Measurements of Photochemical Oxidants at Sindh Industrial Trading Estate of Karachi, Pakistan

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Summary: Continuous measurements of nitrogen oxides (NO and NO_x) and ozone (O_3) were carried out by Air Pollution Monitoring Mobile Laboratory at a sampling site located in the Sindh Industrial Trading Estate (SITE) of Karachi. The average concentration of NO was found to be between 7.1 to 69.9 ppb, NO_x 17.2 to 83.5 ppb, and O_3 from 7.5 to 19.1 ppb. Ambient concentration of NO, NO_x and O_3 are strongly inter related and their dispersion conditions are also discussed. The results obtained at SITE are compared with the data obtained at other industrial areas of Karachi and with the data generated at an uptown area of Karachi, which shows clear formation of ozone during the day time. It is evident that the formation of ozone is dependent upon the time lag in the photochemical process.

Introduction

Population in the increasing number of areas is regularly exposed to air pollution levels above limits set by World Health Organization. It has been estimated that 47 percent population will be living in urban areas by the year 2000 [1]. In 1990, sixty nine cities had a population of 3 million or more, and eighty five cites will probably be in this category by 2000. Tremendous increase in the population, factories, processing industries and transport fleet has adversely affected the quality of air in Karachi. According to 1998 census Karachi has a population of 9.2 million where as in 1947 it was only 0.3 million [2].

The major cause of air pollution is combustion and combustion is essential to man. The impurities in the fuel, poor fuel to air ratio, or too high or too low combustion temperatures causes the formation of side products such as SO_2, NO, CO, fly ash, unburnt hydrocarbons etc. Pollution from fossil fuel burning has regional and global significance. More than 80 percent of sulphur dioxide, 50 percent of nitrogen oxides, and 30 to 40 percent of particulate matter emitted to the atmosphere in USA are produced by fossil fuel fired electric power plants, industrial boiler and residential furnaces. Forty percent of nitrogen oxides and hydrocarbons come from burning gasoline and diesel fuels in cars and trucks. Sulphur in diesel fuel contributes to acid rain while unburnt hydrocarbons, nitrogen oxides and carbon monoxide all contributes to regional pollution [3].

The atmospheres contain oxidants, which are chemically capable of entering into oxidation-reduction type reactions and thereby oxidizing elements or compounds. Ozone as well as most other atmospheric oxidants in polluted air, are formed by chemical reactions which occur among the primary pollutants in presence of sunlight which acts as catalyst. Naturally occurring nitrogen oxides have been estimated to be 990×10^6 tons per year mainly from volcanic emissions and bacterial activity. Anthropogenic sources contribute about 48×10^6 tons per year of nitrogen oxides principally from combustion of fossil fuels. The average half-life of NOx in atmosphere is four days [4]. The total emission of nitrogen oxides (NO and NO_2) from man made sources in Pakistan has been estimated to be 231×10^3 tons per year. An increase of forty one percent emission of nitrogen oxide has been observed during 1980 - 1990 [5].

The human health effects associated with NOx and photochemical oxidants are of importance in urban and industrial areas where usually highest concentration of these pollutants is found. There is some evidence of increased respiratory diseases, decreased lung function and frequent eye irritation in some urban populations as a result of NOx and photochemical oxidant. The situation is further complicated by umbiquitous presence of sulphur dioxide, suspended particulate matter and other pollutants, thus making it more difficult to determine whether health effects are caused by NO_x,

photochemical oxidant or the combination of these and other pollutants [4].

Emission from newly installed small diesel and gas fired power plants in various industries at Sindh Industrial Trading Estate is of great concern. The base line measurement of photochemical oxidants has become imperative. The main objective of this paper is to collect base line data for the largest industrial area of Karachi and to determine the trend of photo-chemical formation at SITE. The generated data is also compared with the data collected from various locations of Karachi.

Results and Discussion

Karachi Long: 67° East, Lat: 25° North on the coast of Arabian Sea is the biggest city of Pakistan and nerve centre of business, commerce and industry of the country, and offers immense employment and business opportunities. Annual growth rate of Karachi is about 6% of which approximately half are new comers from the up country [6]. Karachi has been declared as one of the megacities of the world by Global Environmental Monitoring System (GEMS) [7].

There has been exponential growth of industrial activity in Pakistan. Starting from scratch having only 34 large and 500 medium and small units in the whole region there are about 20,000 small and large industrial units working only in various industrial estates of Karachi [8]. There are some planned industrial estates in Karachi namely Landhi Industrial Trading Estate (LITE), Korangi Industrial Area (KIA), Federal Industrial Area (FIA) and Sindh Industrial Trading Estate (SITE).

Sindh Industrial Trading Estate (SITE) is the largest and oldest industrial area in Pakistan. It was established in the year 1953 [9]. SITE is located in district south of Karachi at Lat: 24° 54′ and Long: 67° 10′. This Estate covers an area of about 4440 acres and has nearly 2000 industrial units of various capacities. Almost all the industries are of medium size and approximately 60 percent of them are textile mills. The others are of diverse type dealing with chemicals, detergents, iron and steel, sulphur refining, vegetable oils, beverages, food products etc. Figure 1 shows the locations of sampling sites.

Continuous measurement of NO, NO_x and O_3 for eight days were carried out in the month of

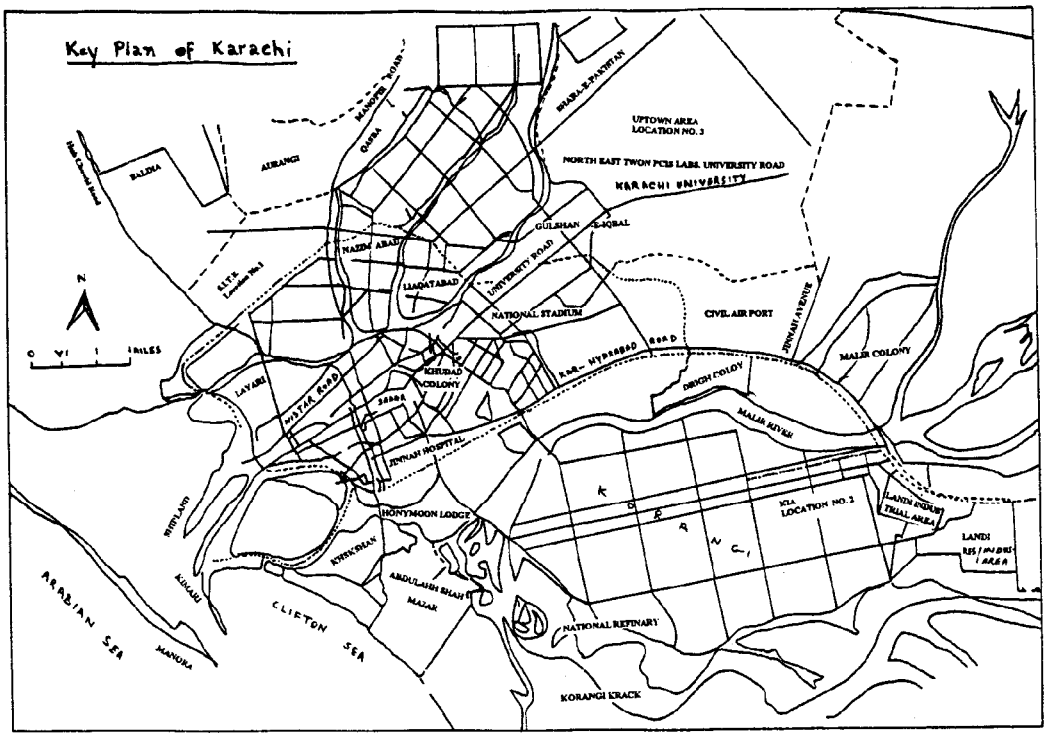

Fig. 1: Key plan of Karachi

February 1998. A SCANAIR software was used for acquisition, editing and recording logical and analogical data from data logger. Fifteen minutes average concentrations of various photochemical oxidants along with solar flux and some meterological parameters measured at SITE is presented in the form of graphs in figure 2 to 10.

The shortage and frequent break down of electric power in the SITE area has compelled the industries to install their own power generating units. These units are mostly diesel and Sui gas fired (Natural gas having 99.9% methane). Diesel fuel engines emit significant quantity of particulate and sulphur dioxide in addition to NOx. Growing number of small power stations being installed in this area motivated us to collect base line data of photochemical oxidants and to study the trend in the ambient air.

The average concentration of ozone was found to be 13.3 ppb where as maximum concentration was 19.1 ppb and minimum 7.5 ppb. The average concentrations of NO and NOx were 31.4 and 44.2 ppb, maximum concentration of NO was 69.9 ppb and NO_x 83.5 ppb where as minimum concentration observed for NO was 7.1 ppb and NO_x 17.2 ppb respectively.

Ambient concentration of NOx,. NO_2 and O_3 are strongly inter related. Nitrogenoxide photolysis forms a vital source of ozone in the troposphere. The chemistry is fundamental to atmospheric chemistry in general. Some possible photochemical reactions and products are presented here

$$NO_2 + \text{UV light} \longrightarrow NO + O \text{ (atomic oxygen)}$$

$$O + O_2 \longrightarrow O_3 \text{ (ozone)}$$

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

NO and NO_2 both have an odd number of electrons, making them reactive. In practice, the majority of the NOx (generally at least 95%) leaves the stack in the form of NO. In the initial stage of plume dispersion NO_2 is formed from NO by two routes. The first is reaction with ozone.

$$NO + O_3 \longrightarrow NO_2 \quad (1)$$

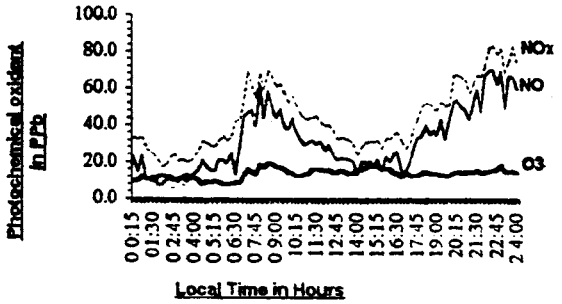

Fig. 2: Average variation of photochemical oxidants at SITE Area.

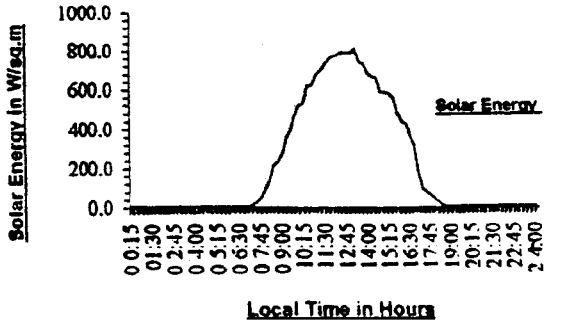

Fig. 3: Average variation in solar energy at SITE Area

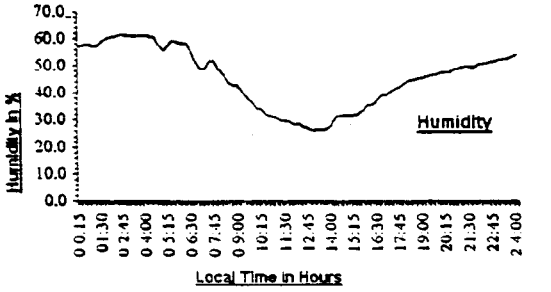

Fig. 4: Average variation in humidity at SITE Area.

The rate constant for this reaction was reported to $K_1 = 55.91 \exp(-1430/T)$ ppm^{-1}, S^{-1} [10]. Direct reaction with oxygen proceeds by a termolecular reaction viz

$$2NO + O_2 \longrightarrow 2NO_2 \quad (2)$$

The rate constant for this reaction is $K_2 = 2.143 \times 10^{-12} \exp(530/T)$ ppm^{-2} S^{-1} [10].

Reaction 2 is of very little importance in the ambient air as it is very rapidly quenched by

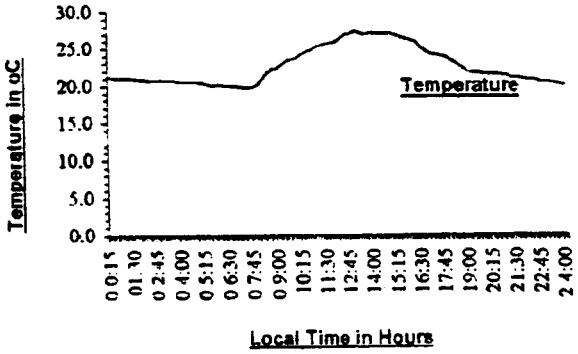

Fig. 5: Average variation in temperature at SITE Area.

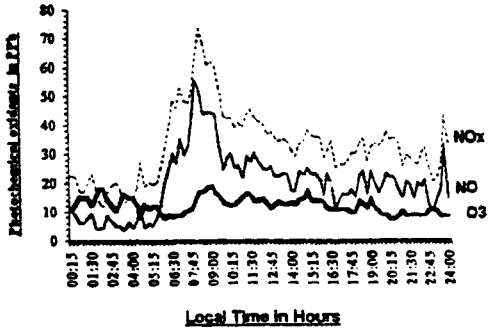

Fig. 6: Average variation of photochemical oxidant at SITE Area on 17/02/98/

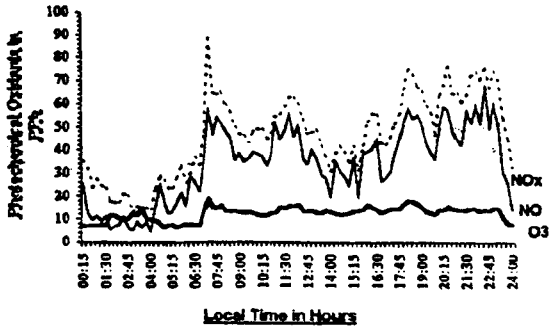

Fig. 7: Average concentration of photochemical at SITE Area on 18/02/98

dilution. In reaction 1 for every molecule of NO_2 produced an O_3 molecule is destroyed. The plume dispersion data and reaction between NO_2 and O_3 just after plume dispersion is still to be verified. Studies carried out in different countries have some difference in the observed results. This may be

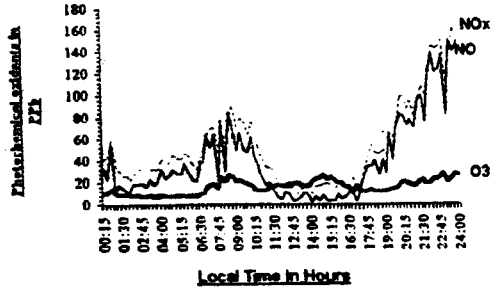

Fig. 8: Average variation of photochemical oxidants at SITE Area on 22/02/98.

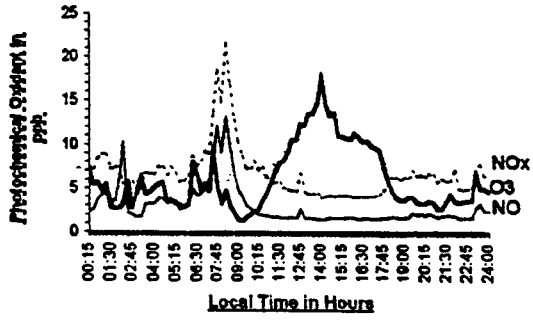

Fig. 9: Average variation of photochemical oxidant at KIA.

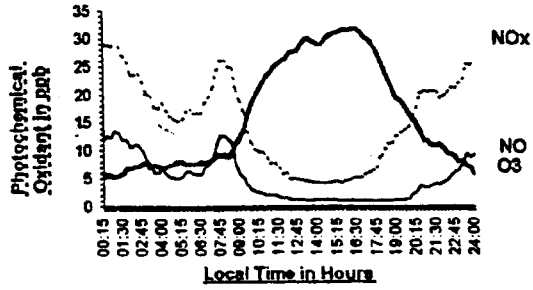

Fig. 10: Average variation of photochemical oxidant at up town Area.

because of ambient air temperature and other local meteorological conditions [11-14]. The photodissociation of O_2 requires solar energy in the region of 0.2μ. However, solar radiation less then 0.29μ does not reach the troposphere having been removed largely by reaction with ozone in stratosphere. Here ozone produced in the lower atmosphere must have some other mechanism. The formation of ozone is usually attributed to nitrogen dioxide because

nitrogen dioxide is highly photo chemically active and dissociates in radiation's below 0.38μ according to the following reaction.

$$NO_2 + hv \longrightarrow NO + O$$

This is one of the most important photo-chemical reaction in the lower atmosphere, since it produces the highly active mono atomic oxygen (O). A global three dimensional transport/chemical model of photochemical oxidants in troposphere since pre-industrial time shows increase in troposphere O_3 with a radiation transfer model. It has also been confirmed that the combined effect of anthropogenic NO_x, CO and CH_4 emissions cause a strong enhancement of O_3 level through out the global troposphere [15].

Figure 2 shows variation between NO, NO_x and O_3 at Sindh Industrial Trading Estate of Karachi. The maximum concentration of NO and NO_x was observed when the wind direction was between 180° to 230° SW and wind speed was less than 2 m/sec. A power generating plant and boiler of pharmaceutical industry was located only 50-75 meters away from the sampling site in the same direction. It shows that most of the NO, NO_x were coming from these combustion sources.

It was reported that at typical ambient air NO concentration the reaction has a time scale of one to a few minutes, while in a recently emitted plume the reaction of NO with O_3 is even more rapid, having a time scale of only a few seconds at typical ambient ozone concentration. Any ozone which mixes into the plume is thus expected to be rapidly destroyed as soon as it comes into molecular contact with NO [16]. It can be seen from Figure 2 that the concentration of ozone during the measurement period was also destroyed by NO scavenging and thus the lower values of ozone in ambient air were observed at SITE. More over the size of emission sources in relation to ambient emissions seem to be of crucial importance. However two mixing time scales must be considered, the rate of molecular diffusion and the rate of turbulent dispersion. Chemical reaction between the mixing species will be limited by the small scale mixing.

Detailed day to day discussion is beyond the scope of this paper. However, typical figures for three days are graphed against local time to illustrate day to day variations of these pollutants. Data for 17/2/98 is presented in figure 6. The maximum concentration was found to be as O_3 18.7 ppb, NO 55.2 ppb and NOx 73.5 ppb. Average wind direction during the day was 211 degree and wind speed 2.8/m.sec. Figure 7 shows the measurements for 18/2/98. Maximum concentration was found to be as O_3 18.8 ppb, NO 68.2 ppb and NOx 88.6 ppb whereas average wind direction during this day was 191 degree and wind speed 4.9 m/sec. Figure 8 presented the diurnal average variation of O_3, NO and NOx for 22/2/98. The maximum concentration of O_3 was 28.4 ppb, NO 48.8 ppb and NO_x 53.1 ppb. Average wind direction during this day was 168 degree and wind speed 1.2 m/sec. Strong interaction between O_3, NO, NO_x is readily apparent when examining diurnal variations of these pollutants from individual days. The formation of ozone is more evident during the day in figure 22/2/98 than figures 17/2/98 and 18/2/98. It may be because the average wind speed on 22/2/98 was only 1.2 m/sec as compared to 2.4 m/sec and 2.8 m/sec for 17th and 18th respectively. The photochemical process is more evident from figure 22/2/98 because of time lag.

The data obtained at SITE, has been compared with the diurnal pattern observed at the second largest industrial area of Karachi which is Korangi Industrial Area (KIA). KIA is located in the South East of Karachi at Lat: 24°-51′, Long:-67°-11′ in the district East. (Location No. 2, Figure 1). The typical photolysis reaction of NO, NO_2 and formation of O_3 in KIA can be seen from figure 9. This data was also generated in the month of February. It can be seen from the figure that the balance between NO, NO_X and O_3 shifts in favour of ozone production, driven by photolysis of NO_2. As a result, ozone concentration reaches its maximum in mid afternoon. The ozone level starts decreasing during early evening as the ultraviolet radiation from the sun also declines. The sampling site at KIA was located about five Km down wind from diesel fire Karachi Electric Supply Corporation power plant of 80 MW/hr. The chemical reaction between the mixing species can clearly observed from the graphs however it was not complete due to time lag. The rate of molecular diffusion and turbulence dispersion was not fully achieved at the sampling site.

Ozone concentration is often elevated downwind of urban area because of the time lag

involved in photochemical processes and NO scavenging in polluted atmosphere. Photochemical oxidants were observed at uptown area of Karachi (location No. 3, Figure 1). This data was also generated in the month of February. The location is about 30 Km down wind from the city centre. Figure 10 shows a distinct ozone production during day time and diurnal pattern was clearly observed. A some what photostationary state may have reached at location 3. Similar phenomena at background urban area was observed during the measurements of urban photochemical oxidants in London [17].

The ratio of NO to O_3 at photostationary state was found to be coherent. No evidence of O_3 production was observed out to their maximum range of 115 kms from the source of emission [18]. However some authors have reported clear O_3 production at a distance of around 100 Kms from the source [19,20].

Experimental

The data presented here was collected with the help of Air Pollution Monitoring Mobile Laboratory designed and fabricated by Environment S.A. France. Air pollution monitoring mobile laboratory is fully equipped with ambient air and particulate monitors designed to measure low concentration of gases such as SO_2, NO, NO_2, NO_x, CO, O_3, HC and particulate matter (PM10) in ambient air. It is also equipped with meteorological sensors mounted on a telescopic mast. These advanced technology instruments are microprocessor regulated and define a homogenous and coherent range. Chemihuminescent analyzer model AC 30M was used for the estimation of NO, NO_x levels. AC30M analyzer is of two-channel type and measure NO and NO_x simultaneously on the same. Sample of air is sucked by a pump located at the end of the circuit. One channel goes directly to reaction chamber (NO channel) and other to converter over (NO_x channel). The NO channel is very accurately regulated to maintain very high efficiency of converter over by a laser perforated synthetic ruby flow regular. The high performance converter over module consists of molybedanium based catalyst heated by a heating coil of total resistance of approximately 380 ohms. The temperature at 350°C is regulated by the electronic control board. Any operation fault detected by microprocessor sets the monitor to a 'converter fault' conditions and breaks the over power supply and cancels the measurement values on NO_x channel. Both the channels are read by a single photo-multiplier tube of high sensitivity to avoid the disadvantage of using two different P.M Tubes. In order to maintain the dark current of photo-multiplier tube within values compatible with minimum measurement range, the PM tube is mounted in a temperature controlled system, which maintains the temperature of PM tube at 12 to 1°C. A high speed chopper is placed before the PM tube which allows to read in succession the reaction chamber for NO, than reaction chamber for NO_x and than the mark (Zero), served time per second. At each complete revolution of chopper, an electrical zero is achieved corresponding to the dark current of PM tube. This is taken into account in signals drift. Further more a high quality filter is located between the chopper and photo-multiplier tube to eliminate emission due to interference by hydrocarbons. Calibration of AC30M was carried out by the microprocessor based portable calibrator VE3M (ISO-6349). The NO_2 DYNACAL, permeation device used for the calibration is certified and traceable to N.I.S.T. standards.

Ozones was measured by a UV photometric ozone monitor, model O_3 41M, which provides continuous ozone measurements. It has its own ozone generator for span gas. Measurement of solar energy was made by obsermet CM5 Pyranometer. An intelligent data logger SAM32 records spot concentrations every second and accumulates these to provide 15-minute average. The logger also monitors instrument alarm and diagnostic functions and controls daily instrument zero/span response checks.

Following are the main characteristics of the instruments.

UV Photometric Ozone Analyzer Model 03 41M

Ozone computerized analyzer with UV energy, temperature and pressure compensation based on Beer Lambert's Law.

Characteristics: .

Measurement ranges:	0.1, 0.25, 0.5, 1.0, 10.0 ppm
Units:	ppm or mg/m^3

Noise:	0.5 ppb (response time 50")
Minimum detectable:	1 ppb (response time 50")
Response time:	10-90" (programmable)
Zero drift:	<1 ppb / 7 days
Span drift:	<1%
Sample flow rate:	1.6 liters/minutes
Ozone generator:	
Concentrations generated:	150 to 75p ppb
Accuracy:	+/- 5%
Total flow rate:	4 Liters/minutes

NO-NOx, Analyzer Model AC 30M

Chemiluminescent AC 30M analyzer is of two channel type. Measurements of NO and NO_x being carried out on practically the same sample. The air sampled by pump placed at circuit, end is led, on the one hand via a converter oven towards the NO_x chamber and on the other hand, directly into NO chamber. The radiation emitted in the NOx chamber is proportional to $NO+NO_2$ (reduced into NO), NO-NO_x analyzer is coupled with serial R232 output, signal processing and continuous zero control by the microprocessors.

Characteristics:

Measurements ranges:	0.1, 0.25, 0.5, 1.0, 10.0 ppm
Units:	ppm or mg/m^3
Noise:	0.17 ppb (response time 90")
Minimum detectable:	0.35 ppb (response time 90")
Response time:	12-120" (programmable)
Zero drift:	<1 ppb/24 hours
Span drift:	<1%/24 hrs
Relative Linearity:	1%
Repeatability:	1%
Sample flow rate:	0.57 liters/minutes
Ozone flow rate:	0.57 liters/minutes
Pressure chamber:	-60 cm/Hg with KNF PM 7837-026 pump
$NO_2 \rightarrow NO$ converter:	molybdenum at 320°C
PM temperature:	regulated at 12 +/- 1°C

Obserment CM5 (Pyranometer)

The pyranometer CM5 is designed for measuring the irradiance on a plane surface, which results from the direct solar radiation and form the diffuse solar radiation incident from the hemisphere above. It complies with the specifications for a "first class" pyranometer, as published in the "Guide to Meteorological Instruments and Methods of Observation" WMO-Geneva, Switzerland.

Characteristics:

Resolution: (small detectable change in Wm-2)	+/-5
Stability: (Percentage of full scale change/year)	+/-2
Cosine response:	<+/-7
Azimuth response:	<+/-5
Temperature response:	+/-2
Non linearity:	+/-2
Spectral sensitivity:	+/-5
Response time (99% response):	<1 min.

Conclusion

The variation of photochemical oxidant observed at SITE shows that the concentration of ozone during the measurement period was destroyed by NO scavenging and lower values of ozone were observed in the ambient air. A short term baseline data generated here may not be applicable beyond the time period monitored. The diurnal pattern of ozone formation of KIA showed typical photolysis reaction of NO, NO_2 and the formation of O_3 in day time. While the measurement carried out at the

uptown area showed clear photochemical production of ozone during day time and a more clear correlation with the solar energy. A distinct photochemical reaction observed here may because of time scale as the observation site is about 30 Km down wind from the emission sources.

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