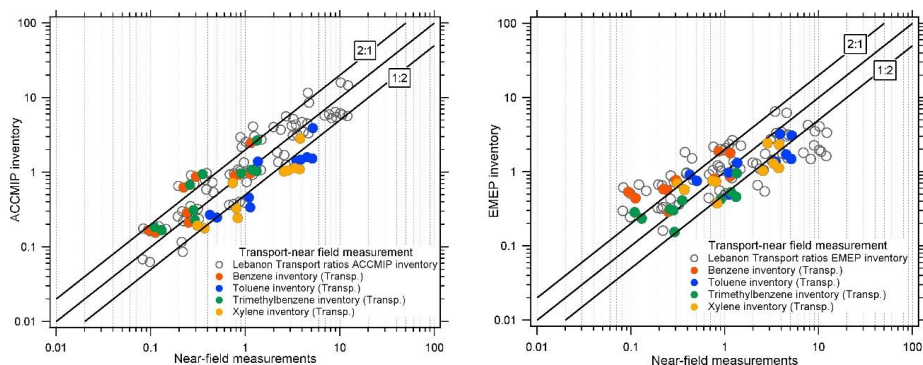
Figure 11: Comparison of the emission ratios of NMVOC vs. NMVOCi from ACCMIP and EMEP to the ER from near-field measurements for the road transport sector, for all data (in grey dots) and for a given NMVOC (colored dots).
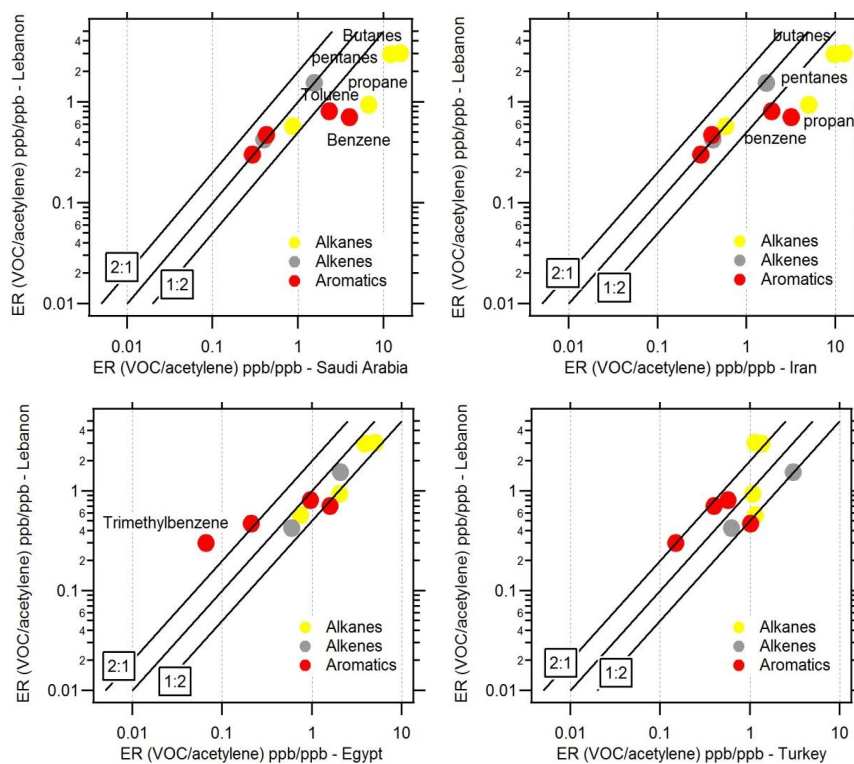

Figure 12: Comparison of the emission ratios from ACCMIP relative to acetylene for all the anthropogenic sectors for five Middle Eastern countries (Lebanon, Egypt, Turkey, Iran, and Saudi Arabia).