Research Paper

Exploring the seasonal NMHC distribution in an urban area of the Middle East during ECOCEM campaigns: very high loadings dominated by local emissions and dynamics

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Environmental context. Non-methane hydrocarbons play an important role in the formation of photochemical oxidants such as ozone. We investigate factors controlling the distribution of non-methane hydrocarbons in an urban area of the Middle East. The study highlights the importance of local emissions and atmospheric dynamics, and the limited effect of photochemistry at the measurement site.

Abstract. Measurements of over 70 C_2-C_{16} non-methane hydrocarbons (NMHCs) were conducted in suburban Beirut (1.3 million inhabitants) in summer 2011 and winter 2012 during the Emission and Chemistry of Organic Carbon in the East Mediterranean (ECOCEM) field campaign. The levels of NMHCs observed exceeded by a factor of two in total volume the levels found in northern mid-latitude megacities (Paris and Los Angeles), especially for the unburned fossil fuel fraction. Regardless of the season, the major compounds, explaining 50 % of the concentrations, were toluene, isopentane, butane, *m*,*p*-xylenes, propane and ethylene, emitted by mobile traffic and gasoline evaporation sources. Most NMHCs show a distinct seasonal cycle, with a summer maximum and a winter minimum, unlike seasonal cycles usually observed in the northern mid-latitude urban areas. We show that NMHC distribution is mainly driven by strong local emissions and local atmospheric dynamics, with no clear evidence of photochemical removal in summer or influence from long-range transport.

Introduction

The Middle East region (MEA) is a hot-spot of photochemical smog as a result of its unique location, an enclosed area, with strong local anthropogenic emissions and highly favourable climatic conditions for photochemistry.[1] Therefore, both ozone and aerosol air-quality limits are often exceeded, in particular during summer.[2] In Lebanon, a developing country in the MEA, located in western Asia on the eastern shore of the Mediterranean Sea, available information and data on air quality are limited to only a few pollutants, and the results show that the concentrations of air pollutants measured exceed the World Health Organization (WHO) recommended values.[3] For instance, Afif et al.[4] reported an annual average concentration of nitrogen dioxide (NO_2) in Beirut of 67 µg m^{-3}, which is higher than the WHO annual recommended value of 40 µg m^{-3}.[3] In addition, high levels of particulate matter, PM_{10} and $PM_{2.5}$, were obtained with annual concentrations of 64 and 20 µg m^{-3} respectively,[5] exceeding WHO guideline values of 20 and 10 µg m^{-3}. As a result, the annual cost of environmental degradation caused by urban air pollution in Lebanon is estimated to be 1.02 % of the annual gross domestic product (GDP).[6]

Non-methane hydrocarbons (NMHCs) present a robust area for research, because they play an important role in the formation of photochemical oxidants such as ozone and
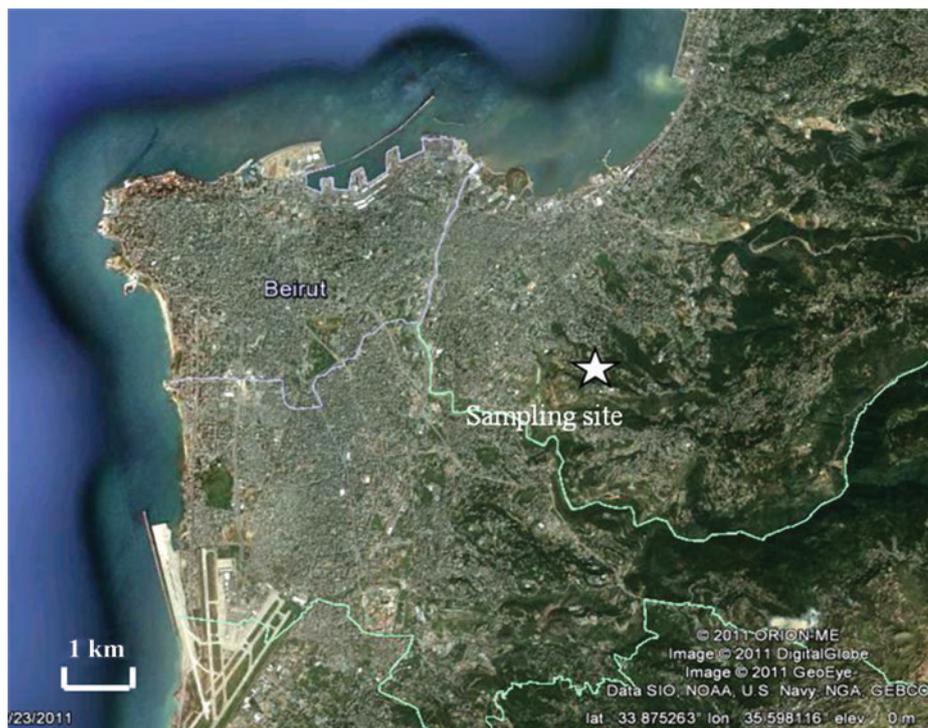
Fig. 1. Sampling site in the eastern suburbs of the city of Beirut.

peroxyacetylnitrate (PAN) in urban areas. NMHCs, particularly intermediate-volatility organic compounds (IVOCs), are also involved in the formation of secondary organic aerosols (SOA).[7,8] In urban areas, NMHCs are typically considered to be the limiting factor of ozone production.[9] Therefore, control strategies for mitigation of ozone levels should focus on local NMHCs emission reduction. Moreover, some species are carcinogenic and mutagenic.[10] Apart from these characteristics, NMHCs include important tracers that can be used to determine air pollutant sources.

To date, there is a paucity of data regarding the NMHCs in the MEA and a lack of ground-based measurements, leading to insufficient evaluation of air pollution in this region. For all those reasons, Lebanon represents a good case study for investigating NMHCs for the first time.

In this context, the main purpose of the present work is to provide useful information on NMHC distribution and the factors that control the seasonal and diel variations of NMHC levels in Lebanon including emission sources, chemical processes and dispersion conditions related to meteorological conditions within the planetary boundary layer (advective and convective transport on a regional or long-range scale).

The present study is based on NMHC observations obtained from two intensive field measurement campaigns within the frame of the Emission and Chemistry of Organic Carbon in the East Mediterranean, Beirut (ECOCEM–Beirut) project conducted during summer 2011 (from 2 to 18 July) and winter 2012 (from 28 January to 12 February).

Experimental procedures

Site description

The measurements were taken on the roof of the Faculty of Sciences building of Saint Joseph University ($33°87'$N, $35°56'$E) (Fig. 1), located in the eastern suburbs of the city of Beirut (6 km south-east of Beirut downtown) at an altitude of 230 m above sea level in summer from 2 to 18 July 2011 and from 28 January to 12 February 2012 in winter. The site is surrounded by a forested pine area and residential premises. Beirut International Airport is located 8 km south-west of the site. The site is appropriately located in order to receive air masses coming from the Greater Beirut Area, which includes the city of Beirut and close suburbs.

Material and methods

NMHCs were continuously analysed by on-line thermal desorption gas chromatography with a flame ionisation detector (TD-GC-FID) provided by Perkin–Elmer Life and Analytical Sciences (Villebon Sur Yvette, France) described elsewhere.[11] The on-line measurements were performed hourly, covering 30 min of ambient air sampling. Approximately 67 NMHCs from C_2 to C_9 comprising alkanes (29), alkenes (19), alkynes (2) and aromatics (17) were identified and quantified. The detection limits (DLs) were calculated based on the signal-to-noise ratio, equal to 3, which is the ratio of the compound signal to the noise measured on a blank. The DLs were ~40 pptv (parts per trillion by volume) for the targeted compounds except for ethane and ethene; both were 90 pptv. A certified National Physical Laboratory (NPL) standard NMHC mixture (~4 ppbv, parts per billion by volume) was used to determine and check the stability of the GC carbon response during both measurement periods.

Off-line measurements of C_5 to C_{16} NMHCs were performed on cartridge samples. Samples were collected onto multibed sorbent cartridges of Carbopack B & C (Sigma–Aldrich Chimie S.a.r.l., St Quentin Fallavier, France), at a 200 mL min^{-1} flow rate for 2 h using the automatic sampler SyPAC (TERA-Environnement, Crolles, France). Samples were first thermodesorbed and then analysed by TD-GC-FID-mass spectrometry (MS). The sampling method is detailed elsewhere.[12] The compounds measured by both instruments, namely alkanes and aromatics, were used to cross-check the quality of the results during the campaigns. The results are highly satisfactory;

Table 1. Mean, median, percentage of values below the detection limit (<DL), maximum and standard deviation of the non-methane hydrocarbon (NMHC) concentrations measured during the summer (n = 298 samples) and winter (n = 179 samples) campaigns (μg m^{-3}) compared with other sites in the Middle East region (MEA)

nd, not detected; TMB, trimethylbenzene

| | Summer | | | | | Winter | | | | | Cairo, Egypt[13] (summer) | Background, Egypt[13] (summer) | Suburban Ankara, Turkey[14] (January 2008–June 2008) |
	Mean	Median	Percentage of values <DL	Maximum	Standard deviation	Mean	Median	Percentage of values <DL	Maximum	Standard deviation	Mean	Mean	Mean
Ethane	1.94	1.92	0	4.99	0.52	3.48	3.55	0	5.17	0.76			
Ethylene	3.86	3.58	0	10.47	2.10	2.40	1.60	0	13.43	2.29			
Propane	4.55	3.67	0	16.09	3.21	5.32	4.61	0	17.05	2.93			
Propene	1.73	1.65	0	5.21	0.95	0.99	0.60	11	6.84	1.09			
Isobutane	2.10	1.74	0	12.88	1.70	4.53	2.17	0	47.08	7.24			
Acetylene	2.43	2.18	0	9.79	1.36	2.31	1.57	0	11.11	1.97			
Butane	8.37	6.15	0	68.29	8.55	8.59	3.93	0	89.75	13.72			
T2-Butene	0.67	0.47	1	6.48	0.64	0.51	0.23	14	4.20	0.69			
1-Butene	1.03	0.89	0	4.21	0.48	0.67	0.38	0	4.88	0.78			
Isobutene	1.09	0.96	0	4.93	0.65	0.76	0.40	0	4.99	0.87			
2,2-Dimethylpropane	0.08	0.06	80	0.45	0.05	0.08	0.06	83	0.47	0.06			
C$_2$-Butene	0.61	0.42	0	6.22	0.62	0.42	0.19	18	3.83	0.60			
Isopentane	12.09	8.30	0	136.03	15.32	6.95	2.50	0	98.73	12.70			
Pentane	2.39	1.80	0	19.63	2.35	1.46	0.76	0	16.31	2.03			
Propyne	0.16	0.15	25	0.65	0.12	0.14	0.09	37	0.75	0.14			
1,3-Butadiene	0.39	0.36	0	1.69	0.23	0.26	0.16	18	1.83	0.26			
3-Methyl-1-butene	0.23	0.18	16	2.69	0.26	0.17	0.06	55	1.91	0.25			
T2-Pentene	0.59	0.41	5	6.43	0.63	0.55	0.23	29	5.65	0.80			
2-Methyl-2-butene	0.59	0.38	8	7.57	0.68	0.06	0.06	100	0.07	0.00			
1-Pentene	0.37	0.26	36	3.65	0.46	0.90	0.39	17	8.35	1.29			
2-Methyl-1-butene	0.56	0.38	4	6.72	0.64	0.35	0.15	34	3.79	0.53			
C$_2$-Pentene	0.32	0.23	13	3.57	0.34	0.30	0.12	40	2.87	0.41			
Isoprene	0.62	0.45	6	2.21	0.48	0.13	0.06	51	0.88	0.12			
2,2-Dimethylbutane	0.89	0.70	2	5.85	0.81	0.22	0.07	64	1.49	0.27			
Cyclopentene	0.09	0.06	71	0.74	0.08	0.07	0.06	88	0.49	0.05			
2,3-Dimethylbutane and cyclopentane	0.88	0.68	2	7.68	0.85	0.45	0.17	40	4.24	0.67			
2-Methylpentane	2.91	2.41	0	19.28	2.40	1.53	0.73	1	13.41	2.04			
3-Methylpentane	1.76	1.47	0	10.84	1.40	0.95	0.45	9	7.93	1.23			
1-Hexene	0.14	0.07	79	1.33	0.17	0.12	0.07	83	0.86	0.13			
Hexane	1.03	0.90	0	6.68	0.80	0.60	0.34	9	4.08	0.75	123.53	8.22	
2,2-Dimethylpentane	0.09	0.08	96	0.46	0.04	0.09	0.08	96	0.21	0.01			
Methylcyclopentane	0.93	0.83	1	3.84	0.65	0.55	0.18	27	4.69	0.79			
2,2,3-Trimethylbutane	0.08	0.08	100	0.08	0.00	0.08	0.08	99	0.16	0.01			
Methylcyclopentene	0.09	0.07	83	0.41	0.07	0.09	0.07	83	0.70	0.07			

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(Continued)

Table 1. (Continued)

	Summer					Winter					Cairo, Egypt[13] (summer)	Background, Egypt[13] (summer)	Suburban Ankara, Turkey[14] (January 2008–June 2008)
	Mean	Median	Percentage of values <DL	Maximum	Standard deviation	Mean	Median	Percentage of values <DL	Maximum	Standard deviation	Mean	Mean	Mean
Benzene	2.00	1.86	0	7.55	1.06	1.72	1.19	0	7.83	1.40	87.20	5.81	2.18
3,3-Dimethylpentane	0.09	0.08	98	0.25	0.01	0.08	0.08	99	0.13	0.00			
Cyclohexane	0.28	0.22	22	1.51	0.22	0.13	0.07	68	0.71	0.12			
2-Methylhexane	1.01	0.92	2	4.72	0.66	0.54	0.23	25	3.79	0.68			0.24
2,3-Dimethylpentane	0.36	0.33	14	1.84	0.25	0.20	0.08	58	1.30	0.22			
3-Methylhexane	1.25	1.13	0	5.43	0.68	0.68	0.40	7	4.04	0.71			0.42
Isooctane	1.83	1.57	0	8.57	1.21	0.98	0.45	16	6.32	1.25			0.09
Heptane	0.73	0.67	0	3.51	0.43	0.40	0.25	19	2.17	0.44	70.61	5.26	0.09
Methylcyclohexane	0.33	0.29	14	1.75	0.24	0.20	0.08	51	1.14	0.22			
2,3,4-Trimethylpentane	0.74	0.67	0	2.86	0.39	0.32	0.13	42	1.91	0.36			
Toluene	14.60	13.25	0	62.00	8.93	8.09	3.95	0	49.98	9.98	213.80	7.48	7.89
3-Methylheptane	0.30	0.29	15	2.14	0.21	0.19	0.10	57	1.66	0.22			
Octane	0.40	0.38	7	1.48	0.23	0.22	0.12	45	1.14	0.21			0.15
Tetrachloroethene	0.75	0.14	69	19.07	2.25	nd	nd	nd	nd	nd			
Ethylbenzene	2.29	2.03	0	9.33	1.36	1.14	0.56	9	6.83	1.39	43.30	2.51	0.85
m,p-Xylenes	7.89	7.06	0	32.60	4.86	3.87	1.87	0	25.25	4.80	140.80	4.11	2.21
Styrene	0.34	0.30	23	1.65	0.26	0.17	0.09	65	1.28	0.18			0.41
o-Xylene	2.78	2.57	0	9.16	1.53	1.35	0.67	9	8.65	1.63	73.77	2.40	0.41
Nonane	0.54	0.48	2	2.14	0.30	0.26	0.11	51	1.56	0.29			0.17
Isopropylbenzene	0.11	0.10	89	0.45	0.05	0.11	0.10	91	0.39	0.04			0.06
Propylbenzene	0.31	0.30	26	1.30	0.21	0.19	0.10	66	1.19	0.21			0.04
m-Ethyltoluene	1.39	1.30	1	5.06	0.83	0.63	0.24	31	4.88	0.86			0.22
p-Ethyltoluene	0.60	0.55	17	2.40	0.38	0.25	0.10	72	1.90	0.32			0.31
1,3,5-Trimethylbenzene	0.69	0.65	13	2.72	0.46	0.31	0.10	50	1.73	0.36	30.61	0.95	0.17
o-Ethyltoluene	0.32	0.25	26	1.35	0.24	0.23	0.10	65	1.79	0.28			0.13
1,2,4-TMB and decane	2.93	2.70	0	10.52	1.56	1.38	0.76	10	10.38	1.66	64.54	1.69	0.49
Isobutylbenzene	0.11	0.11	100	0.11	0.00	0.11	0.11	100	0.11	0.00			0.10
Sec-butylbenzene	0.11	0.11	100	0.11	0.00	0.11	0.11	100	0.11	0.00			
1,2,3-Trimethylbenzene	0.27	0.10	72	1.45	0.32	0.19	0.10	70	1.91	0.22			
Butylbenzene	0.14	0.11	82	0.56	0.08	0.14	0.11	81	0.82	0.09			
Decane	0.47	0.44	0	1.79	0.30	0.33	0.20	1	1.85	0.31			0.22
Undecane	0.07	0.05	9	0.46	0.08	0.30	0.22	1	1.50	0.25			
Dodecane	0.06	0.04	6	0.45	0.07	0.23	0.16	2	1.02	0.18			
Tridecane	0.06	0.04	6	0.73	0.09	0.26	0.21	16	1.05	0.19			
Tetradecane	0.06	0.05	7	0.30	0.05	0.19	0.18	29	1.07	0.19			
Pentadecane	0.06	0.05	11	0.53	0.07	nd	nd	nd	nd	nd			
Hexadecane	0.09	0.03	13	1.01	0.17	nd	nd	nd	nd	nd			

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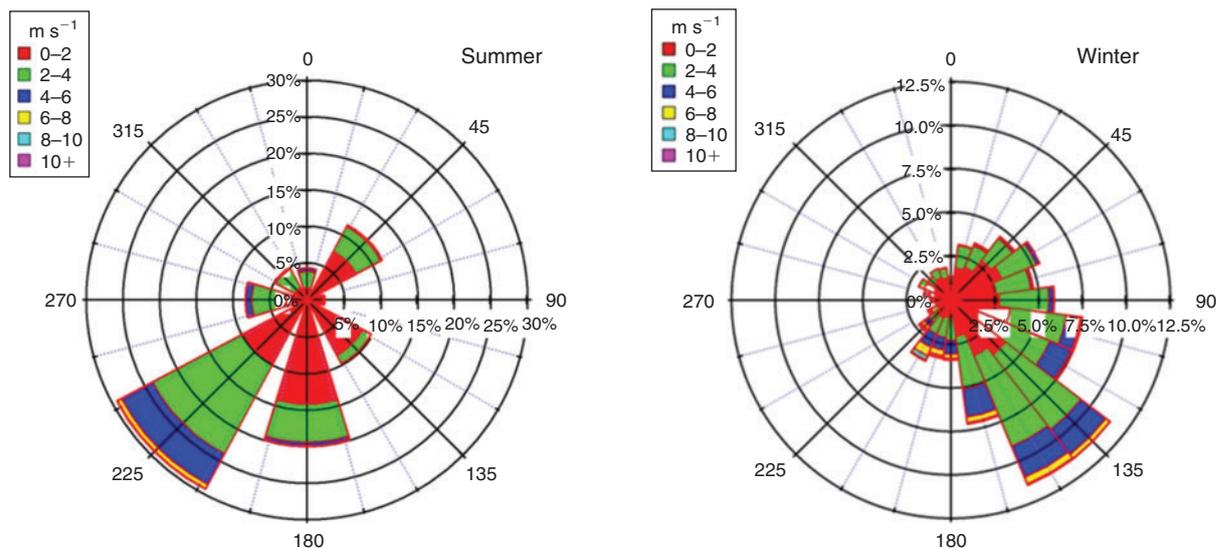
Fig. 2. Wind roses during summer and winter campaigns.

correlation coefficients R were up to 0.90 and slopes are close to 1 for most of the compounds. The off-line measurement results regarding the alkanes C_{10} to C_{16}, as well as the on-line measurements (C_2–C_9), are reported in the current work (Table 1).

Additional measurements of trace gases concentrations including CO, NO_x and O_3 were provided on a 1-min basis by specific analysers. Basic meteorological parameters (wind speed and direction, temperature, relative humidity and atmospheric pressure) were measured on a 1-min basis for the duration of the campaigns.

Results and discussion

Meteorological conditions

Lebanon is characterised by a narrow coastal strip in the western part and is divided by the Lebanon Mountains, which run through the centre of the country approximately NNE to SSW. The coastal region has a Mediterranean climate with land–sea breeze circulation. During the summer measurement campaign, the temperature ranged from 20 to 29 °C with an average of 25 °C ± 2. The average wind speed was low, 2 m s^{-1}, with maximum wind speeds (4–10 m s^{-1}) recorded during the days under south-western wind regimes (Fig. 2) and under northern wind regimes on 3, 7, 8 and 9 July. At night, the wind direction was mostly north-easterly. During the winter measurement campaign, the temperature stayed mild, ranging from 7 to 22 °C with an average of 13 °C ± 2. The average wind speed was still low at 2 m s^{-1} and the wind direction was mostly south-easterly and easterly (Fig. 2). During the winter campaign, periods of heavy rain occurred on 28 to 31 January and 7 to 11 February.

Strong local emissions

High loadings of NMHCs compared with northern mid-latitude megacities

The results of NMHC measurements in the summer and winter seasons are reported in Table 1, including the mean concentrations, median and maximum values, standard deviation and the percentage of values below the detection limit (% < DL). For statistical calculations, data below the DL were replaced by DL/2. The general case for the median/mean ratio of NMHC ambient concentrations is ratios near 1 in summer and below 1 in winter, especially for >C_4 alkanes, C_4–C_5 alkenes
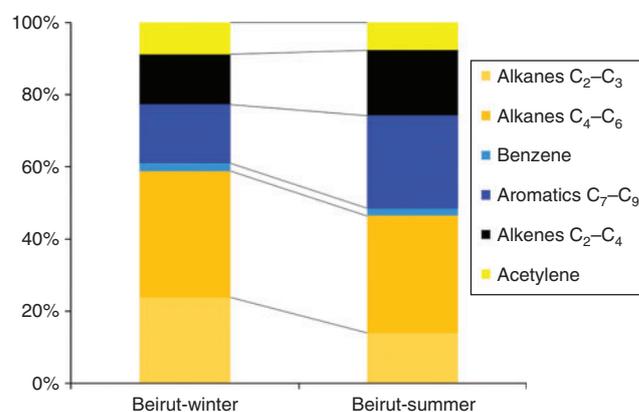
Fig. 3. Non-methane hydrocarbon (NMHC) chemical compositions in volume percentage in Beirut – in winter and in summer.

and aromatics. A median/mean ratio smaller than 1 implies a mean more distant from the median due mainly to high concentrations measured with a low frequency. We also report the mean concentrations of some NMHCs measured in the MEA, specifically in Egypt and in Turkey.[13,14] The concentrations of anthropogenic NMHCs in the Greater Beirut Area with a high population density, compared with Ankara, reaching 21 938 persons km^{-2} in the city of Beirut,[15] are higher than those in suburban Ankara, lower than the levels measured in a background site in Egypt and far lower than those obtained in the most commercial and heaviest-traffic area of greater Cairo because the latter is strongly affected by heavy traffic.

Alkanes followed by aromatics account for 46 and 28 % in summer respectively of the total volume of the measured NMHCs (Fig. 3. In winter, alkanes account for 59 % and aromatics 18 %. Acetylene makes the same contribution in summer and winter of 8–9 %. C_2–C_4 alkenes account for 18 and 14 % in summer and winter respectively. Long-lived alkanes species (ethane and propane) exhibit an enrichment in winter due to the use, among others, of LPG (liquefied petroleum gas) for domestic heating. Conversely, in summer, enrichment is observed for C_7–C_9 aromatics coming mainly from road transport and gasoline evaporation.
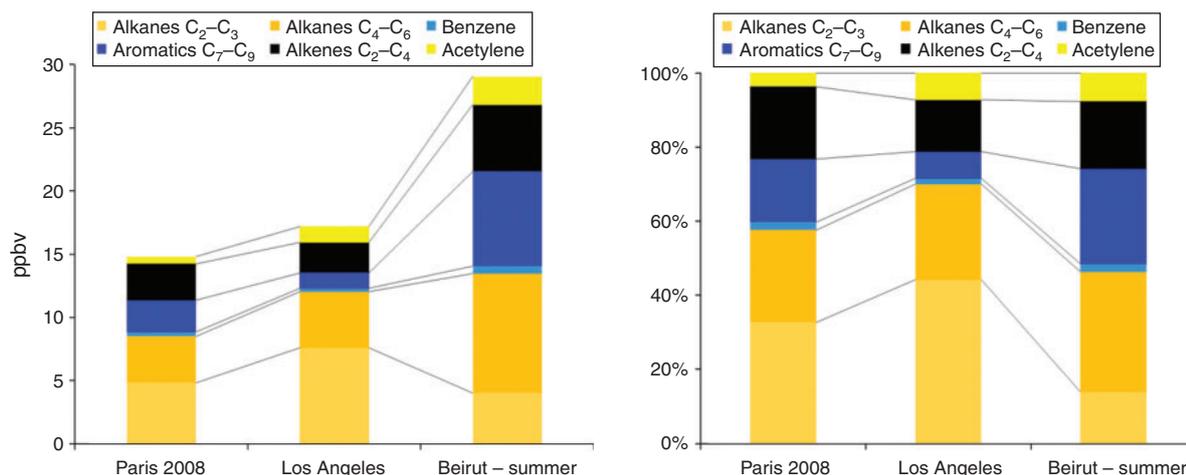
Fig. 4. Non-methane hydrocarbon (NMHC) chemical compositions in parts per billion by volume (ppbv) and in percentage volume in Paris – summer 2008, Los Angeles – spring 2010 and in Beirut – summer 2011.

Fig. 4 shows a comparison of the NMHCs composition in Beirut in summer and in the northern mid-latitude megacities of Paris in summer 2008 (AIRPARIF, Association Interdépartementale pour la gestion du Réseau de mesure de la Pollution Atmosphérique et d'alerte en Région d'Ile-de-France) and Los Angeles in spring 2010. Surprisingly, the NMHC levels in Beirut exceed the levels of northern mid-latitude megacities by a factor of two in total volume. In detail, Beirut exhibits the highest loadings of the C_7–C_9 aromatics and the C_4–C_6 alkanes despite its small surface area and low population (1 300 000 inhabitants) compared with the Paris and Los Angeles megacities (more than 10 000 000 inhabitants). The relative composition (% volume) of the NMHCs is fairly consistent for the three cities. Nevertheless, the contribution of the unburned fossil fuel fraction including C_4–C_6 alkanes and C_7–C_9 aromatics in Beirut in summer is higher than in Los Angeles and Paris. This suggests the importance of temperature-dependent sources in summer in Beirut like fuel evaporation and the absence of updated emission regulations compared with post-industrialised countries. Therefore, the national specifications and standards for air pollutants should be reviewed and adjusted where necessary.

Most of the measured compounds demonstrate a distinct seasonal cycle characterised by a summer maximum and a winter minimum (Table 1), which is different from trends reported previously in urban areas.[16–21] These seasonal fluctuations depend on the variation of the source strength, meteorological conditions and photochemical activity.[22] High temperatures in Beirut may increase the intensity of fuel evaporation from sources especially in summer, leading to the observed high levels of C_5–C_6 alkanes and C_7–C_9 aromatics.[11] The combustion-related compounds with fairly low reactivity with the OH radical (benzene, acetylene) do not exhibit the same trend, even though the reactive species (e.g. ethylene and propene) have higher levels in summer than in winter. This is contrary to what would be expected in winter when high combustion-related emissions occur, caused mainly by the use of residential heating, and in summer, when enhancement of photochemical depletion would lead to low levels of pollutants, yet we obtained opposite results.

Contrary to other primary anthropogenic NMHCs, C_{11}–C_{16} alkanes of intermediate volatility showed lower concentrations in summer compared with winter (Table 1) owing to the use of additional combustion sources, especially for heating. The
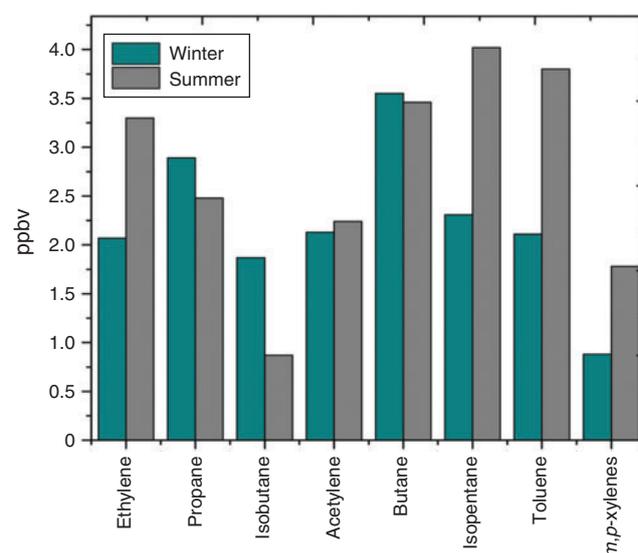
Fig. 5. Mixing ratios of major species in Beirut in winter and in summer campaigns.

levels of C_{10} to C_{16} alkanes in Beirut in summer are lower than those measured in suburban Paris at SIRTA (Site Instrumental de Recherche par Télédétection Atmosphérique) site during the MEGAPOLI (Megacities: Emissions, urban, regional and Global Atmospheric Pollution and climate effects, and Integrated tools for assessment and mitigation) project. However, in winter, the levels in Paris are lower than those in Beirut.[23] The winter season in Paris is colder than in Beirut. Therefore, the IVOCs are adsorbed onto the surface of aerosol particles in Paris whereas in Beirut, they are mainly in the vapour phase during the mild winter season.

Sources governing NMHCs

The major compounds were the same in both seasons in Beirut in terms of average values reported in parts per billion by volume in winter and in summer respectively: toluene, 2.11–3.80; *m,p*-xylenes, 0.88–1.78; isopentane, 2.31–4.02; butane, 3.55–3.46; propane, 2.89–2.48; ethylene, 2.07–3.30; acetylene, 2.13–2.24; and isobutane, 1.87–0.87 (Fig. 5). These compounds are related mainly to mobile traffic and fuel evaporation.[11]
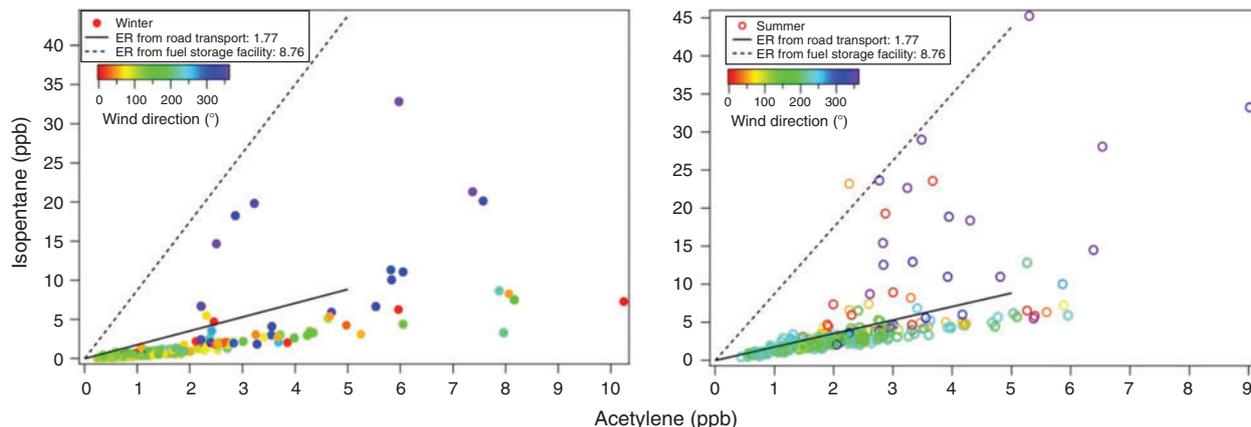
Fig. 6. Scatterplots of isopentane versus acetylene in Beirut in winter and in summer colour-coded by wind direction. The emission ratios (ER) from road transport and from fuel storage facilities are also shown.[11]
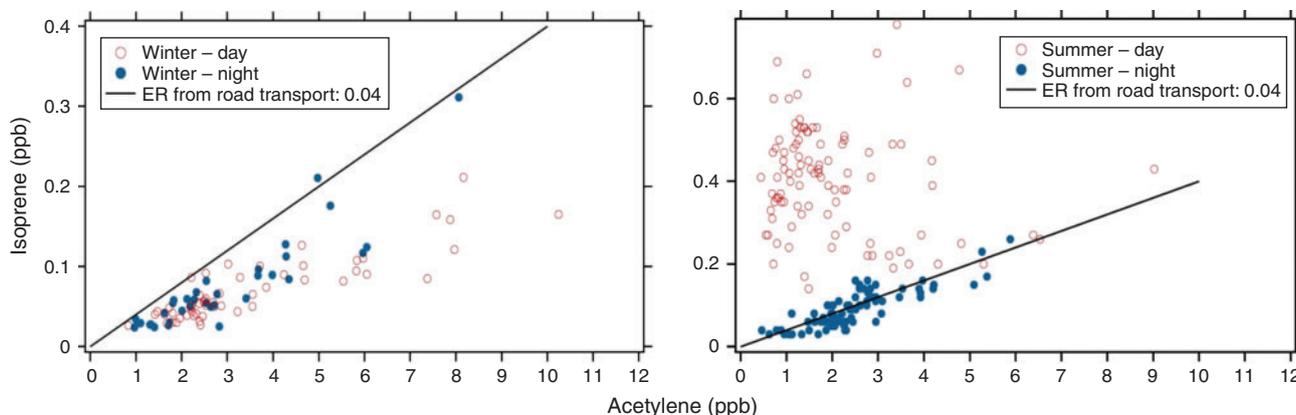
Fig. 7. Scatterplots of isoprene versus acetylene in Beirut in summer and in winter. The solid black line corresponds to the emission ratio (ER) from road transport.[11]

Examining the urban enhancement ratios with appropriate filters like wind direction and time of the day is useful in exploring sources of selected species with the same atmospheric lifetime.[24] First, the scatterplots of isopentane, representing C_4–C_5 alkanes and some alkenes, versus acetylene in summer and in winter reveal the presence of an additional source other than mobile traffic exhaust leading to high levels of isopentane (Fig. 6). Data points that do not lie within the main distribution of points relate to extremely high levels of isopentane originating from the north-wind sector where a fuel storage facility is located.[11] These data points fall within the emission ratio derived from the fuel storage facility emission profile determined in the vicinity of the emission sources in Beirut[11] reported on Fig. 6. The lowest levels are found close to the road transport emission ratio line, which consists of exhaust and evaporative running losses from vehicles.

Second, a correlation is observed between isoprene and acetylene concentrations in summer at night-time and in winter, with data point distribution consistent with the road transport emission ratio determined in the vicinity of this source[11] (Fig. 7). This is indicative of isoprene emission from mobile traffic, as observed in other studies.[25] In contrast, there is a clear increase in isoprene in summer during daytime in line with the temperature, illustrating isoprene emission from local biogenic sources around the site (Fig. 8).

The IVOCs C_{11}–C_{16} alkanes, ranging from 0.20 to 0.30 µg m^{-3} in winter and ∼0.06 µg m^{-3} in summer, can be emitted by vehicles,[26] cooking activities,[27] biomass burning[28] and power generation, which is widely used in Beirut.[29] The time series of C_{11}–C_{16} alkanes in winter, illustrated in Fig. 9 by dodecane, is generally consistent with times series of isopentane and combustion-related compounds like acetylene and ethylbenzene, highlighting combustion sources as the main emitters of these compounds. The analysis of undecane and tridecane with wind direction shows that the increase of species levels does not depend on a specific wind regime. Even though their levels are not as high as other species, their study remains of high importance owing to their high potential for SOA formation.[23]

The results discussed in this section show the importance of local source emissions in Beirut compared with other urban sites in the world. These sources are mostly anthropogenic, related mainly to combustion and fuel evaporation, whereas biogenic sources contribute to isoprene concentrations in summer. In the following sections, other factors, mostly meteorology and photochemistry, that modulate the seasonal variation of the concentrations observed in Beirut will be discussed.

Impact of meteorological conditions and photochemistry

Fig. 10 presents the mean diurnal variations of selected species as well as of wind speed, temperature and photolysis frequency JNO_2 for the summertime and wintertime campaigns.

In winter, the daily time series for most of the compounds related to combustion (benzene, acetylene, ethylene, propylene,
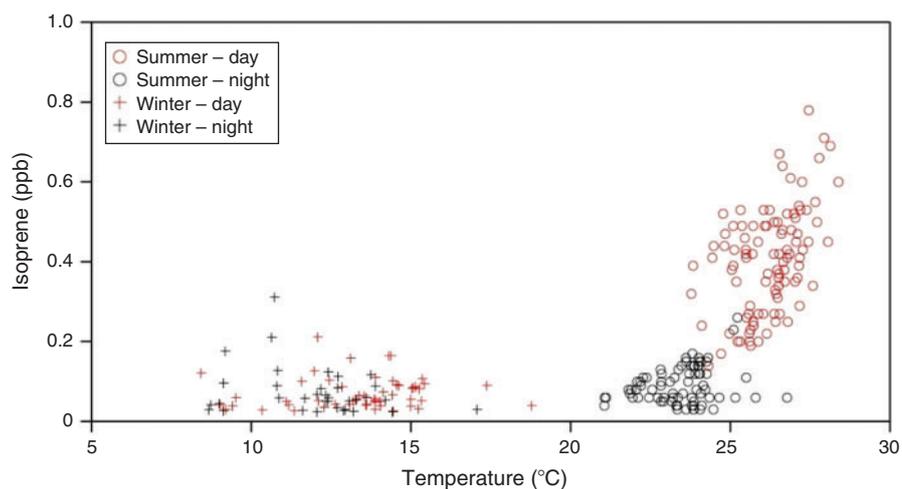
Fig. 8. Scatterplots of isoprene versus temperature in Beirut in summer and in winter.
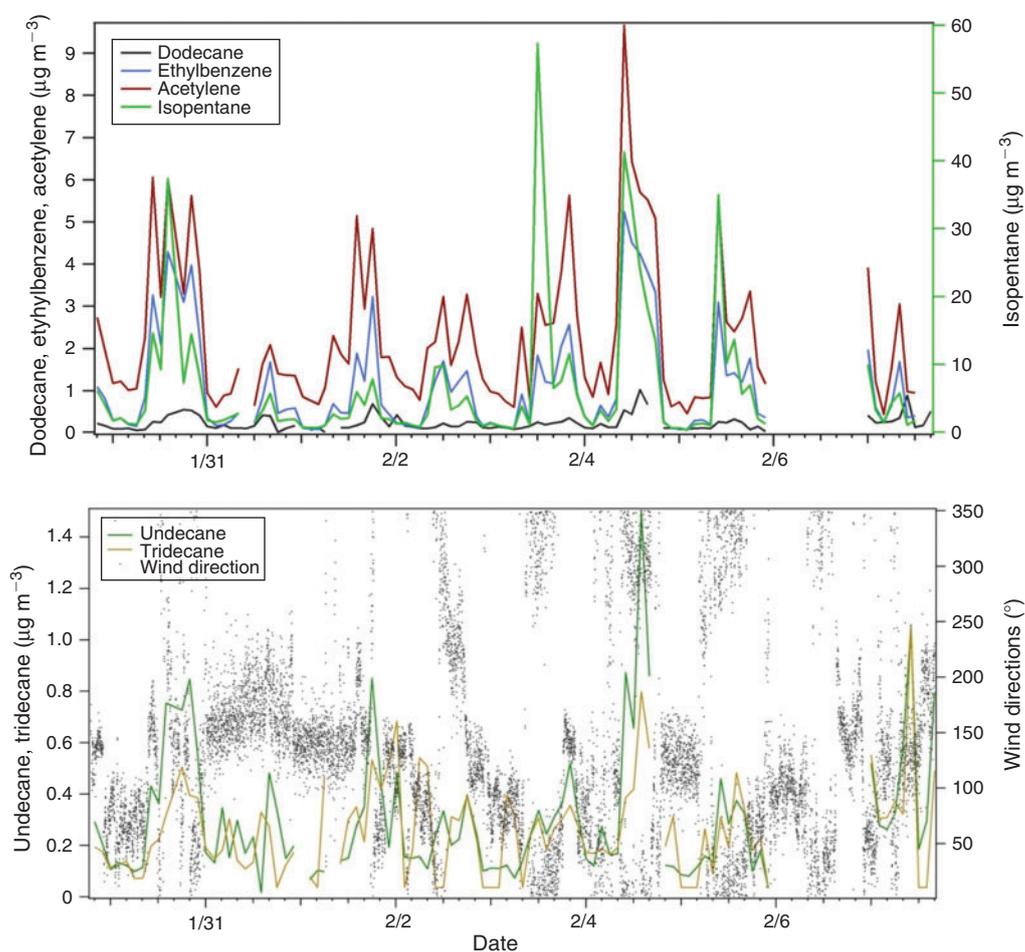
Fig. 9. Wintertime time series of dodecane, ethylbenzene, acetylene, isopentane, undecane, tridecane and wind direction.

m,p-xylenes) are characterised by a first significant increase of concentration at ~0700–0800 hours, a second one at 1400–1500 hours, another increase at 1700–1800 hours and the last peak is observed at 2000–2100 hours in the evening. However, some species related to gasoline evaporation (isopentane, butane, isobutane, butene and toluene) show a significant concentration increase at noon (Fig. 10). According to Waked et al.,[29] the diurnal profile of on-road mobile sources in urban areas in

Lebanon shows a morning peak at ~0700–1000 hours and an evening peak from 1600 to 1800 hours consistent with the increase of the concentrations in the morning and late afternoon. In addition, in winter, additional sources related to domestic heating should be considered because the measurement site is surrounded by a residential area.

In summer, the diurnal time series demonstrate the same morning peak as in winter, and night-time maximum. The

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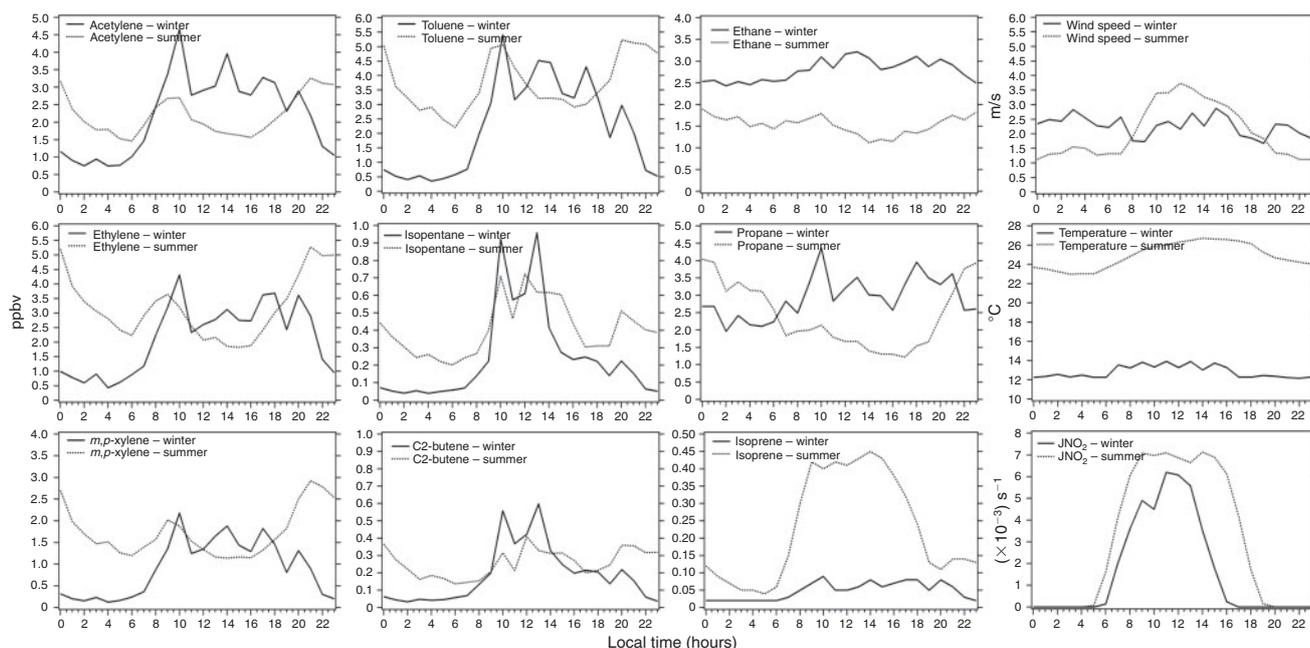
Fig. 10. Diurnal variations of the mixing ratios of acetylene, ethylene, *m,p*-xylenes, toluene, isopentane, cis-2-butene, ethane, propane and isoprene in Beirut, in summer and in winter. The diurnal variations of wind speed, temperature and photolysis frequency (JNO$_2$) in summer and in winter are also presented.

minimum concentration levels are observed at midday and in the afternoon. The morning period (0700–1000 hours) represents the period of least photochemical reactions and highest traffic density. One of the potential reasons for the lowest levels of these hydrocarbons in the noon period (1200–1500 hours) is the enhanced dispersion of air pollutants due to the elevated planetary boundary layer (PBL), which becomes significant from 0900 hours in the morning. Another important reason is the increased average wind speed (Fig. 10), which reaches 3.5 m s^{-1} in the afternoon, leading to greater pollutant dispersion compared with 1 m s^{-1} in the evening. Highest concentrations of C$_4$–C$_5$ alkanes and C$_4$–C$_5$ alkenes were measured during the noon period, coming mainly from gasoline evaporation source emissions, especially from the fuel storage facility, as illustrated previously in Fig. 6. During night-time, values increase owing to the collapse of the PBL height and the low average wind speed of 1 m s^{-1}, which favour higher concentrations of volatile compounds and reduce their dispersion. High night-time levels were observed for all the species, showing the major role of atmospheric dynamics, as well as strong emissions, in modulating the diurnal profile of NMHCs in summer. This is supported by the contrasting diurnal profile of long-lived species like ethane and propane in winter and in summer, where high levels were observed during night-time whereas lowest daytime levels illustrate the effect of the dispersion processes.

As for isoprene, the diurnal variation in winter is similar to that of combustion tracers like acetylene. In summer, the diurnal variation showed high emissions of isoprene during daytime from local biogenic sources, confirming what we previously mentioned.

Reactive species like ethylene, *cis*-2-butene, *m,p*-xylenes and toluene have the same overall diurnal variation as the less reactive species like acetylene (Fig. 10). The reaction of NMHCs with OH$^{\bullet}$[30] is enhanced and reaches a maximum at ~1200 hours owing to the highest solar radiation. The OH$^{\bullet}$-initiated oxidation and, to a lesser extent, O$_3$-initiated

oxidation, are the main pathways for the chemical removal of most NMHCs. Therefore, photochemical removal has to be taken into account especially in summer. The impact of photochemistry was assessed through the comparison of night-time (2300–0700 hours) and daytime (0900–1800 hours) scatterplots during summer[31] and during winter. We assume that there is no photochemistry during night-time and the composition of emissions does not change. The advantage of using the mixing ratios of pairs of ambient NMHC species is that they are not sensitive to dilution and air-mass mixing compared with absolute concentrations themselves.[24] Examining the ratios is useful in exploring the influence of photochemical depletion for compounds with different atmospheric lifetimes. Here the effect of photochemistry is illustrated by the ratio of two reactive compounds, *m,p*-xylenes and ethylene (*m,p*-xylenes and ethylene: rate coefficient with OH$^{\bullet}$ = 23.1 × 10^{-12} and 8.52 × 10^{-12} cm^3 molecule^{-1} s^{-1} respectively),[32] versus acetylene (rate coefficient with OH$^{\bullet}$ = 0.9 × 10^{-12} cm^3 molecule^{-1} s^{-1}).[33]

Scatterplots of selected NMHCs versus acetylene are illustrated in Fig. 11 for summer and winter data sets. For the most reactive compounds, the distribution of the points within the scatterplots is slightly affected by photochemistry for ethylene and *m,p*-xylenes in summer. However, the daytime and night-time scatterplots of *m,p*-xylenes in winter agree pretty well, indicating that emission ratios are not affected by photochemistry. As for benzene, a less-reactive NMHC (rate coefficient with OH$^{\bullet}$ = 1.22 × 10^{-12} cm^3 molecule^{-1} s^{-1}), the night-time and daytime scatterplots cannot be distinguished from each other during both seasons (Fig. 11).

Air mass origins and long-range transport

Long-range transport can significantly contribute to pollutant concentrations in Beirut.[34] According to Waked et al.,[35] the analysis of *FLEXPART* Lagrangian backward trajectories[36] during the same ECOCEM summertime measurement
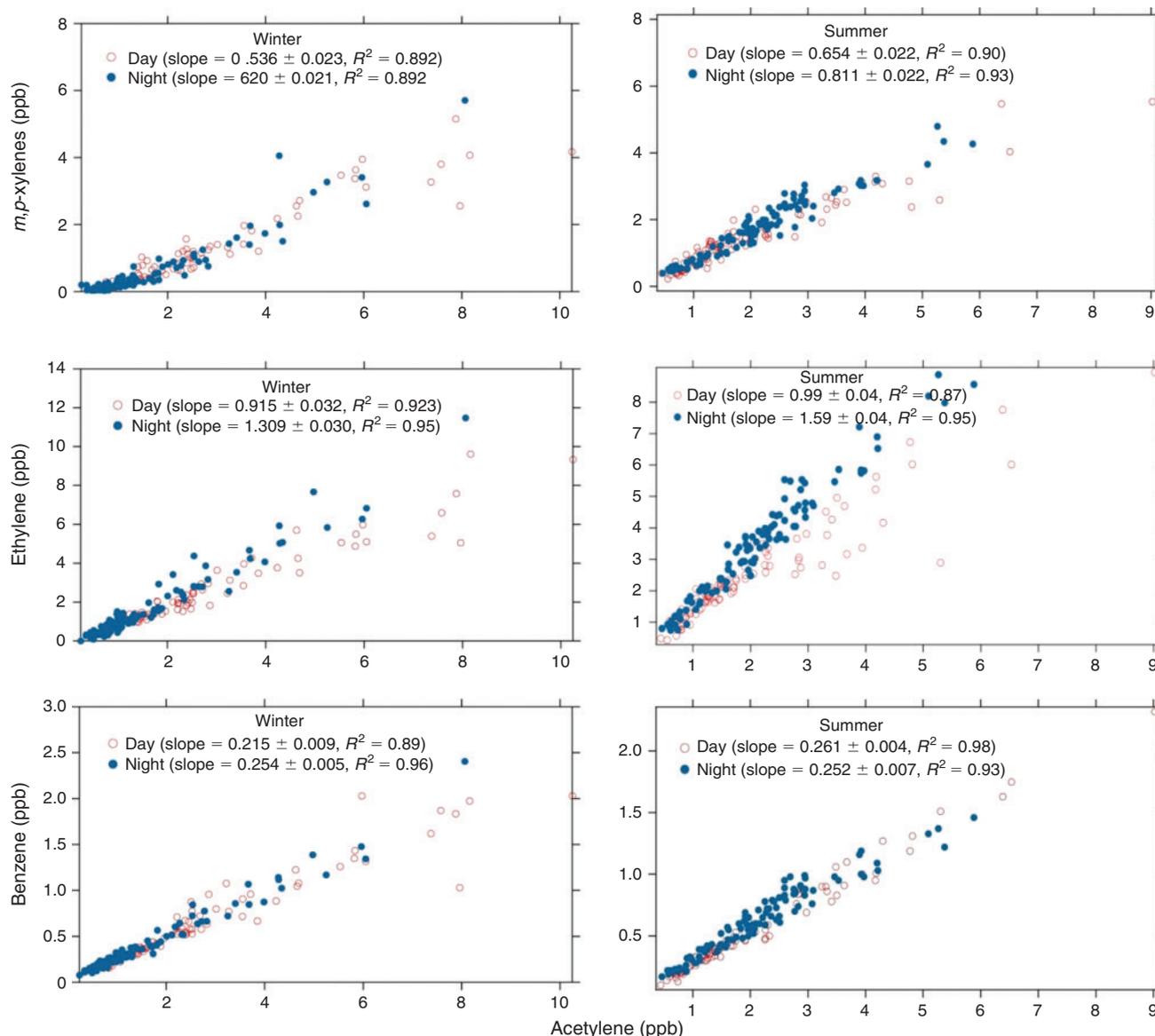
Fig. 11. Scatterplots of selected Non-methane hydrocarbons (NMHCs) (*m,p*-xylenes, ethylene and benzene) versus acetylene in Beirut in winter (on the left) and in summer (on the right).

campaign shows that in summer, OAs (organic aerosols), and particularly biogenic OAs, are associated with long-range transport originating mainly from the Mediterranean Basin and eastern Europe (Turkey). In winter, most of the pollution is associated with local primary emissions and locally formed SOA.[35] The *FLEXPART* model shows that air masses are mostly continental, originating from Turkey and eastern Europe, and the rest come from the Mediterranean basin. Fig. 12 illustrates the surface residence time back-trajectories computed with *FLEXPART*.

Fig. 13 shows the temporal variations of butane, and ethylene and acetylene during the whole summertime campaign as tracers of gasoline evaporation and combustion respectively. Gasoline evaporation and combustion are the two major sources encountered in Beirut; ethylene has a short lifetime whereas butane and acetylene have longer lifetimes of 5 and 13 days respectively with an OH radical concentration of 1.0×10^6 molecules cm^{-3} (24-h average).[32,33] If long-range transport has an influence on

NMHC levels, long-lived species should show a larger increase than short-lived species.[37] Fast short-term variations in high levels of these anthropogenic NMHCs were observed as well as slow variations. No significant increase in long-lived species concentration levels was found when continental air masses reached the sampling site during the whole campaign (e.g. 9, 14 and 17 July), as shown in Fig. 12. This strongly suggests that there is no clear evidence of a long-range transport effect. Hence, reactive and less-reactive NMHCs measured in Beirut during this campaign were mainly emitted locally.

The back-trajectories clusters are quite different in winter. A large fraction of the air masses originates from the Middle East region (Jordan and Syria), from the Mediterranean basin and from Turkey (continental air masses) (Fig. 14). The analysis of the temporal variations in butane, ethylene and acetylene concentrations (Fig. 15) with regard to backward trajectories leads to the same conclusion as in summer with no significant effect from long-range transport.
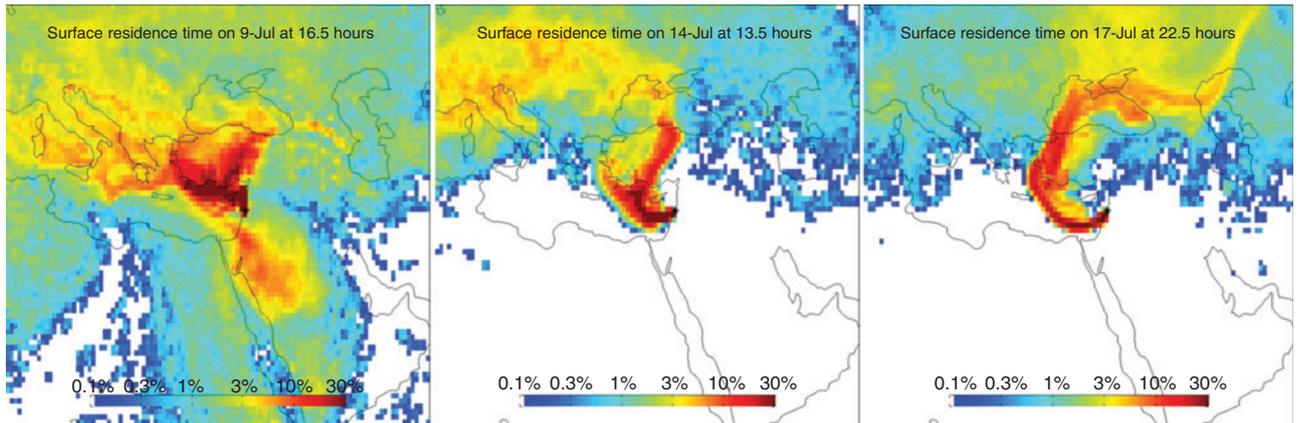
Fig. 12. Surface time residence (%) back-trajectories arriving in Beirut on 9, 14 and 17 July 2011 in terms of grid contributions.
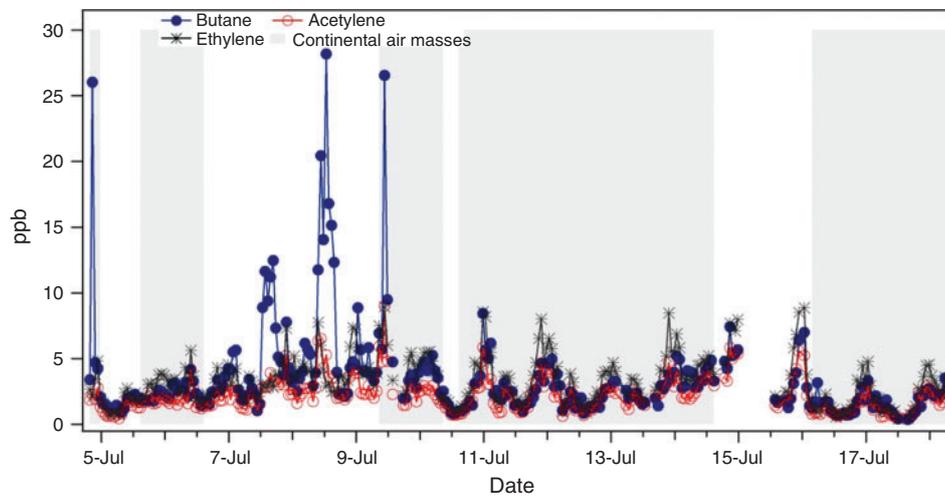
Fig. 13. Summertime time series for butane, ethylene and acetylene. The grey-shaded areas highlight the continental air masses.
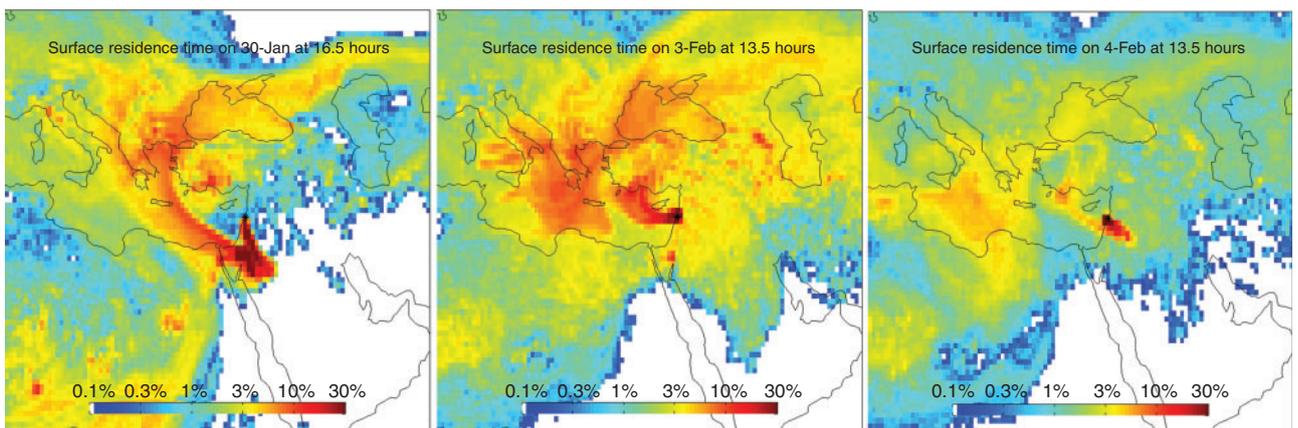
Fig. 14. Surface time residence back-trajectories arriving in Beirut on 30 January, and 3 and 4 February 2012 in terms of grid contributions (%).

Conclusion

For the first time, measurements of more than 70 NMHCs from C_2 to C_{16} were performed at a suburban site in Beirut in two intensive field campaigns in summer 2011 and in winter 2012 within the framework of the ECOCEM project.

The measured average concentrations of NMHCs in summer were found to be higher, by a factor of two in total volume, than levels reported for northern mid-latitude megacities like Paris and Los Angeles.
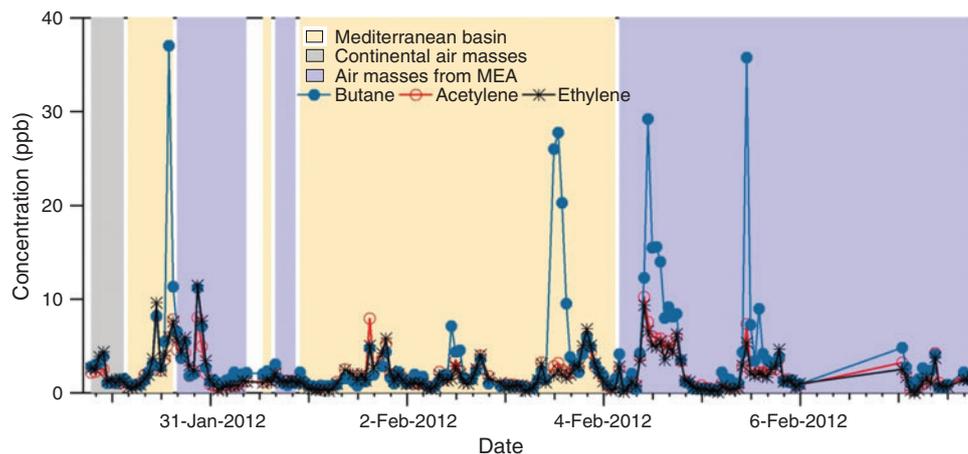
Fig. 15. Wintertime time series for butane, ethylene and acetylene. The grey-shaded areas highlight the continental air masses, blue-shaded areas air masses from the Middle East region (MEA) and light amber area Mediterranean basin air masses.

Toluene, isopentane, butane, *m,p*-xylenes, propane and ethylene were the most abundant NMHCs in Beirut's urban area in summer and in winter, representing almost 50 % of the measured average mixing ratios. Similarly to other urban areas in the world, alkanes were the dominant components of all quantified NMHCs (46 % in summer and 59 % in winter).

The findings further show that there is an observable seasonal variation that affects NMHC levels, characterised by a summer maximum and a winter minimum, unlike seasonal cycles usually observed in northern mid-latitude urban areas. For instance, the levels of some combustion-related reactive species like ethylene and propene were higher in summer than in winter. Furthermore, aromatic compounds show higher concentrations in summer due to mobile traffic emission and gasoline evaporation. Butane, isopentane and pentane emitted from gasoline evaporation also exhibit high concentrations in summer. Other compounds show higher levels in winter, for instance, IVOCs (C_{11}–C_{16} alkanes) emitted mainly by additional combustion sources in winter, ethane, propane, isobutane and some alkenes. This seasonal variation is controlled by a combination of emission sources, dispersion conditions and photochemical removal processes.

The evaporative emissions from gasoline are significant in summer and in winter, affecting the C_4–C_5 alkanes, C_7–C_9 aromatics and C_4–C_5 alkenes fractions in the middle of the day when temperature is the highest.

The duality of the biogenic and vehicle-exhaust origins of isoprene was investigated. Biogenic emissions dominate isoprene daytime concentration in summer whereas vehicle-exhaust emissions govern night-time and wintertime (daytime and night-time) concentrations.

The role of air-mass origin and long-range transport on NMHC levels was also investigated using a Lagrangian model. No significant influence of air-mass origin was found on the concentrations of the longer-lived anthropogenic compounds in summer and in winter.

These results suggest that dilution by atmospheric mixing and strong local emissions dominated by traffic and gasoline evaporation were the leading processes controlling the ambient levels of NMHCs observed in this suburban site. Thus, the influence of long-range transport as well as photochemical depletion is hidden by these strong emissions. However, the effect of the high NMHC levels is potentially of great importance. Therefore, long-term and continuous studies integrating more than one measuring site in the Beirut urban area are of great interest in order to provide information about general tendencies.

The information gathered from the present study has improved our understanding on the tropospheric chemistry of NMHCs and contributes to a better characterisation of air pollution over Beirut. Moreover, the observations are useful for assessing the national atmospheric emission inventory of anthropogenic and biogenic sources established for a base year of 2010 according to the European Environment Agency/European Monitoring and Evaluation Programme (2009) guidelines.[29,38] The present unique data set is of high importance for the MEA where available information on NMHC measurements is scarce but essential for air-quality management and control. Data collected provide decision-makers with reliable guidance in order to mitigate pollution levels and develop appropriate management programs and policies at the national level.

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