

# NO<sub>2</sub>, SO<sub>2</sub>, C<sub>6</sub>H<sub>6</sub>, O<sub>3</sub> AND PM<sub>10</sub> LEVELS WITHIN THE BA-PHALABORWA MUNICIPALITY OF SOUTH AFRICA

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## ABSTRACT

In this case study, the levels of nitrogen dioxide (NO<sub>2</sub>), sulphur dioxide (SO<sub>2</sub>), benzene (H<sub>6</sub>C<sub>6</sub>), tropospheric ozone (O<sub>3</sub>) and particulate matter with aerodynamic diameter of 10 µm (PM<sub>10</sub>) were measured from June to December 2015 to evaluate the air quality status within the Ba-Phalaborwa municipality. Radiello diffusive sampling cartridges were used in duplicates to sample gaseous pollutants at the four selected monitoring sites. The cartridges were exposed for a period of one week (7 days) before being replaced with new unexposed ones. PM<sub>10</sub> pollutant levels were measured continuously at each site with a portable active sampling unit (Met One E-sampler) equipped with meteorological sensors for wind speed and direction. Chemical analyses of all badges were performed by a South African National Accreditation System (SANAS) accredited laboratory. The highest average monthly NO<sub>2</sub> concentrations were measured at sites 3 and 4 with significantly higher concentrations measured during the dry period (18.8 µg/m<sup>3</sup> at site 3 and 14.4 µg/m<sup>3</sup> at site 4 in June) than during the wet period (3.7 µg/m<sup>3</sup> at site 3 and 4.4 µg/m<sup>3</sup> at site 4 in December) and similar trends were also attained at the other two sites. SO<sub>2</sub> and H<sub>6</sub>C<sub>6</sub> average monthly concentration trends were similar to those measured for NO<sub>2</sub>. In contrast to the concentration trends measured for NO<sub>2</sub>, SO<sub>2</sub> and H<sub>6</sub>C<sub>6</sub>, the average monthly concentrations for ozone were relatively low from June to August months. All the gas pollutants measured did not exceed the South African Standards. All monitoring sites experienced episodes of non-compliance with respect to PM<sub>10</sub> national ambient air quality standard of 75 µg/m<sup>3</sup>. The highest PM<sub>10</sub> concentrations recorded were 187.13 µg/m<sup>3</sup> at site 2; 155.48 µg/m<sup>3</sup> at site 1; 140.59 µg/m<sup>3</sup> at site 3 and 101.21 µg/m<sup>3</sup> at site 4. The results provide baseline data to compare with future air quality assessments in Phalaborwa or other similar kinds of study areas.

*Keywords:* air quality, Radiello gas cartridges, NO<sub>2</sub>, SO<sub>2</sub>, C<sub>6</sub>H<sub>6</sub>, O<sub>3</sub>, PM<sub>10</sub>, E-sampler.

## 1 INTRODUCTION

Air pollution is one of the major health, economic and social problems worldwide, particularly in urban areas (WHO [1]). Urban air pollution is estimated to cost approximately 2% of gross domestic product (GDP) in developed countries and 5% in developing countries, as well as being linked to up to one million premature deaths each year along with various cases of respiratory illnesses (WHO [2], Cities Alliance [3], WHO [4]). According to the Organization for Economic Cooperation and Development (OECD) report, air pollution is anticipated to become the biggest environmental cause of mortality worldwide by 2050, overtaking the lack of clean water and poor sanitation (OECD [5]). Air quality, particularly in dense urban industrial areas of South Africa is a national cause for concern. Three national air quality priority areas (areas where air quality standards have been exceeded or are likely to be exceeded) include the Highveld, Vaal Triangle and Waterberg-Bojanala have been declared in terms of section 18 of the Air Quality Act. According to the National Framework for Air Quality Management in the Republic of South Africa (Department of Environmental Affairs and Tourism [6]), Mopani District Municipality is one of the municipalities in Limpopo Province rated as having potentially poor or deteriorating air quality rating. The basis for this rating is mainly the magnitude of industrial and mining activities around the Ba-phalaborwa study area. It is on the same basis, that Ba-Phalaborwa area has been identified as one of the provincial air pollution hotspot area in Limpopo (LEDET [7]). It is



acknowledged in the Ba-Phalaborwa municipal integrated development plan (IDP) (Ba-phalaborwa Municipality [8]) that the municipality does not have reliable information on the severity of air pollution in the area and that the municipality does not have capacity to perform air quality management activities. The objective of this case study is to investigate the levels of NO<sub>2</sub>, SO<sub>2</sub>, C<sub>6</sub>H<sub>6</sub>, O<sub>3</sub> and PM<sub>10</sub> air pollutants within the Ba-Phalaborwa municipality.

## 2 MATERIALS AND METHODS

### 2.1 Study area and location of sampling sites

Ba-Phalaborwa municipality is situated in the Mopani district, halfway up along the length of the Kruger National Park (KNP) in the Limpopo province of South Africa. The geographical coordinates of the area are 23°56'59"S 31°6'35"E (Latitude: -23.95000, Longitude: 31.11000) and it is located at an average altitude of 405 metres above sea level (Ba-phalaborwa Municipality [9]). The town is a mining hub surrounded by two townships (Namakgale and Lulekani) and five tribal authority areas (Mashishimale, Makushane, Ga-Maseke, Majeke and Selwane) on the western direction. South of the town is a base for phosphate and copper mining, process industries, fertilizer, and acid plants. The total area is 193.33 km<sup>2</sup> with a population of approximately 13108 (67.80 inhabitants per km<sup>2</sup>) and 3836 (19.84 per km<sup>2</sup>) households (Stats SA [10]).

This study area experiences subtropical climate with warm to hot temperatures prevailing all year round. Summer days are humid and hot with temperatures often soaring to above 38°C (Ba-phalaborwa, 2014) [8]. The highest recorded temperature was 43°C in January 2006 (LEDET [7], SAWS [11]). The average maximum temperature in summer (October to March) is only 5°C higher than in winter. Winters are dry with cool to cold nights with average temperatures ranging from 9°C to 26°C. During summer the average temperatures vary from 23°C to 35°C with occasional heavy rainfall (Ba-phalaborwa Municipality [9]). The rainfall is low, averaging about 550 mm of rainfall annually. September and October are the driest periods, culminating in rains late in October. The rainy season occurs between November and March, with rainfall mainly occurring as thunderstorms and heavy showers.

### 2.2 Selection of sampling sites

Sampling constitutes the main part of air quality monitoring and it is therefore critical to understand all relevant factors including, amongst others, sampling site location (Senthilnathan [12]). The selected sampling sites should give a representative picture of air quality in the area being investigated. In this study, four monitoring sites were selected for monitoring of air pollutants and measurements of meteorological parameters (Fig. 1). The criteria used for site selection was largely informed by spatial distribution of populations, local air pollution sources, affected receptors and overall land use in the study area. Other considerations included meteorological factors and site logistics such as access to site, security, as well as access to electricity.

Site selection was also attuned to ensure they are representative of areas far from the existing monitoring network, areas where complaints related to air pollution are prevalent, and areas with high population density or heavy traffic volumes (LEDET, 2013). Sites 1 and 2 are located within the residential areas influenced by emissions from domestic activities but are also suspected to be high impact zones for emissions from industrial/mining complex. These sites are located within 5 km radius of the industrial/mining complex, on the northwest





Figure 1: The monitoring sites within the study area.

and west of the complex. Sites 3 and 4 are positioned to monitor emissions from on-road mobile sources at two major intersections entering/exiting Phalaborwa town. These sites are located approximately 6 km northwest and 3 km east of town respectively.

### 2.3 Sample collection and sampling chamber

The selected monitoring sites were attuned to ensure they are representative of the anticipated spatial variation in air pollution in the area (Kanaroglou et al. [13]). Internationally recognized Radiello diffusive passive sampling cartridges were used in duplicates to sample gaseous pollutants ( $\text{NO}_2$ ,  $\text{SO}_2$ ,  $\text{C}_6\text{H}_6$  and  $\text{O}_3$ ) (Radiello [14]). Cartridges were exposed for 7 days before being replaced with new unexposed ones in the period from June to December 2015. Fig. 2 shows a sampling chamber housing exposed cartridges (in blue) and the PM10 inlet with a white cap. Blank Radiello cartridges and filters were submitted to the laboratory for analysis as field or travel blanks together with main samples. Portable active continuous sampling units (Met One E-samplers equipped with meteorological sensors for wind speed and direction) were used to monitor PM10 levels.



Figure 2: Sampling chamber containing Radiello cartridges and a PM10 sampler at each site.

Regular maintenance, leaks, calibrations were undertaken during the sampling period. Chemical analyses of all badges were performed by a South African National Accreditation System (SANAS) accredited laboratory.

### 3 RESULTS AND DISCUSSION

Both temporal and seasonal variations of pollutants of interest were investigated and their probable sources were explored. The influence of wind speed and direction on the air quality was also considered.

#### 3.1 Meteorological data

A summary statistical analysis of the wind data measured at the four continuous monitoring sites is presented in Table 1.

Fig. 3 presents wind roses and wind class frequency distribution graphs for wind speeds and directions observed at site 1, site 2, site 3 and site 4. The figure, together with data in Table 1, clearly indicates the dominance of south-easterly winds which tend to reach speeds of 6 m/s. The highest wind speeds were measured in November, 6.35 m/s at site 1 and 4.89 m/s at site 3 respectively.

Table 1: A summary of daily averaged wind speed and direction data in the study period.

	Site 1		Site 2		Site 3		Site 4	
	Wind speed (m/s)	Wind direction (°)	Wind speed (m/s)	Wind direction (°)	Wind speed (m/s)	Wind direction (°)	Wind speed (m/s)	Wind direction (°)
Average	1.89	160.84	1.56	138.54	2.65	148.81	1.36	160.76
Minimum	0.75	51.98	0.50	0.05	1.38	3.89	0.55	5.30
Maximum	4.89	316.56	3.97	354.67	6.35	358.52	3.42	355.73
Date of min	2015/06/19	2015/11/08	2015/07/03	2015/09/15	2015/07/03	2015/08/13	2015/06/10	2015/12/24
Date of max	2015/09/02	2015/06/14	2015/11/03	2015/12/24	2015/11/03	2015/09/10	2015/09/03	2015/09/15

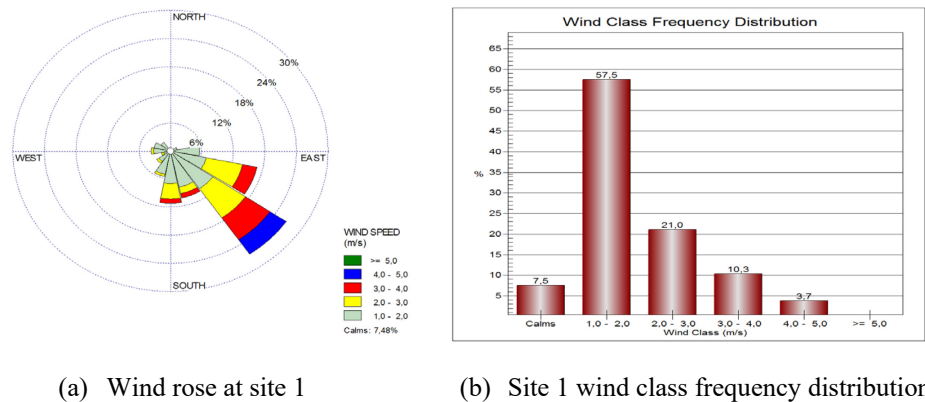
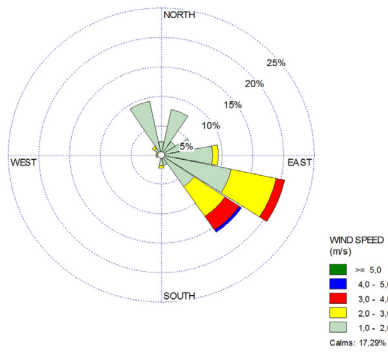
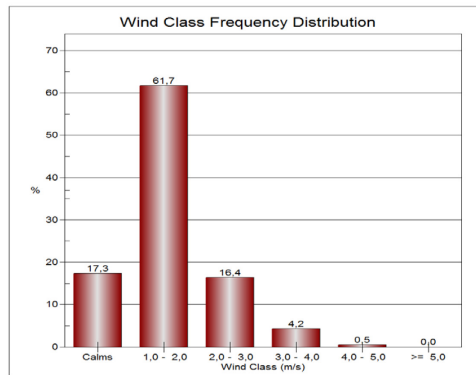


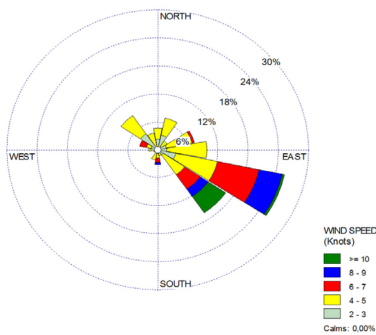
Figure 3: Wind rose and wind class frequency distribution graph observed at site 5, site 6, site 7 and site 8 for the period January to December 2015.



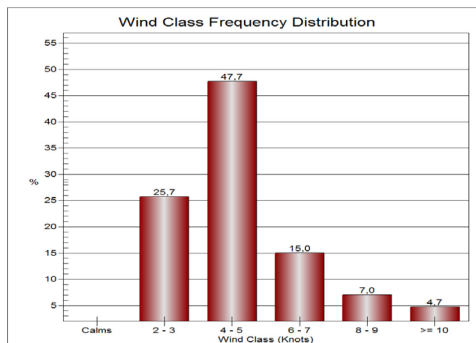
(c) Wind rose at site 2



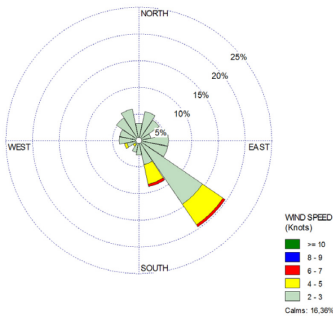
(d) Site 2 Wind class frequency distribution



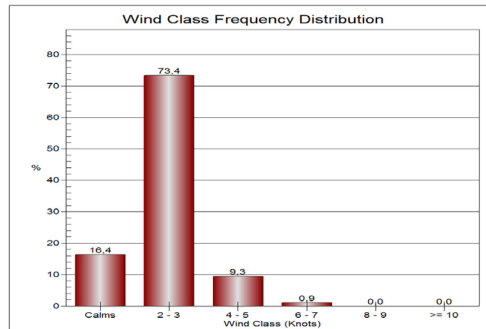
(e) Wind rose at site 3



(f) Site 3 wind class frequency distribution



(g) Wind rose at site 4



(h) Site 4 wind class frequency distribution

Figure 3: Continued.

### 3.2 Nitrogen dioxide data

Fig. 4 shows a plot of a four-week average or monthly average of nitrogen dioxide concentrations. The highest monthly averages were measured in June month with  $12.4 \mu\text{g}/\text{m}^3$  at site 1,  $10.9 \mu\text{g}/\text{m}^3$  at site 2,  $18.8 \mu\text{g}/\text{m}^3$  at site 3 and  $14.4 \mu\text{g}/\text{m}^3$  at site 4. The lowest monthly averages were measured in December with  $3.1 \mu\text{g}/\text{m}^3$  at site 1,  $1.6 \mu\text{g}/\text{m}^3$  at site 2,  $3.7 \mu\text{g}/\text{m}^3$



at site 3 and  $4.4 \mu\text{g}/\text{m}^3$  at site 4. Highest concentrations were measured at sites 3 and 4 which are closed to the main roads. All the concentrations were high during the cold winter months of June and July and decreased gradually with the lowest levels measured between October and December. The South African Standard (SANS [15]) of  $40 \mu\text{g}/\text{m}^3$  was not exceeded.

A summary of the mean, maximum and minimum (in  $\mu\text{g}/\text{m}^3$ ) and standard deviation (SDV) concentrations of nitrogen dioxide measured in that order were 6.66, 12.4, 3.1 and 3.1 at site 1; 5.96, 10.9, 1.6 and 3.3 at site 2; 10.3, 18.8, 3.7 and 5.6 at site 3; 9.54, 15.6, 4.4 and 3.7 at site 4 respectively. All the standard deviations were below 5.0 except the one at site 3.

### 3.3 Sulphur dioxide data

The Fig. 5 shows the weekly average sulphur dioxide concentrations that were measured in duplicates as indicated in columns A and B per site. All the duplicate results are reproducible and give assurance about the accuracy of the results. Fig. 5 shows a plot of a four-week average or monthly average of sulphur dioxide concentrations. The highest monthly averages were measured in June month with  $22.9 \mu\text{g}/\text{m}^3$  at site 1,  $21.9 \mu\text{g}/\text{m}^3$  at site 2,  $29.3 \mu\text{g}/\text{m}^3$  at site 3 and  $25.1 \mu\text{g}/\text{m}^3$  at site 4. The lowest monthly averages were measured in December with  $10.8 \mu\text{g}/\text{m}^3$  at site 1,  $12.1 \mu\text{g}/\text{m}^3$  at site 2,  $15.5 \mu\text{g}/\text{m}^3$  at site 3 and  $13.9 \mu\text{g}/\text{m}^3$  at site 4. Just like in the case of nitrogen dioxide, the highest concentrations were measured at sites 3 and 4 which are closer to the main roads. All the concentrations were high during the cold winter months of June and July and decreased gradually with the lowest levels measured between October and December. The South African Standard (SANS [15]) of  $50 \mu\text{g}/\text{m}^3$  was not exceeded.

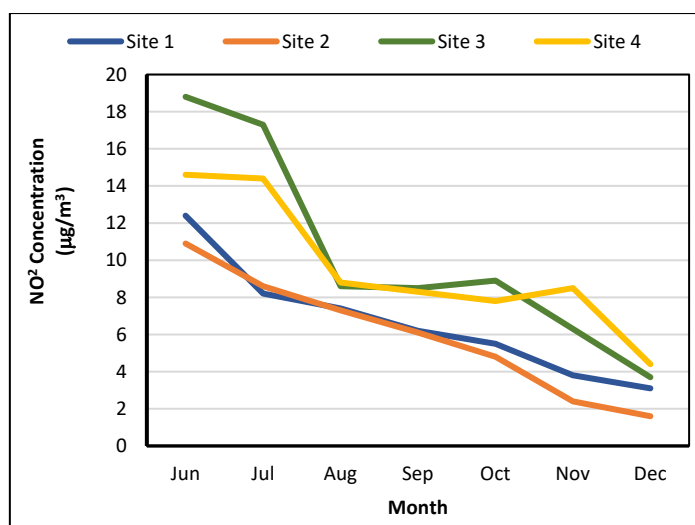


Figure 4: Passive nitrogen dioxide monthly average concentrations.

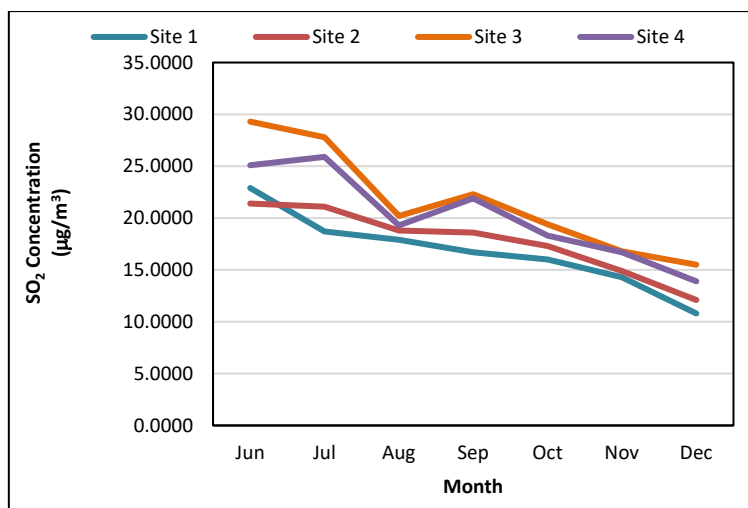


Figure 5: Passive sulphur dioxide monthly average concentrations.

A summary of the mean, maximum and minimum (in  $\mu\text{g}/\text{m}^3$ ) and standard deviation (SDV) concentrations of sulphur dioxide measured in that order were 16.8, 22.9, 10.8 and 3.8 at site 1; 17.7, 21.4, 12.1 and 3.3 at site 2; 21.6, 29.3, 12.1 and 3.3 at site 3; 21.6, 29.3, 15.5 and 5.2 at site 4 respectively. All the standard deviations were below 5.0 except the one at site 3.

### 3.4 Benzene data

The weekly average sulphur dioxide concentrations that were measured in duplicates per site were reproducible and gave assurance about the accuracy of the results. The Fig. 6 below shows a plot of monthly averages of benzene concentrations. The highest monthly averages

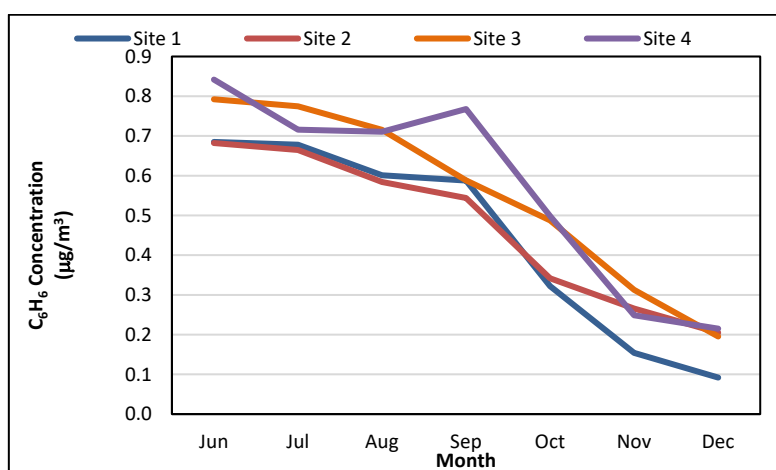


Figure 6: Passive benzene monthly concentrations by location.

were measured between June and September month and decreased sharply from October to December months. The lowest benzene concentrations measured in December were about 10 times lower the concentrations measured in June. Sites 3 and 4 had slightly higher benzene concentrations and could be linked to emissions from vehicles at nearby main roads. The South African Standard (SANS [15]) of  $5.0 \mu\text{g}/\text{m}^3$  was not exceeded. A summary of the mean, maximum and minimum (in ppb) and standard deviation (SDV) concentrations of benzene measured in that order were 0.45, 0.68, 0.09 and 0.25 at site 1; 0.47, 0.68, 0.2 and 0.2 at site 2; 0.55, 0.79, 0.2 and 0.23 at site 3; 0.57, 0.84, 0.22 and 0.25 at site 4 respectively. All the standard deviations were below 5.0.

### 3.5 Ozone data

The weekly average sulphur dioxide concentrations that were measured in duplicates per site were reproducible and gave assurance about the accuracy of the results. Fig. 7 shows a plot of monthly average of ozone concentrations. In contrast to the concentration trends measured in the case of  $\text{NO}_2$ ,  $\text{SO}_2$  and  $\text{H}_6\text{C}_6$ , the average monthly concentrations of ozone were relatively low from June and August months. The highest monthly averages were measured from September to December months. Just like in all previous cases, the highest concentrations were measured at sites 3 and 4 which are closer to the main roads. The South African Standard (SANS [15]) of  $120 \mu\text{g}/\text{m}^3$  was not exceeded. A summary of the mean, maximum and minimum ( $\mu\text{g}/\text{m}^3$ ) and standard deviation (SDV) concentrations of ozone measured in that order were 67.1, 82.4, 54.4 and 12.4 at site 1; 69.7, 83.0, 57.5 and 11.4 at site 2; 79.9, 89.3, 65.3 and 8.7 at site 3; 78.0, 85.9, 62.9 and 8.6 at site 4 respectively. All the standard deviations were high and exceeded 5.0.

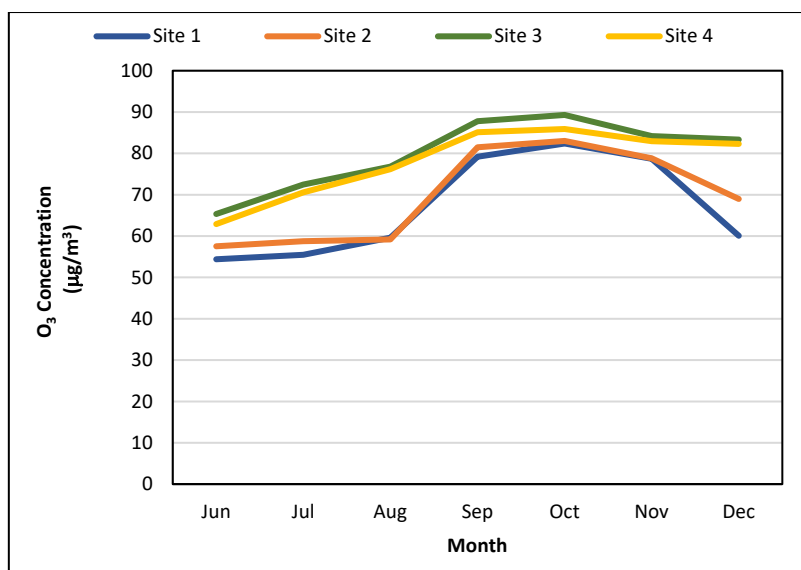


Figure 7: Passive ozone averages concentrations by month.



Overall, the highest concentrations of ozone coincided with the lowest concentrations of ozone precursors like  $\text{NO}_2$  and  $\text{C}_6\text{H}_6$ . This means that the formation of ozone is linked to the destruction of the nitrogen oxide and the benzene compounds. The study area is known to have condition suitable to the formation of photochemical pollution, that is, high temperature, low wind speed and high humidity from September to December wet period. Sunlight catalyse  $\text{NO}_2$  and  $\text{C}_6\text{H}_6$  and form radicals which lead to the formation of ozone through the oxidation process.

### 3.6 E-sampler measurements of particulate matter (PM10)

The PM10 data statistics collected at sites 1, 2, 3 and 4 is presented in Table 2. The average concentrations measured were  $35.24 \mu\text{g}/\text{m}^3$  at site 1;  $40.41 \mu\text{g}/\text{m}^3$  at site 2;  $25.31 \mu\text{g}/\text{m}^3$  at site 3, and  $23.59 \mu\text{g}/\text{m}^3$  at site 4. This information is based on the averaged data recovery of 100% for site 1; 96.4% for site 2; 98.1% for site 3; and 95.3% for site 4. The number of exceedances measured was 22 at site 1, 32 at site 2, 15 at site 3 and 1 at site 4.

Figs. 8–12 show the daily averaged PM10 concentrations recorded from June to December 2015 at site 1 to site 4 respectively. PM 10 concentrations that exceeded the  $75 \mu\text{g}/\text{m}^3$  local standard in June were measured only at site 1 with the following readings per date:  $95.55 \mu\text{g}/\text{m}^3$  on the 1<sup>st</sup>,  $109.094 \mu\text{g}/\text{m}^3$  on the 3<sup>rd</sup>,  $118.416 \mu\text{g}/\text{m}^3$  on the 4<sup>th</sup>,  $97.563 \mu\text{g}/\text{m}^3$  on the 5<sup>th</sup>,  $95.462 \mu\text{g}/\text{m}^3$  on the 9<sup>th</sup>,  $75.805 \mu\text{g}/\text{m}^3$  on the 12<sup>th</sup>,  $81.068 \mu\text{g}/\text{m}^3$  on the 13<sup>th</sup> and  $85.739 \mu\text{g}/\text{m}^3$  on the 14<sup>th</sup> at site 1.

The concentrations that exceeded the local PM10 standard were measured at three sites in July, with site 1 experiencing a total of seven exceedances on days 11, 21, 22, 23, 28, 29 and 30. Site 2 experienced a total of six exceedances on days: 2, 7, 18, 22, 25 and 29. While exceedances at site 3 were only on the 6 and 10 of July. All the sites except site 4 experienced concentration exceedances in August, with site 1 experiencing a total of four exceedances on days 1, 2, 7 and 8. Site 2 experienced non-exceedances only on six days: 1, 2, 9 and 23. While exceedances at site 3 exceedances totalled 13 on days 5 to 10, 13 to 17, 23 and 25 of August. So far, the only concentration that exceeded the local PM10 standard at site 4 was  $101.215 \mu\text{g}/\text{m}^3$  measured on day 6. There were no exceedances measured in during the rainy months of October, November and December because rain tends to remove particulate matter suspended in air.

Table 2: PM10 data statistics and exceedances measured.

Station	Site 1	Site 2	Site 3	Site 4
Average ( $\mu\text{g}/\text{m}^3$ )	35.24	40.41	25.31	23.59
Maximum ( $\mu\text{g}/\text{m}^3$ )	155.48	187.13	140.59	101.21
Minimum ( $\mu\text{g}/\text{m}^3$ )	1.27	0.87	0.21	4.09
Date of maximum	2015/07/11	2015/08/08	2015/08/17	2015/10/06
Exceedances	22	32	15	1
Invalid data	0	13	7	17
Percentage data recovery	100	96.4	98.1	95.3



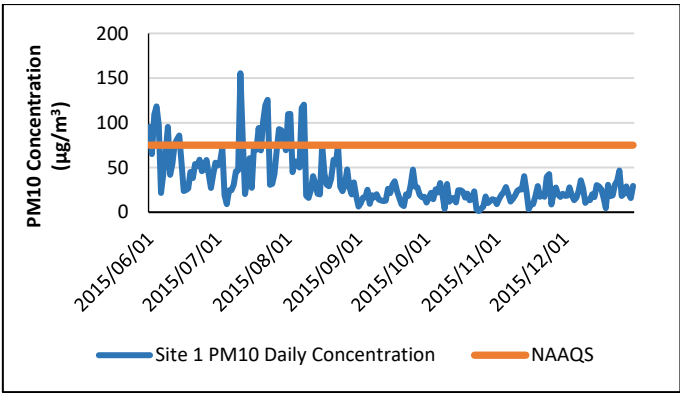


Figure 8: Daily PM10 concentrations recorded at site 1 for the period June to Dec 2015.

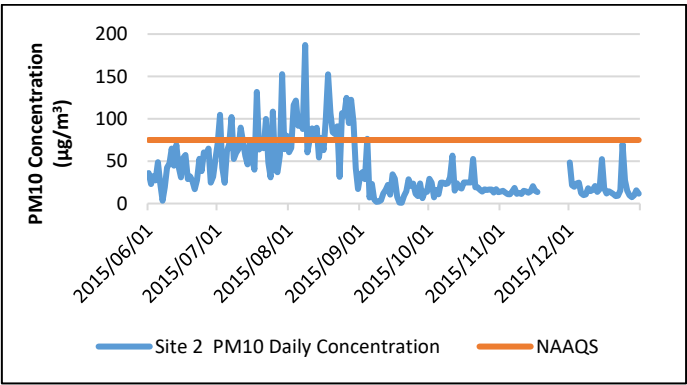


Figure 9: Daily PM10 concentrations recorded at site 2 for the period June to Dec 2015.

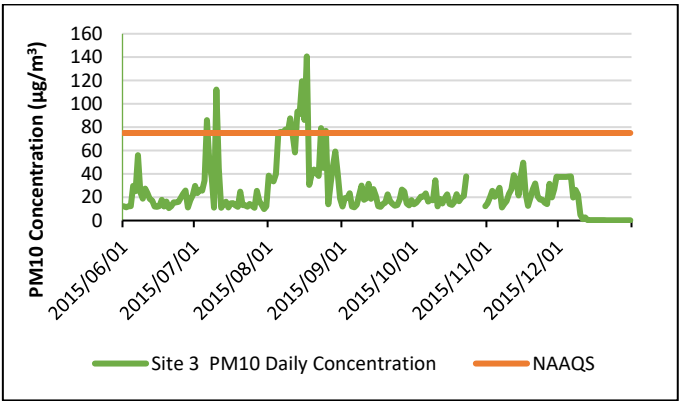


Figure 10: Daily PM10 concentrations recorded at site 3 for the period June to Dec 2015.

The current PM<sub>10</sub> results are relatively higher than those measured in a similar study that was carried out in Vanderbiljpark, a heavily industrialized and polluted region of Gauteng Province. In that study the highest concentration measured was 0.03543  $\mu\text{g}/\text{m}^3$  (Moja [16]).

The seasonal variation of PM<sub>10</sub> concentrations show sites 1 and 2 experiencing highest concentration ranges from June to August with the peaks measured in August for site 2 and July for site 1 (Fig. 11). Site 3 highest concentration was in August. These concentrations peaked during the dry month of June to August. The lowest concentrations flattened from September to December at all monitoring sites.

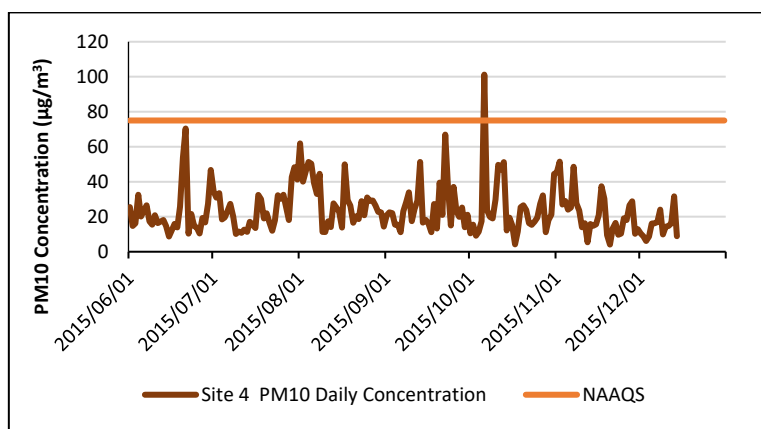


Figure 11: Daily PM<sub>10</sub> concentrations recorded at site 4 for the period June to Dec 2015.

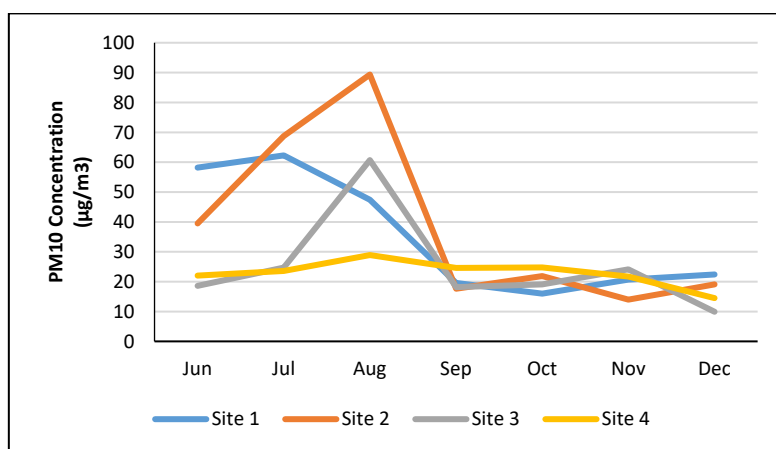


Figure 12: PM<sub>10</sub> monthly concentrations and seasonal variation as Measured by E-sampler at the four sites during the period Jun to Dec 2015.

#### 4 CONCLUSION

This study was able to measure baseline levels of NO<sub>2</sub>, SO<sub>2</sub>, C<sub>6</sub>H<sub>6</sub>, O<sub>3</sub> and PM<sub>10</sub> within the Ba-Phalaborwa study area. The NO<sub>2</sub>, SO<sub>2</sub> and C<sub>6</sub>H<sub>6</sub> gas pollutants measured were high during the dry winter months and dropped significantly during the wet summer months. A drop of NO<sub>2</sub> and C<sub>6</sub>H<sub>6</sub> in summer coincided with a rise in O<sub>3</sub> pollutant. It was not surprising to detect these air pollutants because in a similar study undertaken in the Mpumalanga province, (Zunckel et al. [17]) detected similar pollutants, including carbon monoxide and methane. The study identified sources as power stations, smelters, industries and mining operation. While the levels of NO<sub>2</sub>, SO<sub>2</sub>, C<sub>6</sub>H<sub>6</sub> and O<sub>3</sub> measured in this study were below the local standards, but the presence of ozone precursors (NO<sub>2</sub> and C<sub>6</sub>H<sub>6</sub>) contribute to O<sub>3</sub> and photochemical pollution. The relatively high PM<sub>10</sub> concentrations that exceeded the local standard is of concern because this fraction of particulate matter is inhalable and could have negative effects to those who are exposed to it.

#### ACKNOWLEDGEMENTS

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