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STUDIES OF THE EFFECT OF VOLATILE COMPOUNDS IN ATMOSPHERE OF GREATER CAIRO AREA

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Abstract

Volatile organic compounds (VOCs) have been determined to be human risk factor in urban environments, as well as primary contributors to the formation of photochemical oxidants. Concentrations of VOCs were measured at five monitoring sites located in the greater Cairo area, Egypt, as a part of the air pollution study. On each sampling day, 22 abundant VOCs were collected three times per day (7-9 in the morning, 2-4 afternoon and 8-10 evening) during the period from March 2003 to March 2004, to observe diurnal variations of volatile organic compounds on the air of Greater Cairo area and air quality information system in Egypt. Most of the VOCs species showed diurnal variations with higher concentrations during the morning and evening, and lower concentrations during the afternoon. However, in the afternoon , the concentrations of aromatic compounds, closely correlated with solvent usage such as toluene, ethyl benzene, m-/p- xylene, and o-xylene, were slightly higher than or comparable to those in the morning. This may be due to the increase of evaporative emissions derived from the rise in ambient temperature and additional sources such as the use of solvents in petrol, painting, printing and dry cleaning.

Introduction

After the second world war most countries were in a race to supply their citizen's requirements by increasing industrial and agricultural activities without taking into consideration environmental impacts of these activities. Among the developing countries, Egypt is one of the most active in the industrial and agricultural fields. This leads to a hazardous air pollution problems in some areas which affects not only human health but also Egypt's historical monuments, where, some of which are more than 7000 years old, contain not only the history of Egypt but of all humans.

Volatile organic compounds are organic molecules which are easily vaporized at room temperature without any color, smell or taste. Recently, a number of VOCs have been identified as important cancer risk factors in urban environment [(1)]. These compounds (VOCs) are not routinely monitored in urban air, and no ambient air quality standards have yet been established for them. In addition, through complex photochemical reactions, VOCs contribute to the formation of toxic oxidants such as tropospheric ozone [(2)], and peroxy-acetyl nitrate (PAN).

In urban and industrial areas, many hydrocarbons, including VOCs, are emitted from anthropogenic sources, such as transportation, fossil fuel-burning power plants, chemical plants, petroleum refineries, certain constriction activities, solid waste disposal and burning [3]. There are two main sources for air pollution in Egypt, combustion sources and industrial activity.

Experimental

Monitoring locations

Five air monitoring sites representing different urban communities in the greater Cairo area, Egypt, are chosen :-

- Industrial / Residential Areas:

o -*Shoubra El-Khaima station* is located at north of Cairo, in a heavily industrialized area and is downwind from numerous Pb smelters and other industrial sources. This is one of the most highly polluted areas in the city.

o - *Helwan station* is located at 18 Km south of Mokattam Hill at 114 m above sea level, it impacted by emissions from nearby cement plants and has higher levels than some of the other residential areas.

- Traffic Areas:

- *El-Tahrir Square station*: this site is located downtown, close to the road and has high light- and heavy-duty (bus) traffic.

- Residential Areas:

- *Nasr city station*: it represents a residential area with limited nearby sources

-*The Koba station:* is near to a number of small industrial sources.

Sampling and analytical methods

Sampling was done from March 2003 to March 2004, on each sampling day, 22 abundant VOCs species were collected three times per day (7-9 AM, 2-4 PM and 8-10 PM), to observe diurnal variations of volatile organic compounds on the air of Greater Cairo area. The analysis of VOCs is complicated by the extreme complexity of the mixtures that can be present in the atmosphere. Unidentified air samples obviously can contain many different VOCs of natural and anthropogenic origin. So, the analysis of these samples required highly sensitive analytical techniques in addition to great precautions during sampling in order to avoid losses and contamination of selected elements.

Measurements of VOCs in the field are done by acquiring an air sample in a suitably prepared container and transferring it into the GC-FID. Sample containers (*61 SUMMA canister*) have been made from glass, treated metal and special plastics. Sampling procedures often require that the containers be purged before the air sample is obtained and that the sample be stored in the container above atmospheric pressure [(4)].

Non methane hydrocarbons components (NMHCs) measured by gas chromatography (HP 5890A) with flame ionization detection (FID) (*EPA Method TO-14A, U.S. 1997*), with mass spectra and a specially designed sampling device in the lab.

The Hobira model analyzer (APHA-360) is used for measuring the low contents of the total and non-methane hydrocarbons in ambient air. It uses the principle of flame ionization, where the analyzer's electrometer measures the current generated by the ionization of the carbon atoms in the flame fueled by a hydrogen/ air mixture. The electrometer's output is then computed by electronics in ppm.

$$(HCs + O2 + Catalysts \rightarrow CO2 + H2O)$$

Results And Discussion

To observe diurnal variations of VOCs concentration, the results of the mean concentration of VOCs species measured at El-Tahrir, Helwan, Shoubra El-Khaima, Kobry El-Kobba, and Nasr City sites are summarized in tables (1-3), concerning the daily, monthly, summer, winter and annual mean average concentrations.

The constituents of 22 abundant species of VOCs are summarized in the following:-

1- Total Hydrocarbons groups:- Non-Methane Hydrocarbons and C_2 Compounds
2- Alkanes Group:- Ethane, Propane, n-Butane, iso-Butane, n- Pentane, iso-Pentane, di-methylButane, n-Hexane, n- Nonane and 2-methyl Heptane
3- Alkenes Group:- Ethylene, Propylene and Acetylene
4- Cyclic Group:- Methyl Cyclo Pentane and Tri- Methyl Benzene
5- BTEX Group:- Benzene, Toluene, Ethyl Benzene, o- Xylene and m-/ p- Xylene

Non Methane Hydrocarbons (consists of C_2-C_{11} include Alkanes, Alkenes and Aromatic [(6)]) and C_2 Compounds (includes Ethane, Ethylene, Acetylene) have the highest average concentrations at El Tahrir, due to the high volume of mobile source emissions at this site. Since, there are about two million vehicles on the streets of

greater Cairo making traffic emissions one of the major sources of air pollution especially in the morning and evening. Its concentrations decreases in the following order:-

(El-Tahrir site > Shoubra El-Khaima site > Kobry El-Koba site > Helwan site > Nasr City site)

Ethane, Propane n-/i-Butane and n-/i-Pentane are the most abundant species in alkanes as well as high ranked species among the most 22 abundant species. Ethane is not present in gasoline and known to be released from natural gas and vehicle exhaust [(5)], but it is released to the environment during the manufacture, use and disposal of products associated with the petroleum and natural gas industries. Propane and n-/i-Butane are known to be liquefied petroleum gas (L.P.G.) used for cooking, heating, and fuel for butane-powered vehicles during the winter times[(8)].

n-/i- Butanes are mostly used as fuel for butane powered vehicles, gasoline evaporation and unburned fuel from vehicle exhaust gas are likely to affect high abundance of n-/i- butanes in ambient air in Cairo. Due to the increase of evaporative emissions which associated with high ambient temperature and solvent usage (such as toluene, m-/p xylene, ethyl-benzene, and o-xylene) during daily working hours, the concentration rankings of these compounds closely associated with solvent usage in the morning [(6)].

Pentane is a component of natural gas, lighter and blowtorch fuels and aerosol propellants. It is also an additive in automotive and aviation fuels. It has uses in solvent extraction processes and as a raw material

All plant tissues manufacture ethylene as a growth regulator. It is also released by soil micro-organisms and biomass combustion. Auto and diesel engine emissions, tobacco smoke and emissions from various chemical processes contain ethylene. Its uses includes refrigeration, cutting and welding metals, anesthetics, chemical intermediate and for ripening fruit [(7)].

Pseudocumene (1,2,4 Tri-methyl benzene) is released to the environment from wastes created by the above uses. Also gasoline powered engine emissions; municipal waste treatment plants and coal fired power stations are responsible for pseudocumene release.

The manufacture of elastomers and many pharmaceutical products require hexane as a reaction medium. Hexane is a component of many products associated

with the petroleum and gasoline industries. Release to the environment occurs when petroleum products are used and disposed. Use of paints, varnishes, adhesives and coatings are released hexane by evaporation[8].

Manufacture uses and disposal of petroleum products which releases n-nonane into the environment. Gasoline combustion, vulcanization and extrusion operations during rubber production, printing pastes, paints, varnishes, adhesives and other coatings are also sources of pollution [9].

In the environment, propylene occurs as a natural product from vegetation. It is also a product of combustion of organic matter (biomass burning, motor vehicle exhausts and tobacco smoke) and is released during production and use.

Methyl cyclo-pentane, 2,3 di-methyl butane and 2- methyl heptane occurs naturally in petroleum natural gas which released to the environment by evaporation, wastes, spillage and combustion exhaust. Motor vehicle exhaust is also a large source of pollution.

BTEX groups (benzene - toluene - ethyl benzene - o- xylene - m-/ p- xylene) are emitted from vehicle exhaust and gasoline evaporation, also released from the use of solvents (painting, printing, and dry cleaning). These VOCs containing some species can cause serious individually carcinogenic diseases.

Non methane hydro-carbon, C_2 compounds, n-butane and n- hexane were the most abundant VOCs concentration in Cairo. The maximum and minimum mean concentrations values for non methane hydro-carbon at the different sites were ranged between (1515 – 383 ppb), C2 compounds were ranged between 106 -29 ppb, n- hexane were ranged between 92 -12 ppb, and for n-butane 52 – 30 ppb.

Although propane, n-butane and n-pentane were ranked high in the concentrations based on carbon, their rankings on the OH-reactivity-based scale were low due to the fact that they are relatively less reactive compounds. On the other hand, ethylene, o-xylene and 1,2,4–tri-methyl-benzene were highly reactive species, their concentrations were higher in the OH-reactivity based scale, indicating that high ozone-producing capacity.

Figs. (1 – 22 & 24) showed that, the concentrations ratio of most volatile Organic compounds and carcinogenic VOCs are increases in the following order:-

El-Tahrir site > Shoubra El-Khaima site > Kobry El-Koba site > Nasr City site > Helwan sit).

Highest concentration of BTEX group in all sampling sites was found in El Tahrir (heavy traffic area) and the lowest concentration was in Nasr City. So, BTEX concentrations decreases in the following order:- El-Tahrir site > Shoubra El-Khaima site > Kobry El-Koba site > Nasr City site > Helwan site

The highest concentration ratio of toluene, m/p- xylene and o- xylene to benzene in El-Tahrir site 206, 163, and 58 % respectively, and for ethyl benzene at Nasr City is 84 %. But the lowest concentration ratio of ethyl benzene to benzene has the lowest value at El Tahrir is 46 %, for o-xylene at Nasr City is43 %, for Toluene and m / p – xylene at Helwan is 163 &100 % respectively. Also it increases at the morning and evening but decreases at afternoon, as shown in Fig. (23).

Table (4), showed that the mean outdoor concentrations of aromatic hydrocarbons (ppb) and significance level of their difference in regions with high and low traffic. At sites with high traffic burden the outdoor pollution was statistically significant higher for the total concentration of aromatic hydrocarbons.

The measurements VOCs in the greater Cairo area were compared with exposition data of Berlin, Germany. In table (5), the measurements of the total outdoor pollution level in Cairo is higher than that in Berlin; the percentage composition is very similar [8]. This means that there is resemblance in the pollution sources of both cities. We conclude that the exchange between outdoor and indoor air is more intense in Cairo than in Berlin [10].

Table (6) shows the BTEX data of greater Cairo area in year 2003 /2004 compared to BTEX data in different cities of the world. It was found that greater Cairo comes in the second place after Rome, Italy in the concentrations of BTEX and then the other towns.

Conclusions

Volatile organic compounds have been recognised as one of the principal trace constituents in the atmosphere. They play an important role in photochemical processes in the lower troposphere. In the presence of nitrogen oxides, VOCs contribute to the build-up of ozone and other photochemical oxidants, such as aldehydes. Many of these compounds are often considered to be toxic and some of them, such as benzene, have been identified as important cancer risk factors in urban environment. Large amounts of VOCs are emitted from mobile and stationary sources. Motor vehicles make a significant contribution to ground-level

concentrations of VOCs and it is estimated that 35% of total VOCs emissions are due these sources [11].

Most of the VOCs species showed diurnal variations with higher concentrations during the morning and evening, and lower concentrations during the afternoon. However, later in the morning, the concentrations of aromatic compounds, closely correlated with solvent usage such as toluene, ethyl-benzene, m-/p xylene, and o-xylene, were slightly higher than or comparable to those in the early morning. This may be due to the increase of evaporative emissions derived from the rise in ambient temperature and additional sources such as the use of solvents in painting, printing and dry cleaning. The different modes of traffic and several types of vehicles give rise to numerous levels of the pollutants. Also, the traffic density variation, traffic congestion and traffic flow influenced the concentrations at some of the sites.

Toluene & benzene are the most important species in ozone formation in the greater Cairo area atmosphere during study period. Toluene, m-/p-xylene, o-xylene and ethyl-benzene were largely associated with solvent usage. This suggests that evaporative emission by the use of solvents is a very important factor in ozone formation.

The effect of the BTEX VOCs (toluene, ethyl-benzene, o-xylene, m-/p-xylene and benzene) during the morning, afternoon and evening showed high observed values in the later morning and low observed values in the early morning and evening. This diurnal behavior was probably due to increasing of evaporative emissions associated with high ambient temperature and solvent usage during daily working hours, although toluene and m-/p-xylene are faster destroyed by oxidants than benzene. This may be due to the fact that the contribution of solvent emission of toluene and m-/p-xylene to the ambient VOCs concentrations is higher than that of vehicle-related emissions and loss by photochemical activity during daytime [12].

The results for all of the measured parameters did not exceed the guidelines, when comparing the results with ambient air guidelines obtained from WHO for organic pollutants or the UK ambient air quality guidelines during the period of study from March 2003 to March 2004. The mean average concentrations of benzene were increased over the limit of ambient air guidelines (WHO), The National Air Quality Objective of 5 parts per billion (ppb), measured as a running annual average, to be achieved by 2006.

Table (1): BTEX Pollutant concentration at morning during year 2003/2004

Location	*Concentration (ppb)*) at morning in year 2003/2004				
Site	*Toluene*	*p-/m-Xylene*	*Benzene*	*ethyl Benzene*	*o-xylene*
EL TAHRIR	81.6	64.7	40.2	19.6	24.3
EL-KOBA	42.0	28.7	21.1	15.8	10.8
HELWAN	22.8	15.3	14.8	10.4	9.0
NASR CITY	25.5	16.3	14.5	12.6	8.2
SHOUBRA	48.9	30.4	25.0	17.6	26.4

Table (2): BTEX Pollutant concentration at after noon during year 2003/2004

Location	*Concentration (ppb)*) at afternoon in year 2003/2004				
Site	*Toluene*	*p-/m-Xylene*	*Benzene*	*ethyl Benzene*	*o-xylene*
EL TAHRIR	75.9	62.3	39.0	18.9	22.9
EL-KOBA	39.0	26.9	19.1	14.2	9.9
HELWAN	22.3	13.9	13.9	10.6	8.8
NASR CITY	23.0	14.2	14.0	12.1	6.8
SHOUBRA	43.9	28.7	21.8	15.9	20.6

Table (3): BTEX Pollutant concentration at evening during year 2003/2004

Location	*Concentration (ppb)*) at evening in year 2003/2004				
Site	*Toluene*	*p-/m-Xylene*	*Benzene*	*ethyl Benzene*	*o- xylene*
EL TAHRIR	79.4	62.3	38.4	18.7	22.6
EL-KOBA	39.5	27.0	25.6	14.3	9.5
HELWAN	21.7	13.9	14.4	9.8	8.5
NASR CITY	23.9	14.6	13.7	11.7	6.5
SHOUBRA	45.5	28.8	22.9	15.7	22.7

Table (4): mean outdoor concentrations (µg/m^3) of BTEX VOCs with high and low traffic

Substance	High traffic	Low traffic
benzene	40.4	9.5
toluene	78.7	20.8
ethylbenzene	20.5	9.7
m+p-xylene	65.1	11.1
o-xylene	25.9	4.9

Table (5): VOCs concentrations (µg/m^3) in greater Cairo (Egypt) compared to Berlin, Germany

Compounds	Berlin outdoor	Cairo outdoor
Alkanes	23.4	30.5
Cycloalkanes	9.2	6.2
Aromatics	58.1	56.3

Table(6): BTEX group average concentration (µg/m^3) in greater Cairo compared to some other cities of the world

City	Benzene	Toluene	Ethyl-benzene	M+p Xylene	O- xylene
Cairo	22.95	39.01	15.47	25.85	11.2
Hong Kong	4.85	28.8	3.11	3.18	2.85
Rome Italy	35.5	99.7	17.6	54.6	25.1
Spain	3.43	23.6	3.34	5.08	2.74
UK	6.23	13.8	3.84	11.8	5.73
WHO guideline	16	260	100	100	

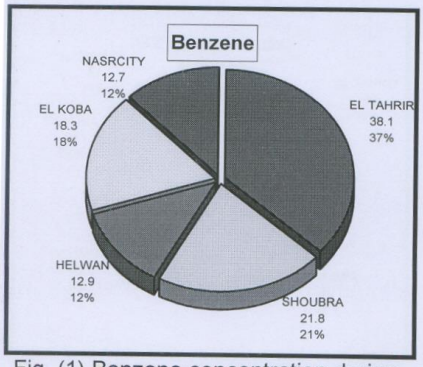


Fig. (1) Benzene concentration during year 2003/2004

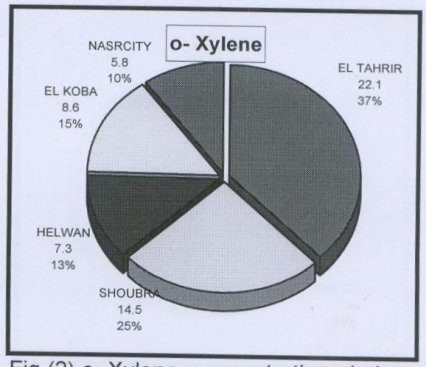


Fig.(2) o- Xylene concentration during year 2003-2004

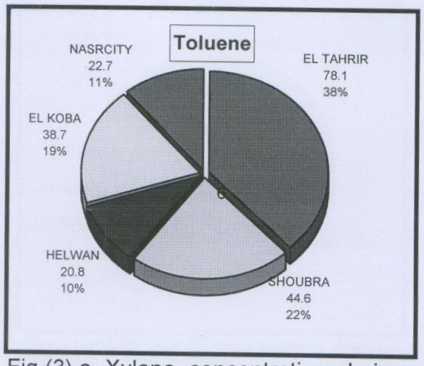


Fig.(3) o- Xylene concentration during year 2003-2004

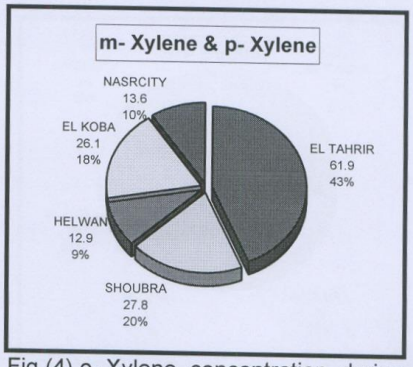


Fig.(4) o- Xylene concentration during year 2003-2004

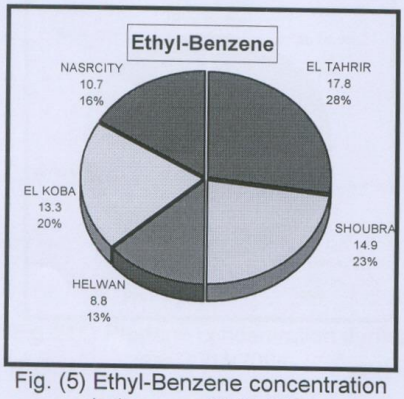


Fig. (5) Ethyl-Benzene concentration during year 2003-2004

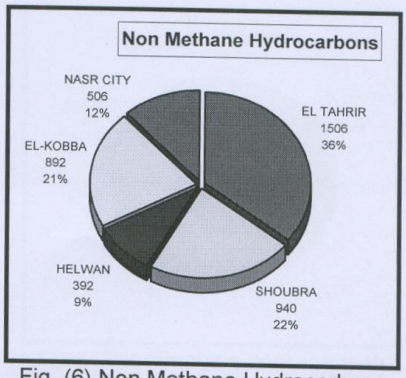


Fig. (6) Non Methane Hydrocarbons concentration during year 2003/2004

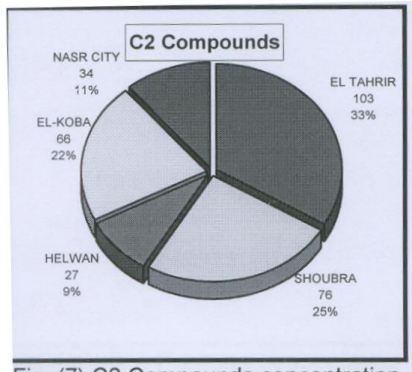


Fig. (7) C2 Compounds concentration during year 2003/2004

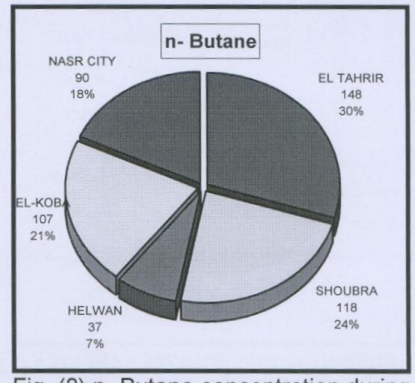


Fig. (8) n- Butane concentration during year 2003/2004

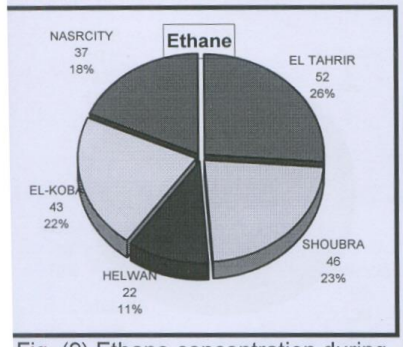


Fig. (9) Ethane concentration during year 2003/2004

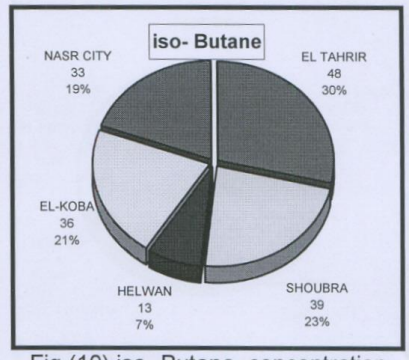
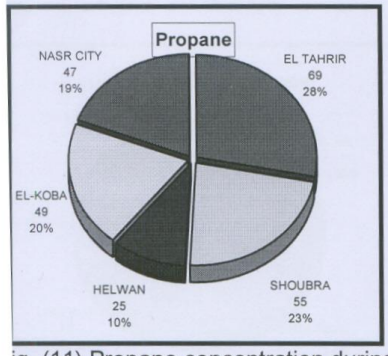


Fig.(10) iso- Butane concentration during year 2003/2004



ig. (11) Propane concentration during year 2003/2004

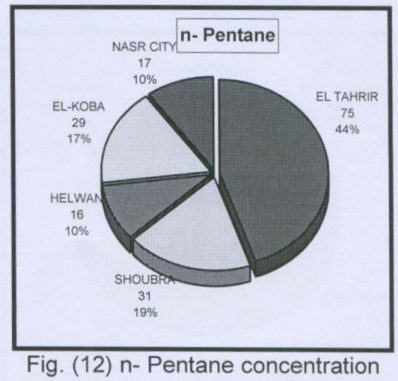


Fig. (12) n- Pentane concentration during year 2003/2004

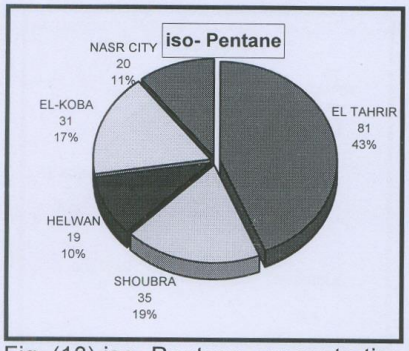


Fig. (13) iso- Pentane concentration during year 2003/2004

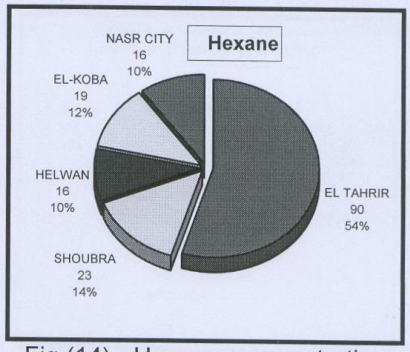


Fig.(14) - Hexane concentration during year 2003/2004

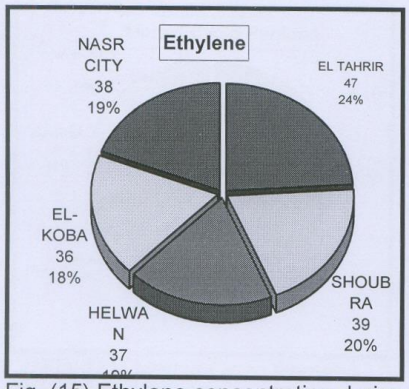


Fig. (15) Ethylene concentration during year 2003/2004

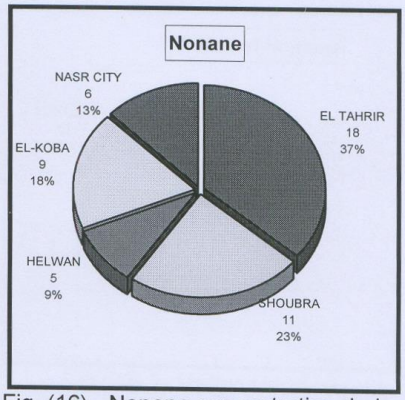


Fig. (16) - Nonane concentration during year 2003/2004

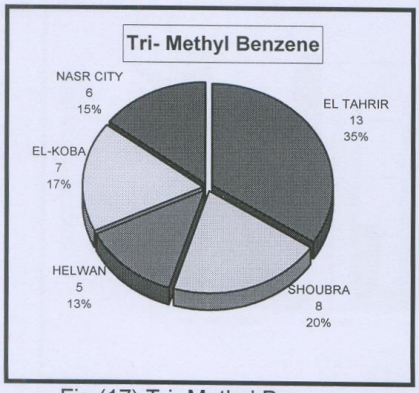


Fig.(17) Tri- Methyl Benzene concentration during year 2003/2004

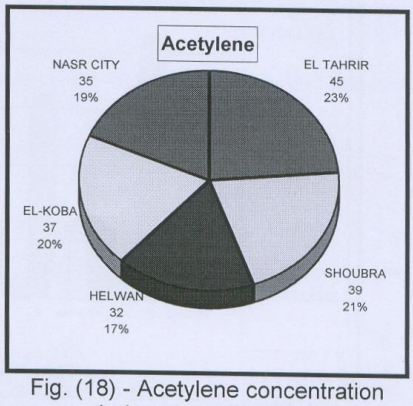


Fig. (18) - Acetylene concentration during year 2003/2004

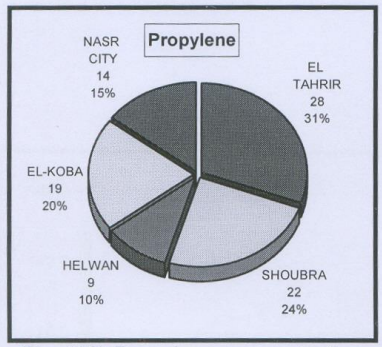


Fig. (19) Propylene concentration during year 2003/2004

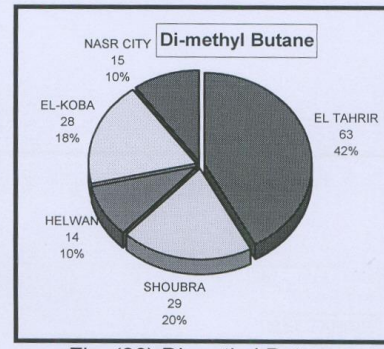


Fig. (20) Di-methyl Butane concentration during year 2003/2004

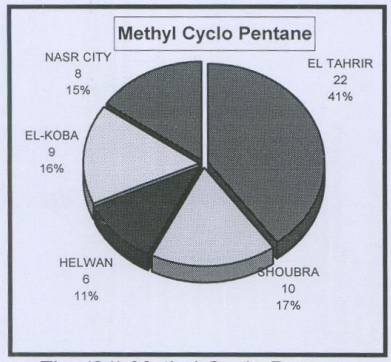


Fig. (21) Methyl Cyclo Pentane concentration during year 2003/2004

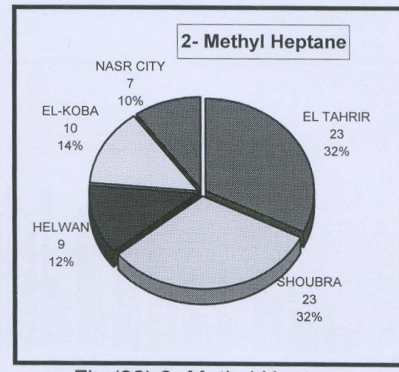


Fig.(22) 2- Methyl Heptane concentration during year 2003/2004

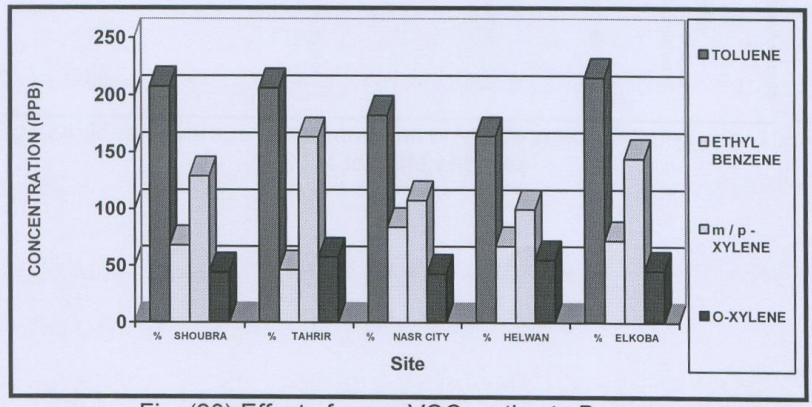


Fig. (23) Effect of some VOCs ratios to Benzene

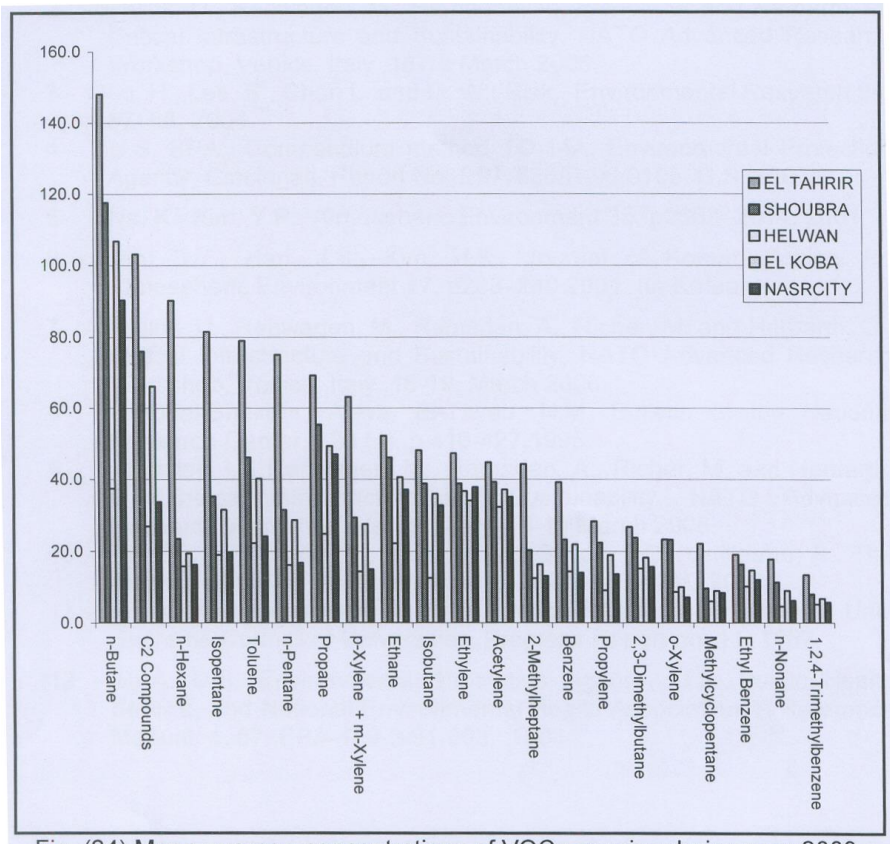


Fig. (24) Mean average concentrations of VOCs species during year 2003-2004 for different sites

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