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Research Article

Determination of Sulphur Dioxide Concentrations in Ambient Air of Some Selected Traffic Areas in Kaduna Metropolis

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Abstract: This research study was aimed at determining concentrations of sulphurdioxide in ambient air of some selected areas viz: industrial area (Kakuri), high vehicler traffic/commercial area (Leventis Roundabout), traveling route (Kawo overhead bridge), Low vehicler traffic area (Tafawa Balewa Roundabout), residential area (Kawo New Extension) and a control site (NFA base) in Kaduna metropolis Nigeria. Air sample was collected at each sampling site by passing ambient air through an impinger bottle containing hydrogen peroxide (absorbent), at a flow-rate of 10 L/min for 30 min using air vacuum pump. The concentration of SO_2 in the resultant solution (absorbent) was determined by titrating against 0.005 moL/dm^3 NaOH solutions. The average SO_2 concentrations in the six sampling stations were within the range 0.16-0.75 ppm, with the highest values of 0.75 and 0.70 ppm at highly industrialized area (Kakuri) and a high traffic area (Leventis roundabout) respectively. The ambient air concentrations of SO_2 depict the pattern; Industrial area (Kakuri) >High vehicler traffic/commercial area (Leventis roundabout) >Traveling route (Kawo overhead bridge) >Low traffic area (Tafawa Balewa roundabout) >Residential area (Kawo New Extension) >Remote area (NAF Base Mando). Except for highly industrial area (Kakuri) and the high traffic area (Leventis), The ambient air SO_2 concentration are within the acceptable limits of United States Environmental Protection Agency (EPA) and Nigeria's Federal Environmental Protection Agency (FEPA) standard limit which is 0.5 ppm for 30 min exposure time.

Keywords: Air pollution, concentration, sulphur dioxide, traffic areas

INTRODUCTION

Classical smog results from large amounts of coal burning in an area caused by mixture of smoke and sulphur dioxide (Ademoroti, 1993; Davis, 2002). Modern smog does not usually come from coal, but from vehicular and industrial emissions that are acted on in the atmosphere by sunlight to form secondary pollutants that also combine with primary emissions to form photochemical smog (Wikipedia, 2009). Motor vehicles are major sources of air pollutants and as industrialization and technological development continue, there will be a corresponding increase in income and hence cities will experience a greater increase in the number of vehicles on the roads (Akpan and Ndoke, 1999). It is not out of place to state that the concentration of these pollutants must have increased tremendously in the past ten years of democratic rule in Nigeria, due to the influx of old and fairly used vehicles into the country following changes in government policy (Abam and Unachukwu, 2009). Poor vehicle maintenance culture and importation of old vehicles which culminate to an automobile fleet dominated by a class of vehicles known as "super emitters" with high emission of harmful pollutants, has raised high this figure of emission concentration (USEPA, 2009). Furthermore, in developing countries the super emitters contribute about 50% of harmful emissions to the entire average emission (BruneKreef, 2005). Sulphur dioxide is also emitted to the atmosphere by natural phenomenon such as volcanic effects and forest fire. Coal and petroleum contain sulphur compound, their combustion generates sulphur dioxide (Wikipedia, 2009). Among the sulphur containing pollutants, SO_2 is the most important. It is one of the criteria pollutants, having been recognized as a major urban pollutant (Davis, 2002). It is estimated that 50% annual global emission of this pollutant (SO_2) is from coal burning and 25 to 30% from oil burning. All the remaining sources, including natural ones like volcanoes and forest fire share the remaining 20 to 25% (Narayanan, 2009). Since the industrial revolution, human activities have contributed significantly to the movement of sulphur from the lithosphere to atmosphere, primarily due to burning of fossil fuels (Wikipedia, 2009).

Transportation is the major source of air pollution accounting for over 80% of total air pollutants (Faize and Sturm, 2000; Abam and Unachukwu, 2009).

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Sulphur dioxide is a chemical irritant that damages mucous lining of the respiratory tract and causes chronic bronchitis in living organism (humans) and also principally responsible for acid rain and it effects (Narayanan, 2009). An epidemiological study in the United States of America has shown that acute exposure to vehicle emission over ten year period reduces lung function among tunnel officers (Koku and Osuntogun, 2007; Michael and Konstantinos, 2008). The world health organization states that 2.4 million people die each year from causes directly attributable to air pollution with 1.5 million of the deaths attributable to indoor air pollution (Duflo *et al*., 2008). A study by the University of Birmingham has shown a strong correlation between pneumonia related deaths and air pollution from motor vehicles (Zoidis, 1999). Air pollution is also emerging as a risk factor for stroke, particularly in developing countries where pollutant levels are highest and worldwide more deaths per year are linked to air pollution than to automobile accidents (Farrah and Robert, 2011). A similar study confirms that there is a prevalence of chronic bronchitis and asthma in street cleaners exposed to vehicle pollutants in concentrations higher than WHO recommended guidelines, thus leading to significant increase in respiratory problems (Rachou-Nelson, 1995). Other related problems include damages to the ecosystem, damage to materials, buildings and the acid rain phenomenon (Weathers and Likens, 2006). Having viewed these consequences, the need to embark on research of this kind becomes obvious and inevitable.

Automobile emission: Products of combustion from automobile emission consist of carbon dioxide, water vapour, nitrogen, oxygen, nitrogen oxides, sulphur dioxide, particulate matter, carbon-monoxide and unburnt hydrocarbons (Kotz and Purcell, 1987). The burning of petrol and diesel oil by motor vehicles, power plant and factories releases a lot of pollutants into the air, for example, every 1000 dm^3 of petrol burnt, an average car releases about 0.15 kg carbon (ii) oxide, 0.01 kg nitrogen oxide, 0.008 kg unburnt hydrocarbons, 0.0005 kg solid particles and 0.0005 kg sulphur (iv) oxide to the atmosphere (Osei, 1990). A stationary car that has its engines still running emits much more pollutants than what is given above (Osei, 1990). The US has witnessed a 33% decrease in emissions of sulphur dioxide between 1993 and 2002 (Chandru, 2006). This improvement resulted from the procedure of flue gas desulphurization. Sulphur dioxide as an air pollutant can be controlled by switching over to low sulphur fuels (natural gas) or by integrated coal gasification cycle, solvent extraction methods or fluidized bed combustion of coal mixed with an adsorbent such as lime or limestone (Magbagbeola, 2001). Sulphur in fuel oil can be removed in high-pressure catalytic reactors, in which hydrogen combines with sulphur to form hydrogen suphide (Jerome, 2000; Wikipedia, 2009). Hydrogen sulphide been toxic is adsorbed by activated carbon and is converted to sulphur dioxide for further disposal (USEPA, 2009). Flue gas desulphurization is achieved by catalytic oxidation using vanadium pentoxide, this catalyst promotes oxidation of SO_2 to SO_3, which can be disposed conveniently. Fuel additives, such as calcium additives, magnesium oxide are being used in gasoline and diesel engines in order to lower the emission of sulphur dioxide gases into the atmosphere (Kaufman *et al*., 2009).

The objectives of this research study are as follows:

- Collecting of air samples at the designated sampling sites
- Determination of so_2 concentrations in the collected sample by titremetric method
- Compare the concentration with the standard values

METHODOLOGY

Description of sampling site: Nigeria is located in West Africa in the map of African continent. Nigeria is located between latitude 4˚ and 14˚ of the equator and longitude 2˚ and 15˚ east of the Greenwich Meridian. Kaduna State is among the 19 Northern States of the Federal Republic of Nigeria, where all the sampling stations of this study are located within the Kaduna metropolis, which is located between latitude 10.9˚ and 10.15˚ north of the equator and between longitude 7.5˚ and 7.9˚ east of the Greenwich Meridian. Kaduna Metropolis is fast becoming a mega city according to Kaduna State Ministry of Environment, because of this fact Kaduna Metropolis is becoming highly congested in automobile traffic in several areas. For this reasons, ambient air quality in Kaduna Metropolis needs to be determined. Sampling stations were chosen with considerations such as Industrial area, high traffic areas, low traffic area, residential area and remote area. Six sampling areas were selected for the study; Kakuri a highly industrialized area, Leventis roundabout a high traffic area with commercial activity nearby, Kawo overhead bridge a relatively high traffic area, Tafawa Balewa roundabout a relatively low traffic area, Kawo new extension a residential area and Behind Nigerian Air Force base a remote area (control site) with relatively very low activity. The keys to the sampling sites are represented on the map of Kaduna metropolis as shown (Fig. 1).

Method of determination:

Preparation of the absorbent (H_2O_2): A buffer solution with a pH of 5 was prepared with sodium

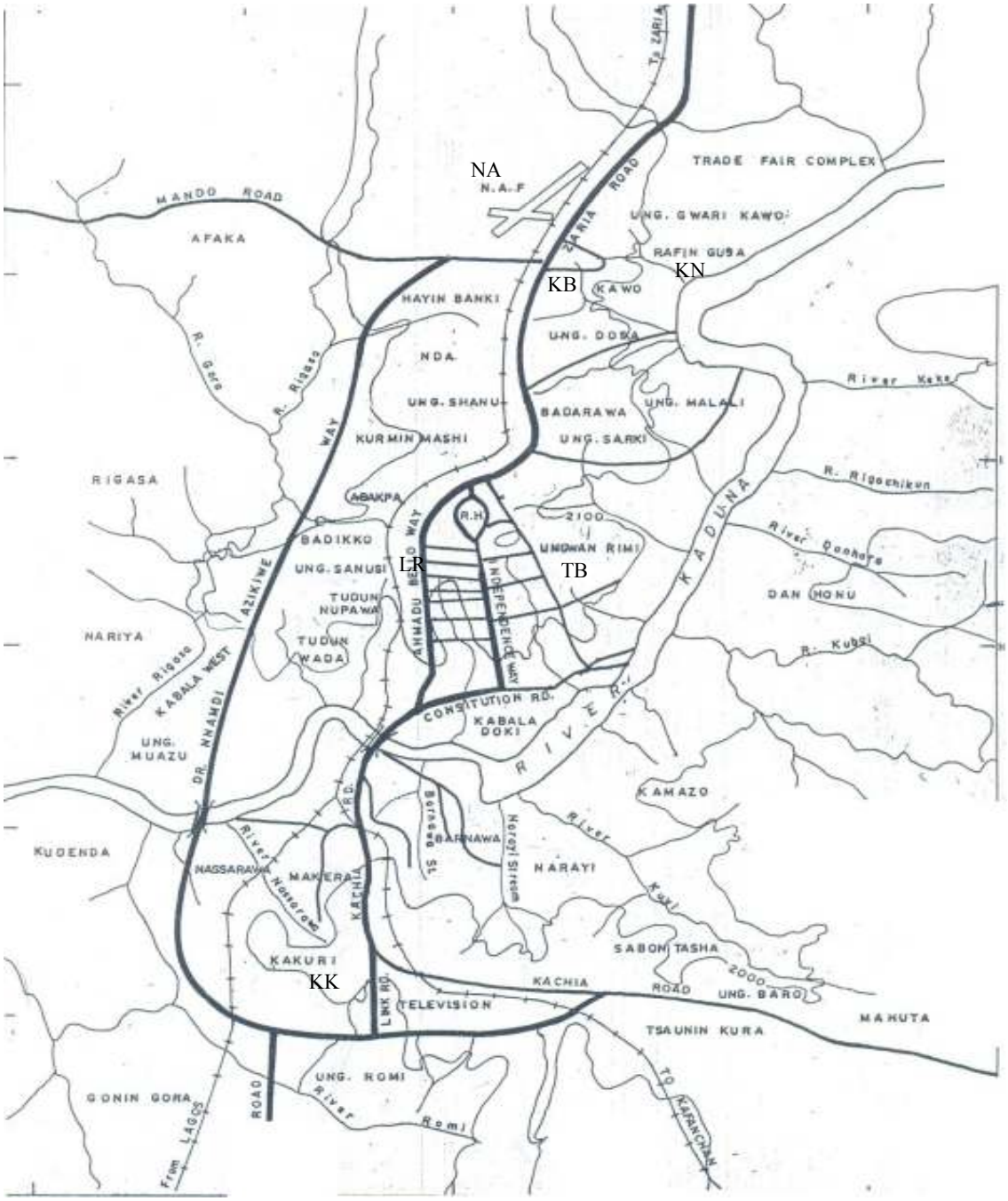

Fig. 1: Map of Kaduna metropolis
LR: Leventis Roundabout; TB: Tafawa Balewa Roundabout; KK: Kakuri Behind Nigerian Breweries; KN: Kawo New Extension; KB: Kawo Overhead Bridge; NA: Behind Nigerian Air Force Base; Mando (control)

acetate and acetic acid. 10.41 g of sodium ethanoate was weighed into a cleaned dried beaker, 4.17 cm^3 ethanoic acids and 18.4 cm^3 of (30% v/v) hydrogen peroxide were added to the beaker. The mixture was dissolved and quantitatively transferred into a 1 liter volumetric flask. The solution was made up to mark with distilled water. The pH of the resultant solution was maintained at 5 in order to prevent the dissolution of carbon dioxide (Abdulraheem *et al*., 2005).

Sampling of sulphur dioxide: Forty cm^3 of the absorbent was measured into a 250 cm^3 impinger bottle, which was connected in series using rubber tubing to the vacuum air pump and equipment set-up, which had the filter holder facing the up-stream direction of the wind. Ambient air was allowed to pass into the absorbent at a flow rate of 10 L/min, for 30 min at hourly intervals from 7.00 am - 6.00 pm. The sampling train was made completely air tight, using a ring screw

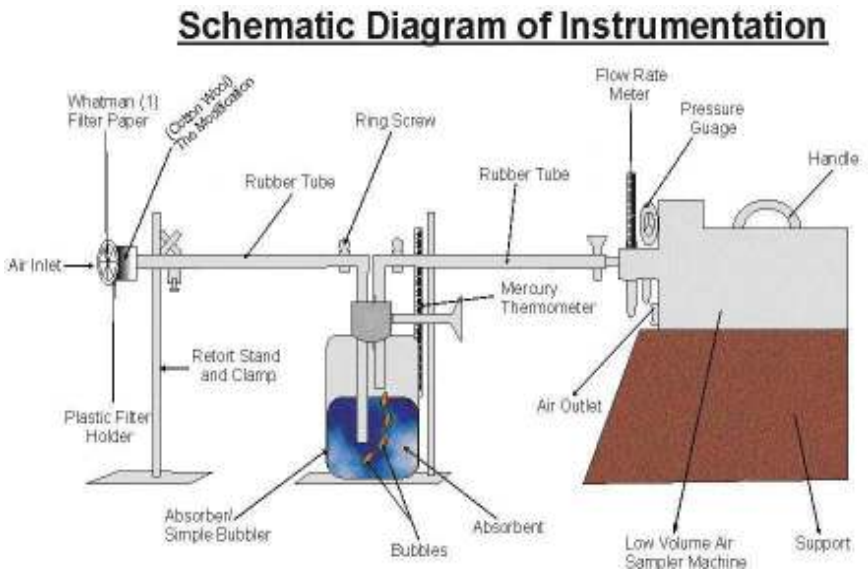

Fig. 2: Air sampling set-up

at all necessary joints. After each hourly sampling, the bubbler was removed carefully and the absorbent solution (sample) was transferred into sample bottle and labeled for analysis. In every sampling, a new filter paper and cotton wool was used, to avoid contamination, chemical reactions on the surface and ultimately to avoid blockage by particulate matter which may reduce the volume of air sampled. Eleven samples were collected from each sampling station within the hours of 7 am to 6 pm, on any sampling day. The pH of the absorbent was maintained at pH 5 with a pH meter before and after sampling. The samples collected were carefully preserved and handled from harsh conditions, by placing the sample bottles in a plastic flask containing ice block to prevent the samples from deteriorating. The samples were then taking to laboratory and stored in a refrigerator at 5°C condition (Lawrebce *et al.*, 2000). A schematic diagram Fig. 2 of the sampling set-up.

Analysis:

Preparation of 0.005 mol/dm^3 NaOH: Fifty cm^3 of a standardized 0.1 moL/dm^3 NaOH stock solution was measured into a 1 liter volumetric flask. It was made up to mark with distilled water, to get a concentration of (0.005 mol/dm^3 NaOH) solution for titration with blank and samples.

Titration: Ten cm^3 reference samples (blanks), containing no sample was pipetted into a clean 250 cm^3 conical flask; a drop of methyl red indicator was added. The blank was titrated with standard sodium hydroxide (0.005 mol/dm^3 NaOH) solution in a 50 cm^3 burette. This was done to take care of the sample matrix of the reagent used for the analyses. Ten cm^3 aliquot of the sample was pipetted into a clean 250 cm^3 conical flask and a drop of methyl red indicator was added. The sample was then titrated with standard alkali 0.005 mol/dm^3 NaOH solutions in a 50 cm^3 burette (Peirce, 1998). The titration was done in triplicate each, for all the samples from the six sampling sites. An average titre was used to calculate the concentration of sulphur dioxide in the sample.

Reaction of the absorbent with SO_2:

$$SO_{2(g)} + H_2O_{2(aq)} \longrightarrow H_2SO_{4(aq)} \quad (1)$$

Equation for the titration:

$$H_2SO_{4(aq)} + 2NaOH_{(aq)} \longrightarrow Na_2SO_{4(aq)} + 2H_2O_{(l)} \quad (2)$$

RESULTS AND DISCUSSION

The results showed six sampling sites, in which SO_2 concentrations in ambient air were determined in Kaduna metropolis, northern Nigeria.

The SO_2 concentration range of Leventis Roundabout was between 0.29-0.90 ppm as shown in Table 1 of the results. The estimated traffic count at Leventis roundabout was 62,423 automobiles within the sampling period (FRSCN, 2010). Comparing the mean SO_2 concentration with USEPA, FEPA standard limit which is 0.5 ppm at 30 min exposure time, Leventis roundabout was found to exceed the limit. From the Fig. 3, there was a steady rise in SO_2 concentration from 7 am to 12 pm and a drop at 12-1 pm and it rises again from 1-6 pm. The reasons for the high SO_2 concentration values from 7 am to 6 pm,

Table 1: Showing the daily SO_2 concentration at the six sampling sites at the various sampling time

Sampling time 30 min	Leventis roundabout SO_2 conc. (ppb)	Kakuri (behind Nigerian breweries) SO_2 conc. (ppb)	Kawo overhead bridge, Kawo.SO_2 conc. (ppb)	Tafawa balewa roundabout, Kaduna. SO_2 conc. (ppb)	Kawo new extension, Kawo Kaduna. SO_2 conc. (ppb)	NAF base (behind) Mando (control). SO_2 conc. (ppb)
7:00 am	290	380	370	290	290	190
8:00 am	480	490	560	290	380	190
9:00 am	680	670	580	390	290	100
10:00 am	780	770	580	590	290	200
11:00 am	790	780	480	490	200	200
12:00 pm	590	790	390	390	200	100
1:00 pm	700	900	500	300	300	100
2:00 pm	800	1000	600	300	400	200
3:00 pm	900	890	600	400	300	200
4:00 pm	800	790	790	500	490	200
5:00 pm	880	790	790	490	390	100

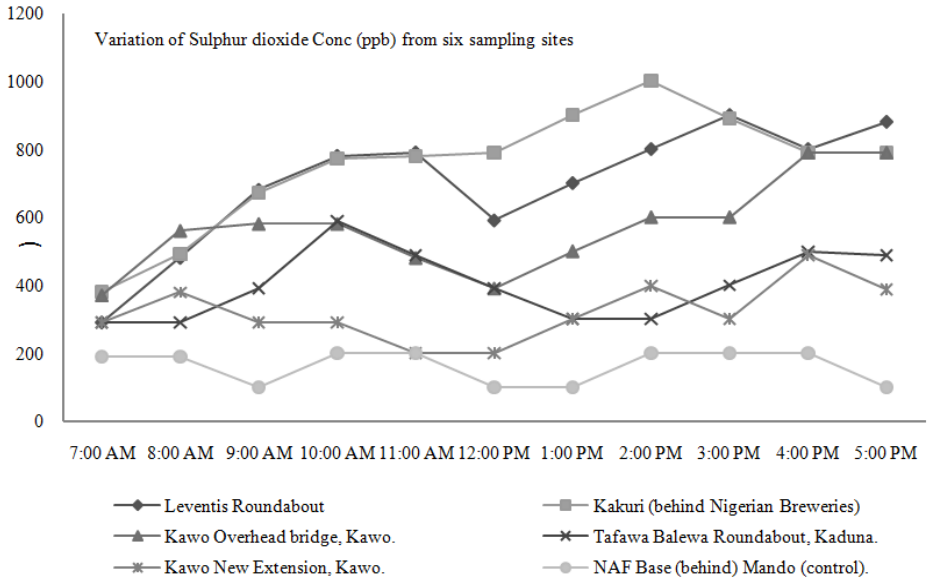

Fig. 3: A graph of SO_2 concentration (ppb) against time (minute), this is showing the trend of SO_2 concentration in the six sampling stations

except for 12-1 pm, was because of high traffic emissions at this area and may be attributed to high traffic volume and commercial activities around this area during sampling. The SO_2 concentration of Kakuri behind Nigerian Breweries range was between 0.38-1.00 ppm as shown in Table 1 of the results. The estimated traffic count at Kakuri route was 66,906 automobiles within the sampling period (FRSCN, 2010). Comparing the mean SO_2 concentration with USEPA, FEPA standard limit which is 0.5 ppm at 30 min exposure time, Kakuri was found to exceed the limit. From the Fig. 3, there was a steady rise of SO_2 concentration from 10 am-3 pm, where the maximum SO_2 concentration of 1.00 ppm was observed in the whole study. At 4-6 pm there was a drop in SO_2 concentration at kakuri, this was because most of the loading trucks were moving away. The reasons for the high SO_2 concentrations at Kakuri may be attributed to high industrial activities, high traffic volume and emissions from power plants. The SO_2 concentration range of Kawo overhead bridge was between 0.37-0.79 ppm as shown in Table 1 of the results. The estimated traffic count at Kawo overhead bridge was 57,831 automobiles within the sampling period (FRSCN, 2010). Comparing the mean SO_2 concentration with USEPA, FEPA standard limit which is 0.5 ppm at 30 min exposure time, Kawo overhead bridge was within the standard limit. Figure 3 shows that SO_2 concentration rises steadily from 7am-10am, the increase was as a result of the period when offices, schools and commercial activities commenced. There was a drop in concentration at 12-1 pm when most workers are in office, students are in school which accounted for less traffic and the concentration rises steadily again from 2-6 pm, at the close of work, school and commercial activity. The increase seen at 4-6 pm was due to high traffic and traveling time via this route. The SO_2 concentration is within standard limit at this area and may be attributed to the overhead bridge which is diverting and decongesting traffic in the area.

The SO_2 concentration range of Tafawa Balewa roundabout was between 0.29-0.59 ppm as shown in Table 1 of the results. The estimated traffic count at

Table 2: Showing the average daily SO_2 concentration at the six sampling sites

S/N	Sampling sites	SO_2 conc. (ppm)	SO_2 conc. (ppb)
1	Leventis roundabout	0.70	700
2	Kakuri behind Nigerian breweries	0.75	750
3	Kawo overhead bridge, Kawo.	0.56	560
4	Tafawa Balewa roundabout	0.40	400
5	Kawo new extension	0.32	320
6	Behind NAF base, Mando (control)	0.16	160
United states (NAAQS) standard limit		0.50	500s
FEPA standard limit		0.51	510

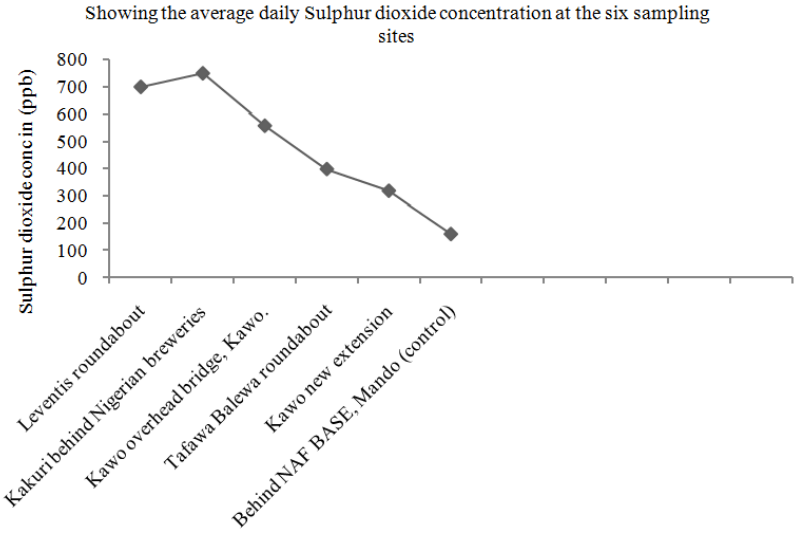

Fig. 4: Showing the average daily SO_2 concentration (ppb) against the sampling sites

Tafawa Balewa roundabout was 12,401 automobiles within the sampling period (FRSCN, 2010). Comparing the mean SO_2 concentration with USEPA, FEPA standard limit, Tafawa Balewa roundabout was found to be within the standard limit. Figure 3 shows that there was a steady rise of SO_2 concentration from 7-10 am due to resumption of schools and offices. There was a drop in SO_2 concentration from 11 am 3 pm and a rise again from 3-6 pm, due to high traffic as a result of the close of work and people returning home. The fact that SO_2 concentration was within standard limit, may be attributed to absence of high traffic volume and commercial activities around this area. The SO_2 concentration range of Kawo new extension was between 0.20-0.49 ppm as shown in Table 1 of the results. The estimated traffic count at Kawo new extension was 9, 307 automobiles within the sampling period. Comparing the mean SO_2 concentration with USEPA, FEPA limit, Kawo new extension was found to be within the limit. In Fig. 3, shows that SO_2 concentration increases from 7-9 am, due to vehicles going to place of work and motor cycles carrying students to school. SO_2 concentration dropped from 10 am to 1 pm due to low domestic activity and traffic and a steady rise of SO_2 concentration from 2-6 pm, due to close of work, school and increase domestic activity i.e., cooking outside the house and use of electric generators. The reasons for the low SO_2 concentration may be attributed to the fact that this is largely a residential area in which most of the emissions was accounted for, by commercial motor cycle popularly known as "okada". The SO_2 concentration range at NAF Base (control) was between 0.10-0.20 ppm as shown in Table 1 of the results. The control site was found to be within the standard limit. The reasons for the low SO_2 concentration may be attributed to the fact that the control site was neither a traffic area nor a residential area, but an open green land. The variation of SO_2 concentrations shown in Fig 3, between 7 am to 6 pm was suspected to be contribution of emission from the electric generator used to power the vacuum pump (air sampler).

Daily average SO_2 concentration at the six sampling sites: The mean concentrations of SO_2 from the six sampling sites are as shown in Table 2 of the results. The average SO_2 concentrations in the six sampling stations were 0.75, 0.70, 0.56, 0.40, 0.32 and 0.16 ppm, respectively. Information of the variation of SO_2 concentrations in the six sampling stations can be seen in Fig. 3 and 4. The ambient air concentrations of SO_2 depict the pattern; Kakuri (behind Nigerian Breweries)

>Leventis Roundabout >Kawo Overhead Bridge >Tafawa Balewa Roundabout >Kawo (new extension) >NAF Base (behind). Comparing the results with United States environmental protection agency and FEPA standard limit which is 0.5 ppm for 30 min exposure time, all the sampling stations were within the acceptable limit except Kakuri and Leventis Roundabout which has high traffic volume, industrial and commercial activities respectively. Kakuri and Leventis roundabout can be said to be polluted areas in Kaduna metropolis, from the results gotten during the research.

CONCLUSION

The research concludes that automobile traffic, emissions and other anthropogenic activities in Kaduna metropolis are responsible for the degree of sulphur dioxide concentration in ambient air of the metropolis. Sulphur dioxide concentrations in the six sampling stations have a direct relationship with the number of traffic counts i.e., the higher the number of automobiles in an area, the higher the sulphur dioxide concentrations. The findings suggest that Kaduna metropolis has super-emitter automobiles, which are responsible for the concentration of pollutants in ambient air. The study further revealed that pollution at traffic intersection is threatening and motor vehicles remains the dominant sources of urban air pollution. Addressing this situation requires a holistic understanding of causal factors related to emissions. Kaduna Metropolis has become highly congested in automobile traffic in several areas. Ambient air quality in Kaduna Metropolis needs to be regularly determined and assured by environmental regulatory authorities or agencies, to avoid health hazards and environmental degradation of the metropolis.

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