10 YEARS OF PHOTO - CHEMICAL SMOG MONITORING IN JOHANNESBURG

H.J. Krohm
Johannesburg City Council : Health, Housing & Urbanisation Department, Laboratory Services
P O Box 1477, Johannesburg 2000

ABSTRACT:
A review is presented on the results of 10 years of air pollution monitoring in Johannesburg, with reference to primary emissions such as nitric oxide (NO), carbon monoxide (CO), non-methane hydrocarbons (NHC) and secondary pollutants such as ozone (O3), nitrogen dioxide (NO2) and peroxy-acetyl nitrate (PAN). Preliminary trend analysis of ozone data shows a rise of ± 1.5 - 2 parts per billion per annum. Average PAN concentrations are above accepted rural values indicating limited photo-chemical smog formation. Spot measurements of sulphur dioxide indicate only low concentrations being present in the city centre.

INTRODUCTION:

Photo-chemical smog monitoring was started at Johannesburg in May 1982 at the City Hall c/o Harrison and President streets. A second station was established in July 1984 at the water reservoir in the southern suburb of South Hills. From June 1986 until May 1989 a third station was maintained at the Northern Sewerage works. Sampling was also conducted at the Rondebult and Bushkoppies sewerage works.

Instrumentation, methodology and air pollution monitoring results in Johannesburg over the period 1982 - 1986 have been discussed by Stevens[1]. The following review covers this period as well as data collected up until August 1992.

AIR POLLUTION: DAILY PROFILES AT CITY HALL, SOUTH HILLS AND NORTHERN WORKS

Figs 1a - 1d and 6d show a typical daily pollution pattern of hourly averages for the South Hills, City Hall and Northern Works monitoring stations.

The City Hall site (Figs 1a, b) exhibits a predominantly automobile generated air pollution pattern with a sharp rise in primary vehicular exhaust pollutants such as nitric oxide (NO), carbon monoxide (CO) and non-methane hydrocarbons (NHC). The morning peak (07:00 - 09:00) and afternoon peak (16:00 - 18:00) coincide with the daily traffic pattern, morning and afternoon rush hour. Ozone is low during rush hour periods due to the scavenging effect of nitric oxide on ozone ($NO + O3 \rightarrow NO2$).

During the latter part of the morning until the early afternoon secondary pollutants such as ozone (O3) and nitrogen dioxide appear. Ozone can rise significantly during the night and early morning, sometimes even eclipsing the mid-day peak.

Good dispersion of air pollutants occurs at the City Hall site as the majority of ozone peaks occur during weekends when very little traffic is present in the city centre, consequently very little nitric oxide is present which can scavenge the ozone. High ozone concentrations due to atmospheric conditions and UV intensity are still predominant (Figs 3, 4).

The South Hills pattern (Fig 1c) is very much different due to the absence of heavy traffic at this site thus much smaller morning and afternoon peaks of primary pollutants are observed. The formation of ozone is largely dependent on the amount of ultra violet light, as ozone maxima mostly occur between 14:00 and 16:00 (Fig 3) and they are fairly evenly distributed for each day of the week, with a slight preference for Saturday (Fig 4).

A smaller O3 peak appears from 21:00 onwards, as is the case at the City Hall, which has given rise to isolated night time ozone maxima.

In the period September 1984 to August 1992 a total of 16 night time (20:00 - 04:00) ozone hourly averages of greater or equal than 0.08 ppm (parts per million) where recorded at South Hills. Fourteen occurrences, or 87% of the total, happened between 17 - 27 October 1984. A single value was recorded on 2 March 1985 and 24 July 1992. The wind direction for these occurrences was predominantly from north-west or north.

These results are not as easily explained but it can be stated that atmospheric conditions can play a role such as the inversion layers. The altitude of Johannesburg can also account for peculiar ozone values as has been found by various authors who measured ozone at high altitude, remote rural sites[2,3]. This is reflected in the data distribution of ozone peaks greater or equal to 0.080 ppm (Figs 2a, 2b). As can be seen some very high isolated ozone values of 0.2 and 0.3 ppm have been recorded at the South Hills site. In contrast, none of these exceptionally high values have ever been recorded at City Hall (Fig 2a), the last ozone value of higher than 0.08 ppm at the City Hall was recorded on the 11 September 1989.

It has been demonstrated by Grosjan and Williams[12] that sites which are 90 - 150 km downwind of a major photo-chemical smog area such as Los Angeles, experience evening and night time ozone maxima, which are caused mainly by emissions from the Los Angeles area and subsequent chemical reactions during transport. As South Hills is downwind of the Johannesburg central area, the persistent night time rise in ozone may in part be due to this phenomenon.

Fig 1 a. CITY HALL : DAILY POLLUTION PATTERNS
SECONDARY POLLUTANTS

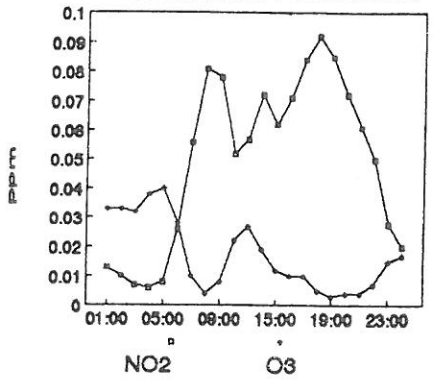


Fig 1 b.
PRIMARY POLLUTANTS

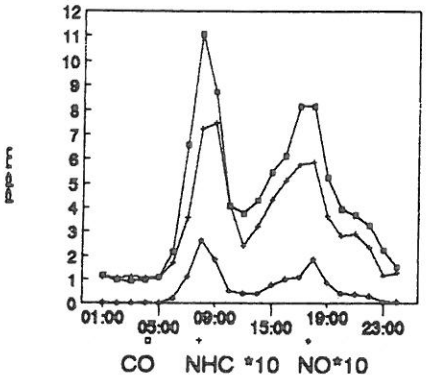


Fig 1 c.
SOUTH HILLS : DAILY POLLUTION PATTERN

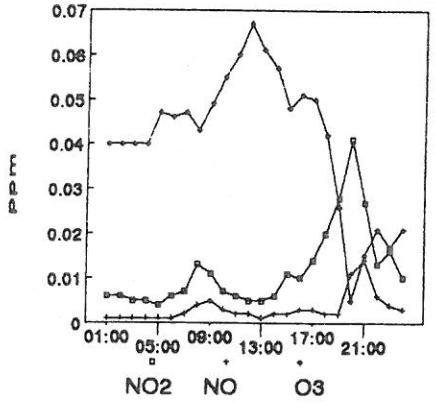


Fig 1 d.
TEMPERATURE AND UV PROFILES

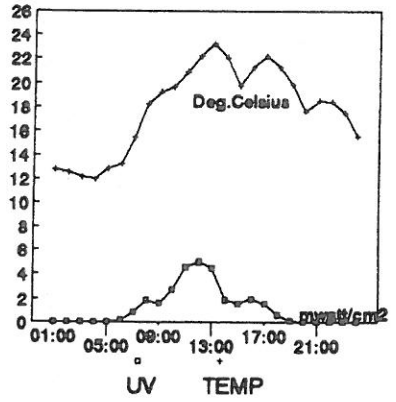


Fig 2 a. CITY HALL : O3 ≥ 0.08 ppm
DATA DISTRIBUTION: 1982 – 1992

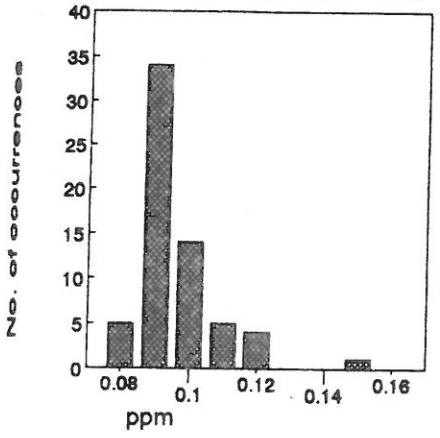


Fig 2 b. SOUTH HILLS : O3 ≥ 0.08 ppm
DATA DISTRIBUTION: 1984 – 1992

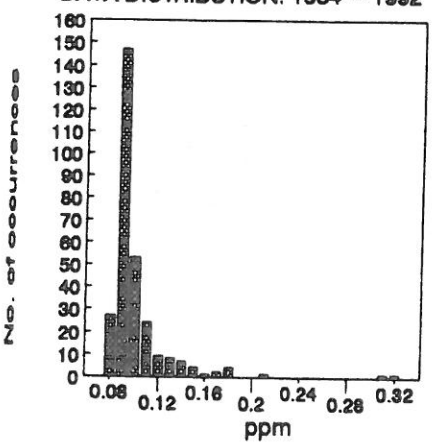


Fig 3 No of Occurrences of O3 ≥ 0.08 ppm against Time of Day

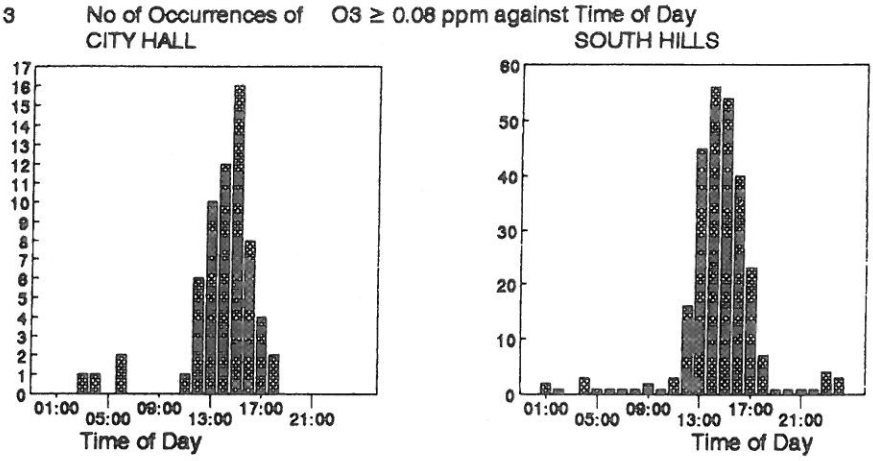


Fig 4 No of Occurrences of O3 ≥ 0.08 ppm against Week Day

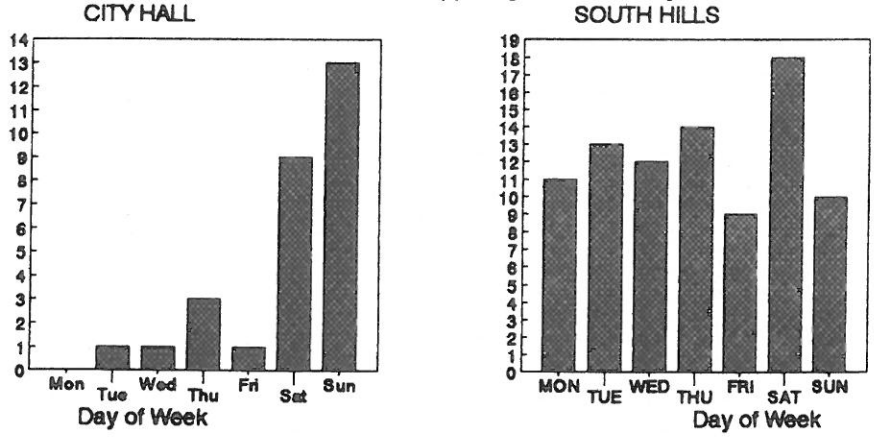


Fig 5 No of Occurrences of O3 ≥ 0.08 ppm against Season of Year

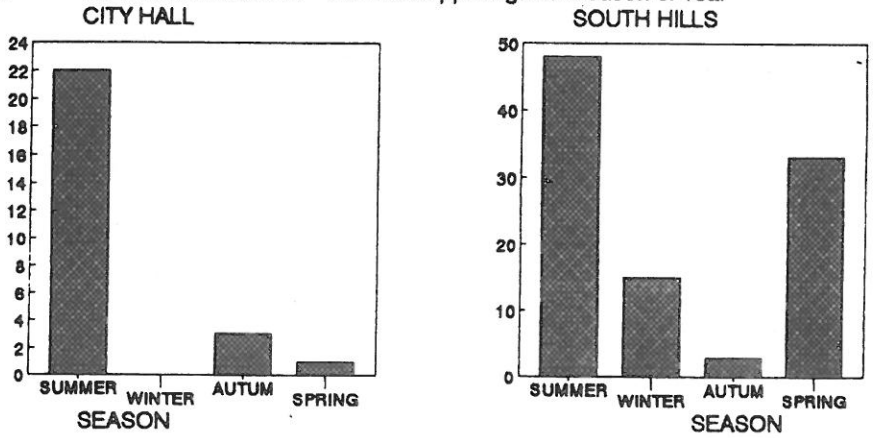


Fig. 6a Northern Works
Data Distribution
O3 > 0.08 ppm

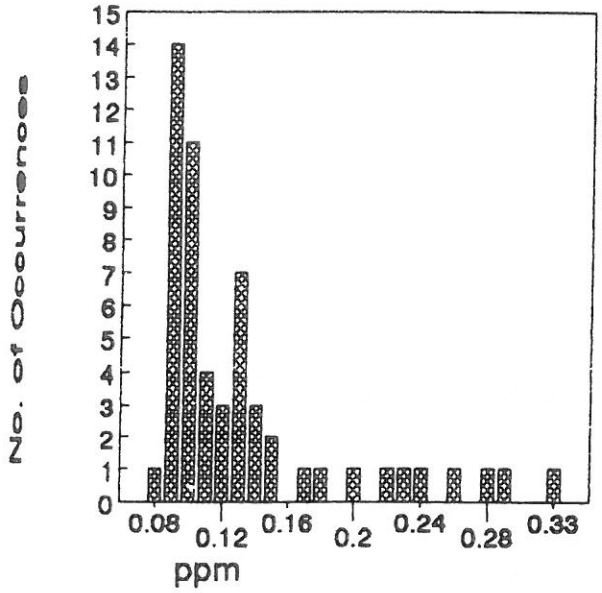


Fig. 6b Northern Works
O3 > 0.08 ppm against Time of Day

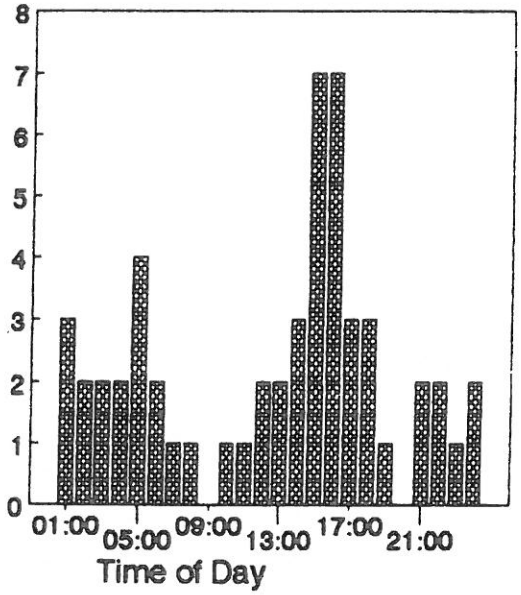


Fig. 6c Northern Works
O3 > 0.08 ppm against Week Day

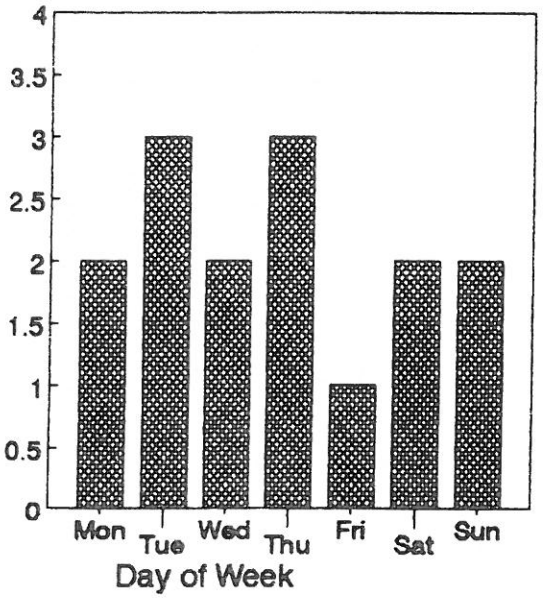
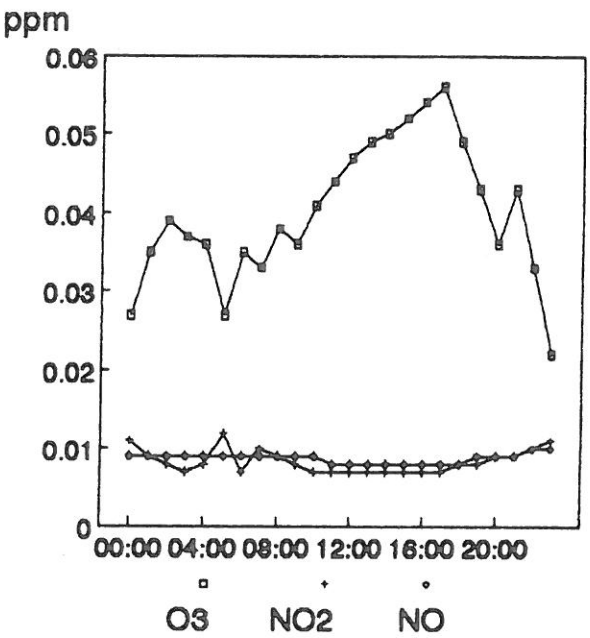


Fig. 6d Daily Pollution Patterns



Seasonal fluctuations in ozone peaks > 0.08 ppm are shown in Fig. 5. Even though most peaks occur in summer (November - March), it is interesting to note that relatively more ozone peaks occur in the spring months September and October at South Hills. An explanation is that these months are warm and dry which favours high ozone formation. In contrast at the City Hall very few ozone maxima occur in spring (Fig. 1e). This can partly be attributed to September and October being windy months with resulting higher dust loads in the air, especially in the city centre, this would be detrimental to ozone formation at this site, as would high windspeed in general due to faster dispersion of pollutants.

The Northern Works site was established primarily to serve as a rural background station, up-wind of the predominant wind direction (from north to south). The daily pollutant profile at Northern Works for peak summer values (Fig 6d) is indicative of a rural pattern, with ozone peaking in the late afternoon. No values of ozone > than 0.08 ppm where measured prior to 1988. An unexplained upsurge in high ozone measurements occurred in August and September 1988, with values in excess of 0.2 and 0.3 ppm being recorded (Fig. 6a), a large proportion night time highs (Fig. 6b) with no specific preference to any day of the week (Fig. 6c).

As a sewerage works can in itself be a source of pollution, due to the emission of NO in the oxidation of urea, ammonia and of methane and non-methane hydrocarbons in the settling and aeration tanks, it was decided to close the station in May 1989. This decision was also necessitated by a lack of serviceable instrumentation.

TREND ANALYSIS OF AIR POLLUTION DATA

Preliminary results for trend analysis of ozone data are shown in Figs 7a, b.

Both daily high and daily average ozone values are considered. The values are split between summer data (September - April) and winter data (May - August). Simple linear regression is performed on each data set.

The results can be summarized as follows:

A slight upward trend in ozone concentrations is detected at South Hills for both the winter and summer data sets. The rise is ± 1.5 - 2 ppb (parts per billion) per year.

The same trend is apparent for the winter ozone values at the City Hall. In contrast, the summer values for City Hall ozone show no trend at all, the best fit line has zero slope.

These results are somewhat surprising. It has been well documented that in the northern hemisphere, ambient levels of air pollutants at rural sites are rising slowly. This appears to be somewhat of a global phenomena, due to the depletion of the stratospheric ozone layer and the accumulation of green house gasses as the direct result of global warming[2].

These observations can be used in part to explain the slow rise in ozone concentrations at the South Hill site and the winter data for the City Hall. The summer time situation at the City Hall appears to be dependent to a larger extent on the presence of primary pollutants such as carbon monoxide, non-methane hydrocarbons and nitric oxide, whose levels have remained fairly constant during the last couple of years.

This is shown in Figs. 8a, b which displays the summer and winter averages and high values of nitric oxide measured during 1982 - 1992. Sundays and public holidays have been removed from the data set, as relatively little traffic is present in the city centre during those days, resulting in low nitric oxide readings. It must be noted that the winter values are substantially higher than the summer values as dry, cold conditions would favour less rapid oxidation of NO to NO2.

MEASUREMENTS OF PEROXY - ACETYL NITRATE (PAN) DURING JUNE - AUGUST 1988

In order to ascertain the extent (if any) of the formation of photo-chemical smog, peroxy acetyl nitrate (PAN) was measured on a 24 and 8 hour average basis at 4 sites, South Hills (southern suburb), Cydna Laboratory (Houghton, northern suburb), Municipal Gasworks (Cottesloe, western suburb) and Bezuidenhout Valley (eastern suburb). Preparation, purification and quantization of PAN standards were performed as described by Nielsen[10]. Results of gaschromatographic analysis of PAN standards and samples from monitoring sites are shown in Figs. 9a, b. The South Hills and Gasworks sites were run on behalf of the CSIR during August 1988. The results for this period are also discussed by Baunuk and Grosser[8].

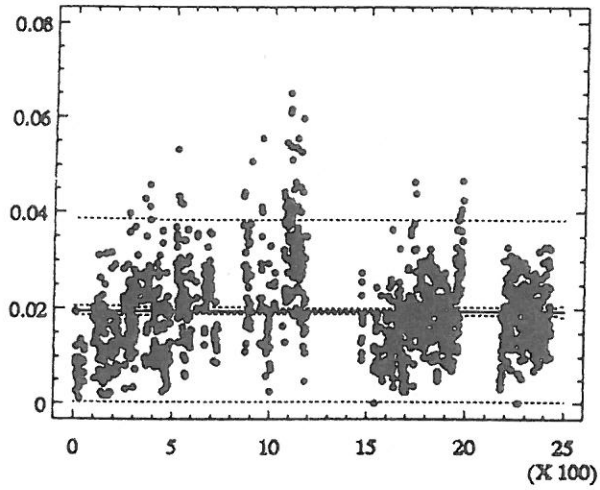
PAN was detected in all but two of the collected samples.

PAN was absent during 10/10 cloud cover, rainy and windy conditions at both the Gasworks and South Hills sites (Figs. 9c). This demonstrates the absolute dependence of PAN formation on UV lights. As PAN is much more stable than ozone, the total absence of PAN under the above conditions, points to the fact that air pollutants are not imported from other sources into the P.W.V. area.

Fig. 7a CITY HALL : OZONE TREND ANALYSIS

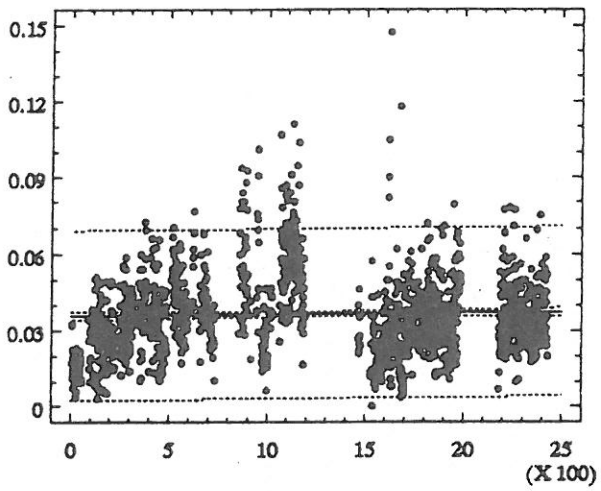
Regression of Summer Ozone Averages in parts per million against summer days

ppm



1984 Summer Days 1992

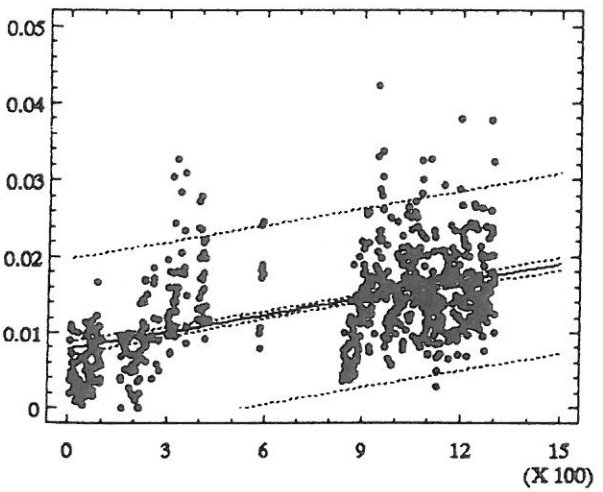
Regression of Summer Ozone Maxima in parts per million against summer days



1984 Summer Days 1992

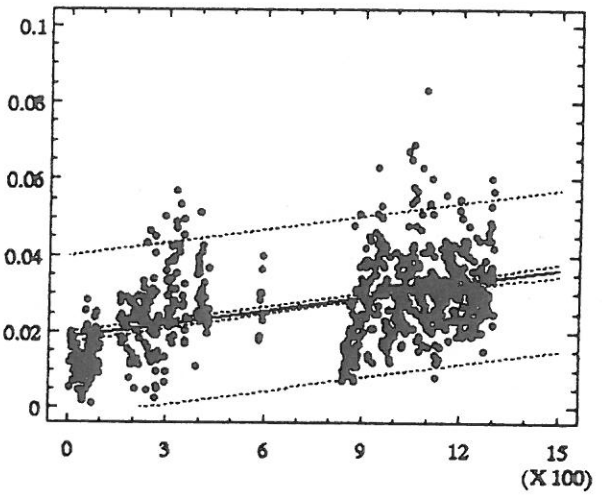
Regression of Winter Ozone Averages in parts per million against winter days

ppm



1984 Winter Days 1992

Regression of Winter Ozone Maxima in parts per million against winter days



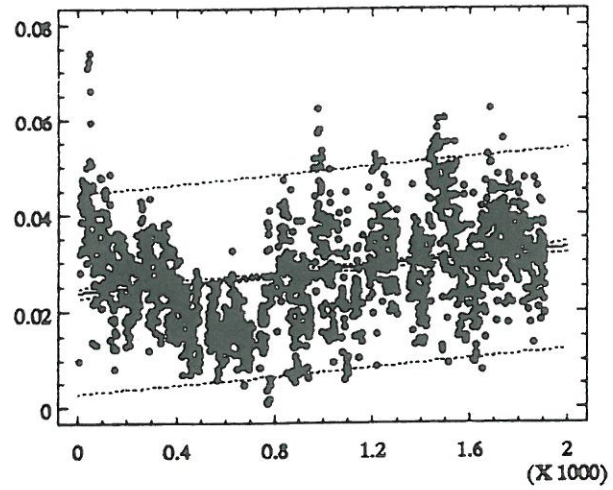
1984 Winter Days 1992

Fig. 7b

SOUTH HILLS : OZONE TREND ANALYSIS

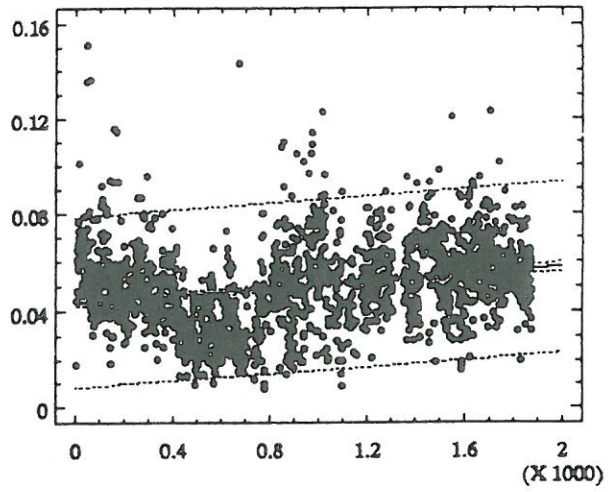
Regression of Summer Ozone Averages in parts per million against Summer days

ppm



1984 **Summer Days** 1992

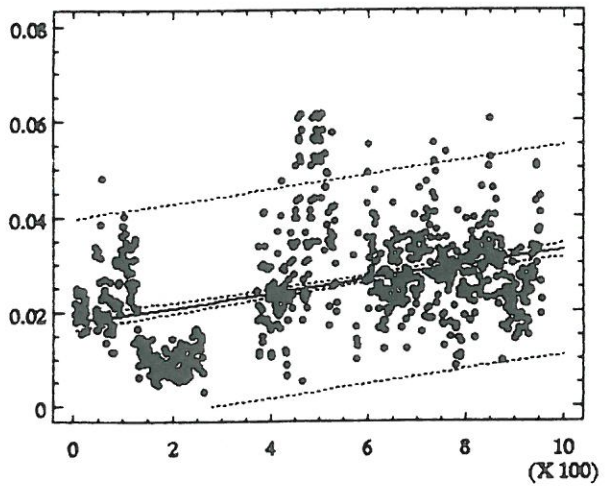
Regression of Summer Ozone Maxima in parts per million against Summer days



1984 **Summer Days** 1992

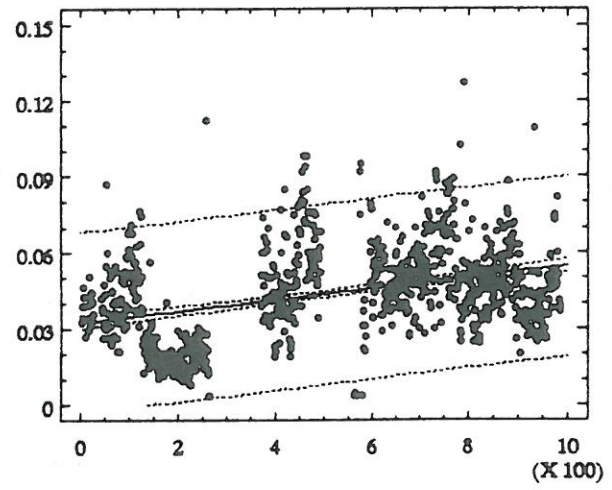
Regression of Winter Ozone Averages in parts per million against winter days

ppm



1984 **Winter Days** 1992

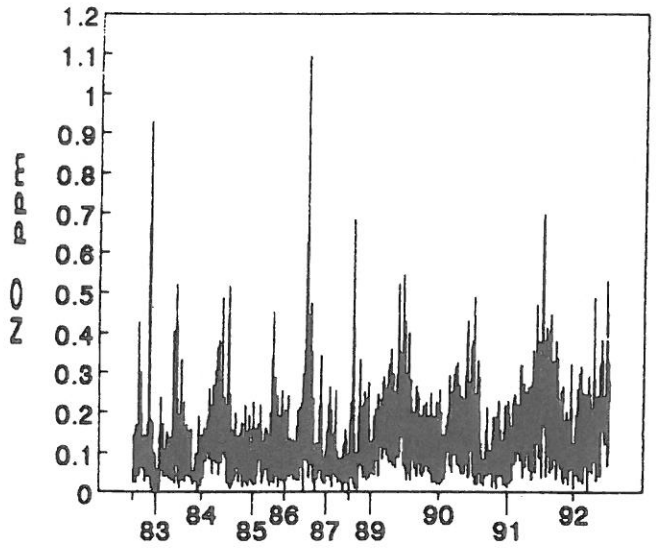
Regression of Winter Ozone Maxima in parts per million against winter days



1984 **Winter Days** 1992

Fig. 8a CITY HALL : NITRIC OXIDE (1982 - 1992)

Summer : Daily Hourly Maximum



Summer : Daily Averages

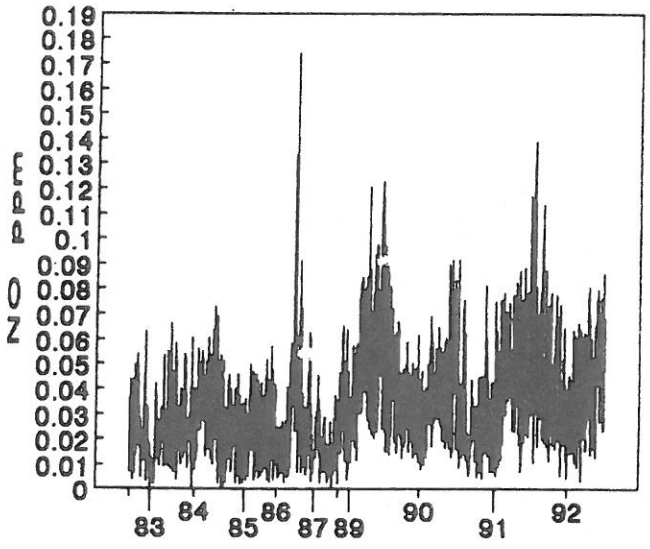
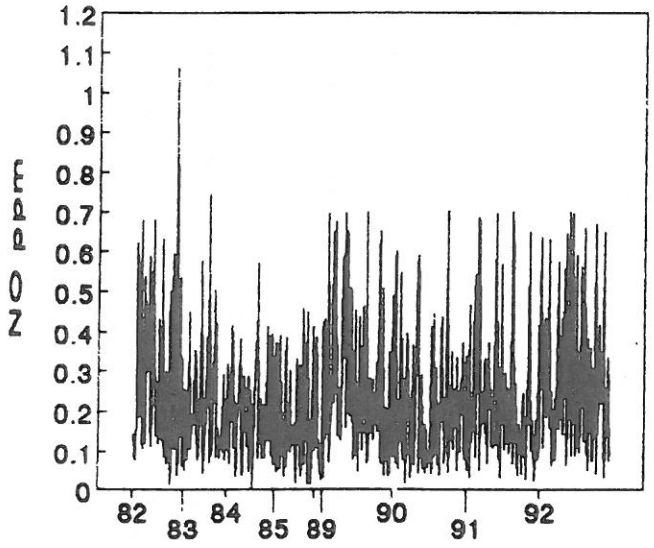


Fig. 8b

Winter : Daily Hourly Maximum



Winter : Daily Averages

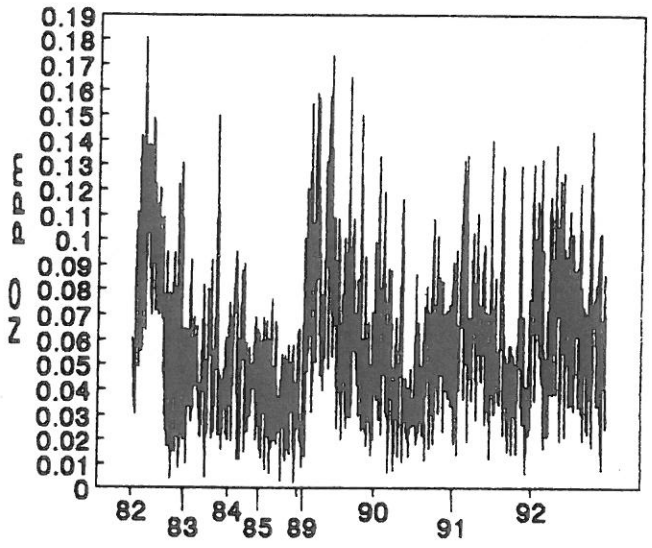


Fig. 9a

Standard PAN solution
(0.1 ug/ml in Hexane)

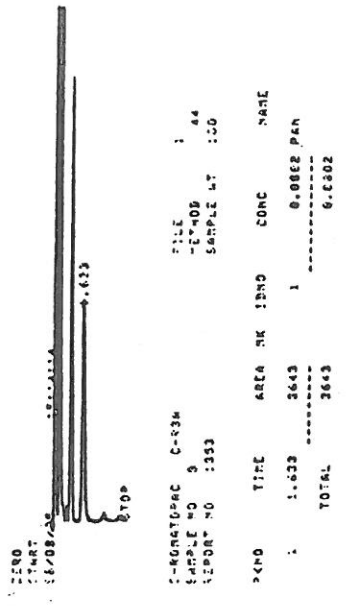


Fig. 9b

Sample: PAN collected at
Bezuidenhout Valley

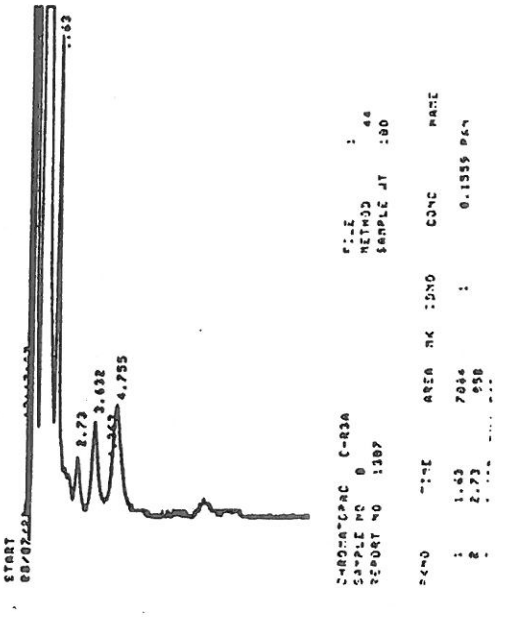


Fig. 9c

Samples: South Hills, Gasworks
Rain, 10/10 Cloud Cover, cold

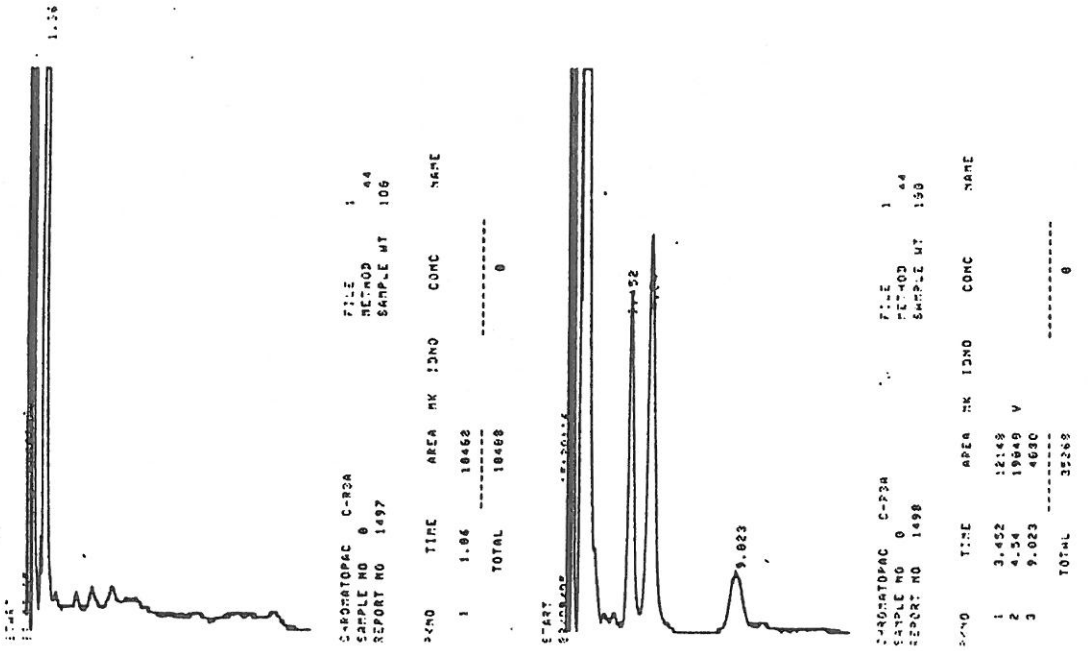


Table 1 summarises the results of PAN measurements at the 4 sites.

TABLE 1 PAN : SUMMARY STATISTICS

SITE	AVG. ppb	MAX. ppb	MIN. ppb
South Hills	0.37	1.1	0
Bez. Valley	0.42	1.2	0.01
Cydna Labs.	0.48	1.5	0.08
Gas Works	0.45	0.9	0

THE IMPORTANCE OF PAN IN AIR POLLUTION MONITORING

This subject has been extensively covered by various authors such as Altshuller[9], Nielsen[10] and Singh[11]. An index of the percentage ratio of PAN and ozone, (PAN/03) x 100, can be used to establish a more accurate pollution index than measuring ozone alone. Sites can be classified on a scale from below 1% to above 7%. Values of below 1 are associated with rural areas, values of 7 and higher occur in highly polluted urban areas such downtown Los Angeles.

Table 2 shows PAN/OZONE x 100 ratios in Johannesburg for June - August 1988, as well as some values measured in North America for both urban and rural remote sites

TABLE 2 RATIO : PAN/O3 *100

SITE	AVG.	MAX.	MIN.
South Hills	1.12	3.2	0

North American values

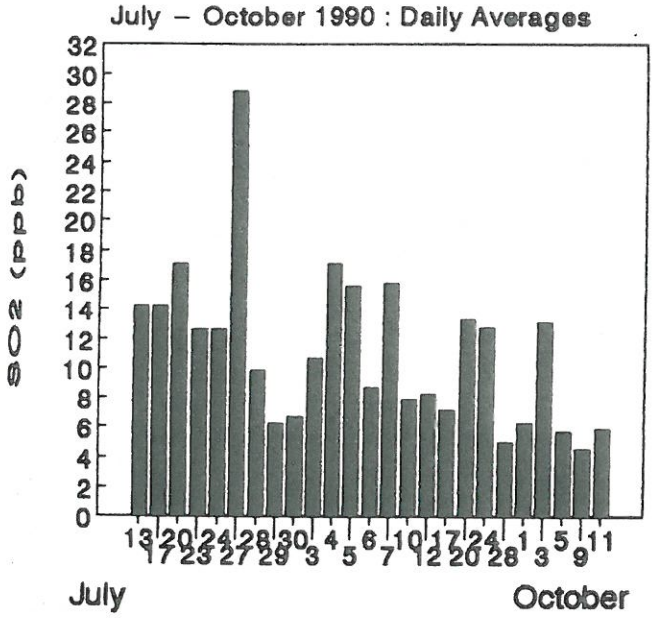
TOWN (URBAN)		PEAK VALUES
Los Angeles	(1960)	7
Pasedena	(1973)	8
Houston	(1976)	3
St.Louis	(1977)	5
RURAL		AVERAGE VALUES
Reese River Remote,high altitude		0.3
Jetmore rural–continental		0.8

The maximum PAN/OZONE x 100 ratio of 3.2 measured at South Hills indicates moderate pollution levels, on par with maximum values measured in Houston, Texas in 1976.

SULPHUR DIOXIDE AT THE CITY HALL

During July to October 1990 sulphur dioxide was measured at the City Hall using potassium hydroxide impregnated filter papers which trap SO2 as sulphite[13,14]. The sulphite is desorbed, oxidised to sulphate and analyzed using Ion Chromatography. The results of this investigation are shown in Fig. 10. SO2 levels are generally low with a maximum 24 hour average value of 28.5 ppb (parts per billion) recorded. The daily average values tend to decrease with the onset of the rainy season. These results indicate that SO2 is not a problem pollutant in the city centre. These results were to be expected as there is no major source of SO2 emission in the Johannesburg central area. The measured SO2 is due to motor car emissions as petrol contains on average 3% sulphur compounds.

Fig. 10 City Hall: Sulphur Dioxide



CONCLUSION

Even though data on pollution levels in Johannesburg has been collected for close to 10 years, no clear cut picture of photo-chemical smog formation has emerged. This is partly due to the following facts:

1. Only 2 monitoring stations have been operated, covering a very small part of the total Johannesburg metropolitan area which could be affected by photo-chemical smog.

2. Large gaps in the data exists, station shut down periods of months or even a year and longer have occurred due mainly to a shortage of funds for instrument repair and maintenance. This has resulted in fragmented data, severely limiting direct comparison between seasons which would be very useful for further statistical manipulations such as time series analysis. It has been shown by several authors[4,5,6,7], that dry and wet years can have a profound effect on ozone levels with dry years leading to a higher incidence of high hourly ozone peaks.

On the basis of the collected data it can however be concluded that:

a) Photo-chemical reactions do take place as indicated by the presence of PAN at levels which are well above documented background values.

b) Ground level ozone values are slowly rising, although it can not be determined what fraction of this rise is directly attributable to photo chemical smog formation.

c) At the moment adequate dispersion of air pollutants occurs as documented by the virtual absence of high ozone peaks (> 0.080 ppm) in the City Centre during week days.

d) Due to the fairly constant emissions of primary pollutants as measured at the City Hall, no dramatic upward trend in air pollution levels would be expected, assuming that no pollutants are imported in significant amounts from sources outside the City. This is confirmed by the PAN measurements which showed a total absence of PAN during overcast, rainy days. This indicates that pollution sources are predominantly of local nature.

REFERENCES

1. Stevens, C.S.; "Automobile Emissions and related Ozone Formation in the greater Johannesburg region." Dissertation for the degree of Master Science, University of the Witwatersrand, Johannesburg, South Africa.

2. Lefon, A.; Shadwick, D.; Feister, W.; Mohnen, V. "Surface-Level Ozone : Climate Change and Evidence for Trends." J. AIR Waste Manag. Assoc. 42 : 136 (1992).

3. Aneja, V.; Claiborn, C.; Li, Z.; Murthy, A.; "Exceedances of the National Ambient Air Quality Standard for Ozone Occurring at a "Pristine" Area Site." J. Air Waste Manag. Assoc. 40 : 217 (1990).

4. Kuntasal, G.; Chang, T.; "Trends and Relationships of O3, NOX and HC in the South Coast Air Basin of California." JAPCA 37 : 1158 (1987).

5. Chock, P.; "Issues Regarding the Ozone Air Quality Standards" J. Air Waste Manag. Assoc. 41 : 148 (1991).

6. Edwards, P.; Wood, F.; Kochenderfer, J.; "Characterization of Ozone during consecutive Drought and Wet years at a rural West Virginia site." J. Air Waste Manag. Assoc. 41 : 1450 (1991).

7. Pagnotti, V.; "Seasonal Ozone Levels and Control by Seasonal Meteorology". J. Air Waste Manag. Assoc. 40 : 206 (1990).

8. Baunuk, I.; Grosser, E.; "Determination of Ambient Peroxyacetyl Nitrate (PAN) concentrations in Pretoria". The Clean Air Journal, Vol. 7 : No. 4 (1987).

9. Altshuller, A.; "Measurements of the Products of Atmospheric Photochemical Reactions in Laboratory Studies and in Ambient Air-Relationships between Ozone and other Products." Atmospheric Environment 17 : 2383 (1983).

10. Nielsen, T.; "A convenient Method for Preparation of Pure Standards of Peroxyacetyl Nitrate for Atmospheric Analyses." Atmospheric Environment 16 : 2447 (1982).

11. Singh, H.; Salas, L.; "Methodology for the Analysis of Peroxyacetyl Nitrate (PAN) in the unpolluted Atmosphere." Atmospheric Environment 17 : 1507 (1983).

12. Grosjan, D.; Williams, E.; "Photochemical Pollution at Two Southern California Smog Receptor Site". J. Air Waste Manag. Assoc. 42 : 805 (1992).

13. Lewin, E.; "Efficiency of 0.5 N KOH Impregnated Filters for SO2 Collection." Atmospheric Environment 11 : 861 (1976).

14. Brocco, D.; Rotatori, M.; Tappa, R.; "Investigation of Dry and Wet Deposition of Air Pollution in a Rural Area." The Science of the Total Environment 54 : 261 (1986).