NITROGEN OXIDES ON THE SOUTH AFRICAN HIGHVELD

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Satellite retrievals have highlighted the South African Highveld as a region with one of the highest nitrogen oxide (NO_x) emission densities in the world. There are numerous sources of NO_x on the Highveld, including coal-fired power stations, petrochemical and other industries, motor vehicles and lightning, but surface measurements of NO_x have not indicated that there is any cause for concern. A number of research initiatives are being undertaken in an attempt to resolve the discrepancy between surface measurements and satellite retrievals of NO_x. An assessment of ground-level concentrations in various environments, including industrial and urban regions, has shown that NO_x levels recorded in the low-income urban area are significantly higher than those recorded downwind of industries or power stations. NO_2 column densities have been remotely sensed over the Highveld using an airborne imaging Differential Optical Absorption Spectrometer (iDOAS), in order to validate the satellite retrievals and investigate individual sources of NO_x. Results from the first campaign show high NO_2 integrated column densities in the immediate vicinity of sources. Well defined plumes can be observed downwind of prominent sources.

Keywords

Nitrogen dioxide, Highveld, DOAS, remote sensing, power stations, satellite

Introduction

The South African Highveld has been identified by satellite retrievals as an area of elevated nitrogen oxide (NO_x) concentration. Nitrogen oxides play a significant role in the chemistry of the atmosphere (Seinfeld and Pandis, 1998). NO_x is linked to the oxidizing effectiveness of the troposphere, directly via its role in the production of 03 and indirectly via its impact on the hydroxy! radical (OH). NO_x is of great concern because it is toxic in the form of nitrogen dioxide (NO2), and tropospheric ozone (O_3) which may be formed from NO_x is a greenhouse gas and is harmful to human health and vegetation. Concern has also been expressed about the high rates of nitrogen deposition and the consequences thereof (Lee *etal,* 1997)

Several research initiatives are currently underway to validate the NO_x 'hotspot' identified by satellite images, and to understand reactive nitrogen on the South African Highveld. NO_x measurements from four ground-based sites across the Highveld have been analysed in an attempt to ascertain baseline NO_x levels in different environments, and an imaging Differential Optical Absorption Spectrometer (iDOAS) has been flown on a research aircraft over the Highveld in order to validate the satellite retrievals and obtain high resolution imagery of NO_2 column densities over the region. Results of these studies will be discussed.

Formation and sources of nitrogen oxides

NO_x (which consists of nitric oxide (NO) and NO_2) is formed when atmospheric nitrogen is oxidised during high temperature combustion (>2000K) and electrical discharges, and by biogenic activity of micro-organisms within soil (Beirle, 2004). NO_x is primarily emitted as NO and rapidly oxidises when it comes into contact with 03 molecules to form NO_2 (equation R2). NO is also oxidized through the reaction with oxygen ($2NO + O_2$ --> $2NO_2$), but the reaction with O_3 dominates at ambient atmospheric conditions (Seinfeld and Pandis, 1998; Beirle, 2004). NO is emitted directly into the troposphere via nitrogen fixation (equation Rl).

$$N2 + O_2 \longrightarrow 2NO \quad (Rl)$$

$$NO + O_3 \dashrightarrow NO_2 + O_2 \quad (R2)$$

Natural tropospheric NO_x concentrations are around 10 - 20 ppt, but concentrations exceeding 200 ppb can be found in urban areas (Leue *et al.*, 2001). NO_x is emitted from sources which provide the high temperature combustion (or microbial action for soil emissions) which is required to split the N_2 molecule which combines with O_2 to create NO_x. Sources of NO_x are both natural and anthropogenic.

Fossil fuel burning

Combustion of fossil fuels is the greatest sources of tropospheric NO_x emissions globally, and it is estimated that NO_x emissions from fossil fuel combustion have more than doubled over the last century (Lee *et al.*, 1997). The high temperature combustion of fossil fuels facilitates the formation of NO. Coal- and gas-fired power stations constitute about a third of global anthropogenic NO_x emissions (Sillman, 2000). Major industrial and power plant sources of NO_x on the Highveld are shown in Figure

Emissions from motor vehicles

Due to the high temperatures in internal combustion engines, atmospheric N_2 combines with O_2 resulting in NO_x formation. It is estimated that 70% of tropospheric NO_x in urban areas comes from motor vehicles. There are usually marked maxima in NO_x concentrations during peak hour traffic times in both the morning and evening (Lal and Patil, 2001).

Aircraft emissions

NO_x emissions from aircraft constitute a very small amount in comparison with other sources (Lee *et al.*, 1997; Beirle, 2004). These emissions are important in the upper troposphere (8-12 km) where intercontinental flights occur (Beirle, 2004).

Lightning

Lightning is the largest natural source of tropospheric NO_x. According to Lee *et al.* (1997) lightning contributes ~12% of total NO_x emissions globally, although this estimate is extremely uncertain. In South Africa, it has been estimated that lightning contributes ~ 25% of tropospheric NO_x over the Highveld (Wenig *et al.*, 2003). High lightning NO_x concentrations are found over parts of the Highveld during summer, due to the nigh intensity of electrical storms (Annegarn *et al*, 2003; Figure 2). The area of highest lightning frequency coincides with the eastern Highveld, where most power stations are concentrated.

Biomass burning

In southern Africa, biomass burning mainly contributes to ambient NO_x concentrations during late winter and spring.

Biogenic soil emissions

NO_x is produced in soils by the biogenic activity of micro-organisms through denitrification (a conversion to free nitrogen) and nitrification (conversion of NH_4^+ into NO_3 - then into NO_2) (Lee *et al.*, 1997; Seinfeld and Pandis, 1998). Soils emit greater concentrations of NO than NO2. The level of NO_x emissions is determined by the soil moisture content. Soils with low moisture content exhibit nitrification, resulting in higher emissions of NO, whilst wetter soils promote denitrification and NO emissions are much lower. Over northern South Africa, drier savanna areas are common, thus the production of NO is favoured (Parsons and Scholes, 1996). However, biogenic soil emissions constitute a small percentage of total NO_x emissions.

Injection from the stratosphere

NO_x that is naturally produced through the destruction of N2O in the stratosphere may be transported into the troposphere in tropopause folding events (Seinfeld and Pandis, 1998). During these events, tongues of stratospheric air push into the troposphere transporting NO_x with them (Seinfeld and Pandis, 1998). These events occur predominantly in spring, but stratospheric injections constitute a very small percentage of NO_x production (Lee *et al*, 1997).

Surface measurements of NO_x

An assessment of surface NO_x levels has been conducted using continuous NO_x measurements collected at four of Eskom's active ambient air quality monitoring stations. These stations are in an industrial area (Elandsfontein); directly (2 km) downwind of a power station (Kendal); in a township (Dhlamini, Soweto); and some distance downwind of the industrialised region (Verkykkop) (Figure 3). Source Apportionment by Diurnal Signature (SADS) analysis (a tool developed by Clive Turner at Eskom to perform source apportionment based on the mean diurnal hourly average pollutant concentrations) has been performed to identify major source types affecting the different regions.

At sites mainly impacted by industrial and power station emissions (Elandsfontein, Kendal and Verkykkop), NO_x concentrations are highest during the day, reflecting the influence of tall stack sources (Figure 4). Surface inversions prevent NO from reaching the ground at night, but pollutants are brought to the surface during the day under convective boundary layer conditions. SADS analysis confirms that tall stacks are the dominant source of NO in the industrial source region, with contributions of 65% and 68% at Elandsfontein and Kendal, respectively (Figure 5).

Nevertheless, average NO_x concentrations are low in and downwind of the industrial region. Average hourly concentrations of NO and NO_2 are less than 7 ppb at Elandsfontein and less than 10 ppb at Kendal (compare to the average annual proposed NO2 ambient air quality standard of 21 ppb). Very low NO_x concentrations (less than 5 ppb) are recorded at Verkykkop due to its distance from NO_x sources. NO2 concentrations at Verkykkop are twice the magnitude of NO concentrations on average, indicating that the airmass is well aged. The source apportionment by diurnal signature indicates that tall stacks, vehicles and background contribute equally to total NO downwind of the Highveld.

NO_x concentrations are significantly higher and the diurnal profile differs at the low-income urban site, where average hourly NO concentrations peak at over 50 ppb in the morning and evening (Figure 4). The morning and evening NO_x peaks reflect the influence of local vehicle emissions and domestic coal combustion at the site. Emissions are highest in the early morning and evening when traffic is heaviest and coal is burnt for cooking and heating, and the accumulation of pollutants is exacerbated by surface temperature inversions which trap the pollutants. The contribution of the low-level sources is confirmed by the SADS analysis, which attributes 96% of the NO to vehicles, domestic burning and background (Figure 5).

The characteristic diurnal cycle in ozone concentrations, with higher ozone concentrations during the day as a result of in-situ production, is evident at all sites (Figure 4). At Verkykkop the ozone diurnal cycle is dampened in comparison to the other regions. Ozone concentrations are generally lower at Kendal and Dhlamini, and increase with distance from the major NO_x sources.

Remote sensing of NO2

Satellite retrievals indicate that NO* emission densities on the Highveld are similar to those in the highly industrialized regions of east Asia, Europe and the north-eastern United States (Figure 6). Satellites also provide evidence of the long-range transport of NO_x from the Highveld over the Indian Ocean (Wenig *et al*, 2003). However, the spatial resolution of the satellite instruments is fairly coarse (tens to hundred of kilometers), and it is not possible to resolve single point sources, or to ascertain with any degree of accuracy the extent of the NO_x 'hotspot' on the Highveld. There is also a discrepancy between satellite and ground-based observations, as surface measurements of NO; are generally low, and do not suggest that NO_2 column densities on the Highveld would be so high.

In order to validate the satellite retrievals on a regional scale and investigate individual sources on a local scale, a project is being conducted by Eskom, the University of the Witwatersrand, the South African Weather Service and the University of Heidelberg, Germany. An imaging Differential Optical Absorption Spectrometer (iDOAS) has been mounted on the South African Weather Service's research aircraft. The iDOAS measures reflected light in the visible and ultraviolet wavelengths, along a line perpendicular to the aircraft track. Combined with the aircraft's forward motion, this produces a two-dimensional image (Figure 7). NO_2 total and tropospheric column densities are retrieved using differential optical absorption spectroscopy. Flights are focused on the Highveld, and coincide with satellite overpasses when possible. Test flights were conducted in October 2006, and a winter campaign was conducted in August 2007. A summer campaign is planned for February 2008.

A flight over the Mpumalanga Highveld was conducted on 5 October 2006. The NO_2 tropospheric column density, as derived from Ozone Measuring Instrument (OMI) data, is shown in Figure 8. NO_2 column densities were highest over the Mpumalanga Highveld, and over the Johannesburg-Pretoria and Vereeniging-Vanderbijl regions (seen as isolated sources to the west of the main hotspot on the satellite image).

The airborne DOAS measurements indicate that there is considerable variation in NO_2 slant column density (SCD) over the Mpumalanga Highveld, however. NO_2 column densities are highest immediately downwind of major sources, and plumes are discernible tens of kilometres downwind of the sources. On this occasion the plumes from Matla, Kriel and Kendal merged to form one large plume which was advected to the east-south-east. It is likely that the joining of the plumes from Matla and Kriel is a common occurrence, since the power stations are situated so close together.

The airborne DOAS can also provide high resolution images, which depict the variability within plumes. The merging of the plumes from Matla and Kriel is seen in Figure 10. The typical expansion of the plume downwind of a source (Majuba power station, in this case) is shown in Figure 11.

Conclusion

Satellite retrievals highlight the South African Highveld as having one of the highest NO2 tropospheric column densities in the world. However, average surface NO_2 levels are generally below the proposed South African ambient air quality standards in industrial regions. NO_x levels are highest in urban areas, where vehicles (and domestic coal combustion in low-income areas) are a significant source of NO_x emissions, and surface temperature exacerbate the accumulation of pollutants. The results of this study suggest that emissions of NO_x in urban areas from vehicles and domestic burning pose a much greater risk to human health than emissions from tall stacks.

High resolution measurements of NO_2 tropospheric column density collected with an airborne DOAS have shown that there is considerable variability in NO_2 column densities over the Highveld, and NO_2 plumes are clearly discernible tens of kilometres downwind of the sources.

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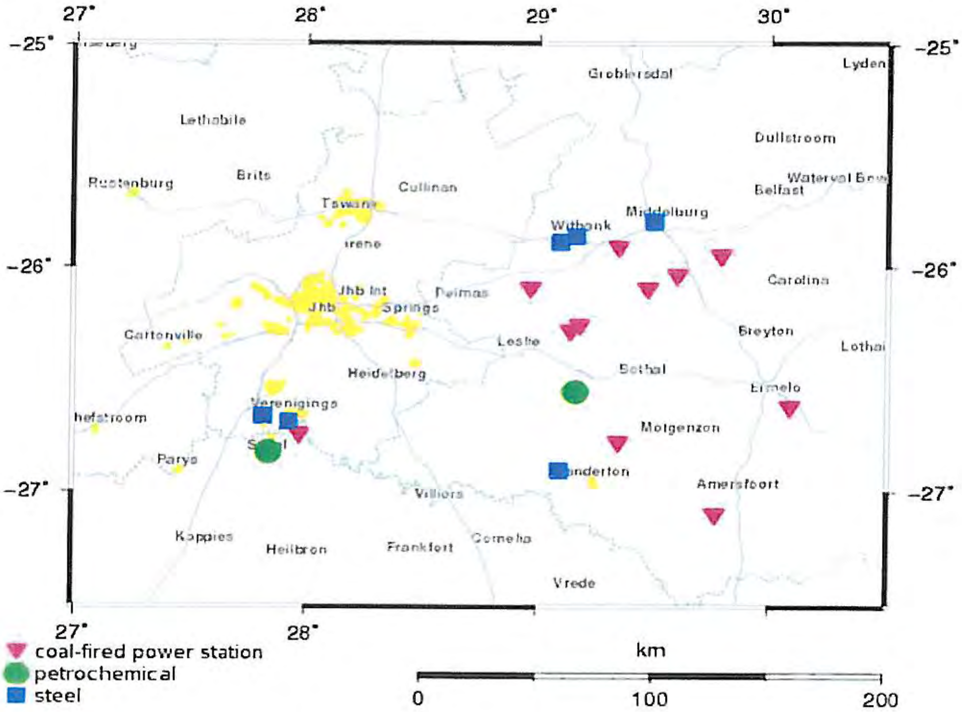

Figure 1: Location of urban areas, power plants and major industries on the South African Highveld (Broccardo *et al.*, 2007)

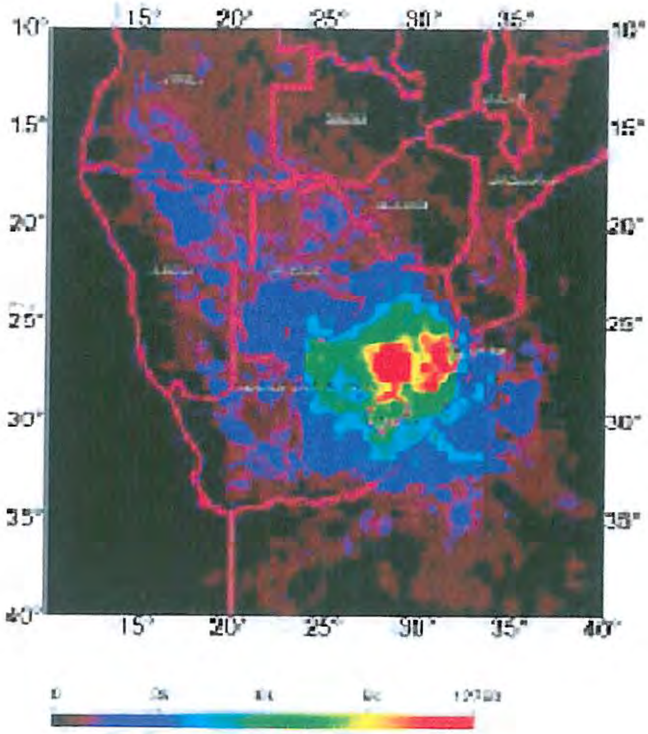

Figure 2: Lightning strike frequency plot (for January 2002) taken from the Lightning Positioning And Tracking System (LPATS) (Annegarn *et al.*, 2003, 4)

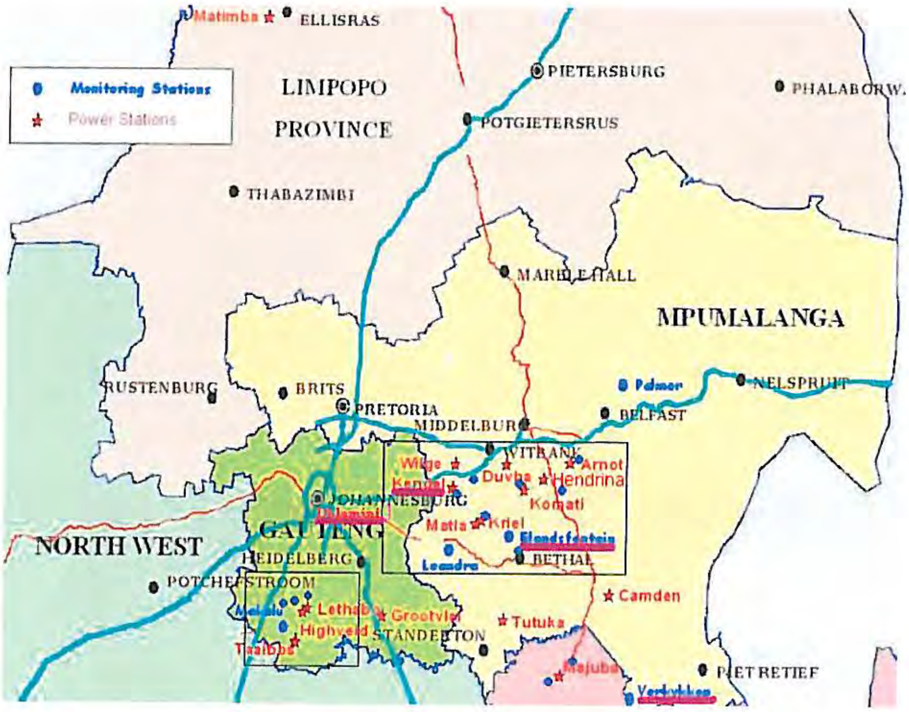

Figure 3: Eskom's power stations and air quality monitoring sites on the South African Highveld. Monitoring sites considered in this study are underlined in pink (Eskom intranet, 2006)

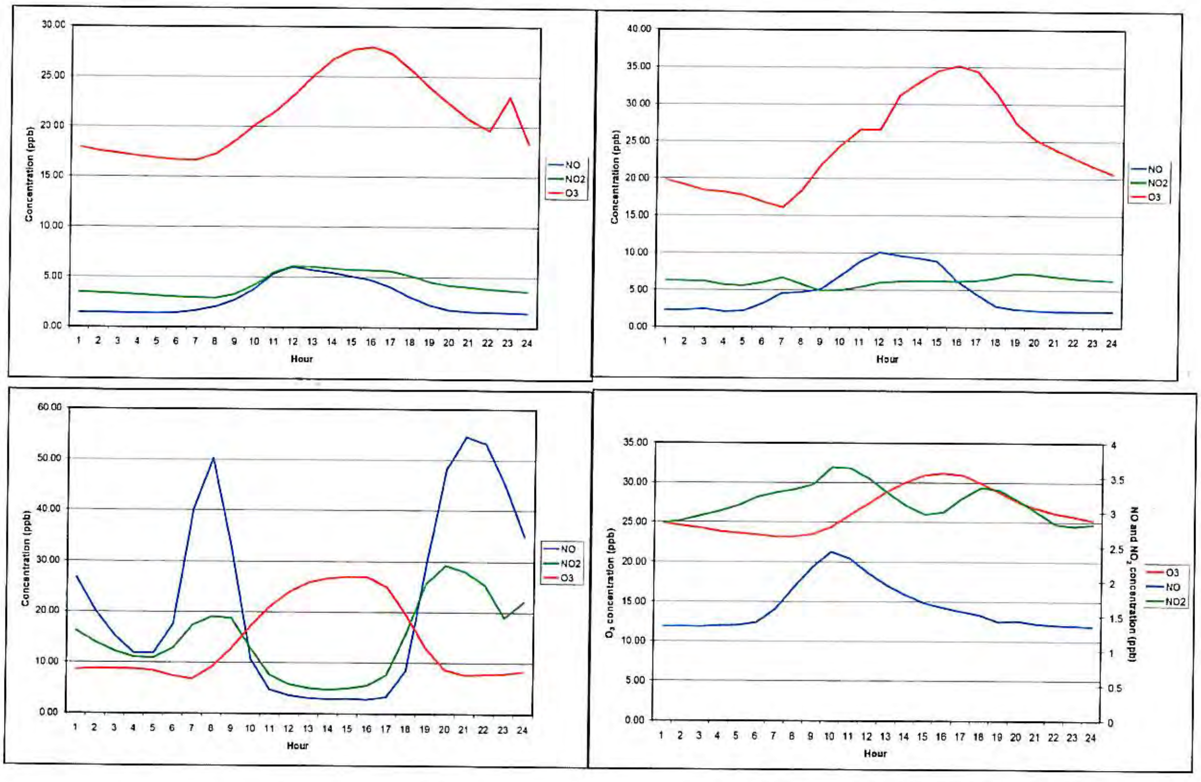

Figure 4: Average hourly NO_x and O_3 concentrations in the industrial region (Elandsfontein; 1990-2005; upper left); directly downwind of a power station (Kendal; 1994-2004; upper right); in a township (Dhlamini; 1991-1992; lower left) and downwind of the Highveld (Verkykkop; 1990-2004; lower right) (Ferguson and Ross, 2006)

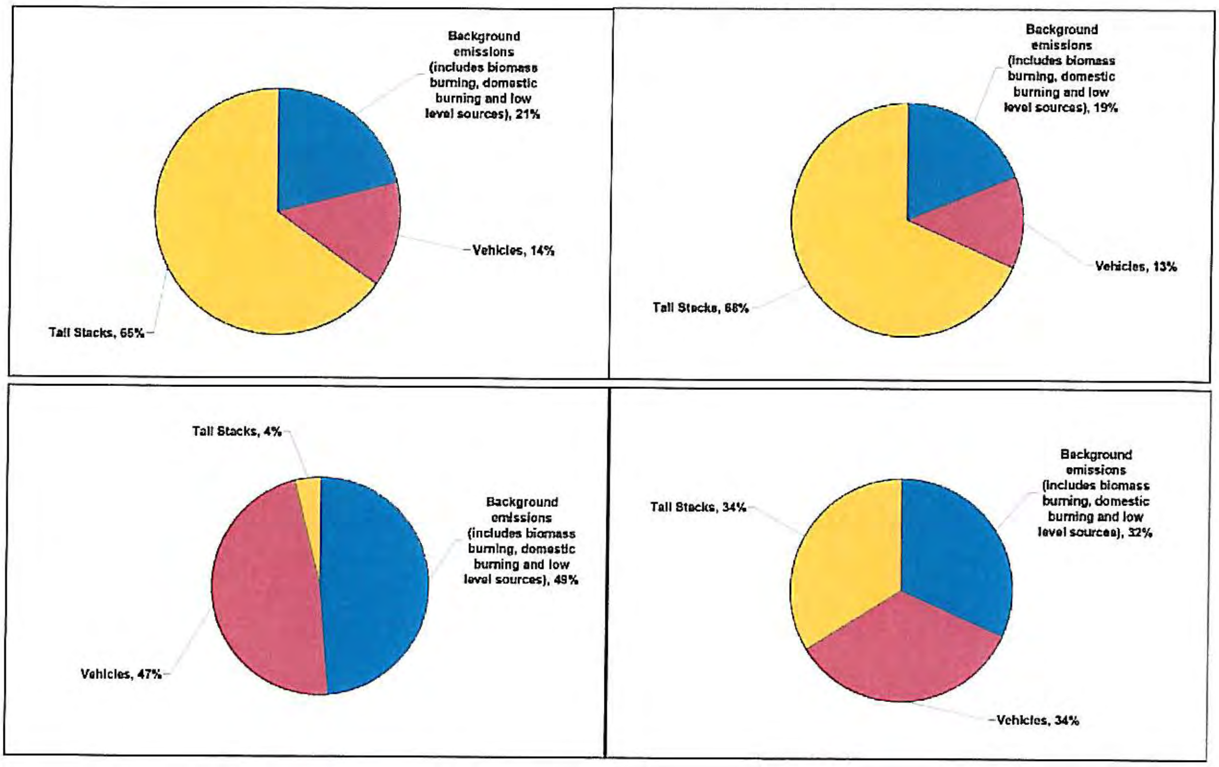

Figure 5: Relative contribution of sources to mean NO concentrations in the industrial region (Elandsfontein; upper left); directly downwind of a power station (Kendal; upper right); in a township (Dhlamini; lower left); and downwind of the Highveld (Verkykkop; lower right) (Ferguson and Ross, 2006)

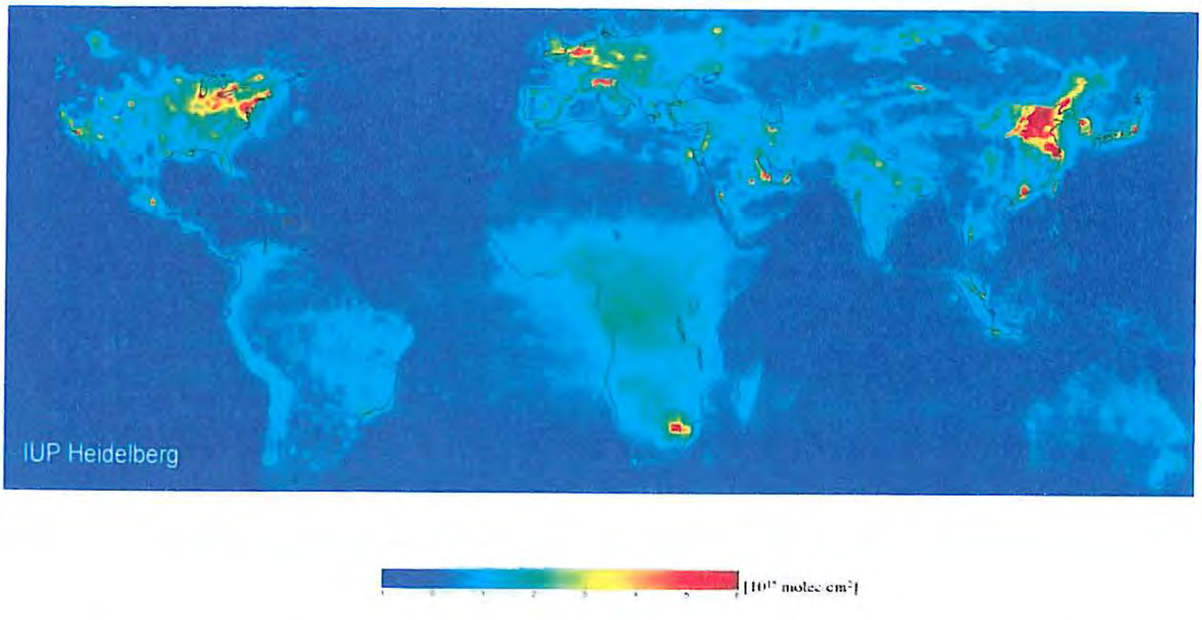

Figure 6: Mean tropospheric vertical column density from SCIAMACHY (January 2003 - June 2004) (http://satellite.iup.uni-heidelberg.de/)

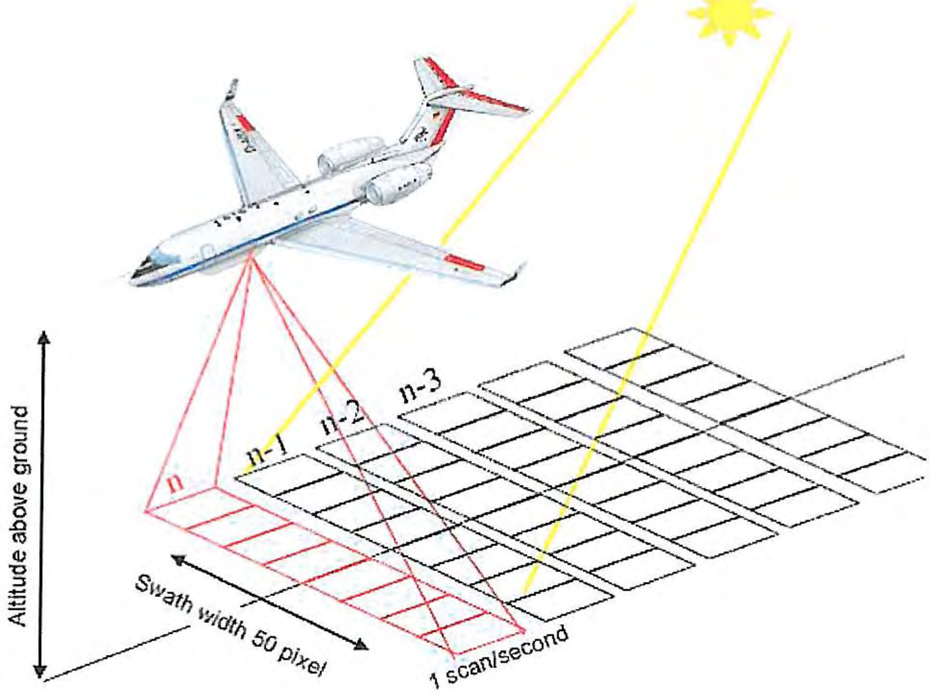

Figure 7: The airborne IDOAS technique (Heue *et al.,* 2007)

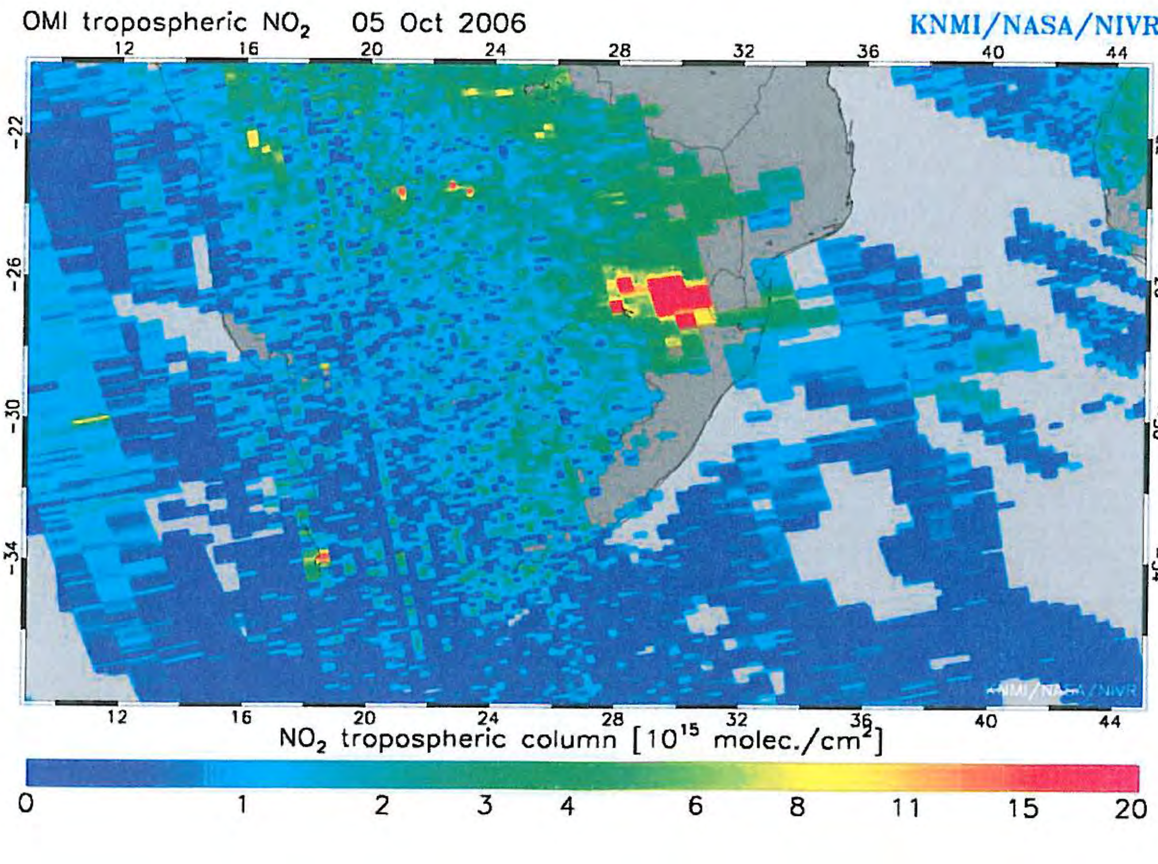

Figure 8: NO_2 tropospheric column density on 5 October 2006, derived from OMI data

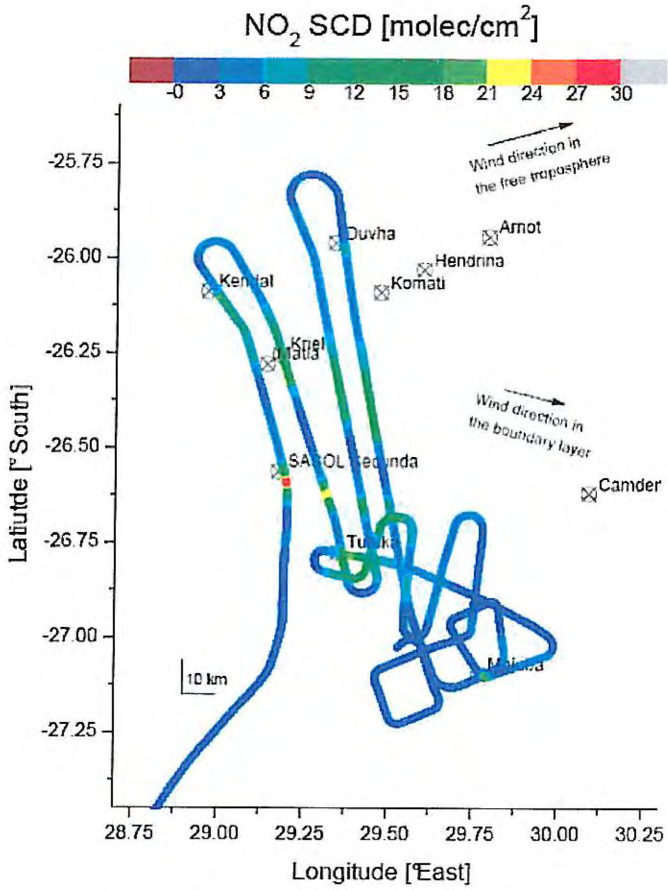

Figure 9: NO_2 SCD on the flight track on 5 October 2006 (Heue *et al.*, 2007)

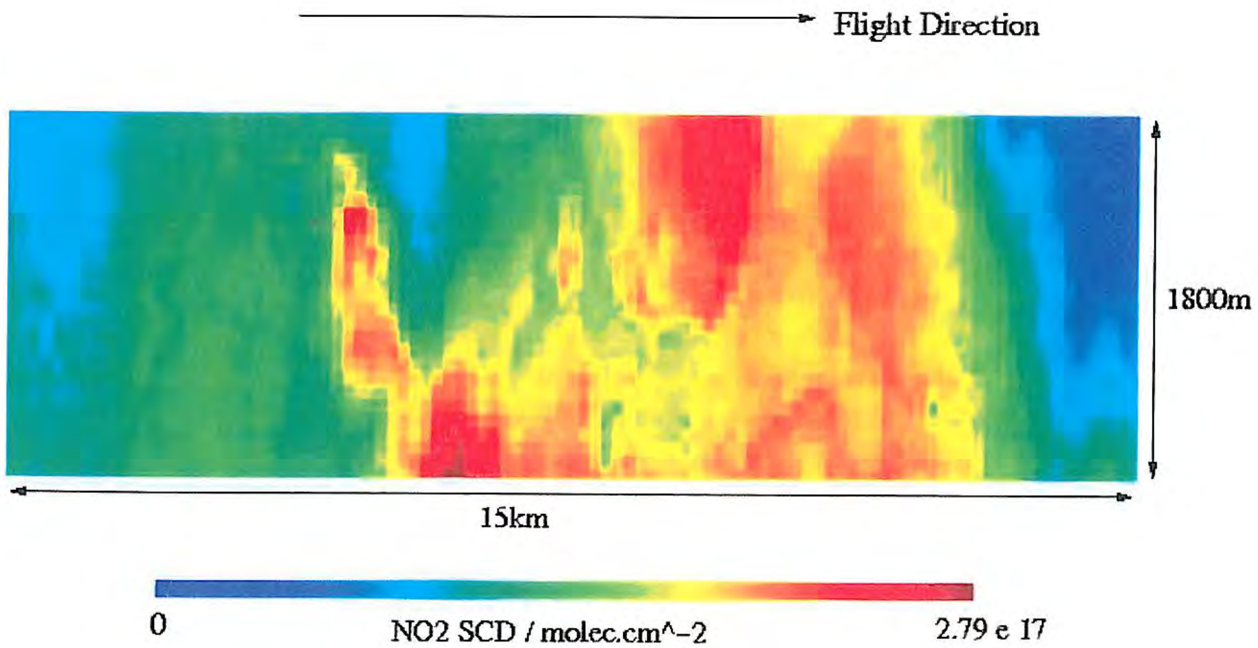

Figure 10: High resolution two-dimensional image of the plumes from Matla and Kriel, from the airborne iDOAS (Broccardo, 2007)

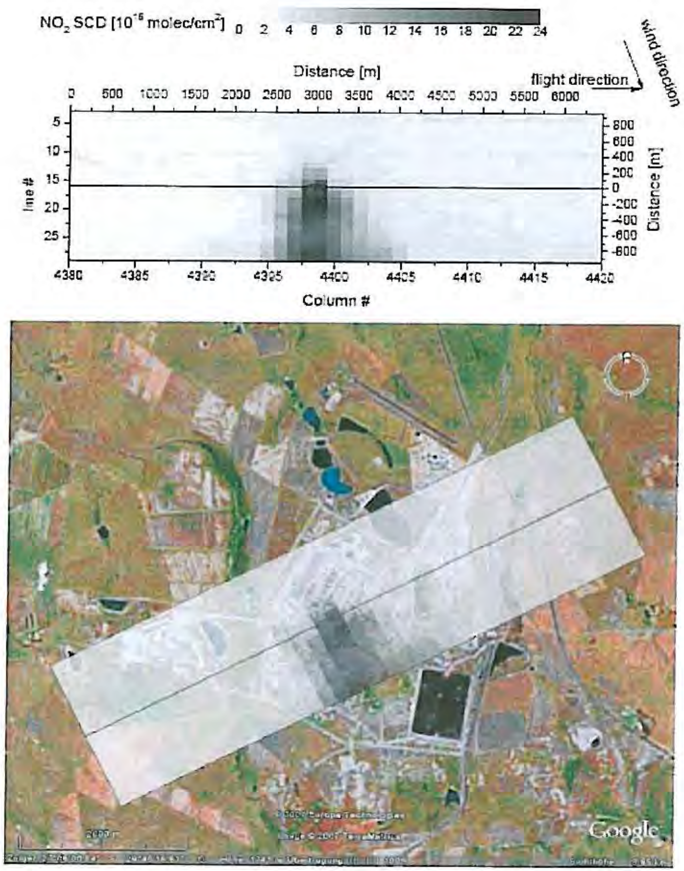

Figure 11: NO_2 SCD near Majuba power station (Heue *et al.*, 2007)