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Concentrations, distributions and critical level exceedance assessment of SO_2, NO_2 and O_3 in South Africa

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Abstract South Africa has been identified as a source of industrial pollution that is significant at a global scale. This study was designed to provide quantitative information, by direct measurement, across northeastern South Africa, which includes the highly industrialised Mpumalanga Highveld. The specific aim of the study was to evaluate whether or not acidic atmospheric pollution poses a threat to soils, plants and water bodies of South Africa. To address this aim, a network of 37 passive sampling sites was established to measure monthly mean concentrations of near-surface SO_2, NO_2 and ozone. The area covered extended over the northern and eastern interior of South Africa while avoiding sources of local emissions such as towns, mines and highways. The field campaign was conducted between August 2005 and September 2007. Spatial distributions and temporal trends for these pollutant gases were assessed. Critical levels analysis comparisons were made against applicable air quality standards, guidelines and limits to evaluate the potential for adverse atmospheric pollution impacts on regional environments. The assessment indicates that only in the central source area of the South African industrial Highveld are some levels exceeded. In remote areas, including the sensitive forested regions of the Drakensberg escarpment, pollutant concentrations are below the critical thresholds for environmental damage.

Keywords South Africa · Exceedance · Industrial pollution · Critical levels

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Introduction

Forest dieback and irreversible acidification of lakes linked to serious loss of fish stocks and other sensitive aquatic species in Scandinavia in the middle of the twentieth century were attributed to deposition of acidic species (acid rain) originating from the UK (Oden 1968). Ever since these experiences became known, there have been global and local concerns that such ecological damage due to acid rain in other regions downwind of large coal-fired power plants and industries are and could be repeated (Kuylenstierna and Hicks 2002; Kuylenstierna et al. 1995, 2001; Kuylenstierna and Chadwick 1989; Whelpdale and Kaiser 1996; Wesely and Hicks 1977).

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Countries in Western Europe and North America responded to air pollution problems and through policies and coordinated measures managed to reduce substantially the emissions of SO_2, the primary acidic precursor, although NO_x emissions still remain a problem. In the meantime, later research has shown that pollutants such as volatile organic compounds and ammonia are also involved in processes that lead to acidification (McCormick 1997).

The science and knowledge on acid pollution has made rapid progress, especially in countries of Western Europe and North America. Most of the industrialised countries operate their own local and countrywide atmospheric monitoring programmes. At the global level, the World Meteorological Organisation (Miller 1992; Georgii 1982) has been operating a Background Monitoring Network, and the UN Environment Programme (UNEP 2008) coordinates global and regional monitoring through its Global Environment Monitoring System. In Europe, monitoring is done under the Cooperative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe under the UNECE (UNECE 2008). Research on emissions has been also performed by the International Institute for Applied Systems Analysis, which has developed an interactive computer simulation called the Regional Air Pollution Information and Simulation. There are several monitoring networks in the USA, such as the National Atmospheric Deposition Program, which collects data from nearly 200 sites across the USA. A major project, called the National Acid Precipitation Program (NAPAP 2008), was launched in 1980 to study the causes and potential effects of acid deposition in and around the USA. The final report was issued in 1990, raising more question than it answered (McCormick 1997).

In contrast to declining SO_2 emissions in Europe and North America in response to stringent government regulation, emissions are rising in many developing nations across the world (McCormick 1997; Held et al. 1996; Galloway 1995). There is an opportunity for policy makers in developing countries to take into account the potential acidification impacts associated with increasing emissions so that they can avoid some of the costly mistakes that have been made during industrial development in Europe and North America. The knowledge obtained in these regions with regard to acidic deposition and the effects of the acidification can be used and adopted to local conditions for this purpose.

Previous experience shows that, in order to manage acid deposition, emissions of the acidifying precursor species need to be controlled. The acidification of soil and surface water has indirect effects, including the cumulative impacts of both wet and dry sulphur (S) and nitrogen (N) deposition. Reducing emissions cannot result in the immediate recovery of affected ecosystems (Bishop and Hultberg 1995), and the major risks of the cumulative effects of acidification in developing countries lie in the future as emissions increase (Kuylenstierna et al. 2001). Therefore, the establishment of quantifiable estimates of acidification of the environment in developing regions still requires attention.

The primary research question for this study is to what extent are industrial emissions from the central power generating region (Mpumalanga Highveld) influencing the concentrations away from the source region, taking into account prevailing circulation of the air masses over the southern African subcontinent?

Very few studies have been undertaken in South Africa on the impacts of gaseous pollutant species on non-commercial vegetation species (Emberson et al. 2001, 2003; Van Tienhoven and Scholes 2003). Past research explored the effects of air pollution on natural vegetation (grassland, Fynbos and *Acacia*), commercial forests (*Eucalyptus* and *Pinus* species) and agricultural crops (maize, sunflowers, dry beans, potatoes, tomato and tobacco). The results from past studies were inconclusive (Van Tienhoven and Scholes 2003; Emberson et al. 2003). More studies need to be undertaken in order to determine critical levels for local vegetation with confidence. Thus, as the second objective, possible exceedances of damage thresholds have been assessed.

Critical levels for vegetation are described in different ways for different pollutants. These are currently expressed as mean concentrations, cumulative exposures or fluxes through plant stomata. Critical levels for vegetation are defined as the

"**concentration**, cumulative exposure or cumulative stomatal flux of atmospheric pollutants above which direct adverse effects on sensitive vegetation may occur according to present knowledge" (Manual on Methodologies and Criteria for Modelling and Mapping Critical Loads 2004). Critical level exceedance can thus show the difference between the critical level and the monitored or modelled air pollutant concentration, cumulative exposure or cumulative flux.

The scope of this study was relatively simple in its design, although extensive in its spatial and temporal extent. It involved establishing a network of passive monitoring sites over the northeastern sector of South Africa and collating monthly concentration samplers over two annual cycles. This was necessary in order to obtain medium term averages, in addition to annual and seasonal variations.

The strategy for selecting sampling locations was designed to capture the regional influences of the industrial pollution, avoiding local influences (towns, industries and highways). The spatial distribution of the concentrations were analysed in order to determine direction and magnitude of the influence of industrial emissions within the study domain. The final step was to assess exceedance of international and local air pollution standards, guidelines and limits, including health-based and vegetation indicators. Literature states that the current pollutant concentrations experienced in many developing countries can result in severe damage to vegetation and that, without appropriate control measures, such damage is likely to worsen if the pollution emissions increase in the future (Emberson et al. 2001). Vegetation (natural and crops) is regarded as the most sensitive component of ecosystems, and thus, the vegetation critical level exceedances were assessed against the concentrations from the monitoring program.

Method

Monthly passive samplers have been exposed at 37 sites for a period of 2 years in the northeastern portion of South Africa. This allowed the concentration distribution of SO_2, NO_x and O_3 to be evaluated from the Mpumalanga Highveld industrial source region. Critical levels were assessed based on measured (mean monthly) pollutant concentrations only. The disadvantage of a relatively long averaging period of 1 month is offset against the advantage of a dense grid of remote measuring locations. In addition, a critical levels survey of the long-term potential damage to the environment from industrial emissions of these gas species has been enabled.

Study design

The air pollutant concentration network for this research was designed for the measurement of SO_2 and NO_2, originating from coal fired power plants on the industrial Highveld, and constrained to lie within the political boundary of South Africa. Although prevailing winds are from the northwest, seasonal stagnation and recirculation necessitated a network design covering the entire inland area of South Africa (Freiman and Piketh 2003). Extension beyond the boundaries of South Africa would have added value but was constrained by practical considerations. The area of concern can be represented geometrically as a 600 × 600-km array rectangle, centred on Witbank, Mpumalanga Province of South Africa.

A reference site, intentionally in the zone of highest pollution, was chosen at the approximate centre of the industrial Highveld. This site, Elandsfontein (site 17), is within visual sight of several of the Mpumalanga coal-fired power stations. Other sources of air pollution in this region include major ore smelters, multiple surface coal mines and a major coal liquefaction and petrochemical complex. Elandsfontein served as an indicator of maximum ground level concentrations of the pollution levels in the industrialised Highveld.

Passive sampling of trace gases

Trace gases were monitored using the passive sampling technology as applied in the International Geosphere Atmosphere Chemistry/Deposition of Biogeochemically Important Trace

Species [IGAC-DEBITS-Africa (IDAF)] network (Pienaar et al. 2003). Such measurements are based on the molecular diffusion of gases and species-specific collection on impregnated filters specific to each pollutant measured. These samplers have been developed according to the DEBITS procedures based on the work of Ferm (1991) and Ferm et al. (1994). While passive monitors have previously been demonstrated in South Africa, these have either been used in remote areas with only a small number of samplers (typically at four to six sites) or in intense urban surveys (Zunckel et al. 2004; Kuylenstierna and Hicks 2002). Passive samplers have been tested and validated since the beginning of 1998 in the IDAF network at six African stations (Al Ourabi and Lacaux 1999; Lacaux 1999). This technique has also been tested in different tropical and subtropical regions (Ferm and Rodhe 1997).

In Ayers et al. (1998), precision of the passive samplers, expressed as mean percentage difference between duplicates, was in the range 5–10% for NO_2 and 10–25% for SO_2. In addition, in Cruz et al. (2004), it is stated that methods precision as a relative standard deviation for three simultaneously applied SO_2 passive samplers was within 10% and, when compared to active monitoring methods under real conditions, used in urban and industrial areas, showed an overall accuracy of 15%. For O_3, error margins of 15% are stated based on comparisons with continuous ozone analyzers (Tang and Lau 2000).

The passive sampling monitoring network

Monitoring sites were selected at integral one-degree grid intersections, with some additional sites positioned at half-degree grid intervals (Fig. 1). To avoid the impacts from local air pollution sources, care was taken to position the sites away from urban centres, industrial point sources or other local disturbances. Samplers were also located away from major roads. Sites were mostly in rural farmland, forestry and natural reserves, sparsely inhabited and often non-electrified locations. In instances were the grid point was close to potential interferences, sites were shifted from the original fixed grid point by distances of not more than 15 km.

Passive samplers where exposed in the field for 30-day intervals, corresponding to calendar months for 2 years (two annual cycles) (September 2005 to August 2007). The monitoring sites were jointly managed with field volunteers who serviced them on a monthly basis. Samples were prepared in the laboratory and couriered or mailed to the site operators.

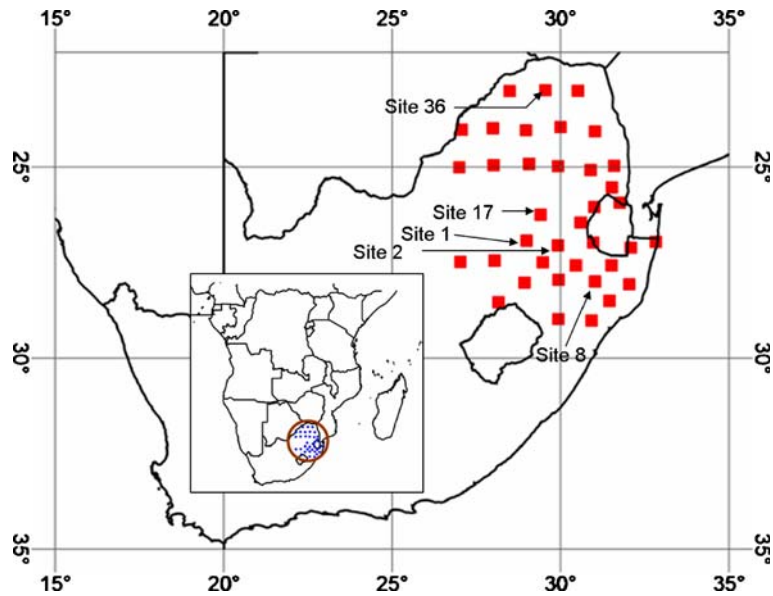

Fig. 1 Extent of the study area within South (larger map) and sub-Saharan Africa (a map *inset*). The sites included in three different sites categories are indicated

Ambient air quality standards and guidelines applied as critical levels

Measured ambient pollutant concentrations have been compared to several sets of appropriate standards. The monitoring interval for all sites was 30 days, and this has been compared with critical levels for averaging periods of 1 month or longer. A range of South African and international air quality standards have been utilised (Table 1). Exceedance of a critical level occurs when the measured mean concentration is greater than the critical level concentration.

The first two sets of standards (NEMA and SANS) are concerned with human (and animal) health protection, while the third (UNECE: CLRTAP 2005) and fourth (UN WHO AOT) are concerned with limits for vegetation. Previous research on the effects of air pollution on vegetation in South Africa was assessed using trace limits specific to South Africa—the reviewed literature did not contain a conclusive value for use as a critical level. Although there is ongoing research on the impact of ozone on vegetation in South Africa, no results had been published by the time this study concluded. No vegetation-specific guidelines or standards for South African vegetation have been legislated. Thus, for the purpose of this assessment, the widely used Convention on Long-Range Transboundary Air Pollution concentration limits were used. Important to emphasise here is that the monthly means do not allow for the calculation of the accumulated hours above the 40 ppb threshold—which is the basis for O_3 AOT40 approach. Thus, for this study, a simplified approach was adopted of using values, 30 and 40 ppb, as threshold limit values with which to compare the monthly mean O_3 values.

Quality assurance and quality control

The use of an accredited atmospheric chemistry laboratory with its own quality assurance and control measures was considered to be of paramount importance. The atmospheric chemistry laboratory of the Atmospheric Chemistry Research Group, of Northwest University (Potchefstroom Campus) as part of the IGBP/IGAC/DEBITS programme of remote deposition monitoring

Table 1 Atmospheric ambient standards and European critical levels used as critical levels for trace gas species SO_2, NO_2 and O_3 in this study

Sources	Averaging period	Applicability	Units	SO_2	NO_2	O_3
SA NEMA: AQA 39 (2004) and SANS: 1929 (2004)	Annual mean	Human (and animal) health	ppm	0.019	0.05	n/a
			$\mu g\ m^{-3}$	50 (50)[b]	95.5[a] (40)[b]	n/a
UN - WHO 2000/2005 AQ Guidelines	Annual mean	Human (and animal health)	ppb	n/a	n/a	n/a
			$\mu g\ m^{-3}$	50[c] (10–30)[d]	40 (40)[b]	n/a
UNECE - CLRTAP (for SO_2 and NO_2)	Annual mean and half-year (winter) mean for (semi)-natural and agricultural vegetation	Agricultural crops	$\mu g\ m^{-3}$	30	30	n/a
		(Semi-) natural vegetation	$\mu g\ m^{-3}$	20		n/a
		Forest ecosystems	$\mu g\ m^{-3}$	20		n/a
		Lichen	$\mu g\ m^{-3}$	10		n/a
UN WHO AOT: Ozone monthly thresholds (cut-off concentration for the AOT 30 and 40 critical levels)	Annual and growing season	Vegetation	Ppb	n/a	n/a	30 and 40[e]

[a]Re-calculated from NEMA standard = 0.05 ppm
[b]Re-calculated from SANS 1929 (2004) standard
[c]WHO Guidelines for the protection of human health (UN WHO 2000)
[d]The critical level of eco-toxic effects (issued by WHO for Europe); a range is given to account for different sensitivities of vegetation types (UN WHO 2000)
[e]Cut-off concentration for the AOT 30 and 40 critical levels, UN WHO Europe (2000)

programme undertook all the laboratory and analysis work.

Each sample was marked with an identification number, enclosed in separate plastic vials (distinct colour for each gaseous species), sealed, and stored in dry, cool pre-packaging for transportation. Samplers were sent to each monitoring site by either registered mail or courier services. After exposures, the samples were retrieved and stored for batch transport to the analytical laboratory. Protocols were communicated and explained to the site operators and volunteers in the field as a set of simple steps.

Throughout the sampling campaign, measures were undertaken for field quality assurance. These ranged from duplicate sampling, seasonal site visits to monitors and procedure inspection of the monitoring campaign. Suspect sampler containers (such as those that were open and those arriving late) were marked and handed to the lab for discarding. As a result, the laboratory established a relatively small number of *not exposed*, *overexposed* and *beyond detection limit* samplers, and those were dealt as per standard laboratory procedures. Furthermore, a number of samplers went missing during transport—these were replaced if notified in time or treated as non-exposures.

The results where divided into two annual cycles, September to August. Rate of valid sample return for the first annual cycle was below 60% and insufficient to meet quality control criteria. However, for the second annual cycle, the data return was above 80% and for the 2-year period was over 70%, which is an adequate return rate on which to derive valid statistical results.

For internal quality control purposes, comparisons were made between the two annual cycles of the monthly, seasonal and annual means. In addition, data analysis included checking for extreme concentrations that prompted the scientific flagging of outliers (greater than two standard deviations). Any samples with concentration values beyond three standard deviations above the mean were excluded from further data analyses. In addition, for readings that exceeded two standard deviations above the mean, the entire chain of sampling, chemical analysis reports and data processing was re-inspected.

Results

Criteria pollution concentrations over the South African Highveld

SO_2 *concentrations and regional distribution*

The mean SO_2 concentrations for the annual cycle September 2006 to August 2007 are presented in Fig. 2. Six locations recorded average concentration above 6 μg m^{-3}. These included Standerton (site 1), Amersfoort (site 2), Piet Retief (site 3), Elandsfontein (site 17), Heilbron (site 18), and Potgietersrus (site 21). These sites are all directly within the main source region, or lie downwind from, the industrial Highveld.

The annual mean concentrations at the remaining sites were all below 6 μg m^{-3}, with the plus one standard deviation lying below 10.5 μg m^{-3}. Those sites with higher variations are downwind of the source areas. These are Standerton (site 1), Piet Retief (site 3), Gluckstad (site 8), Utrecht (site 27), Amsterdam (site 29), and Malelane (site 30). The site at Thabazimbi (site 34) indicated occasional high concentrations of SO_2 despite being to the north of the main sources on the Highveld. The likely sources that contributed the ambient SO_2 are the Thabazimbi iron ore mine and smelter, which were both situated upwind from the site. This site is also impacted by two other possible sources of SO_2, namely the Matimba Power station and the Grootegluk opencast mine, both in Limpopo Province.

The spatial distribution of SO_2 over the Highveld during 2005 and 2006 shows that the highest concentrations are centred directly over the Mpumalanga industrial Highveld. This region is dominated by the influence of high concentrations at Elandsfontein elevated concentrations of SO_2 were also found at Standerton and Amersfoort that are directly downwind of the dominant sources. With the exception of a location NW of Potgietersrus/Mokopane (site 21), the more distant sites have much lower concentrations in both years, while the furthest sites have the lowest concentrations. Potgietersrus (site 21) has two possible influences for slightly higher mean and maximum concentrations. Matimba power station lies ~150 km upwind, while 8 km to the west is

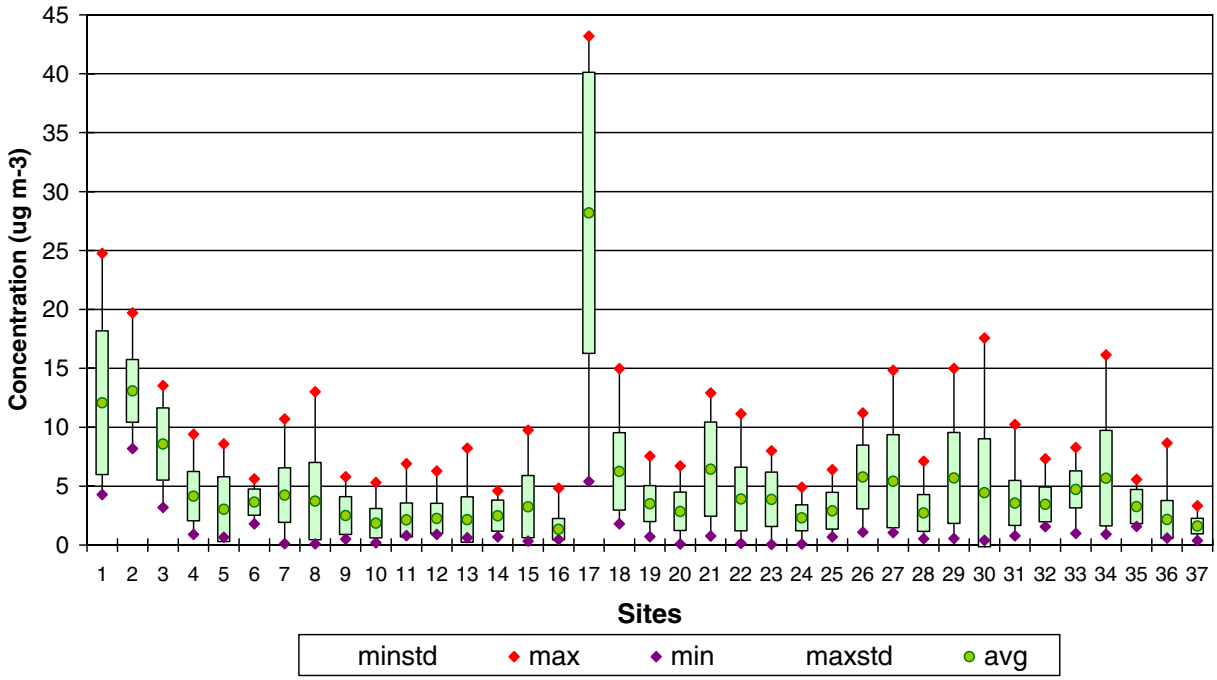

Fig. 2 Two-year mean SO_2 concentrations, standard deviation, maximum and minimum (September 2005 to August 2007)

Mokopane Platinum mine, although it does not appear that this mine has a smelter on site.

Overall, the observation of SO_2 concentrations and the spatial distributions behave as expected and confirm the conclusions from prior studies based on dispersion modelling (Scorgie et al. 2004a, b).

NO_2 *concentrations and regional distribution*

An evaluation of the inter-annual differences for NO_2 showed that concentrations did not diverge substantially from one year to the next, with differences ranging from −0.6 to +0.8 μg m^{-3} (−10% to +52% from 2-year means; Fig. 3). Elandsfontein (site 17) has mean and maximum concentrations much greater than any of the other sites, similar to the spatial distribution of SO_2.

The sites with higher concentrations were positioned either within the industrial Highveld source area, Standerton (sites 1), Amersfoort (site 2) and Elandsfontein (site 17), or were downwind of the source area, Piet Retief (site 3), Harrismith (site 6), Newcastle (site 7) and Gluckstad (site 8). The maximum NO_2 concentration at Elandsfontein (site 17) was only 2.5 times greater than the mean NO_2 at all other sites, whereas for SO_2 concentrations, Elandsfontein (site 17) was 6.5 times greater than the background mean. For the majority of the remaining sites, mean concentrations were between 2 and 3 μg m^{-3}, exceptat Steelpoort (site 23) and Thohoyandou (site 37), which recorded concentrations ∼4 μg m^{-3}. There are chrome–manganese smelters within the Steelpoort valley, which may account for the high NO_x at Steelpoort (site 37). There are no known large industries near Thohoyandou (site 37) and the traffic emissions from a small town such as this should not generate elevated NO_x at a site ∼10 km distant.

This observation confirms that the sites chosen were appropriately remote from direct influences from the main emission points on the industrial Highveld or from other local strong emission sources of NO_x, with the two exceptions noted. The lowest mean NO_2 (1.3 μg m^{-3}) was recorded at Skukuza (site 12) on the Mpumalanga Lowveld. Other low mean NO_2 values, below 2 μg m^{-3},

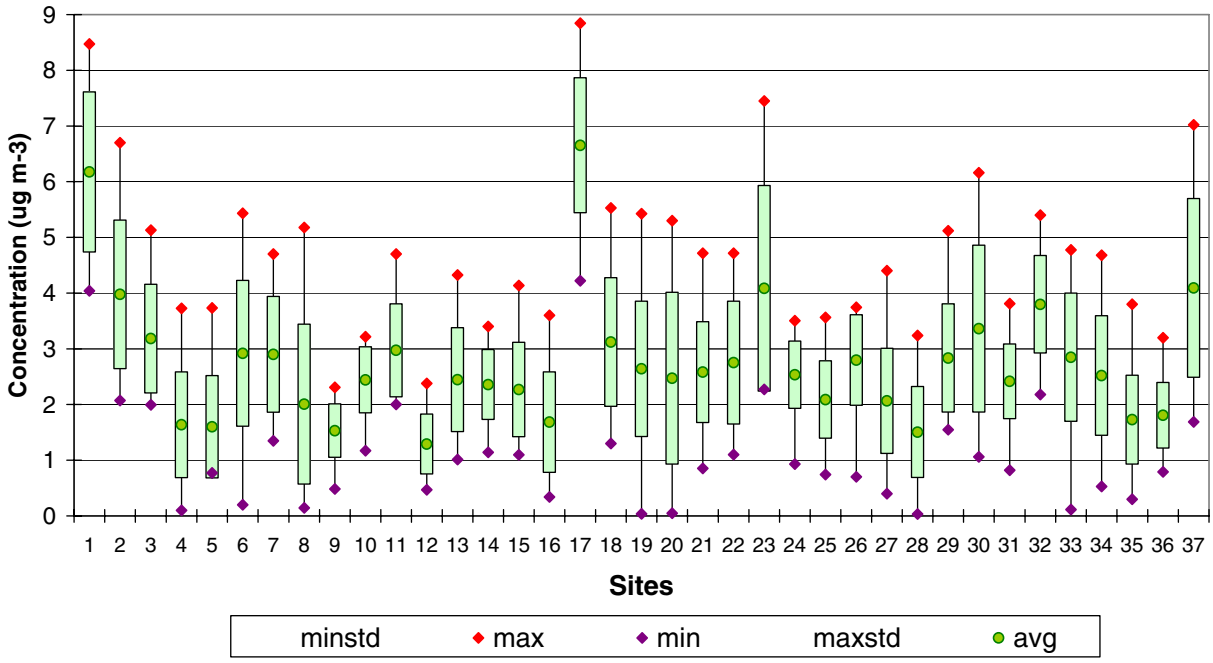

Fig. 3 NO_2 mean, standard deviation, maximum and minimum concentrations over 2 years (September 2005 to August 2007)

occurred at sites Hluhluwe (site 9), Kosi Bay (site 16) and Pongola (site 28), all on the northern KwaZulu–Natal coastal plain, presumably well-ventilated by clean marine air.

For the annual mean NO_2 concentrations, spatial concentrations contours for both annual cycles are compared. The highest NO_2 concentrations at sites on the industrial Highveld close to coal-fired power plants leads to the contours plots with the central red/yellow isopleths almost having a circular distribution, surrounded by otherwise relatively uniformly low background field. Contours for the 2 years of sampling are similar.

The industrial Highveld has been clearly delineated as a zone of elevated NO_2 concentrations. The areas surrounding it show the rapidly decreasing concentrations. For the sites positioned southwest and northwest and to a lesser extent, southeast slightly elevated concentrations are detectable. The overall observation of NO_2 over the study area again compares well to the known transport and dispersion patterns and regional scale dispersion models (Scorgie et al. 2004a, b).

O_3 concentrations and regional distribution

An evaluation of the inter-annual differences for O_3 show that concentrations diverged more from 1 year to the next than for the other gasses analysed. Changes ranged between −6.7 and +2.4 ppb in absolute terms and between −30% and +14% changes from the bi-annual mean in relative terms.

In contrast to wide variations in the mean concentrations at different sites for SO_2 and NO_2, O_3 mean concentrations lie in a narrow band (between 14 and 23 ppb; Fig. 4). For the majority of the sites, the mean measured concentrations were around 20 ppb. The maximum monthly mean concentration of 43 ppb, recorded near Thabazimbi (site 37). Lowest O_3 values were <5 ppb but still well above the detection limit of 0.1 ppb.

Ozone concentrations were *not* enhanced in the central industrial region, as was the case for SO_2 and NO_2. This is expected, as ozone is a secondary pollutant, and the conversion of ozone precursors happens during air transport from source regions. There is no evidence in the medium term averages

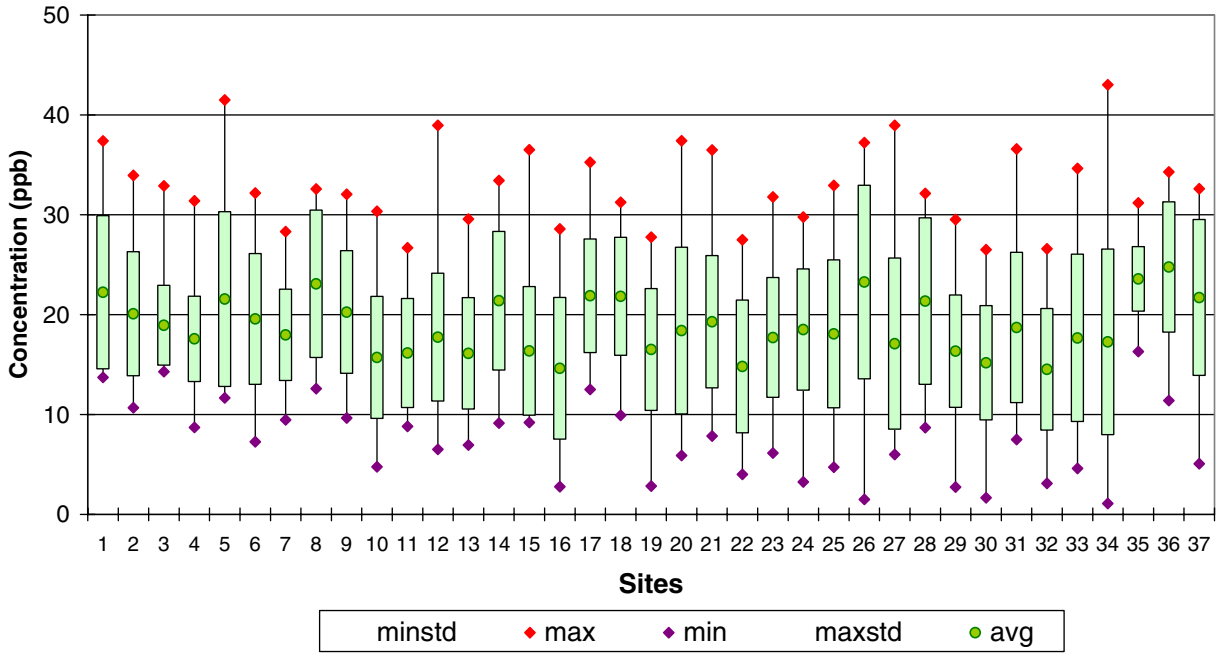

Fig. 4 Mean, standard deviation, maximum and minimum O_3 monthly concentrations for the period September 2005 to August 2007

of enhanced ozone downwind from the Gauteng conurbation. A marginally enhanced concentration of 26 ppb at Standerton (site 1) in September 2005 to August 2006 annual cycle did not recur the following annual cycle September 2006 to August 2007.

The slightly higher concentrations in the northernmost sites Tolwe (site 35), Louis Trichardt (site 36) and Thohoyandou (site 37) may be a real effect. The averages are consistently higher and the standard deviations lower.

Critical (concentration) level exceedance assessment

The exceedance assessments of mean concentrations of SO_2, NO_2, and O_3 against specific mean levels (defined as critical levels) for different periods of measurements are presented in the following section.

Critical level exceedance assessment for SO_2

Comparisons between SO_2 *annual* mean values for each site and critical levels are shown in Fig. 5. Overall, three sites exceeded one or another critical level. The most stringent critical level is for lichen, exceeded at Elandsfontein (site 17), Standerton (site 1) and Amersfoort (site 2). At only one site, Elandsfontein, in the heart of the industrial Highveld, was the CLRTAP critical level for forest and (semi)-natural vegetation exceeded. In addition, SO_2 concentration at this site approached the CLRTAP critical level for agricultural vegetation.

The prevailing winter meteorology is dictated by a lower dispersion potential, so winter months should have higher trace gas concentrations than in summer, for constant emission rates. This general observation is supported by the seasonal concentrations from five representative sites, chosen in the industrial Highveld, downwind from the industrial Highveld and at remote sites. Graphs of seasonal trends for these three categories are shown in Fig. 6. The selected categories of different sites are:

- Remote sites [one far north near Louis Trichardt (site 36), and a site southeast of the industrial Highveld near Gluckstad (site 8)].

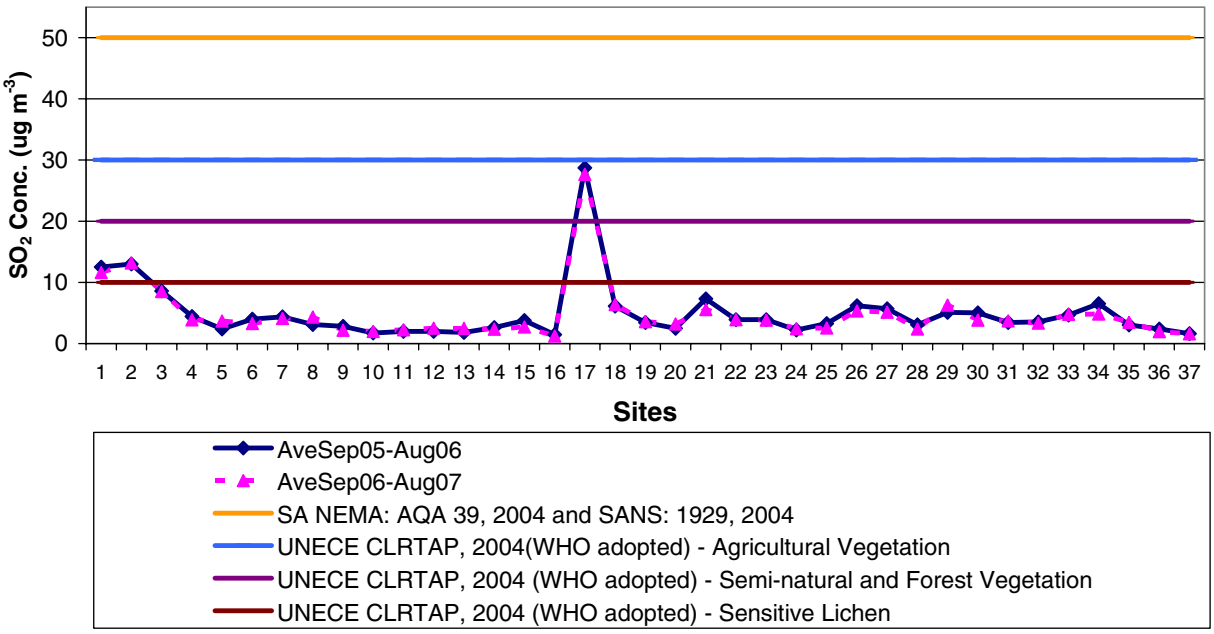

Fig. 5 Annual mean SO_2 concentrations for two annual cycles (September 2005 to August 2006 and September 2006 to August 2007) compared to various annual SO_2 critical levels

- One site in the centre of the industrial Highveld [Elandsfontein, near Kriel (site 17)].
- Two sites downwind from the industrial Highveld (near Standerton (site 1) and near Amersfoort (site 2)].

To highlight the seasonal trends of SO_2, monthly concentrations have been averaged by zone and by 3-month moving averages (Fig. 6). The summer means are lowest and mid-winter means highest. The factor from lowest to highest seasonal

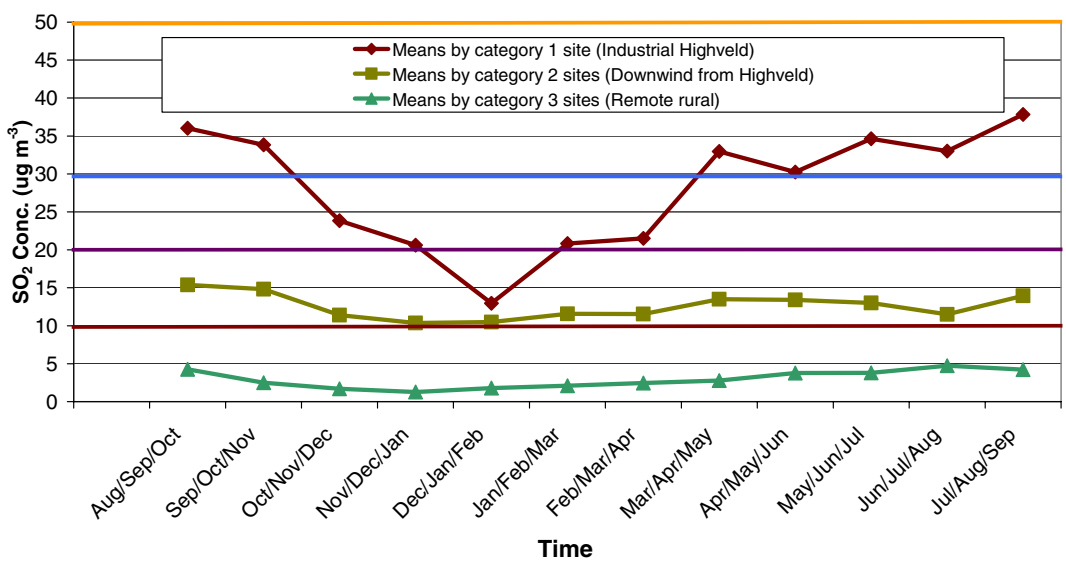

Fig. 6 Moving three-monthly SO_2 means over two annual cycles (September 2005 to August 2006 and September 2006 to August 2007) for three different categories of sites. Different critical levels are the same as in Fig. 5

differences are from ~2 to ~3.5 times greater for the industrial Highveld zone (category 1) while much less marked close to the source areas (category 2) and at remote zones (category 3).

Critical level exceedance assessment for NO_2

There was no exceedance for NO_2 mean annual results for any of the critical levels. The mean annual values of NO_2 for each site were much lower than all the specified critical levels (Fig. 7).

This general observation is supported by the seasonal (3-month moving mean) concentrations from five representative sites, chosen in the industrial Highveld, downwind from the industrial Highveld and at remote sites (Fig. 8). There is little seasonal variation of NO_2 at any of the sites. Once again, the gradient with spatial reduction from the highest in the Highveld centre to the remote rural background is evident.

For the industrial Highveld, seasonal NO_2 concentrations peak during spring and are ~25% higher than the lowest values that occur during summer. For the downwind sites, NO_2 shows no distinct seasonal variation. For remote sites, there is a variation from minimum to maximum of ~80%, with a slight enhancement during summer months.

These relatively constant mean NO_2 concentrations show no trends that would indicate strong influences from lightning produced NO_x (LNO_x). LNO_x peaks strongly in summer over South African Highveld, while lighting frequencies during three winter months comprise <1% (Ojelede et al. 2008). Total LNO_x production in the troposphere over the South African Highveld region was estimated to be ~10% of power plant production (Ojelede et al. 2008).

Critical level exceedance assessment for O_3

Annual mean O_3 values are assessed for exceedance of the annual critical levels for all the sites in Fig. 9. In the case of ozone, no exceedance of the measured annual mean was found for either 40 or 30 ppb concentration thresholds in either of the two annual cycles, although concentrations at several sites were relatively close to the 30 ppb threshold level. If error margins are taken into account, then a few sites only come closer the lower 30 ppb threshold—Standerton (site 1), Gluckstad

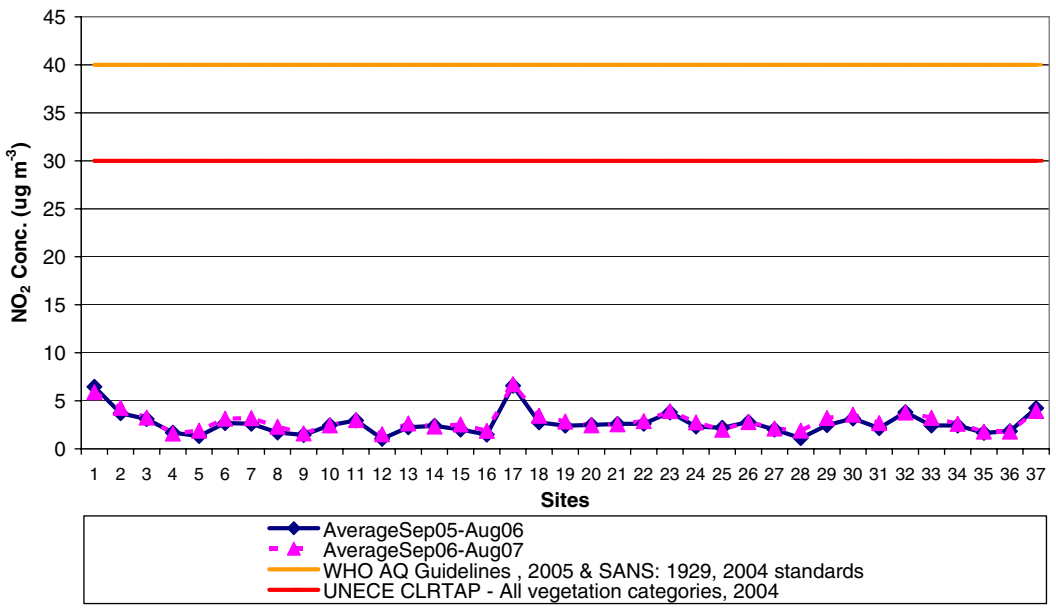

Fig. 7 Mean annual NO_2 concentrations for two annual cycles (September 2005 to August 2006 and September 2006 to August 2007) compared to annual critical levels

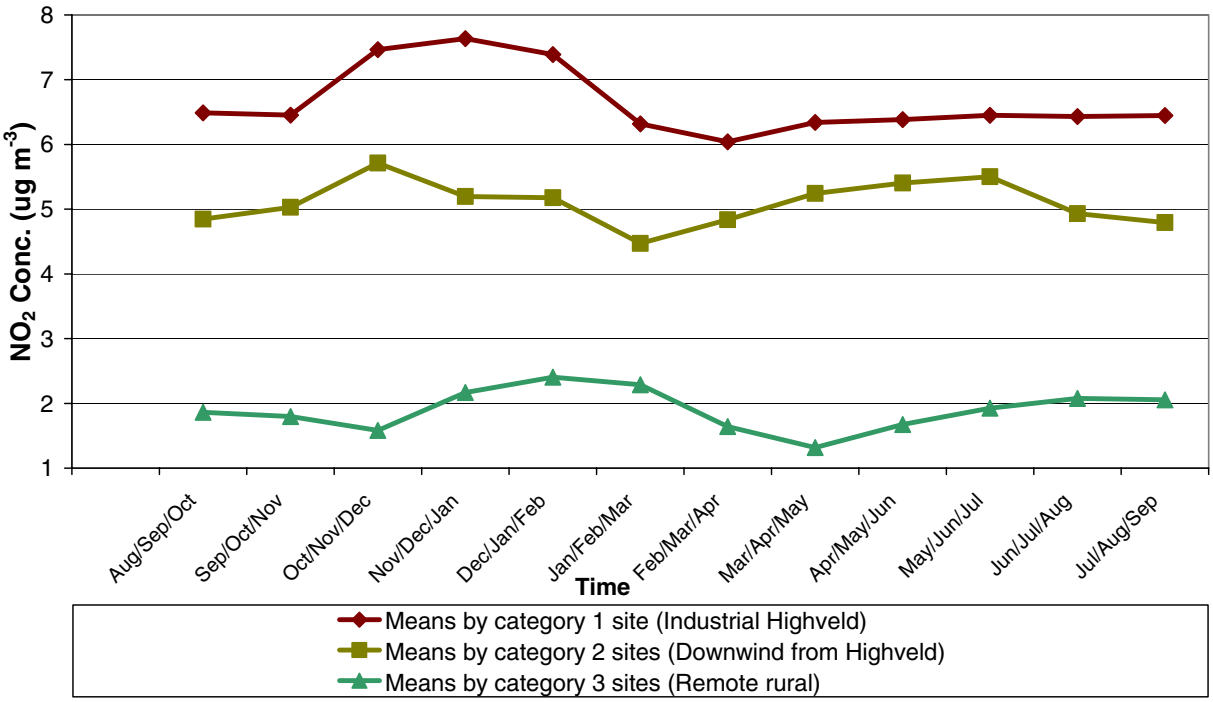

Fig. 8 Thee-month moving average NO_2 concentrations over two annual cycles (September 2005 to August 2006, and September 2006 to August 2007) for three different site categories

(site 8), Memel (site 26), Tolwe (site 35) and Louis Trichardt (site 36)—and not exceeded it.

Seasonal trends at the industrial Highveld, downwind and remote sites are shown in Fig. 10. All three sites show lowest concentrations during winter, as expected.

The remote sites show the strongest summer enhancement of ozone concentration. In contrast,

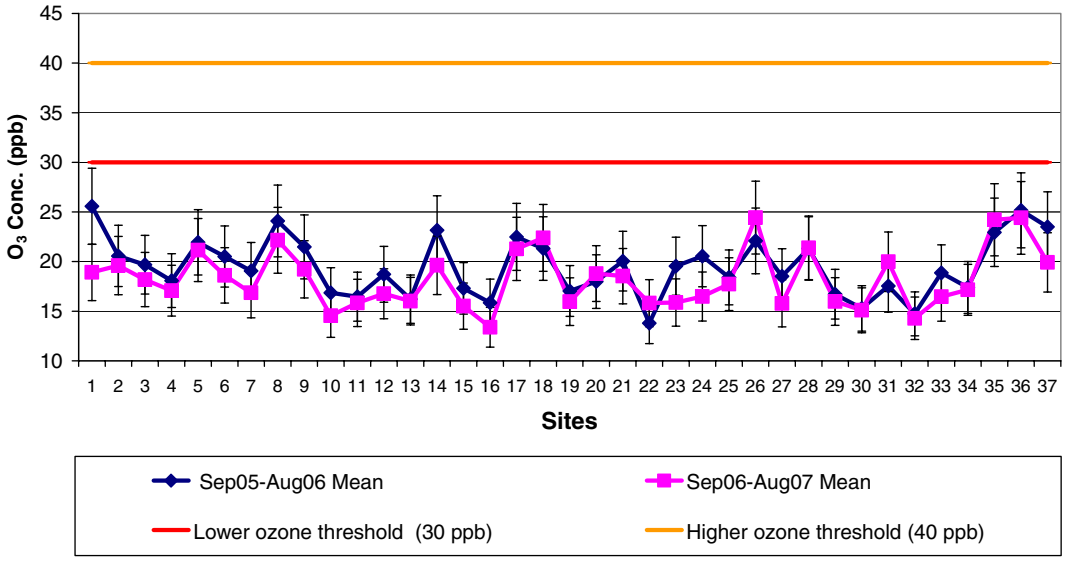

Fig. 9 Mean annual O_3 concentrations for two annual cycles (September 2005 to August 2006 and September 2006 to August 2007) compared to O_3 annual average critical levels. The error bars are set at 15% (Tang and Lau 2000)

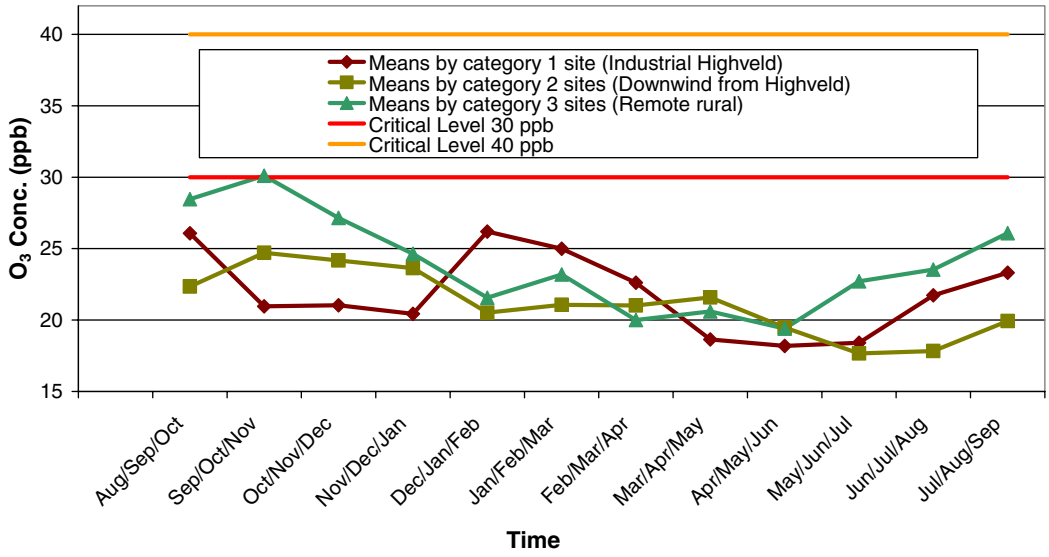

Fig. 10 Three-month moving average O_3 over two annual cycles (September 2005 to August 2006 and September 2006 to August 2007) for three different site categories

the pattern for the industrial Highveld appears erratic and does not follow the common understanding that ozone production in the troposphere is highest during summer due to greater solar radiation. The mean for remote sites and slightly less for the sites downwind from industrial Highveld show the highest records for spring months and secondarily for late winter. However, the industrial Highveld category site shows the highest records for mid-summer months. Increasing ozone concentrations are observed in late winter and early spring. This pattern is logical, as this season has increased pyrogenic ozone precursors from wild fires to the north and within South Africa (Swap et al. 2003) and, together with increased sunlight and daytime, results in higher readings for remote sites. Overall, Fig. 10 shows highly variable regional ozone generation and distribution. Certain temporal and spatial regional trends can be recognised. However, both monthly and long-term averages are below the critical levels.

When the exceedance was assessed through the different sites categories, site category 1 (central industrial Highveld) reached the lower threshold level once in late summer, while sites of category 2 (downwind industrial Highveld) reached it once in late spring only. In category 3 (remote rural), ozone slightly exceeded the lower threshold once in late spring. This temporal trend and spatial pattern confirm ozone assessment findings based on the annual averages.

Discussion and conclusions

The concentrations and spatial distributions for SO_2, NO_2 and O_3 were measured monthly over two annual cycles at 37 sites across the northern and eastern areas of South Africa. Low concentrations were recorded upwind and in areas remote from the Mpumalanga industrial Highveld. Increased concentrations were recorded in the centre and immediately downwind from Highveld source region. Inter-annual differences for SO_2 and NO_2 were not substantial, although SO_2 showed larger inter-annual variations than NO_2. Seasonal trends for SO_2 were apparent, winter having the highest concentrations. Second highest concentrations occurred in spring or autumn, depending on site. For NO_2, the seasonal trends were less obvious. However, summer with late spring and early autumn had slightly elevated levels compared to the remainder of the year.

Ozone concentrations had distinctly different space and time distribution patterns. Increased

concentrations were recorded outside of the industrial pollution area towards the edges of the study area, both south and north, compared to the central area over the Mpumalanga Highveld. In terms of the inter-annual ozone comparison, concentrations for the majority of sites did not fluctuate widely from year to year. In terms of seasonal comparisons, late winter and most of spring had elevated ozone concentrations, with summer lower and autumn the lowest concentrations.

There were multiple exceedances of critical levels for SO_2 in the Highveld industrial source area. Only the lowest critical level was exceeded for the sites located downwind. SO_2 critical levels were not exceeded at the remote locations stations either downwind or upwind from the source. The sites downwind and closer to the industrial Highveld are influenced by SO_2 emissions from known power plant and industrial sources, while remote sites do not show elevated SO_2 distribution.

NO_2 did not exceed any critical level at any site. However, NO_2 concentrations were higher at sites within and downwind of the industrial Highveld source area, compared to remote sites. Although far below the critical levels, a temporal trend is recognizable, indicating relative increases during the summer. Observed seasonal trends of NO_2 do not reflect the known pattern of lightning produced NO_x (strong summer production, close to zero winter production); thus. LNO_x is not expected to be the significant contributor to the observed concentrations. Nevertheless, further investigations of the contribution of LNO_x to the budget of NO_2 in the boundary layer are recommended.

Ozone exceedance of the lowest concentration critical level occurred at several sites. Exceedances occurred for remote sites located both north and southeast off the industrial Highveld. No exceedance of higher critical level was measured. Ozone exceedance for the growing season shows a similar pattern. The representative sites and their means showed that a slight maximum during late winter and early spring. The distribution of ozone is close to uniform on a regional basis, without a localised maximum on the industrial Highveld that was characteristic of SO_2 and NO_2, confirming the mixed origin of ozone precursors and the regional nature of ozone. The most sensitive plant species like lichens will be negatively affected in the central study region.

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