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Indoor and Outdoor Volatile Organic Compounds at Office Buildings in Kuwait

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Abstract: A total of 800 indoor (I) and outdoor (O) air samples from eight large office buildings (LOBs) were analyzed for 78 VOCs using the latest sampling and preconcentration technology. Of these VOCs, 73 and 66 were detected in the I and O samples, respectively, at various levels and proportions. The I/O ratios were >1, and ethanol exhibited the highest ratio of 14.7. The levels of aliphatic hydrocarbons were higher in LOBs located in the southern region of Kuwait, where the majority of industrial activities are located. By contrast, these levels were significantly lower in LOBs located in the northern and far northern regions, where industrial activities are absent. There was evidence of CFCs leaking from HVAC systems in several of the LOBs. BTEX inter-species ratios suggest that vehicular emissions contributed less to the outdoor air composition at the LOB at Jahra compared to other LOBs. Alcohols and carbonyls were the first and second most abundant classes of chemicals, respectively, in the VOC mixtures at the LOBs. None of the VOCs exceeded the recommended air quality limits.

Keywords: air quality, VOCs, indoor air, large office buildings, Kuwait

Introduction

Clean and pollution-free air is a fundamental requirement for human health and well-being. However, due to increased human and industrial activities, air pollution continues to increase and consequently poses a significant threat to health worldwide.[1] Volatile organic compounds (VOCs) are the major group of air pollutants in the ambient and indoor environment. VOCs play a critical role in atmospheric chemistry and contribute greatly to the production of toxic oxidants that are harmful to ecosystems, human health and the atmosphere.

Kuwait is located in the far northwestern region of the Arabian Gulf and is flanked by Saudi Arabia to the south and southwest, Iraq to the north and northwest and the Arabian Gulf to the east. Thus, Kuwait is bordered by sea in the east and surrounded by hot deserts in all other directions. Its most distance points are 170 kilometers (km) east to west and 200 km north to south, with an area of approximately 18 thousand km[2]. The population of Kuwait is currently approximately 3.9 million (3.5 million, 2009 census). Most of the inhabitants live in residential areas concentrated along the coast, which represents approximately 6% of the total area of the country, with a small population in the nearby city of Al-Jahrah (in the northwest).[1] Kuwait has a typical desert climate with comfortably cool winters characterized light rain and long, severe summers in which ambient temperatures reach up to 55 °C in July and August. Kuwait is one of the main producers of crude oil, ranked fourth in production by OPEC,[2] with a production of approximately 3.0 million barrels per day (mbl/d) and a predicted production of 4 mbl/d in 2020.[3] The Shuaiba industrial area (SIA) is located in the southern part of the country and includes three refineries (processing more than 0.93 mbl/d), several petrochemical plants and other conversion industries. In addition, several miscellaneous industrial activities (MIAs) are situated in the vicinity of the SIA (Fig. 1).

Among developed countries, the ambient air in Kuwait has the highest emission levels of VOCs (methane VOCs (MVOCs) and non-methane VOCs (NMVOCs).[4] These emissions are derived from the following sources: (1) six dual-power and desalination plants (with an estimated capacity of 1.61 GW/day of electricity and 2×10^6 m³/day of drinking water); (2) traffic congestion along major highways and

Figure 1. Locations of the large office buildings (LOBs) and power plants within urban areas of Kuwait. (The letters D, E, I, J, R, S, U, and W for the LOBs DT, WE, SI, JA, RG, SR, UH, and AW, respectively. The numbers 1–5 for the power plants. HW1–HW7 for highways. The highlighted areas SIA for Shuaiba industrial area and MIA for miscellaneous industrial activities).

within city streets (332 motor vehicles/1000 resident);[5] (3) flaring activities during the operation of various gas and crude oil production facilities (in the north, west and southeast regions of Kuwait), which emit ninety thousand tons/year of NMVOCs into the atmosphere of Kuwait, including urban areas;[6] and (4) various industrial activities in the SIA and the other MIAs in its vicinity. All of these emissions contribute greatly to the elevated levels of VOCs and other various pollutants in the ambient air of Kuwait. These effects in turn increase the levels of pollutants in indoor air, which depends on the wind direction, wind speed, building location and structural design, as well as the physical and mechanical factors affecting air exchange rates.[7,8]

Indoor air quality (IAQ) in large office buildings (LOBs) is an important factor that has a major impact on the health, comfort, and productivity of employees. LOBs usually contain a multitude of

activities with wide-ranging sources of air pollutants, including toxic gases, VOCs, airborne dust and fungal spores. Depending on the exposure dose and personal susceptibility, exposure to such mixtures of pollutants may produce serious health effects.[9,10] However, low-level and/or short-term exposures may cause a general feeling of unhealthiness and illness, leading to the use of the term "sick-building syndrome" (SBS).

Numerous scientific studies and research projects have been conducted in recent years to assess the ambient air quality in Kuwait,[11–22] and several have examined the IAQ in residential homes.[23–26] A recent study by Alhumood et al[26] assessed the contribution of vehicular traffic emissions of VOCs to indoor and outdoor air quality at 12 houses in 10 residential areas of Kuwait. Although many studies have been published worldwide that have evaluated IAQ as part of the indoor environmental quality (IEQ) in LOBs,[27–35] none have addressed this topic in Kuwait. Because office employees spend most of their waking hours working indoors, it is important to accurately characterize the types, levels and sources of indoor and outdoor pollutants at LOBs. These data are needed to reliably assess the effects of IAQ on employee health and productivity. In addition, a detailed characterization of indoor air pollutants and their indoor/outdoor sources will provide insight into the factors affecting their control and/or elimination. Therefore, this study is intended to (1) investigate both indoor and outdoor levels of VOCs; (2) determine the variability in the chemical composition of the VOCs; (3) determine the variation in their levels among buildings; and (4) identify their major sources whenever possible in the eight selected LOBs, which encompass the commercial and business areas in urban Kuwait. This information will be useful for identifying effective strategies or engineering design for controlling or eliminating indoor sources as well as minimizing contributions from outdoor sources.

Materials and Methods

HPLC-grade volatile- and organic-free water obtained from a Millipore Ultra-Pure Water Purification System (Millipore, Bedford, MA, USA) was used for the humidifier. Ultra-high-purity helium and nitrogen gases (99.9999 grade) were further purified using large Agilent RMSH-2 and RMSN-2 universal traps, respectively (Agilent Technologies Inc., Santa Clara, CA, USA). Helium was used as the carrier gas in the GC and preconcentrator and for cleaning various sampling devices. Nitrogen was used to dilute calibration and internal standards, pressurize samples and prepare blanks. Nitrogen gas from high-pressure liquid nitrogen containers was used to clean canisters and other sampling devices. Liquid carbon dioxide cylinders were used to cool the preconcentrator traps. Entech Micro-QT 6 L silonite fused-silica-lined stainless steel canisters (Entech Instruments Inc., Simi Valley, CA, USA) were used for air sampling, the preparation of calibration and internal standards and for blanks. The Entech 3100A Canister Cleaning System permits cleaning of canisters on a 12-position canister oven manifold by cycling between evacuation and filling with clean humidified nitrogen at 80 °C to rinse contamination out of the canisters. Separate cylinders of certified 1.0 ppm of each of the TO-15 standard calibration gas mixture (specially prepared by Dr. Daniel Reimer, University of Miami, Miami, FL, USA) and the internal standard gases bromochloromethane, 1,4-difluorobenzene, chlorobenzene-d5 and 1,2-dibromobenzene (prepared by Scott Specialty Gases Co., USA) were purchased from Entech Instruments, Inc. The cylinders were plumbed directly to an Entech 4600A Dynamic Diluter, which is designed to dilute the gas blend of either the calibration gas-mixture or the internal standard gases to the required concentration in pure humidified nitrogen diluent in Entech 6 L canisters. The diluter was programmed and automatically controlled using Entech software. The calibration standard canister was used to deliver the required standard concentration levels of the VOC calibration standard samples. The internal standard canister was used to deliver a fixed volume of the four gases to each sample, blank and calibration standard automatically via the Entech 7410 Headspace inlet autosampler before starting the analyte preconcentration process.

Description of sampling sites

Eight LOBs were selected in various urban areas of Kuwait (Fig. 1) to provide a representative sampling scheme for potential sources of air pollution and a good representation of typical indoor environments in Kuwait. The selection of LOB characteristics and location was based on the US-EPA sampling protocol "Standardized EPA Protocol for Characterizing

Indoor Air Quality in Large Office Buildings".[36] Table 1 provides information on these offices and their sampling locations. All of the LOBs have central heating, ventilation and air-conditioning systems (HVAC), with several air handling units (AHU) on each floor. Smoking is not prohibited, and the windows of all offices are kept closed at all times. During the air sampling period, no renovation or refurbishment projects were performed.

Sample collection

Whole air samples were collected passively using cleaned and evacuated 6 L canisters. Canister sampling was performed either in grab mode or time-integrated mode. Entech grab samplers with external filters were used. A pre-calibrated Entech CS1200ES Silonite coated flow controller with the appropriate sapphire orifice (Codes 1–5) (Entech Instruments, Inc.) was installed on the 6 L canister to obtain the required time integrated air sample. The CS1200ES includes a dust filter, rain guard and threaded inlet cover to prevent contamination. Sierra 820 Series Top-Trak™ Mass Flow Meters (Sierra Instruments, Monterey, CA, USA) were used to set the required flow rate for the CS1200ES flow controllers. Flow rates of approximately 12.5 and 4.2 cc/min were used to obtain 8- and 24-hour integrated air samples, respectively. The field sampling was conducted from August 2010 to December 2011 beginning at 7 AM for either 8 or 24 hours. Two sampling points, indoor (I) and outdoor (O), were defined at each of the LOBs. The procedure specified in the EPA sampling protocol[36] was used to select the indoor test area in each building. All test areas were served by an identified HVAC unit and by no more than two AHUs and could not share common ventilation with mechanical or storage rooms or cafeterias. The I sample was collected by placing the sampling canister in the center of the selected test area at a height of 1.5 m above the floor to represent the breathing zone level of a seated person. The O sample was collected simultaneously outside the LOB by placing the sampling canister in a sheltered position as close as possible to the AHU that feeds the selected study area inside the building. Canisters were stored in a contaminant-free environment. Storage time of up to thirty days is recommended.[37] In this study, all of the I and O air samples were analyzed within a maximum period of

Table 1. Information on the large office buildings sampled in this study.

Building →	DT	JA	AW	SI	AE	RG	SR	UH
Location	Downtown Kuwait	Jahra	West Ahmadi	Industrial area	East Ahmadi	Riggae	Sorra south	Ali Sabah Al-Salem
Construction year	1998	1983	1990	1978	2004	1981	2005	1993
Renovation year	–	2005	2003	1998	–	2002	–	2007
Number of floors	25	2	5	2	6	10	8	2
Building area, m²	14,500	6,250	4,400	4,850	24,000	15,500	12,500	2,870
Sampling floor (its area, m²)	Mezzanine (2 open floors)	1	2	2	2	10	3	2
Sampling area, m²	1,400	750	950	1,100	950	1,750	1,400	375
Number of workers	65	51	36	57	55	61	48	25
HVAC location	Penthouse (4th and 5th floors)	Roof	Roof	Roof	Chiller units (outside)	chiller units (outside)	Roof	Roof
Air-handling location	Penthouse, same floor	Roof	Penthouse, same floor	Roof	Penthouse, same floor	Penthouse, same floor	Roof	Roof

one week from the date of collection. The sampling procedure and performance criteria for quality assurance were performed according to US-EPA Compendium Method TO-15.[37]

Analytical procedure

Based on US-EPA method TO-15,[37] an aliquot of the air sample from a canister (nominally 250 cc) was preconcentrated and analyzed for VOCs using an Entech 7150 preconcentrator attached to an Entech 7410 Headspace inlet/7016 tower canister autosampler (Entech Instruments, Inc.) and an Agilent 7890 A/5975 gas chromatograph/mass spectrometer (GC/MS) system (Agilent Technologies, Inc.). The 7150 preconcentrator utilizes 3 + 1stages to perform trapping, matrix management, volume reduction and, finally, splitless injection into the GC/MS using liquid CO_2 cryogenic traps: active SPME (T1), empty Silonite-coated dehydration (T2) and Tenax (T3). In the first stage, initial trapping of the whole sample (or standard) was performed under the following conditions: T1 at 50 °C to trap heavier VOCs, T2 at −30 °C to trap water and T3 at −50 °C to trap lighter VOCs. Water was removed in the second stage by heating T2 to 160 °C while flushing the trap out to a vent. The traps T1 and T3 were maintained at their trapping temperatures during this process, allowing compounds of interest to remain intact while water was eliminated. The third stage allowed the lighter VOCs to dynamically refocus as they were transferred back from T3 to T1, where they were combined with the heavier VOCs by desorbing T3 at 200 °C and cooling T1 to −52 °C. After all of the VOCs were refocused onto T1, they were injected onto the GC column by the rapid heating of T1 to 230 °C. The 7150 injector was also heated to 150 °C to prevent the loss of heavier VOCs during transit to the GC column. The injection time was adjusted at 6 min to ensure complete delivery of heavier VOCs off of T1 through the injector column and onto the GC analytical column (J&W DB-5MS fused silica capillary column of 0.32 mm i.d. and 1 µm film thickness; Agilent Technologies, Inc.) for the separation of VOCs. The column was initially held at 35 °C for 5 min, increased to 110 °C at a rate of 4 °C/min for 0.1 min and increased to 220 °C at a rate of 15 °C/min for 10 min. The separated VOCs were identified in MSD-full scan mode using the following parameters: electron energy, 70 V (nominal);

mass range, 29–280 amu; scan time, as needed to produce at least 10 scans per peak while not exceeding 1 s per scan; and threshold, 200.

Quality control

All of the GC/MS analyses of air samples were performed to meet the technical acceptance criteria of the US-EPA TO-15 method.[37] This included BFB tuning (section 10.4 for details), five-point calibration, continuing calibration response checks, method blank analyses, internal standard response and retention time checks as well as analyte retention time and integration checks. Sample duplicates and triplicates were performed at a frequency of 30% and 5%, respectively, and indicated a precision within ±10%. The method detection limit (MDL) was determined by conducting seven replicate measurements of the 78 compounds of VOCs at concentrations near the expected detection limits (within a factor of five), computing the standard deviation for the seven replicate concentrations and multiplying this value by the Student's t value for 99 percent confidence for seven values of 3.14.[37] Table 2 shows the determined MDL values and frequency of detection for the most abundant VOCs.

Results and Discussion

A total of 800 air samples were simultaneously collected from the I and O sampling areas of the studied LOBs (DT, JA, AW, SI, AE, RG, SR and UH) on 54 different dates during the 17-month period (Table 1 and Fig. 1). The collected samples were analyzed for 78 VOCs, which were grouped into six chemical classes to explore the variability in chemical composition. These groups included the following: (1) six aliphatic hydrocarbons (HCs), (2) 29 halogenated HCs (HHCs), (3) 15 carbonyl compounds (CCs), (4) five alcohols, (5) 16 aromatic compounds (ACs) (comprising 10 aromatic hydrocarbons (AHCs) and six chlorinated AHCs (CAHCs)), (6) and seven miscellaneous compounds. Table 3 presents a statistical summary of the most abundant and most frequently detected compounds in each class of VOCs in the I and O samples collected from each LOB.

The results indicated that 73 and 66 different compounds were detected in the I and O samples, respectively, at various levels and proportions. The number of compounds that were detected in less than

Table 2. Method detection limits (MDLs) of the most abundant volatile organic compounds (VOCs) and its frequency of detection in the indoor (I) and outdoor (O) samples.

S/N	VOC name	% Detection		MDL[a]
		I	O	
I. Aliphatic hydrocarbons (HCs)				
1	Pentane	99.3	99.2	0.4
2	Hexane	95.3	91.2	0.4
3	Propene	100	100	0.3
4	Isoprene	86.3	33.3	0.2
5	*iso*butene	69.1	71.7	0.4
6	1,3-Butadiene (BD)	64.6	42.6	0.2
II. Halogenated aliphatic hydrocarbons (HHCs)				
1	CDFM[b]	97.3	95.2	1.4
2	DCDFM[b]	97.3	95.7	0.1
3	Chloromethane (CM)	91.8	90.5	0.3
4	TCFM[b]	89.5	87.7	0.1
5	Methylene chloride (MC)	63.3	52.6	0.2
III. Carbonyl compounds (CCs)				
1	Acetaldehyde	99.5	100	0.5
2	Acrolein	58.4	34.1	0.3
3	Acetone	99.5	99.7	0.4
4	Propanal	90.5	83.7	0.3
5	Methacrolein (MA)	34.4	18.3	0.2
6	Butanal	59.9	43.6	0.3
7	MEK[b]	52.4	28.8	0.2
8	Pentanal	42.1	20.3	0.2
9	Hexanal	71.8	56.6	0.1
IV. Alcohols				
1	Methanol	99.0	99.0	1.2
2	Ethanol	99.8	89.2	0.3
3	1-Propanol	10.2	2.0	0.3
4	2-Propanol	97.0	97.2	0.4
5	1-Butanol	24.7	20.1	0.4
V. Aromatic compounds (ACs)				
1	Benzene	98.0	95.7	0.2
2	Toluene	98.5	98.7	0.3
3	Ethylbenzene (EB)	91.5	83.7	0.2
4	*m*-Xylene	96.0	92.7	0.3
5	*p*-Xylene	92.8	86.0	0.3
6	Styrene	46.6	22.6	0.3
7	*o*-Xylene	93.8	88.2	0.3
8	1,2,4-TMB[b]	89.3	75.7	0.2
9	p-DCB[b]	22.9	6.0	0.2
VI. Miscellaneous compounds (MCs)				
1	Cyclopentane (CP)	91.3	88.5	0.2
2	Cyclohexane (CH)	66.6	39.8	0.3
3	Acetonitrile (ACN)	87.3	77.2	0.3
4	Vinyl acetate (VA)	28.2	15.8	0.3
5	MTBE[b]	66.8	57.9	0.3

Notes: [a]Concentration in ppbv; [b]chlorodifluoromethane (CDFM), dichlorodifluoromethane (DCDFM), trichlorofluoromethane (TCFM), methyl ethyl ketone (MEK), trimethyl benzene (TMB), dichlorobenzene (DCB), methyl tertiary butyl ether (MTBE).

1%, 5% and 10% of the total samples were 14, 13 and 3, respectively, for the I samples and 11, 11 and 4, respectively, for the O samples. None of the VOCs exceeded either the Kuwait-Environment Public Authority (KU-EPA) air quality limits[38] or the time-weighted average (TWA) threshold limit values recommended by the National Institute for Occupational Safety and Health (NIOSH).[39] The results of each class of VOCs are presented and discussed below.

Aliphatic hydrocarbons (HCs)

Among the HCs, alkenes and alkynes are more highly reactive in atmospheric photochemical reactions than are alkanes. In air pollution studies, alkynes are not of major concern because they are relatively rare in the atmosphere, whereas alkenes are the much more important because they are present in appreciable amounts. The analyzed and detected HCs included the alkenes propene, isobutene, isoprene and 1,3-butadiene (BD) in addition to the alkanes pentane and hexane. As shown in Table 3, the mean values of all six HCs were higher in the I samples than in the O samples; the highest and lowest I/O ratios were found for isobutene and hexane, respectively. In the I and O samples, the highest mean values were found for propene, followed by pentane and isobutene, whereas BD exhibited the lowest values. By contrast, among all LOBs, the highest mean values of the HCs were generally found in the I and O samples for SI and those LOBs located in close proximity (UH, AW and AE), with the exception of the value of 8.6 ppbv for pentane in the I sample for DT (compared to 8.3 ppbv for SI) (Table 4). The I and O samples for SI exhibited the highest mean values of the alkanes pentane and hexane. In addition, SI exhibited the highest recorded values of 627 for propene and 186.2 ppbv for isobutene in the I samples, whereas 151.1 ppbv pentane was detected in the I samples for DT. The lowest mean values of the HCs were found in the I and O samples from JA. These findings may be attributed to the emissions from the industrial activities at SIA and its proximity to the LOBs in the southern part of Kuwait (SI, AW, AE, and UH) and from vehicular emissions from the congested roads at DT. The variations between these LOBs depend on the relative degree of proximity to industrial emission sources, wind speed, wind direction and dispersion level.

Table 3. Summary statistics for the most abundant volatile organic compounds (VOCs) in the indoor (I) and outdoor (O) samples.[a]

S/N	VOC name	Indoor (I)					Outdoor (O)					I/O
		Mean	SD	Median	Min	Max	Mean	SD	Median	Min	Max	
I. Aliphatic hydrocarbons (HCs)												
1	Pentane	5.5	9.7	3.4	0.4	151.1	3.8	5.4	2.3	0.4	45.5	1.4
2	Hexane	1.7	1.7	1.2	0.4	17.5	1.5	1.7	1.0	0.4	15.3	1.1
3	Propene	12.4	32.7	7.7	0.7	627	5.5	5.9	3.8	0.4	51.3	2.3
4	Isoprene	2.0	1.8	1.5	0.2	17.6	0.9	1.2	0.6	0.2	8.7	2.2
5	*iso*butene	5.4	18.6	1.1	0.4	186	1.7	4.2	0.6	0.4	37.2	3.2
6	1,3-Butadiene (BD)	1.0	1.2	0.7	0.2	16.1	0.5	0.9	0.4	0.2	11.4	2.0
II. Halogenated aliphatic hydrocarbons (HHCs)												
1	CDFM[b]	32.9	162	3.6	1.6	1340	10.3	53.7	1.9	1.4	928.0	3.2
2	DCDFM[b]	2.3	2.9	1.2	0.2	20.8	0.8	0.7	0.6	0.2	10.3	2.9
3	Chloromethane (CM)	1.1	2.5	1.0	0.3	48.5	0.8	0.5	0.7	0.3	7.0	1.4
4	TCFM[b]	0.8	2.9	0.4	0.1	51.8	1.0	5.4	0.3	0.1	80.7	0.8
5	Methylene chloride (MC)	1.6	6.4	0.6	0.2	96.9	0.9	1.8	0.5	0.2	18.1	1.8
III. Carbonyl compounds (CCs)												
1	Acetaldehyde	7.7	5.3	6.6	0.5	38.5	4.6	4.0	3.9	0.5	51.1	1.7
2	Acrolein	1.0	1.8	0.6	0.4	24.1	0.7	1.1	0.4	0.3	8.3	1.4
3	Acetone	14.8	29.1	10.1	0.4	520	10.8	19.5	5.9	0.5	270	1.4
4	Propanal	6.1	5.5	4.9	0.3	70.8	3.7	4.2	2.9	0.3	62.4	1.6
5	Methacrolein (MA)	0.8	1.1	0.4	0.2	7.3	1.2	2.0	0.7	0.2	14.6	0.7
6	Butanal	1.4	3.9	0.5	0.3	33.9	1.0	2.4	0.5	0.3	24.2	1.4
7	MEK[b]	2.8	8.6	1.3	0.2	115.0	1.1	1.2	0.6	0.2	8.2	2.5
8	Pentanal	0.5	0.4	0.4	0.2	3.4	0.4	0.3	0.3	0.2	2.3	1.3
9	Hexanal	1.0	2.1	0.7	0.1	34.0	0.6	0.6	0.5	0.1	4.4	1.7
IV. Alcohols												
1	Methanol	35.1	42.1	21.7	1.6	289	23.0	67.6	10.6	1.2	965	1.5
2	Ethanol	112	253	58.1	0.5	4380	7.6	14.8	3.3	0.4	212	14.7
3	1-Propanol	16.8	40.5	6.1	0.3	240	80.8	170	5.6	0.3	486	0.2
4	2-Propanol	12.3	17.3	7.3	0.4	207	5.3	6.5	3.5	0.5	55.4	2.3
5	1-Butanol	2.7	2.1	2.1	0.4	15.3	2.0	1.4	1.4	0.4	6.4	1.4
V. Aromatic compounds (ACs)												
1	Benzene	1.5	1.3	1.2	0.2	11.1	1.3	3.9	0.8	0.2	74.0	1.2
2	Toluene	11.8	22.0	4.4	0.5	185.0	5.1	8.1	2.8	0.5	72.7	2.3
3	Ethylbenzene (EB)	1.4	4.2	0.7	0.2	71.8	0.7	1.0	0.5	0.2	11.0	2.0
4	*m*-Xylene	2.7	8.4	1.3	0.3	145.1	1.6	2.8	0.8	0.3	27.9	1.7
5	*p*-Xylene	1.3	4.0	0.6	0.3	67.4	0.8	1.2	0.4	0.3	10.6	1.6
6	Styrene	1.2	3.5	0.3	0.3	22.7	1.4	3.9	0.3	0.3	32.3	0.9
7	*o*-Xylene	1.5	3.8	0.8	0.3	61.7	0.8	1.2	0.5	0.3	16.3	1.9
8	1,2,4-TMB[b]	1.1	2.4	0.6	0.2	32.4	0.6	1.0	0.4	0.2	14.4	1.8
9	p-DCB[b]	2.5	5.1	0.5	0.2	24.4	2.3	3.5	0.4	0.2	10.0	1.1
VI. Miscellaneous compounds (MCs)												
1	Cyclopentane (CP)	1.8	2.2	1.2	0.2	27.7	1.4	1.9	0.9	0.2	23.5	1.3
2	Cyclohexane (CH)	1.1	6.1	0.5	0.3	99.8	0.6	1.3	0.4	0.3	14.6	1.8
3	Acetonitrile (ACN)	4.1	6.0	2.4	0.5	56.8	3.3	5.8	1.6	0.4	60.2	1.2
4	Vinyl acetate (VA)	0.5	0.4	0.4	0.3	3.1	0.5	0.7	0.3	0.3	5.0	1.0
5	MTBE[b]	0.9	1.2	0.6	0.3	16.6	0.7	1.0	0.5	0.3	13.0	1.3

Notes: [a]Concentration in ppbv; [b]chlorodifluoromethane (CDFM), dichlorodifluoromethane (DCDFM), trichlorofluoromethane (TCFM), methyl ethyl ketone (MEK), trimethyl benzene (TMB), dichlorobenzene (DCB), methyl tertiary butyl ether (MTBE).

Table 4. Variation in the mean values of aliphatic hydrocarbons (HCs) in the indoor (I) and the outdoor (O) samples among studied large office buildings.

Compound	Sample*	DT	JA	AW	SI	AE	RG	SR	UH	All samples
Pentane	I	8.6 ± 21.5	2.0 ± 1.9	6.0 ± 4.5	8.3 ± 9.3	5.4 ± 3.3	3.2 ± 2.8	5.1 ± 4.2	5.3 ± 5.9	5.5 ± 9.7
	O	2.6 ± 3.1	2.1 ± 2.6	5.6 ± 5.2	7.9 ± 10.3	3.9 ± 3.4	2.3 ± 1.8	3.1 ± 2.7	4.0 ± 5.1	3.8 ± 5.4
Hexane	I	1.2 ± 0.9	0.8 ± 0.7	2.1 ± 1.5	3.0 ± 2.9	2.0 ± 1.2	1.2 ± 1.2	1.9 ± 1.5	1.5 ± 1.4	1.7 ± 1.7
	O	1.1 ± 0.9	1.0 ± 1.2	1.8 ± 1.6	2.7 ± 2.7	1.6 ± 1.2	0.9 ± 0.7	1.1 ± 0.9	1.8 ± 2.3	1.5 ± 1.7
Propene	I	6.5 ± 4.2	6.7 ± 7.1	10.9 ± 8.2	18.2 ± 12.3	14.1 ± 8.6	10.1 ± 8.9	9.7 ± 7.2	22.7 ± 83.6	12.4 ± 32.7
	O	3.9 ± 3.1	3.2 ± 3.0	9.8 ± 9.5	8.5 ± 8.4	7.4 ± 6.6	4.1 ± 3.0	4.6 ± 3.6	5.9 ± 6.3	5.5 ± 5.9
Isoprene	I	1.7 ± 1.1	1.6 ± 1.4	1.7 ± 1.3	2.8 ± 2.3	1.6 ± 1.0	2.5 ± 2.7	2.0 ± 1.2	1.6 ± 1.3	2.0 ± 1.8
	O	0.9 ± 1.0	1.8 ± 2.6	1.7 ± 2.0	0.7 ± 0.7	0.8 ± 0.7	0.8 ± 0.7	0.7 ± 0.5	0.6 ± 0.4	0.9 ± 1.2
IsoButene	I	1.8 ± 2.9	2.0 ± 3.2	10.2 ± 21.4	13.8 ± 34.5	5.2 ± 10.6	4.8 ± 13.1	2.1 ± 1.5	8.7 ± 32.4	5.4 ± 18.6
	O	1.1 ± 2.2	1.5 ± 4.5	6.6 ± 10.4	1.9 ± 4.6	0.6 ± 0.7	0.9 ± 1.0	1.3 ± 2.3	2.0 ± 4.2	1.7 ± 4.3
1,3-Butadiene	I	0.7 ± 0.4	0.7 ± 0.8	0.7 ± 0.4	1.1 ± 0.6	0.7 ± 0.4	1.0 ± 0.7	1.1 ± 0.7	1.7 ± 3.0	1.0 ± 1.2
	O	0.4 ± 0.2	0.6 ± 0.8	0.4 ± 0.3	0.4 ± 0.3	0.5 ± 0.3	0.9 ± 2.1	0.6 ± 0.4	0.4 ± 0.3	0.5 ± 0.9

Note: *I: Indoor and O: Outdoor.

A review of Kuwait air quality studies revealed that only hexane (among all HCs) was recorded in indoor and outdoor areas of a house in the Khaldiya residential area, with maximum values of 10.5 and 11.0 ppbv, respectively.[23]

Halogenated aliphatic hydrocarbons (HHCs)

The five HHCs bromodichloromethane, cis-1,3-dichloropropene, 1,2-dibromoethane, 1,1,2,2-tetrachloroethane and 1,1-dichloroethane were not detected in any of the samples. The seven compounds 1,1-dichloroethene, methyl iodide, trans-1,2-dichloroethene, cis-1,2-dichloroethene, 1,1,1-trichloroethane, 1,2-dichloropropane and 1,1,2-trichloroethane were detected in less than 1% of the I samples, with concentrations very close to the MDL. Ten compounds, including vinyl chloride (VC), bromomethane (BM), chloroethane (CE), chloroform (CF), carbon tetrachloride (CTC), trichloroethylene (tri-CE), trans-1,3-dichloropropene (t-DCP) and bromoform (BF), in addition to the chlorofluorocarbons (CFCs) 1,2-dichlorotetrafluoroethane (DCTFE, known as CFC-114) and 1,1,2-trichloro-1,2,2-trifluoroethane (TCTFE, known as CFC-113), were detected in less than 5% of the samples. The I samples of VC and DCTFE exhibited the highest mean values of 2.1 and 1.7 ppbv and the highest recorded values of 9.7 and 14.9 ppbv respectively, whereas less than 0.7 ppbv was detected in the corresponding O samples. Mean values of less than 1.0 ppbv were observed for the other compounds. The compounds 1,2-dichloroethane (DCE) and tetrachloroethylene (TCE) were detected in less than 20% of the samples, with mean values of less than 0.5 ppbv and maximum recorded values of 3.5 and 4.0 ppbv in the I samples from SI and RG, respectively (these data are not included in Table 3).

The percent detections were 55% for methylene chloride (MC) and more than 90% for the compounds chlorodifluoromethane (CDFM), dichlorodifluoromethane (DCDFM), trichlorofluoromethane (TCFM) and chloromethane (CM). The CFCs TCFM and DCDFM, known as CFC-11 and CFC-12, respectively, are used as an aerosol spray propellant and as a refrigerant. Due to concerns regarding their ability to damage the ozone layer, their manufacture was banned in the USA and many other countries in

1996 to comply with the Montreal Protocol.[40] CDFM is a hydroCFC (HCFC) that is known as HCFC-22 (or R-22) and is often used as an alternative to the highly ozone-depleting CFC-11 and CFC-12 because of its relatively low ozone depletion potential (ODP) of 0.055. HCFCs have 80% shorter atmospheric lifetimes and up to 98% less ODP than the corresponding CFCs.[40] CDFM is gradually being phased out in new equipment in the USA under the Montreal Protocol and has been replaced by other non-ozone-depleting alternative refrigerants with lower ODPs, such as propane (R-290).[41]

Table 3 shows that among all of the HHCs, the highest mean values obtained for CDFM in the I and O samples, respectively, were 15-times greater than the values for DCDFM. MC was detected at 1.6 and 0.9 ppbv, whereas the lowest values of 0.8 and 1.0 ppbv corresponded to TCFM in I and O samples, respectively. With the exception of TCFM, the I/O ratio was >1.0, with a maximum value for CDFM, followed by DCDFM. The variation in the mean values of the most abundant HHCs among various LOBs is shown in Figure 2. The mean value of CDFM in the I samples from DT was the highest among the LOBs, followed by those for IS, RG, and very low values for the other LOBs. In addition, DT exhibited the highest mean value of CDFM in the O samples, which was 5-times greater than the next highest level, which was detected at SR (Fig. 2A). Furthermore, DT

exhibited the highest recorded values of CDFM, 1340 and 928 ppbv in the I and O samples, respectively. These high values are the result of significant leakage from the HVAC systems to the indoor air at both DT and SI in addition to the dispersion to the outdoor air from the HVAC systems located at the penthouse of DT (Table 1). Leakage from the HVAC systems at the other LOBs was comparatively low.

As shown in Figure 2B, the highest mean value of DCDFM was detected in the I samples from SI, followed by that from UH. These values are considerably higher than the highest mean value for DCDFM in the O samples (from UH). JA exhibited the lowest values of DCDFM among both the I and O samples. Among the studied LOBs, the maximum recorded values of DCDFM in the I and O samples were detected at SI and UH, respectively, which may be correlated to the presence of these VOCs within the components of HVAC refrigerant gases at these LOBs.

The mean TCFM values in the I and O samples from UH were five- and eight-times greater, respectively, than those at all other LOBs (Fig. 2C). In addition, UH exhibited the maximum recorded values in the I and O samples. The higher TCFM values outdoors relative to indoors at UH (I/O ratio of 0.8) may be attributed to leaking from the HVAC system in addition to dispersion downwind from MIAs located to the north (consistent with the I/O ratio of <1.0) (Fig. 1).
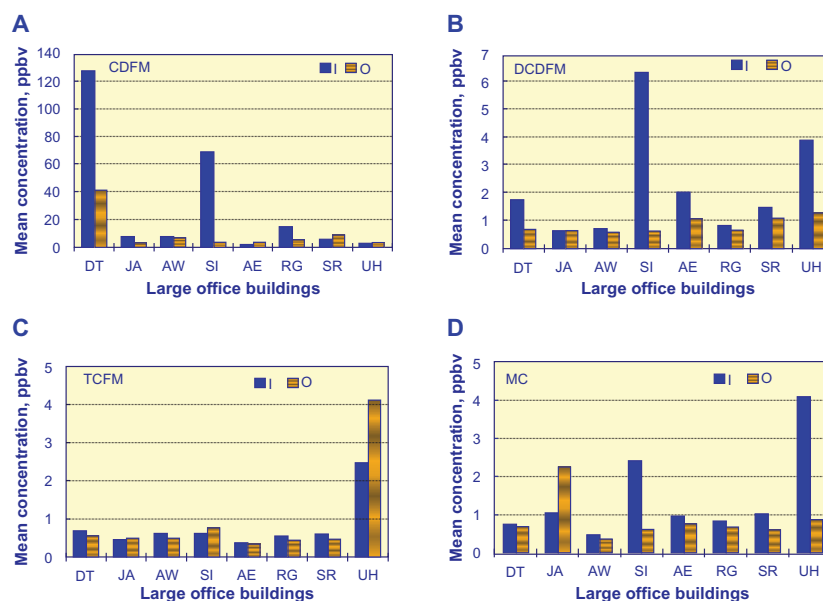
Figure 2. Variation of the mean values of the most abundant halogenated aliphatic hydrocarbons (HHCs) in the indoor (I) and outdoor (O) samples among the studied large office buildings.

Figure 2D shows that among LOBs, the highest mean values of MC in the I and O samples were obtained at UH and JA, with maximum recorded values of 96.6 ppbv (for UH) and 20.2 ppbv (for SI), respectively. These higher values may be explained by the indoor emissions at UH in addition to the emissions from nearby MIAs (Fig. 1).

The mean values of CM in the I and O samples were 1.1 and 0.8 ppbv, respectively (Table 3). UH exhibited the highest mean values of 1.9 and 1.0 ppbv, and the maximum values recorded in I and O samples were 48.5 ppbv and 7.0 ppbv, respectively.

Bouhamra et al[24] reported mean values of 223.1 and 202.9 mg/m^3 for freons (CFCs) in I and O samples, respectively, from residences in Kuwait.
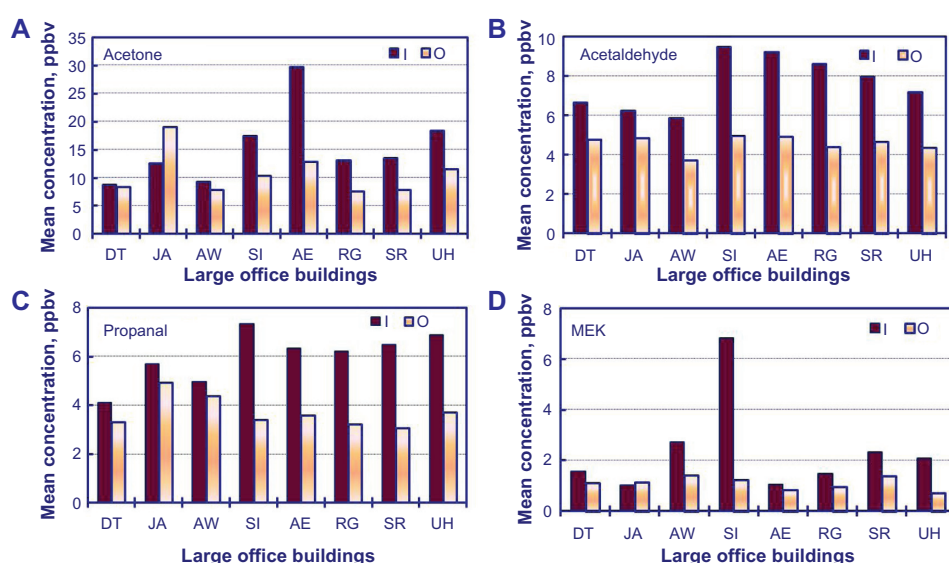
Carbonyl compounds (CCs)

Fifteen CCs were analyzed. Only 2-hexanone and 3-hexanone were not detected in any of the I and O samples, whereas methyl vinyl ketone (MVK), 2-pentanone, 3-pentanone, and 4-methyl-2-pentanone (MP) were detected in less than 10% of the samples. The highest mean value was 0.8 ppbv for 3-pentanone in the I samples and MVK in the O samples, and a maximum value of 6.0 ppbv was recorded for MVK in the O samples (these data are not included in Table 3). The carbonyls acrolein, methacrolein (MA), butanal, pentanal, methyl ethyl ketone (MEK) and hexanal were detected in all samples (I and O) in proportions ranging from 26% (MA) to 60% (hexanal),

with a maximum mean value of 2.8 ppbv for MEK. Acetaldehyde, acetone and propanal were detected in more than 85% of the samples. Table 3 shows that the I/O ratios of the CCs were >1.0 (except MA, which had a ratio of 0.7), with a range of 1.3 (pentanal) to 2.5 (MEK). Among the CCs, acetone exhibited the highest mean values in the I and O samples, followed by acetaldehyde, propanal, and MEK.

The variations in the mean values of the most abundant carbonyls at various LOBs are shown in Figure 3. Acetone showed the highest mean values in the I and O samples from AW and JA, respectively; these buildings also had the highest recorded values of 520 and 270 ppbv. The lowest values were obtained at DT and RG in the I and O samples, respectively (Fig. 3A). With the exception of JA, the mean values of acetone in the I samples for all LOBs were higher than those in the O samples, with I/O ratios ranging from 0.7 for JA to 2.3 for AE, indicative of indoor emission sources for acetone in all of the LOBs. The high outdoor emissions at JA (main hospital of the governorate, with a group of restaurants nearby) may be the main source of the high level of acetone in the O samples for this LOB.

Figure 3B shows that the mean values of acetaldehyde in the I samples were higher than those in the O samples for all LOBs, with little variations in these values among either the I or O samples. The I/O ratio ranged from 1.3 for JA to 2.0 for RG. Among the LOBs, the mean values in the I and O samples

Figure 3. Variation of the mean values of the most abundant carbonyl compounds (CCs) in the indoor (I) and outdoor (O) samples among the studied large office buildings.

from SI were the highest, followed by those at AE; AW exhibited the lowest values, whereas the highest recorded values of 38.5 and 51.1 ppbv were obtained at SI and JA, respectively.

The highest mean values of propanal in the I and O samples were obtained at SI and JA, respectively, while the lowest values were obtained respectively at DT and SR (Fig. 3C). The I/O ratio for propanal ranged from 1.1 for AW to 2.2 for SI. The highest recorded values of propanal in the I and O samples were 70.8 and 62.4 ppbv from UH and JA, respectively.

The I/O ratio for MEK ranged from 0.9 for JA to 5.6 for SI. The highest recorded values of MEK in the I and O samples were 115.0 and 8.2 ppbv, respectively, from SI. Figure 3D shows that among the LOBs, the highest mean values of MBK in the I and O samples were obtained from SI and AW, respectively, and the lowest values were respectively from JA and UH.

No previous air quality studies performed in Kuwait have reported data on the indoor or outdoor levels of CCs.
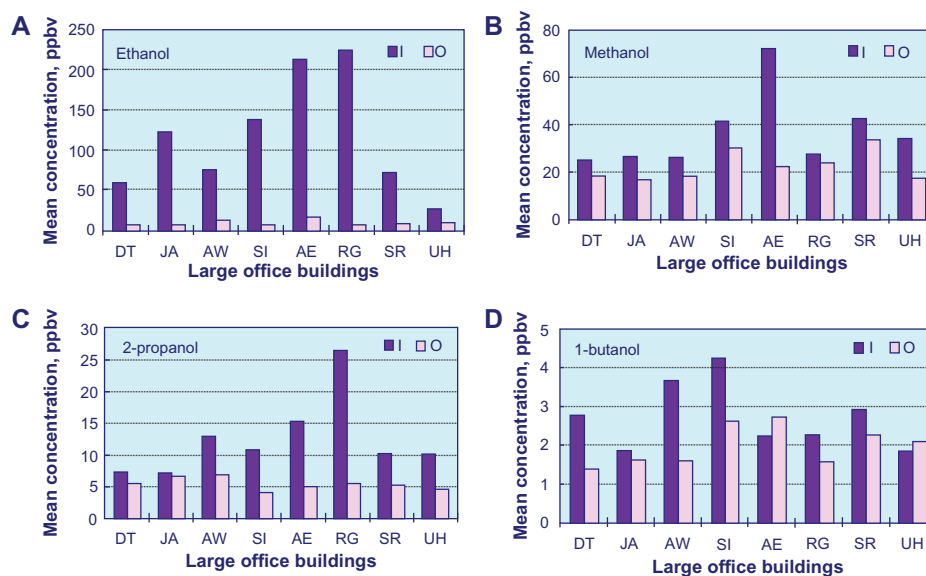
Alcohols

Table 2 shows that the alcohols ethanol, methanol and 2-propanol were detected in more than 95% of the samples, whereas 1-butanol was detected in 13% and 1-propanol was detected in 6%. The mean value of ethanol in the I samples was significantly higher than those of the other alcohols, which were ranked in the order ethanol > methanol > 1-propanol > 2-propanol,

with 1-butanol having the lowest level. The mean values for all alcohols were higher in the I sample than in the O samples (except 1-propanol), with an extremely high I/O ratio (14.7) for ethanol. The mean value of 1-propanol in the O samples was significantly higher than the values of the other alcohols in the O samples (its I/O ratio was 0.2). In addition, it exhibited the lowest detection levels.

Among the studied LOBs, the mean value of ethanol in the I samples from RG was the highest recorded value, followed by that at AE. UH exhibited the lowest value, whereas ethanol values were the highest and lowest in the O samples from AE and SI, respectively (Fig. 4A). The maximum detected values of ethanol in the I and O samples, 4380.3 and 212.3 ppbv, were detected at RG and AE, respectively. The I/O ratio of ethanol ranged from 3 for UH to 34 for RG. The vast difference in ethanol levels between the I and O samples indicates the occurrence of high emissions from indoor sources. Ethanol emissions could be attributed to the oxidation of hydrocarbons and emissions from furniture, copiers, printers and utilities as well as the traditional extensive use of perfumes, fragrances and air fresheners by female Kuwaitis coupled with the high percentage of female employees in the RG and AE offices (which exhibited the highest indoor levels of ethanol).

Methanol exposure may occur during the use of solvents and via the inhalation of ambient air. Vegetation, volcanic emissions, microbes and industrial activities

Figure 4. Variation of the mean values of the most abundant alcohols in the indoor (I) and outdoor (O) samples among the studied large office buildings.

emit methanol to the environment. Methanol was the second most highly detected alcohol (after ethanol), with mean values of 35.1 and 23.0 ppbv in the I and O samples, respectively, and a mean I/O ratio of 1.5 (Table 3). Figure 4B shows that the mean values of methanol in the I samples were slightly higher than those in the O samples for all LOBs. The I/O ratio ranged from 1.3 for SR to 3.2 for AE. In the I samples, the highest mean values were obtained at AE, SR and SI, whereas the lowest value was obtained at DT. SI and AE are located near a methanol plant in the SIA. The indoor source of methanol at AE contributed significantly to the large difference in the level of this alcohol in the I and O samples. In the I and O samples, the maximum detected values at AE and SR were 288.8 and 965.2 ppbv, respectively, which may be attributed to some unknown emission events.

The mean values of 2-propanol in the I samples were higher than those in the O samples, with a mean I/O ratio of 2.3 (Table 3). Among the LOBs, RG exhibited the highest I/O ratio of 4.8, followed by 3.0 for AE; the lowest ratio was detected at JA. In addition, the highest mean values obtained for I and O samples were obtained at RG and AW whereas the lowest values were obtained at JA and SI, respectively (Fig. 4C). The highest recorded values of 2-propanol in the I and O samples were obtained from RG and JA, respectively. These increases may be attributable to indoor emission sources and the absence of casual incidents outdoors.

Table 2 shows that 1-butanol was detected in 20.1% and 24.7% of the I and O samples, with mean values of 2.7 and 2.0 ppbv and maximum recorded values of 15.3 ppbv (for SI) and 6.4 ppbv (for SR), respectively, and a mean I/O ratio of 1.4 (Table 3). Figure 4D shows that among the studied LOBs, the highest mean value of 1-butanol in the I samples was obtained at SI, followed by AW. The values in the O samples were slightly higher than those in the I samples only at AW and UH, with I/O ratios <1.0. For the other LOBs, this ratio ranged from 1.2 for JA to 2.0 for DT.

The frequency of detection of 1-propanol was lowest among the alcohols in the I (10.2%) and O (0.2%) samples, with mean values of 16.8 and 80.3 ppbv, respectively (Table 3). 1-Propanol was not detected in the I samples from DT and SI and in the O samples from AW, RG and UH. The results of the

GC/MS analysis indicated the presence of 1-propanol in one of the O samples from JA (486.4 ppbv) and DT (134.0 ppbv), in addition to a few of the I samples from RG and JA with maximum recorded values of 240.0 and 122.2 ppbv, respectively (data not included in Table 3). The detection of these abnormally high levels of 1-propanol in a few samples may be attributed to its emission from temporary casual incidents.

Previous studies reported that the highest values of methanol in I and O samples of 59 and 65 ppbv, respectively, were obtained at a residential house at Ahmadi (Kuwait).[23] Published data on the levels of other alcohols in ambient and indoor air in Kuwait are not available.

Aromatic compounds (ACs)

The analyzed ACs included the AHCs benzene, toluene, ethylbenzene (EB), o-xylene (o-X), m-xylene (m-X), p-xylene (p-X) (together known as BTEX), styrene, 1,2,3-trimethylbenzene (1,2,3-TMB), 1,2,4-trimethylbenzene (1,2,4-TMB) and 1,3,5-trimethylbenzene (1,3,5-TMB) as well as the CAHCs chlorobenzene (CB), o-dichlorobenzene (o-DCB), m-dichlorobenzene (m-DCB), p-dichlorobenzene (p-DCB), benzyl chloride (BC) and 1,2,4-trichlorobenzene (1,2,4-TCB).

The mean values of the AHCs in the I samples were higher than those in the O samples (except styrene) (Table 3); the highest and lowest I/O ratios were found for toluene and styrene, respectively. Among the AHCs, toluene exhibited the highest mean values in the I and O samples, whereas 1,3,5-TMB exhibited the lowest values.

Among the studied LOBs, SR exhibited the highest mean values for all AHCs in the I samples (except toluene (SI), and styrene (AW)) and in the O samples (except toluene, m-X and p-X (JA), and styrene (AW)) (Table 5). The I/O ratios of all AHCs were >1.0 for all LOBs, with the exception of JA (which ranged from 0.3 for styrene to 1.0 for benzene). UH exhibited the highest ratios for all of the AHCs, with the exception of benzene at AE, toluene at SI, and 1,2,4-TMB at SR. The highest recorded values of o-, m-, and p-xylenes were found in the I samples from UH and in the O samples from SI.

The highest and lowest mean values of styrene in the I and O samples were exhibited by AW and AE, respectively (Table 5). RG and JA exhibited

Table 5. Variation in the mean values of aromatic hydrocarbons (ACs) in the indoor (I) and the outdoor (O) samples among studied large office buildings.

Compound	Sample*	DT	JA	AW	SI	AE	RG	SR	UH
Benzene	I	1.7 ± 1.1	1.1 ± 0.6	0.8 ± 0.4	1.5 ± 1.3	1.2 ± 0.9	1.5 ± 1.0	2.8 ± 2.1	1.1 ± 0.6
	O	1.2 ± 0.7	1.1 ± 1.1	0.8 ± 0.6	1.2 ± 1.5	0.7 ± 0.6	1.1 ± 0.7	2.6 ± 9.8	1.0 ± 0.7
Toluene	I	6.9 ± 8.2	3.8 ± 3.3	4.1 ± 7.1	30.0 ± 36.7	6.9 ± 14.8	8.6 ± 15.5	15.8 ± 16.3	11.3 ± 29.2
	O	5.3 ± 6.3	7.9 ± 13.6	3.0 ± 6.2	4.9 ± 9.4	3.4 ± 3.3	4.6 ± 4.9	5.6 ± 8.3	4.3 ± 5.5
Ethyl-benzene	I	1.4 ± 1.4	0.6 ± 0.4	0.5 ± 0.3	0.9 ± 1.2	0.7 ± 0.5	0.8 ± 0.6	2.7 ± 4.2	2.2 ± 10.0
	O	0.8 ± 0.5	0.7 ± 0.8	0.5 ± 0.3	0.8 ± 1.8	0.4 ± 0.3	0.7 ± 0.4	1.0 ± 1.5	0.5 ± 0.3
o-Xylene	I	1.4 ± 1.1	0.8 ± 0.5	0.6 ± 0.3	1.0 ± 1.5	0.9 ± 0.7	1.0 ± 0.7	3.3 ± 4.5	2.1 ± 8.3
	O	0.9 ± 0.6	1.0 ± 1.2	0.5 ± 0.5	0.9 ± 2.5	0.5 ± 0.4	0.9 ± 0.6	1.1 ± 1.5	0.6 ± 0.4
m-Xylene	I	2.3 ± 1.8	1.3 ± 0.9	0.9 ± 0.5	2.0 ± 2.8	1.5 ± 1.2	1.7 ± 1.3	5.9 ± 9.3	4.3 ± 19.7
	O	1.5 ± 1.1	2.3 ± 4.4	0.8 ± 0.6	1.7 ± 4.2	1.5 ± 3.3	1.4 ± 1.0	1.8 ± 2.6	1.1 ± 0.9
p-Xylene	I	1.0 ± 0.8	0.6 ± 0.4	0.5 ± 0.3	0.8 ± 1.1	0.6 ± 0.5	0.8 ± 0.4	2.8 ± 4.6	1.9 ± 9.0
	O	0.8 ± 0.5	1.0 ± 1.8	0.5 ± 0.5	0.8 ± 1.7	0.8 ± 1.4	0.7 ± 0.5	0.9 ± 1.4	0.5 ± 0.4
Styrene	I	1.1 ± 2.5	1.1 ± 2.1	7.2 ± 9.9	0.4 ± 0.3	0.2 ± 0.1	1.7 ± 4.7	0.5 ± 0.3	2.7 ± 6.4
	O	1.3 ± 2.5	4.3 ± 9.4	10.6 ± 5.6	0.3 ± 0.2	0.3 ± 0.1	0.5 ± 0.6	1.3 ± 3.2	0.5 ± 0.7
1,2,4-TMB	I	0.90 ± 0.7	0.8 ± 1.1	0.4 ± 0.2	0.9 ± 1.3	0.5 ± 0.5	0.7 ± 0.4	2.8 ± 5.5	0.7 ± 0.9
	O	0.6 ± 0.4	0.6 ± 0.7	0.5 ± 0.2	0.8 ± 2.4	0.3 ± 0.2	0.6 ± 0.4	0.8 ± 0.9	0.4 ± 0.2

Note: *I: Indoor and O: Outdoor.

the highest recorded values of styrene in the I and O samples, respectively. Among the studied LOBs, the I/O ratios of styrene were <1.0 at DT, JA, AW, AE, and SR, whereas the highest ratio was detected at UH. The lower levels of styrene in the I samples relative to the O samples illustrate that the main source of styrene emissions was outdoor activities, with no contribution from the indoors, in contrast to the previously discussed VOCs.

Table 3 shows that among the TMB isomers, the isomer 1,2,4-TMB exhibited the highest mean values and the highest recorded values in the I and O samples. Among the studied LOBs, SR exhibited the highest mean values in the I and O samples (Table 5). The I/O ratio for 1,2,4-TMB ranged from 1.1 for SI to 3.6 for SR.

The CAHCs CB, o-DCB, m-DCB and BC were detected in less than 1% of the I and O samples, and 1,2,4-TCB was detected in less than 2.4% of samples with values close to the MDL; p-DCB was detected in 23% and 6% of the I and O samples, with mean values of 2.5 and 2.3 ppbv and maximum recorded values of 24.4 ppbv (at SI) and 10 ppbv (at UH), respectively (data not included in Table 3). In Kuwait, Bouhamra et al[23] reported that the highest recorded values of benzene, toluene and xylenes were 460, 1022 and 886 ppb, respectively, in I samples and 721, 1438 and 989 ppbv in O samples, respectively, for a residential house at Khaldiya, and 480 and 714 ppbv for EB in I and O samples from residential houses in Jabriya and Jahra, respectively. These values are significantly higher than the values observed in this study, which may be due to the differences in activities that occur in residential houses and office buildings.

BTEX and their inter-species correlations

In urban ambient air, the BTEX (benzene (B), toluene (T), EB, and xylenes (Xs)) group of AHCs is one of the major groups of air pollutants and constitutes up to 60% of NMVOCs.[42] This study indicates that the percentages of BTEX/TVOCs were within the range of 3.4%–13.3% for I samples and 5.5%–13.9% for O samples. Studies on source apportionment confirmed that vehicular emissions are the dominant source of AHCs in urban areas[42,43] and that BTEX represents an efficient indicator of the air pollution from these emissions.[44] Good correlations have been reported between the species of BTEX.[45–49]

According to many researchers,[46–50] ratios of toluene to benzene (T/B) of 1.5 to 4.0 are considered an indication of emissions from mobile sources. Zhang et al[51] identified the ratio of (m,p)-Xs to EB (X/E) as an indicator of photochemical age. Regardless of the geographic location, (m,p)-Xs and EB are emitted in urban areas at a ratio of approximately 3.6[52] and are removed from the atmosphere by chemical reaction, deposition and dispersion. However, (m,p)-Xs are removed approximately three-times faster than EB via atmospheric chemical reactions. Therefore, the X/E ratio typically decreases with photochemical aging.[53]

The results of the current study indicate that there are certain similarities between the mean values of TVOCs and BTEX among the studied LOBs as well as between BTEX species in the I and O samples. The differences in the maximum and minimum mean values at various LOBs for both TVOCs (221.2 and 29.3 ppbv for I and O samples, respectively) and BTEX (29.0 and 8.6 ppbv for I and O samples, respectively) exhibited a similar pattern (Fig. 5). These differences were significantly higher in the I samples than in the O samples. Among the studied LOBs, there were significant variations in the mean values of TVOCs in the I samples (Fig. 5A). The highest values were obtained at AE, SI, and RG, whereas the lowest values were obtained at AE and UH. The I/O ratio of the TVOCs was highest for RG (4.6), followed by AE (4.2) and SI (3.8), whereas the ratios for other LOBs ranged from 2.0 for AW (lowest) and 2.3 (highest) for SR. These differences could be attributed to the large variations in the levels of indoor emissions, particularly the emissions of CFCs, alcohols and a number of CCs (as explained above). In particular, these emissions had a significant role in the elevation of TVOC levels in the I samples from AE, SI, RG and DT. The ratio for samples averaged

for all LOBs was 2.9 (Fig. 5A). In contrast to the I samples, the variations in the mean values of the O samples at various LOBs were insignificant. This may be attributable to the unique characteristics of Kuwait (in which urban areas are surrounded by the sea and deserts and occupy only 6% of the total area) and the massive outdoor emissions from flaring processes as well as various industrial and traffic activities. The wind direction and velocity may play a major role in the dispersion of these emissions evenly throughout the ambient air of urban areas due to the relative proximity of these areas (Fig. 1).

As shown in Figure 5B, the pattern of the mean values of BTEX in the I samples is similar to that of TVOCs. Among the studied LOBs and in the I samples, SI exhibited the highest mean value, followed by SR and UH. The lowest mean values were exhibited by AW and JA. In the O samples, the highest mean values were exhibited by JA and SR, whereas the lowest value was obtained for AW. The I/O ratio of BTEX was the highest for SI (3.7) and very similar to the I/O value for TVOCs (3.8), followed by UH (2.9) and SR (2.6), whereas the ratio ranged from 0.6 for JA (lowest) and 1.7 for AE. These ratios could be attributed to the existence of indoor emission sources of BTEX in all of the studied LOBs to varying degrees and the absence of these sources in JA (as indicated by the insignificant variations in TVOCs, as outlined above). In agreement with other studies,[49,54] toluene was found to be the most abundant BTEX species. The ratio percent of T/BTEX varied and ranged from 44% to 72% and 47% to 56% in the I and O samples, respectively. The total-xylenes/BTEX ratio ranged from 16% to 34% and from 28% to 32%, B/BTEX from 9% to 16% and from 13% to 18% and EB/BTEX from 9% to 16% and from 13% to 18% in the I and O samples, respectively.
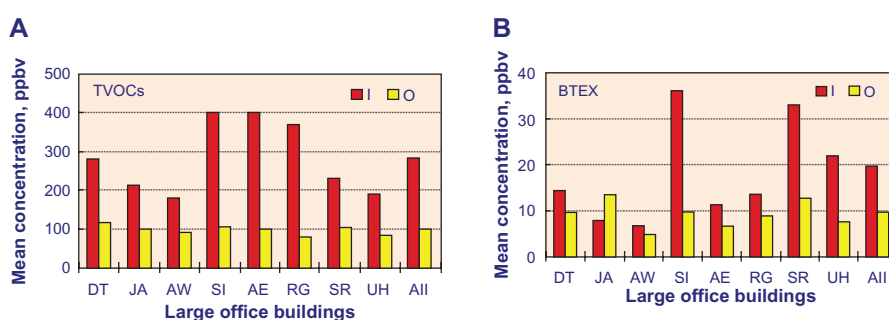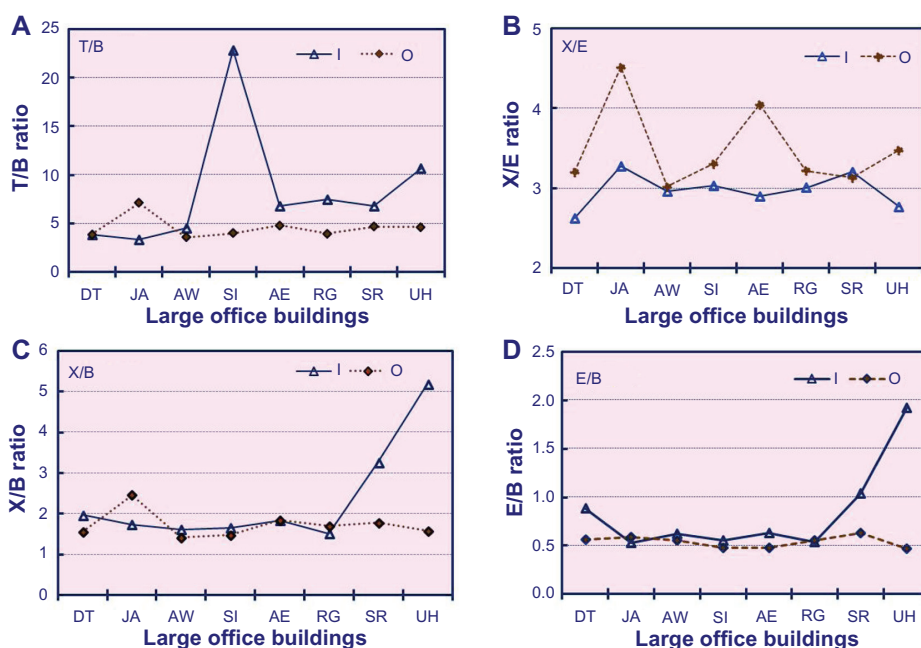

Figure 5. Variation of the mean values of the total volatile organic compounds (TVOCs) and BTEX in the indoor (I) and outdoor (O) samples among the studied large office buildings.

Several authors have used BTEX inter-species ratios as indicators of the sources of VOCs in air.[47–53] The following T/B ratios have been observed in ambient air: 2.5 in Delhi, India,[49] 1.6 in Shanghai, China,[55] 2.8 in Rome, Italy,[56] 2.2 to 4.3 in Windsor, Canada,[48] 4.3 in Ankara, Turkey,[57] and 2.0 in Izmir, Turkey.[58] All of these studies reported that vehicular emissions were a major contributor to VOCs in the ambient air. Higher T/B ratios were recorded for Bangkok-Thailand (10.22),[50] Hong Kong (7.74),[54] Osaka-Japan (7.19) and Sydney-Australia (4.04).[44] The differences in the (T/B) ratios among these cities may reflect differences in their industrial activities, fuel composition and vehicle types. In the present study, the mean T/B ratio for all I and O samples (for all LOBs) was 8.7 and 4.6, respectively. Among the studied LOBs, an extremely high T/B ratio of 22.9 in the I samples was detected at SI, followed by 10.7 for UH, and the lowest ratio of 3.3 was obtained at JA (Fig. 6A). In the O samples, JA exhibited the highest ratio of 7.1 (in contrast to the I samples), and lower but approximately similar values were obtained for the other LOBs (all having ratios ranging from 4.0 to 4.5). The higher T/B ratios in the I samples are attributed to the contribution of toluene from indoor sources; the highest toluene emissions occurred at SI, whereas toluene emissions were absent at JA. For the O samples, it is difficult to define the extent of the contribution of

vehicular emissions to the outdoor air at the OBs due to a lack of data on the chemical composition of the fuel available in Kuwait; however, we can conclude that among the studied LOBs, JA exhibited the lowest contribution from vehicular emissions, with relatively more and variable contributions (approximately similar to each other) for the other LOBs. In addition, the contribution from industrial and flaring sources to the outdoor levels of VOCs at JA is greater than that at the other LOBs.

The X/E ratio indicates transport of VOCs from high-emission sites and is used as an indicator of the age of these VOCs in the atmosphere.[58,59] The rate of (m,p)-xylenes degradation in the atmosphere is much faster than that of EB, with atmospheric life times of three and eight hours, respectively. This difference in reactivity means that as the polluted air travels, the levels of m-, p-xylenes will decrease to a greater extent than those of EB, and consequently, the decrease in the X/E ratio is dependent on the distance from the source. X/E ratios of 3.8, 3.8 and 4.4 have been reported for a tunnel, fresh emissions at a gas station and in an underground garage, respectively.[57] During the course of the current study at the LOBs, the average X/E ratio ranged from 2.6 for DT to 3.3 for JA in the I samples and from 3.1 for SR to 4.5 for JA in the O samples (Fig. 6B). These ratios indicate that the VOC emissions were primarily fresh for JA

Figure 6. Variation of the mean values of the ratios of BTEX species in the indoor (I) and outdoor (O) samples among the studied large office buildings.

and partly aged to varied degrees for other LOBs. This explanation is consistent with the proximity of JA and the relatively remote distance of the other LOBs to the flaring sources to the north while considering the prevailing wind velocity and direction.

The variations in the mean m-, p-xylenes/benzene (X/B) ratios (Fig. 6C) and EB/benzene (E/B) ratios (Fig. 6D) among the LOBs were highly comparable either among the I samples or among the O samples or between the I and O samples for each ratio; however, the X/B ratios (1.6–5.2 (I) and 1.4–2.5 (O)) were greater than the E/B ratios (0.5–1.9 (I) and 0.5–0.6 (O)). With the exception of SR and UH (for the I samples), the ratios X/B and E/B for the I and O samples exhibited comparable low values for all of the LOBs, indicating that there are either high emissions of benzene and/or a greater photochemical degradation of xylenes. However, the higher ratios in the I samples from SR and UH indicate either fewer indoor emissions of benzene and/or less photochemical degradation of xylenes compared to the other LOBs. The higher ratios also imply that xylenes and EB have been transported from the surrounding areas (or emitted from indoors) to SR and UH to a lesser extent than to other LOBs. Hoque et al[49] reported a similar behavior in the urban atmosphere of Delhi, India.

Alhumood et al[26] studied the levels of BTEX species in the indoor and outdoor air of 12 residential houses in Kuwait using a portable HAPSITE GC/MS device. Ranges of 0.5–11.7, 1.0–49.7, 1.0–25.7, 0.1–34.6 and 0.1–27.3 ppb were found for B, T, EB, o-X and p-X, respectively, in the I samples, and ranges of 0.4–5.8, 1.9–30.4, 0.5–17.4, 0.6–29.0 and 0.6–43.9 ppb, respectively, were found in the O samples. The ranges of the I/O ratios for B, T, o-X and p-X were 0.5–6.4, 0.5–3.7, 0.5–3.0 and 0.5–3.3, respectively. Inter-species correlations were not discussed, and these data cannot be compared with the data presented in the current study due of the differences in activities between residential houses and office buildings.

Miscellaneous compounds (MCs)

The MCs included 1,4-dioxane, carbon disulfide (CDS), vinyl acetate (VA), methyl tertiary butyl ether (MTBE), acetonitrile (ACN), and the cyclic hydrocarbons cyclopentane (CP) and cyclohexane (CH). 1,4-Dioxene was detected in only one of the I samples from SI at a very low level of 0.6 ppbv. CDS was detected in 5.2% and 7.8% of the I and O samples, respectively, with mean values of 0.6 and 0.4 ppbv and highest recorded values of 2.2 ppbv (for SR) and 1.9 ppbv (for JA) in I and O samples, respectively (data not included in Table 3).

As shown in Table 2, VA was detected in 28.2% and 15.8% of the I and O samples, with mean values of 0.5 and 0.5 ppbv and highest recorded values of 3.1 ppbv (for RG) and 5.0 ppbv (for SI), respectively (Table 3).

MBTE was detected in 66.8% and 57.9% (Table 2) with mean values of 0.9 and 0.7 ppbv and highest recorded values at RG and SI in the I and O samples, respectively (Table 3). The mean value for MTBE in the I samples for SR was the highest recorded level, followed by thatfor RG, with the lowest value obtained at AW (Table 6). In contrast to all other LOBs, the mean value of MTBE in the O samples from SI was higher than that in the I samples from SI and was also higher than the values in the O samples from the other LOBs.

ACN is commonly used as a solvent, for spinning fibers and in lithium batteries, and the primary airborne emission sources are automobile exhaust and manufacturing facilities. ACN was detected in 87.3% and 77.2% of the I and O samples (Table 2), with mean values of 4.1 and 3.3 ppbv and highest recorded values of 56.8 and 60.2 ppbv (for SI), respectively (Table 3). As shown in Table 6, the mean values in the I samples were higher than those in the O samples for various LOBs (except for UH). In addition, the highest mean values in the I and O samples were obtained at SI, and the variation in the values in the I and O samples was not significant.

The highest recorded values of CP were detected in the I and O samples at RG and SI with detection frequencies of 89% and 91%, respectively (Tables 2 and 3). Table 5 shows that the highest mean values in the I and O samples were obtained at SI, whereas the lowest mean values were obtained at JA. The mean values of CP in the O samples were slightly higher than those in the I samples for both SI and JA.

The mean CH values in the I and O samples from UH were the highest and were significantly high in comparison to those values for all other LOBs (Table 6). The recorded values of 99.8 and 14.6 ppbv in the I and O samples, respectively, from UH were also the highest among the LOBs. CH was detected

Table 6. Variation in the mean values of miscellaneous compounds (MCs) in the indoor (I) and outdoor (O) samples among the studied large office buildings.

Office buildings ↓	Cyclopentane		Cyclohexane		Acetonitrile		MTBE	
	I	O	I	O	I	O	I	O
DT	1.5 ± 0.9	1.0 ± 0.8	0.5 ± 0.3	0.4 ± 0.2	3.9 ± 5.1	2.1 ± 2.4	0.8 ± 0.5	0.7 ± 0.4
JA	0.8 ± 0.6	1.1 ± 1.4	0.5 ± 0.2	0.5 ± 0.4	1.9 ± 1.3	1.9 ± 2.4	0.6 ± 0.7	0.5 ± 0.5
AW	1.5 ± 0.9	1.4 ± 1.1	0.9 ± 0.7	0.5 ± 0.5	4.2 ± 6.9	3.3 ± 6.3	0.5 ± 0.3	0.5 ± 0.4
SI	2.7 ± 2.8	2.8 ± 4.2	1.0 ± 0.9	0.7 ± 0.9	7.0 ± 10.6	6.7 ± 11.6	0.8 ± 0.6	1.3 ± 2.3
AE	1.7 ± 1.1	1.4 ± 1.2	0.8 ± 0.8	0.4 ± 0.3	5.0 ± 3.3	3.5 ± 2.9	0.6 ± 0.4	0.5 ± 0.3
RG	1.7 ± 3.9	1.0 ± 0.6	0.6 ± 0.8	0.4 ± 0.2	3.8 ± 4.3	2.0 ± 2.3	1.1 ± 2.6	0.6 ± 0.3
SR	2.4 ± 1.8	1.2 ± 0.9	0.8 ± 0.4	0.5 ± 0.3	3.8 ± 3.6	2.3 ± 2.1	1.5 ± 1.0	0.7 ± 0.5
UH	1.6 ± 1.8	1.2 ± 1.3	3.5 ± 16.1	1.5 ± 3.3	3.9 ± 7.0	4.8 ± 6.8	0.6 ± 0.9	0.4 ± 0.2

in 40% and 67% of the I and O samples, respectively (Table 2).

The I/O ratio ranged from 1.0 for VA to 1.8 for CH, indicating that there was variation in the degree of indoor emissions between various MCs, with the exception of VA.

Chemical composition of VOCs

Although there was significant variation among the mean values of TVOCs in the I samples and relatively little variation among the O samples from the LOBs (Fig. 5A), there was considerable variation in the chemical composition of the VOC mixtures. Figure 7 shows the variation in the six classes (HCs, HHCs, CCs, alcohols, ACs (AHCs and CAHCs) and MCs) of VOCs in the I and O samples among various LOBs. Alcohols represented the greatest proportion of VOCs for all of the LOBs (second most abundant for DT) in either the I or O samples, ranging from 32% (DT) to 75% (RG) of the TVOCs in the I samples and from 23% (UH) to 44% (AW) of the TVOCs in the O samples. Ethanol was a major contributor to the alcohols class in the I samples, with an average of 63%, whereas 1-propanol contributed to the O samples and represented 68% of the total alcohols among the LOBs.

CCs were the second most abundant class of VOCs (third most abundant for DT and SI), ranging from 8% (DT) to 18% (UH) of the TVOCs in the I samples and from 15% (DT) to 28% (JA) of the TVOCs in the O samples. Acetone and acetaldehyde were the most abundance CCs, representing 41% and 21% of CCs in the I samples and 45% and 19% of CCs in the O samples, respectively, from all LOBs.
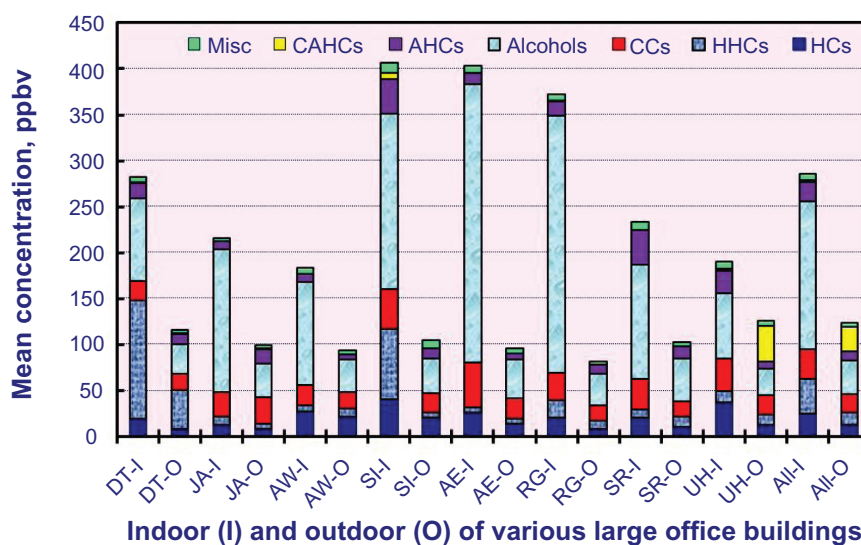
Figure 7. Variation of the mean values of the chemical classes of VOCs in the indoor (I) and outdoor (O) samples among the studied large office buildings.

Unexpectedly, HCs were the third most abundant class of VOCs (fourth most abundant for DT and SI), ranging from 6% (JA) to 19% (UH) of the TVOCs in the I samples and from 8% (DT and JA) to 24% (AW) of the TVOCs in the O samples. Propene and pentane were the most highly represented compounds among the HCs, representing 44% and 20% of HCs in the I samples and 40% and 27% of HCs in the O samples, respectively, from all LOBs.

The HHC levels were highly variable among the studied LOBs, ranging from 2% (AE) to 46% (DT) of the TVOCs in the I samples and from 6% (JA) to 36% (DT) of the TVOCs in the O samples. CDFM was the main contributor, representing 85% and 75% of total HHCs species in the I and O samples, respectively, from all LOBs. Among the LOBs, HHCs were the most abundant class in the I and O samples at DT.

ACs include the AHCs and CAHCs. The contribution of AHCs ranged from 3% (AE) to 16% (SR) of the TVOCs in the I samples and from 6% (AW) to 15% (JA) of the TVOCs in the O samples, with variable abundances among the I and O samples and among the LOBs. Toluene was a major contributor to the AHCs at 47% and 35%, followed by xylenes with 22% and 21% of total AHCs in the I and O samples, respectively, from all LOBs. CAHCs constituted the smallest fraction of TVOCs in all of the LOBs; this class consisted of a single quantified compound, p-DCB. Thus, the contribution of CAHCs was insignificant and cannot be recognized in Figure 7. Its contribution ranged from 0% (AE) to 1.8% (SI) of the TVOCs in the I samples and from 0% (SI, AE, RG, and SR) to 30% (UH) of the TVOCs in the O samples (this abnormality was discussed above).

The MCs class had a minor contribution to the TVOCs, ranging from 1% (JA) to 4% (UH) of the TVOCs in the I samples and from 3% (DT and JA) to 9% (SI) of the TVOCs in the O samples. ACN and CP were the most highly represented compounds among the MCs at 49% and 21% of the total MCs in the I samples and 21% and 22% of the total MCs in the O samples, respectively, from all LOBs.

Conclusions

A study of the levels of 78 VOCs was conducted using a total of 800 samples collected from the indoor and outdoor areas of eight LOBs from August 2010 to December 2011. The analysis of the data from this comprehensive sampling program indicated that (1) 73 and 66 compounds were detected in the I and O samples, respectively, at different levels and in different proportions at various LOBs. None of the VOCs exceeded either the KU-EPA air quality limits or the TWA levels recommended by NIOSH. In addition, (2) the levels of the majority of VOCs were higher in the I samples than in the O samples, with an I/O ratio >1. Ethanol exhibited the highest ratio of 14.7. The ratios were <1 for only four compounds, although these compounds were mainly detected at low levels. The increased VOC concentrations of I samples relative to O samples could be attributed to the existence of indoor emissions from wall paints, carpets, furniture, copiers, printers and other office utilities. In addition, the oxidation of hydrocarbons and the extensive use of perfumes, fragrances and air fresheners may be responsible for the significant increase in indoor ethanol levels relative to outdoor. Moreover, we found that (3) the LOBs at DT and those in the southern part of Kuwait (SI, AW, AE and UH) exhibited the highest levels of HCs, which were attributed to vehicular emissions at DT and industrial emissions from nearby industrial activities in the south. Furthermore, (4) CFCs were detected extremely high levels indoors at several LOBs in comparison to the other HHCs, which was attributed to leakage from HVAC systems. In addition, (5) there was a wide disparity between the mean values of TVOCs in the I samples among LOBs, whereas only small differences between the O samples were observed. The differences among the I samples corresponds to the variation in the levels of indoor emissions, whereas the wind direction and speed may play a major role in the dispersion of these emissions evenly among the ambient air of urban areas because of the relative proximity of these areas. (6) BTEX inter-species ratios, which were used as indicators of the source of airborne VOCs, indicated a lower contribution of vehicular emissions to the outdoor air at JA compared to other LOBs. Moreover, (7) the chemical composition of VOCs revealed that alcohols and carbonyls (oxidized hydrocarbons) were the first and second most abundant classes, respectively. In most cases, HCs and ACs were the third and fourth most abundant classes, respectively, whereas HHC levels were highly variable among the LOBs. Among the chemical classes, ethanol, acetone, acetaldehyde,

propene, pentane, CDFM and toluene were the most abundant compounds in their respective classes.

The data from this study will be useful to health authorities as well as researchers interested in epidemiological studies.

Author Contributions

Conceived and designed the experiments: HFA, AIA, NMA. Analysed the data: HFA, AIA, NMA. Wrote the first draft of the manuscript: AIA. Contributed to the writing of the manuscript: HFA, AIA, NMA. Agree with manuscript results and conclusions: HFA, AIA, NMA. Jointly developed the structure and arguments for the paper: HFA, AIA, NMA. Made critical revisions and approved final version: AIA. All authors reviewed and approved of the final manuscript.

Competing Interests

Author(s) disclose no potential conflicts of interest.

Disclosures and Ethics

As a requirement of publication the authors have provided signed confirmation of their compliance with ethical and legal obligations including but not limited to compliance with ICMJE authorship and competing interests guidelines, that the article is neither under consideration for publication nor published elsewhere, of their compliance with legal and ethical guidelines concerning human and animal research participants (if applicable), and that permission has been obtained for reproduction of any copyrighted material. This article was subject to blind, independent, expert peer review. The reviewers reported no competing interests.

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