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,a], Agnès Borbon[1,b], 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 : Mines Douai, Sciences de l'Atmosphère et Génie de l'Environnement (SAGE), F-59508 Douai CEDEX, France

[b] 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 volatile organic compounds (VOCs) to evaluate the spatial heterogeneity of

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

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

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

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

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

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

11 and are comparable to the ones of the road transport sector from near-field measurements for

12 more than 80% of the species. There is no significant seasonality in ER for more than 90% of

13 the species unlike the seasonality usually observed in other cities worldwide. Regardless of

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

15 cities except for the unburned fuel fraction and ethane. ERs of aromatics (benzene excepted)

16 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.

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). 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_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_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_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_2, CO, NO_x, and NMVOCs).

The same picture is presented by 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 to18 Tg/year according to RCP 8.5 in 2010. 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). 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_x, SO_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 a 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 at 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

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

105   NMVOCs, NH_3, PM_{10} and $PM_{2.5}$, according to EEA/EMEP guidelines (EMEP/EEA, 2009).

106   The NMVOC total emissions in Lebanon were estimated to be 115 Gg for the year 2010.

107   According to this inventory, transport is the main source of NMVOC with a relative

108   contribution of 67% of total emissions of NMVOCs (Waked et al., 2012). In addition, there is

109   a strong need for developing better emission inventories in the Middle East region as a whole

110   (Waked et al., 2013a). The paucity of observations in this region, especially for VOCs and

111   PM composition, is a significant limitation to the achievement of evaluated and accurate

112   emission inventories. Finally, accurate modelling of individual NMVOCs and better

113   understanding of ozone precursors is also important for policy-makers and for the

114   improvement of air quality leading to better estimates of secondary organic aerosols (SOA)

115   formation and ozone levels.

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

117   absence of regional emission inventories for MEA, by the use of detailed observations

118   recently collected in Beirut, Lebanon in the frame of ECOCEM project (Emissions and

119   Chemistry of Organic Carbon in the East Mediterranean) (Salameh et al., 2015). Those

120   observations include detailed near-source field measurements and ambient measurements at a

121   suburban site. We used regional (EMEP) and global (ACCMIP and MACCity) emission

122   inventories downscaled to Lebanon. Two independent methods already applied to Los

123   Angeles basin during the CalNex experiment (Borbon et al., 2013) that take into consideration

124   the effects of chemical removal were used to estimate the urban enhancement emission ratios

125   (ERs) of various NMVOC relative to CO and acetylene for winter and summer. First,

126   calculated ERs are compared to available ERs in other cities worldwide in order to assess the

127   spatial variability of emission composition. Second, calculated ERs are compared to the ones

128   derived from global emission inventories for all the anthropogenic sectors and for the road

129   transport sector. Finally perspectives for the whole Middle East region are discussed.

130

2. Experiment

131   **2. Experiment**

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

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

134   a suburban site, within the ECOCEM project. VOC have been measured by a combination of

135   on-line and off-line techniques (table 1). A set of eight speciated profiles of four major non-

136 methane hydrocarbons (NMHC) sources in Lebanon was proposed by Salameh et al. (2014)

137 by sampling close to emission sources in real-world operating conditions as far as possible.

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

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

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 field campaigns were conducted on the roof of the Faculty of Sciences building of Saint

143 Joseph University located in the eastern suburbs of the city of Beirut from 2 to 18 July 2011

144 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

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

147 residential area. Beirut International Airport is located 8 km southwest of the site and one fuel

148 storage facility is located at 3.6 km North. More details are reported in Salameh et al. (2015).

149 During both measurement periods, NMHCs were continuously analyzed on an hourly basis

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

151 analysis. Additional measurements of trace gases concentrations including CO, NO_x and O_3

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

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

154 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

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

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

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

160 easterly 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

165 and 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   emissions regarding road transport (SNAP 07) is included in this study.

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

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

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

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

175   2010. A seasonal cycle was applied for each sector, and the NMVOC species anthropogenic

176   emissions have been lumped to 13 species (excluding acetylene) using the same methodology

177   for the NMVOCs speciation as used in the ACCMIP dataset.

178   A large number of emission inventories only provide the distribution of total NMVOC

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

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

181   GAINS-4a). We rely on the ACCMIP inventory from ECCAD database which provides a

182   detailed speciation of VOCs including acetylene. ACCMIP global emission inventory covers

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

184   latitude and longitude, based on the combination of the best global and regional available

185   datasets. ACCMIP was developed mainly to provide consistent gridded emissions of reactive

186   gases and aerosols for use in chemistry model simulations needed by climate models for the

187   Climate Model Intercomparison Program 5 (CMIP5) in support of the Intergovernmental

188   Panel on Climate Change (IPCC) Fifth Assessment report (AR5) (Lamarque et al., 2010). 40

189   regions and 12 sectors were used to combine the various sources within this inventory and a

190   set of species including CO, NOx, total and speciated NMVOCs is provided. Speciation of

191   NMVOC emissions is performed using the RETRO (REanalysis of the TROpospheric

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

193   historical period because of the lack of additional information. For all NMVOC species of the

194   RETRO inventory, a factor was calculated only for the year 2000 by dividing the emission of

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

196   grid cell.

197   For comparison with observations, we extracted the emission fluxes (kg/m^2/s) of 11 individual

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

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

200   8 grids is spatially homogeneous for all compounds, we calculated a mean flux for each

201   NMVOC to derive the emission ratio from the inventory. Comparing emission ratios from the

202 inventory to observations collected at one measurement site stays relevant. Indeed the sub-
203 urban site is far enough from strong direct emissions (industrial, road transport) since they can
204 hide the emissions from distant sources, and it receives air masses coming from Greater
205 Beirut Area which includes the city of Beirut and close suburbs.

206

207 **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
210 the values of urban enhancement emission ratios (ER) (see section 5). We report in figures 2
211 and 3 for summer and winter, respectively, the average diurnal normalized profiles to the
212 midnight value of some NMVOC relative to a tracer to examine the relative importance of
213 these processes (Borbon et al., 2013). Acetylene was chosen as a less reactive combustion
214 tracer and its normalized diurnal profile is reported in each panel (grey shaded). The
215 NMVOCs extremely high concentrations have been filtered by removing the northern wind
216 direction events, referring to the identified gasoline evaporation episodic PMF (Positive
217 Matrix Factorization) factor (Salameh et al. 2016), in order to minimize the impact of the
218 local industrial source 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 10:00and accumulation of emissions at
222 night in a shallower boundary layer. The degree of chemical removal during the day is k_{OH}-
223 dependent (k_{OH}: rate coefficient for the reaction with OH) and increases with k_{OH} as
224 illustrated for alkenes and aromatics. At night alkenes and aromatics follows the pattern of
225 acetylene due to common sources, dilution and less photochemistry. Then the importance of
226 daytime maximum and minimum concentrations becomes modulated by chemical removal
227 when k_{OH} is higher than 8.52×10^{-12} cm^3 molecule^{-1} s^{-1} (rate coefficient of ethylene with OH).
228 Compensation of chemical removal at midday by fresh evaporative emission cannot be
229 excluded for aromatics like toluene.

230 In winter the diurnal profiles of NMHCs including acetylene show a unimodal pattern
231 characterized by maximum concentrations in the morning typical of traffic rush hours and a
232 slight decrease until late evening. Contrary to summer, the absence of a midday minimum of
233 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). Aromatic and alkane 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-xylenes 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 inlinear 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).

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

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

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

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

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

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

272 emissions can be derived from nighttime data in the absence of its light-dependent biogenic

273 origin (Borbon et al., 2001). The LRF approach assumes that the composition of urban

274 emissions relative to CO and to acetylene does not change between day and night. For other

275 species, the emission ratios were derived from slopes of LRF for all the data in winter and

276 summer since there is no effect of photochemistry even during the day in summer, and in

277 order to cover the urban mixing of emissions from all the sources. The results are detailed in

278 section 5.4 and summarized in table 2.

279 **5.2. The Photochemical Age method**

280 The photochemical method takes into consideration the photochemical processing of

281 measured ratios of NMVOC with acetylene. We applied this method to all the summertime

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

283 assume that the photochemical removal of NMVOC species is dominated by a reaction with

284 the OH radical. In this method, the ratio of NMVOC with acetylene is plotted versus the

285 photochemical age as shown in Figure 4.

286 The photochemical age of air masses, Δt, is estimated by using the NMVOC ratios following

287 this equation:

288 $$\Delta t = \frac{1}{[OH](k_{135TMB} - k_{benzene})} \times \left[\ln\left(\frac{[135TMB]}{[benzene]}\right)_{t=0} - \ln\left(\frac{[135TMB]}{[benzene]}\right) \right] (1)$$

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

290 (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

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

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

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

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

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

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

297 This emission ratio was derived from a scatter plot of [135TMB] vs. [benzene], it corresponds

298 to the emission enhancement ratio at nighttime data where photochemical processing can be

299 neglected.

300 In figure 4, we report the ratios of measured benzene/acetylene, m,p-xylenes/acetylene, and

301 ethylene/acetylene as a function of the photochemical age. Calculated photochemical age is

302 usually lower than 1h. As expected, the benzene/acetylene ratio remains constant with

303 increasing photochemical age whereas a decrease of m,p-xylenes/acetylene and

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

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

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

307 xylenes/acetylene ratio might be modulated by additional evaporative emissions during the

308 day that counterbalance its chemical removal.

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

310 emission ratio determination illustrated in figure 4 is described as follows for primary

311 NMHCs (equation 2):

312 $$\frac{[NMVOC]}{[C_2H_2]} = ER_{NMVOC} \times \exp[-(k_{NMVOC} - k_{C_2H_2})[OH]\Delta t]\,(2)$$

313 where [NMVOC] and [C$_2$H$_2$] are the volume mixing ratios in ppb of the NMVOC and

314 acetylene respectively; ER$_{NMVOC}$ is the emission ratio of the NMVOC relative to acetylene;

315 k$_{NMVOC}$ and k$_{C2H2}$ are the OH rate coefficients for the reaction of those compounds with OH

316 radical ([OH] = 5.10^6 molecules.cm^{-3}); and Δt is the photochemical age calculated by equation

317 1. The emission ratios of NMVOCs are estimated by extrapolating the photochemical age to

318 zero which is the intercept on the y-axis of the linear fit (figure 4).

319 Following Borbon et al. (2013) and Warneke et al. (2007), the emission ratios determined

320 with the photochemical age method are not affected when reducing or increasing the OH

321 values by a factor of 2.

5.3. Performance of the different methods

323 Figure 5 illustrates the performance of the ER determination methods for the summertime

324 data where ERs from the photochemical age and LRF methods are compared. There is an

325 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 ±30% (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

359 road transport sector (combustion and gasoline evaporation) is the dominating source in both
360 seasons in Beirut.

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

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

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

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

378 Among C2-C5 alkanes and regardless of the season, ER of ethane is much lower in Beirut
379 than Los Angeles, Beijing, and Strasbourg but similar to Saudi Arabia since the natural gas
380 source is not widely used in Lebanon and Middle East countries (Salameh et al., 2015).
381 Regardless of the season, ERs of aromatics are higher in Beirut compared to northern post-
382 industrialized countries and even the Middle Eastern city Mecca. One should note that
383 aromatic differences are quite significant between the two Middle Eastern cities, from a factor
384 of 3 up to a factor of 6 for (m,p)-xylenes. The maximum difference is observed between
385 Beirut and Strasbourg and reached a factor of 10 for m,p-xylenes in winter. Differences are
386 greater in winter than in summer as a consequence of a marked seasonal variability of ER in
387 other cities (Strasbourg and Beijing) in contrast to Beirut. In Beirut, the aromatics are emitted
388 from combustion related sources and from gasoline evaporation which accounts for more than
389 40% in winter as well as in summer (Salameh et al., 2016). ERs of alkenes, which are
390 combustion products, usually agree within a factor of two between Beirut, Los Angeles,

391 Beijing, and Strasbourg in both seasons, except for C4 and C5 alkenes with LA and Beijing;
392 whereas they are higher in Mecca due to their additional evaporative origin (Simpson et al.,
393 2014).

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

395 The emission fluxes (Kg/m^2/s) extracted from ECCAD database are converted to mole
396 emission fluxes, then the NMVOC ratios relative to CO and relative to acetylene are
397 determined.

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

7.1. Emission inventory vs. observations: all anthropogenic sectors

405 To analyze the consistency of the speciation of NMVOCs in the ACCMIP and MACCity
406 global emission inventories, we compared the individual NMVOC relative to CO as well as to
407 acetylene ratios during summer and winter obtained by the LRF method. Figure 8 displays the
408 ratios from the anthropogenic emissions data (ACCMIP and MACCity) and the observations
409 in a logarithmic scale for 11 individual NMVOC species color coded by the NMVOC groups.
410 Except benzene, xylenes to a less extent and long-lived alkanes, ER relative to acetylene
411 agree within a factor of 2 between observations and inventory suggesting that the VOC
412 speciation in ACCMIP is better represented for more reactive VOCs such as alkenes and
413 some aromatics. Regarding ER relative to CO, differences with ACCMIP are significant. A
414 global underestimation by the inventory by a shift towards lower ER over an order of
415 magnitude is observed suggesting an overestimation of CO emissions by ACCMIP.

416 In order to consolidate our conclusions regarding VOC speciation within ACCMIP, we
417 performed the systematic calculation of the ratios of every NMVOC to each of the other
418 NMVOCs (NMVOC$_i$) in the global emission inventory and in the observations (Coll et al.,
419 2010) separately, and then we reported in figure 9, the ERs obtained from ACCMIP versus
420 those obtained from the observations. From figure 9, it appears that benzene is systematically
421 overestimated up to a factor of 5 in ACCMIP and to a lesser extent, pentanes and butanes by a
422 factor >2 whereas xylenes are underestimated in the ACCMIP global emission inventory but

423 not systematically. The other compounds are closer to the line of the slope (= 1), below a
424 factor of 2. Finally, comparisons between ACCMIP and observations (figures 8 and 9)
425 suggest that the overall speciation of anthropogenic sources for major hydrocarbons that act as
426 ozone and SOA precursors in ACCMIP is better represented than the others species but it is
427 still need improvement.

428 **7.2. Emission inventory vs. observations: road transport sector**

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

437 We proceeded as in the previous section by comparing the road transport ER relative to
438 acetylene for all VOCs and individual VOCs from ACCMIP and EMEP emission inventories
439 to the ER from near-field measurements (figures 10 and 11) (Salameh et al., 2014). ERs of
440 alkenes from the road transport sector are usually consistent within a factor of 2 for the
441 regional emission inventory EMEP and the global inventory ACCMIP. In EMEP, benzene
442 and ethane are overestimated whereas butanes are underestimated; while xylenes and toluene
443 are underestimated over a factor of 2 by ACCMIP. At a more detailed level, by calculating the
444 ratios for individual NMVOC, figure 11 confirms that xylenes and toluene are underestimated
445 species by both inventories, and benzene is overestimated by EMEP.

446 **7.3. Perspectives for Middle East region (MEA)**

447 After a focus on Lebanon, the purpose of this last section is to provide some perspectives
448 regarding the whole MEA region. Figure 12 shows the comparison of ER relative to acetylene
449 from the ACCMIP emission inventory considering all the anthropogenic sectors of Lebanon
450 compared to the ones of four other Middle Eastern countries that are expected to be high VOC
451 emitters (Saudi Arabia, Egypt, Iran and Turkey). An overall agreement within a factor of 2 of
452 the ERs is observed between countries of the Mediterranean border (Lebanon, Turkey, and
453 Egypt). However, when comparing Lebanon to other Middle East countries, some gaps are
454 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 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

488 were compared with the corresponding observed ER during both seasons, for all
489 anthropogenic sectors. This comparison suggests that the overall speciation of anthropogenic
490 sources for major hydrocarbons that act as ozone and SOA precursors in ACCMIP is better
491 represented than other species but it is still need improvement.

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

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

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

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

518
519
520

References:

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

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

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

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

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

Borbon, A., Fontaine, H., Veillerot, M.,Locoge, N., Galloo, J.C., andGuillermo, R.: An investigation into the traffic related fraction ofisoprene at an urban location, Atmos. Environ., 35(22), 3749–3760, 2001.

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

557 Boynard, A., Borbon, A., Leonardis, T., Barletta, B., Meinardi, S.,Blake, D. R., and Locoge,
558 N.: Spatial and seasonal variabilityof measured anthropogenic non-methane hydrocarbons in
559 urbanatmospheres: Implication on emission ratios, Atmos. Environ., 82, 258–267,
560 doi:10.1016/j.atmosenv.2013.09.039, 2014.

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

564 de Gouw, J. A., Middlebrook, A. M., Warneke, C., Goldan, P.D., Kuster, W. C., Roberts,
565 J.M., Fehsenfeld, F. C., Worsnop,D. R., Canagaratna, M. R., Pszenny, A. A. P., Keene, W.
566 C.,Marchewka, M., Bertman, S. B., and Bates, T. S.: Budget of organiccarbon in a
567 pollutedatmosphere: Results from the NewEngland Air Quality Study in 2002, J. Geophys.
568 Res.-Atmos.,110, D16305, doi:10.1029/2004jd005623, 2005.

569 deGouw, J., and Warneke, C.: Measurements of volatile organic compounds in the Earth's
570 atmosphere using proton-transfer-reaction mass spectrometry, Mass Spectrom. Rev., 26(2),
571 223–257, 2007.

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

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

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

577 Granier, C., Bessagnet, B., Bond, T., D'Angiola, A., van der Gon, H.D., Frost, G.J., Heil, A.,
578 Kaiser, J.W., Kinne, S., Klimont, Z., Kloster, S., Lamarque,J-F.,Liousse, C., Masui,
579 T.,Meleux, F., Mieville, A.,Ohara, T.,Raut, J.-C.,Riahi, K.,Schultz, M.G., Smith, S.J.,

580   Thompson, A., van Aardenne, J., van der Werf, G.R., and van Vuuren, D.P.: Evolution of
581   anthropogenic and biomass burningemissions of air pollutants at global and regional
582   scalesduring the 1980–2010 period, Climatic Change, 109, 163 - 190, doi: 10.1007/s10584-
583   011-0154-1, 2011.

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

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

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

593   Janssens-Maenhout, G., Petrescu, A., Muntean, M., andBlujdea, V.: Verifying Greenhouse
594   Gas Emissions: Methods to Support International Climate Agreements,Greenhouse Gas
595   Measurement and Management vol. 1, no. 2, p. 132-133, JRC67524, 2011.

596   Kanakidou, M., Mihalopoulos, N., Kindap, T., Im, U., Vrekoussis, M., Gerasopoulos, E.,
597   Dermitzaki, E., Unal, A., Koçak, M., Markakis, K., Melas, D.,Kouvarakis, G., Youssef, A.F.,
598   Richter, A., Hatzianastassiou, N., Hilboll, A., Ebojie, F., Wittrock, F., von Savigny, C.,
599   Burrows, J.P., Ladstaetter-Weissenmayer, A., and Moubasher, H.: Megacities as hot spots of
600   air pollution in the East Mediterranean.Atmospheric Environment 45, 1223 – 1235,
601   doi:10.1016/j.atmosenv.2010.11.048,2011.

602   Kim, S. W., McKeen, S.A., Frost, G.J., Lee, S.H., Trainer, M., Richter, A., Angevine,
603   W. M., Atlas, E., Bianco, L., Boersma, K. F., Brioude, J., Burrows, J. P., de Gouw, J., Fried,
604   A., Gleason, J., Hilboll, A., Mellqvist, J., Peischl, J., Richter, D., Rivera, C., Ryerson,
605   T.,te Lintel Hekkert, S., Walega, J., Warneke, C.,Weibring, P., and Williams, E.: Evaluations
606   of NO_x and highly reactive VOC emission inventories in Texas and their implications for
607   ozone plume simulations during the Texas Air Quality Study 2006, Atmos. Chem. Phys.,
608   11(22), 11,361–11,386, 2011.

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

612   Konovalov, I. B., Beekmann, M., Richter, A., Burrows, J. P., and Hilboll, A.: Multi-annual
613   changes of NO_x emissions in megacity regions: nonlinear trend analysis of satellite
614   measurement based estimates, Atmos. Chem. Phys., 10, 8481–8498, doi:10.5194/acp-10-
615   8481-2010, 2010.

616   Lamarque, J.F., Bond, T.C., Eyring, V., Granier, C., Heil, A., Klimont, Z., Lee, D., Liousse,
617   C., Mieville, A., Owen, B.,Schultz, M.G., Shindell, D., Smith, S.J., Stehfest, E., Van
618   Aardenne, J., Cooper, O.R., Kainuma, M., Mahowald, N.,McConnell, J.R., Naik, V., Riahi,
619   K., and van Vuuren, D.P.: Historical (1850–2000) gridded anthropogenicand biomass burning
620   emissions of reactive gases and aerosols: methodology and application,AtmosChemPhys 10,
621   7017–7039, doi:10.5194/acp-10-7017-2010, 2010.

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

624   Lelieveld, J., Hadjinicolaou, P., Kostopoulou, E., Chenoweth, J., Giannakopoulos,C.,
625   Hannides, C., Lange, M. A., El Maayar, M.,Tanarhte, M., Tyrlis, E., and Xoplaki, E.: Climate
626   change andimpacts in the Eastern Mediterranean and the Middle East, Clim.Chang., 114,
627   667–687, 2012.

628   Lindinger, W., Hansel, A., and Jordan, A.: On-line monitoring of volatile organic compounds
629   at pptv levels by means of proton transfer-reaction mass spectrometry (PTR-MS): Medical
630   applications,food control and environmental research, Int. J. Mass Spectrom., 173(3), 191–
631   241, 1998.

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

635   Martin, R. V., Jacob, D. J., Chance, K., Kurosu, T.P., Palmer, P.I., and Evans, M.J.: Global
636   inventory of nitrogen oxides emissions constrained by space-based observations of NO_2
637   columns, J. Geophys. Res., 108(D17), 4537, doi: 10.1029/2003JD003453, 2003.

638   Parrish, D. D., Kuster, W.C., Shao, M., Yokouchi, Y., Kondo, Y., Goldan, P.D., de Gouw,

639   J.A., Koike, M., and Shirai, T.: Comparison of air pollutant emissions among mega-cities,

640   Atmospheric Environment 43 6435 – 6441, doi:10.1016/j.atmosenv.2009.06.024, 2009.

641   Pozzer, A., Zimmermann, P., Doering, U.M., van Aardenne, J., Tost, H., Dentener, F.,

642   Janssens-Maenhout, G., and Lelieveld, J.: Effects ofbusiness-as-usual anthropogenic

643   emissions on air quality, Atmos. Chem. Phys., 12, 6915–6937, doi:10.5194/acp-12-6915-

644   2012, 2012.

645   Salameh, T., Afif, C., Sauvage, S., Borbon, A., and Locoge, N.: Speciation of Non- Methane

646   Hydrocarbons (NMHC) from anthropogenic sources in Beirut, Lebanon, Environ. Sci.

647   Pollut.R., 21, 10867–10877, doi:10.1007/s11356-014-2978-5, 2014.

648   Salameh, T., Sauvage, S., Afif, C., Borbon, A., Leonardis, T., Brioude, J., Waked, A., and

649   Locoge, N.: Exploring the seasonal NMHC distribution in an urban area of the Middle East

650   during ECOCEM campaigns: very high loadings dominated by local emissions and dynamics,

651   Environ. Chem, 12, 316–328, doi:10.1071/EN14154, 2015.

652   Salameh, T., Sauvage, S., Afif, C., Borbon, A., and Locoge, N.:Source apportionment

653   vs.emissioninventories of non-methane hydrocarbons(NMHC) in an urban area of the

654   MiddleEast: local and global perspectives. Atmos. Chem. Phys., 16, 3595–3607,

655   doi:10.5194/acp-16-3595-2016, 2016.

656   Sauvage, S., Plaisance, H., Locoge, N.,Wroblewski A., Coddeville P., and Galloo,J.C.: Long

657   term measurement and source apportionment ofnon-methane hydrocarbons in three

658   Frenchrural areas. AtmosEnviron 43:2430–2441, 2009.

659   Schultz, M., Rast, S., van het Bolscher, M., Pulles, T., Pereira, J., Spessa, A., Dalsøren, S.,

660   van Nojie, T., andSzopa, S.: REanalysis of the TROpospheric chemical composition over the

661   past 40 years, A long-termglobal modeling study of tropospheric chemistry funded under the

662   5th EU framework programme. Tech.rep., EU-Contract No. EVK2-CT-2002-00170, 2007.

663   Simpson, I.J., Aburizaiza, O.S., Siddique, A., Barletta, B.,Blake, N.J., Gartner, A.,Khwaja, H.,

664   Meinardi, S.,Zeb, J., and Blake, D.R.: Air Quality in Mecca and Surrounding Holy Places in

665   Saudi ArabiaDuring Hajj: Initial Survey. Environ. Sci. Technol. 48, 8529−8537,

666   dx.doi.org/10.1021/es5017476, 2014.

667   Uherek, E., Halenka, T., Borken-Kleefeld, J., Balkanski, Y., Berntsen, T., Borrego, C., Gauss,

668   M., Hoor , P., Juda-Rezler, K., Lelieveld, J., Melas, D., Rypdal, K., Schmid, S.: Transport

669   impacts on atmosphere and climate: Land transport, Atmospheric Environment 44, 4772-

670   4816, 2010.

671   Van Vuuren, D.P., Edmonds, J., Kainuma, M.,Riahi, K., Thomson, A., Hibbard, T., Hurtt,

672   G.C., Kram, T.,Krey, V., Lamarque, J.F.,Masui, T.,Meinshausen,M., Nakicenovic, N., Smith,

673   S.J., and Rose, S.K.:The Representative ConcentrationPathways: an overview, Climatic

674   Change, 109, 5-31, doi:10.1007/s10584-011-0148-z, 2011.

675   Von Schneidemesser, E., Monks, P.S., Gros, V., Gauduin, J., and Sanchez O. :How important

676   is biogenic isoprene in an urban environment? A study in London and Paris, Geophysical

677   Research Letters, Vol. 38, L19804, doi: 10.1029/2011GL048647, 2011.

678   Waked, A., and Afif, C.: Emissions of air pollutants from road transport in Lebanon and other

679   countries in the Middle East region, Atmos Environ 61, 446 – 452, 2012.

680   Waked, A., Afif, C., and Seigneur, C.: An atmospheric emission inventory of anthropogenic

681   and biogenic sources for Lebanon, Atmospheric Environment 50, 88-96, 2012.

682   Waked, A., Seigneur C., Couvidat F., Kim Y., Sartelet K., Afif C., Borbon A., Formenti P.,

683   and Sauvage, S.: Modeling air pollution in Lebanon: evaluation at a suburban site in Beirut

684   during summer, Atmos Chem Phys 13, 5873 – 5886, 2013a.

685   Wang, M., Shao, M., Chen, W., Yuan, B., Lu, S., Zhang, Q., Zeng, L., and Wang, Q.: A

686   temporally and spatially resolved validation of emission inventories by measurements of

687   ambient volatile organic compounds in Beijing, China, Atmos. Chem. Phys., 14, 5871–5891,

688   doi:10.5194/acp-14-5871, 2014.

689   Warneke, C., McKeen, S. A. , de Gouw, J.A., Goldan, P.D., Kuster, W.C., Holloway, J.S.,

690   Williams, E.J., Lerner, B.M., Parrish, D.D., Trainer, M., Fehsenfeld, F.C., Kato, S., Atlas,

691   E.L., Baker, A., and Blake, D.R. :Determination of urban volatile organic compound emission

692   ratios and comparison with an emissions database, J. Geophys. Res., 112, D10S47,

693   doi:10.1029/2006JD007930, 2007.

694   Warneke, C., de Gouw, J. A., Holloway, J. S.,Peischl, J., Ryerson, T. B., Atlas, E., Blake, D.,

695   Trainer, M., and Parrish, D. D.: Multiyear trends in volatile organic compounds in Los

696 Angeles, California: Five decades of decreasing emissions, J. Geophys. Res., 117,
697 D00V17,doi:10.1029/2012JD017899, 2012.

698 Watson, J.G., Chow, J.C., Fujita, E.M.: Review of volatile organic compound source
699 apportionment by chemical mass balance. Atmos Environ 35, 567–1584, 2001.

700 Zanis, P., Hadjinicolaou, P., Pozzer, A., Tyrlis, E., Dafka, S., Mihalopoulos, N., and
701 Lelieveld, J.: Summertime free-tropospheric ozone pool over the
702 easternMediterranean/Middle East, Atmos. Chem. Phys., 14, 115–132, 10.5194/acp-14-115-
703 2014, 2014.

Table 1: Measurements during ECOCEM Campaigns.

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

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

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

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		
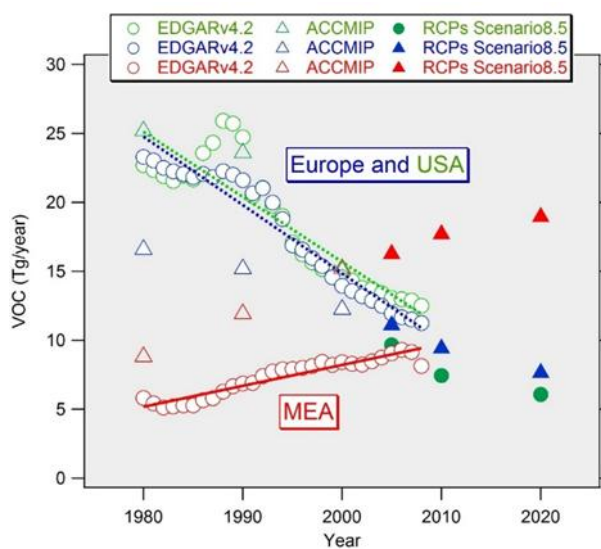
Figure 1: Evolution of the NMVOC anthropogenic total emissions (Tg/year) in the MEA, USA and Europe (OECD Europe and Eastern Europe) from 1980 to 2020 from reference global emission inventories (ECCAD database).
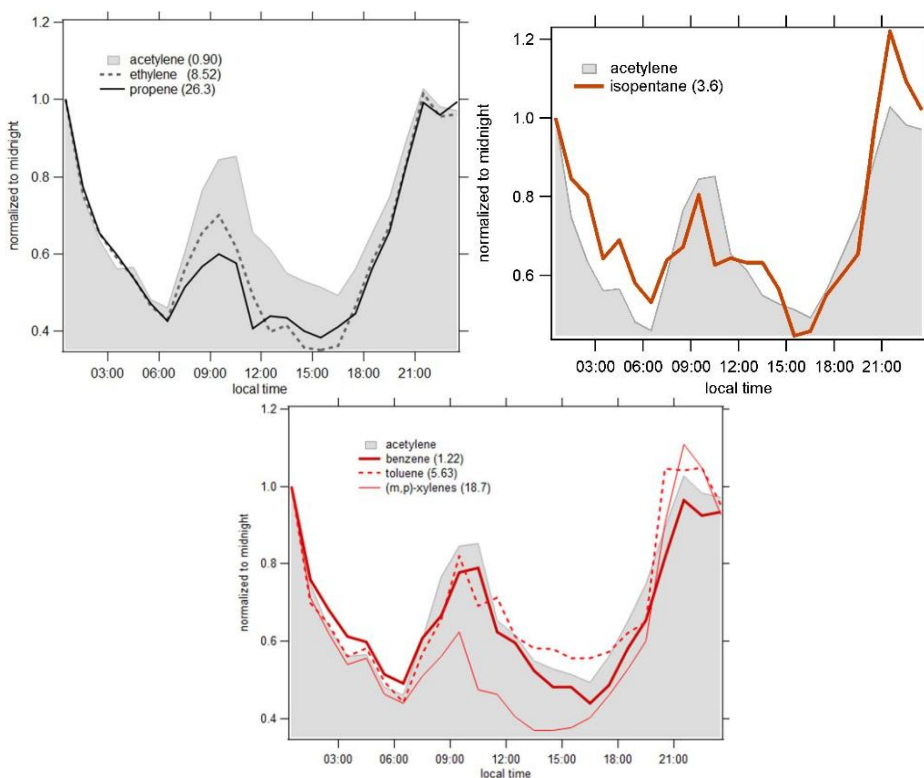
Figure 2: Normalized diurnal profiles of the mixing ratios of selected species to midnight values in summer. Numbers in parentheses are the rate coefficient with OH $\times 10^{-12} cm^3$ molecule^{-1} s^{-1}(Atkinson and Arey2003; Atkinson 2007).
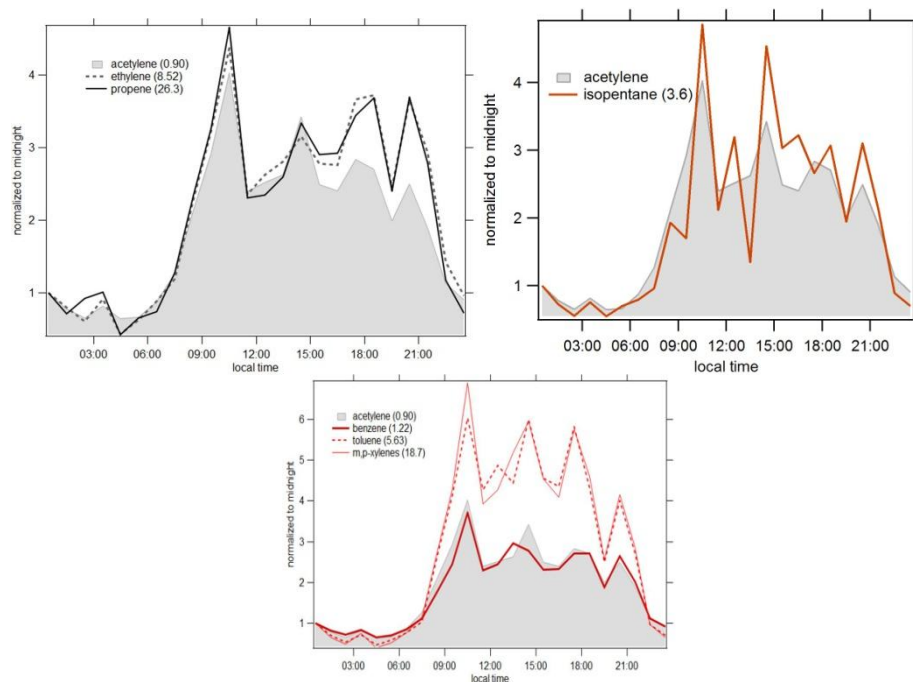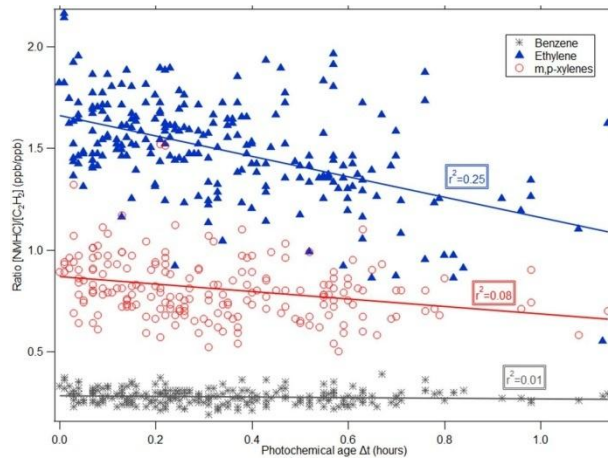

Figure 3: Normalized diurnal profiles of the mixing ratios of selected species to midnight values in winter. Numbers in parentheses are the rate coefficient with OH $\times 10^{-12} cm^3$ molecule^{-1} s^{-1}(Atkinson and Arey2003; Atkinson 2007).

Figure 4: Measured ratios of benzene/acetylene, m,p-xylenes/acetylene, and ethylene/acetylene as a function of photochemical age (hours).
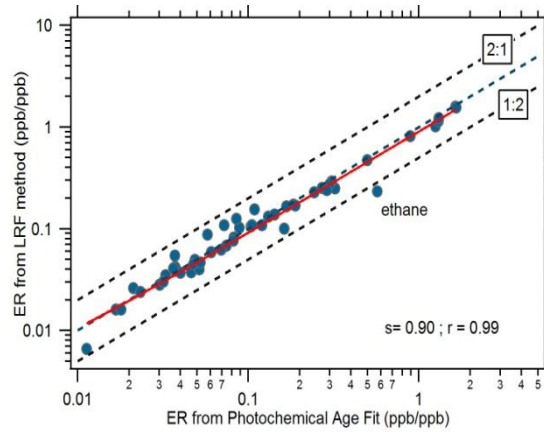
Figure 5: Comparison of the emission ratio (ER) estimated relative to acetylene by the nighttime linear regression fit and the photochemical age fit in summer.
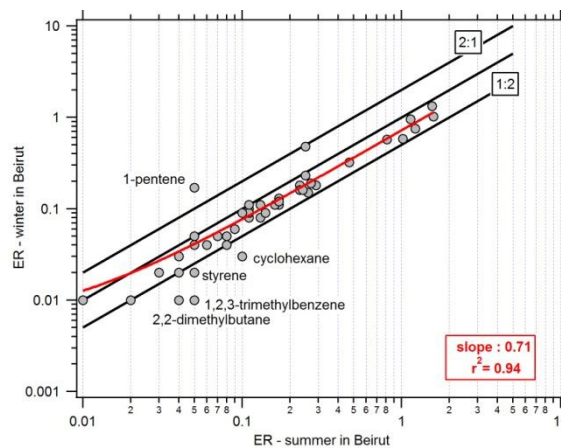
Figure 6: Comparison of summertime and wintertime emission ratios vs. acetylene in Beirut.
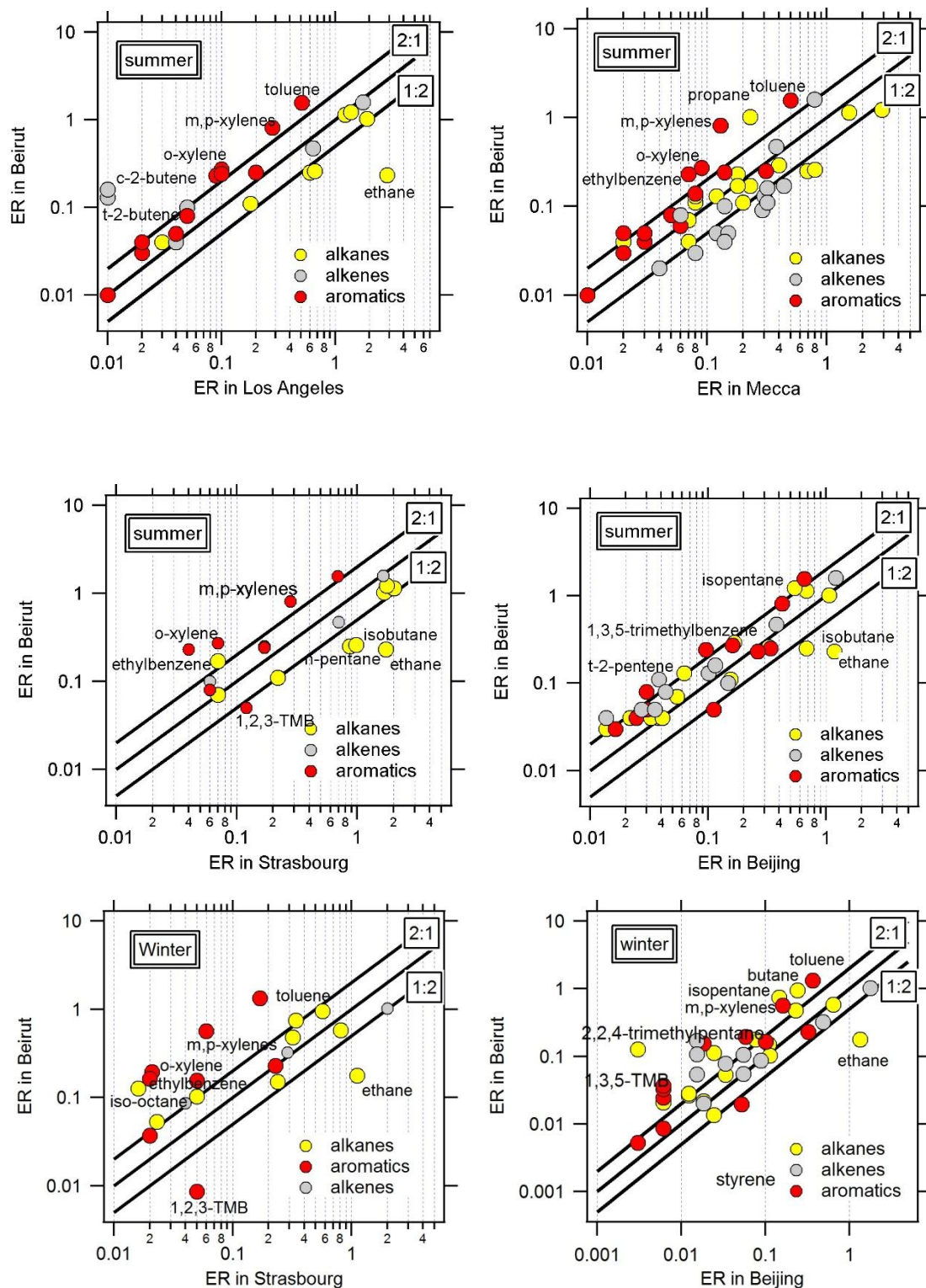
Figure 7: Comparisons of NMVOC emission ratios determined at the Beirut sub-urban site with those for Los Angeles, US (Borbon et al., 2013); Strasbourg, France (Boynard et al., 2014); Beijing, China (wang et al., 2014): and Mecca, Saudi Arabia (Simpson et al., 2014). (TMB: Trimethylbenzene)
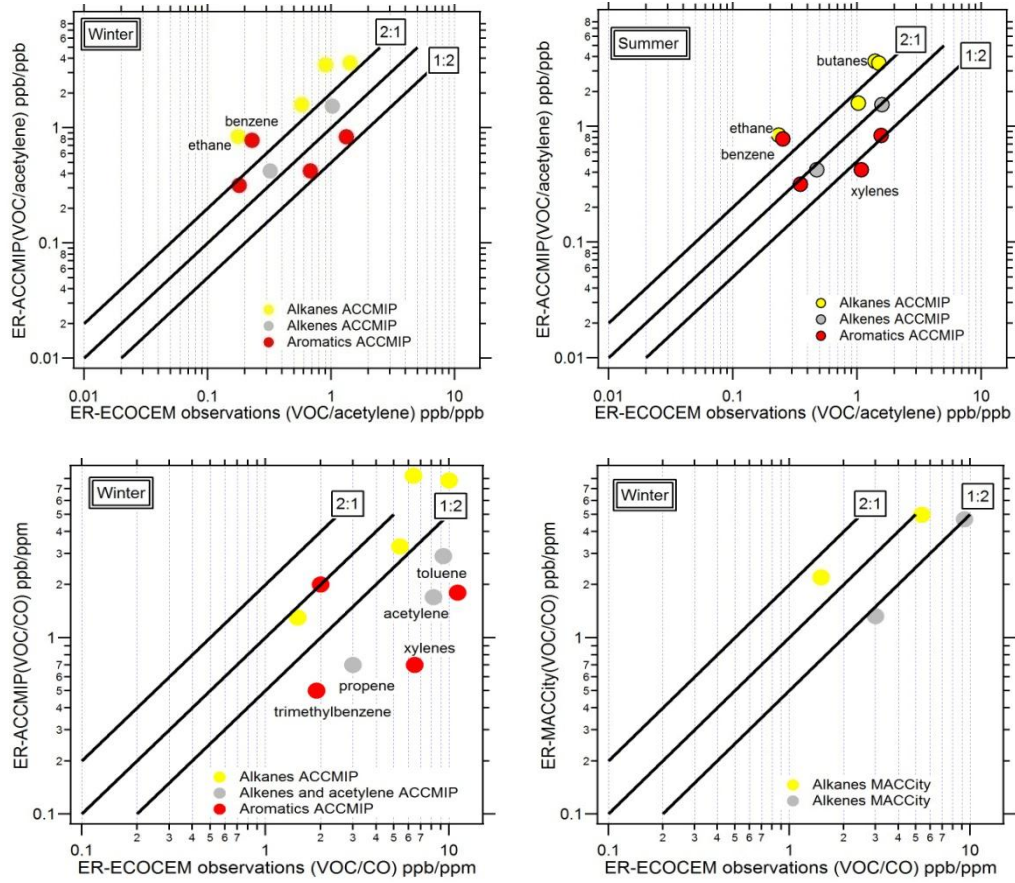
Figure 8: Comparison of the emission ratios from ACCMIP and MACCity to the measured ones by LRF method, in summer and in winter, relative to CO and acetylene, for all the anthropogenic sectors.
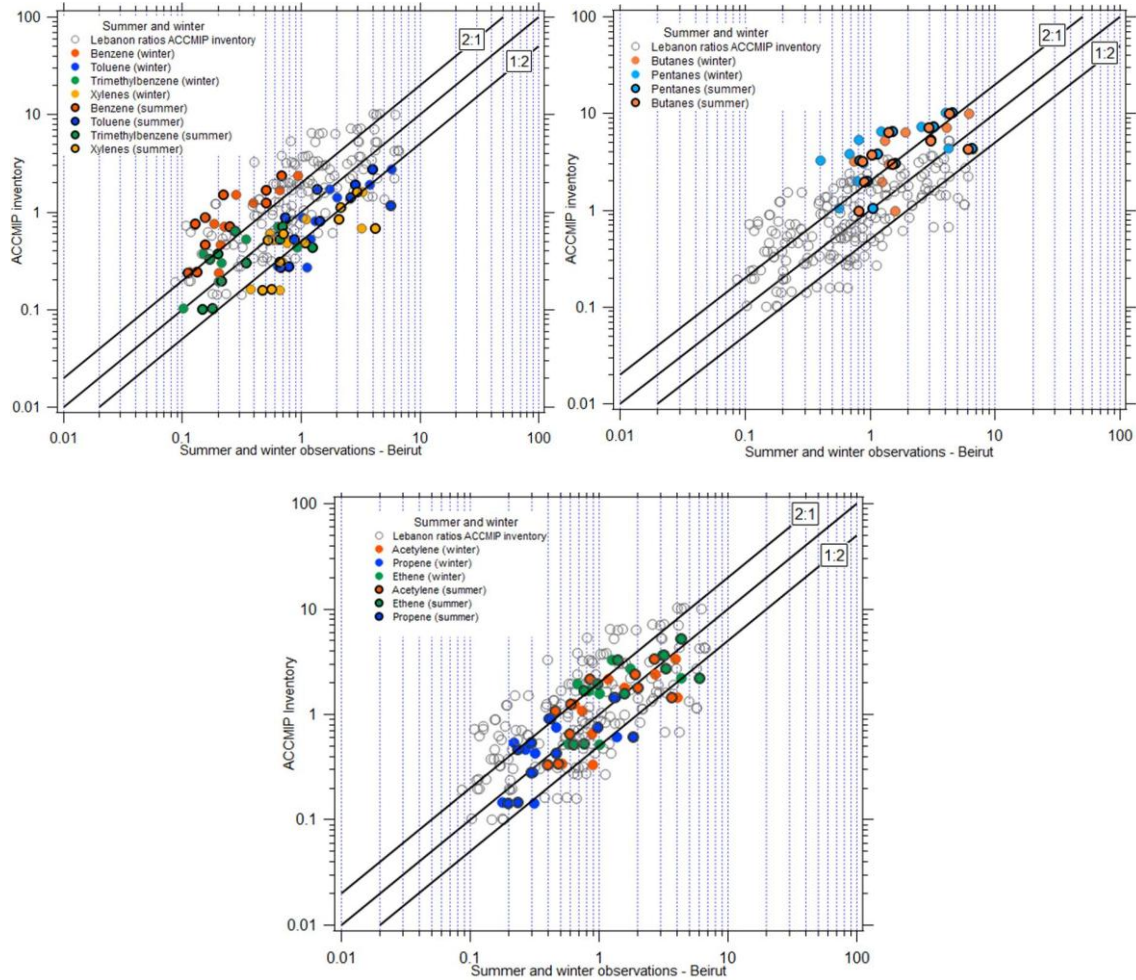
Figure 9: Comparison of the emission ratios of NMVOC vs. NMVOCi from ACCMIP to the measured ones, in summer and in winter, for all the anthropogenic sectors, for all data of all compound classes (in grey dots) and for a given NMVOC (colored dots).
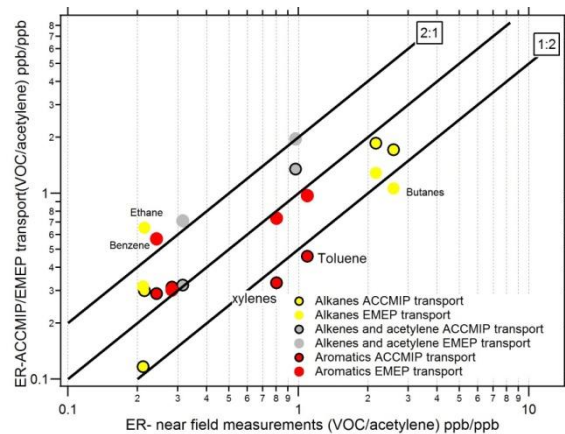

Figure 10: Comparison of the emission ratios relative to acetylene, from ACCMIP and EMEP emission inventories for road transport to the ER from road transport by near-field measurements.
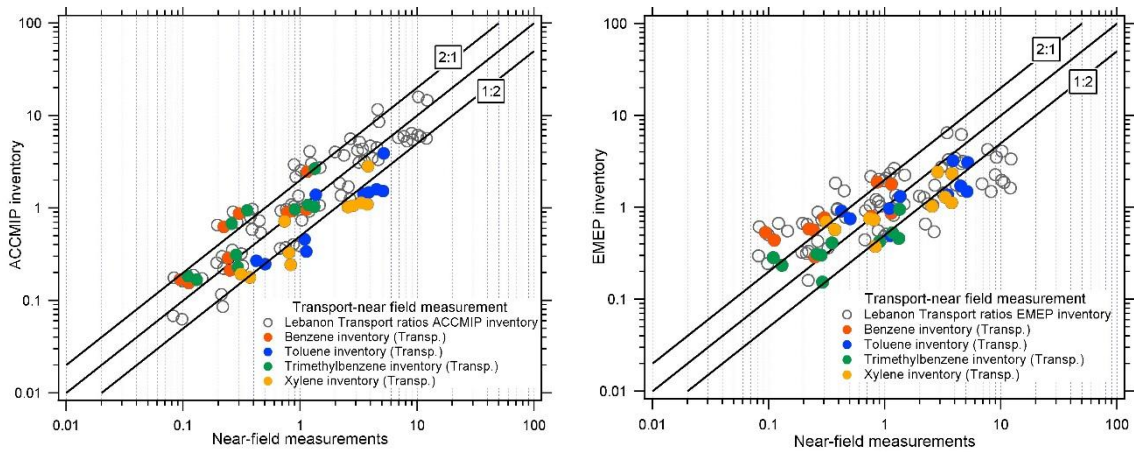
Figure 11: Comparison of the emission ratios of NMVOC vs. NMVOCi from ACCMIP and EMEP to the ER from near-field measurements for the road transport sector, for all data (in grey dots) and for a given NMVOC (colored dots).
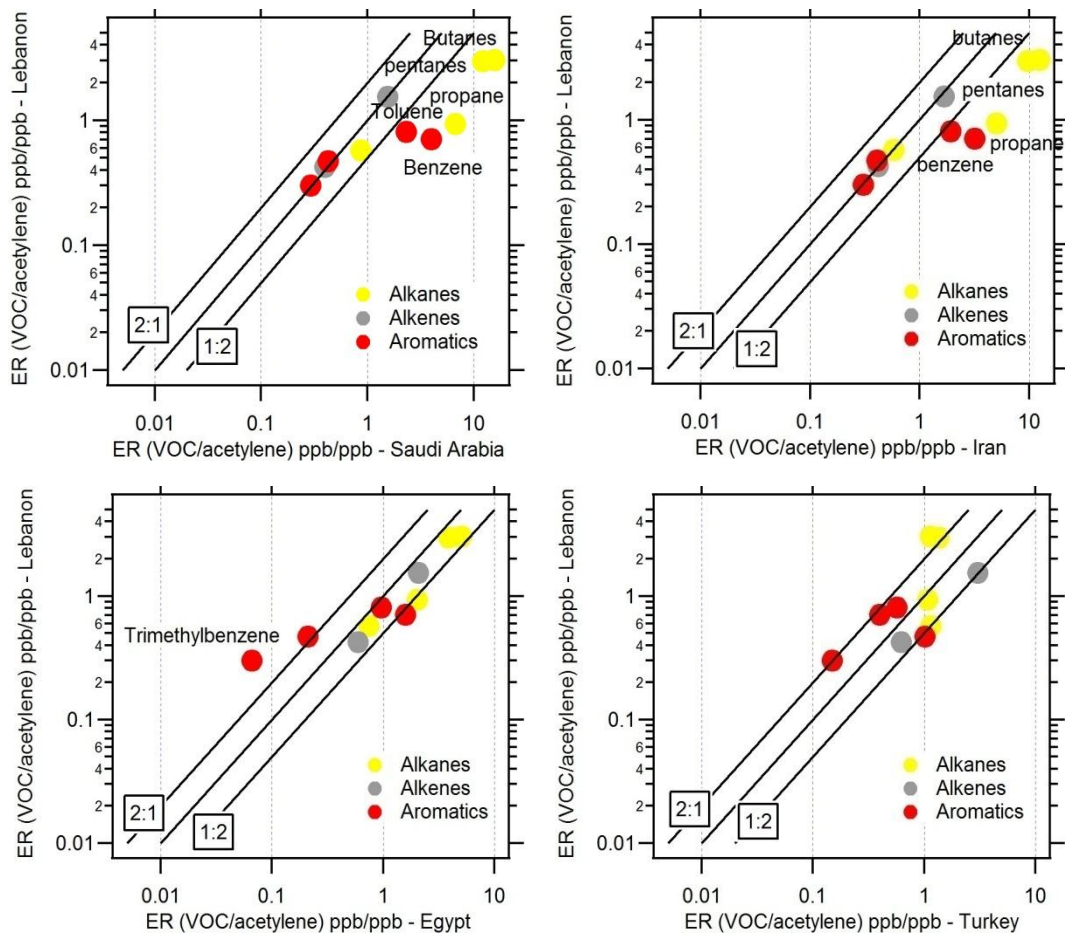

Figure 12: Comparison of the emission ratios from ACCMIP relative to acetylene for all the anthropogenic sectors for five Middle Eastern countries (Lebanon, Egypt, Turkey, Iran, and Saudi Arabia).