Spatial and temporal assessment of gaseous pollutants in the Highveld of South Africa

Diverse natural and anthropogenic activities in the Highveld of South Africa contribute to elevated levels of inorganic and organic gaseous pollutant species. The primary aims of this investigation were to determine spatial and temporal distributions of nitrogen dioxide (NO₂), sulphur dioxide (SO₂) and ozone (O₃), as well as benzene, toluene, ethylbenzene and xylene (BTEX) in this area. Sampling was conducted on a monthly basis for a year at eight strategically selected sites. The highest NO₂, SO₂ and BTEX concentrations were measured at sites with significant local sources and/or sites impacted by more remote sources, as indicated by overlay back trajectories. O₃ concentrations were found to be lower at sites with high levels of NO₂, SO₂ and BTEX. NO₂ and SO₂ peaked during winter, while O₃ peaked in spring. NO₂ and SO₂ temporal concentration variations were ascribed to differences in seasonal meteorological conditions, as well as additional sources in winter. The O₃ peak coincided with a seasonal CO peak, which was identified as an important precursor for O₃ formation. No distinct seasonal trend was observed for BTEX. The annual average concentrations for SO₂, NO₂, O₃ and benzene were below the South African annual standards at all sites.

Introduction

The South African Highveld is known for its diverse anthropogenic activities, which include agriculture, metallurgical and mining operations, power generation (coal-fired power stations), petrochemical operations, coal dumps and transportation. The dry and cold winters (June to August) experienced in the Highveld also result in additional combustion of coal and wood for domestic heating, as well as increased occurrences of biomass burning (veld fires) (July-August). Anthropogenic activities contribute to elevated levels of gaseous pollutants in the atmosphere, which include the inorganic gaseous species nitrogen dioxide (NO₂), sulphur dioxide (SO₂) and ozone (O₃), as well as volatile organic compounds (VOCs) such as benzene, toluene, ethylbenzene and xylene (BTEX). Primary pollutants emitted into the atmosphere can also react and lead to the formation of secondary pollutants. VOCs, for instance, play a significant role in particle formation. VOCs can also act as precursors for ozone formation during photochemical reactions with NO₂, hence modifying the oxidising capacity of the atmosphere.

There are adverse human health effects associated with the abovementioned atmospheric pollutants and they are also harmful to ecosystems. Ozone is highly phytotoxic and can cause damage to crops and native vegetation. NO₂ and SO₂ could have long-term effects such as pulmonary asthma and chronic bronchitis respectively. Benzene is a known carcinogen and is associated with leukemia whereas toluene can cause problems such as foetal malformation.

In the last quarter of 2007 the South African Minister of Environmental Affairs and Tourism proclaimed eastern Gauteng and western Mpumalanga, in terms of the National Environmental Management: Air Quality Act, as a national air pollution hotspot termed the Highveld Priority Area (HPA). The HPA covers a surface of 31 106 km² and has a population of 3.6 million people. This declaration implies that national government takes responsibility for assessing levels of pollution and putting in place emission reduction plans, while local and provincial governments participate in the process. Apart from the local and regional importance of the HPA, satellite-based measurements have also indicated that this area has some of the highest NO₂ concentrations in the world, emphasising the global importance of this region.

In South Africa, whereas very little data exist for VOCs. Currently, measurements of air pollutants usually are carried out by local authorities (municipalities) and certain industries, which do not necessarily give a good spatial representation of larger areas. Most of these data sets are also not published in peer-reviewed journals, which makes it difficult to evaluate the data quality. Therefore, the primary aims of this investigation were to determine spatial and temporal...
distributions of ambient concentrations of NO$_2$, SO$_2$, O$_3$ and BTEX in the Highveld for one year.

Materials and methods

Sampling sites

Eight sampling sites were selected within a sampling grid of 600 km$^2$ as shown in Figure 1. The sites were selected to be representative of the Highveld. The sites were located in Vanderbijlpark, Delmas, Witbank, Ermelo, Carolina, Amersfoort, Standerton and Balfour. The site locations ranged from highly industrialised areas such as Witbank and Vanderbijlpark to the remote rural areas of Carolina and Amersfoort. Apart from localised pollution sources such as traffic emissions, household combustion and small industries, there are also larger pollution sources in this area (Figure 1), which include power stations, a petrochemical plant (Secunda) and metallurgical operations (based mainly in Witbank, Middelburg and Vanderbijlpark). Coal mining activities scattered across the entire sampling area could also be regarded as pollution sources (e.g. from materials handling and spontaneous combustion of coal). Additionally, emissions from the Johannesburg conurbation could also affect the measurement area.

The relevance of this investigation was further enhanced by a recent regional study conducted during 2005–2007, which identified the area under investigation as a pollution hotspot for SO$_2$ and NO$_2$. The eight sites selected for this study gave a higher monitoring resolution for the abovementioned hotspot.

Sampling equipment

Sampling commenced in August 2007 and was conducted for a year. Samples were exposed for a full month for which monthly averages were calculated.

Passive samplers developed and used by the Atmospheric Chemistry Research Group at the North West University were used for NO$_2$, SO$_2$ and O$_3$ measurements. The passive samplers consisted of two plastic snap-on caps with a stainless steel mesh (25 mm o.d., thickness of 160 μm and porosity of 40%), a 175-μm Teflon PTFE filter (GIC, Johannesburg, South Africa) with an outer diameter of 25 mm, a porosity of 85% and an impregnated paper disc (Whatman filter, GIC, Johannesburg, South Africa) at the rear end. The plastic snap-on caps and the stainless steel mesh were manufactured by the instrument makers of the North West University. The mesh and PTFE filter prevented aerosols from diffusing into the sampler. The Whatman filter was impregnated with a specific chemical to react with and trap the pollutant of interest. Samplers were prepared and stored in a freezer prior to sampling. Exposed samplers were stored similarly before analysis.

Tenax TA adsorbent tubes (Sigma-Aldrich, Johannesburg, South Africa), which are commonly used for BTEX sampling, were used in accordance with the US EPA TO-17 Compendium method. The tubes were tested for leaks and preconditioned with helium for 30 min at 350 ºC at a flow rate of 50 cm$^3$/min before they were used. After treatment, the tubes were sealed with Swagelok® brass ¼” caps (P/N 0990-8851, Sigma-Aldrich, Johannesburg, South Africa).
and stored in a freezer. The Swagelok® caps were removed before exposure in the field and replaced with diffusive caps for effective air diffusion into the tubes. In order to attain reproducibility, two samplers for each station were exposed for an entire month. After sampling, the tubes were removed and closed with the Swagelok® caps. Each tube was separately wrapped in aluminium foil and stored in a freezer before analysis.

**Chemical analysis**

Inorganic gaseous species were analysed using two different analytical methods as previously described. SO₂ and O₃ samples were analysed on a Dionex Ion Chromatograph System (ICS-3000, Anatech Instruments, Johannesburg, South Africa) connected to a Micromass AutoMatrix™ time-of-flight mass spectrometer (TOF-MS) detector. The samples were introduced into the gas chromatograph using a PerkinElmer® TurboMatrix™ desorber (Shelton, Connecticut, USA). The equipment was set up and used as prescribed by the US EPA TO-14 Compendium method. A suitable calibration standard (Cat no: 41900-U, Supelco, Taipei, Taiwan), which contained 39 VOC compounds (100 ppb), was used as an external standard.

**Overlay back trajectories**

Individual hourly back trajectories with an arrival height of 100 m were compiled in HYSPLIT 4.8. The duration of each back trajectory was taken as 96 h (i.e. 4 days). An arrival height of 100 m was chosen because the orography in HYSPLIT is not very well defined, thus lower arrival heights could result in increased error margins on individual trajectory calculations. Considering the above, 24 back trajectories per day per site were obtained for the monitoring duration of one year. For each site individual back trajectories generated in HYSPLIT (24 x 365 days) were superimposed in MATLAB 7.8.0. In the overlay back-trajectory graph compiled with MATLAB 7.8.0 a colour code indicates the percentage of trajectories passing over 0.2° x 0.2° grid cells, with red being the highest percentage.

**Results and discussion**

**Spatial distribution**

The spatial distribution of the annual average concentrations of the measured inorganic gases is presented in Figure 2. NO₂ and SO₂ levels were the highest at sites situated in or near industrialised areas. The highest O₃ concentrations were recorded at sites positioned in more rural areas. It is also evident that sites with the highest SO₂ and NO₂ concentrations exhibited the lowest O₃ levels, while higher O₃ concentration coincided with lower SO₂ and NO₂ levels.

Although NO₃ is a precursor for the formation of tropospheric O₃, high NO₂ in polluted areas does not necessarily imply high O₃ levels, because O₃ is rapidly consumed during oxidation of other pollutants. When the pollution dilutes through transportation, O₃ levels will increase if NO₃ and radiation are not limiting factors. For the same reason, virtually no O₃ is observed in a plume close to a point source, while O₃ increases as dispersion occurs.

In an effort to determine the link between sources and measured pollutant species concentrations, overlay back trajectories for the entire 12-month sampling period for every measuring station were generated (Figure 3). Each monitoring station in these figures is indicated by the point where two perpendicular white lines cross. In addition, these white lines also divide the area into sectors aiding the identification of dominating air mass movements towards sampling sites. The black lines in Figure 3 are contour timelines that indicate the average trajectory position in each direction at a given time. The overlay back trajectories obtained indicate that the predominant movement of air masses were from a northerly to easterly direction at most of the measurement sites during the sampling period.

As can be seen in Figure 2, the combined annual average concentrations of NO₂ and SO₂ were the highest at Witbank, which can be partially attributed to industrial and mining activities in the immediate proximity of this highly industrialised area. Major point sources in the immediate vicinity include a host of metallurgical operations i.e. ferrochrome, vanadium, manganese and steel smelters, as
FIGURE 3: Hourly 96-h back-trjectories with 100-m arrival heights for the period from July 2007 to August 2008 for: (a) Witbank, (b) Delmas, (c) Vanderbijlpark, (d) Carolina, (e) Balfour, (f) Standerton, (g) Amersfoort and (h) Ermelo.
well as coal-based industries such as char and electrode paste production. In addition to local sources, anthropogenic activities further away from the site could also contribute to increased NO\textsubscript{2} and SO\textsubscript{2} concentrations. Overlay back trajectories (Figure 3a) for this site show dominant incoming air mass movements from the sector between the north and south-east. In this sector there are several additional major point sources i.e. three coal-fired power stations, as well as ferrochrome and stainless steel plants at Middelburg (about 27 km from Witbank) that could contribute to measured pollutant levels. It can also be expected that smaller industrial, traffic and household sources would contribute to the presence of pollutant species at this site.

The second highest combined annual average concentrations of NO\textsubscript{2} and SO\textsubscript{2} were measured at Delmas. In contrast to Witbank, Delmas is set in rural surroundings suggesting that the relatively high pollutant levels could not be ascribed to major local sources. Overlay back trajectories (Figure 3b) for this site show dominant incoming air mass movements from the sector between the north and south-east. This sector includes Witbank, which implies that the same sources that had an impact on Witbank would have an effect on Delmas, with some dilution, as the two sites are about 62 km apart. In the north to south-easterly sector of Delmas there are, however, also three additional coal-fired power stations and a petrochemical plant that could also contribute to higher levels of NO\textsubscript{2} and SO\textsubscript{2}. It can therefore be concluded that the relatively high pollutant concentrations at Delmas were a direct result of air mass being swept over an area with several major sources.

Relatively high levels of NO\textsubscript{2} and SO\textsubscript{2} were also determined at Vanderbijlpark. This is also a highly industrialised area with numerous significant local sources such as petrochemical industries, steel smelters and a coal-fired power station. Figure 3c shows overlay back trajectories for this site, which indicate that the predominant air mass movement was from the sector between the north and east. The Johannesburg conurbation is within the 12-hour back-trajectory contour to the north-north-east of the measurement site in this sector, which indicates that it could contribute to the relatively high pollutant concentrations. Also, within this dominant sector of air mass movement there are several coal-fired power stations, a petrochemical plant and the metallurgical operations in the Witbank-Middelburg area within the 24-hour back-trajectory contour line.

In contrast to the abovementioned sites (Witbank, Delmas and Vanderbijlpark), the NO\textsubscript{2} and SO\textsubscript{2} concentrations at Carolina were the lowest. Carolina is a small rural town with no major local sources. The overlay back trajectories (Figure 3d) show that there are no major sources (Figure 1) within the 24-hour contour line in the dominant air mass movement sector between the north and south-east. It cannot, however, be regarded as an unpolluted background site because NO\textsubscript{2} and SO\textsubscript{2} levels are higher than those reported for South African background sites.\textsuperscript{23} As previously mentioned, the relatively high O\textsubscript{3} concentrations also indicate that this site is possibly impacted by aged polluted air masses.

Combined SO\textsubscript{2} and NO\textsubscript{2} concentrations at Balfour, Standerton, Amersfoort and Ermelo were lower than those recorded at Witbank, Delmas and Vanderbijlpark, but higher than those measured at Carolina. In general this can be explained by the fact that these stations do not have many significant local sources and are also further removed from most of the major point sources on the Highveld. Overlay back trajectories for these sites (Figure 3e–h) show dominant incoming air mass movements from the sector between north and east for Balfour and Standerton and from the north to south-east sector for Amersfoort and Ermelo.

Similar SO\textsubscript{2} concentrations were measured at Balfour and Standerton, while the annual average NO\textsubscript{2} concentration at Standerton was more than double that determined at Balfour. This can be attributed to the proximity of a single major point source 23 km north-north-east of Standerton (Figure 1). NO\textsubscript{2} has a shorter lifetime in the atmosphere than SO\textsubscript{2}.\textsuperscript{24} As similar emission concentration ratios of large point sources (especially coal-fired power plants) impacting on Balfour and Standerton are present, the longer lifetime of SO\textsubscript{2} results in similar SO\textsubscript{2} levels at both sites. In contrast, the nearby source at Standerton results in higher NO\textsubscript{2} levels. This explanation is supported by the finding that O\textsubscript{3} concentrations were higher at Balfour than at Standerton.

Ermelo and Amersfoort had the same annual SO\textsubscript{2} concentration for the sampling period. The relatively low concentrations measured at Amersfoort were unexpected because there is a point source in close proximity to the measurement site. A plausible explanation is that this point source is not situated in the dominant incoming air mass movements sector, but in the south-west sector. To some extent NO\textsubscript{2} and SO\textsubscript{2} concentrations at Ermelo were anomalies because there are no sources in the dominant incoming air mass sector. The 12-hour back-trajectories contour line does, however, indicate some air mass movements from the westerly region, hence implying impact from the major sources in this area. This is confirmed by the slightly higher concentration of NO\textsubscript{2} which has a shorter lifetime than SO\textsubscript{2}.

The spatial distribution obtained during this investigation can be compared to results obtained during the previous study conducted during 2005–2007 over a larger area in the northern and eastern parts of South Africa.\textsuperscript{26} Both studies included sampling sites at Amersfoort and Standerton. The results obtained at these sites during 2005–2007\textsuperscript{27} are comparable to those measured in this study. Furthermore the 2005–2007 study identified a pollution hotspot in the Highveld. As mentioned previously, the eight sampling sites of the current investigation were situated within this hotspot. The enhanced sampling spatial resolution enabled the identification of a more localised hotspot i.e. the Witbank area.

The spatial distribution of the annual average concentrations of BTEX in the Highveld is shown in Figure 4. A similar spatial trend observed for NO\textsubscript{2} and SO\textsubscript{2} is evident for BTEX.
levels. BTEX concentrations were the highest at Witbank, Delmas and Vanderbijlpark. The concentrations measured at Balfour, Standerton, Amersfoort and Ermelo were lower, with Carolina registering the lowest levels. As indicated previously, the overlay back trajectories in Figure 3 can be used to clarify the link between measured levels, sources and the impact of meteorological conditions. The resemblance between the spatial distributions of BTEX and NO\textsubscript{2}/SO\textsubscript{2} therefore indicate possible corresponding sources for all these species. As the spatial BTEX distribution and linkage to sources (industrialised areas) were similar to that already discussed for SO\textsubscript{2} and NO\textsubscript{2}, in depth discussion on spatial distribution of BTEX is not given.

**Temporal distribution**

The monthly mean concentrations for inorganic gaseous species over the Highveld are shown in Figure 5. The error bars on the graph indicate the maximum and minimum concentrations measured at the different sites during the entire sampling period.

Seasonal trends were observed, with NO\textsubscript{2} and SO\textsubscript{2} peaking during winter while O\textsubscript{3} peaked in spring. Similar trends were observed in a previous investigation.\textsuperscript{14} NO\textsubscript{2} and SO\textsubscript{2} concentration variations can be explained by the difference in meteorological conditions experienced in the Highveld in winter and summer. The warm and wet summers are associated with unstable meteorological conditions, which increase the vertical motion and dispersion in the atmosphere. In addition, rain also scavenges pollutants more frequently from the atmosphere during summer. In contrast, winters are characterised by the formation of surface inversion layers inhibiting vertical atmospheric mixing and effectively trapping the primary pollutants.\textsuperscript{2,25} Increased occurrences of combustion for domestic heating during winter also contribute to elevated levels of SO\textsubscript{2} and NO\textsubscript{2}.

The seasonal variation of O\textsubscript{3} can possibly be ascribed to a combination of various contributing factors. During spring, relatively stable conditions (pre-rain season) still prevail, while there is an increase in photochemical activity (longer days). Several compounds, which are considered to be O\textsubscript{3} precursors, participate in the photochemical reaction with NO\textsubscript{2} in O\textsubscript{3} formation. However, it seems as if CO is probably the most important precursor in the South African context. The importance of CO as a precursor for O\textsubscript{3} formation is well described in the literature.\textsuperscript{26} Other authors\textsuperscript{27} also found CO and O\textsubscript{3} to peak at the same time during the year, i.e. spring, in South Africa. The origin of the CO peak during late winter and early spring can be attributed to the regional increase in biomass burning (veld fires).\textsuperscript{28} Previous investigations\textsuperscript{29,30} also ascribed seasonal trends to these factors, but did not specifically point out the significance of CO as a precursor.

Figure 6 shows the monthly mean concentration for BTEX measured in the Highveld. The error bars indicate the maximum and minimum concentrations for the eight stations. No distinct seasonal trend was observed for BTEX in the Highveld. A possible reason for the low levels of ethylbenzene and xylene can be related to their photochemical reactivity, which leads to faster degradation.\textsuperscript{5}

**Comparison to Ambient Air Quality Standards**

South African National Ambient Air Quality Standards have been established for criteria pollutants, which include SO\textsubscript{2}, NO\textsubscript{2}, O\textsubscript{3} and benzene.\textsuperscript{31} A list of the relevant standards is given in Table 1.

By comparison of the annual average concentrations for all gaseous species measured (Figure 2 and Figure 4) with the standards,\textsuperscript{32} it is evident that levels at all sites were below the annual standards. The results are of particular significance with regard to benzene, which is the only hydrocarbon species included in the new legislation. No national monthly average standards exist for the gaseous pollutant species considered during this investigation. Therefore, no conclusions can be made with regard to the monthly measured values in comparison to a standard.

A comprehensive investigation of benzene levels in the Highveld has been lacking up to now. The results indicate that there were months when values higher than 1.6 ppb (2015 standard\textsuperscript{33}) were measured at individual sites, with the highest value of 6 ppb measured in August 2007 at Standerton. The monthly benzene concentrations are, however, difficult to interpret within the South African legislative context, because no monthly standard for benzene exists in the local legislation. Benzene is currently the only VOC listed as a criteria pollutant in the South African Air Quality Act. It was
evident that toluene was significantly higher than benzene in all instances. Toluene also has negative effects on human health\(^1\) and is a precursor for \(O_3\) and secondary organic aerosols.

**Conclusions**

The highest \(NO_x\), \(SO_x\) and BTEX concentrations were measured at sites with significant local sources and/or sites located...
downwind from major point sources as indicated by dominant air mass movements. The measured O₃ concentrations were found to be inverse of the abovementioned species, that is, sites with high concentrations of NO₂, SO₂ and BTEX exhibited low levels of O₃. Witbank had the highest NOₓ, SO₂ and BTEX concentrations, while Carolina had the lowest. A NOₓ, SO₂ and BTEX hotspot was identified in the Witbank area.

NO₂ and SO₂ peaked during winter while O₃ peaked in spring. NOₓ and SO₂ seasonal concentration variations were ascribed to differences in meteorological conditions, that is, the conditions in winter are more stable than in summer. The O₃ peak coincided with a peak in veld fires, which resulted in elevated levels of CO – an important precursor for O₃. No distinct seasonal trend was observed for BTEX.

The annual average concentrations for SO₂, NOₓ, O₃ and benzene were below the South African annual standards at all sites. Although BTEX measurements were previously conducted in the Highveld, the BTEX data presented in this article is the first comprehensive published temporal and spatial data set.

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References