Dry deposition of sulphur on the Mpumalanga highveld: a pilot study using the inferential method

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A pilot study which uses the inferential method to estimate dry deposition of sulphur on the central Mpumalanga highveld is discussed in this paper. Ambient concentrations of sulphur dioxide, particulates and micro-meteorological measurements from 2 two-week field experiments, one in winter and the other in summer, are used as input to the NOAA/ATDD inferential model. The majority of dry deposited sulphur, 80% and 82% in winter and summer, respectively, comes from SO_2 during the daytime. Smaller contributions come from SO_2 at night and from particulates during the day in both seasons. The contribution to the total dry deposition sulphur load by particulates at night appears to be negligible. Assuming that sulphur precipitation for the two monitoring periods represents a full year, then a dry deposition rate of 8.22 kg S ha^{-1} yr^{-1}, which exceeds the wet deposition rate of 5.7 kg S ha^{-1} yr^{-1}, is recorded for the central Mpumalanga highveld.

Deposition of airborne pollutants on the earth's surface takes place through wet processes such as rainout or washout and cloud or fog deposition, or through dry precipitation processes. Wet deposition has been studied locally in South Africa for many years[1–3] and measurement and analysis techniques are mostly based on those used by the US Environmental Protection Agency and by the Warren Springs Laboratory in the United Kingdom.[4–7] Spatial and temporal variation of rain chemistry is well monitored locally and is understood.[2,3,8,9]

Wet deposition research in South Africa is best summarised by Turner,[3] who presents a seven-year study of rain chemistry and concludes that mean concentrations of sulphate in precipitation at sites on the central highveld resemble those reported by overseas studies in industrial regions. Given the low rainfall of the South African plateau, however, the quantity of these ions precipitated to ground through wet deposition on the highveld is relatively low compared to high rainfall regions of industrialised countries. Average wet deposition SO_4 fluxes for a five-year period on the highveld range from a maximum of 20 kg SO_4 ha^{-1} yr^{-1} south of the Witbank/Middelburg area and decrease southward away from the source region to less than 16 kg SO_4 ha^{-1} yr^{-1} in the southeastern parts of Mpumalanga (former eastern Transvaal). Wet deposition monitoring requires meticulous care, but the procedure is relatively inexpensive and straightforward.

The possible significance of dry deposition in the arid South African climate has been raised in various reports.[3,9,10–13] The South African interior plateau receives mostly summer rainfall on an average of only 60 rain days per year. This suggests that dry deposition processes may be important in this region. A review study[11] in which measured long-term SO_2 concentrations for the central Mpumalanga highveld[1] were linked to plausible deposition velocity (V_d) values suggested that sulphur deposition through dry processes could have values from one half of that from wet deposition to several times this value.

Based on a detailed literature review, Wells[11] suggested applying the inferential method[14–16] on the highveld as for a US site with characteristics approximating local conditions and so improve on previous estimates of deposition velocities and resulting deposition fluxes. The combination of industrial sources on the Mpumalanga highveld coupled with its physical and climatological characteristics make the region unique. The Mpumalanga highveld lies at an elevation exceeding 1500 m and lies in a subtropical high pressure belt. As a result, particularly poor ventilation prevails in this heavy industrialised region.

In this paper, we discuss a pilot study conducted by the CSIR and Eskom on the central Mpumalanga highveld, which uses the inferential method to estimate deposition velocities and dry deposition rates for sulphur. The study provides insights into dry deposition fluxes of sulphur in South Africa. The inferential model used in this study is the FORTRAN version developed by the National Oceanic and Atmospheric Administration's (NOAA) Atmospheric Turbulence and Diffusion Division (ATDD) in Oak Ridge, Tennessee.

The experiment

Field measurements were conducted at Eskom's air quality monitoring site on the central Mpumalanga highveld at Elandsfontein (Fig. 1) during 2 two-week periods, one in winter and the other in summer. The winter period was 27 July to 11 August 1994 and the summer period was 17 – 31 January 1995.

Synoptic conditions

At the start of the winter period, a strong Atlantic Ocean anticyclone (1036 hPa) ridged south of the country to form a bud-off high (1032 hPa) off the east coast on 28 July 1994. This high intensified to 1036 hPa by the following day, and remained east

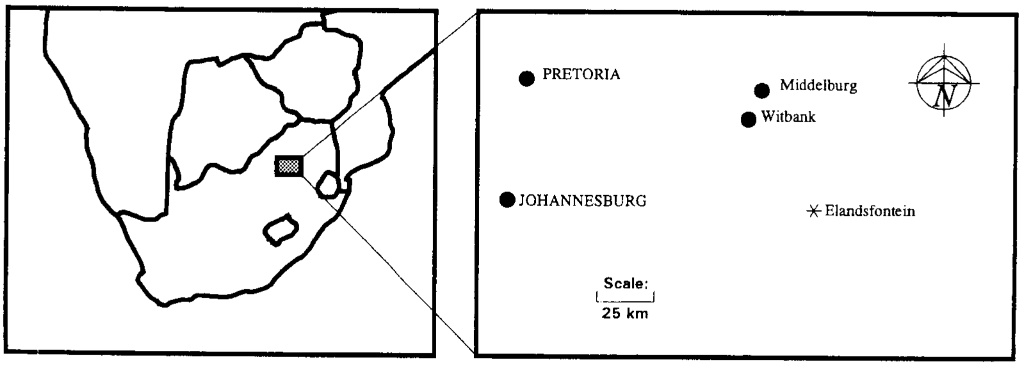

Fig. 1. The shaded block shows the central Mpumalanga highveld (left) with the location of Elandsfontein (right).

of the country until 31 July. Throughout this period, easterly to northeasterly gradient winds prevailed over the highveld. On 1 August 1994, a coastal low and pre-frontal trough caused winds over the southern highveld to veer to the southwest. The frontal system moved across the highveld on 4 August; with a high ridging in behind it, the wind backed from southwesterly to northeasterly. The approach and passage of a second cold front on 8 August again resulted in a period of southwesterly flow. With both stable easterly and unstable frontal weather from the southwest being experienced, the two-week monitoring period was typical of highveld winter conditions. The surface synoptic weather charts at 12:00 GMT on selected days during the winter field experiment and the accompanying 700 hPa geopotential height charts are shown in Fig. 2*a*.

The summer period was mostly characterised by a low pressure trough across the central parts of the country to the west of the highveld. Under these conditions, the flow was mostly from the northeast, with some thunderstorms occurring in the convergent air to the east of the trough. At times, however, the trough was centred over the highveld and winds were westerly and the weather was clear. Generally speaking, the two-week summer monitoring period was typical of highveld summer conditions with hot days and afternoon or evening thunderstorms on four occasions. Figure 2*b* shows the surface synoptic weather charts at 12:00 GMT and the accompanying 700 hPa geopotential height charts on selected days during the experiment.

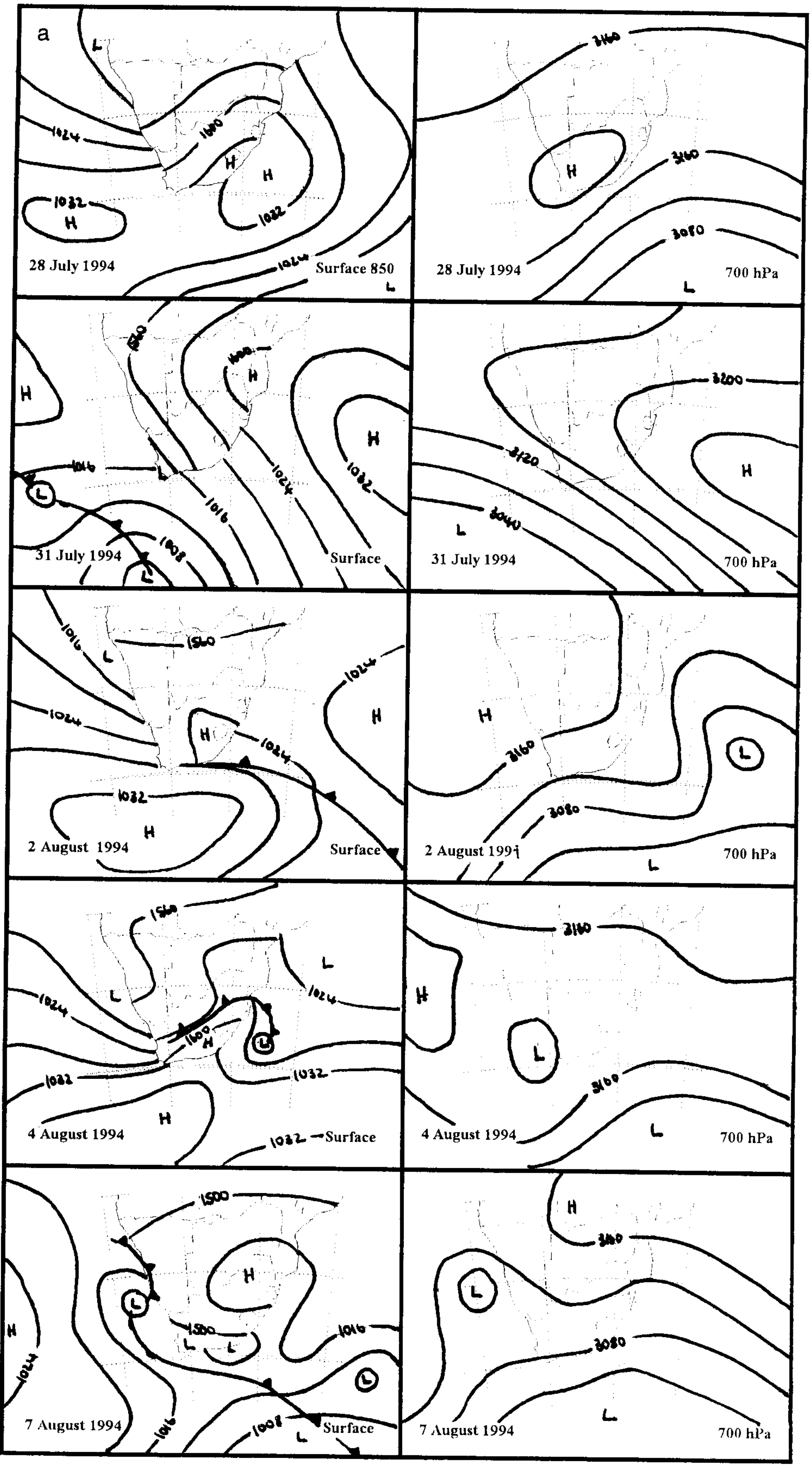

Fig. 2. *a*, The 12:00 GMT synoptic charts (left) showing heights of the 850 hPa geopotential surface over the subcontinent and sea-level isobars over the oceans, and (right) the corresponding 700 hPa geopotential height charts for six selected days during the winter field experiment.

Data

Three types of data were collected at Elandsfontein, namely, sulphur dioxide (SO_2) concentrations, particulate concentrations and micro-meteorological data. SO_2 was monitored continuously by means of a UV-fluorescent analyser which was calibrated before and after both experimental periods by Eskom's NCS accredited calibration laboratory. The continuous measurements were used to calculate 15-min averages. Particulate concentrations were measured by means of two-stage stacked filter units equipped with 8 μm and 0.4 μm Nuclepore filters. Separate filter units were run for the convective daytime period (09:00 to 16:00), for the stable night-time period (22:00 to 06:00) and for each 24-hour period. The sulphate concentrations were determined later using a Dionex ion- chromatograph.

Micro-meteorological parameters were measured using standard equipment. These were wind speed and direction at 10 m

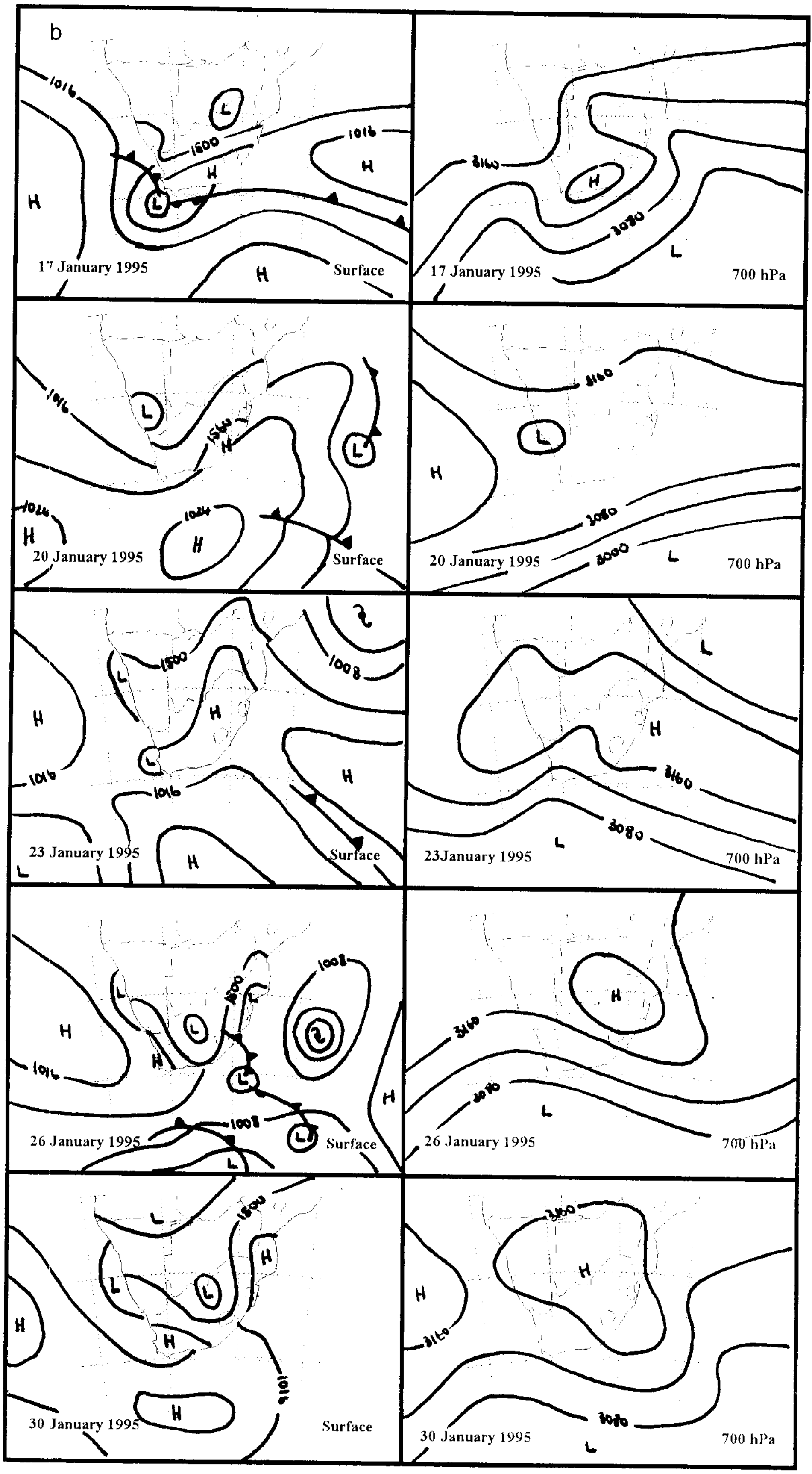

Fig. 2 *b*, The 12:00 GMT synoptic charts (left) showing heights of the 850 hPa geopotential surface over the subcontinent and sea-level isobars over the oceans, and (right) the corresponding 700 hPa geopotential height charts for six selected days during the summer field experiment.

above ground level, the standard deviation of the horizontal wind direction (σ_θ), dry and wet bulb temperature, rainfall and surface wetness (summer only). All the variables were sampled by a Campbell CR-10 data logger every 10 seconds, and were used to calculate the stored 15-min averages. The parameter σ_θ is used by the inferential model as a proxy for turbulence and surface roughness. Global radiation values were obtained from the Irene weather office, approximately 130 km northwest of Elandsfontein. In summer, surface wetness was measured using a coated wetness sensor developed by NOAA/ATDD. Unfortunately, this sensor was not available for the earlier winter monitoring period. Instead, the surface was assumed wet with dew if the dewpoint depression at 1.2 m above ground level was less than 1.5°C. To test the validity of the dewpoint depression method, wetness was calculated in summer and compared with the wetness indicated by the sensor. A correlation coefficient of 0.76 between the two methods provides a degree of confidence in the dewpoint depression approach of determining surface wetness.

The inferential model allows for a ground-cover mix of two vegetation types. A mix of 66% grass and 34% maize was considered to be representative of the highveld region.[17] For each vegetation type the model also requires a maximum leaf area index (LAI) value and a percentage of LAI that describes the growth state of the vegetation canopy. LAI gives a measure of leaf area per unit ground area. Maximum LAI values of 0.3 and 3.5 were used for grass and maize, respectively (R. Scholes, pers. comm.). For the winter period a dormant canopy was modelled as is normal on the highveld, whereas in summer a full canopy was assumed.

Methodology

The factor linking dry deposition of a pollutant to atmospheric concentrations is the deposition velocity (V_d), where

$$V_d = -F/C.$$

F is the dry deposition rate and C the atmospheric concentration of the chemical species of interest. The negative sign conforms with the meteorological convention and indicates a downward flux. V_d can be measured in intensive experimental programmes for some chemical species, or calculated by applying a model driven by field measurements of selected controlling variables. The latter is essentially inferential and referred to as the inferential method,[15,16] that was developed and applied elsewhere to estimate site-specific fluxes of sulphur dioxide, ozone (O_3), nitric acid (HNO_3) and submicron particles.

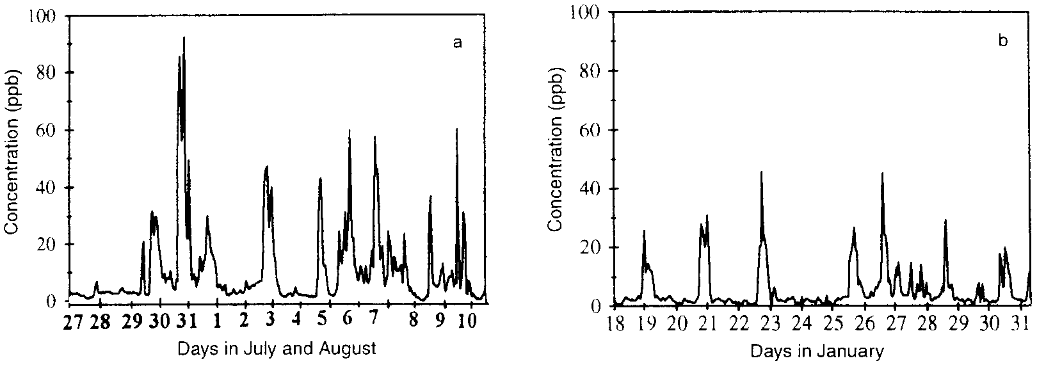

Fig. 3. Ambient SO_2 concentration for *a*, the winter period and *b*, the summer period.

The inferential model makes use of a method of multiple resistances appropriate for describing individual leaves to simulate the vegetation canopy as a whole. The canopy resistance is combined with estimates of aerodynamical and boundary-layer resistance to approximate the total resistance to pollutant transfer. The total resistance to transfer from the atmosphere is

$$R = R_a + R_b + R_c ,$$

where R_a = aerodynamic resistance which is determined by atmospheric properties such as turbulent exchange; R_b = boundary-layer resistance that accounts for pollutant transfer in the vicinity of receptor surfaces affected by the molecular diffusivity; R_c = surface or canopy resistance that combines the consequences of all uptake processes involving individual elements of the surface into a single number that is characteristic of the pollutant and the surface.

The deposition velocity is computed from the total resistance to transfer by the relationship

$$V_d = 1/(R_a + R_b + R_c).$$

The data collected during the 2 two-week periods were used as the basic input information for the NOAA/ATDD inferential model. Although the inferential model computes V_d for the pollutant species listed earlier, the scope of this study considered that for SO_2 and particulates only.

Results

Figures 3*a* and 3*b* show the ambient SO_2 concentrations for the winter and summer periods, respectively. The mean SO_2 concentration during the winter period was 10.7 ppb with a maximum recorded value of 92.3 ppb. In summer the corresponding values were approximately one half of the winter values at 5.4 ppb and 45.5 ppb, respectively. These values are consistent with typical concentrations that have been recorded during long-term observations at this site.[18] Although the summer concentration peaks were smaller and occurred less frequently than in the winter period, the SO_2 concentration records for both seasons exhibited a characteristic diurnal pattern. This has been shown to be associated with the mixing down of plumes emitted from tall power plant stacks within the daytime convective boundary layer.[19]

The SO_4 concentrations calculated from the results of the ion-chromatographic analysis of the daytime and night-time filters are shown in Figs 4*a* and *b*. Similar results were obtained for both winter and summer periods, although the highest concentrations occurred in the former. The fine mode was generally in much greater abundance than the coarse. Furthermore, there appeared to be no tendency for larger concentrations to have formed during the day or the night. The sulphate concentrations measured at Elandsfontein were typical of those recorded in other studies on the highveld.[20,21]

Figures 5*a* and *b* show the modelled deposition velocities for SO_2 for the winter and summer monitoring periods, respectively. The mean predicted deposition velocity for SO_2 during the winter period was 0.150 cm s^{-1} with a maximum value of 0.28 cm s^{-1}. For summer the values were 0.295 cm s^{-1} and 0.61 cm s^{-1}, respectively. These differ by a factor of about two. For both periods the deposition velocity exhibited a distinctive diurnal variation which followed the pattern of observed atmospheric stability. The deposition velocity was low at night during stable boundary layer conditions and reached a maximum in the day during convective boundary layer conditions. Similarly, the proxy for atmospheric stability and mixing induced by surface roughness, σ_θ, showed a strong diurnal character with daytime maxima and minima at night.

The modelled hourly deposition velocities for particulates for the winter and summer periods are shown in Figs 5*c* and *d*, respectively. The mean V_d for the winter period was 0.077 cm s^{-1} with a maximum value of 0.49 cm s^{-1}. For the summer, the values were 0.115 cm s^{-1} and 0.49 cm s^{-1}, respectively. Although there was very little difference between the ranges of modelled V_d values for the two seasons, the mean summer value was larger

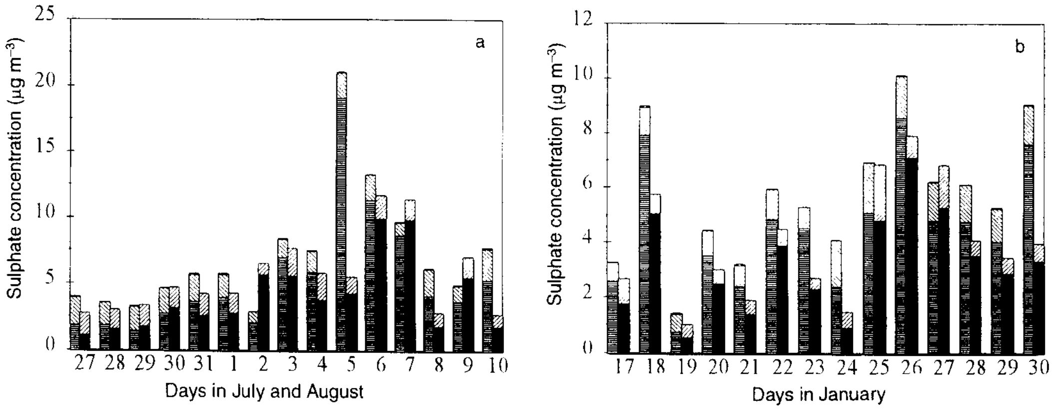

Fig. 4. Ambient particulate sulphate concentrations (in μg m^{-3}) for *a*, the winter period and *b*, the summer period.

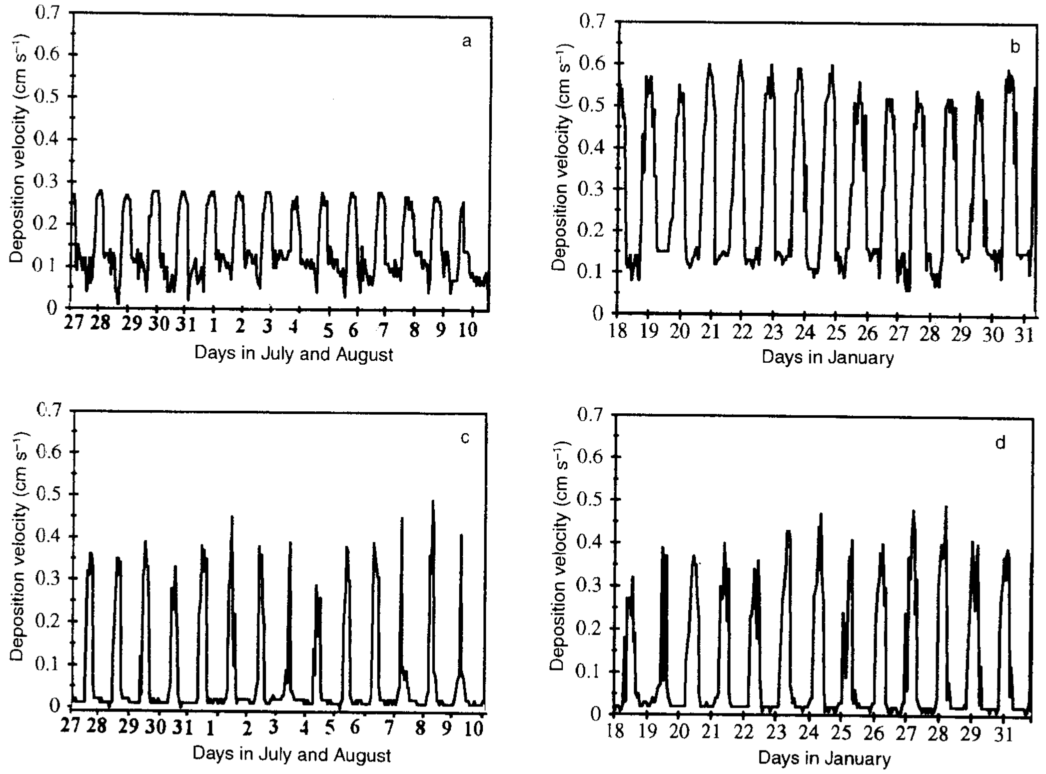

Fig. 5. Deposition velocity for SO_2 for *a*, the winter period and *b*, the summer period, and for particulates for *c*, the winter period and *d*, the summer period.

than that for winter by a factor of about 1.5. In both seasons the diurnal pattern was a prominent feature. Under stable nocturnal boundary layer conditions, V_d approached zero in both seasons, indicating no vertical mixing within the surface inversion layer at night.

The difference in the modelled deposition velocities in winter and summer for SO_2 by a factor of 2 and of 1.5 for particulates is perhaps explained by the variations between the corresponding micro-meteorological parameters in the two seasons. Tests to assess the sensitivity of the inferential model to the various atmospheric parameters showed the largest response to solar radiation and the standard deviation of the horizontal wind direction in both seasons. The other parameters tested had smaller effects on the modelled deposition velocity. For the two-week summer period an average of 66% more solar radiation was received than in winter. Likewise, for summer the mean σ_θ value was 41% higher than in winter. Collectively, these higher summer values could contribute towards larger modelled V_d values for SO_2 and particulates in summer than in winter.

Figures 6*a* and *b* show the hourly SO_2 deposition rates calculated from the model estimated deposition velocities and corresponding measured SO_2 concentrations. The daily mean SO_2 deposition rate calculated from the winter data was 2.067 mg m^{-2} h^{-1} and that calculated from the summer data was 2.073 mg m^{-2} h^{-1}. These similar values imply that the lower deposition velocities in winter were compensated for by the higher SO_2 concentrations. Both the deposition velocity and the SO_2 concentration exhibit strong diurnal variations with the maxima occurring at the same time of day. The resultant deposition values vary by several orders of magnitude between day and night.

The bulk of dry SO_2 deposition occurred during the day and exhibited a large range during a single day and from day to day. This emphasises the need to calculate dry SO_2 deposition on the basis of a minimum of one-hour intervals rather than by using 24-hour or even longer mean values. Sulphur deposition calculated from the mean deposition velocity and concentration values in winter, was 22% lower than that derived from hourly calculations. For the summer data, the corresponding value was 26% lower. At a site where SO_2 exhibited no diurnal cycle, Meyers and Yuen[22] found that the error introduced by using a weekly sampling protocol was random and would sum to zero when combined with dry deposition fluxes for seasonal or annual values. Matt and Meyers[23] reported that dry deposition fluxes could be underestimated by as much as 40% in the growing season when the diurnal cycle of estimated deposition velocity correlated with the measured SO_2 concentrations.

Figures 7*a* and *b* show the overall SO_4 deposition rates. These were calculated from the model estimated V_d values for particu-

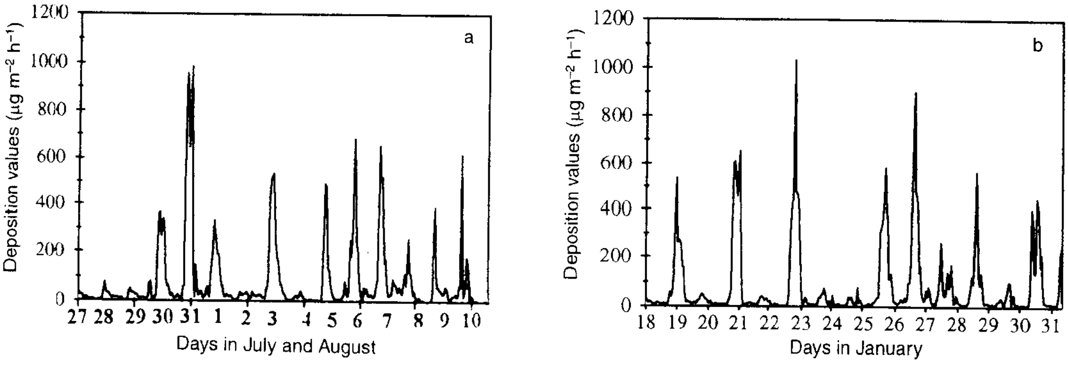

Fig. 6. Hourly deposition rates for SO_2 for *a*, the winter period and *b*, the summer period.

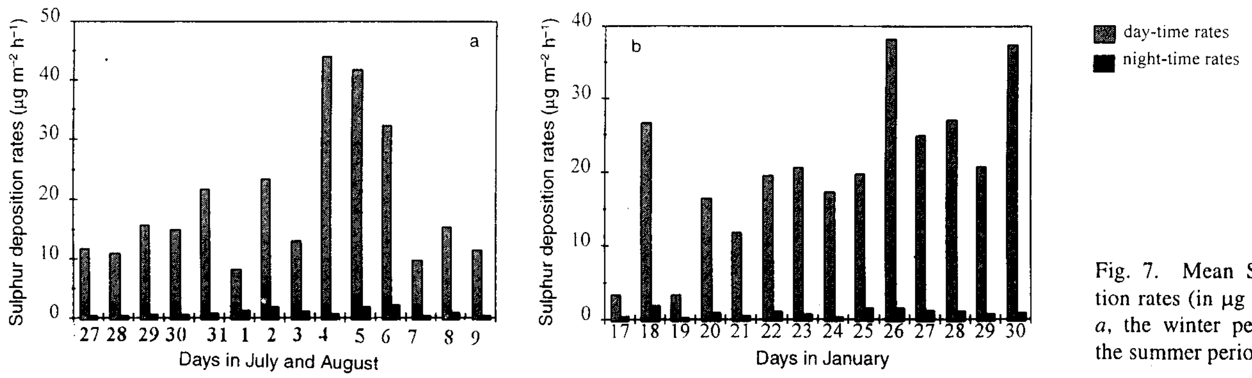

Fig. 7. Mean SO_4 deposition rates (in µg m^{-2} h^{-1}) for *a*, the winter period and *b*, the summer period.

lates and SO_4 concentrations obtained from the analysis of the 24-hour particulate sampler filters. The day and night figures were estimated from the ratio provided by the data from the separate day and nocturnal samplers. It can be clearly seen that virtually all the predicted sulphur deposition from particulates occurred during the day, as was the case for gaseous SO_2. In the case of particulates, however, most of the diurnal variation came from the difference in the modelled day and nocturnal deposition velocities rather than variations between day and night-time concentrations.

The estimated total dry deposition of sulphur for the two periods is shown in Figs 8*a* and *b*. By far the majority of dry-deposited sulphur came from SO_2 during the daytime, to the extent of 80% and 82% in winter and summer, respectively. Smaller contributions were made by SO_2 at night and by particulates during the day in both seasons. The contribution to the total load of dry deposition sulphur by particulates at night appears to be negligible.

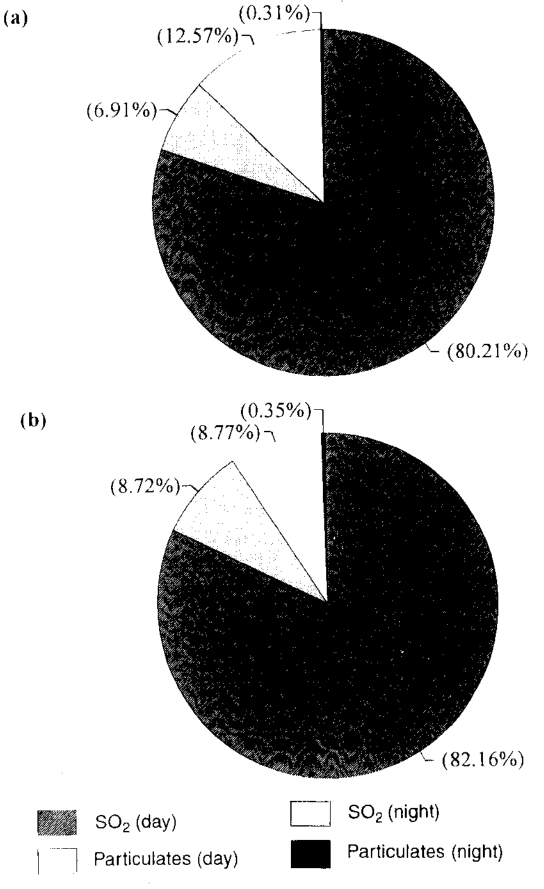

Fig. 8. Relative contributions to the total dry deposition of sulphur by SO_2 and SO_4, (in mg m^{-2} day^{-1}), by day and night in *a*, winter and *b*, summer.

Although wet deposition was not measured at Elandsfontein, there is a wealth of data available for this region in general[3] and concentrations have been found to be consistent over the region as a whole. The nearest wet deposition site to Elandsfontein is at Amersfoort, 100 km to the south-southeast. The reported seven-year mean sulphate concentration for Amersfoort is 58 µeq. l^{-1} in association with a mean annual rainfall of 614 mm. This represents a mean sulphur wet deposition rate of 5.7 kg S ha^{-1} yr^{-1}. If this value is taken as representative of wet deposition at Elandsfontein, and the dry deposition results from the 2 two-week monitoring periods are assumed to represent a full year giving a deposition rate of 8.22 kg S ha^{-1} yr^{-1}, then the estimated total sulphur deposition rate for Elandsfontein is 13.9 kg S ha^{-1} yr^{-1}. The estimated dry deposition of sulphur exceeds the wet, but not by much.

As SO_2 is the biggest single component of precipitated sulphur, the overall sulphur deposition rate will largely follow the regional SO_2 concentration gradient. Thus sites on the periphery of the Mpumalanga highveld, such as the Escarpment region, can be expected to experience lower dry deposition rates than those within the central area. Owing to its central location, the estimated total sulphur deposition rate at Elandsfontein can be expected to be representative of the high end for sites in the Mpumalanga highveld. Compared with published American data,[24] deposition values for Elandsfontein fall well within the reported range (Fig. 9).

Conclusion

This study shows that the inferential technique for estimating dry deposition can be applied on the Mpumalanga highveld. Where the micro-meteorology differed between the two seasons, the difference in ambient SO_2 concentrations provided a compensating effect which resulted in very similar sulphur deposition rates being experienced in summer and winter. This affords a degree of confidence when extrapolating the results to give estimates of annual deposition. However, it cannot be assumed that the 2 two-week monitoring periods were representative of the whole year.

The bulk of dry deposition of SO_2 occurs during the day. This is associated with the mixing down of plumes emitted from tall power plant stacks within the daytime convective boundary layer. The low contributions to dry deposition of sulphur at night are indicative of stable boundary layer conditions and the absence of vertical mixing.

With a wet sulphur deposition rate of 5.7 kg S ha^{-1} yr^{-1} for the Elandsfontein region and an estimated dry deposition rate of 8.22 kg S ha^{-1} yr^{-1}, the total estimated sulphur deposition for the site is 13.9 kg S ha^{-1} yr^{-1}. As expected, the dry deposition rate for sulphur exceeds wet deposition in the central highveld and the values are well within the expected ranges. Estimated sulphur deposition rates compare with published data.

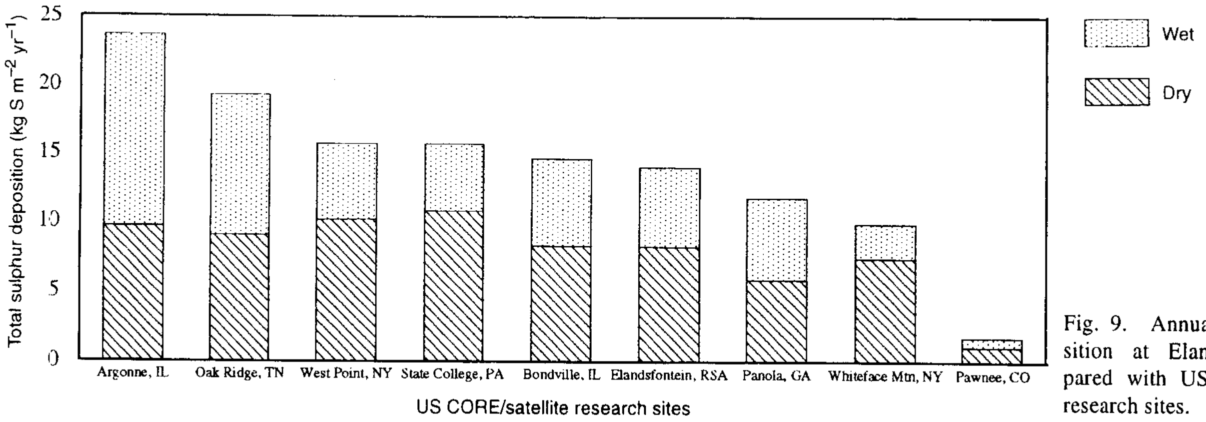

Fig. 9. Annual sulphur deposition at Elandsfontein compared with US CORE/satellite research sites.

Future plans include the installation of two permanent dry deposition monitoring sites on the Mpumalanga highveld by Eskom and seasonal monitoring in the lowveld and on the Mpumalanga Escarpment by the CSIR. These initiatives will expand the scope of the dry deposition work to the three climate regions of Mpumalanga and will build towards a long record of dry deposition for the highveld.

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