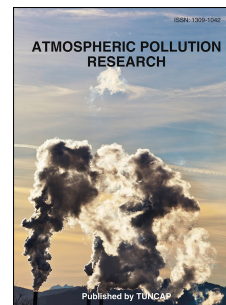


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VOC Tracers from Aircraft Activities at Beirut Rafic Hariri International Airport

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Abstract

1 This is the first study to assess the speciation of 48 VOCs from around 100 commercial aircraft
2 under real operation, as close as possible to aircraft engines during the various modes of the
3 landing/takeoff (LTO) cycles to identify special aircraft fingerprints and markers. Also, Jet A-1
4 kerosene vapor, gasoline exhaust, and the ambient airport concentrations were assessed. Air
5 samples were taken at Beirut Rafic Hariri International Airport inside adsorbent tubes using a
6 portable automatic remote sampler and analyzed using gas chromatographic techniques (GC-MS
7 and GC-FID). Results showed that heavy alkanes (C₈-C₁₄, mainly n-nonane and n-decane), which
8 contributed to about 51 to 64% of the total mass of heavy VOCs emitted by aircraft, and heavy
9 aldehydes (nonanal and decanal) – although to a lesser amount – can be considered as potential
10 tracers for aircraft emissions due to both their exclusive presence in aircraft-related emissions
11 and their absence from gasoline exhaust emissions. On the other hand, the total concentration of
12 heavy alkanes in the airport's ambient air was 47% of the total mass of heavy VOCs measured.
13 No aircraft tracer was identified among the light VOCs (\leq C₇); however, results showed that
14 emissions of light VOCs decrease as the engine power increases. Also, auxiliary power unit
15 (APU) emissions were identified to be of the same order of magnitude as main engine emissions.
16 This study opens the door for future studies aiming at evaluating the impact of airport activities
17 on air quality and human health within or away from the airport vicinity.

Keywords: Air Quality; Aircraft Signature Emissions; Real operation; VOCs; Heavy Alkanes

18 1. Introduction

19 The world combined passenger and cargo traffic, expressed in revenue tonne-kilometres, is
20 expected to grow at the average annual growth rate of 5.0 per cent over the forecast period 2010-
21 2030 (CAEP 9, 2013). This will yield an increase in emissions which can significantly degrade

22 local air quality near airports. The impact of air traffic on local air quality has been the subject of
23 several studies in recent years (Pison and Menut, 2004; Yu *et al.*, 2004; Carslaw *et al.*, 2006;
24 Westerdahl *et al.*, 2008; Dodson *et al.*, 2009). Aircraft engine emissions include non-volatile
25 particulate matter that are harmful to human health and the environment (Barrett *et al.*, 2010;
26 Stettler *et al.*, 2011; Yim *et al.*, 2015) and unburned hydrocarbons (UHCs) which cause adverse
27 health effects on exposed groups (workers, passengers, residents who live near large hubs)
28 (Masiol and Harrison, 2014). UHCs comprise polycyclic aromatic hydrocarbons (PAHs) which
29 are possible human carcinogens (Masiol and Harrison, 2014); as well as volatile organic
30 compounds (VOCs) where the contribution of aircraft to their concentration levels is of
31 particular concern. VOCs are toxic – many of which are even carcinogenic (Wood, 2008),
32 primary precursors of tropospheric ozone formation, and contributors to suspended particulate
33 matter (PM) formation (Masiol and Harrison, 2014).

34 To have a better conception about the impact of aircraft operations on local air quality in the
35 vicinity of airports, the speciation of a wide range of VOCs related to the different modes of
36 engine operation during the Landing/Take-off (LTO) cycle is required. The LTO cycle includes
37 all activities within and near the airport that take place below 3000 feet. This involves taxi, take-
38 off, climb-out, and approach-landing (ICAO, 2011). The flight phase “taxi”, which refers to the
39 “movement of an aircraft on the surface of an aerodrome under its own power, excluding take-
40 off and landing” (ICAO, 2005), includes taxi-in (taxi from runway to parking stand/gate) and
41 taxi-out (taxi from the terminal to runway) (ICAO, 2011). Previous studies (see Table 1) were
42 conducted either during engine tests, where one or few engines were studied (Spicer *et al.*,
43 1992, 1994; Slemr *et al.*, 1998, 2001; Anderson *et al.*, 2006; Beyersdorf *et al.*, 2012), or during
44 real aircraft operations but mainly limited to only one phase of the LTO cycle or to a limited
45 number of assessed VOCs (Herndon *et al.*, 2006; Schürmann *et al.*, 2007; Lelievre, 2009; Zhu
46 *et al.*, 2011) — all covering a limited number of aircraft plumes. Spicer *et al.* has conducted studies
47 on both military (1992) and commercial engines (1994). Results have shown that at low engine
48 power (idle power), the emissions were dominated by cracking products, unburned fuel, and
49 products of incomplete combustion or “combustion-derived”: the major components were
50 ethene, propene, ethyne, and formaldehyde constituting 30-40 % of the total VOCs. At higher
51 engine powers (60-80% of the rated thrust), the concentration of VOCs decreased by a factor of
52 20 to 50, under the effect of combustion, and unburned fuel components disappeared. In
53 accordance with these observations, Anderson *et al.* (2006) reported that VOCs with a higher
54 number of carbon atoms ($nC \geq 4$) dominated at this regime (60 – 80% of the rated thrust) upon
55 studying the emissions of a commercial engine (RB211-535-E4). Studies by Spicer *et al.* (1992,
56 1994) and Slemr *et al.* (1998, 2001) have shown that VOC emissions depend on engine type, use,
57 and maintenance history as well as fuel composition. Limited studies have reported VOC
58 measurements during real aircraft operation. Herndon *et al.* (2006) have conducted
59 measurements on selected organic gas emissions by analyzing wind advected plumes at Boston L
60 ogan International Airport. Schürmann *et al.* (2007) have measured VOCs by sampling diluted
61 gas exhaust for 3 different engines during taxi-out. These measurements have shown higher real-
62 world emissions than those recommended by the International Council Aviation Organization
63 (ICAO) for some engines, but slightly lower values for others. In addition, huge amounts of
64 ethene and propene were detected. Lelievre (2009) have conducted measurements, at 200 m
65 below the flow reactor, on 2 individual aircraft (B757- 200 and one B777-200) during taxi at
66 Paris Charles de Gaulle Airport. Results have shown that the concentrations of alkanes and
67 monoaromatics measured in the plumes were similar but the difference in hydrocarbon

68 concentrations in the two plumes was due to the unsaturated aliphatic compounds.

69 The above studies provide a significant insight into VOC (mainly non-methane hydrocarbon
70 (NMHC)) speciation from aircraft exhaust. However, no special jet exhaust VOC was identified
71 as tracer (Schürmann et al., 2007; Tesseraux, 2004). The identification of aircraft tracers is
72 essential for the assessment of the impact of the airport activities on air quality. Moreover,
73 measurements during engine tests do not reflect the real world aircraft emissions because they do
74 not account for the variations in the aircraft fleet (manufacturer, aircraft type, fuel type, engine
75 thrust, technology, and age) as they were mostly based on individual or few aircraft with
76 controlled operating conditions (thrust, fuel type, etc.). In this manner, they provide conclusions
77 only from samplings from a limited number of engines out of the 300 types of commercial
78 engines present within the commercial aircraft fleet and listed within the ICAO emissions
79 database (ICAO, 2009). Other studies conducted during real aircraft operations either covered
80 one phase of the LTO cycle or were limited to the measurement of few VOCs. In all these
81 studies, available information about the VOC speciation of aircraft auxiliary power unit (APU)
82 emissions is exceedingly sparse. However, APUs, which are small gas turbine engines installed
83 in commercial aircraft to provide electrical power and pneumatic bleed (ICAO, 2011), can
84 represent a significant part of the total emissions at an airport (AERONET III, 2011).

85 Thus, the aim of this research was to identify aircraft tracers by characterizing the relative
86 emissions of 48 VOCs (C₂-C₁₄) from the exhaust of around 100 commercial aircraft under real-
87 world conditions. Measurements included aircraft during the different phases of the LTO-cycle
88 as well as at the gate (APU). For comparison, gasoline exhaust emissions were assessed. The
89 difference in the speciation between aircraft emissions and vehicle emissions will open a door to
90 for future studies to assess the spatial extent of the impact of aircraft activities. Samples were
91 taken at Beirut Airport (Lebanon) and transported to the University of Strasbourg (France) for
92 analysis where gas chromatographic techniques (GC-FID and GC-MS) were used to assess their
93 VOC species contents. To the best of our knowledge, this is the first study covering a wide range
94 of VOCs to assess emissions from a large number of in-use aircraft at various modes of LTO
95 operation.

96 2. Materials and Methods

97 2.1 Study Area

98 The airport of study is Beirut Rafic Hariri International Airport, the only operational
99 commercial airport in Lebanon. It is a midsize commercial and military airport located at 33.82N
100 035.49E, in the Khaldeh suburb about 8 km south of the capital's (Beirut) city center. The west
101 side of the airport is open to the sea while the east side is surrounded by Mount Lebanon where
102 citizens live at close proximity to the airport. Beirut airport has three runways and 14 taxiways.
103 A map of the airport is shown in Fig. 1. The runways are named according to their magnetic
104 heading; and are runways 03/21, 16/34, and 17/35. The surface wind direction is south west
105 throughout most of the year with light wind up to 2.6 m/s, which makes Beirut Airport operates
106 southerly (take-off) and northerly (landing). Runway 21, located to the east of the airport center,
107 is the main departure runway due to the prevalence of southwest wind conditions. It extends to
108 3800 m and is 45 m wide (Lebanese DGCA, 2010) making it well equipped to accommodate a
109 variety of aircraft. Runway 16 is the main landing runway due to the prevalence of wind

110 conditions; while runway 17 is mainly used for landing and take-off of private and military jets.
111 The airport code number is 2E; it handles a wide range of flights (65500 flights/yr for the years
112 2013-2015) including international passenger, air freight, military, and domestic air traffic; it is
113 primarily utilized by the Middle East Airlines (around 50% of the total fleet) (Lebanese DGCA,
114 2015; 2016).

115 2.2 Measurement Sites

116 VOC measurements were carried out in the different locations shown in Fig. 1, namely
117 approach (site 1), idle (site 2), APU (site 3), take-off (site 4), in addition to the airport roof and
118 fuel tanks. These measurement sites were chosen to pursue three different goals, thus 3 different
119 subsets of samples were collected. The first subset aimed at identifying typical fingerprint
120 emissions related to aircraft activities. Air sampling was performed as close as possible to the
121 emission sources, within the constraints of the airport rules, at 5 sites within the airport area. The
122 first series of samples, called “approach”, was taken at the first sequence flash light around 8-9 m
123 below the aircraft performing its approach. The second series, idle, was taken downwind around
124 30 m away (sideways) from the aircraft. The “take-off” site was located at the physical beginning
125 of runway 21 at a distance of 120-190 m behind the aircraft engine at its maximum thrust setting.
126 This location was ideally positioned to capture emissions affected by the take-off thrust. Planes
127 initiate take-off in front of the sampling site and then accelerate southward down the runway and
128 away from the sampling site. At this location, the sampler was placed at a downwind location to
129 capture the aircraft plumes at the prevailing wind conditions. In all of the sites, the wind brought
130 diluted aircraft exhaust to the sampler location. In fact, it was not feasible to obtain exact
131 information regarding thrust settings at each site and for every aircraft. However, estimated
132 thrust settings were determined from pilots and based on the ICAO standard thrust settings.
133 According to ICAO (2011), the thrust levels for idle, approach, and take-off are respectively 7%,
134 30%, and 100% of the rated thrust. However, these values are simplifications used for
135 certification purposes. For example, in real operation, the take-off thrust varies from aircraft to
136 another according to the aircraft type and engine model, flight load, meteorological conditions,
137 runway conditions, etc. (ICAO, 2011). Thus, the “take-off” sample collects a variety of different
138 take-off thrusts which vary between 85 and 100%. At the aircraft gate, the emissions from
139 Garrett-AiResearch (now Honeywell) Model GTCP 331–350C APU on an A330 aircraft were
140 determined by taking the fourth series of air samples at a distance of 10 m downstream from the
141 aircraft tail. For the sake of consistency, samples were taken from the same APU on an A330.
142 The kerosene type fuel used in civil aviation at Beirut Airport is Jet A-1. Jet A-1 vapor was
143 sampled into home-made adsorbent tubes (see section 2.3) by dipping a Teflon tube at the inlet
144 of the autosampler (see section 2.3) inside the valve of the fuel tank (fifth site) at Beirut airport.

145 To compare aircraft emissions to vehicle emissions, it was important to assess VOCs
146 from vehicle exhaust using the same sampling and analysis techniques as the aircraft related
147 samples, and to measure vehicle emissions from the local fuel due to the strong correlation
148 between the fuel composition and VOC emissions (Wang *et al.*, 2013). The main focus was on
149 gasoline exhaust emissions, which were chosen to represent vehicle emissions since the majority
150 of vehicles in Beirut operate on gasoline. In Lebanon, light duty vehicles operate on gasoline
151 while only heavy duty vehicles are allowed to run on diesel that constitute only 4% of the total
152 vehicle fleet (Waked and Afif, 2012). Thus, the second subset aimed at identifying fingerprint

153 gasoline exhaust emissions from gasoline, specifically gasoline type 95 – octane unleaded, that
154 represents 85% of gasoline used in Lebanon for the past 4 years (MoEW, 2017). The vehicle
155 exhaust gas was sampled into adsorbent tubes *via* a Teflon tube from a sampling point located
156 about 30 cm after the tailpipe end. Gasoline exhaust sampling was conducted on Dacia Logan
157 2007 (4 cylinders 1600 cc), which was in good working conditions and is a good stereotype of
158 automobiles currently found in Beirut area. Of course, sampling from gasoline exhaust took
159 place far away from direct aircraft sources.

160 The third subset was taken at the airport roof at the center of the aerodrome to assess the
161 airport ambient concentration. All the samples were collected under the guidance of the airport
162 staff to conduct measurements at the minimal distance permissible from aircraft operations.

163 2.3 Sampling Methodologies

164 Air samples were collected using multi-bed stainless steel thermal desorption tubes
165 suitable for trapping C₂-C₁₂ VOCs. These home-made tubes were fabricated at the University of
166 Strasbourg (EPA, 1999; Liaud Céline, 2014) by packing them with 10 mm Carbosieve™ S-III
167 (60/80 mesh, 100 mg) designed to trap light VOCs from C₂ to C₅; and 35 mm Carbopack™ B
168 column (60/80 mesh, 160 mg) designed to trap heavier C₅-C₁₂ VOCs (Jochmann *et al.*, 2014).
169 The use of these adsorbents together is widespread and commercially found under the name “Air
170 Toxics” (Supelco). These tubes are compatible with Perkin Elmer thermal desorption systems
171 present in the laboratory, and possess similar trapping performance to that of “Air Toxics”. Both
172 seem not at all suitable to trap ethane, ethene, and acetylene at room temperature (Liaud, 2014).
173 In addition, these tubes are not most suitable for n-tridecane and n-tetradecane regarding the
174 recommendations given for carbopack™ B, even if these two compounds were not tested by
175 Liaud (2014). However, due to the sticky nature of the aforementioned heavy VOCs, we
176 assumed that these tubes can still be used to adsorb them (Ras *et al.*, 2009). Note that tubes were
177 sealed with Swagelok end caps fitted with PTFE ferrules. Prior to sampling, tubes were
178 conditioned by thermal cleaning at 350°C under a helium flow rate of 50 mL min⁻¹ for 3 h by
179 using the function “conditioning” of the automated thermal desorber. After conditioning, the
180 tubes were sealed with Swagelok end caps fitted with PTFE ferrules and stored in proper isolated
181 boxes. After sampling, the tubes were immediately sealed, stored in Lebanon in the refrigerator
182 at T < 4°C, and then sent to the University of Strasbourg to be analyzed within 30 days after
183 sampling.

184 Active samples of ambient air and diluted exhaust gases were collected inside thermal
185 desorption tubes using a portable battery-operated automatic sampler (Liaud, 2014) designed in
186 ICPEES (Institute for Chemistry and Processes for Energy, the Environment and Health) - Group
187 of Atmospheric Physical-Chemistry laboratory at the University of Strasbourg. This sampler is
188 composed of a pump located downstream of a mass flow controller that was used to collect a
189 constant flow of air into the empty adsorbent tube. By the very low pressure drop of the low-ΔP-
190 flow mass flow controller (Bronkhorst), this machine was totally adapted to air sampling at
191 atmospheric conditions with a full range of 500 mL min⁻¹, uncertainty of 1% of the full range,
192 and 0.3% precision on the measurement of the mass flow controller. By means of its practical
193 dimensions (width: 61 cm, height: 32 cm, depth: 20 cm, weight: 4 kg) and its battery power
194 supply, this sampler facilitated sampling at any site in the airfield without being constrained with
195 the necessity of electrical supply. Furthermore, its configuration can be operated unmanned with

196 the remote control option which made it possible to control the machine without having to access
197 unsafe sites close to aircraft. The most suitable sampling conditions for a quantitative trapping of
198 the majority of the target VOCs in a 3L sample were sampling at 100 mL min⁻¹ for 30 minutes
199 based on the optimization performed by Liaud (2014). Thus, the sampling flow rate was fixed at
200 100 mL min⁻¹ for most of the samples, whereas the sampling duration varied. To determine the
201 most representative sampling approach for aircraft signature emissions, two sampling strategies
202 were adapted: (i) 30 seconds sampling repeated 6 times to collect emissions from 6 aircraft (30 s
203 × 6) for a total volume of 0.3 L or (ii) continuous 30 min sampling during rush hours for a total
204 volume of 3 L. In both sampling strategies, plumes of 6 aircraft were sampled. Due to the
205 presence of a constant flow of emissions, continuous 3 min-sampling was performed for APU,
206 Jet A-1 vapor, and gasoline exhaust emissions at a total volume of 0.3 L, similar to the 30 s × 6
207 sampling strategy. To measure the ambient airport concentration, samples were taken for a
208 duration of 6 hrs at 25 mL min⁻¹. The choice of a lower flow rate was to avoid the breakthrough
209 of the sampled VOCs through the adsorbents cartridge.

210 VOC measurements were carried out during 2 measurement campaigns performed in
211 October 2014 (2 weeks) and June 2015 (3 weeks). Measurements conducted in October 2014
212 aimed at identifying the speciation of total VOC groups using GC-FID whereas measurements
213 done in June 2015 targeted heavy VOCs using GC-MS for the identification of aircraft tracers. A
214 total of 26 samples were collected: 16 samples from aircraft exhaust, 5 samples from the airport
215 roof, 4 samples from gasoline exhaust, and 1 sample from Jet A-1 vapor were analysed. The
216 engine exhaust samples corresponded to 3 different phases of the LTO cycle (i.e., idle, approach,
217 take-off) as well APU emissions.

218 **2.4 Analytical Methods**

219 **2.4.1 Chemicals and Materials**

220 To prepare liquid calibration curves, by spiking of adsorbent tubes, several reference
221 compounds were purchased from Sigma Aldrich or Fluka with purity ranging mostly from 98 to
222 100%. Propanal, acrolein, pentanal, nonanal, d-limonene, and n-hexane have a purity ranging
223 from 90 to 97%. A liquid standard mixture containing heavy alkanes and monoaromatics was
224 purchased from Supelco (Bellefonte, PA, USA). A 100 mg L⁻¹ liquid standard mixture of BTEX
225 was purchased from Ultra Scientific (North Kingstown, USA). High purity LC-MS methanol
226 (purity > 99.9%), purchased from Fluka, was used to prepare the diluted solutions. Liquid
227 calibration curves were performed with Perkin Elmer stainless steel cartridges obtained from
228 Supelco (Bellefonte, PA, USA) and packed with CarbopackTMB (60/80 mesh, 200 mg). Online
229 calibration was performed with a gas standard mixture composed of light alkanes, alkenes, and
230 one alkyne at 100 ppb (±20%) supplied by the company Air Liquide (Domdidier, Switzerland).
231 This standard gas cylinder was associated with a dilution bench using nitrogen (99.999% purity)
232 obtained from Messer (Puteaux, France). To complete the dilution bench, mass flow controllers
233 were obtained from Bronkhorst (Montigny les Cormeille, France). Helium (99.9995%) and air
234 (99.999%) used for gas chromatography and detectors were also obtained from Messer.
235 Hydrogen was produced by a hydrogen generator HyGen 200 from CLAIND (Lenno, Italy) for
236 flame ionization detectors.

237 To perform calibration curves from gaseous standards, on-line calibration was adopted
238 (Liaud, 2014; Liaud *et al.*, 2014). The standard gas cylinder containing light alkanes, acetylene,
239 and alkenes was diluted from a concentration of 100 ppb with nitrogen gas (99.999% purity), in

240 order to reach targeted concentrations of the order of 0.1 to 20 ppb conventionally encountered in
241 ambient air. On the other hand, liquid spiking was performed to prepare calibration curves for
242 light aldehydes and ketones, d-limonene, chlorinated alkenes, and monoaromatics, using a home-
243 made converted GC injection port, ThermoFinnigan AS3000 (Milan, Italy) with a syringe
244 (Liaud, 2014; Liaud *et al.*, 2014). Because of the sticky nature of heavy alkanes (C₉-C₁₄ in
245 specific) and heavy aldehydes (C₉-C₁₀) on the silica capillary (located between the adsorbent
246 tube and the injector) maintained at room temperature, it was not possible to perform liquid
247 spiking for these VOCs using the converted injection port, and automatic spiking was replaced
248 with manual spiking where the deposition was made directly on the adsorbent tube. For this, 10
249 μL of the previously prepared standard solutions were manually injected with a micropipette,
250 followed by purging the spiked tube for 10 min with N₂ at a flow rate of 50 mL min⁻¹ to remove
251 excess methanol. Liquid standard concentrations ranged from 0.2 to 100 mg L⁻¹ for light
252 aldehydes, ketones, and d-limonene; 20 to 100 mg L⁻¹ for n-nonane and n-undecane; and 100 to
253 500 mg L⁻¹ for nonanal and decanal. As for the mixture which contains heavy alkanes and 4
254 monoaromatics, the concentrations varied between 1.5-7 mg L⁻¹ to 8.5-39 mg L⁻¹. The variation
255 in concentration for each VOC is according to the mass fraction of each component in the
256 mixture. For BTEX, 1,2,4-trimethylbenzene, 1,4-dichlorobenzene, and styrene, the standard
257 concentrations varied between 2.5 and 40 mg L⁻¹.

258 **2.4.2 Analysis Techniques**

259 Analysis was performed on 2 analytical systems to cover the wide range of the target C₂-
260 C₁₄ VOCs. These systems were: (i) ATD-GC-FID: Automated Thermal Desorber (ATD) with
261 capillary gas chromatography (GC) coupled with Flame Ionization Detector (FID) used for the
262 assessment of the total range of VOCs (C₂-C₁₄) and (ii) ATD-GC-MS: Automated Thermal
263 Desorber (ATD) with capillary gas chromatography (GC) coupled with a Mass Selective
264 Detector (MSD) used for the assessment of heavy VOCs (C₈-C₁₄). The total range of target
265 VOCs (except heavy aldehydes) were analyzed by GC-FID by means of its dual column that
266 allows the separation of a wide range of VOCs in a single run as developed by Liaud (2014),
267 especially light VOCs (C₂-C₇), by means of the second analytical column, which could not be
268 separated by GC-MS. However, by using GC-FID it was not possible to quantify benzene (due to
269 co-elution), heavy aldehydes, nor unknown peaks. Thus, GC-MS was used for this purpose.
270 Therefore, both systems were necessary and complementary.

271 Desorption of the analytes retained on the sorbent tubes was carried out using
272 Turbomatrix 350 ATD provided by Perkin Elmer (Waltham, MA, USA). Additional details
273 about the thermal desorption system were given by Liaud (2014).

274 The first analytical system used was a Perkin Elmer gas chromatograph Clarus® 580
275 with a dual column system and twins FID. A capillary column, Perkin Elmer Phase Elite-1, 60 m
276 \times 0.25 mm ID \times 0.25 μm was used to separate heavy VOCs. The second column, Restek Rt®-Q-
277 BOND, 30 m \times 0.32 mm \times 10 μm , allowed the separation of the lightest target VOCs. This
278 analytical chain is equipped with a switching system, Dean switch, which permits the use of one
279 or two chromatographic columns connected in series. The optimization of the chromatographic
280 separation was studied by Liaud (2014). The identification of VOCs was based on the match of
281 the retention times. Quantification was conducted by means of the external standard method.

282 The second analytical system was equipped with a gas chromatograph, 6890N Network
283 coupled to a mass selective detector, 5973N Network MSD provided by Agilent Technologies
284 (Santa Clara, CA, USA). The chromatographic separation of VOCs was conducted on a DB-5MS
285 column (Agilent), 60 m \times 0.25mm \times 1 μ m. This column is non-polar and thus is suitable for the
286 separation of the targeted VOCs. It should be noted that the absence of a second type of column
287 Rt-Q-BOND in this system does not allow the separation of lighter compounds. For the sake of
288 consistency between the two analytical systems, helium flow rate through the system was
289 maintained at 1.2 mL min⁻¹. MSD ChemStation software (Agilent, USA) was used to acquire
290 mass spectrometric data. For quantitative assessment, the extracted ion chromatograms (EICs)
291 were recovered with the target ions and quantification was performed by the use of the external
292 standard method. The most specific fragment ion in the spectra of each identified VOC was
293 determined as the target ion. More details about the optimized analytical conditions for both
294 apparatus are given in table S1 in the supplementary material.

295 All the analytical parameters are reported in Tables S2 and S3 in the supplementary
296 material. Calibrations, prepared *via* both modes of the ATD, showed excellent linearity. For GC-
297 FID, R² values were 0.99 for all VOCs except for propanal (0.98) and acetone (0.98). For GC-
298 MS, R² values were 0.99 for all VOCs except for n-undecane, n-dodecane, and n-tetradecane
299 (0.91-0.94) (refer to tables S2 and S3 in the supplementary material). The limit of detection
300 (LOD) (ng) was calculated as the quantity of analyte (ng) that will yield a signal to noise ratio
301 (S/N) equal to 3. For GC-FID, LOD values varied between 0.03 (n-tetradecane) and 1.4 ng
302 (acrolein and propanal). For GC-MS, LOD values ranged from 0.04 ng for propylbenzene to 4.21
303 ng for n-octane. LOD values were transposed to airborne concentrations (μ g m⁻³) for both given
304 sampling air volumes of 0.3 and 3 L. For a sampling volume of 0.3 L, LOD values varied
305 between 0.10 and 4.58 μ g m⁻³ for GC-FID and between 0.14 (propylbenzene) and 4.21 (n-
306 octane) μ g m⁻³ for GC-MS. For a sampling volume of 3 L, the corresponding LOD values varied
307 between 0.01 and 0.46 μ g m⁻³ (GC-FID) and between 0.01 and 0.42 μ g m⁻³ (GC-MS). For GC-
308 FID (Table S2), the uncertainty of the measured concentrations ranged between 21.0 and 25.3%
309 for most of the VOCs except for acetone (30.4%). For GC-MS (Table S3), the uncertainty of the
310 measured concentrations mostly ranged between 21.8 and 25.7%, with highest values
311 corresponding to n-dodecane (51.9%), n-tetradecane (55.6%), and n-undecane (55.8%) that also
312 possess lower R² values.

313 3. Results and Discussion

314 The 48 VOCs measured mainly represent the most abundant compounds from aircraft
315 emissions according to previous studies, and are divided into different chemical families i.e. light
316 alkanes (C₂-C₇), heavy alkanes (C₈-C₁₄), alkenes (C₂-C₆), light aldehydes and ketones (C₂-C₆),
317 heavy aldehydes (C₉, C₁₀), monoaromatics, and d-limonene. Because sampling conditions could
318 be very different (e.g. meteorology, light, etc.) from one sample to another or from one day to
319 another, the results will often be presented and discussed in terms of percentages and not as
320 quantitative data, as seen in previous studies (Anderson *et al.*, 2006; Lelievre, 2009; Spicer *et al.*,
321 1984). We will first present the total VOC speciation from aircraft exhaust identified using GC-
322 FID (section 3.1), then we present VOC aircraft tracers identified using GC-MS (section 3.2).

323 We have defined a speciation per site by averaging all data collected at the same site and with the
324 same sampling strategy, 30 min or 30 s \times 6. The profile labelled "Aircraft" constitutes the

325 average of samples collected near the aircraft when either the APU or the main turbine engines
326 were running (e.g. samples collected at the sites approach, take-off, and APU). Note that aircraft
327 engines as well as APUs are supplied by the same fuel type stored in the tanks at the aircraft
328 wings i.e. Jet A-1 kerosene fuel (Airbus, 2018; Boeing, 2002). Jet A-1, the most commonly used
329 fuel for commercial aviation around the world, is produced according to an internationally
330 agreed standards with unique physical and chemical properties (ASTM D1655) (IATA, 2015;
331 Ritchie et al., 2003).

332

333 **3.1 Complete Speciation of VOCs**

334 The complete speciation of VOCs was obtained using GC/FID (see Fig. 2). In the case of
335 the 30 s \times 6 “approach”, 4 samples were averaged to assess total VOCs, while 3 samples were
336 averaged to represent the speciation obtained using the 30-min “approach”. The profile labelled
337 “Airport Roof” constitutes of 2 samples taken at the airport roof to assess the ambient airport
338 concentrations affected by the total airport activities including aircraft, ground support
339 equipment (GSE), APU, refueling, etc. Fig. 2 (a) shows that the total concentration of VOC
340 groups in the “Aircraft” source profile taken using the 30 s \times 6 technique has a higher TVOC
341 ($160.8 \mu\text{g m}^{-3}$) than that taken by the 30-min technique ($28.3 \mu\text{g m}^{-3}$). The 30-min samples have
342 a TVOC closer to that of the airport roof ($82.6 \mu\text{g m}^{-3}$) and thus are more representative of
343 ambient airport concentrations rather than aircraft signature emissions. This observation is
344 explained by the fact that with the 30 s \times 6 approach, sampling was done just when the aircraft
345 passed near the sampler to take exclusively (as much as possible) aircraft engine emissions with
346 least interference from the ambient concentration. Results from the 30 s \times 6 approach will be
347 thus chosen in the next paragraphs to discuss the speciation of aircraft emissions at different
348 thrust settings. The detailed results of the measured VOCs, using the 30 s \times 6 approach, in the
349 exhaust at the various modes of the LTO cycle as well as the APU emissions are summarized in
350 Table 2.

351 As seen in Fig. 2 (b), the average aircraft profile, represented by the 30 sec “approach”,
352 was dominated by light aldehydes and ketones (47.7% of TVOCs) followed by alkenes/acetylene
353 (15.8% of TVOC), monoaromatics (14.5% of TVOC), light alkanes (14.7% of TVOC), heavy
354 alkanes (5.7%), and d-Limonene (1.4%). Light aldehydes and alkenes are mainly combustion
355 derived VOCs previously reported as part of the major VOC groups emitted from aircraft
356 exhaust (EPA, 2009a). As illustrated in Fig. 2 (b), the VOC speciation at the “airport roof” was
357 dominated by monoaromatics (38.6%), light alkanes (29%), aldehydes and ketones (16.6%),
358 heavy alkanes (9.1%), alkenes (5.9%), and d-limonene (0.75%). The dominance of
359 monoaromatics and light alkanes is probably enhanced by emissions from vehicles and ground
360 support equipment (GSE) near the airport roof.

361 **3.1.1 Distribution of VOC Groups at Different Engine Powers**

362 Results confirm that VOC compositions in jet exhaust vary with engine power settings
363 (see Fig. 3). As the engine power increased from idle to approach phase, TVOC decreased by a
364 factor of 1.7 from $156 \mu\text{g m}^{-3}$ to $92 \mu\text{g m}^{-3}$. These results could be expected. Indeed, turbine
365 engines primarily emit CO and NMHC species as a result of incomplete combustion of jet fuel
366 (Anderson et al., 2006). The relative amounts of NMHC emissions depend on combustor
367 temperature and pressure, fuel to air ratio, and the extent to which fuel is atomized and mixed

368 with inlet air. VOC emissions are higher at low power settings when the temperature of the air is
369 relatively low and the fuel atomization and mixing process is least efficient. This is also
370 according to ICAO databank sheets for unburned hydrocarbons (UHC) for all modern turbine
371 engines; all engines produce less CO and NMHC emission per kg of fuel burned as their power
372 levels are increased above idle (Anderson *et al.*, 2006). In comparison to our observations,
373 Spicer *et al.* (1994) found that TF-39 and CFM-56-3 engines exhibited larger decreases in
374 NMHC emissions with increasing engine power. These differences, which can be mostly
375 accounted for by the fact that the TF-39 and CFM-56-3 engines produce much higher levels of
376 emissions at idle (low power) than do the newer commercial engines which relates to the
377 significant improvements in engine efficiency and the technical progress to reduce emissions
378 (Masiol and Harrison, 2014).

379 As for aliphatic hydrocarbons, the predominant presence of alkenes and acetylene
380 (unsaturated aliphatic hydrocarbons) over alkanes was observed at idle power (62% of the total
381 aliphatic hydrocarbon species) (see Table 2). The predominance of unsaturated hydrocarbons is
382 consistent with observations previously made by Anderson *et al.* (2006), Spicer *et al.* (1994),
383 and Schürmann *et al.* (2007).

384 The effect of engine thrust settings on the relative contribution of the different families is
385 evident by the decrease in the concentration of alkenes from idle power ($42 \mu\text{g m}^{-3}$) (touchdown)
386 to take-off ($15 \mu\text{g m}^{-3}$), as seen in Fig. 3 (a). Alkenes and alkynes (represented by acetylene) are
387 generally products of incomplete combustion (combustion-derived), and consequently are
388 present at much higher concentrations at idle compared with high power settings (Spicer *et al.*,
389 1990). With higher speed, the contribution of alkanes increased accounting for 68% of the mass
390 of aliphatic HCs (see Table 2). In fact, increasing the engine power drives a lower contribution of
391 unsaturated aliphatic compounds in favor of alkanes and aromatics (Anderson *et al.*, 2006). This
392 increase results from the temperature rise within the combustor. These observations are
393 consistent with those of Lelievre (2009). Another effect of engine power was seen in the increase
394 of the contribution of heavy alkanes from 2 to 8% from approach to take-off, corresponding to 2
395 and $15 \mu\text{g m}^{-3}$ respectively (see Fig. 3 (b)). As mentioned by Anderson *et al.* (2006), at higher
396 engine powers, species with low carbon number disappear, and VOCs with higher carbon
397 numbers become more dominant. These heavier VOCs could be either fuel or combustion
398 derived (Anderson *et al.*, 2006).

399 Finally, for APU emissions, results show that they were of the same order as main engine
400 emissions with TVOC equal to $172 \mu\text{g m}^{-3}$.

401 **3.1.2 Speciation of VOC Groups at Different Engine Powers**

402 The fraction of each species of the VOC family is known as the species “abundance”,
403 presented as a percent of the VOC family (weight %) on the basis of $\mu\text{g m}^{-3}$. The set of species
404 abundances for a source, illustrated in Fig. 4, is known as the “source profile” or “source
405 fingerprint” (Conner *et al.*, 1995; Henry *et al.*, 1994). Information regarding the distribution of
406 emissions by carbon number is important because such data can distinguish the cracking and
407 partial oxidation products from unburned fuel (Spicer, 1990). Light alkanes from aircraft
408 emissions were mainly dominated by propane and isobutene (idle and approach) as illustrated in
409 Fig. 4(a). According to previous studies (Anderson *et al.*, 2006; Schürmann *et al.*, 2007), light
410 alkanes were dominated by ethane and propane at these thrust settings. The fact that ethane

411 contributes less to the light alkane speciation in our study can be attributed to the weak
412 adsorption properties of the used adsorbent. i.e. Carbosieve™ S-III for light VOCs, with C₂
413 molecules, as previously mentioned by Liaud (2014).

414 As shown in Fig. 4(c), ethene, acetylene, and propene clearly dominate the speciation of
415 unsaturated aliphatic hydrocarbons in aircraft emissions, they alone represent 66-88% of the
416 average aliphatic hydrocarbon mass emitted (refer to Table 2). According to experimental and
417 kinetic modelling studies conducted by Dagaut *et al.* (2006), alkene and alkyne emissions are
418 mainly dominated by light compounds (2 to 3 carbon atoms) produced as intermediate products
419 during the oxidation of jet fuel. Also, previous studies conducted during engine tests or in real
420 aircraft operations reported the dominance of C₂-C₃ over unsaturated HCs (Anderson *et al.*,
421 2006; Lelievre, 2009; Schürmann *et al.*, 2007). According to Anderson *et al.* (2006), C₂-C₃
422 compounds constituted 90-92% of unsaturated HC emissions from RB211-535E4. During
423 measurements of real aircraft operations (taxi) by Schürmann *et al.* (2007), C₂-C₃ unsaturated
424 aliphatics constituted 73-91% of the total HC emissions. Another significant alkene is isoprene
425 (see Fig. 4(c)) which has been previously found in both jet and traffic exhaust (Borbon *et al.*,
426 2001). Isoprene, which constitutes between 11-16% of the mass of unsaturated aliphatic
427 hydrocarbons, was previously detected in aircraft exhaust emissions and not in refuelling
428 emissions (Schürmann *et al.* 2007). Thus, it is “combustion-derived”. As for monoaromatics,
429 toluene and m, p-xylene dominated the speciation with approximately equal contributions for the
430 different engine powers (see Fig. 4(d)).

431 As illustrated by Fig. 4(e), aldehydes and ketones (oxygenated VOCs) in aircraft
432 emissions were also dominated by C₂-C₃ compounds. Acetone, acrolein, and propanal
433 constituted between 91-100% of the total oxygenated VOCs. Acrolein and propanal are included
434 in the list of 14 Hazardous Air Pollutants (HAPs) present in the exhaust of aircraft according to
435 the US EPA Clean Air Act (FAA, 2003) and have been identified as major components of jet
436 exhaust (City of Park Ridge, 2000; EPA, 2009a). The highest concentrations of acrolein and
437 propanal were found during take-off and in APU emissions. The concentrations of acrolein
438 ranged between below Detection Limit (bDL) and 112 µg m⁻³ while the concentration of
439 propanal ranged between bDL and 37 µg m⁻³ (Table 2). Acetone has been previously considered
440 as a component of jet engine exhaust (City of Park Ridge, 2000). Other sources that can
441 contribute to acetone levels may be due to maintenance activities performed on planes, like
442 painting and parts cleaning. Butanal and hexanal which have been previously associated with jet
443 exhaust are only present in jet and not in gasoline exhaust (City of Park Ridge, 2000).

444 3.2 Aircraft Tracers

446 The identification of aircraft tracers was investigated using GC/MS technique that is able to
447 quantify VOCs including aromatics and aliphatic compounds with more than 7 carbon atoms in
448 our experimental conditions.

449 We have defined a speciation per site by averaging all data collected at the same site and with the
450 same sampling strategy, 30 min or 30 s × 6. The profile labelled “Aircraft” constitutes the
451 average of samples collected near the aircraft when either the APU or the main turbine engines
452 were running, i.e. samples collected at the sites approach, take-off, and APU. In the case of the
453 30 s × 6 “approach”, 6 samples were averaged to assess heavy VOCs, while 3 samples were
454 averaged to represent the speciation obtained using the 30-min “approach” (see Fig. 5). The

455 profile labelled “Airport Roof” constitutes of 3 samples taken at the airport roof to assess the
456 ambient airport concentrations affected by the total airport activities including aircraft, ground
457 support equipment (GSE), APU, refueling, etc. The profile “Gasoline exhaust” corresponds to
458 the average of 4 samples which represent gasoline exhaust. These gasoline exhaust samples were
459 analyzed only using GC-MS, hence mainly heavy VOCs (monoaromatics; n-alkanes (nC₈-C₁₄);
460 nonanal and decanal) were assessed from gasoline exhaust emissions. Several samples were
461 taken for Jet A-1 vapor, however only 1 sample was analyzed and interpreted, as all the other
462 samples overloaded the GC column and saturated the GC detector.

463

3.2.1 Distribution of Heavy VOCs by Family

465 It is important to assess the VOC distribution of aircraft emissions by family because
466 each family has its different environmental and health effects. Heavy VOCs emitted are broken
467 down into heavy alkanes (C₈-C₁₄), heavy aldehydes (C₉, C₁₀), benzene, and other monoaromatics
468 (see Table 2). The 20 measured VOCs (C₇-C₁₄) using GC-MS were mostly heavy compounds
469 (C₈-C₁₄) accounting for only a portion of aircraft exhaust since the target VOC species covered
470 only a limited range. This range was chosen because it showed significant differences between
471 aircraft and vehicle exhaust during our primary qualitative study.

472 Our objective was to identify emission tracers from aircraft by comparing the emission
473 profile of aircraft engines to that of vehicle exhaust gas. As shown in Fig. 5, the profiles
474 “Aircraft” and “Gasoline exhaust” illustrate significant differences. Indeed, the most prominent
475 difference is the dominance of heavy alkanes (C₈-C₁₄) in the aircraft profiles and their absence
476 from the profile of gasoline. As seen in Fig. 5 (a), the total concentration of heavy alkanes was
477 53 $\mu\text{g m}^{-3}$ for the profile “Aircraft” (30 s \times 6), which accounted for 51% of the total heavy VOCs
478 (Fig. 5 (b)). Similar speciation was observed for the 30-min sampling, where heavy alkanes (C₈-
479 C₁₄) constituted 64% of the mass of aircraft sources with a smaller magnitude of 9.2 $\mu\text{g m}^{-3}$.
480 These observations were in accordance with previous studies, conducted by Liu *et al.* (2008) in
481 China, Lai *et al.* (2011) in Taiwan, Salameh *et al.* (2014) in Beirut-Lebanon, etc. and which
482 reported that gasoline vehicles have negligible emissions of C₉ and higher VOC species. In
483 addition to heavy alkanes, heavy aldehydes (C₉, C₁₀) were present only in aircraft sources with
484 average concentrations of 2.6 and 0.2 $\mu\text{g m}^{-3}$ for the 30 s \times 6 and 30-min approaches
485 respectively. These heavy aldehydes are mainly generated by the atmospheric photo-oxidation of
486 heavy alkanes, kerosene combustion, and/or evaporation of raw fuel. Another difference is that
487 the total concentration of monoaromatics in the profile “Gasoline exhaust” is around 3 times
488 higher than the profile “Aircraft” at 122 and 44 $\mu\text{g m}^{-3}$ respectively (Fig. 5 (a)), which can be
489 attributed to the sampling distance – in addition to fuel type. Benzene dominates the mass
490 emissions in gasoline exhaust (76% of the total mass emissions) (see Fig. 5 (b)) while in aircraft
491 exhaust “other monoaromatics” dominate (82% of the mass of monoaromatics emitted). The
492 absence of heavy alkanes and aldehydes from the VOC speciation of the gasoline exhaust is in
493 accordance with previous studies, which reported that heavy alkanes especially C₈-C₁₄ were
494 negligible or almost not present in gasoline exhaust (Liu *et al.*, 2008; Wang *et al.*, 2013). These
495 results are not surprising because jet aircraft use a kerosene-based fuel (Jet A-1) with a higher
496 overall molecular weight than gasoline. This was confirmed by the analysis of unburned Jet A-1
497 kerosene vapor used in Beirut Airport that showed that heavy alkanes constitute 43% of the mass
498 of heavy VOCs in unburned kerosene vapor (Fig. 5 (b)). Kerosene vapor, in turn, constitutes up
499 to 30% of aircraft emissions (Ritchie *et al.*, 2003). This explains the presence of heavy alkanes as

500 fuel-derived emissions. Heavy aldehydes can be either combustion products or “combustion-
501 derived”(fuel oxidation) or due to unburned fuel. Jet A-1 kerosene fuel may have significant
502 amount of species containing more than 14 carbon atoms, but it was not suitable to measure them
503 because the sampling method involving carbopack B as adsorbent, was adapted for gaseous
504 species up to C₁₂-C₁₄ only. It is known that the average chemical formula for kerosene (Jet A-1)
505 differs from one source to another and ranges from C_{10.9} H_{20.9} to C₁₂ H₂₃ (Dagaut et al., 2006).
506 Conner *et al.* (1995) averaged 2 air samples collected near an aircraft at the gate while refueling
507 and preparing for departure, with running engines. Similar observations were found as heavy
508 alkanes and monoaromatics constituted 66% and 44% of the heavy VOC composition
509 (considering our target heavy VOCs).

510 For the “Airport Roof” profile, 3 measurements were taken during the following times:
511 07:00-13:00; 13:00-19:00; 01:00-07:00 to account for the different airport traffic intensities. As
512 shown in Fig. S1, highest concentrations were found during the noon rush hours between 13:00
513 and 19:00 corresponding to highest airport activities, while lower concentrations were observed
514 between 01:00 and 07:00 corresponding to minimal airport activities. The average heavy TVOC
515 for the 3 measurements at the airport roof was 20.5 µg m⁻³ of which 47% were heavy alkanes,
516 45% monoaromatics, and around 8% heavy aldehydes (see Fig. 5). In all the profiles, benzene
517 had the highest concentration among the monoaromatics except for the airport roof (see Fig. 5).
518 The difference in speciation between VOCs measured in the airport roof for the campaign
519 conducted in October 2014 and that conducted in June 2015 can be probably explained by the
520 difference in time conditions (weather, light, etc.).

521 In Fig. 5, results show that aircraft samples taken using the 30 s × 6 technique have a
522 higher TVOC concentration (107.2 µg m⁻³) than those taken with the 30-min technique (15 µg m⁻³),
523 as found in our previous measurements (GC/FID, see Fig. 2) with the exception of heavy
524 alkanes. Again, it can be deduced that the 30 s × 6 samples (see Table 2) are more representative
525 of aircraft emissions than the 30-min samples which were closer to the airport ambient
526 concentration (82.6 µg m⁻³). Indeed, it is expected and consistent to obtain higher concentrations
527 in aircraft exhausts than in ambient concentrations. The 30-min samples are finally more
528 influenced by ambient concentrations than by aircraft exhaust.

529 3.2.2 Speciation of Heavy VOCs

530 Fig. 6 illustrates the speciation of the identified aircraft tracers, heavy alkanes and heavy
531 aldehydes. The carbon number distribution of Jet A-1 kerosene vapor shows that among the
532 heavy alkanes, C₈-C₉ compounds have the highest mass contribution (95.5%), followed by the
533 contribution of n-decane (3.9%), while n-undecane, n-dodecane, n-tridecane, and n-tetradecane
534 mentioned in decreasing order of contribution all constituted less than 1% of the heavy alkane
535 mass. Both nonanal and decanal were also present in jet vapor (Fig. 6). Upon previous analysis
536 of JP-4 jet fuel by Spicer *et al.* (1984), it was seen that C₇-C₉ dominated the speciation for a wide
537 range of VOCs and low levels of light VOCs were observed. As deduced by Spicer *et al.* (1990),
538 we can conclude that the exhaust species found in C₂-C₆ were probably products of combustion,
539 referred to as “combustion-derived”, and VOCs C₈ and higher were “fuel-derived”. It can be seen
540 that the airport roof source profile is in close resemblance to the samples collected with the 30 s

541 $\times 6$ -approach. In the profiles “Aircraft” (30 s \times 6) and “Airport Roof”, among the heavy alkanes
542 n-nonane and n-decane dominate the speciation: n-nonane contributes to 39.7% and 37.6% of the
543 total mass of heavy alkanes for the “Aircraft” and “Airport Roof” profiles respectively, while n-
544 decane contributes to 30.5% and 33.2% of the total mass of heavy alkanes for the “Aircraft” and
545 “Airport Roof” profiles respectively. The speciation of Jet A-1 kerosene vapor explains the
546 presence of these heavy alkanes in aircraft and airport emissions, as they are components of jet
547 fuel. These results are similar to those obtained within the platform of the airport of Charles De
548 Gaulle, where n-nonane was found to be the dominating species (50%) among C₆-C₉ measured
549 alkanes (Lelievre, 2009). In this study, the speciation of other monoaromatics for “Aircraft” (30 s
550 \times 6) and “gasoline” is dominated by toluene that has a higher contribution in the “Gasoline
551 exhaust” profile (91%) than in the “Aircraft” profile (45%) as shown in Fig. S2 6. 1,2,4-
552 trimethylbenzene, emitted by aircraft as well as vehicles, dominates the airport roof source
553 profile. It is important to note that inhalation of air containing trimethylbenzene can lead to
554 irritation of the respiratory tract, sore throat, headache, wheezing, vomiting, anxiety, tension and
555 may affect the blood.

556 3.2.3 Speciation of Heavy VOCs with Engine Power

557 It should be emphasized that the measurements presented in Fig. S3 7 are not subject to a
558 normative character and that the variety in the conditions (sampling distance, aircraft type,
559 engine type, etc.) does not permit to compare the emission concentrations between the different
560 studies. However, these results illustrate the variability of concentrations and speciation in the
561 plume of the aircraft. Results confirm that VOC compositions decreased with increased engine
562 power settings as can be seen for concentrations of approach (30% of the rated thrust) compared
563 to that of take-off (85-100% of the rated thrust) (Fig. S3). The observed TVOC equal to 216 $\mu\text{g m}^{-3}$
564 m^{-3} for the approach profile decreased by a factor of 3 for the take-off, i.e. down to 75 $\mu\text{g m}^{-3}$.
565 For the same power range, the observed levels of monoaromatics and heavy alkanes decreased
566 by factors of 4 and 5 respectively. The highest drop in concentration was observed for 1,2,4-
567 trimethylbenzene with a factor of 39 (see Table 2).

568 As shown in Fig. S3 7, the concentration of benzene increased from approach (bDL) to
569 take-off (22.5 $\mu\text{g m}^{-3}$) while the concentration of “other monoaromatics” significantly decreased
570 from 85 to 21 $\mu\text{g m}^{-3}$. This is due to the cracking of higher aromatics upon the increase in
571 temperature which leads to less amounts of these species, but increased amounts of benzene
572 (Schürmann *et al.*, 2007). Benzene dominates the mass speciation of the monoaromatics in all the
573 sites except for approach.

574 The speciation of heavy alkanes for approach and APU is dominated by n-nonane (45.1%
575 and 40.2% respectively) and n-decane (27.9% and 59.8% respectively), whereas the take-off
576 profile is dominated by n-undecane (26.0%) and n-decane (21.7%) (see Fig. S4 8(a) in the
577 supplementary information). The heavy alkanes in APU emissions are only n-nonane and n-
578 decane. On the other hand, it is interesting to note that, for the same mode of operation, the
579 speciation of heavy alkanes using GC/MS (Fig. S4 (a)) is similar to that obtained using GC/FID
580 (Fig. 4(b)). For example, with both techniques n-nonane and n-decane dominate the speciation of
581 heavy alkanes for the approach phase, and for APU emissions. Moreover, in both measurements,
582 the speciation for the take-off phase is more distributed as a result of the use of higher engine
583 power. For all these engines powers, the presence of these heavy alkanes is a result of unburned

584 kerosene vapor (Spicer, 1984). It should be noted that emissions during take-off are partially
585 composed of unburned fuel or “fuel-derived”; they contain C₈-C₁₃ alkanes as well as nonanal and
586 decanal coming either from kerosene combustion or from the raw fuel (Ritchie, 2003). Airport
587 roof, which is present between the 2 jetties, is in close proximity to the gates and is consequently
588 affected to a great extent by APU emissions. This explains the dominance of n-nonane (37.6%)
589 and n-decane (33.2%) over the mass of heavy alkanes at this site (see Fig. 6). Nonanal and
590 decanal are also present at the airport roof and are probably oxidation derived. Similarly, higher
591 alkanes (C₈-C₁₄) and nonanal have been found at increased levels at the fence of O’Hare
592 International Airport and was attributed to airport activities (City of Park Ridge, 2000). Decanal
593 has been previously identified as a VOC associated with exhaust from tested commercial aircraft
594 engines (EPA, 2009b).

595 The absence of 1,4-DCB is not surprising as it a chlorinated aromatic compound not
596 expected to be present in combusted fuel. It is worth mentioning that, in addition to heavy
597 alkanes, the following compounds were present at high intensities in take-off and approach
598 source profiles: 1,1,2,3-tetramethylcyclohexane, 1,1,3-trimethylcyclohexane, and 2-butyl-1,1,3-
599 trimethylcyclohexane.

600 3.3 Comparison with Bibliography

601 The comparison of aircraft exhaust emission measurements with previous studies needs to be
602 conducted with caution. Several parameters like the sampling distance, sampling techniques,
603 sampling conditions (real operations or in a test bed), age, model, and type of the engine
604 (commercial or military), can strongly affect the magnitude of the obtained results (Table 2).
605 Therefore, the safest way to compare results is through VOC speciation (expressed in % weight)
606 even though the above mentioned parameters could still play a role in the difference or similarity
607 of results.

608 Fig. S5 presents the comparison of the speciation of VOC groups obtained in this study with
609 those obtained by other studies. To conduct the comparisons, VOCs were reduced to cover
610 exactly the same species for all the studies. Thus, in Fig. S5 light alkanes are constituted of
611 ethane, propane, n-heptane; aldehydes/ketones are constituted of acrolein, propanal and acetone;
612 monoaromatics include toluene, ethyl benzene, m, p-xylene and o-xylene; and heavy alkanes are
613 constituted of nC₈-nC₁₂ straight chain alkanes. Comparisons were divided into comparisons with
614 engines tests (Fig. S5 (a), (b), (c)) and comparisons with measurements taken under real aircraft
615 operation that took place during taxi or idle power (Lelievre, 2009; Schürmann *et al.*, 2007). This
616 study is probably the first study to cover this range of VOC species at different thrust settings
617 measured under real conditions. As a reminder, according to ICAO (2008), the thrust levels for
618 idle, approach, and take-off are respectively 7%, 30%, and 80% of the rated thrust. However, in
619 real operation, the take-off thrust varies from aircraft to another according to the aircraft type and
620 engine model, flight load, meteorological conditions, runway conditions, etc. Thus, in reality, the
621 “take-off” sample collects a variety of different take-off thrusts which vary between 85 and
622 100% (Dennis Ting, 2009).

623 Fig. S5 (a) presents the comparison of the total VOC groups obtained in this study, at the average
624 of 3 powers, with that of Spicer *et al.* (1994). Fig. S5 (b) presents the comparison of total VOC
625 groups obtained in this study (minus aldehydes and ketones) with that obtained by Spicer *et al.*
626 (1994), Lelievre (2009), and Anderson *et al.* (2006). It can be seen that alkenes dominate the

627 VOC mass in the results obtained by Spicer *et al.* (Fig. S5 (a)), whereas light aldehydes/ketones
628 dominate the speciation in our study. On the other hand, by comparing our results to those
629 obtained by Lelievre, a similar speciation can be seen upon averaging the idle and approach
630 powers, whereas results obtained by Anderson *et al.* (2006) and Spicer *et al.* (1994) still show
631 higher domination of alkenes. This is probably due to the difference in the sampling location;
632 contrary to the mentioned studies in which sampling was done behind the engine exhaust as
633 small distances (0.3-30 m) behind the engine, sampling in our study was done either sideways at
634 relatively smaller distances (17-32 m to the left) or behind (130-190 m behind) to be able to
635 sample several aircraft in real operation without interfering with aircraft operations. The
636 difference can be also attributed to the difference in emissions between the CFM-56 engine
637 studied by Spicer *et al.* (1994), RB211-535E4 measured by Anderson *et al.* (2006), and our
638 averaged emissions for several engine types. The difference in emissions at idle power measured
639 in our study and taxi emissions measured during real aircraft operation by Schürmann *et al.*
640 (2007) can be related to the difference in aircraft type, age, engine type, etc. However, results
641 obtained by Schürmann *et al.* are of the same order as our results.

642 Finally, Fig. S5 (c) presents the speciation of heavy alkanes and monoaromatics measured in this
643 study (GC/FID and GC/MS) compared to the results obtained with Spicer *et al.* (1994), Lelievre,
644 and Eickhoff (1998). It can be seen that the speciation obtained in this study (GC/MS) is very
645 similar to that obtained by Eickhoff for the averaged test run of the engine CFM56-3B1, while
646 the speciation obtained with GC/FID (34% heavy alkanes) is similar to that obtained with CF6-
647 50C2/E2.

648 Fig. S5 (d) presents the comparison between results obtained in this study at idle power, to real
649 measurements taken for real in-use aircraft. A similar speciation is observed between our study
650 and that obtained by Lelievre (2009). Results obtained by Schürmann *et al.* (2007) (representing
651 3 aircraft engines) show a higher contribution of alkenes and heavy alkanes and a less
652 contribution of light alkanes.

653 4. Conclusion

654 To the best of our knowledge, this is the first study covering a wide range of VOCs to
655 assess emissions from a large number of in-use aircraft at various real modes of operation, as
656 close as possible to jet emissions. Results have shown that heavy alkanes and heavy aldehydes
657 may be the best tracers to distinguish jet exhaust emissions from gasoline sources in air quality
658 monitoring studies. These differences in the types of VOCs emitted act as “fingerprints” for the
659 sources. The main reason for the presence of heavy alkanes is that jet aircraft use a kerosene
660 based fuel (Jet A-1) that is mainly composed of heavy alkanes (11-14 carbon atoms) in contrast
661 to gasoline fuel. On the other hand, the presence of heavy aldehydes is due to both kerosene
662 combustion and the photo-oxidation of heavy alkanes. The identification of jet exhaust tracers
663 opens the door for future studies aiming at identifying the spatial extent of the impact of airport
664 activities in environments polluted by vehicle and aircraft emissions. On the other hand, the 30 s
665 × 6 sampling approach using a specific remote autosampler was proven to be more representative
666 of aircraft sources than the 30-min approach.

667 In the present work, alkanes, alkenes, alkynes (represented by acetylene), aldehydes, and
668 ketones were detected in jet exhaust as observed by Spicer *et al.* (1994). Since jet fuel is mainly

669 composed of long heavy alkanes, then the presence of light VOCs in aircraft exhaust was a result
670 of incomplete combustion rather than being unburned fuel. As for the total speciation of VOCs,
671 results confirmed the dominance of light aldehydes and ketones, followed by alkenes.

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List of Figures

Fig. 1. Top view of Beirut Rafic Hariri International Airport showing the sampling sites used in this study.

Fig. 2. VOC distribution by compound class determined by GC-FID from measurements performed in October 2014. (a) VOCs concentrations, (b) weight %.

This figure illustrates the distribution of average aircraft emissions using 2 sampling approaches (30 seconds repeated 6 times or continuous 30 min sampling at 100 mL min^{-1}), and average airport roof concentrations at a sampling duration of 30 min at 100 mL min^{-1} .

Fig. 3. Total VOC distributions by compound class determined by GC-FID for jet exhaust emissions at different modes of operation and for APU emissions. (a) VOCs concentrations, (b) weight %

This figure illustrates the total VOC distribution of average jet emissions during approach, idle, take-off, and from APU. The approach, idle, and take-off emissions were assessed by sampling for 30 seconds repeated 6 times, whereas the APU emissions were taken by continuous sampling for 3 min. The sampling rate was 100 mL min^{-1} .

Fig. 4. Speciation of VOCs by family obtained by GC-FID: (a) light alkanes, (b) heavy alkanes ($n\text{C}_8$ - $n\text{C}_{14}$: n-octane, n-nonane, n-decane, n-undecane, n-dodecane, n-tridecane, n-tetradecane) (c) light alkenes/acetylene, (d) monoaromatics, (e) light aldehydes and ketones. This figure illustrates the speciation of jet emissions during approach, idle, take-off and as well as APU emissions upon sampling for 30 seconds repeated 6 times at 100 mL min^{-1} .

Fig. 5. Heavy VOC groups determined by GC-MS from measurements conducted in June 2015. (a) VOCs concentrations, (b) weight %

This figure illustrates the distribution of jet fuel vapor emissions, average aircraft emissions using 2 sampling approaches (30 seconds repeated 6 times or continuous 30 min sampling at 100 mL min^{-1}), average airport roof concentrations at a sampling duration of 6 hr at 25 mL min^{-1} , and average gasoline exhaust emissions at a sampling duration of 30 min at 100 mL min^{-1} .

Fig. 6. Speciation of heavy alkanes ($n\text{C}_8$ - $n\text{C}_{14}$: n-octane, n-nonane, n-decane, n-undecane, n-dodecane, n-tridecane, n-tetradecane) and aldehydes (nonanal and decanal).

Fig. 1

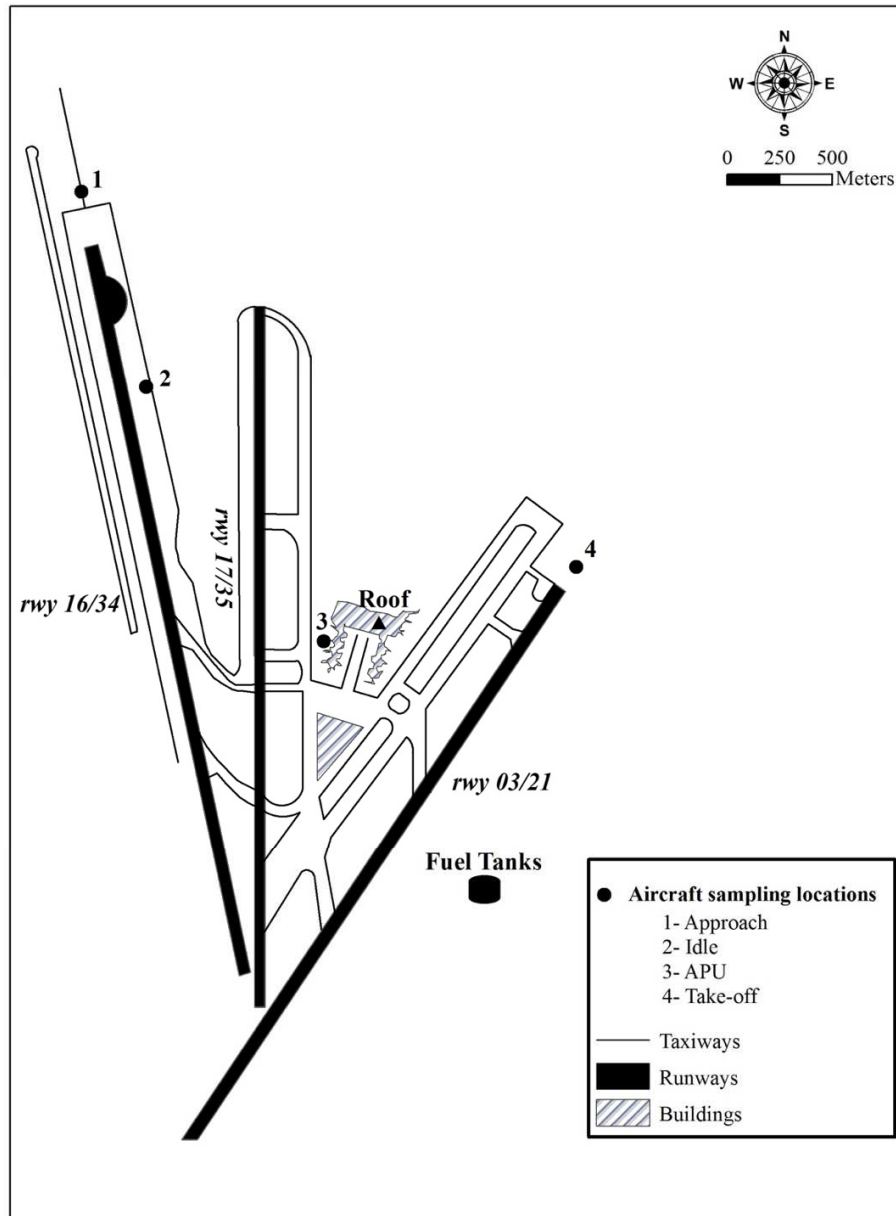
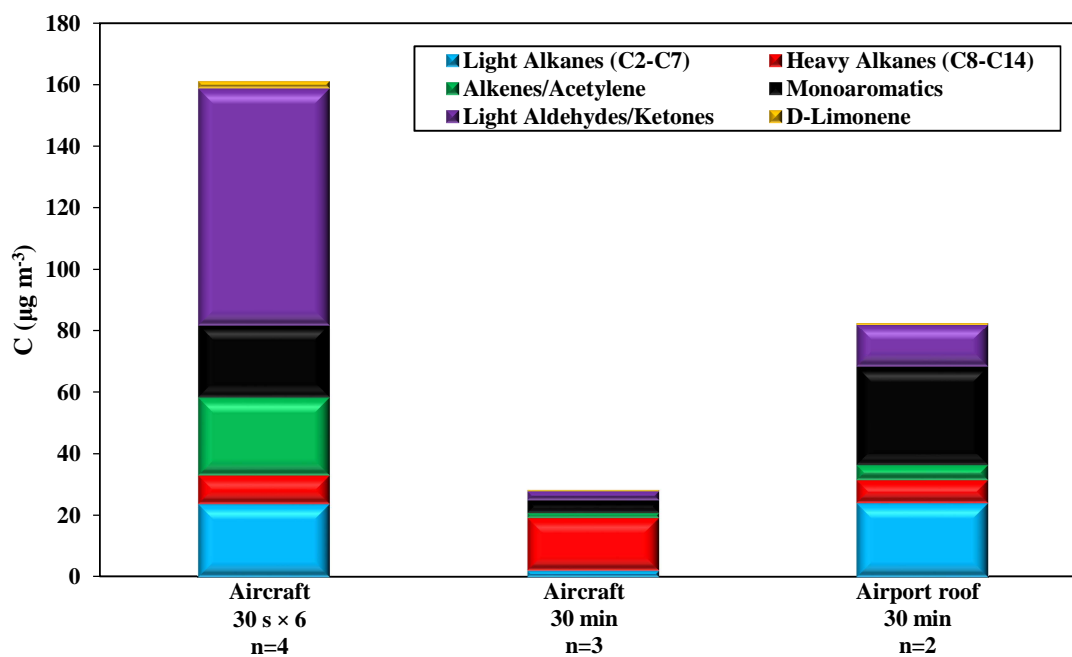
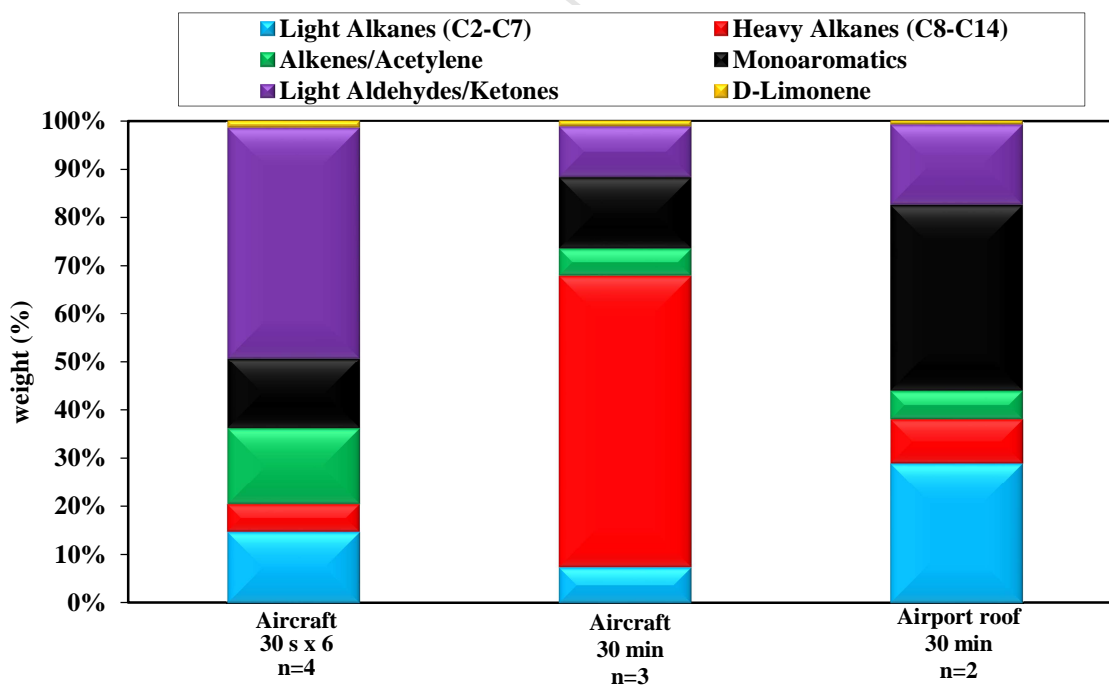


Fig. 2

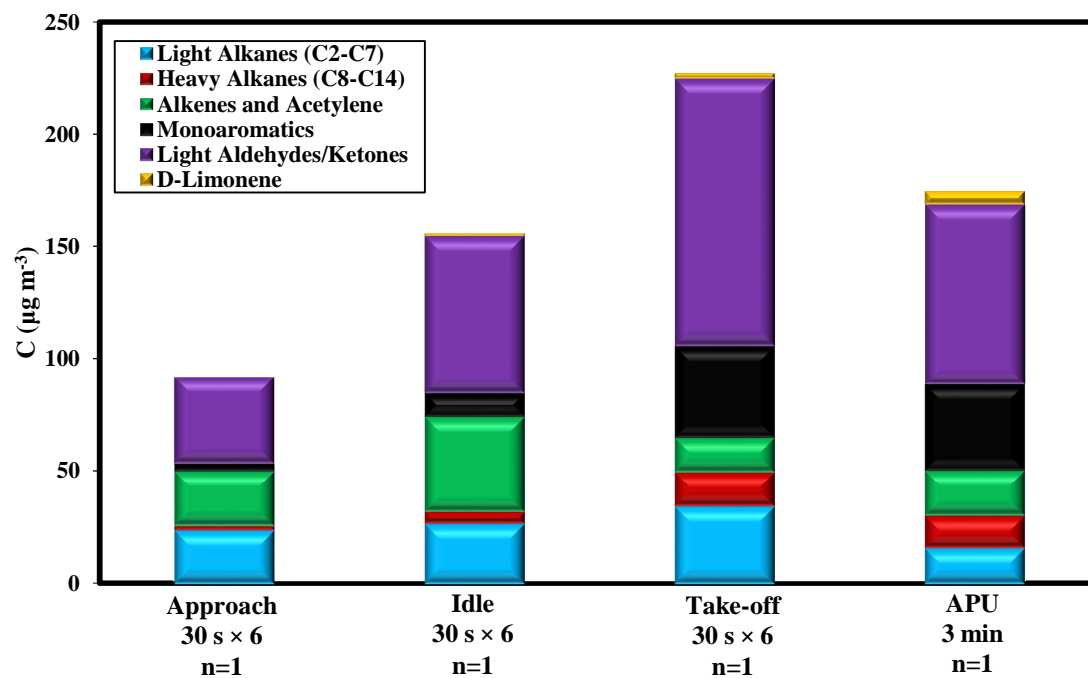


(a)

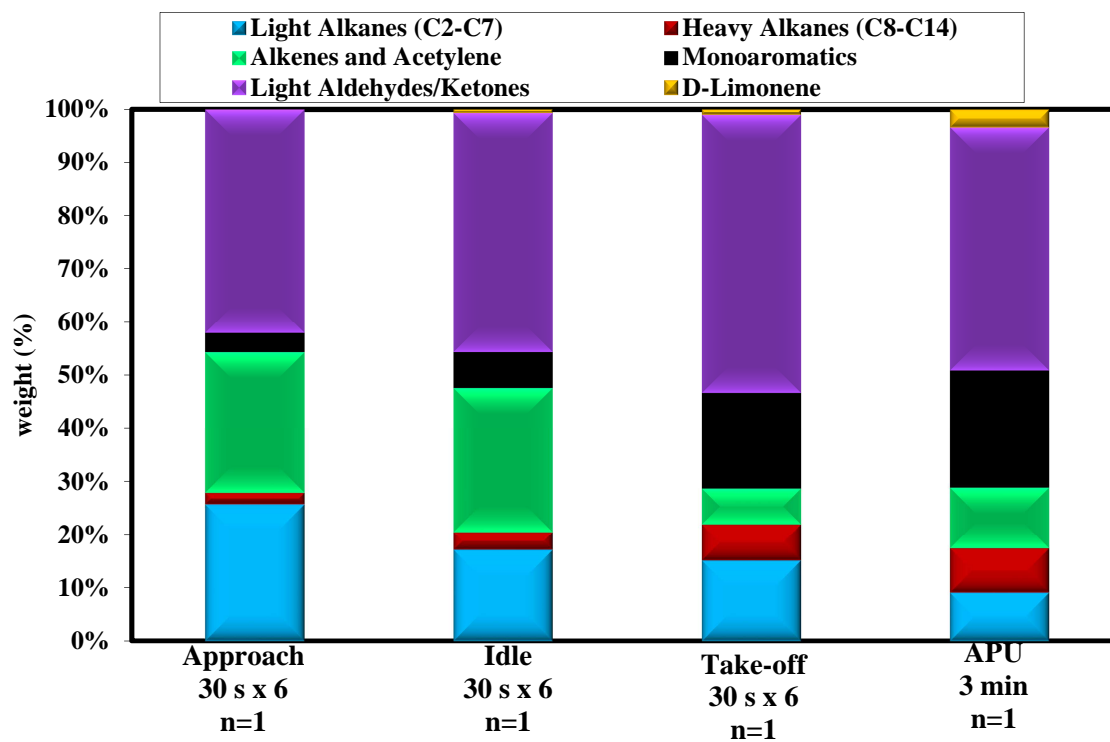


(b)

Fig. 3



(a)



(b)

Fig. 4

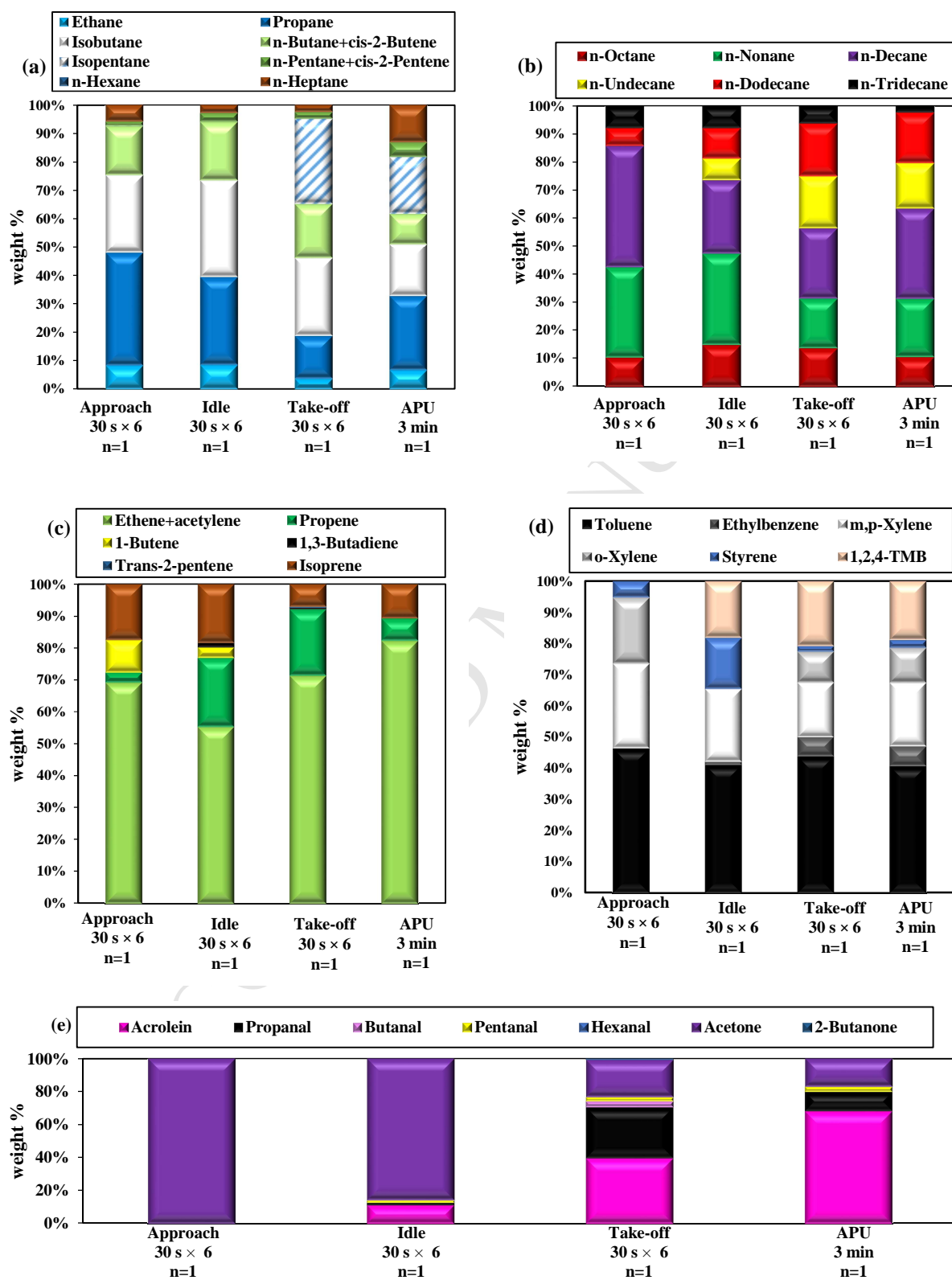
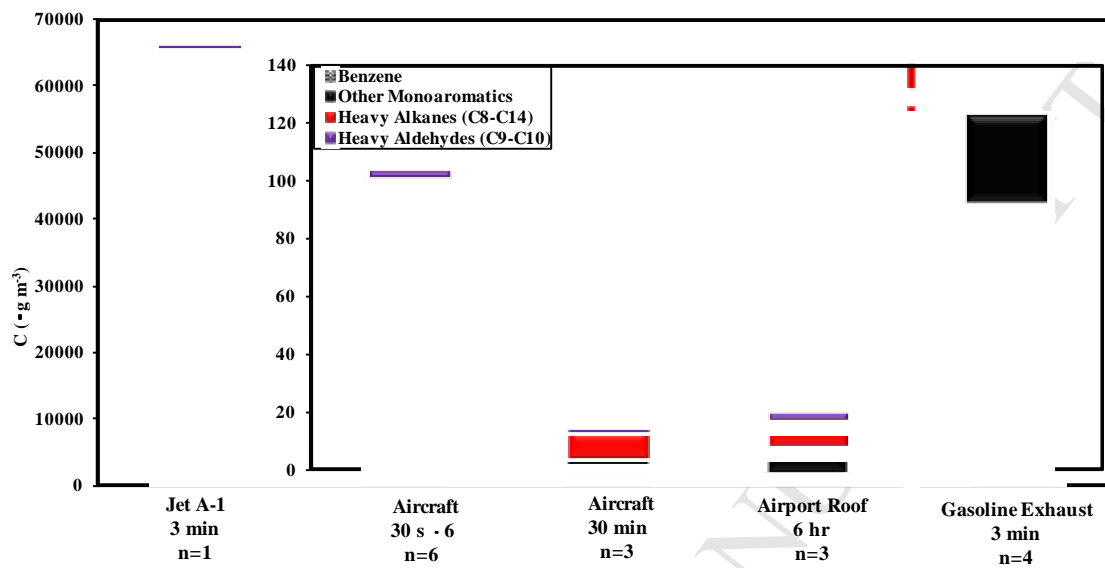
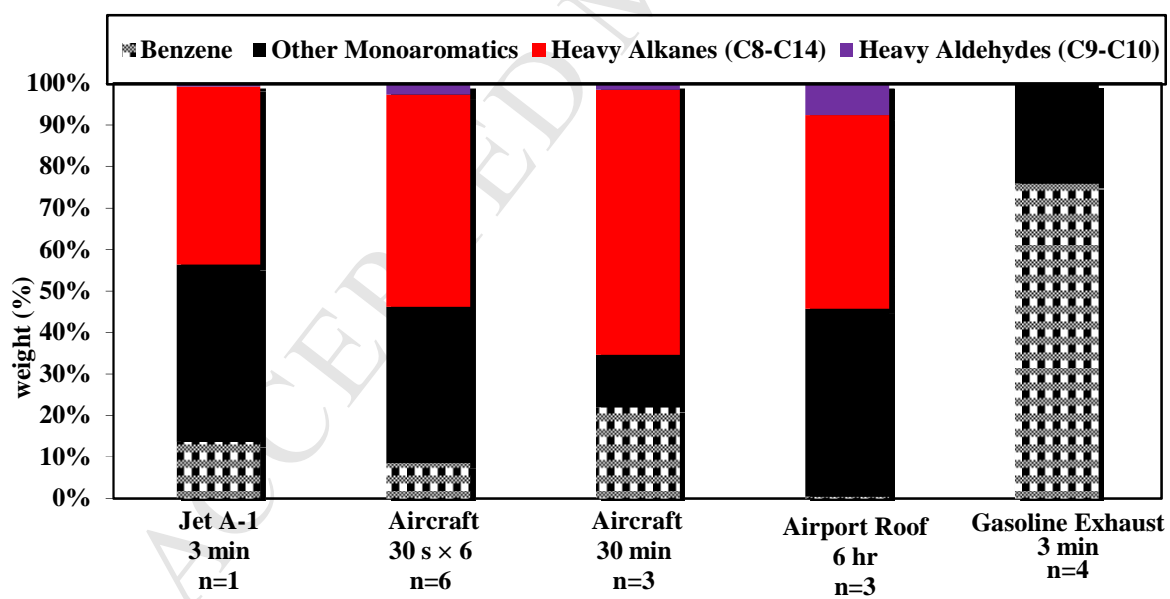


Fig. 5



(a)



(b)

Fig. 6

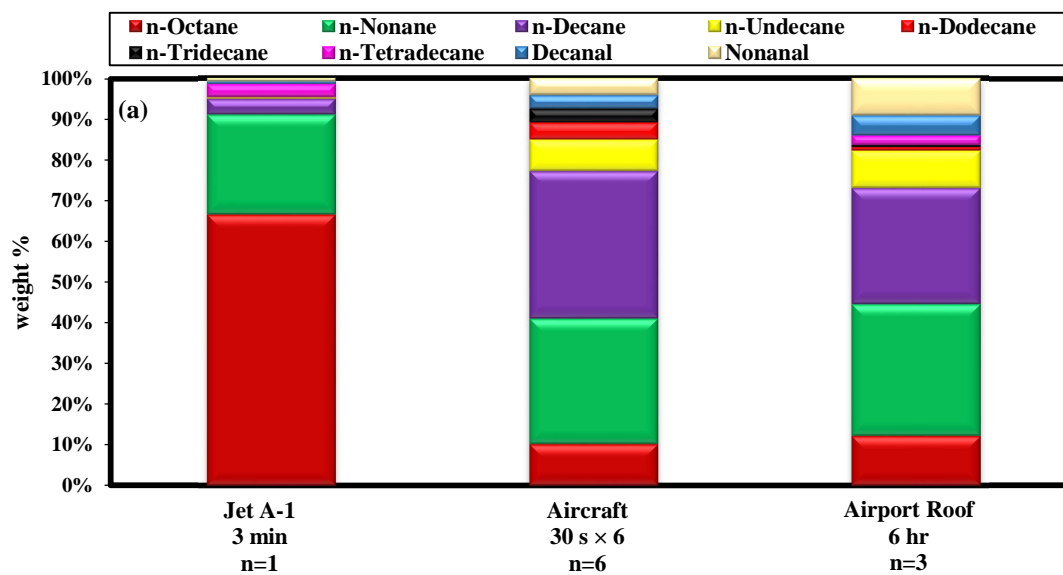


Table 1. Literature studies assessing emissions from engine tests or during real aircraft operation

<i>Engine Tests</i>						
Spicer <i>et al.</i>, (1984, 1994)	TF-39 (Military TF of Lockheed C-5) and CFM-56 (TF)	Total HCs, C ₂ to C ₁₇ organics, aldehydes	Sampling rake 0.3-0.6 behind the engine. Experimental: non-dispersive infrared instruments, chemiluminescence, FID, polymeric adsorbent (XAD) and DNP cartridges	[GC/MS, GC/FID], On-Line Cryogenic Trap/GC, canister [GC/MS], Total HC Analyser	Idle, 30%, 80%; [JP-4; JP-5; JP-8]	
Spicer <i>et al.</i>, (1992)	2 Engines: F101, used on the B-1B aircraft, and the F110, used on the F-16C and F-16D aircraft.	Total HCs, individual organic species	Samples collected from each engine using a probe positioned just behind the exhaust	-	4 power settings from idle to intermediate power	
EXCAVATE: Anderson <i>et al.</i> (2006)	NASA Boeing 757; Engine: Rolls Royce RB-211-535E4 (TF)	Gaseous carbon species	10 m behind the engine exit plane.	Canister, GC/MS	4-7%; 26%; 47%; 61%; [JP-5 low and high S]	
APEX-3: Knighton <i>et al.</i> (2007); Kinsey (2009); Timko <i>et al.</i> (2010)	B737-300, ERJ-145, A300, B775, plus Learjet Model 25. Engines: CFM56-3B1, AE3007A1E, plus others	CO ₂ , HC, PM _{2.5}	Sampling: 30 m downstream of the engines Experimental: continuous and time-integrated instruments: IR	PTR-MS	4%, 7%, 15%, 30%, 45%, 65%, 85%, 100%, Jet A	
Eichkoff (1998)	CF6-50C2/E2, CFM56-3B1	103 organic compounds	30 m	GC-MS	Average load	
<i>Real Aircraft Operation</i>						
Herndon <i>et al.</i> (2006)	Regional jets, B737s, MD88s, and B757s	Formaldehyde, acetaldehyde, benzene, and toluene	Continuous analysis through a sample port located on the front of the truck.	PTR-MS	Idle, taxi, approach (or landing), and take-off	
Schürmann <i>et al.</i> (2007)	Engines from 3 aircraft	VOCs	50-100 m behind an aircraft, at a height of 1 m	Canister/GC-FID	Taxi, ignition	
Zhu <i>et al.</i> (2011)	-	VOCs: butadiene, benzene, acrolein, Formaldehyde,	At blast fence (140 m from the take-off)	Canister	Take-off	
Lelievre (2009)	B757- 200, B777-200	VOCs	200 m below the flow reactor	Canister, ATD-GC-FID	Taxi	

Table 2. Volatile organic compounds in jet engine emissions (units converted to $\mu\text{g m}^{-3}$)
(Spicer *et al.*, 1994; Eichkoff, 1998; Anderson *et al.*, 2006; Schürmann *et al.*, 2007)

	<i>This Study</i> ^a							<i>Spicer</i>			<i>Eichkoff</i> ^b	<i>Anderson (RB211-535E4)</i>			<i>Schürmann</i>
Sampling distance (m)/position wrt engine	10 m/ down- stream		17 m/ left	8-9 m/ below		130-190m/ behind		0.3-0.6 m/behind			30 m/ behind	1 m behind			50 -100 m behind
Engine Status*/ Flight mode	APU A330 (GC-FID)	APU A330 (GC-MS)	Touch down (GC-FID)	Approach (GC-FID)	Approach (GC-MS)	Take-off (GC-FID)	Take-off (GC-MS)	Idle	30%	80%	Averaged run	4-7%	26%	61%	Taxi
n-Octane	1.52	bDL	0.78	0.21	22.10	2.10	3.31	664.96	bDL	bDL	0-120				0.56-11.74
n-Nonane	2.97	6.53	1.70	0.64	55.96	2.72	bDL	746.63	53.33	bDL	20-760				1.13-35.96
n-Decane	4.66	9.70	1.39	0.87	34.63	3.88	3.77	4259.53	76.91	11.83	30-1480				-
n-Undecane	2.32	bDL	0.40	n.d.	8.62	2.83	4.52	6499.38	58.49	129.99	30-1010	-	-	-	-
n-Dodecane	2.57	bDL	0.57	0.13	2.67	2.87	2.90	7365.62	502.85	297.46	20-850				-
n-Tridecane	0.36	bDL	0.42	0.16	bDL	0.97	2.89	9275.49	114.99	168.65	20-570				-
n-Tetradecane	bDL	bDL	bDL	bDL	bDL	bDL	bDL	7754.12	156.73	164.98	20-270				-
Nonanal	-	bDL	-	-	bDL	-	2.37	-	-	-	-	-	-	-	-
Decanal	-	bDL	-	-	2.02	-	3.60	-	-	-	-	-	-	-	-
Benzene	-	3.74	-	-	bDL	-	22.52	13413.48	64.96	64.96	60-690	36.70	1.17	1.62	7.77-39.20
Toluene	15.69	3.63	4.35	1.59	9.98	17.94	10.77	5976.65	38.31	-	70-260	15.55	3.60	3.14	6.06-28.37
Ethylbenzene	2.45	0.24	0.11	n.d.	4.99	2.59	2.47	1854.1	bDL	bDL	10-180	2.87	0.57	0.44	1.42-12.19
m, p-Xylene	7.92	0.77	2.48	0.94	13.66	7.18	3.16	3001.6	bDL	bDL	20-450	6.40	1.77	2.25	4.03-25.90
o-Xylene	4.32	1.95	n.d.	0.72	13.06	4.06	2.70	1765.6	bDL	bDL	10-350	4.99	1.28	1.46	1.89-17.97
Styrene	0.95	0.62	1.74	0.18	0.45	0.71	0.37	3291.23	43.31	-	10-90	-	-	-	1.75-17.95
1,2,4-TMB	7.25	1.92	1.91	n.d.	36.67	8.47	0.95	-	-	-	-	3.55	1.85	2.05	-
1,4-DCB	-	bDL	-	-	bDL	-	bDL	-	-	-	-	-	-	-	-
Propyllbenzene	-	0.59	-	-	2.36	-	0.11	-	-	-	-	-	-	-	-
Butylbenzene	-	0.53	-	-	4.19	-	0.18	-	-	-	-	-	-	-	-
Acrolein	54.74	-	7.87	bDL	-	46.87	-	9790.10	23.31	23.31	62-190				
Propanal	9.23	-	bDL	bDL	-	37.23	-	2897.96	24.15	24.15	-				
Butanal	bDL	-	bDL	bDL	-	4.18	-	-	-	-	-	-	-	-	-
Pentanal	2.44	-	1.00	bDL	-	2.87	-	-	-	-	-	-	-	-	-
Hexanal	bDL	-	bDL	bDL	-	bDL	-	-	-	-	-	-	-	-	-
Acetone	13.67	-	60.37	38.75	-	26.92	-	1473.13	386.40	166.63	-	-	-	-	-
2-Butanone	bDL	-	bDL	bDL	-	0.87	-	-	-	-	-	-	-	-	-

Table 2. (Continued): Volatile organic compounds in jet engine emissions (units converted to $\mu\text{g m}^{-3}$)

Sampling distance (m)/position wrt engine	<i>This Study^a</i>							<i>Spicer</i>			<i>Eichkoff^b</i>	<i>Anderson (RB211-535E4)</i>			<i>Schürmann</i>
	10 m/ down- stream		17 m/ left	8-9 m/ below		130-190m/ behind		0.3-0.6 m/behind			30 m/ behind	1 m behind			50 -100 m behind
Engine Status*/ Flight mode	APU A330 (GC-FID)	APU A330 (GC-MS)	Idle (GC-FID)	Approach (GC-FID)	Approach (GC-MS)	Take-off (GC-FID)	Take-off (GC-MS)	Idle	30%	80%	Averaged run	4-7%	26%	61%	Taxi
D-Limonene	5.90	-	1.00	bDL	-	2.29	-	-	-	-	-	-	-	-	-
Ethane	1.05	-	2.23	1.94	-	1.23	-	1388	50.01	bDL	-	21.51	3.93	2.40	4.46-24.51
Propane	4.08	-	8.15	9.31	-	5.14	-	312	18.34	bDL	-	9.11	3.12	1.93	2.75-5.15
Isobutane	2.90	-	9.07	4.05	-	6.56	-	-	-	-	-	1.81	0.77	0.65	0.39-3.24
n-Butane+cis-2-Butene	1.69	-	5.44	6.46	-	9.30	-	-	-	-	-	8.14	2.27	1.74	1.80-9.73
Isopentane	3.14	-	bDL	0.35	-	0.80	-	-	-	-	-	3.45	1.32	0.81	1.80-49.52
n-Pentane+cis-2-Pentene	0.81	-	0.82	bDL	-	10.18	-	-	-	-	-	1.05	0.45	0.30	1.15-7.14
n-Hexane	bDL	-	bDL	bDL	-	bDL	-	-	-	-	-	0.79	0.36	0.36	0.33-1.45
n-Heptane	2.07	bDL	0.77	1.40	4.80	0.87	8.73	583.34	bDL	bDL	10-50	7.71	2.54	8.54	0.31-0.98
Ethene +Acetylene	16.28	-	20.30	16.73	-	10.57	-	48892	bDL	bDL	-	579.66	2.40	1.78	58.37-191.13
Propene	1.39	-	7.88	0.74	-	3.08	-	18092	18	bDL	-	118.98	0.38	0.42	18.89-159.55
1-Butene	bDL	-	1.20	2.45	-	bDL	-	9332	23	47	-	31.03	0.12	0.16	4.64-43.18**
1,3-Butadiene	bDL	-	0.53	bDL	-	0.07	-	8974	bDL	22.5	-	34.19	bDL	bDL	bDL-11.11
Trans-2-Butene	bDL	-	0.86	bDL	-	0.80	-	11120***	23***	bDL	-	3.13	0.12	0.05	0.56-5.42
1-Pentene	bDL	-	2.64	0.27	-	bDL	-	5161	bDL	bDL	-	-	-	-	bDL-19.95
Trans-2-Pentene	bDL	-	bDL	bDL	-	bDL	-	-	-	-	-	-	-	-	bDL-3.91
Isoprene	2.10	-	6.69	4.21	-	1.04	-	-	-	-	-	7.00	0.11	bDL	0.84-9.43
1-Hexene	bDL	-	2.20	bDL	-	bDL	-	5879	35	-	-	-	-	-	-
TVOC ($\mu\text{g m}^{-3}$)	174.7	30.2	155.9	92.11	216.2	227.2	75.3	113311	601	283	62-190	820	15	10	140-400

^aNote that concentrations presented for this study correspond to samples taken using the 30 s \times 6 approach

^bCF6-50C2/E2, CFM56-3B1

*Engine power setting is given in percent of maximum rated thrust.

**1-Butene coelutes with propyne

***cis-2-butene + trans-2-butene

bDL: below Detection Limit

1

ACCEPTED MANUSCRIPT

Research highlights

- 48 VOCs were measured from commercial aircraft under real operation.
- Heavy alkanes and aldehydes were identified as aircraft exhaust tracers.
- Airport ambient VOCs concentrations are influenced by jet emissions.
- APU VOCs emissions are of the same order of magnitude as main jet engine emissions.