

## Sulphur Dioxide Characterization in Ambient Air for Calabar, Nigeria

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The present investigation was carried out for the Characterization of Sulphur dioxide (SO<sub>2</sub>) in Calabar, Nigeria. The measured concentration of SO<sub>2</sub> as recorded in this research is above the World Health Organization (WHO) standard. For air quality index, Marina Resort station was found to be “moderately polluted” with AQI of 157.20. The remaining five (5) stations were classified as “poor” with the AQI ranging from 214 to 229. Basin Authority showed the highest positive correlation of SO<sub>2</sub> and relative humidity, with R = 0.753. This shows that at Basin Authority station, relative humidity had the greatest effect on SO<sub>2</sub>. The highest correlation between SO<sub>2</sub> and wind speed was obtained at basin authority with R = 0.609. Wind speed also had effect on SO<sub>2</sub> in that station. Marina resort recorded the highest negative correlation of SO<sub>2</sub> and temperature, with R = -0.643. Basin Authority recorded the highest positive correlation with R = 0.631. Hence the best model for the prediction of SO<sub>2</sub> for Calabar is 5 – 10 – 1. This translates to, five (5) input variables that include; SO<sub>2</sub>, wind speed, temperature, relative humidity and total suspended particulate matter (TSP), ten (10) hidden neurons in the neural network and one (1) target variable which is SO<sub>2</sub>.

**Keywords:** Sulphur dioxide, relative humidity, correlation, neural network.

## INTRODUCTION

The quality of air we breathe is directly linked to the concentration of certain chemicals in ambient or indoor air. These chemicals are called pollutants. Sulfur dioxide ( $\text{SO}_2$ ) is one of the pollutants set aside by the World Health Organization (WHO, 2005) as a criteria pollutant. A criteria pollutant is a pollutant that could cause harm or injury to living things and the environment. Sulfur is assimilated by living organisms and is then released as a product of metabolism. The most important sulfur gases in the atmosphere are  $\text{SO}_2$ ,  $\text{H}_2\text{S}$ , dimethyl sulfide ( $\text{CH}_3\text{SCH}_3$  or DMS for short), COS, and carbon disulfide ( $\text{CS}_2$ ). The principal natural sources of  $\text{SO}_2$  are the oxidation of DMS and  $\text{H}_2\text{S}$ . Volcanoes and biomass burning are also sources of atmospheric  $\text{SO}_2$  (Wallace and Hobbs, 2006). Important sources also include power plants, smelters, petroleum refineries, and pulp and paper mills (Lutgens and Tarbuck, 2013; Olatunji et al., 2015). Road side vulcanizers also produce  $\text{SO}_2$  (Gobo et al., 2012). However, the largest source of  $\text{SO}_2$  is fossil fuel combustion. This is because  $\text{SO}_2$  constitutes 18% of the quantity of gases and smoke discharged daily into the atmosphere (Asuoha and Osu, 2015). In summary, the anthropogenic  $\text{SO}_2$  emissions worldwide amount to 70-80 million tons per year, while the natural emissions have been estimated to be 18-70 million tons per year (Abdul Raheem et al., 2009). United States Environmental Protection Agency (EPA, 2006) states that  $\text{SO}_2$  reacts with other compounds in the atmosphere to form fine particles that reduce visibility. Except for marine aerosols, the masses of which are dominated by sodium chloride, sulfate is one of the prime contributors to the mass of atmospheric aerosols. These aerosols which are also called particulate matter, are categorized as follows;  $\text{PM}_{2.5}$  are aerosols that have diameter less than or equal to 2.5  $\mu\text{m}$ .  $\text{PM}_{10}$  are aerosols that have diameter 10  $\mu\text{m}$  or less and Total Suspended Particulate (TSP) which has diameter 30  $\mu\text{m}$  or less. High concentrations of  $\text{SO}_2$  can result in temporary breathing impairment for asthmatic children and adults who are active outdoors. Short-term exposures of asthmatic individuals to elevated  $\text{SO}_2$  levels while at moderate exertion may result in reduced lung function that may be accompanied by such symptoms as wheezing, chest tightness, or shortness of breath. Other effects that have been associated with longer-term exposures to high concentrations of  $\text{SO}_2$ , in conjunction with high levels

of particulate matter, include respiratory illness and aggravation of existing cardiovascular disease (Lutgens and Tarbuck, 2013). Deposition of aerosols can stain and damage stone and other materials such as statues and monuments. This is because  $\text{SO}_2$  is one of the precursors of acid rain. It causes the formation of microscopic acid aerosols.  $\text{SO}_2$  also contributes to climate change (Ljubisa et al., 2011). The emissions of Sulphur dioxide ( $\text{SO}_2$ ) into the air and the subsequent impact on the environment and health from the consumption of refined petroleum products in Nigeria could be mitigated, if there is proper and consistent investigation (Olatunji et al., 2015). Due to this serious need to mitigate the high mortality and morbidity rate associated with  $\text{SO}_2$  together with the aerosols they produce, there is a serious need to characterize  $\text{SO}_2$  in ambient air for Calabar, Nigeria.

## MATERIALS AND METHOD

The equipment used for the measurements is the Gas Analyser – Aeroqual series 500 – ENV which comes with the Aeroqual  $\text{SO}_2$  0 – 10 ppm Model 1905152 – 006. The equipment was purchased as part of TETFUND Assisted Air Quality Project. Another set of data for this research was obtained by an AQM65 Equipment, Micro-climate – Extech 4-in 1 Environmental Meter Model 45170 for measuring Wind speed, Air Temperature, and Relative Humidity. The data for this research were obtained in two parts. The first was obtained from the mobile Aeroqual hand-held devices while the second part was obtained from the stationary AQM65 device stationed at the University of Calabar Main Station. The data from the mobile devices were obtained at specific time intervals and at specific days. The days data were taken are; 23/05/2015, 06/06/2016, 20/06/2016, 04/07/2016, 18/07/2016, 1/08/2016, 15/08/2016 and 29/08/2016. The extended project covered fifty (50) stations within the stipulated time-frame hence the monitoring of the pollutants in the selected stations fell on the selected dates. On the other hand, the AQM65 stationary device was programmed by the company to record data at a minute by minute interval. The machine could also be re-programmed to record data at an hourly interval. For the purpose of this research, the data was obtained in a minute by minute interval. The data from both devices were

**Table1.** Mean concentration of Sulphur dioxide for the study location.

Location	Mean	Median	1 <sup>st</sup> Quartile	3 <sup>rd</sup> Quartile
Army Junction	0.3912	0.4200	0.3300	0.4800
Basin Authority	0.3513	0.3100	0.2125	0.4150
Goodluck Bypass	0.3463	0.3450	0.2175	0.4250
Ikalkaukwa Market	0.3450	0.3250	0.2125	0.4000
Marina Resort	0.2350	0.2550	0.1425	0.2925
Tinapa Resort	0.3050	0.3050	0.2175	0.3675

presented as monthly means. For the purpose of these research, six locations within Calabar metropolis were selected for the mobile data taking. These stations include; Army Junction, Basin Authority, Goodluck Johnathan Bypass, Ikaika Ukwa Market, Marina and Tinapa Resorts. Linear Regression Method was used to establish the correlation between meteorological parameters and Sulphur dioxide (SO<sub>2</sub>). Artificial neural network algorithm was used for SO<sub>2</sub> prediction. Five variables were used as input variables in the neural network toolbox. These variables include; SO<sub>2</sub>, TSP, wind speed, relative humidity and temperature. SO<sub>2</sub> was used as the target variable. 75% of the data was used for training, 15% was used for validation and 15% was used for testing. During the training of the data, the number of neurons was varied from 10 to 100. All the work related to statistical analysis and visualization was carried out with R Data Analysis Software.

## RESULTS AND DISCUSSION

Characterization of SO<sub>2</sub> in ambient air has been carried out in Calabar, Nigeria. **Table 1** shows the mean concentration of SO<sub>2</sub> for the study locations. It can be seen from the table that the mean concentration of SO<sub>2</sub> at Army Junction was 0.39 ppm, at Basin Authority it was 0.35 ppm, at Goodluck Johnathan Bypass it was 0.35 ppm, at Ikalka Ukwa Market it was 0.35 ppm, at Marina Resort it was 0.24 ppm and at Tinapa Resort it was 0.31 ppm. the measured concentration of SO<sub>2</sub> as recorded in this research is above the WHO (2005) standard of 0.009 ppm 24 hrs standard as well as 0.213 ppm 10 minutes standard. These values are high compared to that of Kano which ranged from 0.001 to 0.002 ppm (Ayodele and Abubakah, 2010). In Ilorin, Nigeria, SO<sub>2</sub> concentration was measured as 1.29 ±0.17 ppb in the

wet season and 7.17 ±0.87 ppb in the dry season (Abdul Raheem et al., 2009). In APO District in Federal Capital Territory, Abuja, Nigeria, it ranged from 0.60 to 0.66 ppm (Ishaya et al., 2017). In Orlu, Imo State, Nigeria, SO<sub>2</sub> was found to be within the range of 0.17 – 0.75 ppm (Chizoruo et al., 2017). In Ibadan, Oyo State, it was found to be within the range of 0.009 – 0.02 ppm (Ipeaiyeda and Adegboyega, 2017). In Umuahia, Abia State, SO<sub>2</sub> concentration which was measured from vehicular emissions was 0.44ppm.

**Figure 1** shows a graph of the mean concentration of SO<sub>2</sub> as measured in the study locations. The graph shows that 20% of the SO<sub>2</sub> concentration was measured at Army Junction. That makes Army Junction the most polluted in terms of SO<sub>2</sub>. Marina Resort had 12% of the concentration making it the least polluted. **Figure 2** shows SO<sub>2</sub> concentration as measured from the different study locations. This can be comparable to the measurements at Abuja Campus of the University of Port Harcourt which recorded a concentration of 0.25 ppm in April 2019 and 0.63 ppm in March of 2019 (Ugbebor et al., 2019). The mean concentration of SO<sub>2</sub> is presented in **Table 1**. Also presented are the median, 1<sup>st</sup> Quartile and 3<sup>rd</sup> Quartile values.

## AIR QUALITY INDEX

### AQI Equation

$$Ip = \frac{IHi - ILo}{BPHi - BPLo} (Cp - BPLo) + Lo \text{ ----- equation (1)}$$

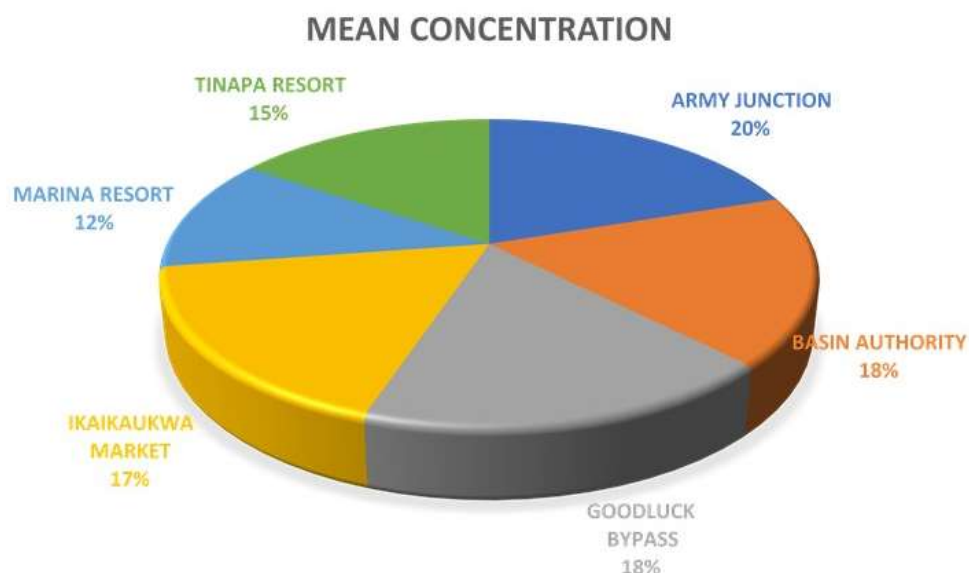
Where: IP = the index for pollutant P

CP = the rounded concentration of pollutant P

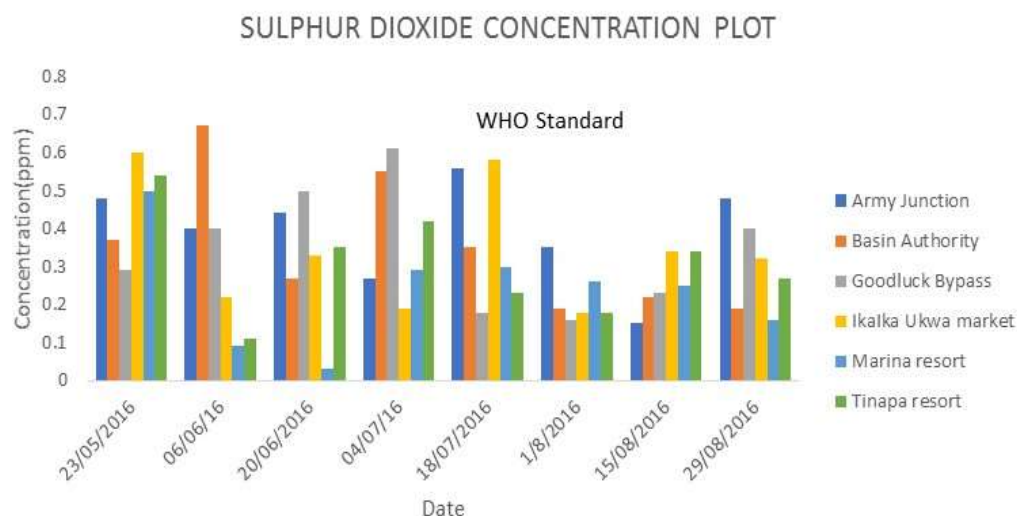
BPHi = the breakpoint that is greater than or equal to CP

BPLo = the breakpoint that is less than or equal to CP

IHi = the AQI value corresponding to BPHi



**Figure 1.** Mean concentration of Sulphur dioxide.



**Figure 2.** Concentration of SO<sub>2</sub> at different stations.

ILo = the AQI value corresponding to BPLo

Ip is the AQI that is to be calculated based on the pollutant. Cp is the concentration of the pollutant rounded to a reasonable decimal. BPHi is the breakpoint that is greater than or equal to the rounded concentration of the pollutants. BPLo is the breakpoint that is less than or equal to the rounded concentration of the pollutant Cp. IHi is the AQI value that corresponds to BPHi. While ILo is the AQI value

that corresponds to BPLo. The measured concentration of the four pollutants was used in the computation of the AQI. The AQI was based on the breakpoints published by the United States EPA (2006).

Air quality index (AQI) is a number issued by the Government or/and the stakeholders in the environmental sector, to inform the public on the state of the air in which they are breathing. It is an

**Table 2.** break points for the different pollutants (USEPA, 2006).

O <sub>3</sub> (ppm) 8-hour	O <sub>3</sub> (ppm) 1-hour	PM <sub>2.5</sub> (µg/m <sup>3</sup> )	PM <sub>10</sub> (µg/m <sup>3</sup> )	CO (ppm)	SO <sub>2</sub> (ppm)	NO <sub>2</sub> (ppm)	AQI	Category
0.000– 0.064	-	0.0 – 15.4	0 – 54	0.0 – 4.4	0.00 – 0.034	( <sup>2</sup> )	0 -50	Good
0.065 – 0.084	-	15.5 – 40.4	55 – 154	4.5 – 9.4	0.035 – 0.144	( <sup>2</sup> )	51 – 100	Moderate
0.085 – 0.104	0.125 – 0.164	40.5 – 65.4	155 – 254	9.5 - 12.4	0.145 – 0.224	( <sup>2</sup> )	101 – 150	Unhealthy For sensitive groups
0.105 – 0.124	0.165 – 0.204	65.5 – 150.4	255 – 354	12.5 – 15.4	0.225 – 0.304	( <sup>2</sup> )	151 – 200	Unhealthy
0.125 – 0.374	0.205 – 0.404	150.5 – 250.4	355 – 424	15.5 – 30.4	0.305 – 0.604	0.65 – 1.24	201 – 300	Very unhealthy
( <sup>3</sup> )	0.405 – 0.504	250.5 – 350.4	425 – 504	30.5 – 40.4	0.605 – 0.804	1.25 – 1.64	301 – 400	Hazardous
( <sup>3</sup> )	0.505 – 0.604	350.5 – 500.4	505 - 604	40.5 – 50.4	0.805 – 1.004	1.65 – 2.04	401 - 500	Hazardous

NOTE: NO<sub>2</sub> has no short-term NAAQS and can generate an AQI only above a value of 200.

**Table 3.** AQI Categorization Table.

Category	AQI	Description of Ambient Air
I	0-50	Good
II	51-100	Moderate
III	101- 150	Unhealthy for sensitive groups
IV	151-200	Unhealthy
V	201-300	Very unhealthy
VI	301-400	Hazardous
VII	401-500	Hazardous

indication on how safe the air is. For this research, air quality is calculated using equation 1. **Table 2** shows the breakpoint of all the criteria pollutants as published by the United States EPA (2006). These break points are used in the estimation of the AQI. The air quality categorization is presented on **Table 3**. The result shows that only Marina Resort station

was found to be “moderately polluted” with AQI of 157.20 and the remaining five (5) stations were classified as “poor” with the AQI ranging from 214 to 229. This result is presented in **Table 4**. This shows that the quality of air is poor in Calabar considering SO<sub>2</sub>. This is comparable with the AQI for SO<sub>2</sub> in APO District in the Federal Capital Territory, Abuja, Nigeria which was categorized as very poor (Ishaya et al., 2017).

## CORRELATION OF SO<sub>2</sub> WITH METEOROLOGICAL PARAMETERS

### Effect of Meteorology on Sulphur Dioxide

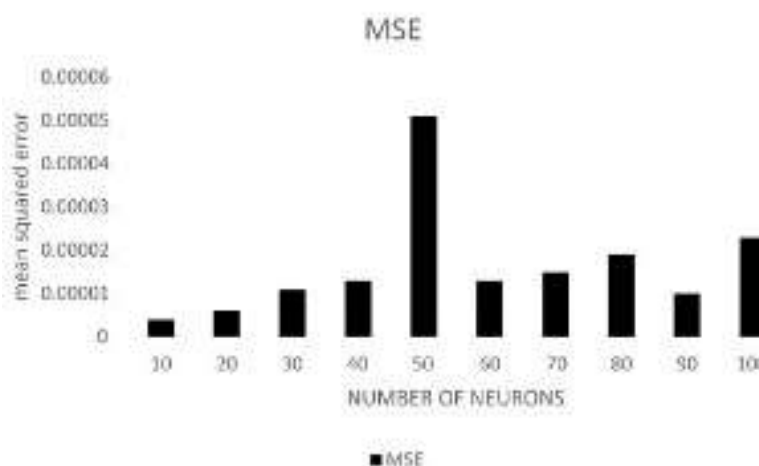
Correlation was made between SO<sub>2</sub> and the meteorological parameters. This is shown in **Table 5**. The result shows that at basin Authority, the highest positive correlation was with SO<sub>2</sub> and relative

**Table 4.** AQI table for the study locations.

Location	Air quality index	AQI category
Army Junction	229.54	Poor
Basin Authority	216.33	Poor
Goodluck bypass	214.67	Poor
Ikalkaukwa market	214.24	Poor
Marina Resort	157.20	Moderately Polluted
Tinapa Resort	201	Poor

**Table 5.** AQI correlation of SO<sub>2</sub> with meteorology.

Location	SO <sub>2</sub> vs WS	SO <sub>2</sub> vs RH	SO <sub>2</sub> vs TEMP
Army Junction	0.198	-0.222	0.221
Basin Authority	0.609	0.753	0.631
Goodluck Bypass	-0.534	-0.323	0.250
Ikalkaukwa Market	-0.165	0.642	0.561
Marina Resort	0.495	0.716	-0.643
Tinapa Resort	0.198	0.639	-0.333

**Figure 3.** Plot of the mean squared error (MSE) with the number of hidden neurons.

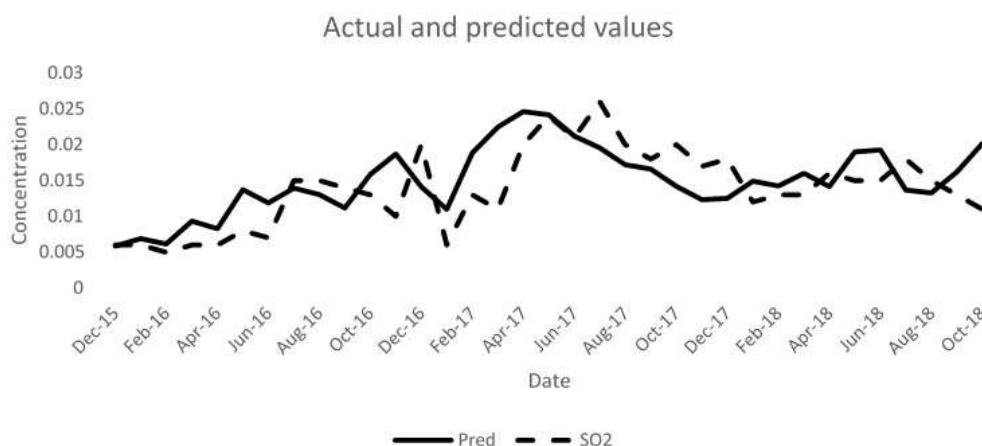
humidity, with  $R = 0.753$ . This shows that at Basin Authority station, relative humidity had the greatest effect on SO<sub>2</sub>. The highest correlation between SO<sub>2</sub> and wind speed was obtained at basin authority with  $R = 0.609$  which shows that wind speed also had effect on SO<sub>2</sub> in that station. Marina Resort recorded the highest negative correlation of SO<sub>2</sub> and temperature, with  $R = -0.643$  and Basin Authority recorded the highest positive correlation with  $R =$

0.631. The positive correlation with meteorological parameters was recorded by (Nwokocha et al., 2015). Ljubisa et al., 2011, also recorded strong correlation of SO<sub>2</sub> with temperature.

### Modelling and Prediction of So<sub>2</sub>

Figure 3 shows a histogram plot of the mean squared error (MSE) and the number of hidden neurons used





**Figure 4.** Plot of actual and predicted values of SO<sub>2</sub>

in the training of the network. The graph shows that the neural network performed better when the hidden neurons were set to ten. Hence the best model for the prediction of SO<sub>2</sub> for Calabar is 5 – 10 – 1. This translates to, five (5) input variables that include; SO<sub>2</sub>, wind speed, temperature, relative humidity and total suspended particulate matter (TSP), ten (10) hidden neurons in the neural network and one (1) target variable which is SO<sub>2</sub>. The output of the neural network which is predicted values were plotted with the actual values of SO<sub>2</sub>. The plot is shown in **Figure 4**.

## CONCLUSION

The following conclusion has been drawn in this research. The concentration of SO<sub>2</sub> in Calabar has over-shot the WHO (2005) threshold limits of 0.008 ppm for 24 hrs and 0.188 ppm for 10 minutes measurement. The air quality in Calabar based on SO<sub>2</sub> is poor. This may be very dangerous to the health of Calabar residents. The best model for the prediction of SO<sub>2</sub> is 5 – 10 – 1. This model will help scientist in the accurate prediction of SO<sub>2</sub> concentration in Calabar and locations with the same meteorological conditions as Calabar.

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