Comparisons of Meso-Scale Air Pollution Dispersion Modelling of SO_2, NO_2 and O_3 Using Regional-Scale Monitoring Results

M Josipovic[1], HJ Annegarn[1], GD Fourie[2], M Zunckel[3], MA Kneen[1]
1. Department of Geography, Environmental Management & Energy Studies, Uni versity of Johannesburg,
2. Sasol Technology Research and Development – Atmospheric Impact Research Group
3. CSIR Environmentek/uMoya-NILU

Abstract

Results of a regional-scale monitoring campaign were compared with two meso-scale to sub-continental modelling studies, for SO_2 and NO_2 and O_3 respectively (Fourie, 2006, Zunckel *et al.*, 2006, van Tienhoven et al., 2006, Van Tienhoven and Zunckel, 2004). However, a direct validation of the monitored results with modelled results could not be carried out, as available modelling studies dealt with different periods from the monitoring study.

For this study, three monitoring sites were selected for comparison with modelling results. These sites were strategically selected to be representative of the entire region. Site Elandsfontein in the centre of the industrial Highveld, site Amersfoort, downwind from the central pollution source region and site Louis Trichardt, a remote site. Sulphur, nitrogen and ozone species comparisons were considered in turn. The comparisons were carried out for equivalent annual (and seasonal) cycles. The comparisons produced mixed results. For sulphur and nitrogen species in most cases, depending on site and season, modelling results ranged between significant underestimates to overestimates. Ozone modelling almost always overestimated the concentrations compared to the measured results.

Despite several limiting factors, constraining the reliability of the comparisons between the modelled and measured results, they were important as the distribution of the gases showed patterns that imply understanding of the source and fate of these pollutants. The uncertainty in the magnitude of the model inaccuracies as well as margin of error of the measured data remained. Thus a modelling validation is recommended using the concurrent period with fewer uncertainties.

Keywords: Monitoring, modelling, concentrations, depositions, dry, wet, SO_2, NO_2 and O_3, Highveld, comparison.

1. Modelled and Measured Comparison

An optimal application of atmospheric (numerical) models should include, besides its calibration, eventual evaluation with relevant air quality monitoring data, in order to determine its applicability and minimise future (forecasting) errors. The measured concentration data derived from a monitoring project, with derived computations of dry and wet deposition, provided results for comparisons with two suitable regional scale sets of the modelled concentration and deposition results. The comparisons of the monthly measured sulphur and nitrogen compounds are presented for two annual cycles and for seasonal periods for concentrations, and for dry and wet depositions. A regional scale ozone concentration comparison was carried out of modelled versus monthly measured project data, for two growing seasons, as the modelling data did not extend to a full annual cycle (Zunckel *et al.*, 2006).

2. Comparison of modelled and measured results for sulphur and nitrogen

Modelled concentrations were compared to monthly measured results for 12 months, January to December. The seasonal averages of the measured monthly concentrations were calculated by averaging each month during the entire observation period, January 2005 to September 2007. Some monthly means were the average of

three, others of two months; depending on how many times a particular month occurred during the monitoring campaign. The modelled results for sulphur and nitrogen concentrations and depositions were derived from "Modelling the Long-range Transport and Transformation of Air Pollutants over the Southern African Region", the doctoral thesis of Fourie (2006). A long-range air pollution transport and diffusion model with atmospheric chemistry was developed, using a combined Lagrangian-Eulerian approach. Fourie ran his modelling for the period January to December 2000.

Presented is a comparison of the measured results averaged over the period 2005 to 2007, to the modelled results that used the meteorological data for 2000 and emission inventories from two sources from circa 1995 and 2000. Methodologically such a comparison could be challenged. For this it is important to state important assumptions that preceded the comparison:

- It is assumed that the source activity has not changed significantly between the modelled and measured years – a reasonable assumption as there have been no new large power plants commissioned or decommissioned.

- As the averaging periods used are monthly, obvious daily variations in meteorology are averaged out. However, it is assumed that there are no significant inter-annual variations in synoptic meteorology. This might be a weak assumption, as significant changes in air transport patterns occur depending on the phase of the ENSO cycle, as recently shown by Kanyanga (2008).

Acknowledging these possible weaknesses, the comparison is made as a first step towards validating the most recent available regional modelling estimates against the only available set of comprehensive regional measured concentrations.

For sulphur and nitrogen, tabulated modelled concentrations and depositions were available at three regional locations corresponding to the monitoring sites for this project – Amersfoort (**AF**), Elandsfontein (**EF**) and Louis Trichardt (**LT**).

2.1. Comparison of annual average SO_2 ambient concentrations

The model concentrations *under-estimated* the measured concentrations significantly at these locations. This could be due to the coarse resolution of the modelling domain leading to smoothing of the peak plume impacts. Alternatively, the differences may be due to inter-annual synoptic meteorological differences, which affect the transport and fate of the pollutants.

In terms of absolute and relevant number differences (the annual concentration means), they are given in Table 1.

Table 1: SO_2 mean annual concentration comparison for all three sites

Sites	*SO_2 annual mean (2000) modelled ($\mu g\ m^{-3}$)*	*SO_2 annual mean (Jan05-Sep07) measured ($\mu g\ m^{-3}$)*	***Relative difference (modelled – measured) / measured (%)***
AF	*5.1*	*12*	***-58%***
EF	*17*	*29*	***-41%***
LT	*0.6*	*2.1*	***-71%***

2.2. Comparison of annual sulphur dry deposition rates

The sulphur dry deposition results were compared in a similar way. For this comparison the resulting values were for the period from September 2006 to August 2007 (one annual cycle) while the modelled data compared was for the time period from January to December 2000 (Table 2).

Table 2: Sulphur dry deposition modelled (SO_2 and SO_4^{-2}) and measured (SO_2) comparison

Site	Modelled dry S deposition (2000) (kg $ha^{-1}\ yr^{-1}$)	Measured dry S deposition (Sep06-Aug07) (kg $ha^{-1}\ yr^{-1}$)	Relative difference (modelled – measured) / measured (%)
AF	3.3	3.7	-2%
EF	9.7	8.3	16%
LT	0.56	0.60	-1%

The strong influence of different deposition velocity rates (V_d), for modelling and to convert measured concentrations from this work (applied to both S and N species) seems to be the reason, which resulted in the modelling depositions being closer to measurements than for the comparison of modelling and measured concentration data. The V_d values used by Fourie (2006) from which the modelling results are derived are higher than the Vd values from Mphepya (2002) applied to measured results for inferential depositions. If the same V_d values were chosen, the modelled and measured deposition rates would differ by a factor of two.

2.3 Comparison of sulphur annual wet deposition rates

The measured wet deposition results are derived from calculating the measured concentration of the species of interest in the rain and the precipitation rate. The rain chemistry data was obtained from a long-term (ten-year) Eskom network of precipitation monitoring for the study region (Turner and de Beer, 1996). As the wet deposition is highly dependant on rainfall that varies considerably between years, comparisons of wet deposition rates show much more variability. Both sulphur and nitrogen wet deposition species should show a strong deposition correlation with the annual differences and particularly seasonality of rainfall. (Table 3)

Table 3: Wet sulphate deposition comparison for three sites

Sites	Modelled mean annual SO_4^{-2} (kg ha^{-1} yr^{-1})	Measured (Sep06-Aug07) mean annual SO_4^{-2} (kg ha^{-1} yr^{-1})	(modelled – measured) / measured (%)
AF	6.3	3.7	69%
EF	14	4.4	218%
LT	1.9	1.0	98%

The modelling overestimated the measurement for all three sites but this is not significant as changes in the precipitation measured during the monitoring and modelling periods explain these differences (Figure 1).

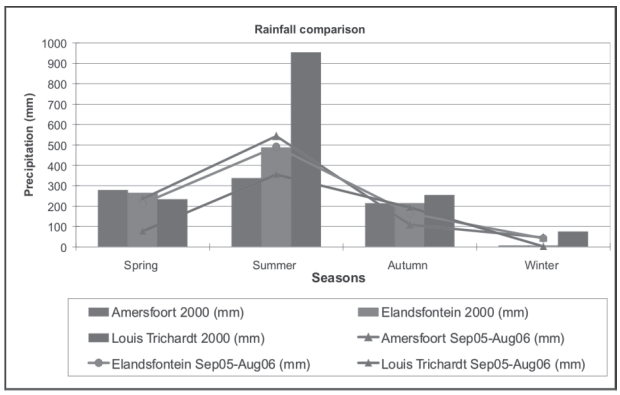

Figure 1: Seasonal rainfall comparison for three representative sites.

However, the substantial difference between the relative difference in wet sulphate deposition and relative difference in the rainfall data does not fully support a near-levelled sulphate deposition in winter with the rest of the seasons either for the Louis Trichardt site or for other two sites.

2.4 Comparison of annual average NO_2 concentrations

The annual mean of the modelled concentrations is substantially higher than the measured value for Elandsfontein (industrial Highveld), while the opposite is the case for Louis Trichardt (remote rural). The difference for Amersfoort (downwind off Industrial Highveld) is small (Table 4).

Table 4: NO_2 mean annual concentration comparison for all three sites

Sites	Modelled NO_2 annual mean (2000) (µg m^{-3})	Measured NO_2 annual mean (Sep05-Aug07) (µg m^{-3})	(Modelled – measured) /measured (%)
AF	*4.3*	*3.9*	10%
EF	*13*	*6.7*	88%
LT	*0.90*	*1.8*	-50%

2.5.Comparison of annual nitrogen dry deposition rates

The nitrogen dry deposition rates were based on measurements during the period from September 2006 to August 2007(one annual cycle), while the modelled deposition results cover the time-frame from January to December 2000.

The nitrogen dry deposition rates (which directly depend on the atmospheric concentrations for their results) have similar patterns to the concentration annual comparison (Table 4). The large modelling *overestimation* relative to measurements for Elandsfontein sites is a stark contrast to the moderate *underestimation at the* Louis Trichardt site and similar results for Amersfoort. A possible cause could be that in the modelled dry nitrogen deposition, nitrous oxide (NO) deposition was included in the calculation as a separate species, which amounted to a substantial portion of total N deposition. For the measured dry deposition calculation, only NO_2 concentrations were available. Close to the source region, the fresh emissions might be anticipated to still have a high fraction of unprocessed NO present. The site in the central industrial Highveld (Elandsfontein, site 17) has much higher modelled values (88%) while the values for remote site (where there would be little unconverted NO) is under-matched by ~50% (Table 5). See next page.

Table 5: Nitrogen modelled and measured dry deposition comparison

Sites	Modelled cumulative N dry deposition (2000) (kg ha^{-1} yr^{-1})	Measured cumulative N dry deposition (2006/2007) (kg ha^{-1} yr^{-1})	(Modelled – measured) /measured (%)
AF	0.64	0.62	3%
EF	1.9	1.01	88%
LT	0.13	0.27	-52%

2.6..Comparison of average annual nitrogen wet deposition rates

The nitrogen *wet deposition* pattern shows that the modelled results overestimate the measured results for all three sites (Table 6).

Table 6: Nitrogen cumulative wet deposition for all three sites

Sites	Modelled N cumulative wet deposition (2000) (kg ha^{-1} yr^{-1})	Measured N cumulative wet deposition (2006/2007) (kg ha^{-1} yr^{-1})	(Modelled – Measured) /Measured (%)
AF	2.7	1.41	94%
EF	5.1	1.66	208%
LT	1.1	0.43	149%

A comparison of precipitation data show that the precipitation for the modelled period is higher than the precipitation sum for the measured period for two of three sites (Elandsfontein and Louis Trichardt) (Figure 1). Thus, *overestimation* of wet nitrogen deposition is greater than expected for Louis Trichardt, indicating possible systematic model *overestimation* for the distant site(s).

3. Comparison of modelled and measured concentrations of ozone

The measured ozone concentrations for South African growing season were compared with the ozone modelling concentrations from the Cross Border Air Pollution Impact Assessment Project (CAPIA). The Comprehensive Air Quality Model with extensions (CAMx), version 4.00 (ENVIRON, 2003), was used by the CAPIA modellers. The measured results were compared numerically and spatially. The CAPIA modelling results were supplied by the Natural Resources and the Environment Division of Council for Scientific and Industrial Research (CSIR) (Zunckel *et al.*, 2006, van Tienhoven *et al.*, 2006).

Comparable growing seasons October through April (2005 to 2007) were extracted for analysis. CSIR ozone modelling results were available for October 2000 to April 2001.

A comparison diagram for the comparable growing seasons shows significant disparity for most of the sites (Figure 2).

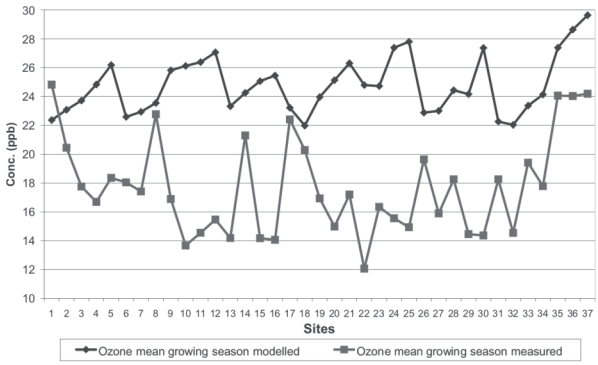

Figure 2: Comparison of ozone concentrations modelled for the growing season (Oct00-Apr01) to measured concentrations, averaged for the two growing seasons (Oct05-Apr06 & Oct06-Apr07), for all monitored sites

There is no satisfying agreement between the monitored and modelled concentrations in the seasonal averages over all sites, although both measurement and modelling indicate a zone of relatively elevated ozone concentrations for the northernmost sites (sites 35, 36 and 37, in northern Limpopo Province). The modelling over-estimated the concentrations over entire region except for site 1.

The differences varied from site to site and ranged from -10 % to +106 % below or above the measurement mean. The mean variation between modelled and measured was 33% *overestimation*. However, the absolute and relative differences between the modelling and measurements for ozone were of smaller amplitude in comparison with the differences established for sulphur and nitrogen concentrations.

Despite a few outlying modelled concentrations, the differences between measured and modelled concentrations are generally less than 5 ppb. During the mid-summer months, December 2000 to March 2001, the modelled surface ozone concentrations are consistently higher than the measured values. This is possibly attributed to higher biogenic emissions during the summer

resulting in higher modelled ozone (Zunckel *et al.*, 2006).

Several inherent limits had to be accepted preventing better comparison for ozone between the CAPIA project and ozone measured for this study. The modelling took into account ten daylight hours per day for five days a month, extrapolated into a monthly mean average. As daylight ozone concentrations are inevitably higher than night time values, this selection of daily modelling hours could already explain much of the discrepancy between modelled and measured values (mean 33% overestimation). While the measurements were taken from the monitoring stations positioned at 1.5 m above surface, the CAMx model provided an estimate of the concentrations in a grid block of 2 500 km^2 and a 70 m deep lower tropospheric layer. Also, anthropogenic emissions used in CAPIA project did not include all emission sources. The biogenic emissions were limited to only three volatile organic compounds (VOC) species emissions, while emissions from biomass burning sources were entirely excluded.

The influence of the air transport on oxidation of ozone precursors and other strong local (and regionally positioned) sources such as biogenic and pyrogenic are likely to have significant impact on ozone concentrations and distributions (at least for the sites positioned in the northern zone of the study area – Limpopo region) (van Tienhoven and Scholes, 2003, Zunckel *et al.*, 2006). Some relatively elevated concentrations areas were also recorded in places south and southeast of the study area (comparable to the increased concentrations in the north of the study area but more isolated in time). No clear cause could be established through this study. One possibility under consideration includes the transport (and transformation) of ozone precursors from the central industrial area mixed with locally generated ozone precursors of mixed origin: anthropogenic, biogenic and pyrogenic.

Overall ozone observations confirm prior spatial modelling (although not its maxima) results. A broad area of increased concentrations in far north of South Africa confirms existence of slightly elevated concentrations in comparison to the central study region. In addition, the modelled-measured matching for this sub-region confirms seasonality of ozone peaks and their origin, positioned far north, distant from the central anthropogenic pollution source region, but downwind of the main pyrogenic and on-path of the Highveld re-circulated air mass stream.

4. Measured and modelled comparison conclusions

In most cases, modelled SO_2 concentrations underestimated the measured values. The modelled dry deposition rates of S (SO_2 and SO_4^{2-}) were approximately equal to the calculated rates based on measured concentrations. The modelled S wet deposition rate (SO_4^{2-}) comparison although varied from site to site generally overestimated the results based on the measured parameters for all compared sites and seasons. The wet deposition comparison gave a larger range of differences, but most of these disparities could be explained by variations in the precipitation.

NO_2 concentrations were generally overestimated. The NO_2 dry deposition rates *overestimated* the measurements for the central and close downwind site but *underestimated* for the remote site Wet modelled deposition rates (NO_3^-) *overestimated* the rates inferred from concentrations from this study (NO_3^- only) for all compared sites in all compared seasons.

One interesting finding is that the modelled seasonal trends are less well matched with the evidence from measured (and calculated on the basis of the measurements) seasonal trends for all three species (S, N and O_3). It is possible that such differences are a reflection of differences in the meteorological information for the different years. Ideally, further research would be valuable to establish more accurately reasons for seasonal disparities.

The modelled ozone concentrations overestimated the measurements results. However, the absolute and relative differences in ozone were of smaller amplitude in comparison with the differences established for sulphur and nitrogen. The agreement between the modelled and the measured ozone concentrations was closer at the northern background stations. Both modelling and measurements have traced areas of increased ozone concentrations for the northern region of South Africa. Several limiting factors constrain the reliability of the comparison between the modelled and measured ozone. These factors were considered to have increased uncertainties.

The different air transport as well as differing annual meteorology influenced those differences. Long-term air mass movement research was taken into account. However, strong links between the air mass movements from the central, Industrial Highveld region with the ground level concentration of the studied trace gas species were not apparent. In contrast, rainfall differences were much more recognisable, more so in annual than seasonal modelled results.

Ideally modelling should be repeated for a period corresponding to the measurement period in order to give a more accurate assessment. However, the general patterns predicted by the modelling were shown in the monitoring results and they confirm that the general understanding of the emissions and their fate is accurate.

Acknowledgments

The study was a joint project of Department of Geography, Environmental Management and Energy Studies, University of Johannesburg; Climatology Research Group, University of the Witwatersrand, Johannesburg, and Atmospheric Chemistry Research Group, North-West University, Potchefstroom. Thanks are extended to all those involved, with special thanks to Dr K. Martins for the laboratory work conducted at the North West University and Mr Warren Carter from CSIR for supplying the CAPIA extract data.

The study was funded jointly by Anglo American Corp, Eskom and Sasol, with matching contributions from the Department of Trade and Industry's THRIP programme. M. Josipovic acknowledges the support of a NRF Grant Holder's Bursary, an Oppenheimer Memorial Trust Fellowship (16068) and a Sasol Fund supplementary bursary through the Faculty of Science, UJ. The work was supported in part by an NRF Focus Area Project grant to HJA - Sustainability Studies using GIS & Remote Sensing FA2005040600018.

References

Fourie D.G. 2006, 'Modelling the Long-range Transport and Transformation of Air Pollutants over the Southern African Region', PhD thesis, North-West University, Potchefstroom, South Africa.

Kanyanga J.K. 2008, 'Atmosphere-Biosphere Interactions: El Niño Southern Oscillation (ENSO) and Atmospheric Transport over Southern Africa', PhD thesis, University of Johannesburg, Johannesburg.

Mphepya N.J. 2002, 'Atmospheric Deposition Characteristics of Sulphur and Nitrogen Compounds in South Africa', PhD thesis, The Potchefstroom University for Christian Higher Education, Potchefstroom, South Africa.

Turner C.R. and de Beer G. H. 1996, A Review of Ten Years' Rain Quality Data from the South African Interior, Report TRR/S96/1341, Eskom, Johannesburg, South Africa.

Van Tienhoven A.M. and Scholes M.C. 2003, 'Air pollution impacts on vegetation in South Africa', in L.D. Emberson, M.R. Ashmore, F. Murray (eds), *Air Pollution Impacts on Crops and Forests: a Global Assessment*, Imperial College Press, London, UK, pp. 237–262.

Van Tienhoven A.M. Zunckel M., Emberson L., Koosailee A. & Otter L. 2006, 'Preliminary Assessment of Risk of Ozone Impacts to Maize (Zea Mays) in southern Africa', *Environmental Pollution* **140**: 220–230.

Van Tienhoven A.M. and Zunckel M. 2004, 'Cross-border air pollution in SADC Region', Report No. ENV-D-C 2004-017, Department of Science and Technology, internet accessed January 2006, http://dbn.csir.co.za/capia/documents/Final_Report.pdf.

Zunckel M., Koosailee A. Yarwood, G., Maure G, Venjonoka K., van Tienhoven A.M. & Otter L. 2006, 'Modelled surface ozone over southern Africa during the Cross Border Air Pollution Impact Assessment Project', *Environmental Modelling & Software, **21***: 911–924.