



Article

An Assessment of Indoor Air Quality in the Arrivals Hall of Beirut–Rafic Hariri International Airport: Monitoring of VOCs and NO₂

Tharwat Mokalled ^{1,2,*}, Jocelyne Adjizian Gérard ¹, Maher Abboud ³, Céline Liaud ², Rouba Nasreddine ^{2,4} and Stéphane Le Calvé ^{2,4}

- Geography Department, Saint Joseph University, Beirut 1104 2020, Lebanon; jocelyne.gerard@usj.edu.lb
- ² Group of Atmospheric Chemistry, The Institute of Chemistry and Processes for Energy, Environment and Health (ICPEES, UMR 7515 CNRS/UdS), 67087 Strasbourg, France; liaudceline@gmail.com (C.L.); rouba.nasreddine@gmail.com (R.N.); slecalve@unistra.fr (S.L.C.)
- Unité de Recherche Environnement, Génomique et Protéomique (UR-EGP), Faculté des Sciences, Université Saint-Joseph, Beyrouth 1107 2050, Lebanon; maher.abboud@usj.edu.lb
- ⁴ In'Air Solutions, 67000 Strasbourg, France
- * Correspondence: tharwatmokalled@live.com

Abstract: In Beirut–Rafic Hariri International Airport (RHIA), airport employees stay at least 12 h inside the airport's buildings and suffer from respiratory symptoms. Additionally, direct openings exist between the apron and the arrivals hall providing a pathway for contaminated air to enter the buildings. Hence, we study the impact of Beirut–RHIA's activities on the indoor air of the arrivals hall (impact on employees and passengers) during June, November, and October 2014. Due to their impacts on air quality and human health, assessing of the concentrations of nitrogen dioxide (NO₂) and Volatile Organic Compounds (VOCs) was the target of our study by using gas chromatographic techniques (GC-MS and GC-FID) for VOCs and calorimetric methods for NO₂ concentrations. NO₂ levels indicated a probable hazard to the health of passengers and employees, while measured VOC levels did not present any risks except for acrolein. This is the first study to assess the speciation of a large number of VOCs (46 VOCs) for airport indoor air while revealing a very interesting correlation between aircraft number and the concentrations of VOC groups (namely heavy alkanes, aldehydes and ketones, and monoaromatics). Moreover, this is the first study in Lebanon to assess the speciation of a large number of VOCs in indoor air.

Keywords: indoor air pollution; Volatile Organic Compounds (VOCs); heavy alkanes; nitrogen dioxide (NO₂); airport; Beirut



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1. Introduction

According to the World Health Organization (WHO), exposure to air pollution is considered to be the biggest single environmental risk to human health [1]. This includes exposure not only to outdoor air pollution but also to indoor air pollution which causes globally 4.3 million deaths a year [2]. As a result, indoor air quality (IAQ) has increasingly gained concern over the last two decades. Exposure to indoor air pollutants can lead to a wide range of adverse health outcomes in both children and adults, from respiratory illnesses to cancer [3].

Several studies were conducted to assess indoor air quality [4,5] in preschools [6] and schools [7], residential apartments [8,9], and households [10]. Some of these studies have shown seasonality of indoor volatile organic compound (VOC) concentrations [4], i.e., for alkanes, BTEX (Benzene, Toluene, Ethylbenzene, and Xylenes), and terpenes measured in ten apartments in Cairo, higher indoor concentrations being observed in winter and lower values in summer [11]. This observation is consistent with measurements done inside apartments in Germany [9] with completely different climate and building characteristics.

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Even though airport buildings are ventilated using potentially very polluted outdoor air, indoor air was not the main focus in airports so far. However, airport indoor air pollution can impact both airport personnel and the public/passengers [12] and should be considered because most spend the majority of their time indoors. Indoor sources include combustion sources, smoking, cleaning solutions, building materials, and furniture (e.g., formaldehyde released from pressed-wood products). In addition to these sources, indoor air pollution can intensify if inadequate ventilation exists, and insufficient outdoor air is allowed to mix with the indoor air [13], or if improper filtration systems are utilized to reduce the contamination from outdoor air. Some studies have measured concentration levels inside airport buildings [14–16].

There is scarcity in studies targeting indoor air quality in airport buildings (see Table 1). Among the studies in line with our objective, it was reported that the airport hall in Strasbourg, France has a relatively clean environment, with formaldehyde and acetaldehyde levels not exceeding 20 and 10 µg m⁻³, respectively [14]. On the other hand, levels of polycyclic aromatic hydrocarbons (PAHs) inside an Italian airport—mainly benzo (b + j + k) fluoranthene and benzo [a]-pyrene concentrations—were of concern [15]. Pleil et al. [17] examined the relative exposures to JP-8 fuel (military jet fuel) vapor at the U.S. Air Force, by measuring the concentrations of nC_6 – nC_{12} as and monoaromatics in indoor base shops (break rooms, office areas, etc.) being the main constituents of JP-8 fuel. Results showed that indoor air concentrations measured inside the Air Force base shops were similar to the outdoor levels in Los Angeles (used as an indicator of urban exposure) except for an obvious elevation of the JP-8 fingerprint compounds n-nonane, n-decane, and n-undecane. However, these levels were 5-10 times lower than ambient air concentrations. Tasakas et al. [16] assessed the indoor air quality at the Control Tower of Athens International Airport by measuring carbon monoxide, formaldehyde, and VOCs—more particularly, benzene. Contrary to the results found by Pleil et al. [17], results highlighted that even though indoor concentrations never exceeded the established limits for indoor environments, all pollutant concentrations determined were substantially higher than those outdoors [16] due to emissions from indoor sources such as smoking, carpets, furniture and human emanations including breathing and body odour. In fact, smoking activity increased total VOCs (TVOCs) concentrations by 2.5 times compared to concentrations measured during a non-smoking period. In addition to the above, several studies assessed the impact of smoking on the indoor air quality at several airports [18,19]. Zanni et al. [20]. assessed IAQ in the airport of Bologna (Italy), by monitoring the Temperature, Relative Humidity, the total VOC concentrations and Particle Matter by means of a set of sensors as a prototypical example of a large regional airport. The study identified a positive correlation between indoor and outdoor gaseous concentrations, attributed to airside activities but they did not provide any VOC speciation. Although the aforementioned studies were done to assess indoor air quality at airports; however, none of these studies assessed the speciation of a large number of VOCs (e.g., 46 VOCs in this work) at different seasons but where just limited to only few VOCs or TVOC measurements.

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Table 1. Previous Studies Performed on Indoor Air in Airports.

Pollutants	Concentrations Ranges Mean (min-max)	Time/Number of Samples	Technique	Location	Reference	
Heavy alkanes (nC ₈ -nC ₁₂) Light alkanes (nC ₄ , nC ₇) Monoaromatics Chlorinated Alkenes	Light alkanes (nC_4 , nC_7) 24.22 $\mu g m^{-3}$ Monoaromatics 23.73 $\mu g m^{-3}$		Canisters/GC-MS	U.S. Air Force Break rooms, offices	Pleil et al. [17]	
Formaldehyde Acetaldehyde	$10.8 (8.8-13.0) \mu g m^{-3}$ $3.5 (2.0-4.3) \mu g m^{-3}$	June–September 2004 and September 2004– January 2005 (n = 4)	DNPH/HPLC (active sampling)	Strasbourg airport— Arrivals Hall	Marchand et al. [14]	
Polycyclic aromatic hydrocarbons (PAH)			Quartz fiber, a polyurethane foam, and an XAD-2 layer /GC-MS	Italian airport Terminal C Sierra C "Terminal C departure area"	Iavicoli et al. [15]	
Carbon Monoxide $0.18-6.41~\text{mg m}^{-3}$ Formaldehyde $5.5-26.1~\mu\text{g m}^{-3}$ Total VOCs $\text{bDL}^c-542~\mu\text{g m}^{-3}$ Benzene $\text{bDL}^d-379~\mu\text{g m}^{-3}$		April–September 2003	CO: Automatic infrared analysers HCHO: DNPH/HPLC TVOCs and benzene: Radiello type passive samplers/GC-FID	Control Tower of Athens International Airport	Tsakas and Siskos [16]	
Odorous Gases * PM _{2.5} PM ₁ Total VOC	0.39 ppm (0.09–2.2) ** 1872 pcs/L (1660–4066) ** 5595 pcs/L (4642–27541) ** 0.11 ppm (0.04–0.73) **	2 months (30 days per location) summer 2017	Gas and PM Sensors	Arrivals and departure areas of Bologna Airport (Italy)	Zanni et al. [20]	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		July, October, November 2014 (n = 20)	VOCs: Thermal desorption tubes/GC-FID NO ₂ : Passam tubes/UV-VIS spectrophotometer	Arrivals Hall at Beirut–Rafic Hariri International Airport	This work	

a: concentrations measured in Terminal C; bDLb: below detection limit (0.1 ng m $^{-3}$); bDLc: below detection limit (3.97 μ g m $^{-3}$); bDLd: below detection limit (2.74 μ g m $^{-3}$); e: concentrations measured in July and November 2014 (regular ventilation); * toluene, hydrogen sulphide, ethanol, and ammonia; ** concentrations measured in the arrivals area.

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In Lebanon, Beirut–Rafic Hariri International Airport (RHIA) emitted 454.8 t of NO_x, 50.7 t of NO₂, 404.1 t of NO, and 24.4 t of VOCs in 2012 [21]. Airport employees at Beirut–Rafic Hariri International Airport (RHIA) staying at least 12 h inside Beirut airport's buildings suffer from respiratory symptoms [22]. Additionally, direct openings exist between the apron and the arrivals hall providing a pathway for very contaminated air to enter the buildings. In addition to the scarcity of studies worldwide, no study has previously studied airport indoor air by measuring this wide range of 46 VOCs, as a function of aircraft traffic. In Lebanon, no prior study has assessed (i) the impact of Beirut–RHIA's activities on its indoor air quality nor (ii) the speciation of a large number of VOCs in non-airport indoor air. Therefore, the aim of this study was to identify the impact of airport activities on the indoor air quality of the arrivals hall to better evaluate the exposure of passengers/airport employees to the gaseous pollutants, which opens the door for adapting mitigation measures to protect the indoor environment and health of the passengers and airport personnel.

2. Materials and Methods

2.1. Study Area

The airport of study is Beirut–RHIA, the only operational commercial airport in Lebanon, located in the Khaldeh suburb about 8 km south of the capital's (Beirut) city center (Figure 1a). The airport is located on the eastern coast of the Mediterranean Sea, hence affected by a Mediterranean climate. To the east of the airport, Mount Lebanon—a mountain range sloping up to 2500 m—is located. Excluding its western side (Mediterranean Sea), Beirut Airport is embedded in a very urbanized area. Additionally, its eastern side is in close proximity to an industrial zone.

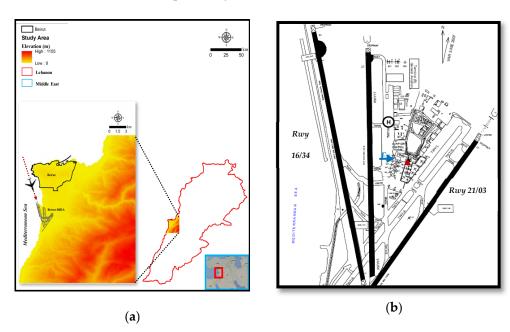


Figure 1. (a) Study Area (Beirut–Rafic Hariri International Airport). Note that the red dotted line reflects the main jet trajectory used for landing in Beirut–RHIA; (b) Top view of Beirut–Rafic Hariri International Airport, taken from Lebanese DGCA [23] (A: Arrivals Hall, Rwy: runway).

2.2. Sampling Site

Indoor sampling was conducted inside the arrivals hall at Beirut–RHIA (see Figure 1b). The arrivals hall is the area of an airport where the incoming passengers arrive and spend at least 1 h. Moreover, at RHIA it has the same indoor air quality as that of the offices and duty-free shops located in the same airport section—where employees spend at least 12 h/day.

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In Beirut Airport, ventilation takes place as follows: for each room there exists an air climate unit located inside a mechanical room not necessarily adjacent to the room. Within this air climate unit, the system of ventilation works in the following manner: 80% of the returning indoor air (return duct) is mixed with 20% of fresh outdoor air which are afterwards filtered with Aluminium filter (to remove big dust particles and protect the air bag filter from being clogged) and an air bag filter (to trap particles that are 0.3–1.0 microns in diameter including bacteria, most tobacco smoke, droplet nuclei (sneeze), and dust particles). According to the required indoor temperature, this air is heated or cooled before it enters the indoor room again through the supply duct [24]. It is important to note that the temperature inside the arrivals' hall is almost constant throughout the year (around 22–23 °C). The aforementioned information has been retrieved from the Mechanical Department at the Middle East Airport Services.

2.3. Sampling Methodologies

VOCs air samples were collected using multi-bed stainless steel thermal desorption tubes fabricated at the University of Strasbourg [24,25]. These homemade tubes, compatible with Perkin Elmer thermal desorption systems present in the laboratory, are suitable for trapping C₂–C₁₂ VOCs, by means of packing them with 10 mm CarbosieveTM S-III (60/80 mesh, 100 mg) to trap light VOCs from C_2 to C_5 ; and 35 mm Carbopack TM B column (60/80 mesh, 160 mg) to trap heavier C_5 – C_{12} VOCs [26]. It is worth noting that their trapping efficiency resembles that of the commercially used "Air Toxics" (Supelco) adsorbent tubes, being less efficient to trap ethane, ethylene, and acetylene at room temperature and n-tridecane and n-tetradecane as per the recommendations given for carbopackTM B [24]. Nevertheless, we presumed that these tubes can still be used to adsorb the aforementioned heavy VOCs with sticky nature [27]. Before sampling, tubes were conditioned by using the function "conditioning" of the automated thermal desorber: thermal cleaning at 350 °C under a helium flow rate of 50 mL min⁻¹ for 3 h. 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, then transferred to the University of Strasbourg for analysis within 30 days after sampling.

Active samples of indoor air were collected in thermal desorption tubes via two different sampling devices with a similar principle of operation: a one-channel autosampler and an eight-channel programmable device [24], designed by ICPEES (Institute for Chemistry and Processes for Energy, the Environment and Health)—Group of Atmospheric Physical-Chemistry laboratory at the University of Strasbourg. These devices operate as follows: the pump outlet located downstream a very low pressure drop (low- Δ P) mass flow controller (Bronkhorst) is connected to the adsorbent tube to ensure a constant flow of air into the tube. This design renders these machines suitable for air sampling at atmospheric conditions with a full range of 500 mL min⁻¹, uncertainty of 1% of the full range, and 0.3% precision on the measurement of the mass flow controller. Based on previous experimental optimization experiments conducted to attain quantitative trapping of the majority of the target VOCs [24], we adopted optimal sampling conditions at a rate of 100 mL min⁻¹ for 30 min (total sampled volume of 3 L). The sampling height was 1.5–2 m above ground, approximately at the breathing zone level of employees and passengers.

VOCs measurements were carried out during the summer of 2014 over 2 days in July using an eight-channel programmable autosampler, and during the fall/winter of 2014 over 2 days in October and 2 days in November using a portable battery-operated autosampler collecting a total of 20 air samples. Sampling times (Table S1 in the Supplementary Material) were set to take account for the different levels of activity at the airport (low traffic, rush hours, morning hours, etc.). The number of samples obtained was subject to the fact that all campaigns conducted within the airport vicinity required official permissions from the Directorate General of Civil Aviation (DGCA) and Airport Security; the number of samples taken as well as sampling locations were restricted due to security reasons. During the

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summer campaign, VOCs samples were taken by inserting a Teflon tube in the return duct to assess the VOCs concentrations in the returning indoor air from the arrivals hall using the programmable eight-channel autosampler, whereas the one-channel sampler was used to take samples directly from the arrivals hall during the fall/winter campaigns (Figure S1 in the Supplementary Material). During the campaign conducted in October, an exceptional malfunction in the air conditioning system took place, which necessitated the change of the ventilation procedure from mixing 20% fresh outdoor air with 80% returning indoor air, to mixing 50% fresh outdoor air with 50% indoor air.

To measure NO_2 concentrations, air samples were taken using Passam passive samplers placed in polypropylene cages (see Figure S2). These cages were tied to the ceiling of arrivals hall at a height of 2.5 m above floor level to measure indoor NO_2 levels. To assess average NO_2 concentration of the fresh outdoor air that supplies the arrivals hall, a cage (1.5 m above floor level) was tied adjacent to the window through which fresh air enters before getting mixed with the returning indoor air, as previously mentioned. NO_2 sampling took place just outside the arrivals hall to measure the NO_2 levels (2.8 m above floor level) of the air that enters into the arrivals hall through openings associated with the conveyor belts. These openings lead to the flow of contaminated air from the ramp into the arrivals hall. All NO_2 measurements (Table S2 in the Supplementary Material) were taken simultaneously with both VOCs winter campaigns as well as during summer 2015.

2.4. Analytical Methods

2.4.1. Chemicals and Materials

Spiking of adsorbent tubes was implemented to prepare liquid calibration curves of several reference compounds with 98 to 100% purity, listed as follows: (i) Propanal, acrolein, pentanal, nonanal, d-limonene, and n-hexane with a purity ranging from 90 to 97%. (ii) A liquid standard mixture containing heavy alkanes and monoaromatics obtained from Supelco (Bellefonte, PA, USA). (iii) A 100 mg L⁻¹ liquid standard mixture of BTEX from Ultra Scientific (North Kingstown, USA). (iv) High purity LC-MS methanol (purity > 99.9%), from Fluka, was used to prepare the diluted solutions. Perkin Elmer stainless steel cartridges obtained from Supelco (Bellefonte, PA, USA) and packed with Carbopack™B (60/80 mesh, 200 mg), were used for liquid calibrations. Online calibrations were performed with a gas standard mixture composed of light alkanes, alkenes, and one alkyne at 100 ppb ($\pm 20\%$) 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 Cormeille, France). Helium (99.9995%) and air (99.999%) used for gas chromatography and Flame Ionization Detectors (FID) were also obtained from Messer. Hydrogen was produced by a hydrogen generator HyGen 200 from CLAIND (Lenno, Italy) for FID.

Calibration curves for gaseous standards were performed via on-line calibrations [24,28]. Light alkanes, acetylene, and alkenes were diluted from a concentration of 100 ppb with nitrogen gas (99.999% purity) to simulate ambient air concentrations between 0.1 and 20 ppb. On the other hand, calibration curves for light aldehydes/ketones, d-limonene, chlorinated alkenes, and monoaromatics, were performed via liquid spiking with a syringe using a homemade converted GC injection port, ThermoFinnigan AS3000 (Milan, Italy) [24,28]. Since automatic liquid spiking was not feasible to perform for heavy alkanes (C9–C14 in specific) and heavy aldehydes (C9–C10) on the silica capillary maintained at room temperature due to their sticky nature, it was replaced with manual spiking whereby VOCs were directly deposited on the adsorbent tube as follows: 10 μ L 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. The range of liquid standard concentrations for light aldehydes, ketones, and d-limonene was between 0.2 and 100 mg L⁻¹; between 20 and 100 mg L⁻¹ for n-nonane and n-undecane; and between 100 and 500 mg L⁻¹ for nonanal and decanal. As for the

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mixture comprising the heavy alkanes and four monoaromatics, the concentrations varied between 1.5–7 mg $\rm L^{-1}$ to 8.5–39 mg $\rm L^{-1}$. The concentration of each VOC varied as per the mass fraction of this 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 $\rm L^{-1}$.

2.4.2. Analysis Techniques

VOC Measurements and Analysis

VOC samples were analysed using an ATD-GC-FID, i.e., Automated Thermal Desorber (ATD) with capillary gas chromatography (GC) coupled with Flame Ionization Detector (FID) to detect/quantify the total range of VOCs (C₂–C₁₄). Desorption of the analytes held on the sorbent tubes was carried out using Turbomatrix 350 ATD provided by Perkin Elmer (Waltham, MA, USA). For more details on the thermal desorption system, please refer to Liaud [24]. The analytical system used was a Perkin Elmer gas chromatograph Clarus 580 (Perkin Elmer, Villebon-sur-Yvette, France) with a dual column system and twins FID. This analytical chain, by means of a switching system called Dean switch, allows the use of one or two chromatographic columns connected in series. Two different gas separation columns were utilized to cover the whole range of VOCs, as follows: (i) A capillary column, Perkin Elmer Phase Elite-1, 60 m \times 0.25 mm ID \times 0.25 μ m was used to separate heavy VOCs; (ii) the second column Restek Rt[®]-Q-BOND (Restek, Lisses, France), 30 m \times 0.32 mm \times 10 μ m, was installed to separate the lightest target VOCs. The aforementioned chromatographic separation was optimized by Liaud [28]. VOCs were identified on the basis of matching the retention times, and quantification was conducted according to the external standard method. All the analytical parameters are reported in Tables S3 and S4 in the supplementary material. Calibrations, prepared via both modes of the ATD, showed excellent linearity: R² values were 0.99 for all VOCs except for propanal (0.98) and acetone (0.98). 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. As presented in Tables S3 and S4, LOD values were lowest for n-tetradecane (0.03 ng) and highest for acrolein and propanal (1.4 ng during both calibrations). LOD values were transposed to airborne concentrations (μg m⁻³) for a sampling air volume of 3 L: The corresponding LOD values varied then between 0.01 and $0.46 \mu g m^{-3}$. The uncertainty of the measured concentrations was evaluated as follows (Equation (1)):

$$\frac{\Delta C}{C} = \frac{\Delta a}{a} + \frac{\Delta b}{b} + \frac{\Delta V_{sample}}{V_{sample}} \tag{1}$$

where:

 $\frac{\Delta a}{a}$ and $\frac{\Delta b}{b}$ are the relative errors on the slope and intercept by considering the equation of the fit straight line obtained during calibration: y=ax+b, where Δa and Δb are equal to 2 times the value of the standard deviations of the slope and intercept, respectively. For most of the VOCs, b=0.

 $\frac{\Delta V_{sample}}{V_{sample}}$ is the relative uncertainty of the sampled volume (V).

where:

 $V = D \times t$

The uncertainty of the flow rate (D) is the sum of the uncertainty of the measurement (i.e., 0.3%) and the uncertainty of the full scale (1%).

In the case of 30-min sampling, Δt is assumed to be equal to 3 s:

$$\frac{\Delta t}{t} = \frac{3}{1800} \times 100 = 0.16\% \tag{2}$$

Thus, the uncertainty of the sampled volume was:

$$\frac{\Delta V_{sample}}{V_{sample}} = \frac{dt}{t} + \frac{dD}{D} = 0.16\% + 0.3\% + 1\% = 1.46\%$$
 (3)

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For June calibrations (Table S3), most of the relative errors on the slope ($\Delta a/a$) were below 6% which correspond to a relative uncertainty ($\Delta C/C$) of 7.5%, except for propanal ($\Delta a/a = 0.124$, i.e., 12.4% of calibration uncertainty) and acetone ($\Delta a/a = 0.069$) with corresponding uncertainties on the measured concentrations equal to 13.8% and 8.5%, respectively, according to Equation (1). As for October calibrations (see Table S4), $\Delta a/a$ values of the most investigated VOCs were below 0.053 (5.3%) implying a total uncertainty of 6.7% on the measured concentrations, except for 1,2,4-trimethylbenzene (1,2,4-TMB) which exhibited a $\Delta a/a$ value of 0.1655 (i.e., 16.5% of uncertainty) and acetone which exhibited a $\Delta a/a$ value of 0.104 (i.e., 10.4% of uncertainty), respectively resulting in 18.1% and 11.9% uncertainty on their measured concentrations.

Statistical Methods

The identification of VOCs was based on the matching of retention times, and the quantification was performed by the use of the external standard method using the software *Totalchrom*. The standard deviation, coefficient of variation, minimum, median, maximum, and third quartile were calculated for each VOC. Moreover, Pearson's correlations and p-values have been calculated in Microsoft Excel taking into account a subset of the heavy alkanes (C_8 – C_{11}) and monoaromatics quantified in the indoor rooms, as it is an important method to determine common sources for these VOCs [29,30].

Nitrogen Dioxide Measurements and Analysis

As for the collected NO_2 , they were spectrophotometrically quantified based on the well-established Saltzman method [31]. Accordingly, NO_2 is transformed into nitrite ions after the reaction with triethanolamine (TEA) present in Passam tubes with 1:1 conversion to form a product called TEA- NO_2 [32]. Once sampled, TEA- NO_2 was extracted from Passam tube with 2 mL of a colored reagent—sulfanilamide (SA)/N(-(1naphthyl) ethylenediamine dihydrochloride (NED). Derivatization proceeds when nitrite is converted to an azo dye by means of its reaction with SA/NED. The sample was then stirred vigorously for 3 min by a vortex to allow the nitrite to dissolve in the solution and was then left for two hours to allow the derivatization to be completed. The NO_2 -captured reddish purple azo dye was afterwards determined by colorimetry using a Nicolet 300 spectrophotometer at 540.0 nm. The detection limit is equal to 2–5 μ g m⁻³ for a sampling time of 8–24 h, and 0.3 μ g m⁻³ for a sampling time between 1 and 4 weeks [33]. The uncertainty in the measured values due to sampling and experimental analysis is equal to 28.1% and 19% for sampling times of 8–48 h and 1–4 weeks, respectively, determined when measured data using Passam tubes were compared to chemiluminescence reference data [33].

3. Results

3.1. Variation of TVOCs between the Campaigns

As previously mentioned, the first campaign in the arrivals hall was conducted during summer (June 2014), the second campaign (October 2014) during fall/winter with no rain preceding, while the third fall/winter campaign (November 2014) was conducted on a rainy day. Another variable to consider is the change in the ventilation procedure during the campaign that took place in October 2014 where the supply duct contained 50% fresh outdoor air mixed with 50% returned indoor air (and not 20% fresh outdoor air mixed with 80% recycled air as usual).

All VOCs concentrations ($\mu g \ m^{-3}$) presented in this section were measured using GC-FID. n-Tetradecane was not detected (n.d.) in our samples. The mean total VOC concentrations ($\mu g \ m^{-3}$), as well as the concentrations of the individual VOC groups, measured inside the arrivals hall at Beirut Airport during the three measurement campaigns are presented in Figure 2, whereas descriptive statistics are presented in Tables S5 and S6. The mean TVOC concentration decreased by 35% between the summer (98 $\mu g \ m^{-3}$) and the fall/winter (November) campaign (64 $\mu g \ m^{-3}$). In fact, the decrease occurred in the concentration of total monoaromatics (31.4 to 10.1 $\mu g \ m^{-3}$), aldehydes and ketones (32.6 to 9.5 $\mu g \ m^{-3}$), alkenes (8.8 to 5.5 $\mu g \ m^{-3}$), and d-limonene (2.8 to 0.6 $\mu g \ m^{-3}$). Whereas the

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concentration of light alkanes doubled from summer to winter (11.3 to 22.7 μg m⁻³), and the concentration of heavy alkanes increased slightly from 11.5 to 14.9 μg m⁻³ (Figure 2 and Tables S5 and S6). During the summer campaign, the major contributors to TVOC concentrations were aldehydes (32.6 μg m⁻³, 33%) whereas light alkanes (22.7 μg m⁻³, 35%) were the major contributors in winter (Figure 2 and Tables S5 and S6). It is important to note there are three variables between the campaigns conducted in June and November which can explain the obtained results: (i) the method of sampling was through the duct which carries the air entering the indoor room during the summer campaign, whereas sampling during the fall/winter campaign took place inside the arrivals hall, (ii) samples were taken during a rainy day in November; (iii) stronger photochemical reactions take place in the summer.

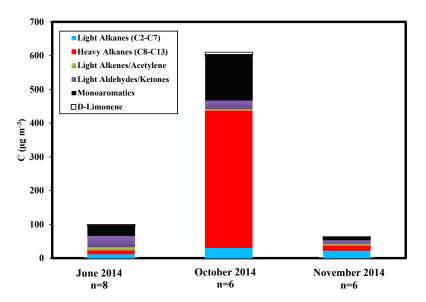


Figure 2. Variation of VOC concentrations ($\mu g \ m^{-3}$) by VOC class between the three indoor campaigns, determined by GC-FID from measurements conducted at the arrivals hall (Beirut Airport, 2014). This figure illustrates the distribution of average concentrations by sampling for 30 min at 100 mL min⁻¹. Note that n-tetradecane (heavy alkane, C_{14}) was not detected during the measurement campaigns.

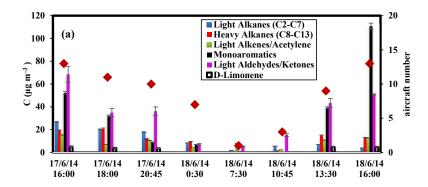
Despite these different conditions, it is remarkable to observe very similar TVOC indoor concentrations and the occurrence of the same VOCs.

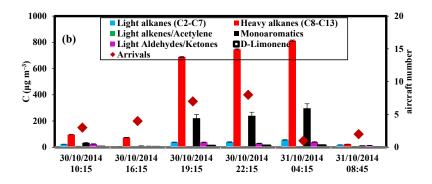
An exceptional incident took place on 30–31 October 2014, where the air conditioning units malfunctioned that necessitated the pumping of 50% of fresh outdoor air instead of 20% (usual conditions) in order to provide cooling effects by allowing more outdoor air to enter. This implied that more outdoor pollutants (rich with aircraft exhaust and other airport-related emissions) were injected into the arrivals hall and got confined inside. The most prominent result was the enormous increase of the concentration of heavy alkanes up to 407 µg m⁻³, around 40 times that of the other two campaigns, contributing by 66% of the TVOCs measured (Figure 2 and Tables S5 and S6) and remarkably mimicking the speciation observed in aircraft signature measurements presented in our previous work [34,35]. The other VOCs family affected by this irregular ventilation was the monoaromatics, reaching a concentration of 135 µg m⁻³. It is important to note that light alkanes, alkenes, and d-limonene remained in the same order of magnitude as the other campaigns. To conclude, these results provide additional evidence that heavy alkanes can serve as the major aircraft signature emissions in air measurement affected by aggregate airport emissions—as found in our previous work as well as in the literature [17,34–36]—which elevated dramatically when more outdoor emissions were allowed to enter indoors.

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3.2. Temporal Variations of VOC Groups

Figure 3 presents the temporal variations of the concentrations of VOC families and their correlation to the number of arriving aircraft, calculated by counting the number of aircraft arriving within the past 2 h before the end of the sampling. According to Figure 3, a very interesting correlation exists between the number of arriving aircraft with the concentrations of VOCs, specifically for heavy alkanes, aldehydes and ketones and monoaromatics. For example, at 16:00 on 17/6/2014 (see Figure 3a) the concentrations of heavy alkanes, light aldehydes/ketones, and monoaromatics (combustion products) are maximum (rush hour). Afterwards, these concentrations decrease gradually until they become very low at 07:30 (very low traffic) and increase again to reach another maximum at 16:00 (rush hour). Additionally, at 04:15 on 31/10/2014 (see Figure 3b), the concentrations of the aforementioned VOCs peaked due to the precedence of night-time rush traffic.





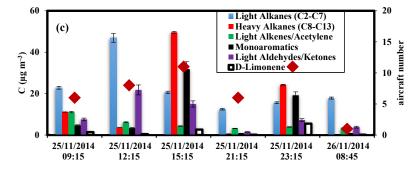


Figure 3. Temporal Variation of VOC groups determined by GC-FID from measurements taken in the arrivals hall during (a) June 2014, (b) October 2014, and (c) November 2014. This figure illustrates the distribution of average concentrations by sampling for 30 min at 100 mL min⁻¹. Note that n-tetradecane (heavy alkane, C_{14}) was not detected during the indoor measurement campaigns. The red diamonds correspond to the number of aircraft arriving within the past 2 h before the end of the sampling. Error bars represent the absolute uncertainty (μg m⁻³) per VOC family, calculated as the sum of absolute uncertainties (Δc) of the individual VOCs.

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In fact, this direct effect of aircraft activity on indoor concentrations is also influenced by the presence of large openings at the baggage belts that provide a pathway for contaminated air near the aircraft gates. The influence of aircraft traffic is also shown in Figure 3b where huge concentrations of heavy alkanes entered the arrivals hall when the fresh outdoor air flux was increased up to 50%. Again, maxima of heavy alkane concentrations were observed in November 2014 for the third campaign during rush traffic (see Figure 3c).

3.3. VOCs Speciation

Descriptive statistics of VOCs ($\mu g \ m^{-3}$) measured in the arrivals hall at Beirut Airport during the three campaigns are summarized in Tables S5 and S6. The occurrence of a VOC, in percent, describes the proportion of the dataset in which the VOC was detected. As presented in Tables S5 and S6, the percentage occurrence was more than 60% for most VOCs (June 2014) except for tetrachloroethene and hexanal. Propanal (10.9 $\mu g \ m^{-3}$), toluene (10.3 $\mu g \ m^{-3}$), acetone (9.3 $\mu g \ m^{-3}$), n-butane and cis-2-butene (6.5 $\mu g \ m^{-3}$), ethene and acetylene (4.5 $\mu g \ m^{-3}$), listed in descending order of predominance, were the most abundant VOCs measured in indoor air during the summer campaign.

During the first fall/winter campaign (October 2014), affected to a great extent by outdoor emissions, the most abundant VOCs were n-decane, n-undecane, and n-nonane with mean concentrations of 134.9, 105.5, and 79.3 $\mu g\ m^{-3}$, respectively, followed by 1,2,4-TMB (67.1 $\mu g\ m^{-3}$), n-octane (43.5 $\mu g\ m^{-3}$), and n-dodecane (37.8 $\mu g\ m^{-3}$) (see Table S5). This confirms again the role of heavy alkanes (C8–C12) as signature emissions from aircraft and airport activities.

During the second fall/winter campaign (November 2014), the most abundant VOCs were acetone (6.8 μ g m⁻³), n-hexane (6.5 μ g m⁻³), n-nonane (5.7 μ g m⁻³), n-decane (4.0 μ g m⁻³), 1,2,4-TMB (3.6 μ g m⁻³), ethylene and acetylene (2.21 μ g m⁻³) (see Table S6).

All these values were below the occupational exposure limits set by the National Institute of Scientific Research (INRS) in France [37]. The U.S. EPA has listed 14 airport-related HAPs (Hazardous Air Pollutants), generally defined as those pollutants that are known or suspected of being able to cause serious health effects such as cancer, birth defects, etc. Ten individual HAPs comprise the vast majority of HAPs [38,39], five of which were assessed in this study which are (listed in descending order of importance): acrolein, 1,3-butadiene, toluene, xylenes, and propanal. In this study, the average concentration levels for these species were below the acute toxicity criteria reported by Wood [39] except for acrolein which was found to be above the reference exposure level (0.19 μ g m⁻³) for short-term exposure with average concentrations of 5.01 μ g m⁻³ (between 0 and 15.86 μ g m⁻³) during the summer campaign, 4.57 μ g m⁻³ (between 1.98 and 7.8 μ g m⁻³) during the campaign conducted in 30–31 October 2015, and 1.11 μ g m⁻³ (0–2.47 μ g m⁻³) during the campaign conducted in 25–26 November 2015, which may pose a health hazard for passengers and the airport employees.

Figure 4 presents the temporal variations of individual VOCs concentrations for the most abundant families (i.e., heavy alkanes, light alkanes, aromatics and light aldehydes/ketones) for the campaign conducted in November 2014. These individual VOCs concentrations also exhibit temporal variations related to aircraft activity, mostly heavy alkanes (nC_9 and nC_{10}) and monoaromatics (xylenes and 1,2,4-TMB).

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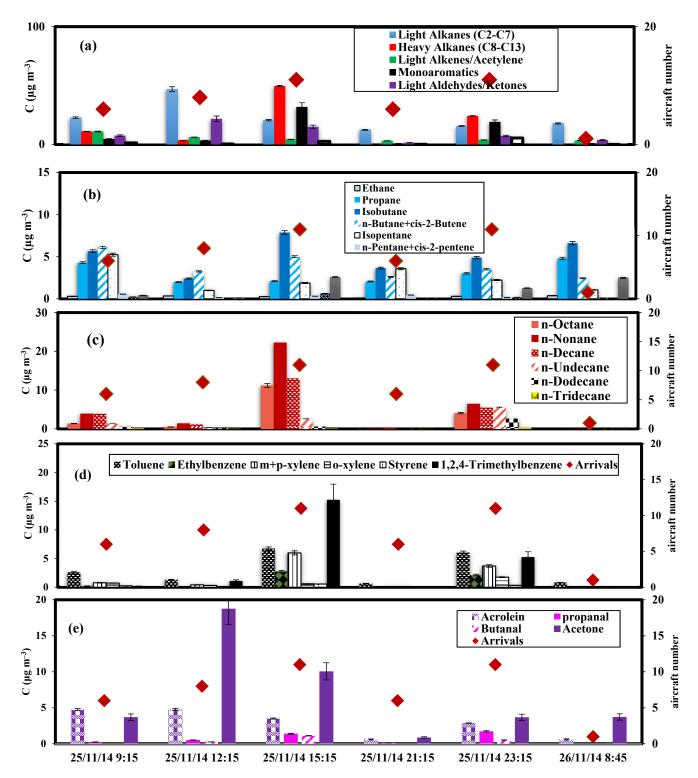
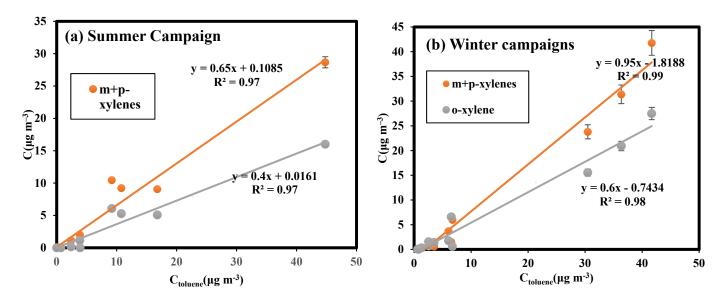


Figure 4. Temporal Variations of individual VOCs concentrations classified by family determined by GC-FID from measurements performed in the arrivals hall campaign (Beirut Airport, 25–26 November 2014) (a) Total VOC families, (b) Light alkanes, (c) Heavy alkanes, (d) monoaromatics (e) light aldehydes and ketones. These concentrations were obtained from sampling for 30 min at 100 mL min⁻¹. Note that n-tetradecane (heavy alkane, C_{14}) was not detected during the indoor measurement campaigns. The red diamonds correspond to the number of aircraft arriving within the past 2 h before the end of the sampling. Error bars represent the absolute uncertainty (μ g m⁻³) per VOC family, calculated as the sum of absolute uncertainties (Δ c) of the individual VOCs.

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3.4. Correlation Analysis of VOCs Concentrations

Pearson's correlations and p-values have been calculated taking into account a subset of the heavy alkanes (C_8 – C_{11}) and monoaromatics quantified in the arrivals hall, as it is an important method to determine common sources for these VOCs [29,30]. The most significant correlations between measured VOCs during summer and winter are shown in Figures 5 and 6, whereas Pearson's correlation coefficients of VOCs quantified inside the arrivals hall at Beirut Airport, taken during summer (June) and winter (October/November) 2014 are given in Table 2. Note that the presence of an asterisk (*) indicates that the correlations are statistically insignificant (p > 0.05), while a double asterisk (**) indicates strong (r > 0.8) and statistically significant (p < 0.05) correlations.



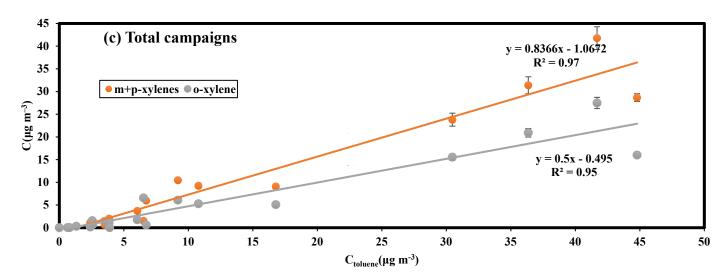


Figure 5. Examples of very strong correlations: the correlation between the indoor concentrations (μ g m⁻³) of xylenes (m,p-xylenes and o-xylene) and toluene at the arrivals hall in Beirut Airport during (a) Summer (17–18 June 2014), (b) Fall/Winter (30–31 October 2014 and 25–26 November 2014), and (c) Total Campaigns. For the correlation, each set of data had the same weighting. Error bars represent the absolute uncertainties (μ g m⁻³) of m,p- and o-xylene.

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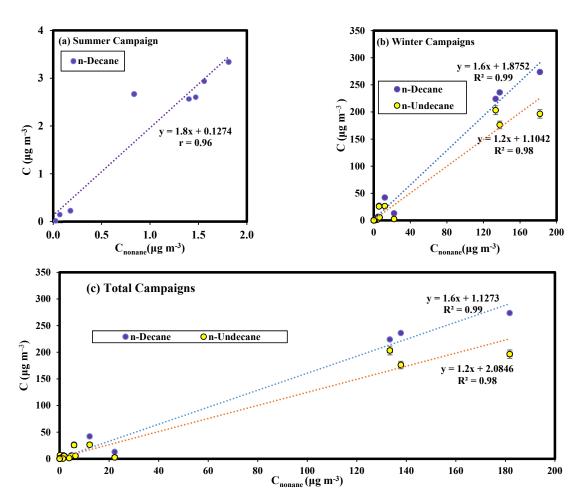


Figure 6. Examples of strong and very strong correlations: the correlation between the indoor concentrations (μ g m⁻³) of n-nonane, n-decane, and n-undecane at the arrivals hall in Beirut Airport during the different measurement campaigns: (a) Summer (17–18 June 2014), (b) Fall/Winter (30–31 October 2014 and 25–26 November 2014), (c) Total Campaigns. For the correlation, each set of data had the same weighting. Error bars represent the absolute uncertainties (μ g m⁻³) of VOCs.

Table 2. Pearson's Correlation Coefficients of VOCs Quantified inside the Arrivals Hall at Beirut Airport, taken during summer (June; Upper Half of the table) and winter (October/November; bottom half of the table) 2014.

VOC	1. n- Octane	2. n- Nonane	3. n- Decane	4. n- Undecane	5. Toluene	6. Ethyl- benzene	7. m,p- Xylene	8. o-Xylene	9. Styrene	10. 1,2,4- TMB
1. n-Octane	1									
2. n-Nonane	0.68 *	1								
3. n-Decane	0.63 *	0.96 **	1							
4. n-Undecane	0.42 *	0.59 *	0.59	1						
5. Toluene	0.13 *	0.76	0.67	0.34	1					
6. Ethylbenzene	0.35 *	0.73	0.66	0.49	0.52	1				
7. m,p-Xylene	0.27 *	0.81 **	0.72	0.39	0.97	0.59	1			
8. o-Xylene	0.29 *	0.83 **	0.74	0.38	0.97	0.60	1	1		
9. Styrene	0.27 *	0.23 *	0.12 *	0.45 *	0.65 *	0.07 *	0.56 *	0.52 *	1	
10. 1,2,4-TMB	0.08 *	0.66	0.54	0.38	0.96 **	0.38	0.92 **	0.91 **	0.80 **	1
1. n-Octane	1									
2. n-Nonane	0.99 **	1								
3. n-Decane	0.98 **	0.99 **	1							
4. n-Undecane	0.97 **	0.98 **	0.99 **	1						
5. Toluene	0.99 **	0.99 **	0.99 **	0.98 **	1					
6. Ethylbenzene	0.99 **	0.98 **	0.96 **	0.96 **	0.99 **	1				
7. m+p-Xylene	1 **	0.99 **	0.97 **	0.96 **	0.99 **	1 **	1			
8. o-Xylene	0.99 **	0.97 **	0.97 **	0.97 **	0.98 **	0.98 **	0.98 **	1		
9. Styrene	0.71	0.75	0.79	0.75	0.72	0.62	0.66	0.72	1	
10. 1,2,4-TMB	0.99 **	1 **	0.99 **	0.98 **	0.99 **	0.96 **	0.98 **	0.96 **	0.78	1

^{*} The presence of an asterix (*) indicates that p > 0.05 (statistically insignificant); ** A value of p < 0.05 indicates statistically significant correlations. If the Partial correlation coefficient (r) > 0.8 with p < 0.05, a strong correlation was considered to be present.

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Results show that the correlations between VOCs measured during summer are much weaker (lower correlation coefficients) and less statistically significant (most *p*-values are above 0.05) than those measured in winter campaigns (Table 2). There is no doubt that indoor VOCs levels are affected by outdoor air. In summer, when solar radiation is maximum, the variation of outdoor VOC concentrations is affected by both their photo-oxidation reactions with the hydroxyl radical, in addition to their emissions from different sources. By contrast, during winter when the rate of these photo-oxidation reactions is minimal, the changes in VOC concentrations would be majorly affected by the variations in source emissions rather than by photochemistry. It has been previously reported that the tropospheric lifetimes of VOCs are 20 times shorter in summer than in winter, considering OH radical reaction as the rate determining step in the photo-oxidative degradation of VOCs [40,41].

As presented in Table 2, the correlations between VOCs measured during the summer campaign ranged between very weak (r = 0.08 for 1,2,4-TMB and n-octane) and very strong (r = 1 for o-xylene and m, p-xylene) correlations. These results are not surprising. During summer, the photochemical reactions of VOCs are intensified and consequently strongly contribute to the production/loss processes of VOCs, depending on the rate constant of each VOC. For example, the rate constant of 1,2,4-TMB (32.5 \pm 5.0 $\times 10^{-12}~\rm cm^3$ molecule $^{-1}~\rm s^{-1}$) for its reaction with OH radical is 4 times higher than that of n-octane (8.11 \times 10 $^{-12}~\rm cm^3$ molecule $^{-1}~\rm s^{-1}$) at T = 296–298 K (around 25 °C) which leads to a faster degradation of the former [42,43]. Consequently, the sink caused by OH radicals will lead to a faster variation of 1,2,4-TMB concentrations than n-octane.

The correlation coefficients during the winter campaigns ranged between 0.62 (styrene/ethylbenzene) and 1 (m, p-xylene/n-octane, m, p-xylene/ethylbenzene, and 1,2,4-TMB/n-nonane). This implies that all the correlations listed are classified as "strong" or "very strong" correlations.

Despite the seasonal differences, some VOCs correlate similarly throughout summer and winter. For example, m, p-xylene and o-xylene present a very strong correlation with toluene with r equal to 0.97 and 0.95, respectively (three campaigns) (Figure 5). A similar very strong correlation exists between aircraft tracers, namely n-nonane and n-decane if the three campaigns are taken into account (r = 0.99) (Figure 6c). This is explained by the fact that they have similar tropospheric lifetimes and same primary emission sources. On the other hand, examples of weakly correlated VOCs are styrene and n-nonane during the summer campaign.

3.5. NO₂ Concentrations

Average NO₂ concentrations (µg m⁻³) measured in the maintenance room and the arrivals hall are presented in Table 3. The uncertainty in the measured values due to both sampling and experimental analysis is equal to 28.1% (sampling time: 8-48 h) or 19% (sampling time: 1-4 week)—determined when measured data using Passam tubes were compared to chemiluminescence reference data [33]. Results show that NO₂ concentrations exceeded 40 $\mu g m^{-3}$ in the arrivals hall at two out of 4 measurement campaigns to reach values of 41.6 μ g m⁻³ (26–27 October 2014) and 48.4 μ g m⁻³ (24–29 June 2015), followed by 36.1 μg m⁻³ (25–26 November 2014). These results are threatening since these valuesalthough weekly average concentrations—indicate a big probability that the annual mean NO₂ concentrations might be either above or slightly below the World Health Organization (WHO) annual guideline value for indoor NO₂ of 40 μ g m⁻³ [44], which risks the health of passengers in the arrivals hall. Most importantly, are the airport personnel who stay a minimum of 12 h per day in the offices and duty-free shops adjacent to the measurement location. Three sources contribute to pollutant concentrations in the arrivals hall: (i) The return flow from the indoor room itself, (ii) fresh outdoor air measured in the mechanical room, and (iii) the air that flows from the ramp into the arrivals hall through the openings associated with the conveyor belts. Table 3 presents NO₂ concentrations of the fresh air $(52.3 \, \mu \mathrm{g \, m^{-3}})$ and the outdoor air $(64.2 \, \mu \mathrm{g \, m^{-3}})$ measured in 30–31 October 2014 which are

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already above the annual threshold value of $40 \,\mu g \, m^{-3}$ [44] and which consequently contribute to the elevated concentrations in the arrivals hall. Similar observations were found in June 2015 with mean indoor NO_2 concentration of $48.4 \,\mu g \, m^{-3}$ and a corresponding concentration of $49.5 \,\mu g \, m^{-3}$ measured outdoors near the conveyor belt. These results are very significant, as they can point at the causes for pulmonary diseases that Beirut airport employees suffer from, especially workers in the ramp [22].

Table 3. Measured NO₂ concentrations (μ g m⁻³) during the campaigns conducted in the arrivals hall (Beirut Airport, 2014–2015). Measurements were taken by passive methods at durations of 24 h or one week. Errors correspond to uncertainties of NO₂ concentrations due to both sampling and analysis estimated at 28.1% (sampling time: 8–48 h) or 19% (sampling time: 1–4 week) according to Passam (2017).

NO ₂ (μg m ⁻³)	30–31 October 2014	25–26 November 2014	17-24 June 2015	24–29 June 2015
Indoor	41.6 ± 11.7	36.1 ± 10.1	34.0 ± 6.5	48.4 ± 9.2
Outdoor Baggage	64.2 ± 18.0	NA	49.0 ± 9.3	49.5 ± 9.4
Fresh Air	52.3 ± 14.7	20.6 ± 5.8	NA	NA

NA: Not Available due to logistical reasons.

4. Discussion

Even though airport buildings are ventilated using potentially very polluted outdoor air, indoor air was not the main focus in airports so far [13]. Therefore, comparison of our results with previous studies is rather very limited. To the best of our knowledge, this study is the first to assess the speciation and temporal variations of 46 VOCs inside airport buildings. This is also the first detailed indoor VOC study conducted in Lebanon, so it was not possible to compare our results with other indoor Lebanese institutions.

Table 4 presents a comparison between measurements taken in this study (arrivals hall) and those measured by Pleil et al. [17] taking into account the subset of common VOCs measured. To assess the relative exposures to JP-8 fuel (military jet fuel) vapor, Pleil et al. [17] measured C_6 – C_{12} alkanes as well as monoaromatics (the main constituents of JP-8 fuel) in the Air Force base shops (break rooms, office areas, etc.) using a battery-operated machine. Indoor concentrations in the Air Force base shops represent the average of 5 samples taken in July 1997 and February 1998. Therefore, to conduct a comparison, the arrivals hall summer (June) and fall/winter (November) campaign were averaged.

Table 4. Comparison of our data with those obtained by Pleil et al. [17] (Concentrations measured by Pleil et al. were converted from ppb to $\mu g m^{-3}$).

VOC Group	voc	This Study Arrivals Hall June/November 2014 (n = 14)	Pleil et al., 2000 U.S. Air Force base (AFB) Break rooms, offices July 1997, February 1998 (n = 5)
	n-Octane	2.92	0.85
TT A 11	n-Nonane	3.31	6.33
Heavy Alkanes	n-Decane	2.89	15.94
	n-Undecane	2.90	16.49
	Toluene	6.65	9.62
	Ethylbenzene	3.44	1.77
Monoaromatics	m,p-Xylene	4.29	4.46
	o-Xylene	2.16	3.05
	Styrene	0.31	1.43
Chloroalkenes	Tetrachloroethene	0.17	0.48
	n-Butane	5.17	13.85
Links Alleann	n-Pentane	0.53	8.28
Light Alkanes	n-Hexane	0.54	1.51
	n-Heptane	1.13	0.58
	TVOC (μg m ⁻³)	36.41	84.64

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Results show the mean TVOC concentration measured by Pleil et al. [17] (84.6 μg m⁻³) was around double that measured in the arrivals hall (36.4 μg m⁻³). This is most probably a result of the heavy rain that occurred during sampling in the arrivals hall (wet deposition). However, in both studies, heavy alkanes and monoaromatics dominated the total VOC speciation, both constituting 79% of the total VOC mass in the arrivals hall (33% and 46%, respectively) and 71% of the total VOC mass measured by Pleil et al. [17] (47% and 24%, respectively).

5. Conclusions

This is the first study that covers 46 VOCs measured inside an airport arrival's hall to understand the impact of airport activities on the airport personnel and passengers. Moreover, it is the first study that correlates air traffic emissions with levels of indoor air pollutants. This is explained by the strong relation between the concentration of various VOC groups—especially aircraft tracers—and aircraft number in the arrivals hall, due to the presence of direct openings that provides a pathway for air from the ramp into the arrivals hall.

In addition, NO_2 concentrations hinted at a potential risk to the health of airport employees and passengers since some measurements were slightly higher than the threshold annual value of $40~\mu g~m^{-3}$.

These results highlight the need to enhance the air filtration and ventilation systems in airports to maintain a healthy indoor air quality and protect the health of the employees.

At Beirut airport, it therefore seems obvious that indoor air pollution is directly impacted by the quality of the outdoor air. While adapting clean energy technologies for aircraft is still underway, non-polluting alternative solutions operating with electricity or hydrogen (fuel cell) can now be envisaged for vehicles used on the ground, such as refuelling vehicles, vehicles used for luggage and buses for passengers. This could partially improve the quality of the air outside and ultimately inside the airport buildings.

Supplementary Materials: The following are available online at https://www.mdpi.com/2073-443 3/12/3/400/s1, Table S1: Sampling schedule for indoor VOC measurements, using adsorbent tubes and automatic samplers, at the arrivals hall in Beirut Airport (2014), Figure S1: (a) Sampling through the opening in the return duct at the mechanical room at which the air climate unit for the arrivals hall is installed (Beirut Airport, June 2014); (b) one-channel autosampler during the winter campaign and NO₂ cage, Figure S2. Installation of polyethylene cage (red square) (a) in the mechanical room to measure NO₂ levels in fresh air supplying the arrivals hall at Beirut Airport; and (b) near the baggage loaders to measure NO₂ levels in the air that enters from the ramp into the arrivals hall through openings, Table S2: Sampling schedule for NO₂ measurements at the arrivals hall, Table S3: GC-FID analytical performance parameters (June 2014), Table S4: GC-FID analytical performance parameters (October 2014), Table S5: Statistical distribution of gaseous pollutants data measured during the two campaigns conducted in the arrivals hall at Beirut Airport (June and October 2014), Table S6: Statistical distribution of gaseous pollutants data measured during the two campaigns conducted in the arrivals hall at Beirut Airport (November, 2014).

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Data Availability Statement: The data presented in this study are available on request from the corresponding author. The data are not publicly available because the authors want to keep priority for conference presentations.

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Conflicts of Interest: The authors declare no conflict of interest.

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