SEASONAL VARIATION AND TRENDS OF ATMOSPHERIC PARTICULATES ON THE SOUTH AFRICAN HIGHVELD: 1982 - 1990

G Held[2], G M Snyman[2] and H Scheifinger[3]

1. Environmental Sciences, Eskom Technology Research and Investigations, Private Bag 40175, Cleveland 2022
2. Consultant, P O Box 731342, Lynnwood Ridge, 0040
3. Institut für Meteorologie und Geophysik, Universität Wien, Austria

SYNOPSIS

Atmospheric particulates on the Highveld have been sampled since 1982, using stacked filters (8 and 0,4 µm pore size) exposed for 24 hour periods. The filters were analysed by ion chromatography and concentrations for five species (sulphate, nitrate, chloride, phosphate and fluoride) determined. During the eight years of monitoring intermittent measurements were made at 34 sites with up to 20 samplers being deployed simultaneously. During 1985 continuous monitoring was initiated. Four of the sites were at elevated points (up to 300m above the surrounding terrain) and significantly higher concentrations of most species were found there. For instance, at the elevated Verkykkop site mean monthly concentrations of the order of two to three times those measured at surface sites were obtained.

During the period May 1985 to March 1990 primary particulates (fluoride, chloride and phosphate) displayed only non-seasonal variations at the ground-level sites. In contrast to findings in the northern hemisphere, the seasonal variation of nitrates is well developed with a maximum during early spring. The seasonal variation of sulphates is less pronounced than that of nitrates and the maximum occurs during summer. A good correlation with various meteorological parameters could be found.

At the elevated Verkykkop site the seasonal variation of all particulate species is represented by a bimodal distribution with spring and autumn maxima. Good correlation with meteorological variables indicates that synoptic-scale transport mechanisms govern the particulate level at the escarpment.

Trend analyses based on monthly mean concentrations of sulphates, chlorides and nitrates for observations spanning at least four years indicated that any trends detected were statistically not significant. Similar resultes were obtained from 31-day moving averages.

INTRODUCTION

The variation in concentration of airborne pollutants should in theory be related to the concentration of primary pollutants emitted by the major sources. The seasonal variation in temperature, humidity and hours of sunshine should also be of prime importance in controlling the processes responsible for the conversion of primary pollutants to secondary ones, as well as for horizontal and vertical dispersion.

Thus, the various measurements made in the northern hemisphere should have shown that lower SO_2 levels from lowered emissions should lead to lower SO_4^{2-} during summertime and vice versa[1]. In the USA levels measured at an elevated site at Whiteface Mountain[2], were similar to those measured at lower sites. The maximum values for SO_2 and NO_2 were found in winter, with SO_2 and, to a lesser extent NO_2 showing seasonal variations. In contrast to SO_4^{2-} no trend was observed for NO_3^-. In the Netherlands no seasonal variation could be found for SO_4^{2-}, NO_3^- and Cl^-.[3] In the Southern African context it should be expected that with the emission of primary pollutants being reasonably steady throughout the year, only the weather should influence the concentrations of secondary pollutants. Chemical reactivity should be at its highest during the summer months as a result of the increased temperature, higher humidity and longer hours of sunlight. On the other hand it would be expected that, in the summer rainfall region, more of the pollutants would be removed by wash-out during thunderstorms. During the dry winter it is conceivable that conversion will be much slower. Very little is, however, known about deposition of pollutants during the dry season. A further complication is introduced by the seasonal variation in the height of the mixing layer, providing a greater volume for dispersion and thus lower concentrations during summer. However, convective processes are stronger in summer, resulting in plumes from tall stacks being brought down to ground level more often. In a previous publication[4] it was shown that primary pollutants were subject to a distinct seasonal variation as observed over a three year period, while the secondary pollutant sulphate showed no such variation for a one year period. The present investigation has concentrated on data available for much longer periods.

DATA BASE

The CSIR measured aerosol particulates in the atmosphere of the Highveld and determined the concentrations of sulphate, nitrate, phosphate, chloride and fluoride by means of stacked filters and ion-chromatography. Samplers consisted of a rack with eight positions for filter holders which were coupled to an eight position valve. This valve was time activated to change at midnight every day. Air was sucked through the filter stacks by means of a pump. The filters were from Nucleopore and had 8 µm and 0,4 µm pore size, respectively. The filters were removed once a week and returned to the laboratory for analysis[5]. This work was started in the winter of 1982.

At first, measurements were limited to the winter periods as it was assumed that the highest concentrations of pollutants would occur during this period. This was based on the fact that large amounts of visible pollution would be trapped, either in the surface inversion or under a low-level elevated inversion and that more pollutants were emitted into the air when residential heating from coal burning appliances was at its highest.

After having performed measurements in Witbank (Figure 1) during the summer of 1983/84[6] it was decided to extend the monitoring period to encompass the whole year. At this stage the sampling area was expanded to

cover most of the Eastern Transvaal Highveld and a portion of the northern Orange Free State. The data from this network was used to investigate possible seasonal variations and trends in ambient concentrations.

During the eight years of monitoring samplers were placed at 34 sites (Figure 1). However, certain sites were abandoned and the samplers moved to other sites. This means that some sites were only in operation for one or two years, depending on their positions and purpose. At any one stage up to 20 samplers were deployed simultaneously within the network. Observations were terminated by the CSIR at the end of March 1990.

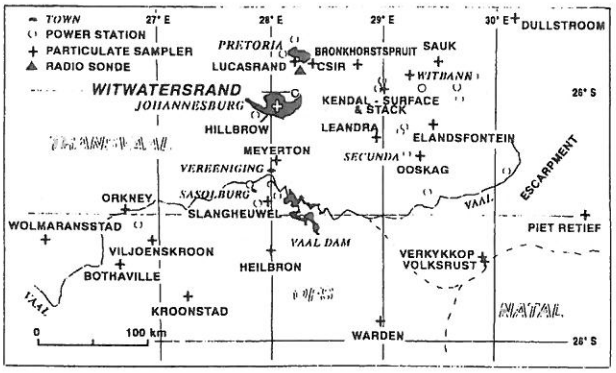


Figure 1. The aerosol monitoring network 1982 - 1990

SEASONAL VARIATIONS

Ground Level Sites

For the purpose of a detailed statistical analysis to investigate seasonal variations in the ambient concentrations of the various aerosol species and to establish possible correlations with meteorological parameters[7], only the period of May 1985 to March 1990 was initially taken into consideration. The reasons for this were that continuous monitoring only commenced in May 1985 and this data was readily available on the CSIR mainframe computer for the necessary mathematical manipulations.

The aerosol species which were measured can be divided into three distinct groups each with their own characteristics. These groups are a) the primary pollutants (fluoride, chloride and phosphate) and secondary pollutants b) nitrate and c) sulphate. The first group shows a distinct non-seasonal variation for the period of observation (Figure 2). It is possible that this is due to distinct local sources for these primary pollutants. For example it is known that a source of phosphates existed in the Meyerton area when the measurements were made and that fluoride is emitted by metallurgical and fertilizer plants which are scattered in the Highveld[7].

Nitrate concentrations follow a very distinct seasonal variation with minimum values recorded during January/February and maximum values during August/September (Figure 3a). The mean values calculated for the entire network varied from a minimum of 0,28 $\mu g.m^{-3}$ in summer to a maximum high of 1,2 $\mu g.m^{-3}$ during winter period. A build-up of the pollutant seems to occur over a period of 6 months from about February to August while the decline is quicker, extending only over a four month period from about September until January. Peak values occurred during a period varying from a week to a month while minimum concentrations were only observed for a few days (Figure 3a). Thus, nitrates behave in a completely different manner to that in the northern hemisphere. On the Highveld the concentrations are highest during the cooler months and therefore appear to be more dependent on atmospheric physics rather than on chemical reactivity.

In the case of sulphates (Figure 3b) the seasonal pattern is hidden behind the episodes of relatively high concentrations and not as distinct as for nitrates. A period of a few weeks, where the highest values were consistently recorded, can, however, be observed any time between August and April, ie during summer, but hardly ever from May to July. Conversely a period of several weeks can be found between June and September when values were low, ie during the winter months. The maximum average values were recorded as 6,0 $\mu g.m^{-3}$ while the minima were in the region of 2,5 $\mu g.m^{-3}$. It must be remembered that these values are for the ground-level sites and not for any of the elevated sites.

A clear cut relationship exists between the various meteorological parameters and sulphate aerosol (Figure 4). This analysis is based on the assumption that the Irene soundings are more or less representative for the Highveld area. Daily arithmetic means of various meteorological parameters were calculated for the layer from the surface to 750 hPa and smoothed by applying a 31-day moving average procedure. During the warmer months higher sulphate concentrations seem to be produced when the sub-tropical to tropical, moist warm air masses move into the sub-continent. It would appear that the formation of oxidants in the gas and liquid phases is enhanced by these factors as well as the higher possibility for photochemical reactions. This does however not seem to affect any of the other species.

Monthly averages for the entire network, including the earlier observations from 1982 onwards, confirm the detailed analysis set out above which was based on 31-day moving averages for the five-year period of continuous monitoring.

Elevated Sites

As a result of a decision to enlarge the monitoring area in an effort to trace the movement of the secondary pollutants, a sampling site was established on Verkykkop (a hill outside Volksrust, Figure 1) during 1985. This proved to be fortuitous because distinct differences between the socalled "ground-level" sites and this elevated position were found with respect to seasonal variations. This led to short-term measurements at places such as the Kendal Power Station stack, the Hillbrow tower and the Lucasrand tower[8].

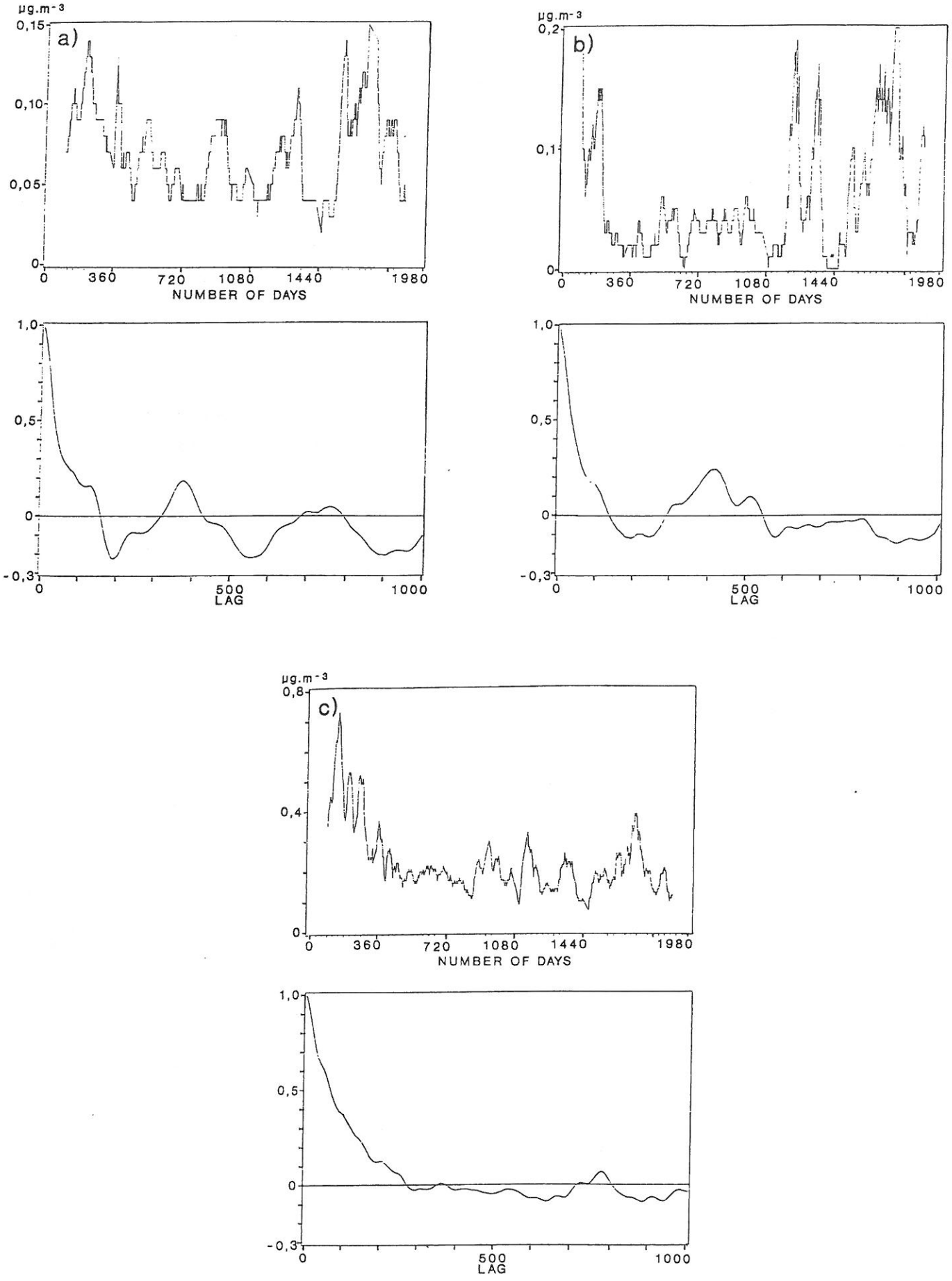


Figure 2. Seasonal variation of primary atmospheric particulate pollutants (mean over total network area) from 1985 to March 1990, 31 day moving average (top) and auto correlation coefficients for lags 0 to 1000 (bottom). a) Fluorides b) Phosphates c) Chlorides

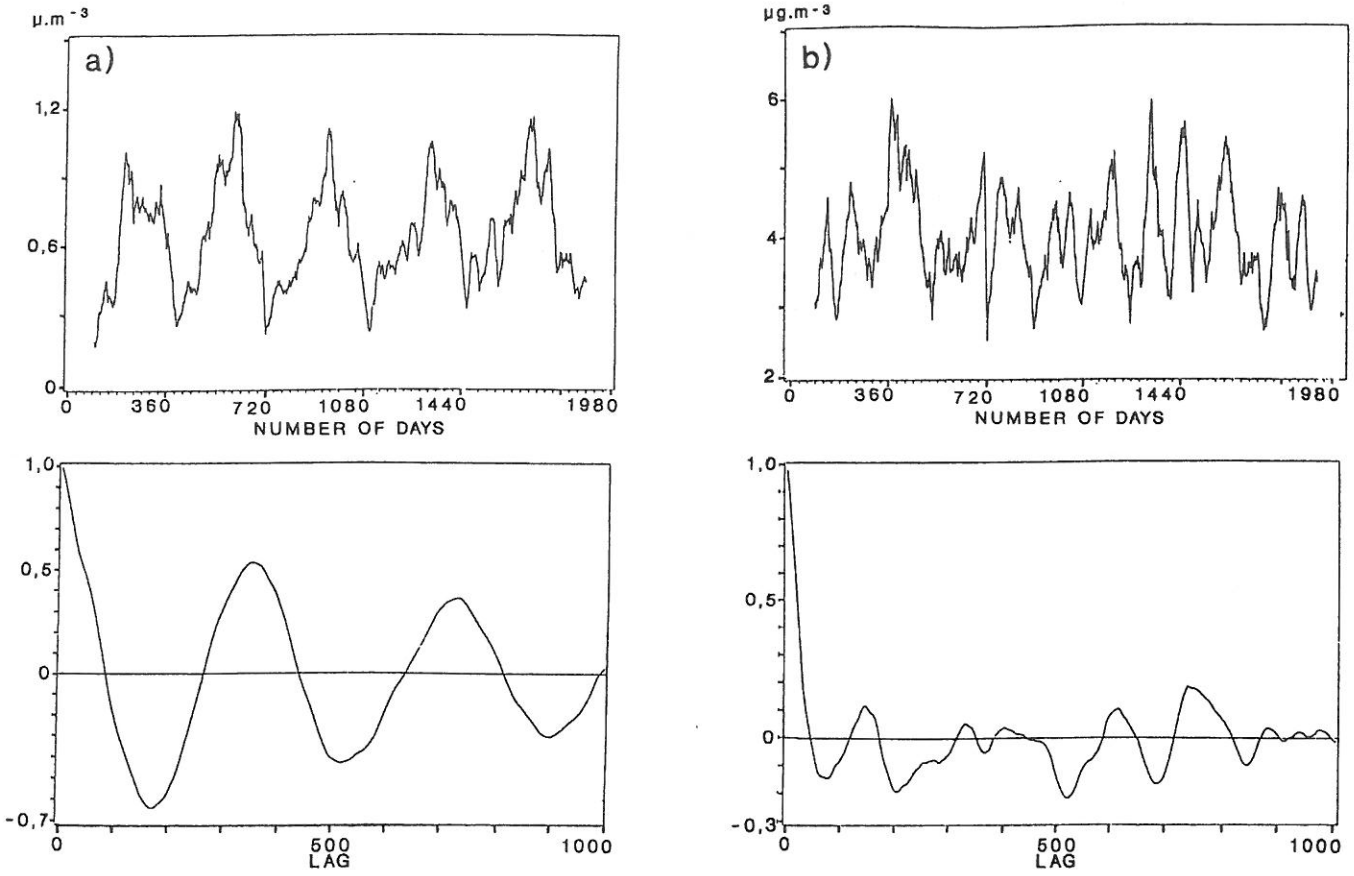


Figure 3. Seasonal variation of secondary atmospheric particulate pollutants and auto correlation coefficients as described in Figure 2. a) Nitrates b) Sulphates

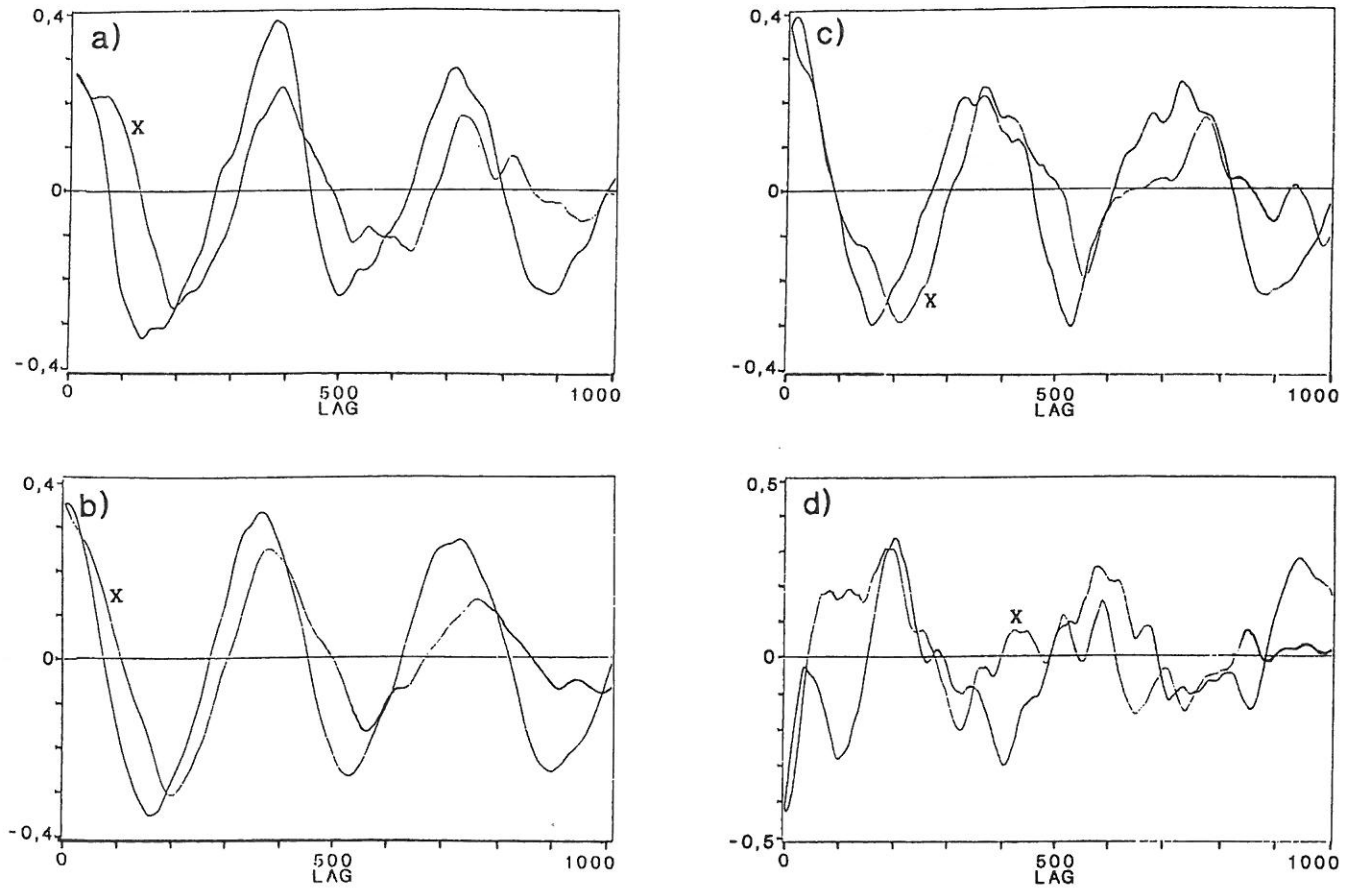


Figure 4. Cross-correlation coefficients between the time series of sulphates (mean over total network area) and various meteorological parameters and vice versa for lags 0 to 1000. a) Temperature b) Vapour pressure c) Relative humidity d) Wind speed

All the measured species show a double wave with the first minimum occurring during January and February and the first maximum during March to June. The second minimum occurs during the period May to July, whilst the second maximum occurs between September and November. Figure 5 shows the seasonal variation for chloride, nitrate and sulphate. The anions follow the same pattern without any phase shift between them as can be seen from the cross-correlation coefficients in Figure 6. As a consequence any cross-correlation between the values found at the surface stations and those at Verkykkop is very weak (Figure 7a shows results for sulphate) with the exception of nitrate. The mean maximum concentration of nitrate at Verkykkop in spring lags the surface maxima by about four weeks, thus giving a well developed positive correlation (Figure 7b).

Fluorides and nitrates can be regarded as a group because their relationship with meteorological parameters coincides to a marked degree. Cross-correlation coefficients are shown between nitrates and various meteorological parameters in Figures 8a, b, c. Sulphate and chloride can also be seen as a group as their behaviour is similar but different from the other two (sulphate has been used as example in Figures 8d, e, f). Apart from quantitative differences the seasonal variation of the anions is in phase with temperature, vapour pressure and relative humidity. The winter minima of temperature coincide with anion minima and the increase in spring coincides with the rise in temperature, while the autumn decrease in concentrations coincides with the decrease in temperature during this period.

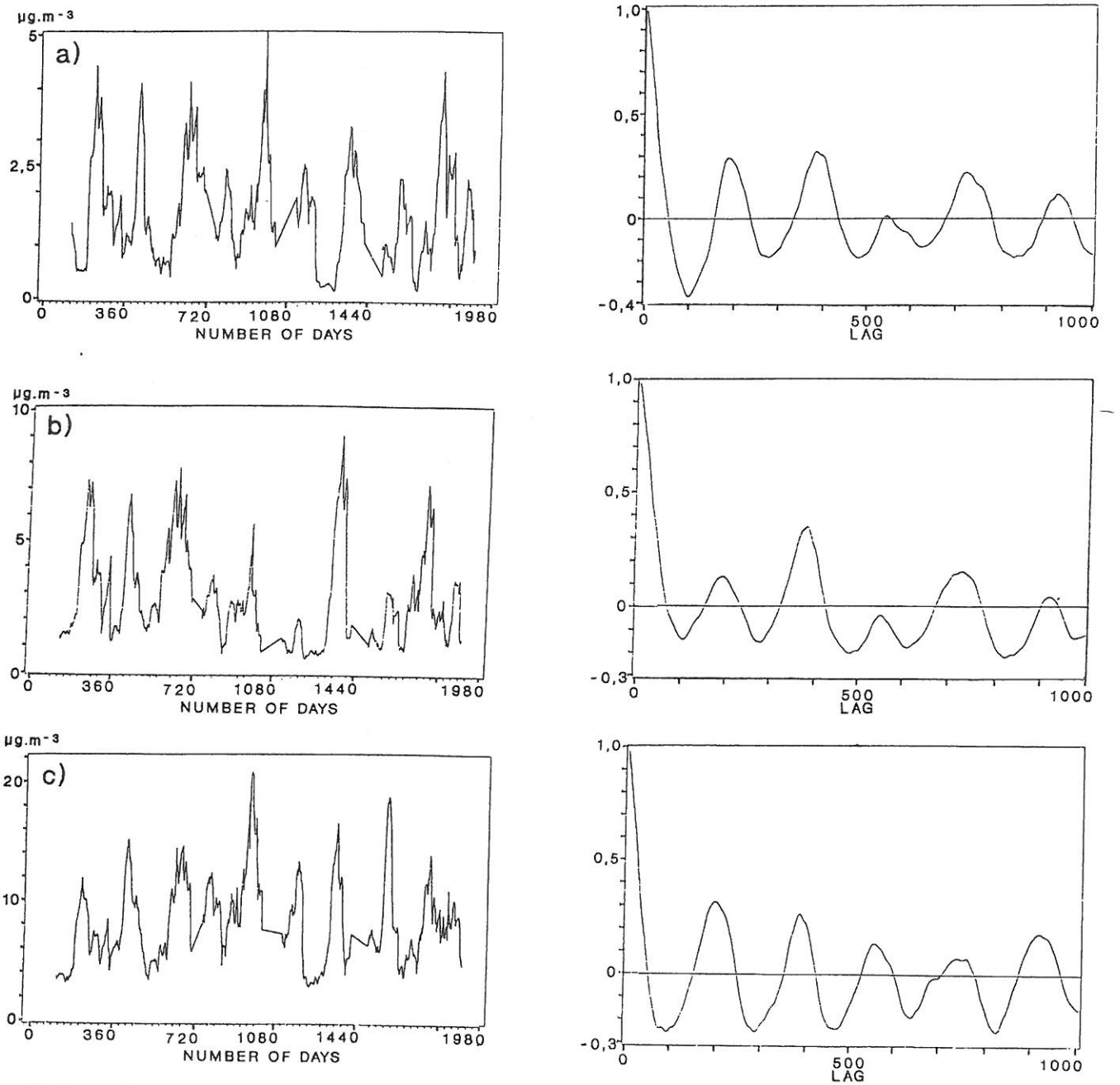


Figure 5. Seasonal variation of atmospheric particulates at Verkykkop from may 1985 to March 1990, 31 day moving average (top) and auto correlation coefficients for lags 0 to 1000 (bottom).
a) Chlorides b) Nitrates c) Sulphates

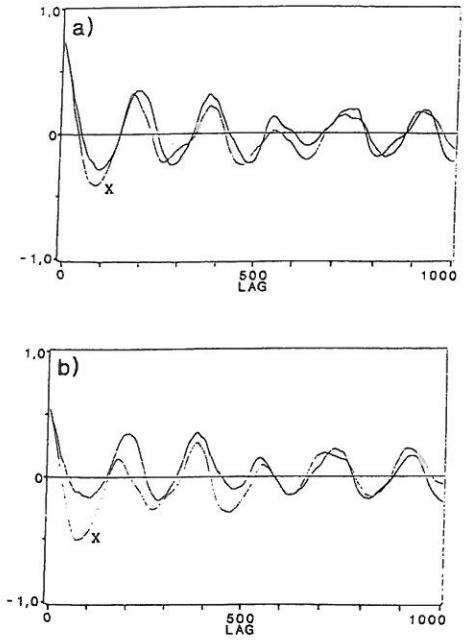


Figure 6. Cross-correlation coefficients between the time series of chlorides and sulphates (top) and nitrates and sulphates (bottom) for lags 0 to 1000 at Verkykkop.

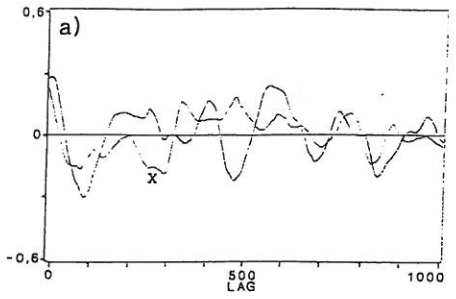
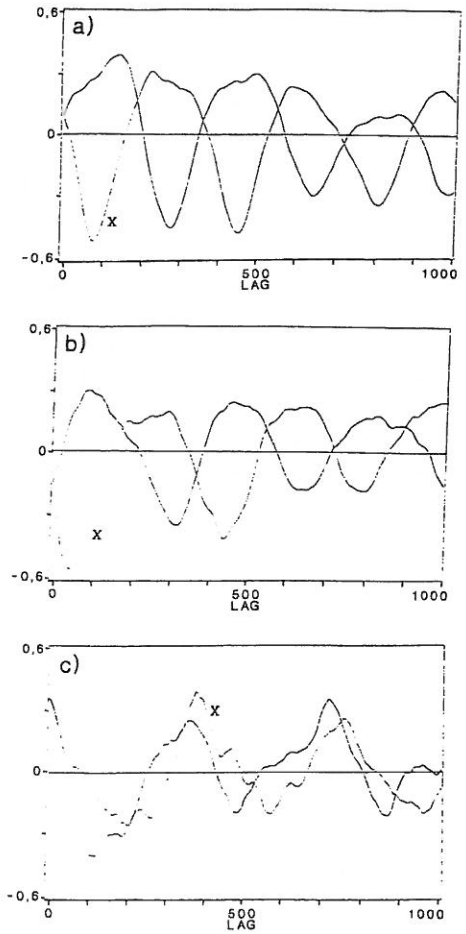


Figure 7. Cross-correlation coefficients between the time series of secondary pollutants at the surface stations (mean over total network area) and at Verkykkop for lags 0 to 1000. a) Sulphates b) Nitrates



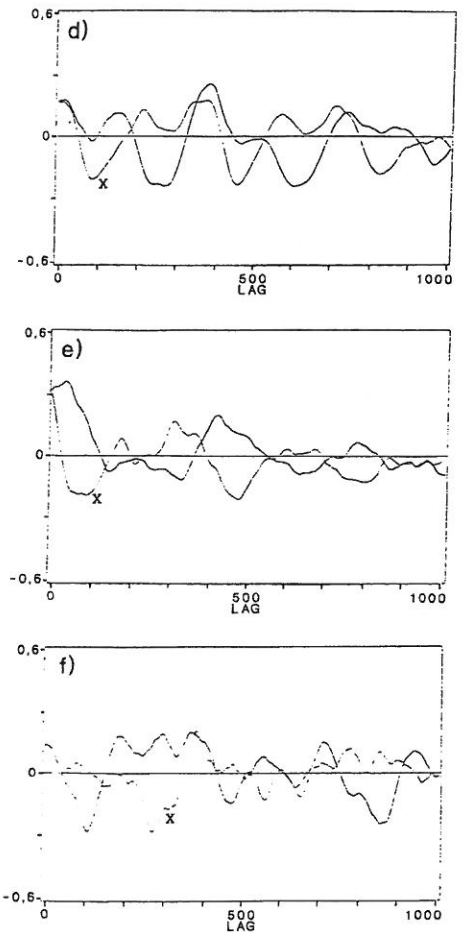


Figure 8. Cross-correlation coefficients between the time series of secondary pollutants at Verkykkop and meteorological parameters and vice versa for lags 0 to 1000. Nitrates versus a) temperature b) relative humidity c) wind speed. Sulphates versus d) temperature e) relative humidity f) wind speed

The double wave character of the particulates at Verkykkop and the weak correlation of the aerosols at the surface must lead to the conclusion that they are governed by different mechanisms. There is also strong evidence that atmospheric transport dominates atmospheric chemistry at the elevated monitoring sites.

The very high concentrations of both secondary (up to 64 $\mu g.m^{-3}$ for SO_4^{2-}) and primary pollutants observed at this site can only be explained by accumulation at a high altitude (above 300 m AGL) of a layer or layers of pollutants as well as recirculation on a regional scale[5], which is in contrast to the generally expected well-mixed convective boundary layer. The fact that these high values are mostly observed during March to June and again from September to November confirms the existence of such a postulated reservoir of pollutants aloft, since these are the periods of highest baroclinic instability in the atmosphere, coinciding with the bimodal seasonal variation of cut-off lows.[7,9]

TRENDS FROM 1982 TO 1992

A more in-depth study of possible trends in concentrations of aerosol pollutants in the atmosphere over the South African Highveld can now be undertaken. The area covered by the measurement network of the CSIR includes most of the Transvaal Highveld and the northern Orange Free State. The major industrial and residential developments in South Africa, as well as large areas of the platteland and areas which were perceived to be pristine, fall within this area. It can, however, be stated that there was no site within the network area that was totally unaffected by the aerosol pollutants measured.

For this analysis all available data in the form of monthly means of sulphate, nitrate and chloride have been utilised, including the resultes for Elandsfontein and Verkykkop from a twelve-month study during 1991/92.[10] Considering ground level sites only, the ratios between the highest and lowest measured concentrations for a specific pollutant which were obtained are shown in Table 1.

From Table 1 it is evident that a single source for the phosphates exists at Meyerton. Fluorides show two distinct areas, one near Meyerton, and another one near Elandsfontein. Two distict sources are apparent for chlorides, one near Viljoenskroon, pointing to a local source and the other one at Volksrust, which could be due to maritime influences. Nitrates as well as sulphates are more or less evenly distributed over the whole area.[7]

The results from the trend analysis (simple linear regression) are summarised in Table 2. Chlorides show a slight decrease at all sites, but it is only significant at Oosskag, Leandra and Slangheuwel. Likewise sulphates seem to have a mostly negative trend, while the nitrates show a marginal increase at most sites. However, considering both the correlation coefficients and significances, none of these trends are statistically significant. The slopes of the regression lines were generally very small and varied up to 0,12 for sulphates, 0,07 for nitrates and 0,11 for chlorides with the corresponding signs. An exponential fit of the data yielded even worse correlations.

The findings presented above are consistent with results obtained from 31-day moving averages based on surface network means for the period of continuous monitoring.

Table 1. *Ratios between highest and lowest concentrations at ground level of each particulate measured on the Highveld*

Aerosol	Highest	Lowest	Ratio
F^-	Meyerton	Piet Retief	7,4
Cl^-	Viljoenskroon	Dullstroom	4,7
PO_4^{3-}	Meyerton	Wolmaransstad	107,8
NO_3^-	Elandsfontein	Warden	6,8
SO_4^{2-}	Meyerton	Wolmaransstad	2,0

Table 2. *Trend analysis for sites which were in operation for at least four years. However, observations were not necessarily continuous during the period indicated.*

Station	Start	End	Sulphates corr. coef.	Sulphates signi-ficance	Nitrates corr. coef.	Nitrates signi-ficance	Chlorides corr. coef.	Chlorides signi-ficance
CSIR	05/83	03/90	-0,17	0,17	-0,03	0,81	-0,36	0,00
SAUK	05/82	11/87	-0,16	0,30	0,29	0,58	-0,30	0,05
Elandsfontein	05/82	03/92	-0,22	0,11	0,28	0,04	-0,34	0,01
Oosskag	05/82	11/87	-0,17	0,30	0,15	0,33	-0,50	0,00
Leandra	05/82	11/87	-0,23	0,14	0,21	0,19	-0,58	0,00
Slangheuwel	09/84	11/88	0,02	0,90	0,26	0,09	-0,55	0,00
Heilbron	09/84	03/90	-0,17	0,20	0,28	0,31	-0,39	0,00
Kroonstad	09/84	03/90	-0,17	0,22	-0,03	0,85	-0,17	0,20
Verkykkop	06/85	03/92	-0,06	0,63	-0,02	0,88	-0,26	0,05

CONCLUSIONS

It has become clear that short term measurements which are undertaken over limited areas cannot produce sufficient data to enable one to find seasonal variations or trends. It has been shown that various seasonal variations exist for three distinct groups of pollutants measured continuously over a period of five years on the Highveld.

At ground level the primary pollutants (fluorides, chlorides and phosphates), show a distinct non-seasonal variation which could be attributed to the influence of local sources. Nitrates show maximum values during spring and minimum values during the summer. Sulphates display a seasonal pattern which is partly hidden by episodes of relatively high concentrations, with consistently high values during summer and lower values during the winter period.

There is also a definite difference between the concentrations of pollutants measured at the "ground level" sites and those at approximately 300 m AGL (for instance Verkykkop and Kendal stack). At these elevated sites seasonal variations are much more pronounced than those at ground level. This has led to the assumption that different meteorological parameters control the transport of the pollutants and the resulting concentrations. At elevated sites all five species follow a bimodal seasonal variation with the first maximum occurring more or less during autumn and the second one during spring and early summer.

Although marginal downward and upward trends for sulphates and nitrates, respectively, have been found at most sites during the monitoring periods, they are statistically not significant. Chlorides show a slight decrease at all sites, but the trend is only meaningful at three of the nine sites analysed.

ACKNOWLEDGEMENTS

The results presented in this paper are based on data which had been collected as part of an investigation into air pollution levels in the Eastern Transvaal Highveld and the northern Orange Free State, which was initiated by the then Office of the Prime Minister: Physical Planning Branch (now Department of Development Planning). Since 1984, the project had also been financially supported by the Department of National Health and Population Development through the Foundation for Research Development with contributions from other Government Departments and the CSIR.

The authors were employed by Ematek, CSIR, until April 1992 and permission for publication of this paper was granted by both Eskom and the CSIR.

REFERENCES

1. Altschuler A P 1973. Sulphur dioxide and sulphate. *Environmental Science and Technology* 7, 709-712.

2. Hidy M, Mueller P K and Tong E Y (1978). Spatial and Temporal Distribution of Airborne Sulphates in Parts of the United States. *Atmos Env* 12, 735-752.

3. Janssen L H I M, Visser H and Romer F G (1989). Analysis of large scale sulphate, nitrate, chloride and ammonium concentrations in the Netherlands using an aerosol measuring network. *Atmos Env* 23(12), 2783-2796.

4. Snyman G M, Turner G S M, Wells R B, Ellerbeck R H and Dos Santos A (1987). Seasonal variations in airborne sulphate pollution on the South African Highveld. *SA J Sci* 83, 541-544.

5. Held, G, Scheifinger H and Snyman G M (1993). Recirculation of pollutants in the atmosphere of the South African Highveld. *SA J Sci* (in print).

6. Snyman G M, Ellerbeck R H and Wells R B (1984). *Witbank air pollution load - summer 1983/84.* Report to the Dept of Health, CSIR Report ATMOS/84/9, 1-57.

7. Scheifinger H (1993). *Particulate climatology of the South African Highveld.* PhD thesis accepted at the University of Vienna.

8. Danford I R and Hong Y (1989). Episodes of high concentrations of pollutants at Verkykkop and Kendal. *Proceedings of 1989 NACA Air Pollution Conference on "Charting a Course for the 90's",* Cape Town, 9-10 November 1989, 215-224.

9. Taljaard J J (1985). *Cut-off lows in the South African region.* Technical Paper No 14, Department of Transport, Weather Bureau, 1-153.

10. Taljaard J F and Zunckel M (1992). *Comparative study of pollutants in the Eastern Transvaal (June 1991 - May 1992).* Final Report to Eskom T-R-I, Confidential CSIR Report EMA-C 91174.E.