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VOC Tracers from Aircraft Activities at Beirut Rafic Hariri International Airport

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Abstract

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

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

1. Introduction

The world combined passenger and cargo traffic, expressed in revenue tonne-kilometres, is expected to grow at the average annual growth rate of 5.0 per cent over the forecast period 2010-2030 (CAEP 9, 2013). This will yield an increase in emissions which can significantly degrade...
local air quality near airports. The impact of air traffic on local air quality has been the subject of several studies in recent years (Pison and Menut, 2004; Yu et al., 2004; Carslaw et al., 2006; Westerdahl et al., 2008; Dodson et al., 2009). Aircraft engine emissions include non-volatile particulate matter that are harmful to human health and the environment (Barrett et al., 2010; Stettler et al., 2011; Yim et al., 2015) and unburned hydrocarbons (UHCs) which cause adverse health effects on exposed groups (workers, passengers, residents who live near large hubs) (Masiol and Harrison, 2014). UHCs comprise polycyclic aromatic hydrocarbons (PAHs) which are possible human carcinogens (Masiol and Harrison, 2014); as well as volatile organic compounds (VOCs) where the contribution of aircraft to their concentration levels is of particular concern. VOCs are toxic – many of which are even carcinogenic (Wood, 2008), primary precursors of tropospheric ozone formation, and contributors to suspended particulate matter (PM) formation (Masiol and Harrison, 2014).

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

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

Thus, the aim of this research was to identify aircraft tracers by characterizing the relative emissions of 48 VOCs (C$_2$-C$_{14}$) from the exhaust of around 100 commercial aircraft under real-world conditions. Measurements included aircraft during the different phases of the LTO-cycle as well as at the gate (APU). For comparison, gasoline exhaust emissions were assessed. The difference in the speciation between aircraft emissions and vehicle emissions will open a door to for future studies to assess the spatial extent of the impact of aircraft activities. Samples were taken at Beirut Airport (Lebanon) and transported to the University of Strasbourg (France) for analysis where gas chromatographic techniques (GC-FID and GC-MS) were used to assess their VOC species contents. To the best of our knowledge, this is the first study covering a wide range of VOCs to assess emissions from a large number of in-use aircraft at various modes of LTO operation.

2. Materials and Methods

2.1 Study Area

The airport of study is Beirut Rafic Hariri International Airport, the only operational commercial airport in Lebanon. It is a midsize commercial and military airport located at 33.82N 035.49E, in the Khaldeh suburb about 8 km south of the capital’s (Beirut) city center. The west side of the airport is open to the sea while the east side is surrounded by Mount Lebanon where citizens live at close proximity to the airport. Beirut airport has three runways and 14 taxiways. A map of the airport is shown in Fig. 1. The runways are named according to their magnetic heading; and are runways 03/21, 16/34, and 17/35. The surface wind direction is south west throughout most of the year with light wind up to 2.6 m/s, which makes Beirut Airport operates southerly (take-off) and northerly (landing). Runway 21, located to the east of the airport center, is the main departure runway due to the prevalence of southwest wind conditions. It extends to 3800 m and is 45 m wide (Lebanese DGCA, 2010) making it well equipped to accommodate a variety of aircraft. Runway 16 is the main landing runway due to the prevalence of wind...
conditions; while runway 17 is mainly used for landing and take-off of private and military jets. The airport code number is 2E; it handles a wide range of flights (65500 flights/yr for the years 2013-2015) including international passenger, air freight, military, and domestic air traffic; it is primarily utilized by the Middle East Airlines (around 50% of the total fleet) (Lebanese DGCA, 2015; 2016).

2.2 Measurement Sites

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

To compare aircraft emissions to vehicle emissions, it was important to assess VOCs from vehicle exhaust using the same sampling and analysis techniques as the aircraft related samples, and to measure vehicle emissions from the local fuel due to the strong correlation between the fuel composition and VOC emissions (Wang et al., 2013). The main focus was on gasoline exhaust emissions, which were chosen to represent vehicle emissions since the majority of vehicles in Beirut operate on gasoline. In Lebanon, light duty vehicles operate on gasoline while only heavy duty vehicles are allowed to run on diesel that constitute only 4% of the total vehicle fleet (Waked and Afif, 2012). Thus, the second subset aimed at identifying fingerprint
gasoline exhaust emissions from gasoline, specifically gasoline type 95 – octane unleaded, that represents 85% of gasoline used in Lebanon for the past 4 years (MoEW, 2017). The vehicle exhaust gas was sampled into adsorbent tubes via a Teflon tube from a sampling point located about 30 cm after the tailpipe end. Gasoline exhaust sampling was conducted on Dacia Logan 2007 (4 cylinders 1600 cc), which was in good working conditions and is a good stereotype of automobiles currently found in Beirut area. Of course, sampling from gasoline exhaust took place far away from direct aircraft sources.

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

2.3 Sampling Methodologies

Air samples were collected using multi-bed stainless steel thermal desorption tubes suitable for trapping C\textsubscript{2}-C\textsubscript{12} VOCs. These home-made tubes were fabricated at the University of Strasbourg (EPA, 1999; Liaud Céline, 2014) by packing them with 10 mm Carbosieve\textsuperscript{TM} S-III (60/80 mesh, 100 mg) designed to trap light VOCs from C\textsubscript{2} to C\textsubscript{5}; and 35 mm Carbopack\textsuperscript{TM} B column (60/80 mesh, 160 mg) designed to trap heavier C\textsubscript{5}-C\textsubscript{12} VOCs (Jochmann \textit{et al.}, 2014). The use of these adsorbents together is widespread and commercially found under the name “Air Toxics” (Supelco). These tubes are compatible with Perkin Elmer thermal desorption systems present in the laboratory, and possess similar trapping performance to that of “Air Toxics”. Both seem not at all suitable to trap ethane, ethene, and acetylene at room temperature (Liaud, 2014). In addition, these tubes are not most suitable for n-tridecane and n-tetradecane regarding the recommendations given for carbopack\textsuperscript{TM} B, even if these two compounds were not tested by Liaud (2014). However, due to the sticky nature of the aforementioned heavy VOCs, we assumed that these tubes can still be used to adsorb them (Ras \textit{et al.}, 2009). Note that tubes were sealed with Swagelok end caps fitted with PTFE ferrules. Prior to sampling, tubes were conditioned by thermal cleaning at 350°C under a helium flow rate of 50 mL min\textsuperscript{-1} for 3 h by using the function “conditioning” of the automated thermal desorber. After conditioning, the tubes were sealed with Swagelok end caps fitted with PTFE ferrules and stored in proper isolated boxes. After sampling, the tubes were immediately sealed, stored in Lebanon in the refrigerator at T < 4°C, and then sent to the University of Strasbourg to be analyzed within 30 days after sampling.

Active samples of ambient air and diluted exhaust gases were collected inside thermal desorption tubes using a portable battery-operated automatic sampler (Liaud, 2014) designed in ICPEES (Institute for Chemistry and Processes for Energy, the Environment and Health) - Group of Atmospheric Physical-Chemistry laboratory at the University of Strasbourg. This sampler is composed of a pump located downstream of a mass flow controller that was used to collect a constant flow of air into the empty adsorbent tube. By the very low pressure drop of the low-\(\Delta P\)-flow mass flow controller (Bronkhorst), this machine was totally adapted to air sampling at atmospheric conditions with a full range of 500 mL min\textsuperscript{-1}, uncertainty of 1% of the full range, and 0.3% precision on the measurement of the mass flow controller. By means of its practical dimensions (width: 61 cm, height: 32 cm, depth: 20 cm, weight: 4 kg) and its battery power supply, this sampler facilitated sampling at any site in the airfield without being constrained with the necessity of electrical supply. Furthermore, its configuration can be operated unmanned with
the remote control option which made it possible to control the machine without having to access unsafe sites close to aircraft. The most suitable sampling conditions for a quantitative trapping of the majority of the target VOCs in a 3L sample were sampling at 100 mL min$^{-1}$ for 30 minutes based on the optimization performed by Liaud (2014). Thus, the sampling flow rate was fixed at 100 mL min$^{-1}$ for most of the samples, whereas the sampling duration varied. To determine the most representative sampling approach for aircraft signature emissions, two sampling strategies were adapted: (i) 30 seconds sampling repeated 6 times to collect emissions from 6 aircraft (30 s × 6) for a total volume of 0.3 L or (ii) continuous 30 min sampling during rush hours for a total volume of 3 L. In both sampling strategies, plumes of 6 aircraft were sampled. Due to the presence of a constant flow of emissions, continuous 3 min-sampling was performed for APU, Jet A-1 vapor, and gasoline exhaust emissions at a total volume of 0.3 L, similar to the 30 s × 6 sampling strategy. To measure the ambient airport concentration, samples were taken for a duration of 6 hrs at 25 mL min$^{-1}$. The choice of a lower flow rate was to avoid the breakthrough of the sampled VOCs through the adsorbents cartridge.

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

2.4 Analytical Methods

2.4.1 Chemicals and Materials

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

To perform calibration curves from gaseous standards, on-line calibration was adopted (Liaud, 2014; Liaud et al., 2014). The standard gas cylinder containing light alkanes, acetylene, and alkenes was diluted from a concentration of 100 ppb with nitrogen gas (99.999% purity), in
order to reach targeted concentrations of the order of 0.1 to 20 ppb conventionally encountered in ambient air. On the other hand, liquid spiking was performed to prepare calibration curves for light aldehydes and ketones, d-limonene, chlorinated alkenes, and monoaromatics, using a homemade converted GC injection port, ThermoFinnigan AS3000 (Milan, Italy) with a syringe (Liaud, 2014; Liaud et al., 2014). Because of the sticky nature of heavy alkanes (C₉-C₁₄ in specific) and heavy aldehydes (C₉-C₁₀) on the silica capillary (located between the adsorbent tube and the injector) maintained at room temperature, it was not possible to perform liquid spiking for these VOCs using the converted injection port, and automatic spiking was replaced with manual spiking where the deposition was made directly on the adsorbent tube. For this, 10 µL of the previously prepared standard solutions were manually injected with a micropipette, followed by purging the spiked tube for 10 min with N₂ at a flow rate of 50 mL min⁻¹ to remove excess methanol. Liquid standard concentrations ranged from 0.2 to 100 mg L⁻¹ for light aldehydes, ketones, and d-limonene; 20 to 100 mg L⁻¹ for n-nonane and n-undecane; and 100 to 500 mg L⁻¹ for nonanal and decanal. As for the mixture which contains heavy alkanes and 4 monoaromatics, the concentrations varied between 1.5-7 mg L⁻¹ to 8.5-39 mg L⁻¹. The variation in concentration for each VOC is according to the mass fraction of each component in the mixture. For BTEX, 1,2,4-trimethylbenzene, 1,4-dichlorobenzene, and styrene, the standard concentrations varied between 2.5 and 40 mg L⁻¹.

### 2.4.2 Analysis Techniques

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

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

The first analytical system used was a Perkin Elmer gas chromatograph Clarus® 580 with a dual column system and twins FID. A capillary column, Perkin Elmer Phase Elite-1, 60 m × 0.25 mm ID × 0.25 µm was used to separate heavy VOCs. The second column, Restek Rt®-Q-BOND, 30 m × 0.32 mm × 10 µm, allowed the separation of the lightest target VOCs. This analytical chain is equipped with a switching system, Dean switch, which permits the use of one or two chromatographic columns connected in series. The optimization of the chromatographic separation was studied by Liaud (2014). The identification of VOCs was based on the match of the retention times. Quantification was conducted by means of the external standard method.
The second analytical system was equipped with a gas chromatograph, 6890N Network coupled to a mass selective detector, 5973N Network MSD provided by Agilent Technologies (Santa Clara, CA, USA). The chromatographic separation of VOCs was conducted on a DB-5MS column (Agilent), 60 m × 0.25mm × 1µm. This column is non-polar and thus is suitable for the separation of the targeted VOCs. It should be noted that the absence of a second type of column Rt-Q-BOND in this system does not allow the separation of lighter compounds. For the sake of consistency between the two analytical systems, helium flow rate through the system was maintained at 1.2 mL min\(^{-1}\). MSD ChemStation software (Agilent, USA) was used to acquire mass spectrometric data. For quantitative assessment, the extracted ion chromatograms (EICs) were recovered with the target ions and quantification was performed by the use of the external standard method. The most specific fragment ion in the spectra of each identified VOC was determined as the target ion. More details about the optimized analytical conditions for both apparatus are given in table S1 in the supplementary material.

All the analytical parameters are reported in Tables S2 and S3 in the supplementary material. Calibrations, prepared via both modes of the ATD, showed excellent linearity. For GC-FID, \(R^2\) values were 0.99 for all VOCs except for propional (0.98) and acetone (0.98). For GC-MS, \(R^2\) values were 0.99 for all VOCs except for n-undecane, n-dodecane, and n-tetradecane (0.91-0.94) (refer to tables S2 and S3 in the supplementary material). The limit of detection (LOD) (ng) was calculated as the quantity of analyte (ng) that will yield a signal to noise ratio (S/N) equal to 3. For GC-FID, LOD values varied between 0.03 (n-tetradecane) and 1.4 ng (acrolein and propional). For GC-MS, LOD values ranged from 0.04 ng for propylbenzene to 4.21 ng for n-octane. LOD values were transposed to airborne concentrations (µg m\(^{-3}\)) for both given sampling air volumes of 0.3 and 3 L. For a sampling volume of 0.3 L, LOD values varied between 0.10 and 4.58 µg m\(^{-3}\) for GC-FID and between 0.14 (propylbenzene) and 4.21 (n-octane) µg m\(^{-3}\) for GC-MS. For a sampling volume of 3 L, the corresponding LOD values varied between 0.01 and 0.46 µg m\(^{-3}\) (GC-FID) and between 0.01 and 0.42 µg m\(^{-3}\) (GC-MS). For GC-FID (Table S2), the uncertainty of the measured concentrations ranged between 21.0 and 25.3% for most of the VOCs except for acetone (30.4%). For GC-MS (Table S3), the uncertainty of the measured concentrations mostly ranged between 21.8 and 25.7%, with highest values corresponding to n-dodecane (51.9%), n-tetradecane (55.6%), and n-undecane (55.8%) that also possess lower \(R^2\) values.

3. Results and Discussion

The 48 VOCs measured mainly represent the most abundant compounds from aircraft emissions according to previous studies, and are divided into different chemical families i.e. light alkanes (C\(_2\)-C\(_7\)), heavy alkanes (C\(_8\)-C\(_{14}\)), alkenes (C\(_2\)-C\(_6\)), light aldehydes and ketones (C\(_2\)-C\(_6\)), heavy aldehydes (C\(_9\), C\(_{10}\)), monoaromatics, and d-limonene. Because sampling conditions could be very different (e.g. meteorology, light, etc.) from one sample to another or from one day to another, the results will often be presented and discussed in terms of percentages and not as quantitative data, as seen in previous studies (Anderson et al., 2006; Lelievre, 2009; Spicer et al., 1984). We will first present the total VOC speciation from aircraft exhaust identified using GC-FID (section 3.1), then we present VOC aircraft tracers identified using GC-MS (section 3.2).

We have defined a speciation per site by averaging all data collected at the same site and with the same sampling strategy, 30 min or 30 s × 6. The profile labelled “Aircraft” constitutes the
average of samples collected near the aircraft when either the APU or the main turbine engines were running (e.g. samples collected at the sites approach, take-off, and APU). Note that aircraft engines as well as APUs are supplied by the same fuel type stored in the tanks at the aircraft wings i.e. Jet A-1 kerosene fuel (Airbus, 2018; Boeing, 2002). Jet A-1, the most commonly used fuel for commercial aviation around the world, is produced according to an internationally agreed standards with unique physical and chemical properties (ASTM D1655) (IATA, 2015; Ritchie et al., 2003).

\section*{3.1 Complete Speciation of VOCs}

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

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

\subsection*{3.1.1 Distribution of VOC Groups at Different Engine Powers}

Results confirm that VOC compositions in jet exhaust vary with engine power settings (see Fig. 3). As the engine power increased from idle to approach phase, TVOC decreased by a factor of 1.7 from 156 µg m\(^{-3}\) to 92 µg m\(^{-3}\). These results could be expected. Indeed, turbine engines primarily emit CO and NMHC species as a result of incomplete combustion of jet fuel (Anderson et al., 2006). The relative amounts of NMHC emissions depend on combustor temperature and pressure, fuel to air ratio, and the extent to which fuel is atomized and mixed...
with inlet air. VOC emissions are higher at low power settings when the temperature of the air is relatively low and the fuel atomization and mixing process is least efficient. This is also according to ICAO databank sheets for unburned hydrocarbons (UHC) for all modern turbine engines; all engines produce less CO and NMHC emission per kg of fuel burned as their power levels are increased above idle (Anderson et al., 2006). In comparison to our observations, Spicer et al. (1994) found that TF-39 and CFM-56-3 engines exhibited larger decreases in NMHC emissions with increasing engine power. These differences, which can be mostly accounted for by the fact that the TF-39 and CFM-56-3 engines produce much higher levels of emissions at idle (low power) than do the newer commercial engines which relates to the significant improvements in engine efficiency and the technical progress to reduce emissions (Masiol and Harrison, 2014).

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

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

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

### 3.1.2 Speciation of VOC Groups at Different Engine Powers

The fraction of each species of the VOC family is known as the species “abundance”, presented as a percent of the VOC family (weight %) on the basis of µg m$^{-3}$. The set of species abundances for a source, illustrated in Fig. 4, is known as the “source profile” or “source fingerprint” (Conner et al., 1995; Henry et al., 1994). Information regarding the distribution of emissions by carbon number is important because such data can distinguish the cracking and partial oxidation products from unburned fuel (Spicer, 1990). Light alkanes from aircraft emissions were mainly dominated by propane and isobutene (idle and approach) as illustrated in Fig. 4(a). According to previous studies (Anderson et al., 2006; Schürmann et al., 2007), light alkanes were dominated by ethane and propane at these thrust settings. The fact that ethane
contributes less to the light alkane speciation in our study can be attributed to the weak adsorption properties of the used adsorbent, i.e. Carbosieve® S-III for light VOCs, with C₂ molecules, as previously mentioned by Liaud (2014).

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

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

### 3.2 Aircraft Tracers

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

We have defined a speciation per site by averaging all data collected at the same site and with the same sampling strategy, 30 min or 30 s × 6. The profile labelled “Aircraft” constitutes the average of samples collected near the aircraft when either the APU or the main turbine engines were running, i.e. samples collected at the sites approach, take-off, and APU. In the case of the 30 s × 6 “approach”, 6 samples were averaged to assess heavy VOCs, while 3 samples were averaged to represent the speciation obtained using the 30-min “approach” (see Fig. 5). The
profile labelled “Airport Roof” constitutes of 3 samples taken at the airport roof to assess the ambient airport concentrations affected by the total airport activities including aircraft, ground support equipment (GSE), APU, refueling, etc. The profile “Gasoline exhaust” corresponds to the average of 4 samples which represent gasoline exhaust. These gasoline exhaust samples were analyzed only using GC-MS, hence mainly heavy VOCs (monoaromatics; n-alkanes (nC\textsubscript{8}-C\textsubscript{14}); nonanal and decanal) were assessed from gasoline exhaust emissions. Several samples were taken for Jet A-1 vapor, however only 1 sample was analyzed and interpreted, as all the other samples overloaded the GC column and saturated the GC detector.

3.2.1 Distribution of Heavy VOCs by Family

It is important to assess the VOC distribution of aircraft emissions by family because each family has its different environmental and health effects. Heavy VOCs emitted are broken down into heavy alkanes (C\textsubscript{8}-C\textsubscript{14}), heavy aldehydes (C\textsubscript{9}, C\textsubscript{10}), benzene, and other monoaromatics (see Table 2). The 20 measured VOCs (C\textsubscript{7}-C\textsubscript{14}) using GC-MS were mostly heavy compounds (C\textsubscript{8}-C\textsubscript{14}) accounting for only a portion of aircraft exhaust since the target VOC species covered only a limited range. This range was chosen because it showed significant differences between aircraft and vehicle exhaust during our primary qualitative study.

Our objective was to identify emission tracers from aircraft by comparing the emission profile of aircraft engines to that of vehicle exhaust gas. As shown in Fig. 5, the profiles “Aircraft” and “Gasoline exhaust” illustrate significant differences. Indeed, the most prominent difference is the dominance of heavy alkanes (C\textsubscript{8}-C\textsubscript{14}) in the aircraft profiles and their absence from the profile of gasoline. As seen in Fig. 5 (a), the total concentration of heavy alkanes was 53 \(\mu\)g m\(^{-3}\) for the profile “Aircraft” (30 s \(\times\) 6), which accounted for 51% of the total heavy VOCs (Fig. 5 (b)). Similar speciation was observed for the 30-min sampling, where heavy alkanes (C\textsubscript{8}-C\textsubscript{14}) constituted 64% of the mass of aircraft sources with a smaller magnitude of 9.2 \(\mu\)g m\(^{-3}\). These observations were in accordance with previous studies, conducted by Liu et al. (2008) in China, Lai et al. (2011) in Taiwan, Salameh et al. (2014) in Beirut-Lebanon, etc. and which reported that gasoline vehicles have negligible emissions of C\textsubscript{9} and higher VOC species. In addition to heavy alkanes, heavy aldehydes (C\textsubscript{9}, C\textsubscript{10}) were present only in aircraft sources with average concentrations of 2.6 and 0.2 \(\mu\)g m\(^{-3}\) for the 30 s \(\times\) 6 and 30-min approaches respectively. These heavy aldehydes are mainly generated by the atmospheric photo-oxidation of heavy alkanes, kerosene combustion, and/or evaporation of raw fuel. Another difference is that the total concentration of monoaromatics in the profile “Gasoline exhaust” is around 3 times higher than the profile “Aircraft” at 122 and 44 \(\mu\)g m\(^{-3}\) respectively (Fig. 5 (a)), which can be attributed to the sampling distance – in addition to fuel type. Benzene dominates the mass emissions in gasoline exhaust (76% of the total mass emissions) (see Fig. 5 (b)) while in aircraft exhaust “other monoaromatics” dominate (82% of the mass of monoaromatics emitted). The absence of heavy alkanes and aldehydes from the VOC speciation of the gasoline exhaust is in accordance with previous studies, which reported that heavy alkanes especially C\textsubscript{8}-C\textsubscript{14} were negligible or almost not present in gasoline exhaust (Liu et al., 2008; Wang et al., 2013). These results are not surprising because jet aircraft use a kerosene-based fuel (Jet A-1) with a higher overall molecular weight than gasoline. This was confirmed by the analysis of unburned Jet A-1 kerosene vapor used in Beirut Airport that showed that heavy alkanes constitute 43% of the mass of heavy VOCs in unburned kerosene vapor (Fig. 5 (b)). Kerosene vapor, in turn, constitutes up to 30% of aircraft emissions (Ritchie et al., 2003). This explains the presence of heavy alkanes as
fuel-derived emissions. Heavy aldehydes can be either combustion products or “combustion-derived” (fuel oxidation) or due to unburned fuel. Jet A-1 kerosene fuel may have significant amount of species containing more than 14 carbon atoms, but it was not suitable to measure them because the sampling method involving carbopack B as adsorbent, was adapted for gaseous species up to C12-C14 only. It is known that the average chemical formula for kerosene (Jet A-1) differs from one source to another and ranges from C10.9H20.9 to C12H23 (Dagaut et al., 2006). Conner et al. (1995) averaged 2 air samples collected near an aircraft at the gate while refueling and preparing for departure, with running engines. Similar observations were found as heavy alkanes and monoaromatics constituted 66% and 44% of the heavy VOC composition (considering our target heavy VOCs).

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

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

### 3.2.2 Speciation of Heavy VOCs

Fig. 6 illustrates the speciation of the identified aircraft tracers, heavy alkanes and heavy aldehydes. The carbon number distribution of Jet A-1 kerosene vapor shows that among the heavy alkanes, C₈-C₉ compounds have the highest mass contribution (95.5%), followed by the contribution of n-decane (3.9%), while n-undecane, n-dodecane, n-tridecane, and n-tetradecane mentioned in decreasing order of contribution all constituted less than 1% of the heavy alkane mass. Both nonanal and decanal were also present in jet vapor (Fig. 6). Upon previous analysis of JP-4 jet fuel by Spicer et al. (1984), it was seen that C₇-C₉ dominated the speciation for a wide range of VOCs and low levels of light VOCs were observed. As deduced by Spicer et al. (1990), we can conclude that the exhaust species found in C₂-C₆ were probably products of combustion, referred to as “combustion-derived”, and VOCs C₈ and higher were “fuel-derived”. It can be seen that the airport roof source profile is in close resemblance to the samples collected with the 30 s
In the profiles “Aircraft” (30 s × 6) and “Airport Roof”, among the heavy alkanes n-nonane and n-decane dominate the speciation: n-nonane contributes to 39.7% and 37.6% of the total mass of heavy alkanes for the “Aircraft” and “Airport Roof” profiles respectively, while n-decane contributes to 30.5% and 33.2% of the total mass of heavy alkanes for the “Aircraft” and “Airport Roof” profiles respectively. The speciation of Jet A-1 kerosene vapor explains the presence of these heavy alkanes in aircraft and airport emissions, as they are components of jet fuel. These results are similar to those obtained within the platform of the airport of Charles De Gaulle, where n-nonane was found to be the dominating species (50%) among C6-C9 measured alkanes (Lelievre, 2009). In this study, the speciation of other monoaromatics for “Aircraft” (30 s × 6) and “gasoline” is dominated by toluene that has a higher contribution in the “Gasoline exhaust” profile (91%) than in the “Aircraft” profile (45%) as shown in Fig. S2 6. 1,2,4-trimethylbenzene, emitted by aircraft as well as vehicles, dominates the airport roof source profile. It is important to note that inhalation of air containing trimethylbenzene can lead to irritation of the respiratory tract, sore throat, headache, wheezing, vomiting, anxiety, tension and may affect the blood.

### 3.2.3 Speciation of Heavy VOCs with Engine Power

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

As shown in Fig. S3 7, the concentration of benzene increased from approach (bDL) to take-off (22.5 µg m⁻³) while the concentration of “other monoaromatics” significantly decreased from 85 to 21 µg m⁻³. This is due to the cracking of higher aromatics upon the increase in temperature which leads to less amounts of these species, but increased amounts of benzene (Schürmann et al., 2007). Benzene dominates the mass speciation of the monoaromatics in all the sites except for approach.

The speciation of heavy alkanes for approach and APU is dominated by n-nonane (45.1% and 40.2% respectively) and n-decane (27.9% and 59.8% respectively), whereas the take-off profile is dominated by n-undecane (26.0%) and n-decane (21.7%) (see Fig. S4 8(a) in the supplementary information). The heavy alkanes in APU emissions are only n-nonane and n-decane. On the other hand, it is interesting to note that, for the same mode of operation, the speciation of heavy alkanes using GC/MS (Fig. S4 (a)) is similar to that obtained using GC/FID (Fig. 4r(b)). For example, with both techniques n-nonane and n-decane dominate the speciation of heavy alkanes for the approach phase, and for APU emissions. Moreover, in both measurements, the speciation for the take-off phase is more distributed as a result of the use of higher engine power. For all these engines powers, the presence of these heavy alkanes is a result of unburned
kerosene vapor (Spicer, 1984). It should be noted that emissions during take-off are partially composed of unburned fuel or “fuel-derived”; they contain $C_8$-$C_{13}$ alkanes as well as nonanal and decanal coming either from kerosene combustion or from the raw fuel (Ritchie, 2003). Airport roof, which is present between the 2 jetties, is in close proximity to the gates and is consequently affected to a great extent by APU emissions. This explains the dominance of n-nonane (37.6%) and n-decane (33.2%) over the mass of heavy alkanes at this site (see Fig. 6). Nonanal and decanal are also present at the airport roof and are probably oxidation derived. Similarly, higher alkanes ($C_8$-$C_{14}$) and nonanal have been found at increased levels at the fence of O’Hare International Airport and was attributed to airport activities (City of Park Ridge, 2000). Decanal has been previously identified as a VOC associated with exhaust from tested commercial aircraft engines (EPA, 2009b).

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

### 3.3 Comparison with Bibliography

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

Fig. S5 presents the comparison of the speciation of VOC groups obtained in this study with those obtained by other studies. To conduct the comparisons, VOCs were reduced to cover exactly the same species for all the studies. Thus, in Fig. S5 light alkanes are constituted of ethane, propane, n-heptane; aldehydes/ketones are constituted of acrolein, propanal and acetone; monoaromatics include toluene, ethyl benzene, m, p-xylene and o-xylene; and heavy alkanes are constituted of $nC_8$-$nC_{12}$ straight chain alkanes. Comparisons were divided into comparisons with engines tests (Fig. S5 (a), (b), (c)) and comparisons with measurements taken under real aircraft operation that took place during taxi or idle power (Lelievre, 2009; Schürmann et al., 2007). This study is probably the first study to cover this range of VOC species at different thrust settings measured under real conditions. As a reminder, according to ICAO (2008), the thrust levels for idle, approach, and take-off are respectively 7%, 30%, and 80% of the rated thrust. However, in real operation, the take-off thrust varies from aircraft to another according to the aircraft type and engine model, flight load, meteorological conditions, runway conditions, etc. Thus, in reality, the “take-off” sample collects a variety of different take-off thrusts which vary between 85 and 100% (Dennis Ting, 2009).

Fig. S5 (a) presents the comparison of the total VOC groups obtained in this study, at the average of 3 powers, with that of Spicer et al. (1994). Fig. S5 (b) presents the comparison of total VOC groups obtained in this study (minus aldehydes and ketones) with that obtained by Spicer et al. (1994), Lelievre (2009), and Anderson et al. (2006). It can be seen that alkenes dominate the
VOC mass in the results obtained by Spicer et al. (Fig. S5 (a)), whereas light aldehydes/ketones dominate the speciation in our study. On the other hand, by comparing our results to those obtained by Lelievre, a similar speciation can be seen upon averaging the idle and approach powers, whereas results obtained by Anderson et al. (2006) and Spicer et al. (1994) still show higher domination of alkenes. This is probably due to the difference in the sampling location; contrary to the mentioned studies in which sampling was done behind the engine exhaust as small distances (0.3-30 m) behind the engine, sampling in our study was done either sideways at relatively smaller distances (17-32 m to the left) or behind (130-190 m behind) to be able to sample several aircraft in real operation without interfering with aircraft operations. The difference can be also attributed to the difference in emissions between the CFM-56 engine studied by Spicer et al. (1994), RB211-535E4 measured by Anderson et al. (2006), and our averaged emissions for several engine types. The difference in emissions at idle power measured in our study and taxi emissions measured during real aircraft operation by Schürmann et al. (2007) can be related to the difference in aircraft type, age, engine type, etc. However, results obtained by Schürmann et al. are of the same order as our results.

Finally, Fig. S5 (c) presents the speciation of heavy alkanes and monoaromatics measured in this study (GC/FID and GC/MS) compared to the results obtained with Spicer et al. (1994), Lelievre, and Eickhoff (1998). It can be seen that the speciation obtained in this study (GC/MS) is very similar to that obtained by Eickhoff for the averaged test run of the engine CFM56-3B1, while the speciation obtained with GC/FID (34% heavy alkanes) is similar to that obtained with CF6-50C2/E2. Fig. S5 (d) presents the comparison between results obtained in this study at idle power, to real measurements taken for real in-use aircraft. A similar speciation is observed between our study and that obtained by Lelievre (2009). Results obtained by Schürmann et al. (2007) (representing 3 aircraft engines) show a higher contribution of alkenes and heavy alkanes and a less contribution of light alkanes.

4. Conclusion

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

In the present work, alkanes, alkenes, alkynes (represented by acetylene), aldehydes, and ketones were detected in jet exhaust as observed by Spicer et al. (1994). Since jet fuel is mainly
composed of long heavy alkanes, then the presence of light VOCs in aircraft exhaust was a result of incomplete combustion rather than being unburned fuel. As for the total speciation of VOCs, results confirmed the dominance of light aldehydes and ketones, followed by alkenes.

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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 (nC₈-nC₁₄: 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 (nC₈-nC₁₄: n-octane, n-nonane, n-decane, n-undecane, n-dodecane, n-tridecane, n-tetradecane) and aldehydes (nonanal and decanal).
Fig. 1
Fig. 2

(a) Bar chart showing the concentration of different compounds in various samples. The x-axis represents the type of sample (Aircraft 30 s x 6, Aircraft 30 min, Airport roof 30 min) and the y-axis represents the concentration in mg m⁻². The compounds are Light Alkanes (C2-C7), Heavy Alkanes (C8-C14), Alkenes/Acetylene, Monoaromatics, Light Aldehydes/Ketones, and D-Limonene.

(b) Stacked bar chart showing the weight percentage of different compounds in various samples. The x-axis represents the type of sample (Aircraft 30 s x 6, Aircraft 30 min, Airport roof 30 min) and the y-axis represents the weight percentage. The compounds are Light Alkanes (C2-C7), Heavy Alkanes (C8-C14), Alkenes/Acetylene, Monoaromatics, Light Aldehydes/Ketones, and D-Limonene.
Fig. 3

(a) 

(b)
Fig. 5

(a) 

(b)
Fig. 6

![Graph showing weight percentages of various compounds over different time periods and locations.](image-url)
Table 1. Literature studies assessing emissions from engine tests or during real aircraft operation

<table>
<thead>
<tr>
<th>Study</th>
<th>Engine/EngineTarget Compounds</th>
<th>Sampling system</th>
<th>Analytical methods</th>
<th>Tested Regimes</th>
<th>Literature Study Details</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Engine Tests</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spicer et al. (1984, 1994)</td>
<td>TF-39 (Military TF of Lockheed C-5) and CFM-56 (TF)</td>
<td>Total HCs, C_2 to C_{17} organics, aldehydes</td>
<td>Sampling rake 0.3-0.6 behind the engine. Experimental: non-dispersive infrared instruments, chemiluminescence, FID, polymeric adsorbent (XAD) and DNPH cartridges</td>
<td>GC/MS, GC/FID, On-Line Cryogenic Trap/GC, canister GC/MS, Total HC Analyser</td>
<td>Idle, 30%; 10%: [JP-4; JP-5; JP-8]</td>
</tr>
<tr>
<td>Spicer et al. (1992)</td>
<td>2 Engines: F101, used on the B-1B aircraft, and the F110, used on the F-16C and F-16D aircraft.</td>
<td>Total HCs, individual organic species</td>
<td>Samples collected from each engine using a probe positioned just behind the exhaust</td>
<td>-</td>
<td>4 power settings from idle to intermediate power</td>
</tr>
<tr>
<td>EXCAVATE: Anderson et al. (2006)</td>
<td>NASA Boeing 757; Engine: Rolls Royce RB-211-535E4 (TF)</td>
<td>Gaseous carbon species</td>
<td>10 m behind the engine exit plane.</td>
<td>Canister, GC/MS</td>
<td>4-7%; 26%; 47%; 61%; [JP-5 low and high S]</td>
</tr>
<tr>
<td>APEX-3: Knighton et al. (2007); Kinsey (2009); Timko et al. (2010)</td>
<td>B737-300, ERJ-145, A300, B775, plus Learjet Model 25. Engines: CFM56-3B1, AE3007A1E, plus others</td>
<td>CO_2, HC, PM_{2.5}</td>
<td>Sampling: 30 m downstream of the engines Experimental: continuous and time-integrated instruments: IR</td>
<td>PTR-MS</td>
<td>4%, 7%, 15%, 30%, 45%, 65%, 85%, 100%, Jet A</td>
</tr>
<tr>
<td>Eichkoff (1998)</td>
<td>CF6-50C2/E2, CFM56-3B1</td>
<td>103 organic compounds</td>
<td>30 m</td>
<td>GC-MS</td>
<td>Average load</td>
</tr>
<tr>
<td><strong>Real Aircraft Operation</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Herndon et al. (2006)</td>
<td>Regional jets, B737s, MD88s, and B757s</td>
<td>Formaldehyde, acetaldehyde, benzene, and toluene</td>
<td>Continuous analysis through a sample port located on the front of the truck.</td>
<td>PTR-MS</td>
<td>Idle, taxi, approach (or landing), and take-off</td>
</tr>
<tr>
<td>Schürmann et al. (2007)</td>
<td>Engines from aircraft</td>
<td>3 VOCs</td>
<td>50-100 m behind an aircraft, at a height of 1 m</td>
<td>Canister/GC-FID</td>
<td>Taxi, ignition</td>
</tr>
<tr>
<td>Zhu et al. (2011)</td>
<td>VOCs: butadiene, benzene, acrolein, Formaldehyde,</td>
<td>At blast fence (140 m from the take-off)</td>
<td>Canister</td>
<td>Take-off</td>
<td></td>
</tr>
<tr>
<td>Lelievre (2009)</td>
<td>B757-200, B777-200</td>
<td>VOCs</td>
<td>200 m below the flow reactor</td>
<td>Canister, ATD-GC-FID</td>
<td>Taxi</td>
</tr>
</tbody>
</table>
Table 2. Volatile organic compounds in jet engine emissions (units converted to µg m$^{-3}$) (Spicer et al., 1994; Eichkoff, 1998; Anderson et al., 2006; Schürmann et al., 2007)

<table>
<thead>
<tr>
<th>Sampling distance (m)/position wrt engine</th>
<th>This Study$^a$</th>
<th>Spicer</th>
<th>Eichkoff$^b$</th>
<th>Anderson (RB211-535E4)</th>
<th>Schürmann</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 m/ down-stream</td>
<td>17 m/ left</td>
<td>8-9 m/ below</td>
<td>130-190m/ behind</td>
<td>0.3-0.6 m/behind</td>
<td>30 m/ behind</td>
</tr>
<tr>
<td><strong>Engine Status/ Flight mode</strong></td>
<td><strong>APU A330 (GC-FID)</strong></td>
<td><strong>APU A330 (GC-MS)</strong></td>
<td><strong>Touch down (GC-FID)</strong></td>
<td><strong>Approach (GC-MS)</strong></td>
<td><strong>Take-off (GC-FID)</strong></td>
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<tr>
<td>n-Octane</td>
<td>1.52</td>
<td>2.97</td>
<td>4.66</td>
<td>2.32</td>
<td>2.57</td>
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<tr>
<td>n-Nonane</td>
<td>6.3</td>
<td>1.70</td>
<td>1.39</td>
<td>0.57</td>
<td>0.57</td>
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<tr>
<td>n-Decane</td>
<td>1.70</td>
<td>0.64</td>
<td>0.87</td>
<td>0.13</td>
<td>0.16</td>
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<tr>
<td>n-Undecane</td>
<td>1.90</td>
<td>55.96</td>
<td>34.63</td>
<td>2.67</td>
<td>bDL</td>
</tr>
<tr>
<td>n-Dodecane</td>
<td>2.21</td>
<td>3.10</td>
<td>1.70</td>
<td>0.53</td>
<td>-</td>
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<tr>
<td>n-Tridecane</td>
<td>22.10</td>
<td>55.96</td>
<td>34.63</td>
<td>2.89</td>
<td>0.37</td>
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<tr>
<td>n-Tetradecane</td>
<td>664.96</td>
<td>53.33</td>
<td>76.91</td>
<td>1.00</td>
<td>1.00</td>
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<tr>
<td>Nonanal</td>
<td>-</td>
<td>bDL</td>
<td>-</td>
<td>bDL</td>
<td>-</td>
</tr>
<tr>
<td>Decanal</td>
<td>-</td>
<td>bDL</td>
<td>-</td>
<td>bDL</td>
<td>-</td>
</tr>
<tr>
<td>Benzene</td>
<td>3.74</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Toluene</td>
<td>15.69</td>
<td>3.63</td>
<td>4.35</td>
<td>4.09</td>
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<tr>
<td>Ethylbenzene</td>
<td>2.45</td>
<td>0.24</td>
<td>0.11</td>
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<td>0.72</td>
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<td>m, p-Xylene</td>
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<td>0.77</td>
<td>2.48</td>
<td>0.57</td>
<td>0.95</td>
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<tr>
<td>o-Xylene</td>
<td>4.32</td>
<td>0.19</td>
<td>2.64</td>
<td>0.76</td>
<td>0.72</td>
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<tr>
<td>Styrene</td>
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<td>0.62</td>
<td>1.74</td>
<td>0.57</td>
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<tr>
<td>1,2,4-TMB</td>
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<td>1.91</td>
<td>0.95</td>
<td>0.59</td>
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<td>1,4-DCB</td>
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<td>bDL</td>
<td>-</td>
<td>bDL</td>
<td>-</td>
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<tr>
<td>Propylbenzene</td>
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<td>-</td>
<td>0.59</td>
<td>-</td>
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<tr>
<td>Butylbenzene</td>
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<td>0.53</td>
<td>-</td>
<td>0.53</td>
<td>-</td>
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<tr>
<td>Acrolein</td>
<td>54.73</td>
<td>-</td>
<td>7.87</td>
<td>bDL</td>
<td>-</td>
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<tr>
<td>Propanal</td>
<td>9.23</td>
<td>-</td>
<td>bDL</td>
<td>bDL</td>
<td>-</td>
</tr>
<tr>
<td>Butanal</td>
<td>-</td>
<td>bDL</td>
<td>-</td>
<td>bDL</td>
<td>-</td>
</tr>
<tr>
<td>Pentanal</td>
<td>2.44</td>
<td>-</td>
<td>1.00</td>
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<tr>
<td>Hexanal</td>
<td>bDL</td>
<td>4.18</td>
<td>2.87</td>
<td>bDL</td>
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<tr>
<td>Acetone</td>
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<td>60.37</td>
<td>38.75</td>
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<tr>
<td>2-Butanone</td>
<td>bDL</td>
<td>-</td>
<td>bDL</td>
<td>1473.13</td>
<td>386.40</td>
</tr>
</tbody>
</table>
Table 2. (Continued): Volatile organic compounds in jet engine emissions (units converted to $\mu g m^{-3}$)

<table>
<thead>
<tr>
<th>Sampling distance (m)</th>
<th>This Study</th>
<th>Spicer</th>
<th>Eichkoff</th>
<th>Anderson (RB211-535E4)</th>
<th>Sch{&quot;u}rmann</th>
</tr>
</thead>
<tbody>
<tr>
<td>(position wrt engine)</td>
<td>APU A330 (GC-FID)</td>
<td>APU A330 (GC-MS)</td>
<td>Approach (GC-FID)</td>
<td>Approach (GC-MS)</td>
<td>Take-off (GC-FID)</td>
</tr>
<tr>
<td>Engine Status*</td>
<td>Flight mode</td>
<td>10 m/ down-stream</td>
<td>17 m/ left</td>
<td>8-9 m/ below</td>
<td>130-190 m/ behind</td>
</tr>
<tr>
<td>D-Limonene</td>
<td>5.90</td>
<td>1.00</td>
<td>bDL</td>
<td>2.29</td>
<td>-</td>
</tr>
<tr>
<td>Ethane</td>
<td>1.03</td>
<td>-</td>
<td>2.23</td>
<td>1.94</td>
<td>-</td>
</tr>
<tr>
<td>Propane</td>
<td>4.08</td>
<td>-</td>
<td>8.15</td>
<td>9.31</td>
<td>-</td>
</tr>
<tr>
<td>Isobutane</td>
<td>2.90</td>
<td>-</td>
<td>9.07</td>
<td>4.05</td>
<td>-</td>
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<tr>
<td>n-Butane+ cis-2-Butene</td>
<td>1.69</td>
<td>-</td>
<td>5.44</td>
<td>6.46</td>
<td>-</td>
</tr>
<tr>
<td>Isopentane</td>
<td>3.14</td>
<td>-</td>
<td>bDL</td>
<td>0.35</td>
<td>-</td>
</tr>
<tr>
<td>n-Pentane+ cis-2-Pentene</td>
<td>0.81</td>
<td>-</td>
<td>0.82</td>
<td>bDL</td>
<td>-</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>bDL</td>
<td>-</td>
<td>bDL</td>
<td>-</td>
<td>-</td>
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<tr>
<td>n-Heptane</td>
<td>2.07</td>
<td>bDL</td>
<td>0.77</td>
<td>1.40</td>
<td>4.80</td>
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<tr>
<td>Propene</td>
<td>1.39</td>
<td>-</td>
<td>7.88</td>
<td>0.74</td>
<td>3.08</td>
</tr>
<tr>
<td>1-Butene</td>
<td>bDL</td>
<td>-</td>
<td>1.20</td>
<td>2.45</td>
<td>bDL</td>
</tr>
<tr>
<td>1,3-Butadiene</td>
<td>bDL</td>
<td>-</td>
<td>0.53</td>
<td>bDL</td>
<td>-</td>
</tr>
<tr>
<td>Trans-2-Butene</td>
<td>bDL</td>
<td>-</td>
<td>0.86</td>
<td>bDL</td>
<td>-</td>
</tr>
<tr>
<td>1-Pentene</td>
<td>bDL</td>
<td>-</td>
<td>2.64</td>
<td>0.27</td>
<td>bDL</td>
</tr>
<tr>
<td>Trans-2-Pentene</td>
<td>bDL</td>
<td>-</td>
<td>bDL</td>
<td>-</td>
<td>bDL</td>
</tr>
<tr>
<td>Isoprene</td>
<td>bDL</td>
<td>-</td>
<td>6.69</td>
<td>4.21</td>
<td>1.04</td>
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<tr>
<td>1-Hexene</td>
<td>bDL</td>
<td>-</td>
<td>2.20</td>
<td>bDL</td>
<td>-</td>
</tr>
<tr>
<td>TVOC ($\mu g m^{-3}$)</td>
<td>174.7</td>
<td>30.2</td>
<td>155.9</td>
<td>92.11</td>
<td>216.2</td>
</tr>
</tbody>
</table>

*Note that concentrations presented for this study correspond to samples taken using the 30 s × 6 approach

bDF6-50C2/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
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.