DETERMINATION OF AMBIENT PEROXYACETYL NITRATE (PAN) CONCENTRATIONS IN PRETORIA

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SUMMARY
Peroxyacetyl nitrate (PAN) was trapped from ambient air at two sites in Pretoria and determined by gas chromatography. Average monthly daytime concentrations during a few winter and summer months were found to be in the range of 0,18–0,66 ppb. These levels were well below phytotoxical limits and indicate photochemical activity similar to what has been observed in European, Canadian and lesser polluted USA cities. The need for further investigation in high traffic density areas is suggested.

OPSOMMING
Peroksieasetielnitraat (PAN) is opgevang uit die omgewingslug by twee plekke in Pretoria en deur gaschromatografie bepaal. Die maandelikse gemiddelde konsentrasie gedurende die dag was in die omgewing van 0,18–0,66 ppb. Hierdie vlakke is ver onder fitotoksiese grense en dui op fotochemiese aktiwiteit soortgelyk aan dit wat in Europese, Kanadese en die minder besoedelde stede van die VSA waargeneem word. Daar bestaan 'n behoefte aan verdere metings in gebiede met hoë verkeersdigthede.

1. INTRODUCTION

Peroxyacetyl nitrate (PAN) is an important component of photochemical smog. It is formed in the atmosphere by the action of sunlight on hydrocarbons and nitrogen oxides[1]. A large number of reactions are involved, leading via acetaldehyde to the peroxyacetyl radical which finally reacts with nitrogen dioxide to form PAN[2].

PAN is a lachrymator[3], a possible agent in the formation of skin cancer[4] and a phytoxicant[1,5]. Considerable loss of agricultural crops caused by exposure to PAN has been reported[6] in southern California. It has been accepted, that PAN levels of over 15 ppb lasting four or more hours can damage plants[5]. Potentially phytotoxic PAN concentrations have been observed in areas with high traffic density in California[5,6] and Australia[7]. Levels reported from western Europe and eastern North America are generally five to ten times lower[8].

The ingredients for PAN formation, including hydrocarbons and NO_2 from motor vehicles and especially sunshine, are abundant in Pretoria. Moreover, petrol distributed in the area has been blended with ethyl alcohol, which could be partially oxidized to acetaldehyde, a major precursor of PAN.

To gain more information about PAN formation in South Africa a preliminary survey was conducted in Pretoria during a few winter and summer months 1986 and 1987.

2. ANALYTICAL TECHNIQUES

In this investigation a new analytical technique, developed by the author[9], based on cold trapping of PAN in hexane, was used. The air to be analysed was bubbled through hexane at dry ice temperature and the PAN content of the solution determined by gas chromatography. The excellent stability of PAN in hexane at low temperature allowed transport and storage of ample extracts as well as of standards prepared in hexane. The entire analytical procedure is described in greater detail in an internal CSIR report[10].

Samplers were placed in the mobile laboratories (caravans) used for monitoring traffic pollutants in Sunnyside (Mears and Park Streets corner) and Mooikloof (Pretoria East Cemetery). The first site is in a high traffic density area, the second is peripheral, about 15 km south east of the city centre in the path of the prevailing wind. The samplers were activated by electric time switches, mostly on week days during daytime hours.

3. RESULTS

The results were calculated by relating the PAN content of the sample extracts, as determined by gas chromatography, to the volume of the air passing through the bubblers. The concentrations obtained in mass per volume were then converted into mixing ratios (volume per volume) taking into account the sampling pressure (average barometric pressure in Pretoria) and temperature (average in the air-conditioned caravans).

Monthly averages of PAN mixing ratios were calculated from daily values and are listed in Table 1. The daily values together with other parameters (ozone and nitrogen oxides levels, solar radiation, atmospheric temperature and precipitation) are given in an internal CSIR report[9].

TABLE 1

Monthly average PAN mixing ratios (excluding weekends)

Site	Year	Month	PAN (ppb) and No. of samples Morning	Afternoon	Daytime
Sunnyside	1986	May			0,537 (19)a
		June			0,428 (21)b
		Jul	0,326 (9)	0,404 (12)	0,515 (13)
		Aug			0,355 (21)
		Dec	0,143 (12)	0,230 (14)	0,195 (12)
	1987	Jan	0,126 (19)	0,233 (18)	0,180 (18)
		Feb	0,184 (19)	0,365 (18)	0,277 (18)
Mooikloof	1986	Jul	0,474 (8)	0,709 (18)	0,656 (8)
		Aug	0,380 (18)	0,466 (18)	0,427 (18)
		Dec			0,237 (16)
	1987	Jan			0,261 (19)
		Feb			0,301 (19)

NOTE:
Morning (6–12 h), afternoon (12–18 h), daytime (6–18 h) except a (9–17 h) and b (9–19 h).

The present investigation showed that the average daytime PAN mixing ratio during a few winter and summer months was 0,30 ppb in Sunnyside and 0,38 ppb in Mooikloof. The range of monthly daytime averages was 0,18–0,52 ppb and 0,24–0,66 ppb respectively. The highest level for 6 h samples was 1,69 ppb (10 samples over 1,00 ppb) and for 8 or 12 h samples 1,22 ppb (5 samples over 1,00 ppb). The levels were almost always higher during the afternoon than the morning. Lowest levels were observed during the night (26 samples). PAN concentrations were found to be almost twice as high during winter at both sampling sites. The levels were generally somewhat higher at Mooikloof.

4. CONCLUSIONS

PAN mixing ratios found in Pretoria indicate considerably lower photochemical pollution than those reported from some Californian and Australian cities. The Pretoria results seem to be in the range of what was observed in the European, Canadian and lesser polluted USA cities.

However, there are indications that the Sunnyside levels could have been negatively affected by the abundance of a primary pollutant. It is known that high NO levels or more correctly high ratios of NO to NO_2 levels inhibit the formation of ozone and PAN. Since the ratios of NO to NO_2 levels in Sunnyside were high, about six times higher than in Mooikloof, one could expect that ozone and PAN levels are affected. Indeed, ozone values in Sunnyside were found to be about a third of those in Mooikloof. The high NO levels in Sunnyside must have been caused by the proximity of the sampling site to the streets and thus the exhaust gases from motor vehicles. These gases contain nitrogen oxides and specifically as NO.

The higher winter levels of PAN at both sampling sites, contradicting reports from other parts of the world could be explained by the striking differences in meteorological conditions. Most cities, where higher summer levels were found have cold winters with frequent rain and cloud cover. Pretoria winters are mild, especially during the daytime, clouds and are virtually absent and global radiation is intensive due to high altitude (1350 m) and low latitude (25°42'S). Lastly, in Pretoria during wintertime, the accumulation of pollutants is common as it is caused by frequent low thermal inversions.

It is suggested that future investigations should be concentrated on suspect areas, e.g. where traffic pollutants are high (hydrocarbons, ozone) and during periods when atmospheric dispersion is low.

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