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Ambient levels of volatile organic compounds in the atmosphere of Greater Cairo

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Abstract

Ambient volatile organic compounds (VOCs) samples were collected at three locations, two in urban areas in Greater Cairo (Ramsis and Haram) and background one in rural area in Menofiya province (Kafr El-Akram), during the period of June, 2004–August, 2004. The highest concentrations of VOCs were found in Ramsis, whereas the lowest concentrations were detected in Kafr El-Akram, and the difference in mean concentrations were statistically significant ($p < 0.001$). Among all of the measured VOCs species, the contribution of individual VOC to the total VOCs concentration were very similar in Ramsis and Haram locations, toluene was the most abundant compound followed by (m, p)-xylene. This similarity implies a similar emission sources of VOCs in both urban locations, vehicle exhausts are the dominant one. Greater Cairo has high levels of volatile aromatic hydrocarbons compared with many polluted cities in the world. The BTEX (benzene: toluene: ethylbenzene: xylenes) concentration ratios were (2.01:4.94:1:4.95), (2.03:4.91:1:4.87) and (2.31:2.98:1:2.59) in Ramsis, Haram and Kafr El-Akram, respectively. The average toluene/benzene (T/B), (m, p)-xylene/benzene ((m, p)-X/B) and o-xylene/benzene (o-X/B) concentration ratios were 2.45, 1.61and 0.85, respectively in Ramsis and 2.42, 1.61 and 0.78, respectively in Haram. The ratios in both urban locations were of the same magnitude and close to those obtained from automotive exhausts, indicating that the ambient BTEX originate mainly from motor vehicle emissions. However, the (T/B), ((m, p)-X/B) and (o-X/B) concentration ratios were 1.29, 0.71 and 0.41 in Kafr El-Akram, respectively. These ratios were lower than those found in Ramsis and Haram locations and in automotive exhaust, suggesting that the BTEX in Kafr El-Akram do not come from a local source and are exclusively results from the diffusion and dispersion of VOCs produced from the traffic density in the surrounding cities. Significant positive correlation coefficients ($p < 0.001$) were found between the concentrations of BTEX compounds at the three sampling locations. The diurnal variation of VOCs concentrations in Ramsis location showed two daily peaks linked to traffic density.
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Keywords: VOCs; Urban/rural areas; BTEX ratio; BTEX correlation; Diurnal variation; Air quality in Greater Cairo

1. Introduction

High rate of industrialization/urbanization process, especially in developing countries, leads to an increase in the emission of many types of air pollutants due to fossil fuel combustion. Volatile organic compounds (VOCs) are one of the most important groups of air pollutants in the urban atmosphere because they can cause significant risk to human health. Many VOCs have been reported to be toxic, carcinogenic or mutagenic (Duce et al,

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1983; Edgerton et al., 1989; Sweet and Vermette, 1992; Kostiainen, 1995; Mukund et al., 1996). In addition, the presence of VOCs in the atmosphere play an important role in the formation of ground level ozone, photochemical oxidants and smog episodes (Monod et al., 2001) and they are harmful to the ecosystem (Derwent, 1995; Kuran and Sojak, 1996; Dewulf and Van Langenhove, 1997; Atkinson, 2000). In addition, ozone and photochemical oxidants lead to an increase in the formation and fate of airborne toxic chemicals and fine particles (Finlayson-Pitts and Pitts Jr., 1997).

The sources of VOCs are both anthropogenic and natural. The major anthropogenic sources in the urban environment are vehicle exhaust, gasoline evaporation, emissions from the use of solvents, and gas leakage from natural gas and liquefied petroleum gas (LPG) (Fujita et al., 1995; Jose et al., 1998; Kourtidis et al., 1999; Derwent et al., 2000; Srivastava et al., 2005). The levels of VOCs in the ambient air are related to the fuels used, vehicle types and ages, flow rates and speeds of traffic as well as road and environmental conditions in the city (Paul, 1997). The increased aromatics, olefins and other organic compounds in fuels used in vehicles lead to an increase in the emission of aromatic VOCs, especially from vehicles which are not supplied with catalytic converters (Singh et al., 1985; Perry and Gee, 1994). Volatile aromatic hydrocarbons represent a significant fraction of gasoline and other fuels as well as automobile exhausts (Yamamoto et al., 2000). Benzene, toluene and xylenes are the most abundant among the aromatic volatile hydrocarbons (Singh et al., 1985; Brocco et al., 1997).

Aromatic VOCs in the atmosphere have a high photochemical ozone creation potential. They take part in photochemical reactions and are major sources of radicals which can oxidize $NO–NO_2$, the precursor of ozone (Finlayson-Pitts and Pitts Jr., 2000; Reis et al., 2000). Among the aromatic volatile hydrocarbons (benzene, toluene, ethylbenzene and xylenes), xylenes are considered the more reactive species with respect to ethylbenzene, whereas benzene has a lower reactivity and more stable in the atmosphere, due to its relatively longer lifetime (Calvert et al., 2000; Hsieh and Tsai, 2003). Xylenes ((m, p)-xylene plus o-xylene) are the most dominant contributor to ozone formation among BTEX (Na et al., 2005). The (m, p)-xylene/ethylbenzene concentration ratio is used to investigate the extent of photochemical reactivity in the atmosphere and to estimate the photochemical age of air mass (Nelson and Quigley, 1984; Monod et al., 2001; Hsieh and Tsai, 2003).

There is a lack of information on VOCs concentrations in Greater Cairo. Previous studies on air pollution in Greater Cairo had been focused on gaseous pollutants like SO_2, NO_2, NH_3, O_3 and total oxidants, and suspended particulate matter and its chemical composition (Khoder, 1997, 2002; Hassan, 2000). These studies indicate that the photochemical smog occurs in Cairo atmosphere during the summer season, especially around noon. Therefore, it is very important to evaluate the concentration levels and variation of VOCs in Cairo atmosphere. This will help in setting a proper strategy to control the ground level ozone, photochemical oxidants and smog episodes build up in the future.

Therefore, the present study aims to measure the levels of ambient VOCs in three sampling locations, two in urban areas in Greater Cairo and background one in rural area in Menofiya province, and to study the diurnal variation of VOCs concentrations at the most polluted location (Ramsis).

It should be noted that the present study is a part of the plan designed by the Air Pollution Research Department, National Research Centre to investigate the ambient air quality in Greater Cairo.

2. Materials and methods

2.1. Sampling sites and periods

Greater Cairo region lies to the south of Delta in the Nile basin. In the last century, urbanization and industrialization have been rapidly increased, causing an increase in the pollution of Cairo atmosphere. Greater Cairo region (Cairo, Giza & Shoubra El-Khiema cities) houses more than 11.30 million inhabitants. About 52% of the industries and about 40% of electrical power stations in Egypt are found in Greater Cairo, besides more than 1.30 million vehicles are running in the streets of the Greater city (Nasralla, 2001). Consequently, it is considered one of the most polluted megacities in the world. Vehicle fuels used in Greater Cairo are mainly unleaded gasoline and diesel, and some vehicles are using compressed natural gas (CNG).

Menofiya is one of the biggest provinces in the Nile Delta with a total population of about 3.50 million. The major activities of the inhabitants are usually associated with the agriculture and some

light industries are frequently distributed in some cities of the province.

Climatologically, both Greater Cairo and Menofiya province are located in the subtropical climatic region. The general climate of both two cities is cold, moist and rainy in winter (December–February), whereas during summer (June–August), it is characterized by high temperature, high solar radiation, clear sky and rainless. Nights are generally cool and, during the winter, quite damp; radiational cooling often leads to shallow, stable inversions. Temperature ranged from 27 to 36 °C with a mean value of 33 °C during the period of study.

Three sampling locations were chosen for VOCs measurements in the present study, two in urban areas in Greater Cairo and background one in rural area in Menofiya province (Fig. 1). Sampling sites in Greater Cairo were selected according to traffic densities. The first location was in the city centre of Cairo (Ramsis), it is the most commercial and heaviest traffic area in Greater Cairo. The second one was in the urban area in Giza (Haram), located to the southeast of the city centre of Cairo, it is characterized by relatively high traffic density. Each sampling location was close to the major traffic road. On the other hand, the third location which was selected to represent a background rural area is located in Menofiya province, namely Kafr El-Akram, about 55 km to the north of Cairo.

Sampling was carried out at a height of approximately 6 m above the ground level. One daytime sample (09.00–21.00 h) was collected weekly at each of the three sampling locations, during June 2004–August 2004. In addition, only during four days (once every week during July 2004) the samples were collected in a 3-h interval from 09.00 to 21.00 h to observe the diurnal variation of VOCs concentrations at Ramsis location. The morning period (09.00–12.00 h) represents the period of lowest photochemical reactions and highest traffic density. The noon period (12.00–15.00 h) represents the time of intense vertical mixing (high dispersion) and the period of highest photochemical reactions. The afternoon period (15.00–18.00 h) represents the late period of photochemical reactions and the other highest traffic density. The evening period (18.00–21.00 h) represents the period follows the photochemical reaction and the low traffic density.

2.2. Sampling and analysis

Ambient VOCs samples were collected according to a standard method developed by NIOSH using activated charcoal tubes (ORBO[TM]-32 activated coconut charcoal (20/40)) for the collection (NIOSH, 1996). The collection tubes (Supelco, Inc., Bellefonte, PA) contained 150 mg of coconut charcoal sub-divided into two portions of 100 and 50 mg: the front portion of 100 mg was used to collect the VOCs, while the 50 mg backup section was intended to determine if solvent breakthrough occurred from the front section. Air was drawn through the charcoal tubes, using a pump calibrated to draw 0.20 L min^{-1}. After sampling time, the charcoal tube was removed from the sampling train and two open sides were tightly closed using special caps to avoid any desorption. During the sampling procedure, one charcoal tube was opened at the sample site and then the ends capped, which served as a blank. The samples and blanks tubes were put into special plastic bags that were tightly closed and kept at −10 °C in a freezer until processed, not more
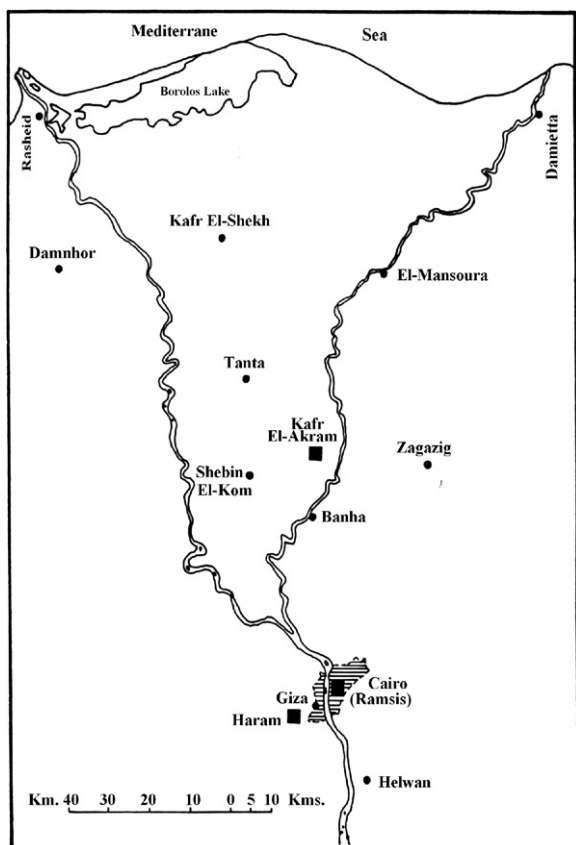

Fig. 1. Map showing the location of the sampling sites (■): Ramsis (City centre of Cairo), Haram (urban) and Kafr El-Akram (rural).

than 15 days. Before analysis, all samples and blanks were taken from the freezer, contents of both sections of the adsorber tubes were transferred to glass test tubes containing 2.00 ml of distilled carbon disulfide (CS_2). The tubes were shaken by using a mechanical shaker and leave it sitting for at least 1 h to obtain the final sample solution. Immediately after this, a 2 µl aliquot was withdrawn from the samples, including the blank samples, and injected into a Hewlett-Packard gas chromatography (GC) (Model HP6890), fitted with a flame ionization detector (FID). A HP-5 (30 m × 320 µm × 0.25 µm) capillary column was used with hydrogen as carrier gas and temperature programming from 30 °C (5 min) to 250 °C at 10 °C min^{-1}. The instrument was checked on daily basis based on the drift in retention times and responses of selected compounds in the standard calibration mixture injection. The concentrations of the target VOC species were quantified by an external standard calibration. To prepare the calibration solution, revised PVOC/GRO mix and individual *n*-hexane and *n*-heptane liquid standards (Supelco, Inc., Bellefonte, PA) were used. Five standard solutions were prepared by injection of aliquot portions of the different compounds into 2 ml of the same CS_2 as used for the sample vials. These standard solutions were used to produce calibration curves and were analysed with the samples. For all measured VOCs, good correlation was found with $R^2 > 0.995$. The relative standard deviation (RSD) for replicate analyses of the calibration standard for all measured VOCs varied from 4% to 5%. The detection limit of each compound was calculated from the data of seven replicate measurements of low concentration samples and observed from their standard deviation. The method detection limits ranged from 0.2 to 0.5 µg m^{-3} for the target VOCs.

2.3. Quality assurance/quality control

The quality assurance and quality control (QA/QC) procedure included laboratory and field blanks, parallel samples and duplicate measurements of samples. Five laboratory blanks and five field blanks were tested with no significant contamination found for any of target VOCs. Ten replicate field samples were collected at one of the sampling location (Ramsis) from 09.00 to 21.00 h. The RSD for replicate analyses of all the field samples varied from 6% to 8% for all measured VOCs. The VOC

recovery after extraction with CS_2 was determined by injecting a known amount of the compounds selected for study directly onto the 100 mg portion of charcoal in five unused tubes. The sealed vials containing the charcoal were allowed to stand overnight to ensure complete absorption of the VOCs onto the charcoal. A parallel blank of 100 mg charcoal was handled in the same manner except that no compound was added to it. The 100 mg portion of charcoal was then removed and placed in a septum sealed vial for analyses as above. The five treated charcoal samples and blank were desorbed and analysed in exactly the same manner as the sample tubes, and the recovery amount of each VOC was determined. The recoveries ranged from 92% (1,2,4-Trimethylbenzene) to 97% (benzene). Loss of VOCs during storage of samples was also investigated. Eight samples were simultaneously collected from 09.00 to 21.00 h. Half of the samples were measured immediately after sampling. The remaining samples were stored at −10 °C in a freezer for 15 days and then measured. The losses were found to be negligible. The amount of target VOCs measured in the backup section of charcoal tubes (50 mg) was less than 5% of the total concentration in both sections, so, it is considered that no breakthrough of the target VOCs occurred for the sampling condition.

3. Results and discussion

3.1. VOCs concentrations in the urban and rural areas

The minimum, maximum, median and arithmetic mean daytime concentrations of VOCs measured in the urban (Ramsis and Haram) and rural (Kafr El-Akram) areas are summarized in Table 1. From this table, it can be observed that, the maximum concentrations of VOCs were found in the urban areas, whereas the minimum levels were detected in the rural area, and the differences in mean concentrations were statistically significant ($p < 0.001$). This is due to the higher emission of VOCs from traffic emissions and fuel evaporations in urban areas. The mean concentrations of *n*-hexane, *n*-heptane, benzene, toluene, ethylbenzene, (*m, p*)-xylene, *o*-xylene, 1,3,5-trimethylbenzene and 1,2,4-trimethylbenzene were 123.53, 70.61, 87.20, 213.80, 43.30, 140.80, 73.77, 30.61 and 64.54 µg m^{-3}, respectively in Ramsis, i.e. 2.05, 2.06 ,1.89, 1.91, 1.90,1.89, 2.04, 1.96 and 1.95 times higher than

those found in Haram, respectively, and 15.03, 13.42, 15.01, 28.58, 17.25, 34.26, 30.74, 32.22 and 38.19 times higher than those found in Kafr El–Akram, respectively. The observed high levels of VOCs in Ramsis is due to the high traffic density, since Ramsis is the most commercial and heaviest traffic area in greater Cairo. In the present study, significant positive correlations ($p < 0.05$) were found between the daytime temperature and the concentrations of the measured VOCs at Ramsis and Haram locations, the correlation coefficients (r) ranged from 0.59 to 0.67 at Ramsis and from 0.58 to 0.65 at Haram. These results confirmed that higher temperature causes more gasoline evaporation. The increase in traffic density will increase both exhaust and vehicle evaporative emission (Nelson and Quigley, 1982). Motor exhaust emissions were the dominant sources of VOCs (Edgerton et al., 1989).

Benzene is a carcinogenic compound causing leukaemia. The WHO has estimated that a life time exposure of $1\,\mu g\,m^{-3}$ of benzene leads to about six cases of leukaemia per million inhabitants (WHO, 1999). For a city such as Greater Cairo with a population of about 11.30 million and average benzene levels of $67\,\mu g\,m^{-3}$, about 4542 additional cases of leukaemia would be expected in the city. Such approximation may indicate the importance of considering the potential effects of high levels of VOCs in the Greater Cairo and the necessity of applying pollution control measures on VOCs emissions in the city.

The contribution of individual VOC to the total VOCs concentration at Ramsis, Haram and Kafr El-Akram locations are represented graphically in Fig. 2(a)–(c). From this figure, it can be noticed that the distributions of VOCs in Ramsis and Haram are very similar, with toluene as the most abundant compound followed by (m, p)-xylene, n-hexane, benzene, o-xylene, n-heptane, 1,2,4-trimethylbenzene, ethylbenzene and 1,3,5-trimethylbenzene, respectively (Fig. 2(a) and (b)). Moreover, the contribution of individual volatile aromatic hydrocarbon to total volatile aromatic hydrocarbons in Ramsis and Haram locations were also similar. The mean distributions of aromatic volatile compounds for Ramsis and Haram, were, respectively: 32.69% and 32.85% for toluene, 21.53% and 21.92% for (m, p)-xylene, 13.33% and 13.58% for benzene, 11.28% and 10.64% for o-xylene, 9.87% and 9.72% for 1,2,4 trimethylbenzene, 6.62% and 6.69% for ethylbenzene and 4.68% and 4.59% for 1,3,5 trimethylbenzene. This similarity in distribu-
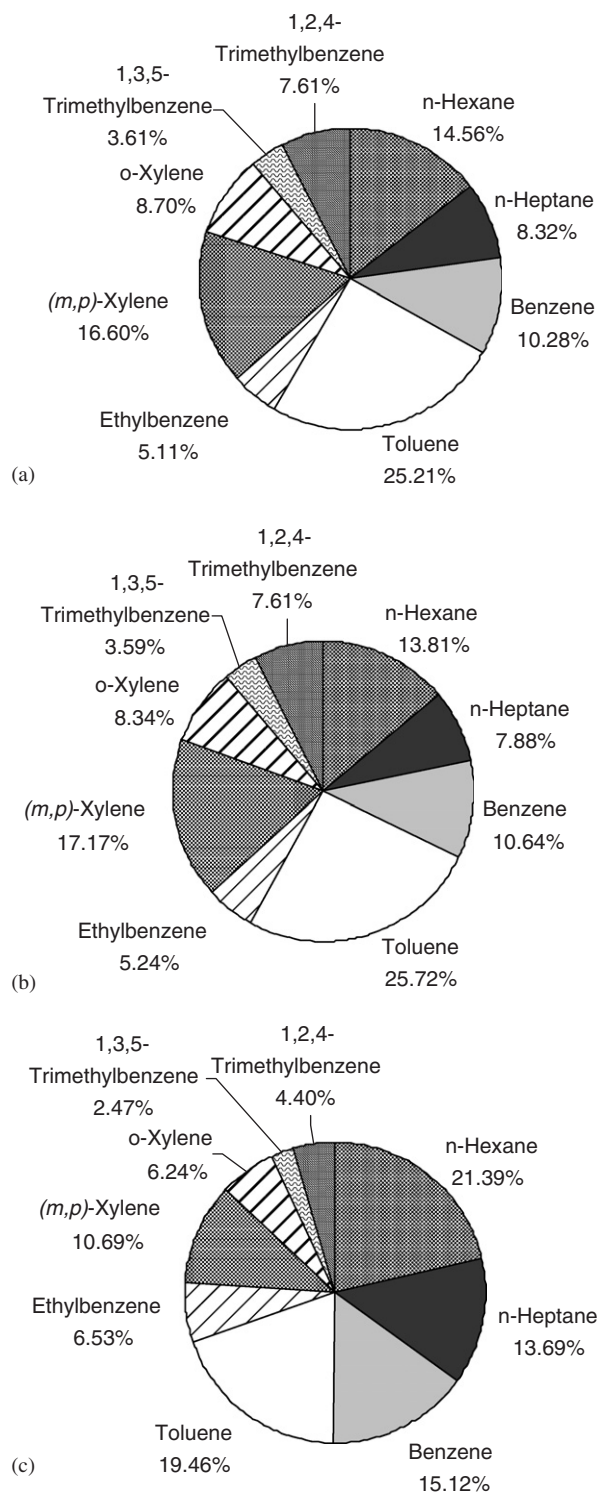

Fig. 2. Average contribution of individual VOC to total VOCs concentrations at Ramsis (a); Haram (b) and Kafr El-Akram (c) locations.

tion implies a similar emission source of VOCs in both urban locations in Greater Cairo, vehicle exhaust emissions are the dominant one. The above results agree with the fact that toluene is the most dominant species in many emission sources of aromatic VOCs (i.e., vehicle exhaust, solvent usage, gasoline evaporation, fossil fuel combustion, landfill, tobacco smoke, adhesives, etc.) (Sack et al., 1992; Kim and Kim, 2002; Na et al., 2004, 2005; Baek and Jenkins, 2004).

At the rural location (Kafr El-Akram), n-hexane was found to be the most abundant VOCs followed by toluene, benzene, n-heptane, (m, p)-xylene, ethylbenzene, o-xylene, 1,2,4-trimethylbenzene and 1,3,5-trimethylbenzene, respectively (Fig. 2(c)). In addition, the contribution of individual volatile aromatic hydrocarbons to total volatile aromatic hydrocarbons were 29.98% for toluene, 23.29% for benzene, 16.47% for (m, p)-xylene, 10.06% for ethylbenzene, 9.62% for o-xylene, 6.77% for 1,2,4-trimethylbenzene and 3.81% for 1,3,5-trimethylbenzene. These results show differences in the distributions in the total VOCs and volatile aromatic hydrocarbons in the rural area compared with the urban ones (Ramsis and Haram). This suggests a considerable difference in the nature of VOCs pollution in these areas, since rural area is far from point sources and there were no significant anthropogenic sources of VOCs.

3.2. Comparison of BTEX levels in Greater Cairo with other cities in the world

The average concentrations of BTEX in both urban areas in Greater Cairo were compared with

those found in urban areas in other cities (Nelson and Quigley, 1982; Tsujino and Kuwata, 1993; Brocco et al., 1997; Gee and Sollars, 1998; Muezzinoglu et al., 2001; Lee et al., 2002). As shown in Fig. 3, BTEX levels in Greater Cairo were much higher when compared with those reported for Santiago, Sao Paulo, Caracas, Sydney, Rome, Osaka and Hong Kong. Moreover, the average benzene, (m, p)-xylene and o-xylene concentrations in Greater Cairo were much higher than those found in Manila and Bangkok. The average toluene concentration was similar to that reported for Manila and relatively lowers than that found in Bangkok. Compared with Izmir, Greater Cairo has relatively higher levels of benzene, toluene and (m, p)-xylene and lower level of o-xylene. Generally, BTEX concentrations profile described in Fig. 3 shows that Greater Cairo is at high ranges among the 11 cities.

3.3. BTEX concentration ratios

The BTEX (benzene: toluene: ethylbenzene: xylenes) concentration ratios were calculated to compare the VOCs emission sources among the three sampling locations. The BTEX ratios in Ramsis (2.01:4.94:1:4.95) and Haram (2.03:4.91:1:4.87) were similar, both sites might be affected by similar sources. On the other hand, the BTEX ratio was (2.31:2.98:1:2.59) in Kafr El-Akram, indicating that this rural site might be affected by emission sources far from the sampling location, such as those associated with transportation activities. The ratios of BTEX reported in other studies were (3:4:1:4) for vehicle exhaust and (3:5:1:4) in the
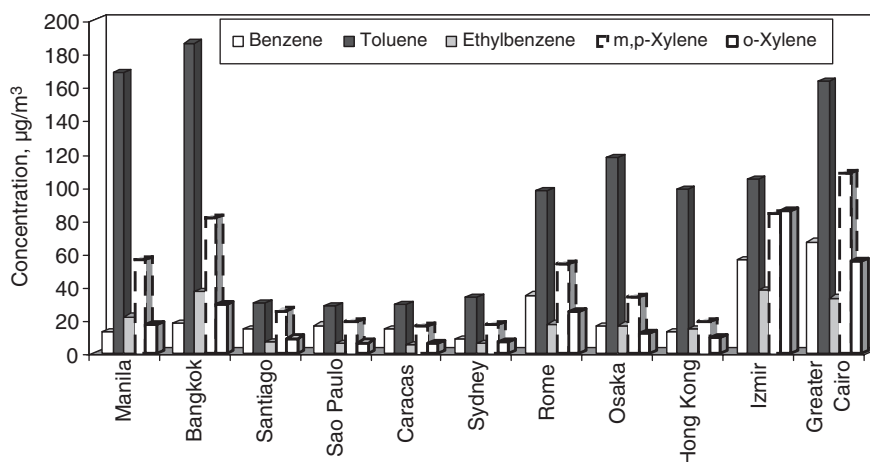

Fig. 3. Comparison of BTEX concentrations for eleven cities including Greater Cairo.

tunnel in Taiwan (Taipei city) (Chiang et al., 1996), and (2.9:4.3:1:4.6) in China (Guangzhou city) (Wang et al., 2002).

Some of the VOC species in the atmosphere are used as indicators of the age of the air mass and tracers for emission sources. Evaluation of toluene/benzene (T/B), (m,p)-xylene/benzene $((m,p)$-X/B), o-xylene/benzene $(o$-X/B) and (m,p)-xylene/ethylbenzene $((m,p)$-X/E) concentration ratios is useful for characterizing the distance of vehicular emission sources and for estimating the photochemical age of the air mass (Derwent et al., 2000; Monod et al., 2001). In the present study, the maximum (T/B), $((m,p)$-X/B), $(o$-X/B) and $((m,p)$-X/E) concentration ratios were found in Ramsis and Haram locations, where an intense traffic exists, whereas the minimum ones were detected in Kafr El-Akram, which is far from the intense traffic. The average ratios were 2.45, 1.61and 0.85 in Ramsis and 2.42, 1.61 and 0.78 in Haram for (T/B), $((m,p)$-X/B) and $(o$-X/B), respectively, (Tables 1 and 2). In addition, the $((m,p)$-X/E) ratios were 3.25 in Ramsis and 3.28 in Haram. The ratios at both sites were nearly of the same magnitude and the (T/B), $((m,p)$-X/B) and $(o$-X/B) ratios were close to those obtained from automotive exhausts (Table 2), thereby confirming an origin of the pollution of BTEX at both sites. The (T/B) ratios in both sites were nearly similar to those found in many cities such as in Rome (2.80), Izmir (1.87-2), Santiago (2.01) and Caracas (2.04) (Brocco et al., 1997; Hartmann et al., 1997; Muezzinoglu et al., 2001; Gee and Sollars, 1998). On the other hand, our results are lower than those found in Manila (13.33), Bangkok (10.22), Hong Kong (7.74), Osaka (7.19) and Sydney (4.04) (Nelson and Quigley, 1982; Tsujino and Kuwata, 1993; Gee and Sollars, 1998; Lee et al., 2002). The differences of (T/B) ratios among these cities may reflect a difference between their vehicle types, fuel composition and industrial activities.

Kafr El-Akram is located far from traffic density; it is not exposed to direct emission from an adjacent road. Therefore, the concentration of VOCs measured in Kafr El-Akram is exclusively a result from diffusion and dispersion of VOCs produced from the traffic density in the surrounding cities. The time required for the transportation of the VOCs allows for significant photochemical reactions/degradation of reactive compounds such as xylenes and toluene to take place, causing a reduction of toluene and xylenes concentrations at Kafr El-Akram compared with benzene. The (T/B), $((m,p)$-X/B) and $(o$-X/B)

ratios were 1.29, 0.71 and 0.41, respectively in Kafr El-Akram (Table 2). In addition, the $((m,p)$-X/E) ratio was 1.64. These ratios were lower than those found in Ramsis and Haram sites. These results confirm that the BTEX in Kafr El-Akram do not come from a local source and the more reactive isomers of xylene and toluene have been exposed to photochemical degradation for some time during transport of these pollutants from the surrounding cities. This is in agreement with IIgen et al (2001) and Monod et al (2001) who reported that the photochemical degradation of toluene and the isomeric xylene is faster than that of benzene and this degradation is favoured by long transport distances. The lower ratios of (T/B) and xylenes/benzene (X/B) at the rural area in Venezuela are due to the faster reaction of OH with toluene and xylene, with respect to benzene (Holzinger et al., 2001). The (T/B) ratio decreased as the distance from pollution source increased (Gelencser et al., 1997; Simon et al., 2004). A lower $((m,p)$-X/E) ratio implies an aged air parcel (Hsieh and Tsai, 2003).

3.4. BTEX correlations

Since benzene and other volatile aromatic hydrocarbons measured in this study were mainly from motor vehicle emissions, their ambient concentrations are likely to be correlated. Significant positive correlation coefficients ($r > 0.87$, $p < 0.001$) were found between the concentrations of benzene and other BTEX species at Ramsis and Haram locations (Table 3), benzene can be used as a marker for other volatile aromatic hydrocarbons in heavy traffic areas. The significant positive correlations ($r > 0.87$, $p < 0.001$) between the concentrations of BTEX compounds at Ramsis and Haram sites suggest that BTEX originate from similar sources, i.e. traffic emissions. The most dominant contributing source of BTEX in urban areas is vehicles exhaust gases (Lawryk and Weisel, 1996; Jose et al., 1998).

At Kafr El-Akram site, although no nearby point sources of BTEX affected the correlations, significant positive correlation coefficients ($r > 0.78$, $p < 0.001$) were found between the concentrations of BTEX compounds (Table 3). This indicates that the rural background area received BTEX from the surrounding cities and predominantly related to the traffic emissions.

Table 1
Daytime concentrations ($\mu g\,m^{-3}$) of VOCs at the three sampling locations (12-h average)

	n-hexane	n-heptane	Benzene	Toluene	Ethylbenzene	(m,p)-xylene	o-xylene	1,3,5-trimethylbenzene	1,2,4-trimethylbenzene
Ramsis (N = 12)									
Minimum	78.33	48.24	72.35	159.65	30.36	102.55	49.42	24.51	48.24
Maximum	161.52	92.41	107.37	263.44	59.53	171.61	98.71	38.57	86.55
Median	122.46	69.28	87.45	214.52	42.25	140.44	72.38	30.42	64.33
Arithmetic mean	123.53	70.61	87.20	213.80	43.30	140.80	73.77	30.61	64.54
Arithmetic standard deviation	20.62	12.09	10.07	34.78	7.40	21.81	12.45	4.33	10.49
Haram (N = 12)									
Minimum	39.44	24.54	33.33	78.41	16.61	51.51	26.62	11.23	24.43
Maximum	76.62	46.23	58.56	138.69	32.48	99.64	46.53	20.43	44.51
Median	59.32	34.62	46.54	110.23	23.55	73.45	34.95	16.22	32.27
Arithmetic mean	60.21	34.23	46.23	111.80	22.77	74.62	36.23	15.62	33.08
Arithmetic standard deviation	9.33	6.43	7.37	18.94	3.86	12.45	5.43	2.66	5.65
Kafr El-Akram (N = 12)									
Minimum	3.46	2.89	3.10	3.29	1.24	2.00	0.98	0.60	0.80
Maximum	14.11	10.68	10.91	15.10	5.55	9.22	5.12	2.26	3.75
Median	7.66	4.50	4.40	6.49	1.97	3.57	2.04	0.70	1.34
Arithmetic mean	8.22	5.26	5.81	7.48	2.51	4.11	2.40	0.95	1.69
Arithmetic standard deviation	3.16	2.43	2.61	4.13	1.38	2.39	1.45	0.52	0.98

N: Number of daytime samples.

Table 2
Toluene/benzene (T/B), (m, p)-xylene/benzene $((m, p)$-X/B) and o-xylene/benzene $(o$-X/B) concentration ratios at the three sampling locations

	Ramsis	Haram	Kafr El-Akram	Automotive exhaust
Toluene/benzene	2.45	2.42	1.29	2.70[a]
(m, p)-xylene/benzene	1.61	1.61	0.71	1.80[b]
o-xylene/benzene	0.85	0.78	0.41	0.90[c]

[a]Brocco et al. (1997) and Guicherit (1997).
[b]Stevenson et al. (1997).
[c]Guicherit (1997).

Table 3
Summary of BTEX correlation coefficients (r) at the three sampling locations[a]

	Benzene	Toluene	Ethylbenzene	(m, p)-xylene	o-xylene
Ramsis $(N = 12)$					
Benzene	1				
Toluene	0.93	1			
Ethylbenzene	0.93	0.91	1		
(m, p)-xylene	0.94	0.95	0.91	1	
o-xylene	0.90	0.90	0.92	0.95	1
Haram $(N = 12)$					
Benzene	1				
Toluene	0.95	1			
Ethylbenzene	0.87	0.89	1		
(m, p)-xylene	0.91	0.92	0.93	1	
o-xylene	0.91	0.92	0.91	0.97	1
Kafr El-Akram $(N = 12)$					
Benzene	1				
Toluene	0.90	1			
Ethylbenzene	0.90	0.85	1		
(m, p)-xylene	0.88	0.81	0.86	1	
o-xylene	0.86	0.78	0.79	0.92	

N: number of samples in statistical analysis.
[a]Significant $(p < 0.001)$.

3.5. Diurnal variation of VOCs at Ramsis location

The diurnal variation of VOCs, BTEX and non BTEX compounds, concentrations at Ramsis location are shown in Fig. 4(a) and (b). The variations in the concentrations of these pollutants during the daytime hours were found to follow the similar patterns. These results indicate that these compounds have a similar source and dispersion mechanisms. The concentration of BTEX and non BTEX increased during the 09.00–12.00 h period, and then decreased to minimum during the 12.00–15.00 h period. After that time, the concentrations increased again during the 15.00–18.00 h

period, and finally decreased slightly during the 18.00–21.00 h period. The morning peaks of BTEX and non BTEX during the 09.00–12.00 h period were due to the high traffic density in that period. On the other hand, the decrease in the concentrations of these compounds during the 12.00–15.00 h period were probably due to the decrease of the traffic density and increase in dilution caused by the decrease in atmospheric stability owing to the heating of the earth surface and the increase in wind speed. During the 15.00–18.00 h period, the concentrations of BTEX and non BTEX increased again because the traffic density is increased. After that time, the concentrations decreased due
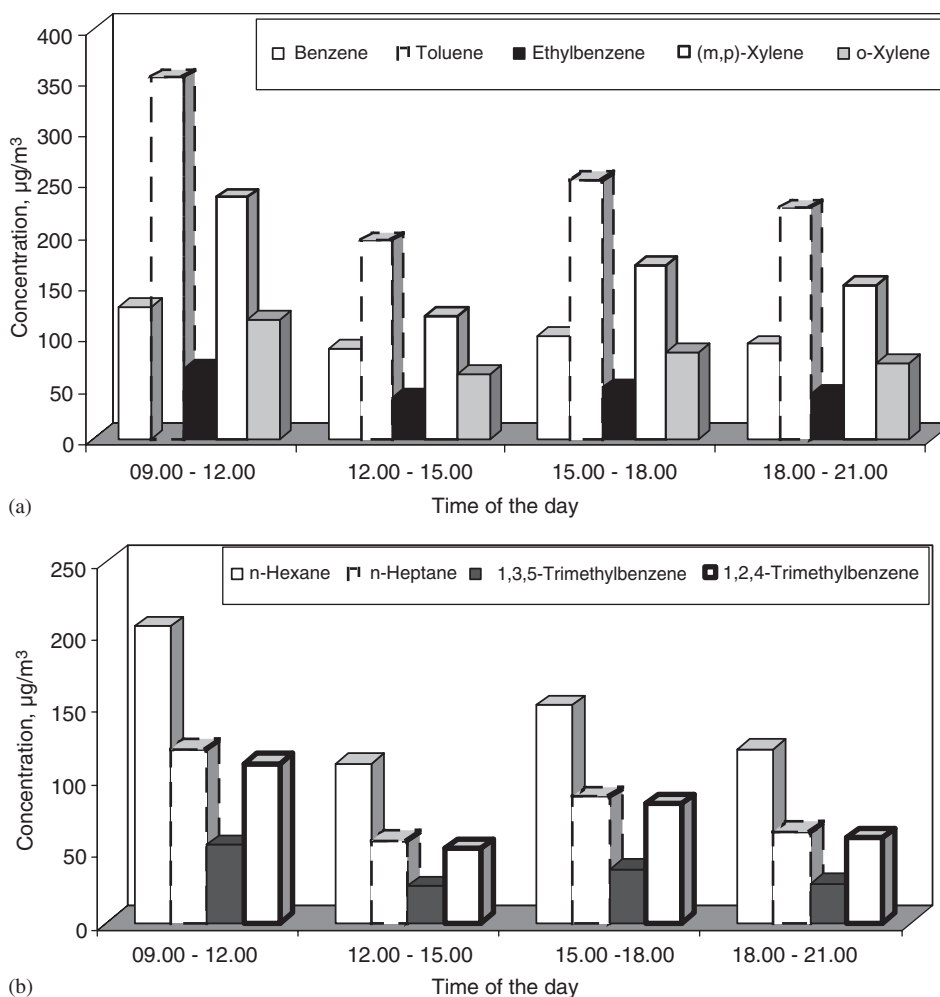
Fig. 4. Diurnal variation of BTEX (a) and non BTEX (b) concentrations at Ramsis location.

to decrease of traffic density. The profile of BTEX and non BTEX during the daytime hours suggests that vehicle exhaust emissions are the main source of VOCs. This is in agreement with Liu et al. (2000) and Ho et al. (2004) who found that the diurnal variations of VOCs concentrations showed two peaks associated with traffic density. The concentrations of VOCs vary with hours of the day and they were directly related to the variations of traffic flow (Muezzinoglu et al., 2001). The levels of aromatic hydrocarbons exhibit a daily variation linked to traffic rush hours (Yamamoto et al., 2000).

3.6. Diurnal variation of BTEX ratios

BTEX concentration ratios were nearly similar during the whole sampling periods, with the mean ratios of (1.88:5.17:1:5.16) during the 09.00–12.00 h period, (2.20:4.83:1:4.58) during the 12.00–15.00 h period, (2.00:5.04:1:5.06) during the 15.00–18.00 h period and (2.09:5.11:1:5.09) during the 18.00–21.00 h period. In addition, the diurnal variations of (T/B), ((m, p)-X/B), (o-X/B) and ((m, p)-X/E) ratios were nearly similar during the daytime hours, with the average ratios ranging from 2.20 to 2.75 for (T/B), 1.36–1.83 for ((m, p)-X/B), 0.72–0.91 for (o-X/B) and 3.00–3.45 for ((m, p)-X/E). The similarity in these ratios during the whole sampling periods suggests a common source of these pollutants, mainly traffic emissions. In addition, the photochemical reactions/degradation of the more reactive aromatic hydrocarbons (toluene and isomers of xylene) during the daytime hours was not significant because the sampling location was close to the traffic roadside.

4. Conclusions and recommendations

Ambient VOCs play a critical role in the atmospheric chemistry. These pollutants lead to an increase of the formation of ozone, photochemical oxidants and smog episodes which are harmful to human health, ecosystem and atmosphere.

The levels of VOCs were determined at three locations, two in the urban areas in Greater Cairo (Ramsis and Haram) and background one in the rural area in Menofiya province (Kafr El-Akram). The mean concentrations of *n*-hexane, *n*-heptane, benzene, toluene, ethylbenzene, (*m*, *p*)-xylene, *o*-xylene, 1,3,5-trimethylbenzene and 1,2,4-trimethylbenzene were 123.53, 70.61, 87.20, 213.80, 43.30, 140.80, 73.77, 30.61 and 64.54 $\mu g\,m^{-3}$, respectively in Ramsis. Total average concentration of VOCs in the city centre of Cairo (Ramsis) was about 1.95 times higher than those found in other urban site, i.e. Haram and 22.10 times than those found in background site, i.e. Kafr El-Akram. Toluene has the highest levels of VOCs in both urban areas, whereas *n*-hexane has the highest levels in the rural area. The contribution of individual VOC to the total VOCs concentration and the ratios between different BTEX species indicate that vehicular emissions are the dominant source of VOCs in both urban locations in Greater Cairo. This is confirmed by the significant positive correlations between the concentrations of BTEX compounds in both urban areas. On the other side, the significant positive correlations between the concentrations of BTEX compounds in rural area suggest that the background area received BTEX from the surrounding cities and predominantly related to traffic emissions. The variation in the concentrations of BTEX and non BTEX compounds during the daytime hours were found to follow a similar patterns and had two daily peaks associated with traffic density.

The results of this study indicate that the high levels of VOCs in Greater Cairo are sufficient to represent a degree of risk to the local population and a more comprehensive study over a long period of time and during the four seasons of the year would be required to better quantifying the problem. In addition, it is necessary to adopt drastic measures concerning motor vehicles, either by reducing traffic or introducing emission control devices, to reduce the ambient levels of VOCs in Greater Cairo.

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