SO_2 seasonal variation and assessment of Ozone Monitoring Instrument (OMI) measurements at Sharpeville (27.86° E; 26.68° S) a South African ground-based station

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In this study, seasonal, inter-annual variations of sulphur dioxide (SO_2) were analysed for Sharpeville, South Africa (27.86° E; 26.68° S) for the period 2007-2013. Sharpeville is a residential site located within a highly industrialised region. Inter-annual variations were investigated by analysis of data collated by a Ground-based (GB) instrument as well as the SO_2 retrievals recorded by the Ozone Monitoring Instrument (OMI), a satellite-based sensor. The Planetary Boundary Layer (PBL) SO_2 vertical column data recorded by OMI were converted to surface SO_2 volume mixing ratios using the pressure difference between surface and PBL. Accordingly, the OMI derived SO_2 measurements overestimated GB values and showed a good correlation with GB data in the austral winter. Besides this, the overall comparisons i.e. their daily, seasonal and yearly correlation studies found that OMI derived measurements was in better agreement with GB regardless of its moderate relative percentage of difference with GB. The seasonal variations of SO_2 demonstrated that GB and OMI derived measurements followed a general pattern of increasing trend from autumn until late winter and decreased from the onset of spring,

however the latter showed unique high SO_2 levels in summer. Together with this, the inter-annual variations of both computations displayed a small decrement in SO_2 values during the period 2011-2013. This however proved to be a stable variation when compared to other countries.

Keywords: SO_2, Ground-based, Ozone Monitoring Instrument, Correlation, seasonal and inter-annual variations

1. Introduction

Several satellite-based instruments are currently in operation to meet the increasing demand for air pollution monitoring. They have the advantage of providing wide spatial coverage of continuous data and location of hot spot regions compared to Ground-based (GB) measurements. They are utilised in a variety of applications such as monitoring of unpredictable emissions from volcanoes, ships and biogenic sources; trans-boundary emissions; intercontinental transport of dust aerosols and other pollutants (Streets et al. 2013). Satellite instruments also serve as a major tool in investigating the seasonal and inter-annual trends of a pollutant over long time periods on a local, regional, zonal and even global scale. However, satellite-borne instruments have some basic disadvantages related to uncertainties in the retrieval algorithms and the instruments themselves, which can lead to random and systematic errors (Duncan et al. 2014). Their temporal resolution is reduced because of their limited overpass timings and as a result, they may not be able to record outlying values or anomalies. These data gaps can be filled up only by anticipated geostationary satellites such as the forthcoming Tropospheric Emissions: Monitoring of Pollution (TEMPO) which is planned to be launched in 2018. TEMPO will remain in a geostationary orbit over North America to continuously measure pollutant levels on an hourly basis (Chance 2013). At present, it is only possible to relate satellite data with data from GB instruments and the output of air quality models in order to determine a well-defined profile of atmospheric pollutants. Many approaches are therefore possible to study the atmospheric lower strata, namely the lower tropospheric and planetary boundary layers, with the aid of satellite measurements.

In a study conducted on global volcanic SO_2 emissions from 2005 to 2012, it was shown that Ozone Monitoring Instrument (OMI) detected about 50 volcanic eruptions. The largest OMI based volcanic SO_2 sources during this time period were from eight continuously

degassing volcanoes in the tropics (Ge et al. 2016). In another study based on volcanic SO_2 from the 2014 to 2015 eruption at the Holuhraun lava in Iceland, it was demonstrated that OMI could trace down the high SO_2 plumes similar to those detected by air quality monitoring stations and thereby disproved the notion that the retrieval of OMI in high latitudinal regions is demanding (Schmidt et al. 2015). OMI observations of SO_2 emissions from two Peruvian copper smelters and active volcanoes in Ecuador and Southern Colombia between September 2004 and June 2005 confirmed that OMI could detect both natural and anthropogenic SO_2 sources (Carn et al. 2007).

Global maps of OMI mean total SO_2 columns between 2004 and 2009, showed high emission anthropogenic point sources over Asia such as the Persian Gulf region and India. In addition to this, OMI detected weak SO_2 signals from shipping routes near the Red sea and Gibraltar (Theys et al. 2015). It has been shown that the choice of appropriate Air Mass Factor (AMF) in the OMI retrievals plays a vital role in reducing the bias (Bauduin et al. 2016). The relative change in the percentage of SO_2 emissions based on OMI measurements found that there was 70% -80% and 40%-50% decline in SO_2 emissions during the period 2005-2014 over USA and European sources respectively, while an 80% increase was observed over India. However, large emitting source regions in Middle East, Mexico, Russia, and South Africa showed fixed up trends (Fioletov et al. 2016). Finally, it has been estimated that nearly 6%-12% of total global anthropogenic SO_2 emissions has been accounted for by the Persian Gulf regions (McLinden et al. 2016).The annual mean SO_2 column simulations with GEOS-Chem (global 3-D chemical transport model (CTM) from the Goddard Earth Observing System (GEOS)) chemical transport model for 2006 shows that anthropogenic SO_2 emissions contribute to nearly 1×10^{16} molecules cm^{-2} in the industrialised regions of Highveld, South Africa and the whole fraction of SO_2 column is from these anthropogenic emissions (Lee et al. 2011). In this study, our objective is to compare the OMI SO_2 measurements at a South African site against GB measurements. Based on our knowledge, the study would be one of a few of its kind that explores the applicability of SO_2 satellite measurements in Africa/Southern Hemisphere and likely the first comprehensive comparative study on the assessment of long-term GB and OMI SO_2 measurements made in South Africa. Prior to this study there were a few comparative studies using in-situ measurements and research aircrafts, which have been carried out on a short timescale (Sinha et al. 2003).

The major scope of this investigation is the comparative study between the GB and OMI satellite SO_2 data, where the latter is converted into comparable units by following the

application of Josipovic et al. 2013 who has adopted from Ziemke et al. (2006). Based on this comparison, it can be inferred if the adopted method correlates better with the GB results and whether the OMI satellite SO_2 measurements can be used as proxy concentrations in areas of GB station shortfall places. A further aim of this work is to study SO_2 seasonal variation over Sharpeville (South Africa) using, data sets from OMI derived measurements and GB data. It should be noted that since OMI data is available for 2004 to 2013 and GB data available for 2007 to 2013, the comparative study was performed for the period 2007 to 2013. However, SO_2 seasonal variations were studied individually according to their respective available measurement time periods.

2. Location, Data and Methodology

2.1.Location of Ground-based station

The SA GB SO_2 measurement station selected is Sharpeville. Sharpeville station was chosen as it is the station with the highest number of paired (both OMI overpass and GB) data sets available. The monitoring station is located in Sharpeville, Sedibeng Municipality, in the Gauteng province of South Africa at 26.68° S 27.86° E (see. Figure 1(*a*)). Sharpeville is situated in the Vaal Triangle Airshed Priority Area managed by the Department of Environmental Affairs. The major sources of pollution in this area are residential fuel burning and the industrialised urban areas of Vereeniging, Sasolburg and Vanderbijlpark. Lethabo coal-fired power station is also located near Sharpeville. Figure 1(*b*) shows an enlarged view of Sharpeville and its nearby industrial sites.

2.2.Ground-based instrumentation

The instrument used at the GB station is the Thermo Electron 43i SO_2 analyser. It is a pulsed fluorescence SO_2 analyser and employs the principle of fluorescence by adopting the absorption in the ultraviolet light region, i.e. UV light is allowed to pass through the fluorescent chamber, where SO_2 molecules absorb in this range thereby emitting decay radiation, which is sensed by a photomultiplier tube. The amount of energy emitted is measured in terms of electric voltage by the electronic signal processors and is directly proportional to the SO_2 concentration. The instrument was maintained under South African

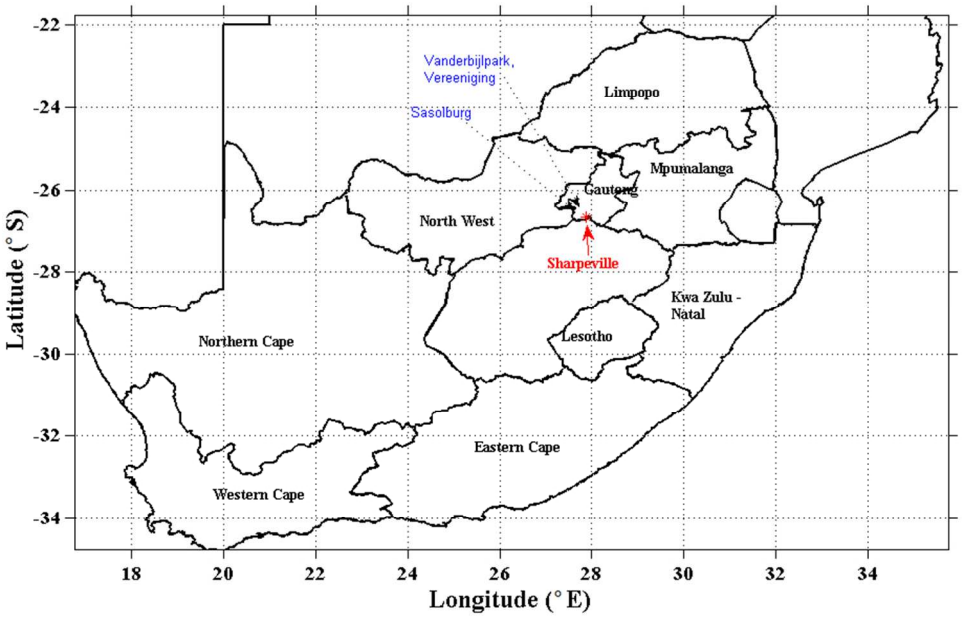

Figure 1(a). Geographical map of South Africa depicting the Geo-location of the Sharpeville ground station. 252x159mm (96 x 96 DPI)

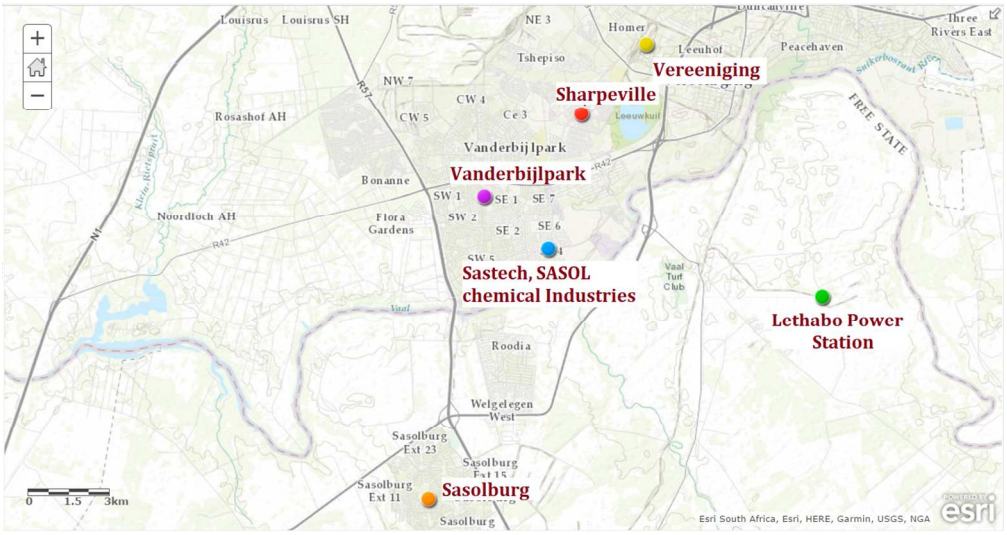

Figure 1(b). Map of Sharpeville and its neighbourhood industries and Lethabo power station (created through web-ArcGIS)

390x206mm (96 x 96 DPI)

National Accreditation System and routinely calibrated on a bi-monthly basis. The precision of the instrument is around 1 ppbv with zero drift value less than 1 ppbv and a response time of approximately 60 seconds with a detection limit of about 2 ppbv.

2.3.Ground-based data

Measurements of SO_2 at Sharpeville were performed by the South African Weather Service (SAWS) and archived in the South African Air Quality Information System (SAAQIS). In this investigation, GB SO_2 data starting from 23 March 2007 to 31 January 2014 was used and this high resolution data was averaged hourly for each day to give a total of 24 data points per day. The following data gaps should be noted: 16 February 2009 to 7 March 2009; 21 February 2010 to 21 June 2010; 22 January 2011 to 20 May 2011; 5 September 2012 to 11 September 2012; and 21 May 2013 to 27 May 2013. In order to improve the quality of data and accuracy of results, data validation was carried out. In this process, 70% data completeness was followed, namely data points having a zero or negative value were discarded as well as missing data points. The data gaps and anomalies were filtered out in order to obtain uniformity in the data sets programmatically. The daily means were calculated from the hourly averaged data for each day from March 2007 to January 2014. The calculated daily means were assumed to be within the standard deviation of hourly recorded data. The reason for calculating daily averages was to increase the uniformity in the data set as some hourly data were missing. Thereafter, individual monthly means were obtained by calculating the monthly mean for each year of the time period in order to evaluate inter-seasonal variations. The overall monthly means were calculated to investigate overall seasonal variation. This was accomplished by sorting the data with respect to monthly measurements discounting the years of measurement (for example, all January values were combined for all the years from 2008 to 2014 and the resultant mean was calculated for the corresponding month) and their corresponding mean and standard deviation were obtained. The measurements which had high positive and negative anomalies were removed (those over/below the mean $\pm 2\sigma$ (standard deviation)).

2.4.Satellite–based instrument (OMI) and retrieval of SO_2 data

The satellite-based instrument used in this study is the OMI. When compared to other satellites the unique features of OMI are the high spatial resolution of about 13 km × 24 km and its daily global coverage. The Global Ozone Monitoring Experiment (GOME) has a spatial resolution of 320 km × 40 km (Boersma et al. 2006, 1) whereas the Scanning Imaging

Absorption Spectrometer for Atmospheric Cartography (SCIAMACHY) has 60 km × 30 km and it takes about 6 days for complete global coverage (Blond et al. 2007). Thus, the daily measurements of OMI help in forecasting the air quality, near real-time monitoring, transport of pollutants and sudden increase in pollution levels that are associated with public health issues. The fine spatial resolution of OMI allows regional scale mapping of highly polluted areas (1). In OMI, reflected solar radiation is measured in the ultraviolet (UV) and visible regions with a spectral range between 270 nm and 500 nm. The UV channel has two sub-channels with UV-1 (270-310 nm) and UV-2 (310-365 nm) and a spectral resolution of 0.5 nm. This permits the measurement of concentrations of several trace gases in the atmosphere. The spectral band used for SO_2 measurements is from 310.5-340 nm (UV-2 band). A newly improved retrieval algorithm based on Principal Component Analysis (PCA) to radiance data, has been used in this study. Based on this technique, the SO_2 retrieval quality using the PCA algorithm is greatly improved when compared to its predecessor the Band Residual Difference (BRD) algorithm, in particular, the negative bias seen under cloudy conditions has been eliminated with the use of PCA (OMSO2 README File 2008). Further information on this algorithm is fully explained in the referred OMI SO_2 data product document (OMSO2 README File 2008). The errors and biases have been largely decreased with the use of the PCA algorithm (nearly 2 orders of magnitude) when compared to the BRD algorithm. This demonstrates the applicability of this technique (Li et al. 2013), it can also be applied to determine a wider range of point source emissions. An estimated uncertainty limit of $approximately$ 0.5 DU is expected by OMI SO_2 measurements over the latitudinal regions between 30 □S and 30□N (OMSO2README File 2008). In addition, the errors due to row anomaly where blockage in the field of view and light scattering affects track positions (Fioletov et al. 2011) has been undertaken and corresponding values are disregarded (GES DISC, News)

In this investigation, the daily '$OMSO_2$ product' from 2004 to 2013 is used. The level 2 OMI SO_2 product with version 003 was accessed from the National Aeronautics and Space Administration (NASA) Goddard Earth Sciences (GES) Data and Information Services Center (DISC) (http://disc.sci.gsfc.nasa.gov/Aura/data-holdings/OMI/omso2_v003.shtml). The radiation calibrations of this data product are improved compared to the previous version (Krotkov and Li 2012). The $OMSO_2$ product has four distinct categories of the vertical distribution of SO_2 namely planetary boundary layer (PBL); lower tropospheric; middle tropospheric; upper tropospheric and stratospheric SO_2 (OMSO2 README File 2008). In

order to perform further analysis, the OMI PBL SO_2 data for the Sharpeville region (26.68˚ S and 27.86˚ E) were extracted from the global OMI SO_2 data. The OMI satellite measurements over Sharpeville were selected with a discrepancy in sampling grid of 0.125˚ × 0.125˚ (i.e. 27.86˚ ±0.125˚ E and 26.68˚ ±0.125˚ S). As instructed in the OMI data manual, data was discarded if the Radiative Cloud Fraction (RCF) was more than 0.2 and the Solar Zenith Angle (SZA) greater than 50□ (OMI Data User's Guide 2012). It is noted that there is a data gap in June for every year of this investigation as there was no satellite overpass during this month for the location under study.

In order to perform a reasonable comparison of the OMI SO_2 data expressed as vertical column density (VCD) with its corresponding GB measurement which was recorded in volume mixing ratios (VMR), the OMI SO_2 PBL VCD were extracted down to surface level values assuming well mixed layers. In this method, the VCD in the PBL layer were converted into VMR into parts per million volume (ppmv) by using the pressure difference between the surface and top of the PBL layer (Josipovic 2009; Josipovic et al. 2013 as adjusted from Ziemke, Chandra, and Bhartia 2001; Ziemke et al. 2006). The equation for this conversion follows the above basic assumption but at two different pressure levels, i.e.

$$\Delta\Omega \approx 0.79 \int_{P_S(\mathrm{hpa})}^{P_{BL}(\mathrm{hpa})} \mathrm{x\,(ppmv)}.\,dP_{atm}(\mathrm{hpa})$$

$$X_{VMR} = 1.27 \times \left[\frac{VCD_{PBL}}{(P_S - P_{BL})}\right] \quad (1)$$

Where:

VCD_{PBL} is the Daily OMI PBL columnar SO_2 in DU, and P_S and P_{BL} denote the hourly atmospheric pressure in hPa at the surface layer and top of the boundary layer respectively corresponding to the satellite overpass timings. Daily OMI PBL columnar SO_2 measurements stand here for the entire atmosphere. In this investigation hourly surface pressure, PBL pressure data using Modern ERA-Retrospective Analysis for Research and Applications (MERRA) (Reichle 2012) was obtained for the same OMI satellite overpass timings, i.e. local noontime for the same period (2004 to 2013).

The anomalies in data and data gaps were discarded by calculating the overall mean (regardless of the day, month and year) and the corresponding standard deviation (σ) i.e. daily mean values have been checked with the above obtained overall mean and $\pm 2\sigma$. Since our primary objective was to extract climatological results and thus to avoid extreme high and low values, the data have been discarded if the values were lower or higher than the overall

mean and $\pm 2\sigma$ level. Such a criterion has been followed in earlier research for a sub-tropical station at Reunion Island when extracting ozone climatology from GB measurements (Sivakumar et al. 2007; Toihir et al. 2015). Similar to GB data, daily mean variations were also estimated by calculating the mean of the daily columnar values for the corresponding station latitude and longitude zones and then extracting down to surface ppbv values by the application of equation (1).

RESULTS

3.1. *Comparative study between Ground-based and OMI derived measurements*

3.1.1. Daily mean comparisons:

The scatter plot between GB hourly mean values around the OMI overpass timings (i.e. mean values of hourly GB data before, after and during overpass) and OMI derived SO_2 measurements is shown in Figure 2. It is evident from the figure that OMI derived measurements showed a better linear relationship with GB data with a regression coefficient of $approximately\ 0.3$.

We also calculated the difference between GB data and OMI derived measurements (figure not shown). The mean difference between them was found to be -1.08 ppbv, which indicated that the satellite data overestimated values recorded at the surface. The observed difference might also be influenced by the input parameters (i.e. pressure values) used in these calculations and the assumptions employed while obtaining OMI PBL SO_2 including the height elevation. It should be noted here that Sharpeville has elevation (mean sea level) altitude of about 1.5 km.

3.1.2.Inter-annual mean comparisons

3.1.2.1.Inter-annual variations: According to the inter-annual variations, the highest SO_2 values of GB and OMI derived measurements were only in winter periods of all the selected years. This further proved that pollutants accumulate at surface levels during the winter period. GB underestimated OMI derived measurements in most of the cases, which is illustrated in Figure 3. This result was similar to the study conducted on SO_2 emissions from major power plants in Turkey (Firatli and Kaynak-Tezel 2015). They have found that the difference between OMI (level 2 and based on PCA algorithm) and GB measured SO_2 were high nearer to the location of electric generation power plants. The average SO_2 mean

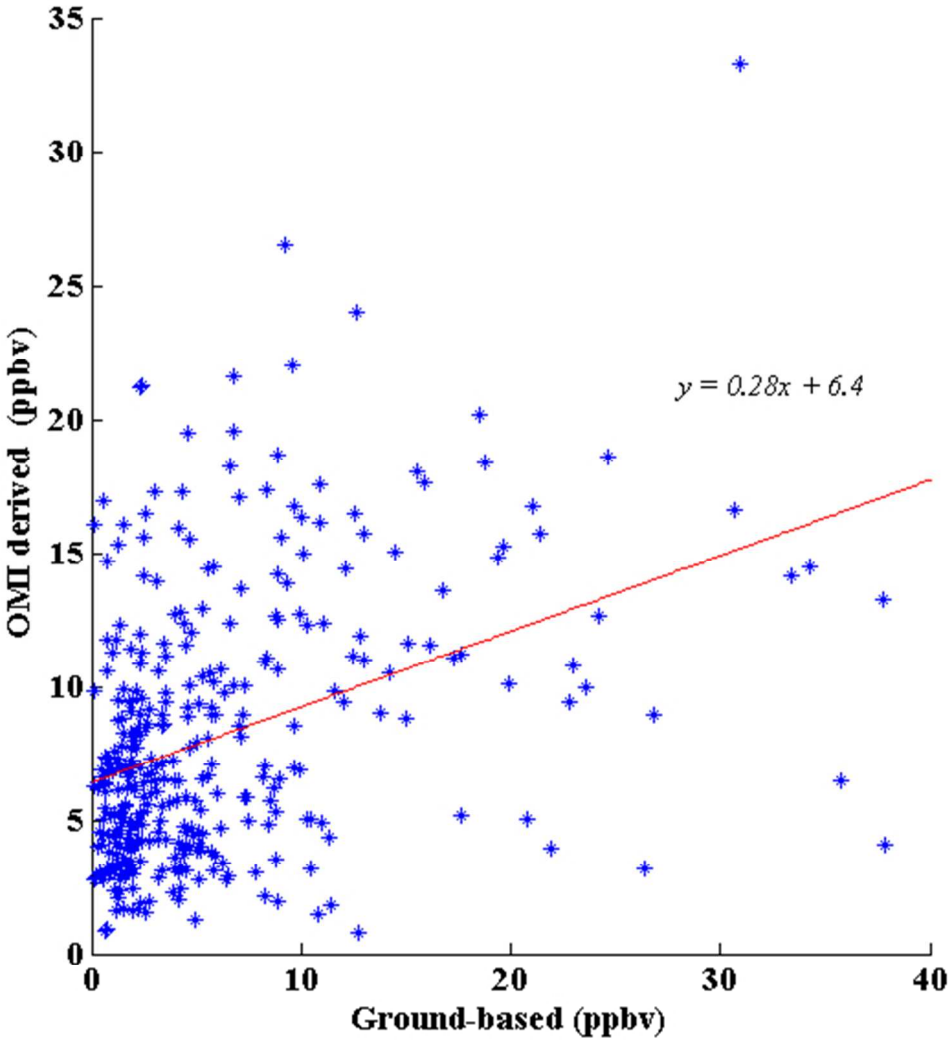

Figure 2. Scatter plots between Ground-based hourly mean values around the OMI overpass time and OMI derived SO2 measurements. The regression line slope (red line) represents the correlation coefficient of approximately 30 %.

144x160mm (96 x 96 DPI)

differences from 2007 to 2013, between OMI and GB was found to be $approximately$ 2.24 ppbv, however the difference is found to be within the standard deviations (see Figure-3, vertical lines). These results were similar to those obtained by Lee et al. (2011). According to their estimation, OMI SO_2 columns and the bottom-up GEOS-chem model varied by a factor of 2 in the Highveld region during their study period of 2006, this was approximately equivalent to the present study. The scatter plot of OMI derived measurements (figure not given) is similar to that of daily mean scatter plot with a regression slope of about 0.42.

3.1.2.2.Yearly correlation: The yearly correlation analysis between GB and OMI derived measurements was done based on their monthly mean SO_2 values (Table 1). Based on the results, years 2007, 2008, 2010 and 2013 showed high correlation *r* values of $approximately$ 0.7, which was a good correlative result, whereas other years had a poor *r* value.

However, it is noteworthy that the *r* value between their annual averages was 0.80.

3.1.3. Seasonal comparisons

3.1.3.1. Seasonal Variations: The seasonally based comparisons indicated that GB and OMI derived measurements exhibited a fair seasonal variation. During summer, OMI derived calculations gave higher values and indicated a well marked difference with GB measurements as demonstrated in Figure 4. Both the SO_2 datasets (i.e. derived from GB and OMI) showed a general increasing trend between autumn (during April) and winter (during July), with a few exceptional cases, such as in March and August, where OMI derived measurements and GB data decreased, respectively. GB measurements thus showed a winter peak similar to that of the Vaal Triangle spatial SO_2 average concentration (Ncipha 2011). During spring, OMI data decreased steadily through the entire spring period. GB measurements also showed a rapid decreasing trend in October corresponding to a decrease of about 2 ppbv, this was followed in November by a slight increase. The deviations from the mean values ($\pm$ 1σ) found to be almost similar for both OMI and GB. This observation was similar to the seasonal trends estimated by Laakso et al. (2012, 3), in Elandsfontein (about 180 km from Sharpeville) between 2009 and 2011, where high SO_2 levels occurred in

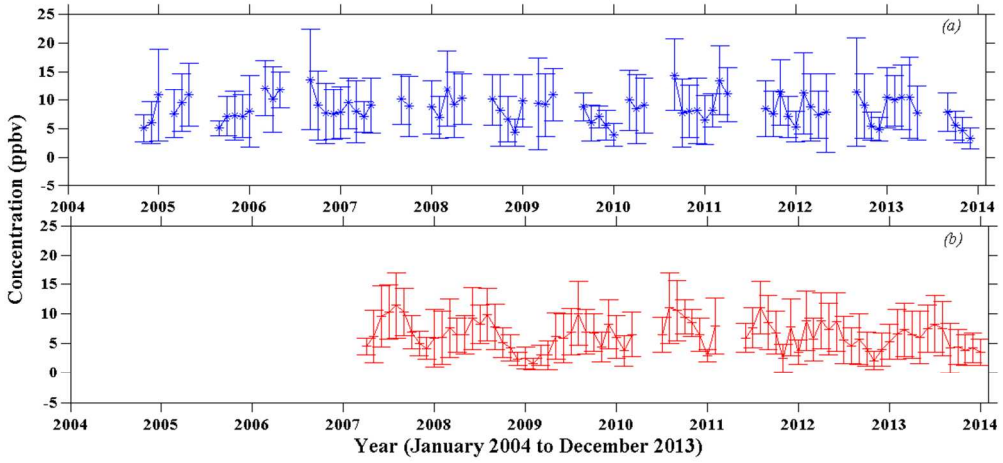

Figure 3. Year to year SO2 variations by OMI derived (a) and Ground-based (b). Vertical lines represent ±1 standard deviation.

305x144mm (96 x 96 DPI)

Table 1. Correlation Coefficient (*r*) between Ground-based and OMI derived SO_2 measurements based on their monthly SO_2 averages for different year

Years	2007	2008	2009	2010	2011	2012	2013
	0.89	0.65	-0.42	0.65	-0.20	0.46	0.87

Table 2. Correlation Coefficient (*r*) between Ground-based and OMI derived SO_2 measurements based on their monthly SO_2 averages for various seasons

Season	Autumn	Winter	Spring	Summer
	-0.10	0.6	0.21	0.38

winter and early spring. Monthly mean values in winter were more than 20 ppbv as the site was impacted by a substantial number of industries and power stations. The SO_2 mean values in this study were at minimum levels during October–December (summer) when rainfall was a maximum (Janowiak 1988; Davis 2011; 3). Further, it has been noted from a study conducted on atmospheric transport by South African Fire-Atmosphere Research Initiative (SAFARI) in 1992, that during the spring season the main subsidence induced stable layer in the middle troposphere at a height of about 3.5 km above the surface was persistent throughout almost the entire period, whereas the lowest inversion layer at a height of about 1.5 km above the surface was frequently broken down by the passage of westerly wave disturbances. The wind speed was also maintained at high levels. These factors might lead to less accumulation of surface SO_2 and frequent long range transport, thereby lowering GB and OMI derived measurements of SO_2 values (Garstang et al. 1996). The average seasonal mean difference of surface SO_2 during the entire period between GB and OMI derived measurements was -2.32, whereas the relative percentage of difference was approximately -34.5%.

Therefore, the results suggest that OMI derived measurements overestimated GB SO_2 measurements throughout the entire period. It has been observed that OMI derived data was not compatible with GB especially in late spring and autumn where they both sometimes followed opposite trends.

3.1.3.2. Seasonal correlation coefficient: The correlation coefficients (*r*) between GB and OMI derived measurements was calculated using the monthly mean SO_2 values of GB and OMI data for each season (Table 2). The results of correlation assessments are as follows:

Winter and summer had an average *r* value of nearly 0.6 and 0.38 respectively, whereas the transitional periods namely spring had a lower *r* value of 0.21 and autumn had lower negative *r* value. It is notable that *r* values based on daily means for all the seasons were $approximately$ 0.4 and had a good correlative result as shown in Figures 5(a) and (b), (c) and (d), in particular for spring and winter.

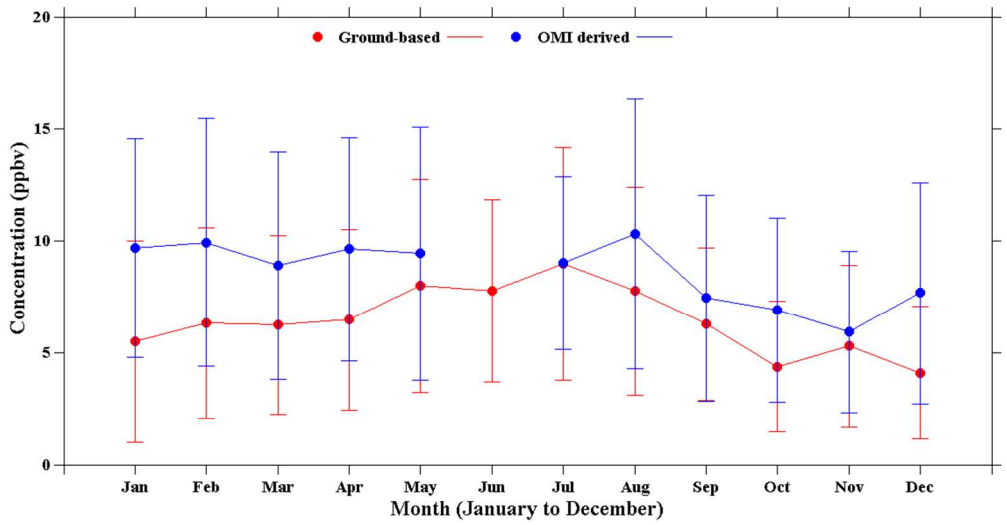

Figure 4. Overall seasonal SO2 variations of Ground-based and OMI derived SO2 measurements with data gap in June in OMI data. Vertical lines represent ±1 standard deviation.
302x156mm (96 x 96 DPI)

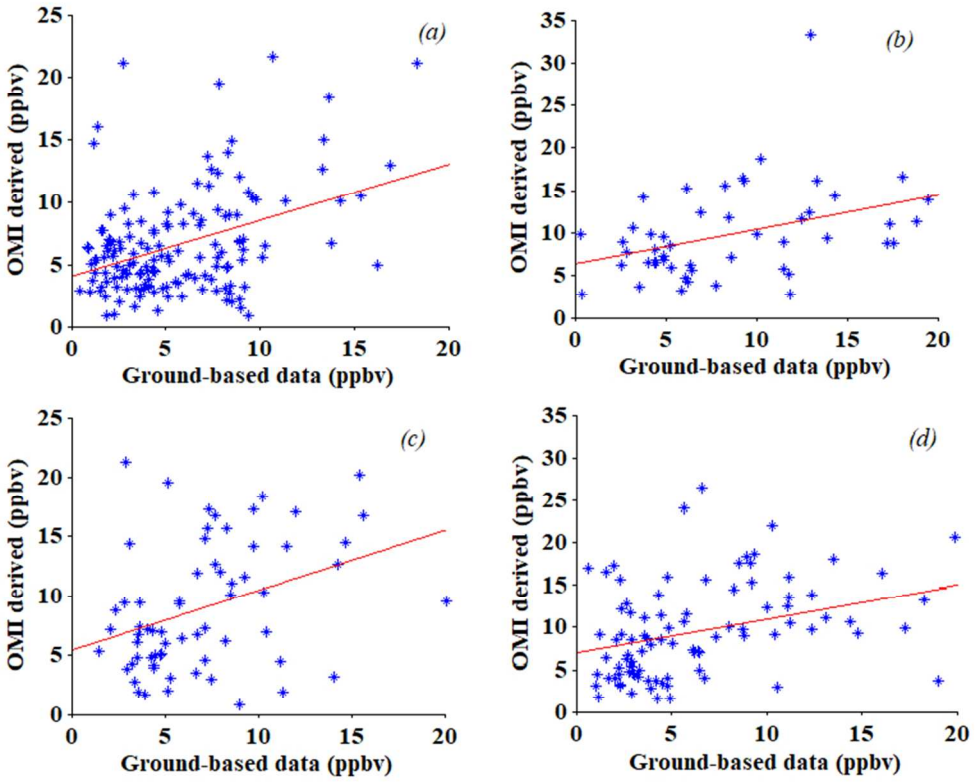

Figure 5. Scatter plots based on daily mean of Ground-based and OMI derived SO2 measurements in spring (a); winter (b); autumn (c) and summer (d).
207x167mm (96 x 96 DPI)

Thus, the seasonal correlative studies showed that winter had the best correlative result between the two types of measurements. This is an interesting result as the surface based measurements of SO_2 cannot be a representative of the PBL in winter, as factors such as stable inversion layer, low surface albedo and high pressure could have negative effects.

3.2 SO_2 variations from satellite-borne measurements

3.2.1.OMI Daily Mean: The daily mean values for OMI derived SO_2 measurements are plotted in the Figure 6. The obtained results are as follows:

Nearly 75% of the SO_2 values remained below 20 ppbv. The ranges were between 5 and 20 ppbv. The occurrence of values exceeding 20 ppbv was both in late summer and in winter periods, unlike GB where high values occurred only in winter and rarely in summer. This was similar to the results obtained over the global SO_2 level in 2006 by Lee et al. (2011). In their study, the same level 2 PBL SO_2 data product was used, but the retrieval algorithm was BRD. According to their results, a weak seasonal variation was exhibited, however high SO_2 columns were seen in the central region of South Africa, both in summer and in winter. The highest SO_2 value measured by OMI in this study was noted in July 2012 with a corresponding value of 33 ppbv.

3.2.2.OMI annual variations: The annual (year to year) variations of OMI derived SO_2 measurements is shown in Figure 7. The figure is overlaid with GB SO_2 measurements for comparative purposes. It is noted from the figure that a decreasing trend in the last three years corresponding to approximately 15% reduction in SO_2 average was observed by GB between 2011 and 2013. In addition to this, OMI derived measurements had two sharp rises in SO_2 value one in 2006 and other in 2010, but after this there was a gradual decrease in SO_2 level similar to GB and reached minimum level in 2013. A 17% decrement was seen, during 2011-2013. However, this decreasing trend was relatively small when compared to other countries like U.S.A and Europe, where more than 40% emission reduction was made over the period 2005 to 2010 (Klimont, Smith, and Cofala 2013), but still resembled that of the Middle East where about 20% decreasing trend was estimated by OMI for the period 2010 to 2013

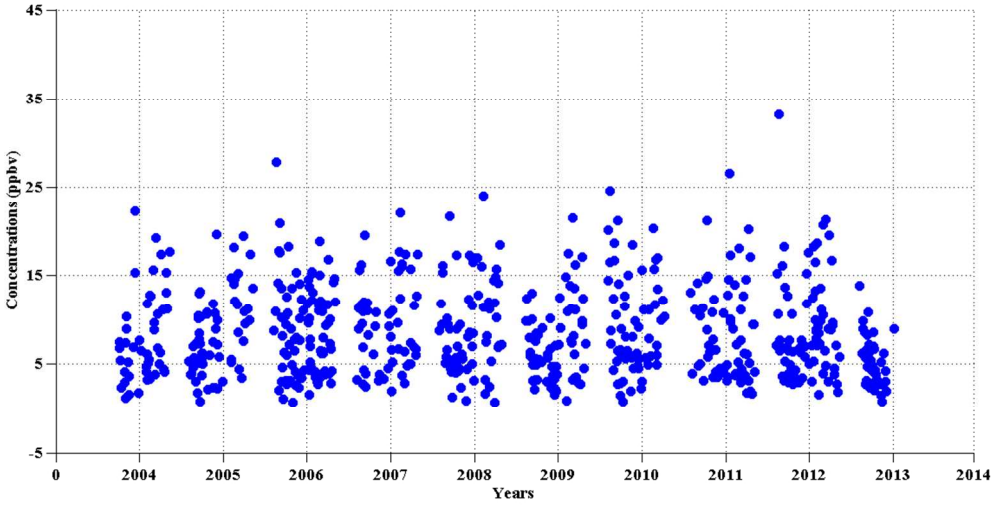

Figure 6. Daily mean SO2 variations based on OMI derived measurements. 305x156mm (96 x 96 DPI)

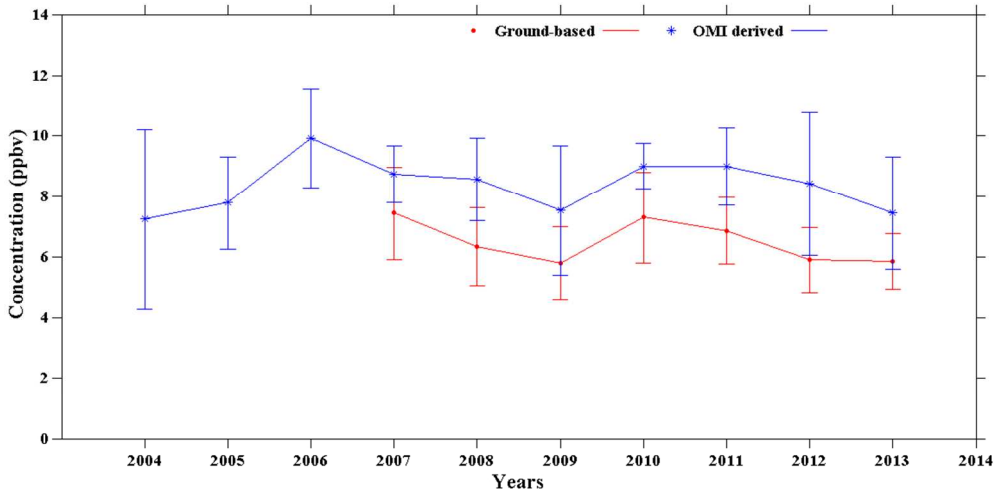

Figure 7. Inter-annual variations of Ground-based and OMI derived measurements of SO2. Vertical lines represent ±1 standard deviation.
306x154mm (96 x 96 DPI)

(Krotkov et al. 2015). The overall average SO_2 values from 2004 to 2013 for OMI derived measurements was 8.5 ppbv a thus it had $approximately$ 1.5 DU. This was slightly higher than that estimated by Theys et al. (2015). They applied the Differential Optical Absorption Spectroscopy (DOAS) algorithm to OMI SO_2 data. In their study on the global distribution of SO_2 columns, they found that the overall average of the SO_2 columnar amount from 2004 to 2009 in the Highveld region was $approximately$ 1 DU. This might be due to the removal of more biases by principal components and strong SO_2 spectra in PCA technique.

3.2.2.3. OMI seasonal variations: The intra-seasonal variations of OMI derived SO_2 measurements with vertical lines representing ± 1 standard deviation is displayed in Figure 8 for four different seasons (see. Figure 8*a-d*). The obtained main results are as follows:

The SO_2 values ranged between 4.4 ppbv and 15 ppbv. In contrast to GB data, only 60% of the values were within 10ppbv. The outliers occurred during summer and winter periods. The year 2010 had the highest SO_2 mean value of about 14.4 ppbv in winter. The standard deviation ranged from approximately2 ppbv to 9 ppbv. The fact that the deviation was found to be higher in winter which could be due to fewer measurements as there were no measurements recorded during June and July. The overall mean standard deviation during the entire time period was $approximately$ 4 ppbv.

Thus, it is evident that the SO_2 values were high when compared to GB data. Furthermore, the number of outliers above 10 ppbv was greater with approximately 13. This was in contradiction with GB SO_2 outliers, which were 6 in total. However, the OMI derived SO_2 measurements had a mean standard deviation of $approximately$ 4 ppbv (equivalent to $approximately$ 0.8 DU) which was insignificant with the expected root mean square of approximately 0.5 DU by PCA algorithm over the regions between 30°S and 30°N (See..OMSO2 README File, 2008).

The overall seasonal variations of OMI derived SO_2 measurements showed that the SO_2 mean values did not exceed 10 ppbv for all the seasons except in winter (August) where it reached 13.5 ppbv. The values were $\approx 9 \pm 3.5$ ppbv throughout the entire period, excluding the spring and early summer, where they were lower than below 8 ppbv. The lowest value of 4.5 ppbv was recorded in spring 2013.

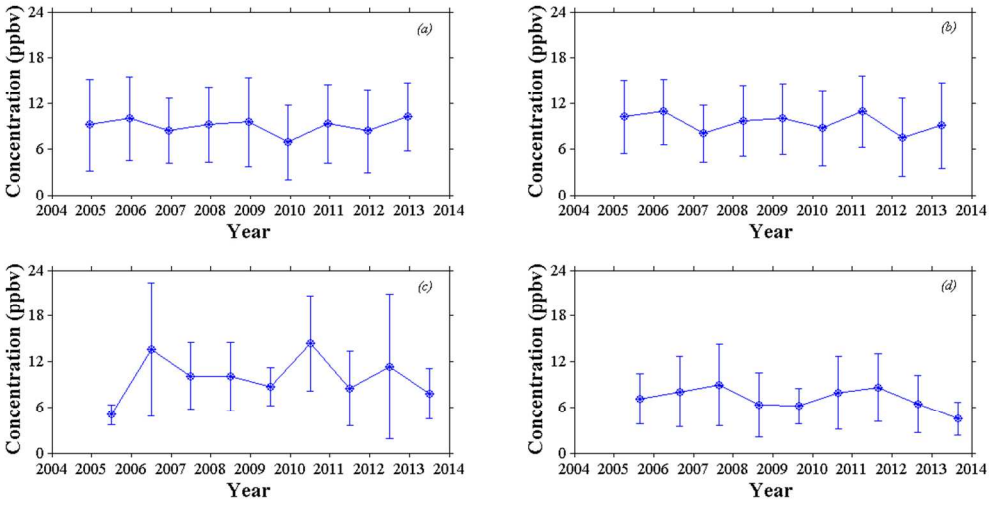

Figure 8. Inter-seasonal variations of OMI derived measurements depicting monthly SO2 averages in four main seasons where Top left (a) summer (Dec-Feb); Top Right (b) autumn (Mar-May); Bottom Left (c) winter (Jun-Aug); spring (Sep-Nov), based on the data from Dec 2004-Dec 2013. Summer mean values calculated for the December (corresponding year), January to February of the following years. Vertical lines represent ±1 standard deviations.

304x161mm (96 x 96 DPI)

4. Discussion and conclusion

The outcome of this study illustrates two important findings. Firstly, it was found that both the estimations from GB data and OMI surface-based measurements showed higher SO_2 values in winter and secondly, in summer only OMI surface-based measurements showed higher SO_2 values. Several meteorological factors play a vital role with respect to this observation. The wind speed estimation in this investigation, found that wind speed was low in winter and also noted high pressure exists during this period, which is characterised by calm conditions. The prevalence of low wind speed controls the horizontal transport of pollutants (Annegarn and Scorgie, 1997) and thus the surface SO_2 rise from January until July. After the post winter period until early summer, the wind speed increased. This could lead to long range transport and dispersion of pollutants thereby lowering SO_2 amounts in these periods. Apart from this, periodic recirculation of air from the Highveld region occurs mostly in the lower troposphere (800-700 hPa) (Freiman and Piketh 2003, 5). When this re-circulated air mixes with the pre-existing ground level SO_2 rich air, this could lead to high surface level episodes in winter. A contrasting phenomenon occurs in summer when the recirculation of air from the Highveld was more frequent in the upper troposphere (600-500 hPa) than the surface level (5). In addition, the 500 hPa stable layer was more frequent and persistent, whereas the lowest 700 hPa was eroded frequently by easterly waves in summer (Freiman and Tyson 2000). Apart from this, in summer the convergence of air masses occur by two main principal mechanisms namely Congo air boundary and Intertropical Convergence Zone (ITCZ). These two convergence systems in summer bring thunderstorms and frequent uplift of air (Kruger et al. 2010). These climatological conditions prevailing in winter and summer support our findings for higher SO_2 values in winter by both the measurements whereas in summer by OMI only. Furthermore, Li et al. (2013) have indicated that the newly developed PCA algorithm is able to capture SO_2 variations even on daily time scales. Thus the daily mean comparisons in this study also proved that the OMI surface-based method Upper Range Limit (URL) were equivalent and they even exceeded that of the GB amount in some cases and therefore could measure increase in SO_2 values similar to GB data (especially in winter) on a daily basis.

In a study conducted on the relationship between the SO_2 concentration and the meteorological conditions prevailing in the North China Plain during winter periods of 2006 - 2015, they found that the top 10% percentile of high SO_2 days detected by OMI were highly

influenced by increase in geopotential metre (gpm) height over 850 hpa, high surface pressure and relative humidity, warm temperature, slow wind speed. According to them, high gpm was the major causative source for the observed higher SO_2 levels, as it led to more stagnant conditions and thus hindered the dispersal of air. In addition, they noticed increased SO_2 concentration when the precipitation was slightly drier. They also observed a good agreement between OMI measurements and chemistry transport model SO_2 emissions during winter while a non-linear relationship existed when SO_2 emissions were compared with the ground based SO_2 measurements. It was suggested that the background meteorological parameters play a major role for such discrepancies (Calkins et al. 2016).

It should be noted that since the monitoring station was located near to some major industrial sources, an analysis on seasonal variation of wind direction should be estimated and hence the meridional and zonal wind velocity for the time period from 2004 to 2013 were obtained from MERRA data over the site location (figures are not shown). It has been identified from both meridional and zonal wind velocity that during January to March, the wind direction was north easterly, whereas from April to December, it was north westerly. These results were similar to those obtained by a study conducted on Air quality impact assessment at Vanderbijlpark works during January 2005 to December 2007 where the annual average wind rose were predominantly from north westerly and easterly direction, but in contrast, in winter both north westerly and south westerly winds prevailed (Watson and Thompson, 2014). In another study on population exposure to pollutants in the VAAL Triangle, the seasonal average wind rose in Vereeniging during 1994-1997 showed that northerly to north-north westerly winds predominated in winter, whereas in summer, easterly winds were dominant (Liebenberg,1999). Thus, this study also found that the majority of wind flow was from northerly to north westerly direction in almost all seasons. These events might have carried additional SO_2 amounts from its neighbouring industrial sites like Vereeniging CBD and Arcelo- Mittal Vanderbijlpark works rather than aiding dilution.

The overall results of this study showed that OMI derived method followed a similar trend equivalent to its counterpart i.e. the GB data, although they differ in magnitudes, where several meteorological parameters, physical and chemical complexity in the PBL layer acts as a barrier for OMI's retrieval. Thus, it can be concluded that OMI data in lieu of GB quantitative SO_2 measurement may be used in conjunction with air pollution models in order to clearly monitor the seasonal or monthly SO_2 trends qualitatively in places where there is

no GB monitoring station. However, this study must be extended to many more ground site measurements for higher confidence in such methods.

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