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PHYSICOCHEMICAL EFFECT OF OZONE IN ATMOSPHERE OF GREATER CAIRO AREA

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Abstract

The surface Ozone has been determined to be human risk factor in urban environments, as well as a contributor to the formation of photochemical oxidants. Where the surface ozone is not a primary pollutant (i.e. not emitted directly by human activity), but it is produced through the action of sunlight on primary pollutants such as nitrogen oxides and hydrocarbons. Concentrations of ozone were measured at five monitoring sites located in the greater Cairo area, Egypt, as a part of the air pollution study for the effect of the volatile organic compounds and nitrogen oxides on surface ozone.

For each site, during the period from March 2003 to March 2004, we collected forty eight Ozone samples per day (every half hours), daily samples of nitrogen oxides (Nitrogen oxide & Nitrogen dioxide) and 22 abundant volatile organic compounds (VOCs) three times per day (7-9 in the morning, 2-4 afternoon and 8-10 evening).

The average ozone concentrations were found to be higher in the afternoon than in morning and nights. The morning rush hours are marked by an increase in the primary emission of NO and hydrocarbons. In the evening and night, ozone is destroyed by NO generated locally by unburned hydrocarbons from industry, traffic and thermal power plants.

Introduction

Egypt is one of the most active in the industrial and agricultural fields, which may leads to hazardous air pollution problems in some areas. This affects not only the human health but also the historical monuments. These historical monuments, some of which are more than 7000 years old, represent not only Egyptian history but all world human history.

There are two main sources for air pollution in Egypt: combustion sources and industrial activity [(1)]. 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 construction activities, solid waste disposals and burnings [(2)]. Air pollution in Cairo is caused by pollutants emitted from more than 12600 industrial establishments, two million motor vehicles, open burning of solid wastes, and combustion of eight million tons

of fuel annually in power stations, industries, furnaces etc. and the number grows by a significant amount each year [3].

Depending on where ozone is found**,** it can be good or bad. Good ozone is a gas that occurs in the upper atmosphere (stratosphere) from 10 to 30 miles above the Earth's surface, where it shields us from the sun's harmful Ultraviolet rays [4]. But at ground level (troposphere) bad ozone is formed when pollutants emitted (by cars, power plants, industrial boilers, refineries, chemical plants, and other sources) react chemically in the presence of sunlight (UVB < 320 nm). The ground surface ozone is not a primary pollutant (i.e. not emitted directly by human activity) but it is produced through the action of sunlight (through the photochemical reactions) on primary pollutants such as nitrogen oxides (NO_X) and volatile organic compounds.

$$NO_2 + O_2 + \text{sun light} \longrightarrow NO + O_3$$

$$NO + VOCs \longrightarrow NO_2$$

But in the dark, the reaction reverses and destroys ozone.

$$NO + O_3 \longrightarrow NO_2 + O_2.$$

Surface ozone is occurring roughly from May to September, when sunny, warm weather is dominating. Ozone formation is extremely sensitive to sunlight, as well as being influenced by other factors. The higher levels of ozone generally occur in the afternoon after the temperature has risen and the precursors have had time to react. Ground level ozone concentrations then fall off during the night. Cars and other vehicles are the largest source of ozone precursors. Other important sources include industrial facilities, power plants, gasoline-powered, evaporation of cleaners, paints, and other chemicals [5]**.** Ozone can damage the agricultural crops, forests, and wilderness areas, also damages materials such as nylons, rubber, and certain fabrics.

Nitrogen gas is the major gas in the atmosphere, accounting for 78% of atmospheric volume. Two oxides of nitrogen; Nitric oxide (NO) and Nitrogen dioxide (NO_2) are considered important air pollutants. The Nitrogen oxides pollutants are formed during high temperature combustion processes from the oxidation of nitrogen in the air or fuel. The main sources of NO_x (NO and NO_2) are road transport (approximately 47%), rising in urban areas where traffic is heaviest, power generation (22 %, like the power stations, furnaces and boilers using fossil fuel which present in Shoubra El-Khaima site) as well as domestic sources (4%, as examples, home heaters and gas cookers can produce nitrogen dioxide inside homes). Also large industrial sources have a significant impact. Nitrogen oxides can destroy stones used in buildings, statues, monuments, etc [6].

Volatile organic compounds are organic molecules that are mainly composed of carbon and hydrogen atoms (hydrocarbons). These are easily vaporized at room temperature without any color, smell, or taste. Recently, a number of volatile organic compounds have been identified as important cancer risk factors in urban environment [7]. These compounds 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 sources in urban areas include vehicle exhaust gas, gasoline evaporation, natural gas emissions and solvent use. VOCs contribute to the formation of toxic oxidants such as tropospheric ozone, and peroxy-acetyl nitrate, VOCs can cause serious health problems such as cancer, also some VOCs such as formaldehyde and ethylene may harm plants [8].

Experimental

The monitoring site locations of Ambient Air Quality

Five representative sampling sites were chosen to study the effect of VOCs and NOx on ozone in the greater Cairo area.

- Residential Areas: *Nasr city station*: represents a residential area with limited nearby sources.
- Traffic Areas: *El-Tahrir Square station*: located downtown, close to the road and has high light- and heavy-duty (bus) traffic.
- Industrial / Residential Areas: *The Koba station:* near a number of small industrial sources. *Helwan station* impacted by emissions from nearby cement plants and has higher levels than some of the other residential areas. on *Shoubra El-Khaima station*, in a heavily industrialized area downwind from numerous industrial sources. This is one of the most highly polluted areas in the city.

Meteorological conditions of Greater Cairo area

The meteorological conditions were measured at the measurement sites during the study period, where the average atmospheric pressure was remarkably constant. The mean value was 1010 mbar relative humidity during that period varying between 15 and 85% during day and night with a mean value of 47%. This was accompanied by temperature fluctuation between 9 and 36 ^{o}C, with a mean value of 22 ^{o}C. Annual mean rainfall is only 22 mm, as rains typically occur only during the winter months. Finally, we consider these factors are constant during the study and not included in our readings due to the stability of the meteorological conditions of greater Cairo area most of the year.

Sampling and analytical methods

During the period from March 2003 to March 2004, Samples were collected from ozone precursor (every half hour) and 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. Also, Nitrogen oxides samples were collected one time daily.

For Ozone estimation , the air sample was taken continuously by a pump placed at the end of the circuit, passes first through a teflon dust filter, then flows to the optical chamber either directly or through an ozone selective filter (commutation every 5 seconds). UV Photometric Ambient Ozone Instrument (O 41 M) is capable of measuring ambient level of ozone concentration on a continuous, real time basis. The UV photometer determines ozone concentration by measuring the attenuation of light due to presence ozone in the absorption cell, at wavelength of 254 nm. The concentration of ozone is directly related to the difference between UV absorption due to the gas sample and UV absorption due to the ozone-free sample.

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 [(13)]. Non methane hydrocarbons components (NMHCs) are 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 in ppm.

$$HCs + O_2 + Catalyst \longrightarrow CO_2 + H_2O.$$

Chemiluminescence nitrogen oxide Analyzer Model AC 31 M is used to measure the continuous concentration of NO and NOx by detection of the light emitted when NO is oxidized to activated NO_2 in the presence of ozone produced from ambient air:

$$NO + O_3 \longrightarrow NO_2 + O_2 + h\nu$$

Results And Discussion

Ozone measured at the earth's surface plays a key role in the chemical cycling of gases in the troposphere, and it contributes to greenhouse warming. Its concentrations appear to be increasing due to human activities and careful measurements must be made to verify these changes and track those that may occur in the future.

When we breathe air unpolluted by human activities, we usually take in about 10 to 15 parts of ozone per billion parts of air (10 -15 ppb). However, pollution from human activities has elevated levels of the ozone we breathe. Surface ozone measurements have increased considerably since the onset of the Industrial Revolution. Spring and summer ozone concentrations in many regions reach above 125 ppb during episodes of excessive heat and stagnant air. The U.S. Environmental Protection Agency (EPA) has established 80 ppb of ozone exposure over eight hours as the National Ambient Air Quality Standard, but recognizes the possibility that ozone exposure at lower levels over several years can significantly impair human health, especially the health of children [(9)].

Figs. (1-3) show that, the concentration ratio of ozone at early morning and evening at El-Tahrir, El-Koba sites during summer season is higher than winter season, due to traffic pollution which increases the percentage of volatiles organic compounds, but approximately the same in Helwan and Nasr city. At afternoon the concentration ratio of ozone at most sites in winter season are little less than in summer season, except in Shoubra El-Khaima and Helwan site which is higher in summer season due to formation of ozone from its constituent in presence of sun light. Meteorological conditions combined with emissions of air pollutants gave rise to high concentrations in central part of Cairo.

The concentrations of different pollutants considerably varied according to location and time. Where, the time of day is a very important factor in the amount of photochemical present [(10)]. In the early morning hours and the late afternoon (at about 18:00h), the daily of ozone level are rapidly decreased due to formation the

photochemical smog cycle and destruction of ozone by NO generated locally by unburned hydrocarbons from industry, traffic and thermal power plants. Photochemical ozone production was monitored in the daytime and ozone destruction was monitored in the night time. The typical ozone concentrations in clean remote atmospheres range from 20-40 ppb in the evening and at night, Fig (4) illustrates the daily variation for relative pollutant concentration during summer season.

The mean concentration values for Ozone are sensitively classified from low (< 50 ppb) to moderate (50 – 89) according to the ambient air quality values as given by Law no. 4 for Egypt (1994). The mean concentration values gradually decreases in the following order:-

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

The most important compounds are nitrogen oxides (NO, NO2), which play a crucial role in determining the ozone concentration in the air, especially during the daytime, which accelerate photolysis of NO_2 and gives O_3 as the by-product.

With increasing solar radiation in the morning rush hour the photochemical reaction accelerates[(11)] and increases the primary emissions of NO and Hydrocarbons. , but at night there are no UV photons, so that NO can no longer be formed by photolysis and continues to be used up by reaction with O_3, the concentrations of NO and O_3 therefore decline.

Figures 5 and 6 show that, the concentration ratio of NO_X in traffic and industrial pollution area are high, like El-Tahrir, Shoubra and Helwan in summer and winter, due to presence of factories emissions and traffic emissions, The presidential areas have low concentrations of NO, like Nasr City and Kobry El-Koba.

From the results of different sites, the mean average concentration values of Nitrogen oxides are classified as low <150 ppb according to the Ambient Air Quality Limit values as given by Law no.4 for Egypt (1994).

Volatile organic compounds (VOCs) 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 as (35%) of the total VOCs emissions [5].

Most of the VOCs species showed diurnal variations (higher concentrations during the morning and evening, and lower concentrations during the afternoon). However, later in the morning, the concentrations of aromatic compounds were slightly higher than solvent usage such as toluene, ethyl-benzene, m-/p xylene, and o- Xylene 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 types of vehicles give rise to the many pollutants. Also, the traffic density variation, traffic congestion and traffic flow influenced the concentrations at some of the sites.

Most of the 22 abundant species in VOCs have the highest average concentrations at El Tahrir, due to the high volume of mobile source emissions at this site as shown in figure (7). where about two million vehicles are making traffic emissions one of the major sources of air pollution in greater Cairo, 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)

BTEX groups [12] (Benzene - Toluene - Ethyl Benzene - o- Xylene - m-/ p- Xylene) are emitted from vehicle exhaust and gasoline evaporation, and also released from the use of solvents (painting, printing, and dry cleaning). These VOCs contain some species can cause serious individual carcinogenic diseases. Toluene & Benzene are the most important species for 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. Figure (8) shows that, the highest concentration of BTEX group in all sampling sites was found in El Tahrir (heavy traffic area) while the lowest concentration was in Nasr City. The BTEX concentration ratios decreases in the following order:-

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

Table (1) 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 [13]. The results for all the measured parameters did not exceed the guidelines, when comparing with ambient air guidelines of WHO for organic pollutants or the UK ambient air quality guidelines during the period of study from March 2003 to March 2004 [14]. The average concentrations of Benzene were higher 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 (2) indicates that, the sensitivity classification of the mean average concentration values for ozone during the study period were low (<50 ppb) to moderate (50-89 ppb) according to the Egyptian Ambient Air Quality Limit values as given by Law no. 4 for Egypt (1994).

There are more than 2 million vehicles now in Greater Cairo area [15], and that number grows by a significant amount each year. So, the government takes a comprehensive approach to reduce pollution from motor vehicles, by the emission Inspection and Maintenance programs (I/M) which are expected to have a big payoff in reducing air pollution from cars.

Conclusion

During the year from March 2003 to March 2004, the average ozone concentration at afternoon are higher than morning and night, in the morning rush hours is marked by an increase in the primary emission of NO and hydrocarbons, with increasing solar radiation, the photochemical reactions accelerate, and at evening and night ozone is destroyed by NO generated locally by unburned hydrocarbons from industry, traffic and thermal power plants.

Also, in early morning traffic increases the emissions of both nitrogen oxides and VOCs as people drive to work, later in the morning, traffic goes down and the nitrogen oxides and volatile organic compounds begin to be react forming nitrogen dioxide, and increasing its concentration. As the sunlight becomes more intense later in the day, nitrogen dioxide is broken down and its by-products form increasing concentrations of ozone. At the same time, some of the nitrogen dioxide can react with the volatile organic compounds to produce toxic chemicals. As the sun goes down, the production of ozone is halted. The ozone that remains in the atmosphere is

then consumed by several different reactions. The average ozone concentration at summer are higher than in winter, and the maximum values of ozone concentration appear in June and July when the longest days occur with most intense sunlight .

The results for all the measured parameters did not exceed the guidelines, when comparing the result 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, and in the second place after Rome Italy in the concentrations of BTEX and then the other towns.

Automobile emissions contribute to the production of ground level ozone and can cause serious upper respiratory ailments and cardio vascular disorders, particularly among the elderly and young children. Also, in highly traffic crowded areas, the mean average concentration 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.

EPA believes that control of hydrocarbon and nitrogen oxide emissions is the most promising strategy for reducing ozone levels in most urban areas. Toward that end, the government takes a comprehensive approach to reduce pollution from motor vehicles, by the emission Inspection and Maintenance programs (I/M) which are expected to have a big payoff in reducing air pollution from cars. Also, the government will establish more stringent limits on gasoline volatility, control hydrocarbon vapors that evaporate during vehicle refueling, tighten tailpipe emission standards, and require improvements in Inspection and Maintenance programs.

Recommendation

We recommend some regional strategies for reducing ground-level ozone namely,

- Reducing NO_x emissions from power plants and industrial combustion sources.
- Using low-emission cars and trucks.
- Using "cleaner" gasoline.
- Improving vehicle inspection programs.

Table (1) 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 guide line	16	260	100	100	

Table (2) Average concentration pollutant (ppb) in greater Cairo compared to the WHO standard.

Ambient Air Quality Limit values as given by Law no. 4 for Egypt (1994) compared to the worild Health Organization (WHO) air quality guideline values.				
Pollutant	Time	Actual Max. Conc. (ppb)	Maximum Limit Value (ppb)	
Ntrogen Dioxide (NO_2)	1 hour	219	200	400
	24 hours		-	150
Ozone (O_3)	1 hour	120	150-200	200
	8 hours	80	120	120

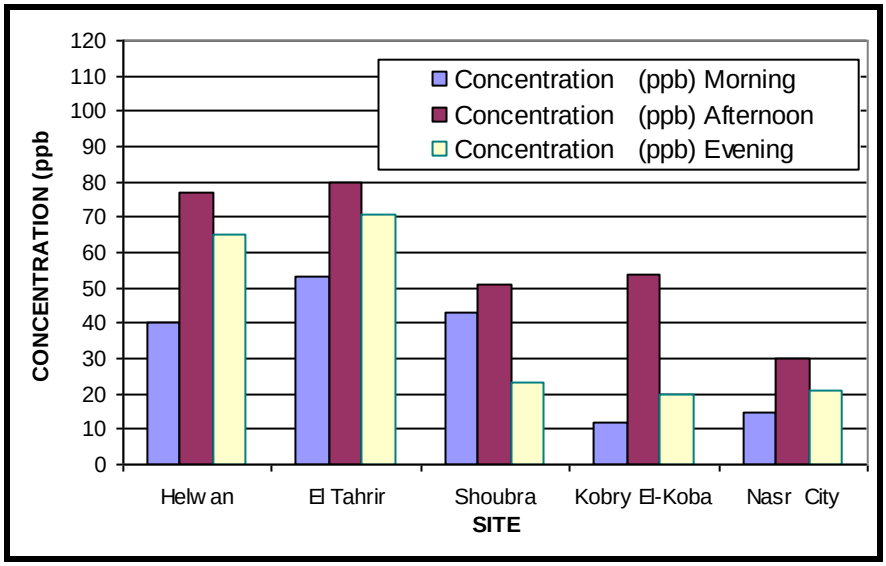

Fig. (1) Ozone concentration of the different sites in summer.

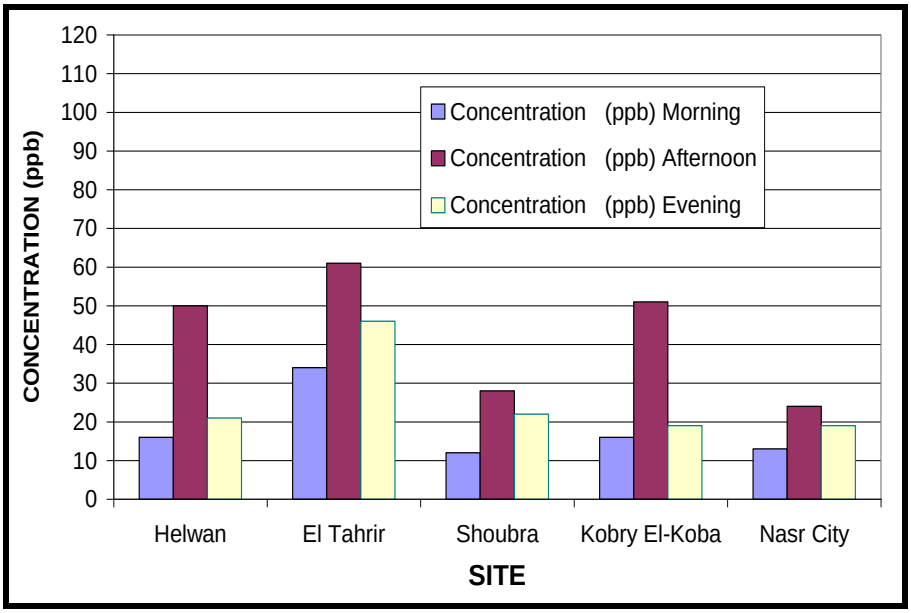

Fig. (2) Ozone concentration of the different sites in winter .

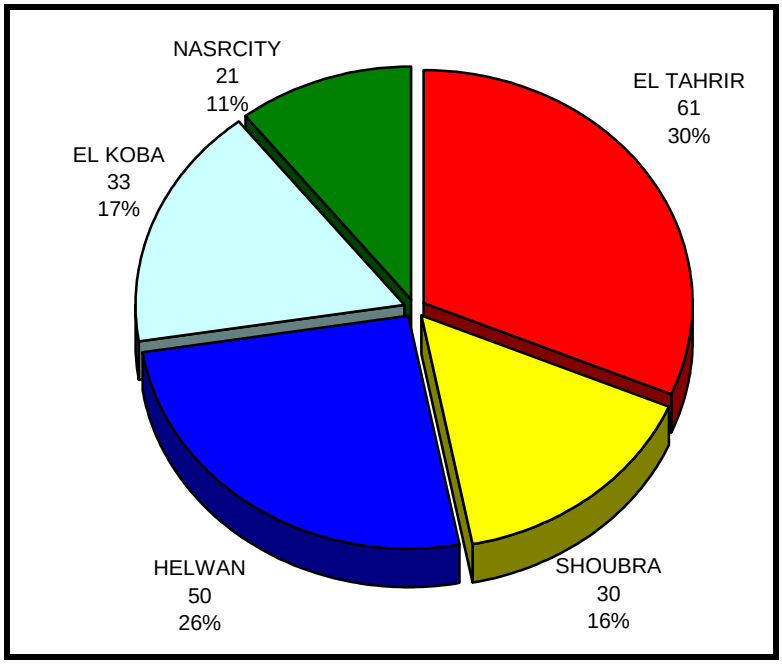

Fig. (3) Percentage of O3 concentration for the different sites in year 2003 -2004.

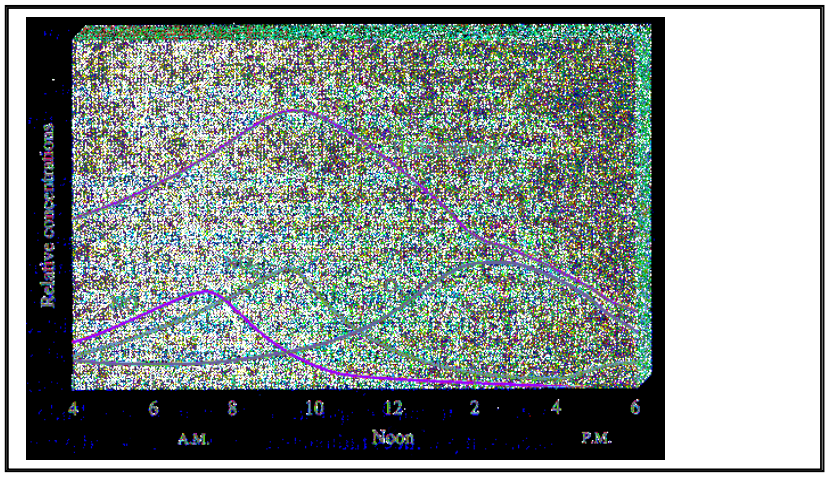

Fig. (4) Relative pollutant concentration during summer season .

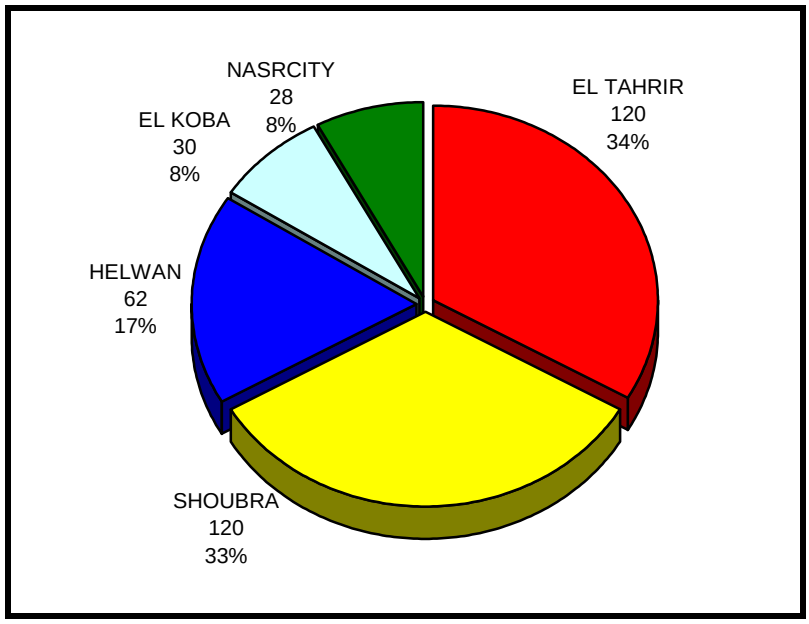

Fig. (5) Percentage of NO concentration for the different sites in year 2003 – 2004.

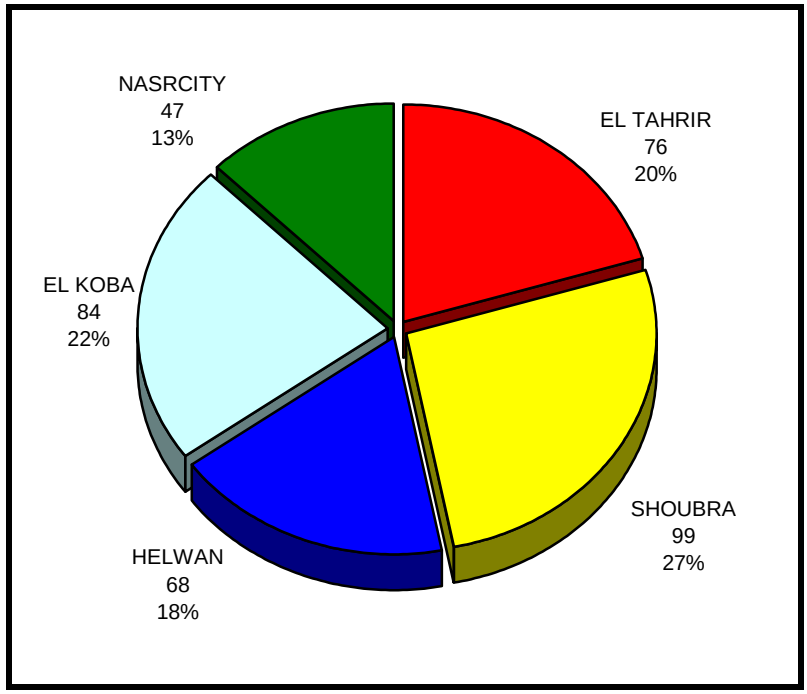

Fig. (6) Percentage of NO2 concentration for the different sites in year 2003 – 2004.

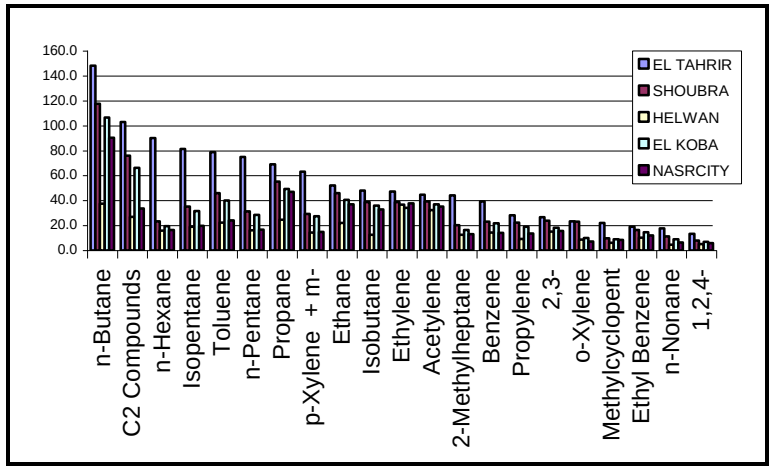

Fig.(7) Mean average concentrations of VOCs species during year 2003-2004 for different sites.

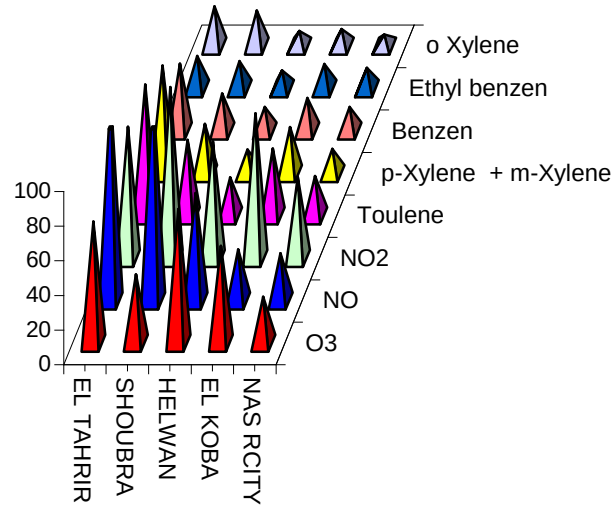

Fig. (8) Concentration of air pollutant (ppb) at after noon in year 2003/2004.

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