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Seasonal Variations of Air Quality Measures in Warri and Effurun, Delta State, Nigeria

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Abstract

Air quality in Urban Cities like Warri and Effurun has been deteriorating over time. The distribution levels of air pollutants in the Warri and Effurun environments may be related to both natural and man-made factors. In addition to evaluating the quality of rainwater with regard to pH, heavy metals (Fe, Pb, Cd, As, Hg, CU, Zn), and some anions (Cl-, NO_3-, SO_{42}-, CO_{32}-), this project study aims to investigate, using standard methods, variations in concentrations of major air criteria pollutants such as carbon monoxide (CO), nitrogen dioxide (NO_2), sulphur dioxide (SO_2), carbon dioxide (CO_2), and total particulate matter. The seasonal air quality was monitored in four major locations each in Effurun and Warri during the rainy and dry seasons from March, 2020 to February, 2021 and the quality of the rain water was assessed during the period of the seasons (March – October for the rainy season and November – February for the dry season). The concentration of the air pollutants was assessed using an automatic digital multi gas tester (Aeroqual Air Tester S200) while the physicochemical properties of the rain water were assessed using appropriate standard methods. The results for the pollutants shows that the concentration of pollutants is higher during the dry season as compared to the rainy season as can be seen that the mean concentration of NO_2, SO_2, CO, CO_2 and TSPM at station E_1 in Effurun of 0.018µg/m^3, 0.78µg/m^3, 0.028µg/m^3, 0.0028µg/m^3, 128.50µg/m^3 during the dry season is higher than that of 0.012µg/m^3, 0.25µg/m^3, 0.020µg/m^3, 0.0018µg/m^3, 99.50µg/$m^3$of the rainy season at the same station E_1. This trend follows for other stations. Of all the stations monitored station E seems to have the highest concentration of the various pollutants this might be attributed to its proximity to the WRPC where there is a lot of anthropogenic activities there apart from the refinery and the petroleum depot situated there. Apart from the TSPM which had the highest concentration range of 56.35 – 99.50µg/m^3 during the rainy season and 78.50– 128.50µg/m^3 during the dry season; SO_2 among the gaseous pollutants has the highest concentration range of 0.18 – 0.78µg/m^3 during the dry season and 0.09–0.25µg/m^3 during the rainy season. The concentration range of 0.0027–0.008µg/m^3 in the dry season and 0.0012–0.0035µg/m^3 in the rainy season for NO_2 is the least. The rainwater's physicochemical studies indicate that it has a mean PH value of 6.04, which indicates a slightly acidic content and much more acidic during the months of the dry season than that of the rainy season with the month of January (5.3) most acidic of all the Months. Of all the parameters only Arsenic has no value for any month as the concentration of arsenic was below the instrument detection limit of 0.3 mg/L.

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INTRODUCTION

Variations in the number of seasons and the uniqueness of some months that make up the summer and winter seasons—also referred to as

the "heating" season—are linked to variations in air pollution. Higher air pollution levels in different months of the year are related to the kind of climate, which in turn is related to various atmospheric conditions in those months, variations in the weather on any given day, and human activities. For a certain amount of time, the emergence of these conditions causes varying degrees of air pollution.

Seasonal air quality monitoring is the methodical measurement and observation of ambient air pollutants with the goal of determining the source of the pollution (causal analysis) and/or assessing the exposure of vulnerable receptors (people, animals, plants, and artwork) based on standards and guidelines derived from observed effects. Since it is impossible to isolate natural protective barriers for atmospheric air, it is crucial to regulate and analyze the effects of certain pollutants not only globally but also continentally, nationally, and locally [1].

Worldwide, air pollution is a serious threat to public health that affects both industrialized and developing nations. The environment and human health are being harmed by the constant global emission of ever-increasing amounts of potentially hazardous gases and particles into the atmosphere. In many places across the world, the issue of air pollution poses a severe threat to environmental health [3]. As urban motor traffic increases, the level of air pollution increases, especially in densely built-up areas. In addition, emissions with great space-time variability, as well as pollutants with variations in atmospheric dispersion and the increasing number of worldwide industrialization has led to the problem of air pollution [4], cause variable concentration fields of a complex nature within cities. Metoeorological conditions affect the dispersion of air pollutants [5]. Air pollution is influenced by a number of variables, including pollutant emissions, transportation and transformation, and meteorological circumstances [6, 7]. Research has demonstrated that air pollution emissions and meteorological factors influence the temporal and spatial ordering of air pollutants as well as dominating trends in pollutant concentrations [8]. Favorable weather has a significant impact on the environmental capacity and dispersal circumstances, which in turn affects the air criteria [9].

High level of air pollution exhibits substantial regional variation [10].

More than 80% of the people who live in urban areas which are monitored for air quality have exceeded the air quality levels given under the WHO standards [11]. One of the biggest environmental hazards to people, the general public's health, the ecology, and economies is air pollution [12–14].

To make effective urban air quality management programs comprehensive information about the seasonal and diurnal variations of pollutant concentrations in different areas of a city is needed [15].

The World Health Organization (WHO) recognized the issue of poor air quality and projected in 2012 that approximately 7 million fatalities were linked to living in places with dirty air. The level of urban air pollution is of vital interest to city inhabitants, since polluted air can be a source of potential danger for the population and environment. Unfortunately, many important human activities cause air pollution.

Urban air pollution is dispersed non-uniformly throughout a city. Increased concentrations of pollutants are frequently observed near pollution sources. The primary sources of air pollution include automobile traffic, several technical activities, and combustion processes [2]. As urban motor traffic increases, the level of air pollution increases, especially in densely built-up areas. In addition, emissions with great space-time variability, as well as pollutants with variations in atmospheric dispersion, cause variable concentration fields of a complex nature within cities.

The kinetics of hazardous material dispersion in the air and the geographical or temporal variance of their emissions both affect ambient air pollution concentrations. Consequently, there are noticeable fluctuations in concentrations on a daily and annual basis. Determining all these various variations in air quality (or, to put it statistically, the population of air quality states) in a unified manner is nearly impossible. As a result, measurements of ambient air pollution concentrations are inherently random in terms of both space and time. Urban areas almost everywhere in the world have high levels of air pollution. Urban air quality varies greatly between regions and cities, with one of the main contributing variables being the presence of local sources like anthropogenic pollutants. The urban environment is exposed to significant numbers of precursors and reactants due to the large emissions of carbon monoxide (CO), nitrogen oxides (NOx), and volatile organic compounds (VOCs).

These emissions also result in significant chemical turnover rates. According to [16], photochemical air pollution is a major issue in certain places where increased traffic has led to excessive emissions of NOx, organic compounds, and particulates. The study of meteorological parameters is essential in comprehending the fluctuations in the concentrations and dispersion of air pollutants. Aerosol composition and diurnal concentrations of air pollutants are also influenced by meteorological driving variables [17]. The variations and patterns of pollutants, including NOx, PM10 (particulate matter smaller than 10 μm), and SO2, are impacted by land cover, as well as different economic factors, population patterns, and meteorological factors.

Precipitation is inherently acidic due to the atmospheric concentration of carbon dioxide.
Rain and other precipitation may become more acidic as a result of the sulfur dioxide and nitrogen oxides released during the burning of fossil fuels, such as coal, oil, and gas. Sulfur dioxide and nitrogen oxides can come from combustion sources or from natural sources such volcanoes, seas, biological decomposition, and forest fires. Emissions of acidifying pollutants from human sources have skyrocketed in recent decades due to the growing demand for power and the increase in the number of motor vehicles, especially since the 1950s. The majority of these pollutants originate from the northern hemisphere, specifically from North America and Europe. These countries consequently frequently experience acidic precipitation.

However, scientists have not yet examined these variations, although this would provide more complete information on urban air pollution and ultimately would help scientists and urban planners devise better solutions to the problems of urban air pollution and population exposure.

Study Area

The study area is Warri-Effurun metropolitan twin cities in Warri South and Uvwie Local Government Areas, Delta state, Nigeria. The highly populated twin Cities is an oil hub in the Niger

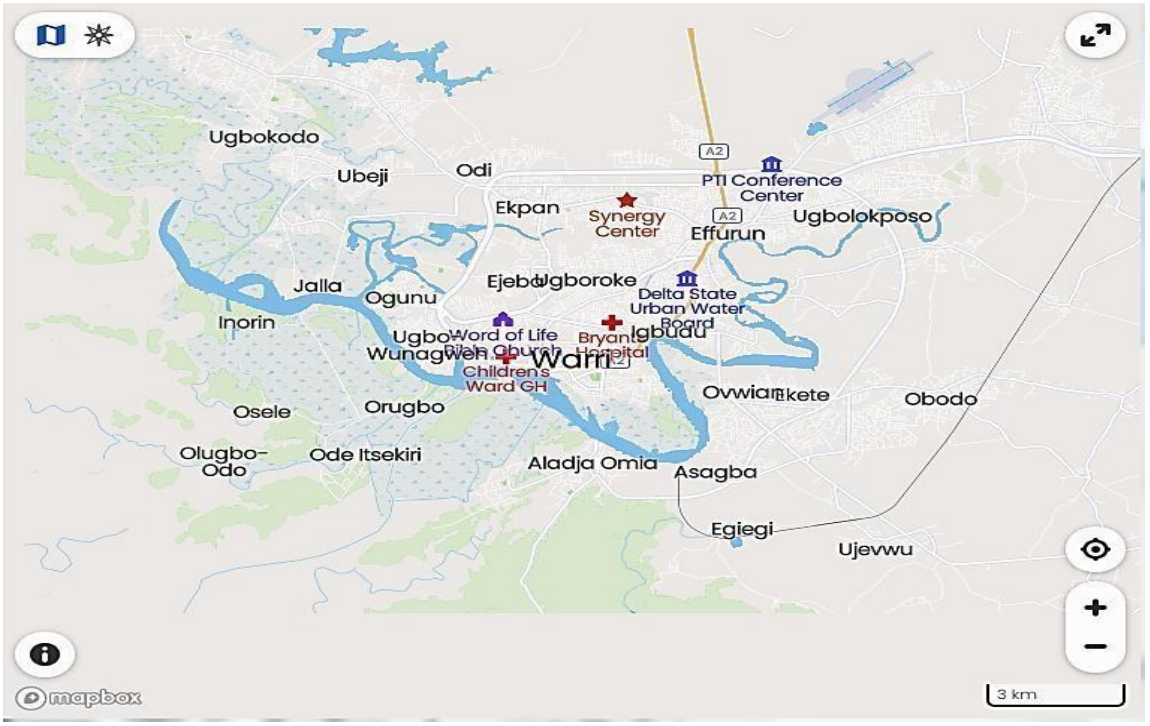

Figure 1. Map of Warri, Warri south west local government area.

Delta region and houses numerous industries with tremendous high traffic activities. The conjoined Cities, lie within Latitude 5.525368 (5° 31'31.325") and Longitude 5.777101(5° 46'37.564") and Latitude 5.556(5°33'22") and Longitude 5.785(5°47'4") for Warri and Effurun respectively.

The eight geo-referenced sampling points were carefully selected for this study based on the anthropogenic activities operational within the study areas. Figures 1, 2.

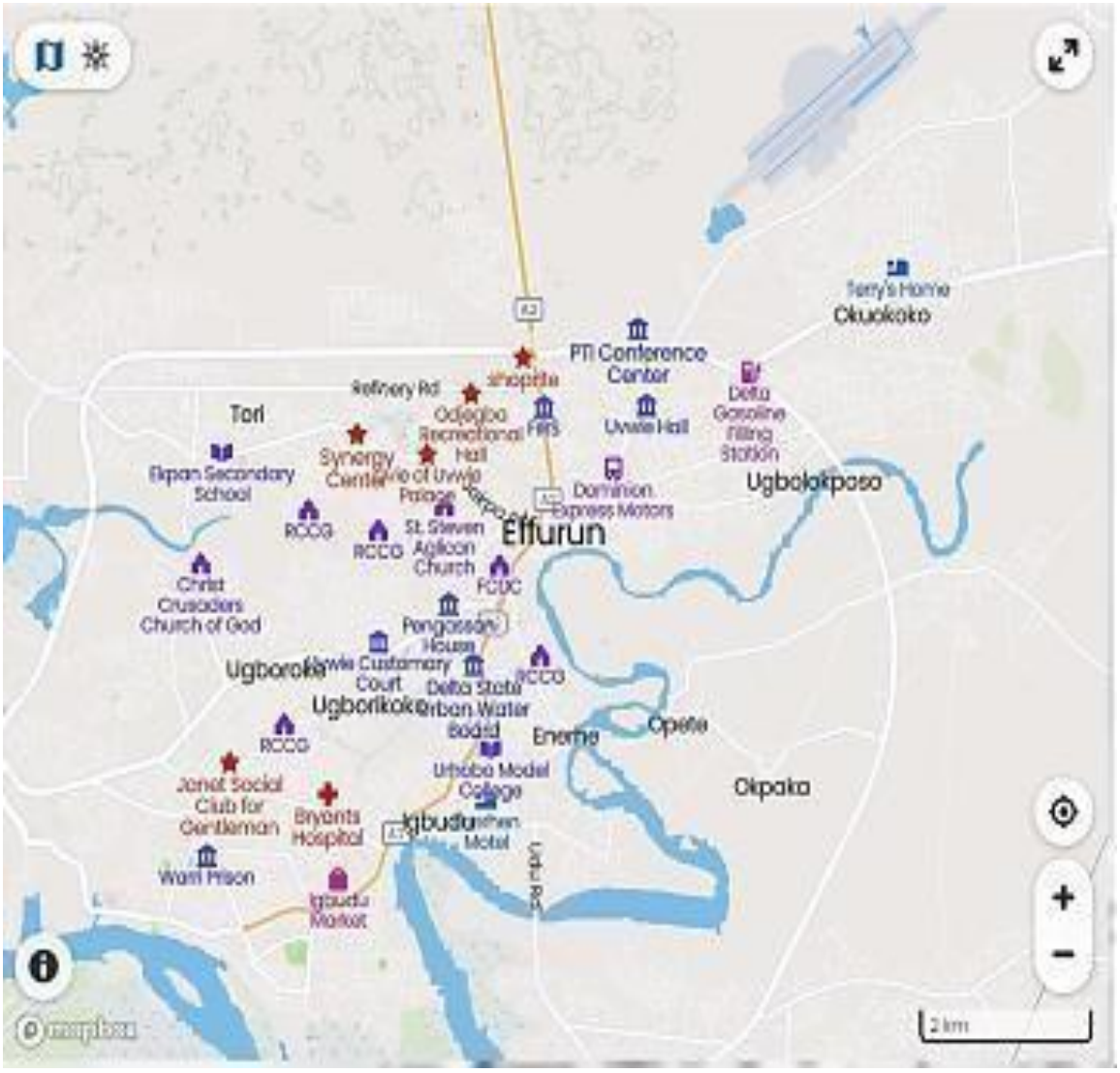

Figure 2. Map of Effurun, Uvwie local government.

Parameters for Quality Measure

The following parameters will be monitored during the course of this project work.

For air quality, carbon monoxide (CO), Carbon dioxide (CO_2), nitrogen dioxide (NO_2), sulphur dioxide (SO_2), Chlorine (Cl_2) and total particulate matter will be analysed, while for rain water quality. The pH, heavy metals (Fe, Pb, Cd, As, Hg, Cu, Zn) and some anions (Cl^-, NO_3^- SO_4^{2-}, CO_3^{2-}) will be analysed and will be use to assess the quality of rain water.

Rain Quality Assessment

As a result of atmospheric carbon dioxide, precipitation is inherently acidic. Acidity in rain and other precipitations can be increased by burning fossil fuels, such as coal, oil, and gas, which releases sulfur dioxide and nitrogen oxides. Natural sources of sulfur dioxide and nitrogen oxides include volcanoes, seas, biological decomposition, forest fires, and combustion sources.

Emissions of acidifying pollutants from human sources have skyrocketed in recent decades due to the growing demand for power and the increase in the number of motor vehicles, especially since the 1950s. North America and Europe are the main emitters of these pollutants in the northern hemisphere. These countries consequently frequently experience acidic precipitation.

The following characteristics of the rainwater in Effurun and Warrri will be evaluated: pH, Cl-, SO_{42}-, NO_3- CO_{32}-, Fe, Pb, Cd, Cu, Zn, As, and Hg. Table 1.

Table 1. Names of sampling points and their coordinates.

S/N	Name of Station	Station code	Coordinate (Deg Min Sec)	Coordinate (Decimal Degree)	Description of sampling points
1.	Ugbuwangue	W1	05º 31'32"N 05º 43'8"E	5.525758N 5.719057E	This is a densely populated area off the NPA expressway. The Ugbuwangue market is situated here and there are lots of traffic and human activities.
2.	Deco road	W2	05º 31'30"N 05º 45'45"E	5.523247N 5.764527E	Deco road in Okumagba avenue of Warri has a lot of activities going on. It is the hub of electronic sales in Warri so there is usually congestion of traffic there.
3.	Warri Main Market	W3	05º 34'33"N 05º 44'44"E	5.513663N 5.745725E	This is the biggest market in Warri where there are lot of activities. The market is usually congested from mid –morning till in the evening.
4.	Okere	W4	05º 31'35"N 05º 44'33"E	5.509396N 5.752567E	Ajamimogha where the sample were collected is situated in Okere road of Warri. A lot of activities takes place. We have several churches and schools here. The Olu of Warri palace is located here.
5.	Ekpan	E1	05º 34'9"N 05º 43'41"E	5.569478N 5.728035E	Ekpan in Effurun hosts the famous Warri Refinery and Petrochemical Company (WRPC) and as such activities pertaining to oil and gas goes on steadily.
6.	PTI Road	E2	05º 34'12"N 05º 47'47"E	5.570064N 5.796837E	The Petroleum Training Institute (PTI) is located here as well as the Effurun market. Close to this place is Jakpa junction where is a lot of traffic.
7.	Enerhen Junction	E3	05º 32'29"N 05º 46'58"E	5.541490N 5.782754E	Enerhen Junction in Effurun is famous for its traffic congestion all day round. It is the boundary between Effurun and Warri.
8.	Ugbomro	E4	05º 33'53"N 05º 49'19"E	5.564866N 5.822254E	Ugbomro hosts the Federal University of Petroleum Resources (FUPRE). There are lot of human activities here and there are usually traffic congestion here. Since it was avillage in Effurun before the University was created, there are local activities such as smoking of fish and roasting of meat as well.

MATERIALS AND METHODS

Sample Locations

Sample Collection

Sulfur dioxide (SO_2), nitrogen dioxide (NO_2), carbon monoxide (CO), carbon dioxide (CO_2), and total particle matter were examined for air quality, while rainwater quality was examined. The PH, heavy metals (Fe, Pb, Cd, As, Hg, Cu, and Zn) and some anions (Cl^-, NO_3^-, SO_4^{2-}, CO_3^{2-}) were analysed and the result was used to assess the quality of rain water Figure 3.

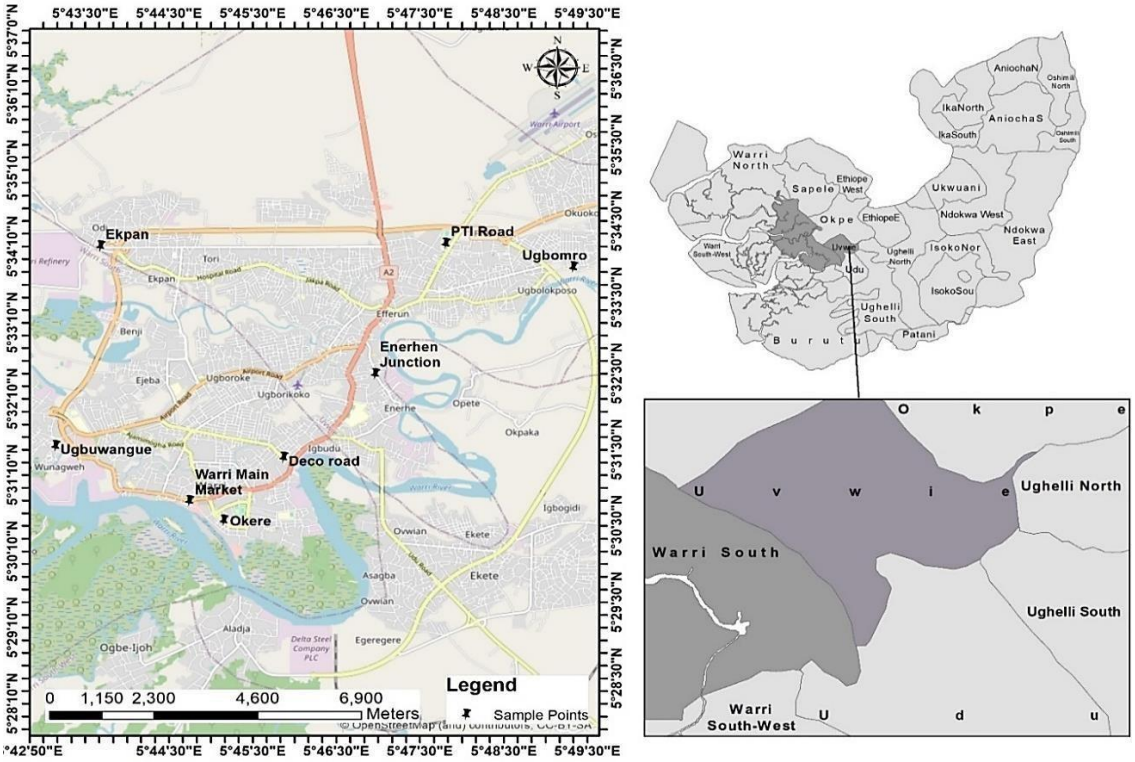

Figure 3. Map of the sampling points.

Fourteen weeks of data from eight selected stations, namely Ugbuwangwe (W_1), Deco Road (W_2), Warri main market (W_3) and Okere (W_4) all in Warri, while data from Ekpan (E_1), PTI road (E_2), Enerhen Junction (E_3) and Ugbomro (E_4) all in Effurun were analysed for temporal trend variations. Measurement of air pollutants were carried out on seasonal basis from all the eight selected stations and average data were collected at one-hour interval between 7.0am 15.0pm (on 8-hourly) on each monitoring day. Hourly time data were collected using the gas monitoring equipment for over a period from March – October (Rainy Season) and from November – February (Dry Season) from the various sampling points.

Monitoring of Gaseous Pollutants

The pollutants gases, CO, CO_2, NO_2, and SO_2 were monitored at each sampling point using gas monitoring equipment of Aeroqual air tester series S200 to collect air samples at a height of 1.2m above the ground level and then analysed.

The apparatus uses a variety of sensors to identify gasses. It is equipped with Gas Sensitive Semi-Conductor (GSS) sensors to measure and examine various airborne contaminants. It works by sucking in and examining the air sample for three to five minutes, after which the findings are shown on the screen.

The Aeroqual Air Quality tester S200 does not require field calibration prior to use as it is fully calibrated at the factory (A. Hassan, 2018).

Collection of Particulate Matter

A particulate sampler, CW-HAT200 The total particulate matter was measured using an aeroqual device that shows particle concentrations in micrograms per cubic meter (μg/m3). The instruments measured particulate matter by light scattering method.

Collection of Rain water

The rain water samples were collected in an open field where there is no interaction/interference of

buildings. The samples were collected every day of the week of sampling in a sample container of high-density polyethylene bottles by first rinsing the bottles with the rain water sample and then the bottles were placed uninterrupted in the open for it to almost filled up, that is, the bottles were filled to within one to two inches from the top. The sample bottles were then retrieved, capped and stored in a refrigerator at 4ºC according to standard practice and thereafter composition of the samples were made for that particular week. The samples for the heavy metals were fixed with 1ml of Concentrated HNO_3 and the analysis were performed before six months which is the holding time for most metals. The samples for the anions Cl^-, SO_4^{2-}, NO_3^-, and CO_3^{2-} were stored in the refrigerator at 4ºC and analysed not later than one week after composition of the samples. The pH of the rain water samples was determined immediately or eight hours after collection of samples as the case may be.

Analysis of gaseous Pollutants

The air quality parameters of CO, CO_2, NO_2, SO_2 and total particulate matter been measured were analysed using Aeroqual air tester series S200. The apparatus uses a variety of sensors to identify gasses. It is equipped with Gas Sensitive Semi-Conductor (GSS) sensors to measure and examine various airborne contaminants.

It works by sucking in and examining the air sample for three to five minutes, after which the findings are shown on the screen. The Aeroqual Air Quality tester S200 doesn't need to be field calibrated before use because it is completely factory calibrated.

Analysis of Rain Water

pH Determination

The pH of the rain water was determined using electrometric method according to SM 4500-H+ B method by APHA (2017).

After calibrating the pH-Meter with the buffers, the electrode(s) and glassware were rinsed with deionized waterFor the pH test, 100 ml of the sample was properly measured and put in a 150 ml beaker. The rinsed electrode was then placed in the rain water sample. Before analysis, all samples were let to reach room temperature in the firmly sealed vial. The pH was analysed within 5 minutes of uncapping the sample bottles since the sample would still be subjected to further analyses. A magnetic stirrer was used to very gently mix the sample. It required a maximum of three minutes for the reading to stabilize.When stable, the sample pH was recorded to the nearest 0.01 pH unit.

Determination of Fe, Pb, Cd, As, Hg, Cu, Zn) in rain Water

The analysis of the above heavy metals was done using Agilent Atomic Absorption Spectrophotometer (AAS). Agilent Technologies 200 series AA was used. The following methods were used: Fe (ASTM D1068), Pb (ASTM D3559), Cu (ASTM D3558), Zn (ASTM D1691), Cd (ASTM D3557 -17), Hg (ASTM D3223-12), As (ASTM D2972 - 15).

Every heavy metal method involved creating a stock solution from the reference standard solution using the dilution formula (C1V1=C2V2), where C1 is the stock solution's concentration, V1 is the stock solution's volume needed for dilution to the working standard's concentration, C2 is the working or calibration standard's concentration, and V2 is the volume of the volumetric flask needed for the dilution. From there, standard solutions of the various metals were created in accordance with the AAS cook book. The instrument was then calibrated using these series of standards according to metal of interest.

For Fe and Pb, for example 2, 4, 6, 8 ppm were used to calibrate the AAS.

A calibration curve of absorption versus concentration which was a straight-line graph in accordance with Beer and Lambert's law was obtained for each of the metals. The sample was then aspirated directly into the AAS after filtering with Whatman No 42-filter paper since the rain water was cleared and free from debris and concentration of each element was obtained.

Analysis of Sulphate (SO^{2-}_4)

The analysis of sulphate was carried out using Turbidimetric method (ASTM D 516-16).

Calibration Curve

From the stock solution, 5.0, 10.0, 15.0, and 20.0ppm standard solutions were prepared for the calibration curve using dilution formula.

Next, a 250 ml conical flask was filled with 100 ml of the rainwater sample, 20 ml of the buffer solution, and mixed with a magnetic stirrer. A tablespoon of BaCl2 crystal was added and swirled for 602 seconds at a steady speed. The solution was then poured into cell of the spectrophotometer and measurement taken at an absorbance of 420nm. Blank, standards and sample were treated alike.

Analysis of Nitrate (NO^-_3)

The Analysis was carried out by using UV Spectrophotometric Screening Method ($SM4500 - NO^-_3$).

Analysis of Chloride (Cl^-)

Analysis of chloride was done using Mohr's method (Silver Nitrate Titrimetric) according to ASTM D512-12.

10mls of the sample was measured into the 250ml conical flask, 3 drops of Potassium Chromate indicator were then added. This was then titrated with $AgNO_3$ to brick red precipitate. The procedure was repeated for the blank sample using deionised water.

Calculation

$$\text{mg/l Cl-} = \frac{(\text{A - B}) \times \text{M AgNO}_3 \times 35450}{\text{Volume of Sample}}$$

Where:

A = ml titration for sample
B = ml titration for blank
M = Molarity of $AgNO_3$

Analysis of Alkalinity as Carbonates (CO^{2-}_3)

Alkalinity of the rain water was determined using titrimetric method (SM 2320 B).

Samples of rainwater collected in milliliters were mixed with two to three drops of Phenolphthalein indicator. Two to three drops of methyl orange indicator were added and titrated until the color changed from yellow to orange because there had been no change in color.

Calculation and Report

$$\text{Phenolphthalein Alkalinity } (CO^{2-}_3) = \frac{\text{Titre Vol.} \times \text{M acid} \times 30 \times 1000}{\text{Volume of Sample}}$$

$$\text{Bicarbonate } (HCO^-_3)\ \text{mg/l} = \frac{\text{Titre Vol.} \times \text{M acid} \times 61 \times 1000}{\text{Volume of Sample}}$$

RESULTS AND DISCUSSION

The physicochemical characteristics of the rainwater samples and the numerous contaminants found in the air samples were analyzed, and the tabulated findings are shown in the tables and figures below.

Table 1, 2 shows the mean concentration of the physicochemical parameters of the rain water samples for different months in the year while Tables 3 and 4 shows the mean concentration of the air pollutants considered for dry and wet seasons respectively.

Physicochemical Analysis of the Rain Water

The results obtained for the analysis of various physiological parameters of the monthly rain water samples and the various pollutants of the air were as tabulated in the tables and figures below.

Table 2 shows the concentration of the physicochemical parameter of pH Chloride, Sulphate, Nitrate, Carbonate, Iron, Lead, Cadmium, Copper, Zinc, Arsenic and Mercury of the average monthly rainfall for the period of dry season (November – February) and the wet season (March – October).

Table 2. Results of analysis of the physicochemical parameters of the rain water.

Month	pH	Cl^- (mg/L)	SO_4^{2-} (mg/L)	NO_3^- (mg/L)	CO_3^{2-} (mg/L)	Fe (mg/L)	Pb (mg/L)	Cd (mg/L)	Cu (mg/L)	Zn (mg/L)	As (mg/L)	Hg (mg/L)
Jan.	5.3	16.25	6.30	3.45	0.90	0.02	0.05	0.003	0.0028	0.0056	<0.3	0.0025
Feb.	5.45	21.50	6.70	3.50	0.95	0.025	0.06	0.0025	0.0031	0.008	<0.3	0.0019
March	5.4	32.75	6.50	3.75	1.0	0.03	0.04	0.002	0.003	0.0075	<0.3	0.0010
April	5.6	25.25	6.40	3.50	0.95	0.025	0.02	0.003	0.006	0.0068	<0.3	0.0018
May	5.8	22.50	4.80	3.45	0.75	0.02	<0.01	0.01	0.002	0.0067	<0.3	0.0020
June	6.5	22.75	4.50	3.40	0.60	0.01	0.06	0.01	0.0025	0.0023	<0.3	0.0010
July	6.65	20.15	4.00	3.00	0.48	0.01	<0.01	<0.002	0.002	0.002	<0.3	<0.001
August	6.73	23.50	2.80	2.45	0.45	<0.006	0.03	0.015	0.0015	0.0019	<0.3	<0.001
Sept.	6.77	21.50	3.50	1.75	0.43	<0.006	0.01	0.01	0.001	0.0025	<0.3	<0.001
Oct	6.82	19.00	2.00	0.90	0.40	<0.006	<0.01	<0.002	0.0023	0.0031	<0.3	<0.001
Nov.	5.9	18.75	6.32	2.78	0.58	0.015	0.01	0.002	0.0019	0.0025	<0.3	0.0015
Dec.	5.6	17.55	6.35	2.40	0.85	0.025	0.04	0.0025	0.0026	0.0047	<0.3	0.0020

Air Quality for Dry Season (November – February)

Table 3 shows the concentration of the air pollutants of NO_2, SO_2, CO, CO_2 and TSM of the various sampling points for the dry season (February – November).

Table 3. Results of the air quality analysis for dry season.

Sampling Points	NO_2 (µg/m^3)	SO_2 (µg/m^3)	CO (µg/m^3)	CO_2 (µg/m^3)	TSPM (µg/m^3)
W_1	0.003	0.29	0.0215	0.0010	92.30
W_2	0.005	0.25	0.018	0.0008	85.40
W_3	0.008	0.33	0.020	0.0014	101.32
W_4	0.0027	0.18	0.013	0.0018	78.50
E_1	0.018	0.78	0.028	0.0028	128.50
E_2	0.005	0.35	0.0205	0.0019	118.40
E_3	0.007	0.28	0.015	0.0015	105.50
E_4	0.0035	0.22	0.014	0.0009	96.52

Air Quality for Rainy Season (March – October)

Table 4 shows the concentration of the air pollutants of NO_2, SO_2, CO, CO_2 and TSM of the various

sampling points for the wet season (March – October).

Figure 4 shows the annual mean values of physicochemical parameters of rainfall in Warri and Effurun.

Table 4. Results of analysis of air quality for the rainy season.

Sampling Points	NO_2 (µg/m^3)	SO_2 (µg/m^3)	CO (µg/m^3)	CO_2 (µg/m^3)	TSPM (µg/m^3)
W_1	0.0015	0.19	0.018	0.0009	83.56
W_2	0.002	0.13	0.014	0.0005	67.20
W_3	0.0035	0.18	0.013	0.0010	95.83
W_4	0.0013	0.09	0.012	0.0012	56.35
E_1	0.012	0.25	0.020	0.0018	99.50
E_2	0.0025	0.20	0.018	0.0011	89.65
E_3	0.003	0.19	0.017	0.0009	79.34
E_4	0.0012	0.13	0.011	0.0008	80.44

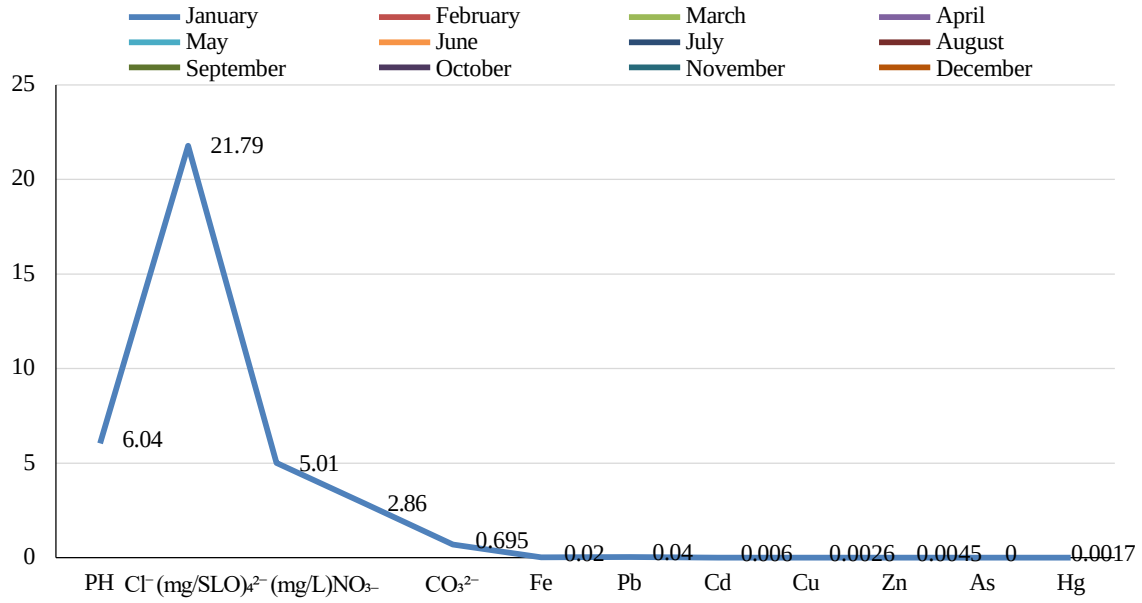

Figure 4. Annual mean values of physicochemical parameters of rainfall in Warri and Effurun.

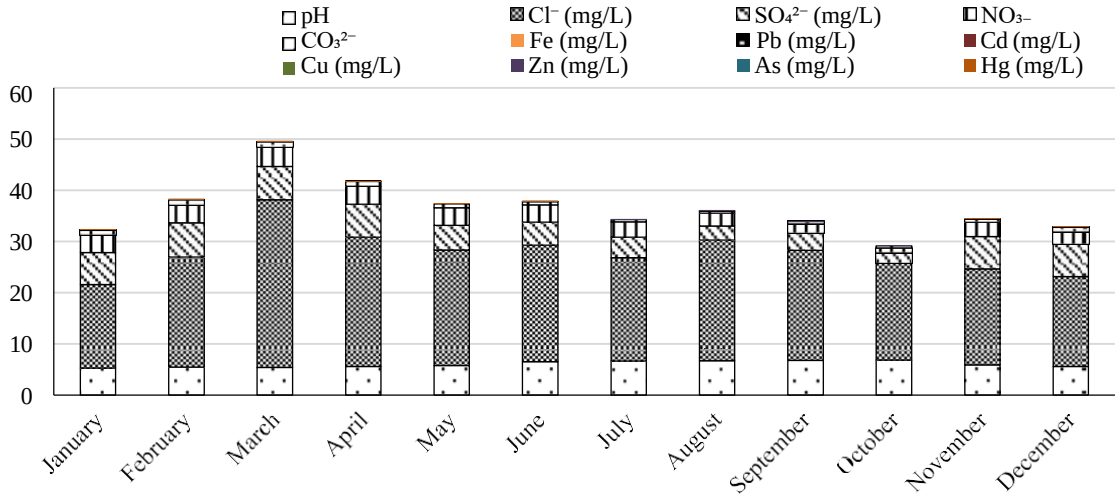

Figure 5. (a) Mean Values of Physico Chemical Parameters of Rainfall of Different Months in a Year.

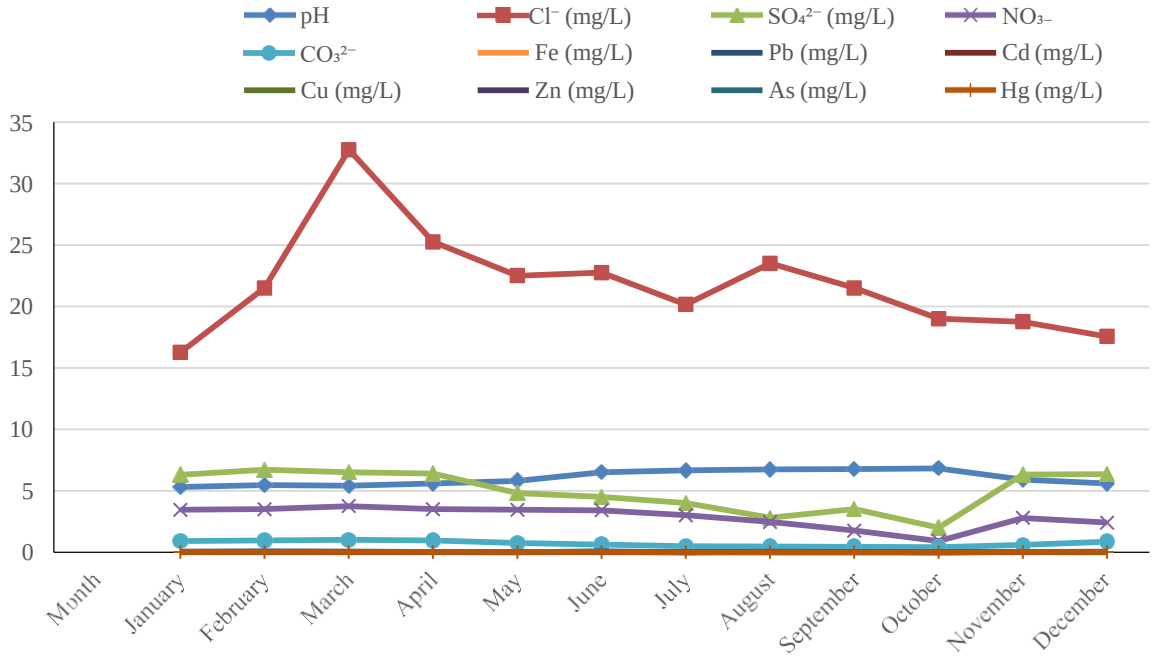

Figure 5. (b) Trends of the physicochemical parameters of the rain water considered over various months of the year in Warri and Effurun.

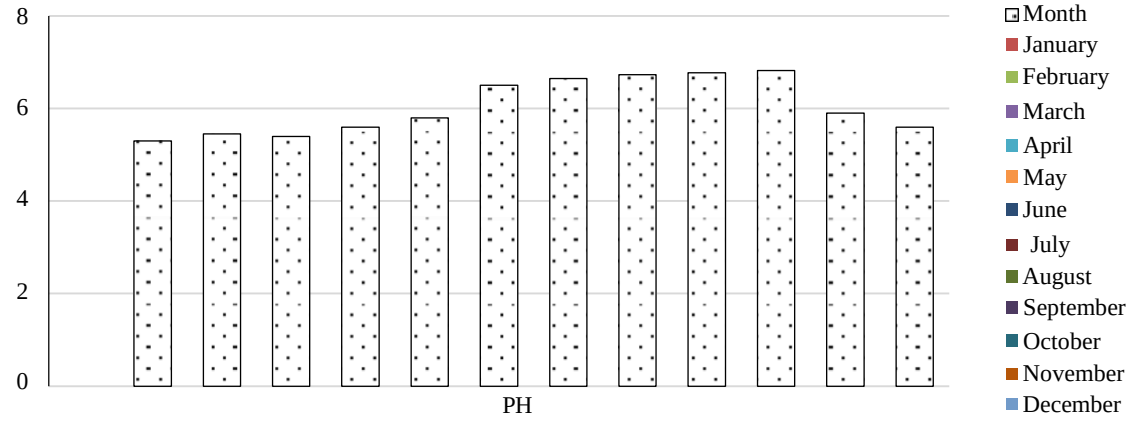

Figure 6. (a) Mean value of pH for different months.

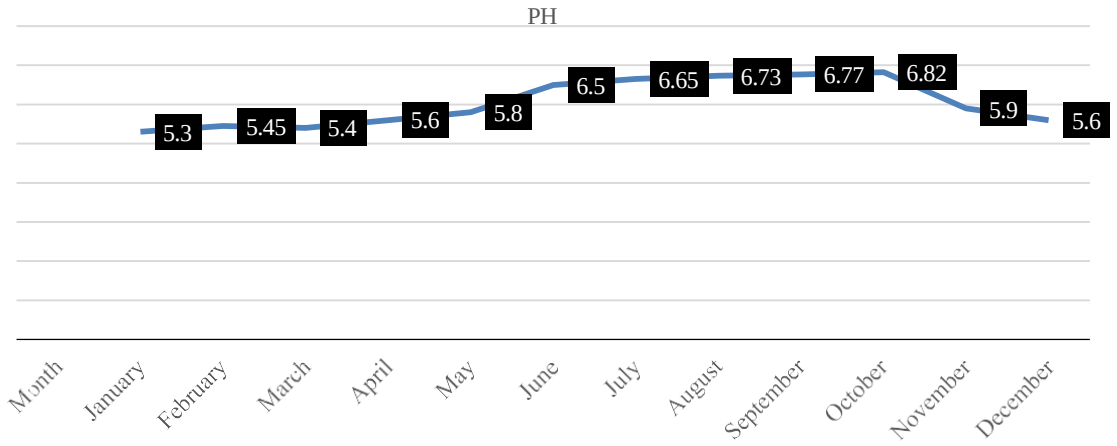

Figure 6. (b) Trends of the pH over different months of the year.

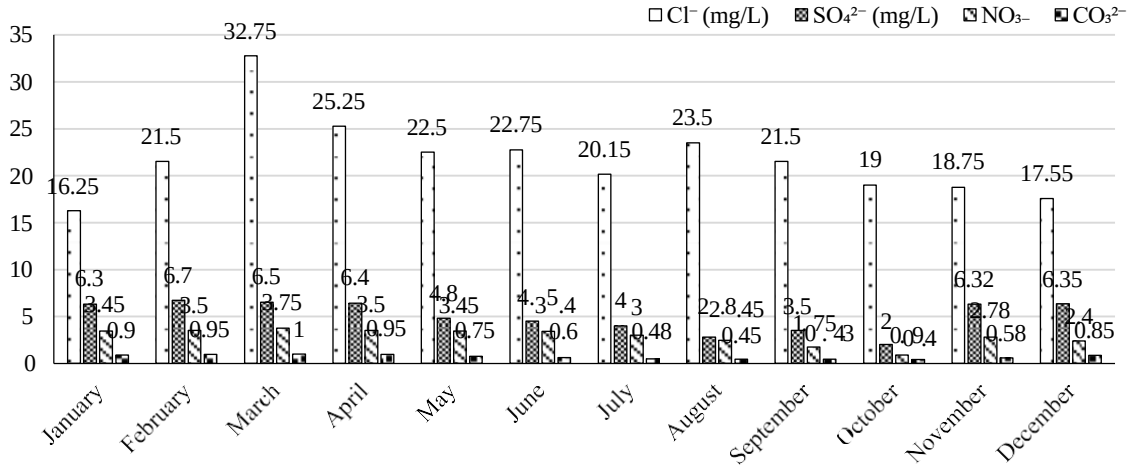

Figure 7. (a) Mean values of Cl^-, SO_4^{2-}, NO_3^- and CO_3^{2-} for different months.

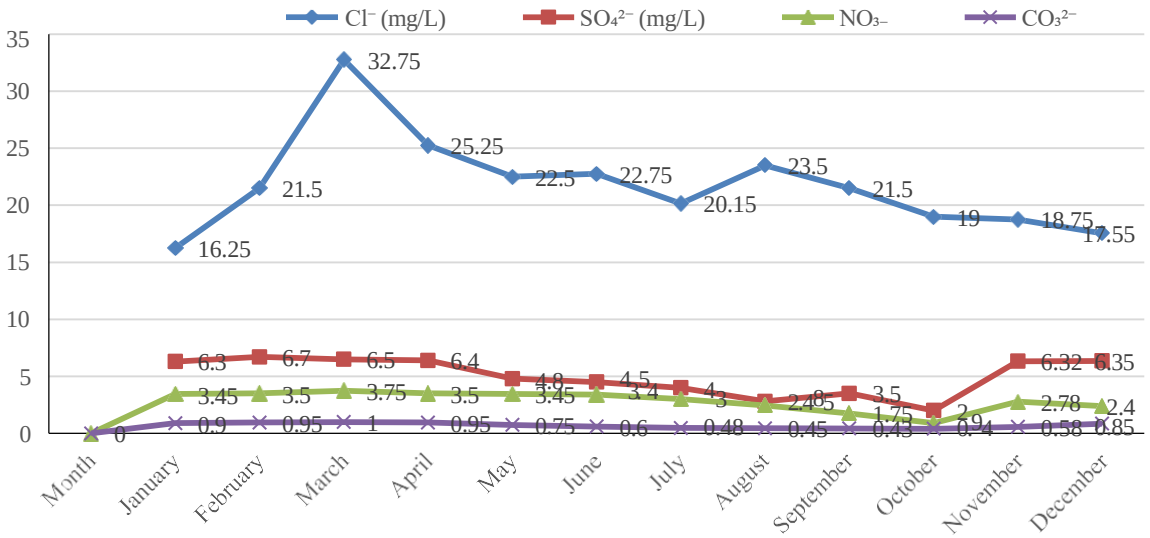

Figure 7. (b) Trends of Cl^-, SO_4^{2-}, NO_3^- and CO_3^{2-} of various months of the year.

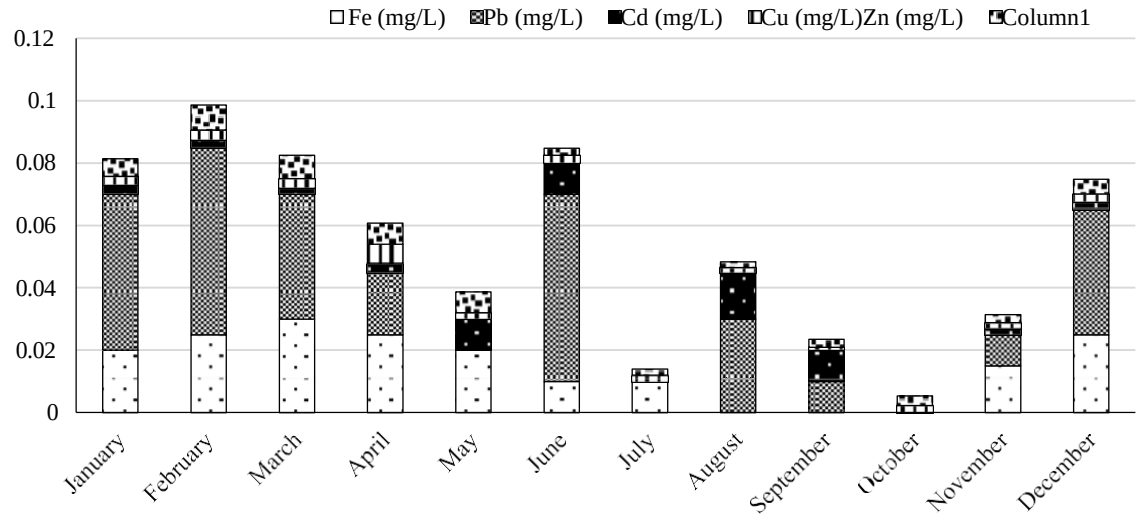

Figure 8. (a) Mean values of the heavy metals: Fe, Pb, Cd, Cu, Zn, As and Hg for different months.

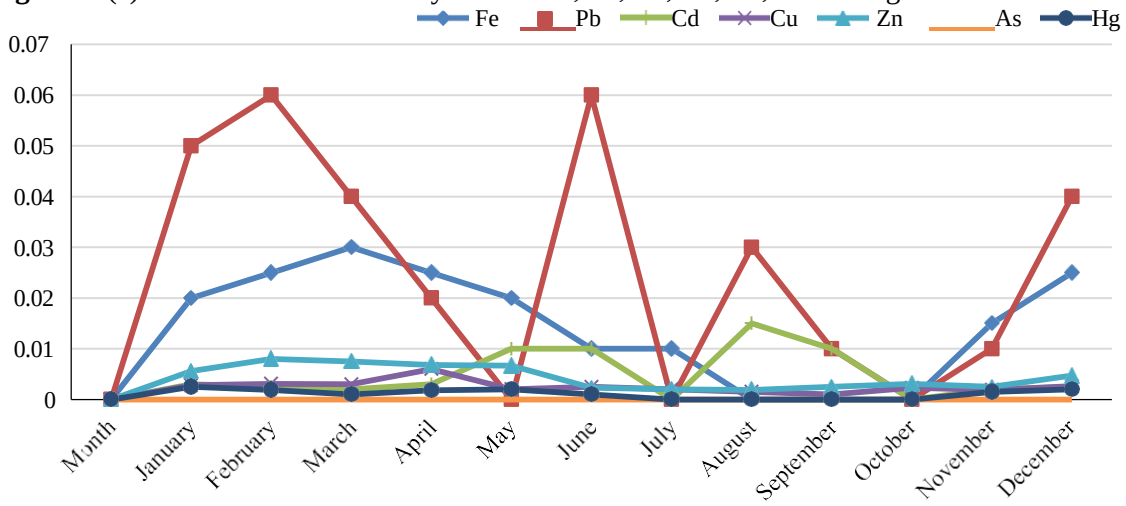

Figure 8. (b) Trends of the heavy metals over different months of the year

Plots of the Results of the Pollutants for the Dry Season

Figure 5a shows the mean values of physicochemical parameters of rainfall in different months in a year.

Figure 5b shows the trends of the physicochemical parameters of rain water considered over various months of the year in Warri and Effurun.

Figure 6a shows the mean value of pH for different months in a year and Figure 6b shows the trends of the pH of rain water over different months of the year.

Figure 7a shows the mean values of the anions, Cl^-, SO_4^{2-}, NO_3^- and CO_3^{2-} for different months of the year while

Figure 7b shows the trends of these anions over the year.

Figure 8a shows the mean values of the heavy Metals Fe, Pb, Cd, Cu, Zn, As and Hg for the different months of the year.

Figure 8b shows the trends of these heavy metals over the period.

Figure 9a shows the mean values of the air pollutants for the dry season in Effurun and Warri.

Figure 9b shows the trends of these pollutants over the period of the dry season.

Figures 10a and 10b shows the mean values and trends of NO_2 over the period of dry season respectively.

Figures 11a and 11b shows the mean values and trends of SO_2 over the period of dry season respectively.

Figure 12a shows the mean values of CO over the period of dry season and Figure 12b shows the trends of CO over the period.

Figure 13a shows the mean values of CO_2 over the period of dry season and Figure 13b shows the trend of CO_2 over the period.

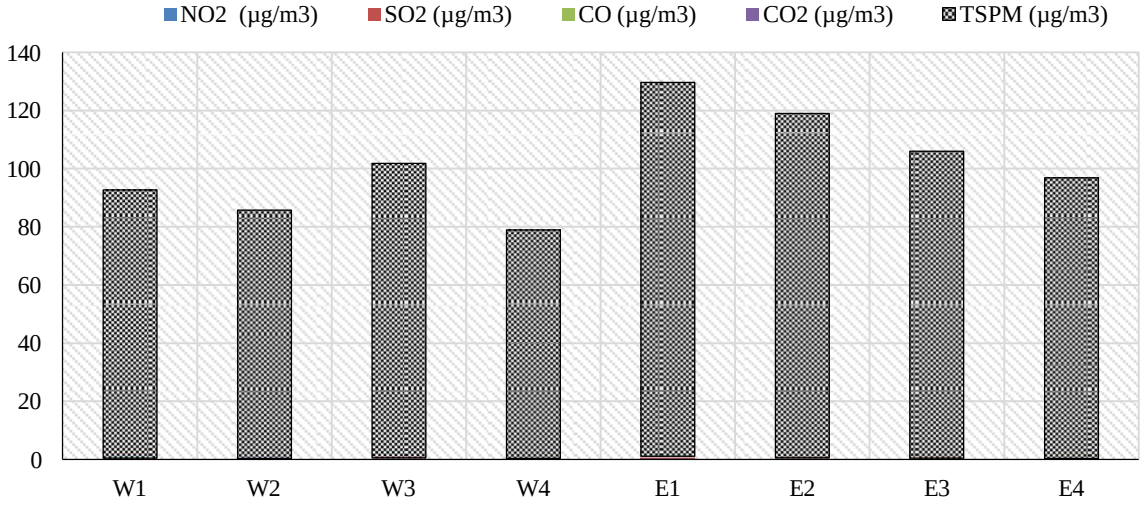

Figure 9. (a) Mean Values of the Air Pollutants for the Dry Season in Effurun and Warri.

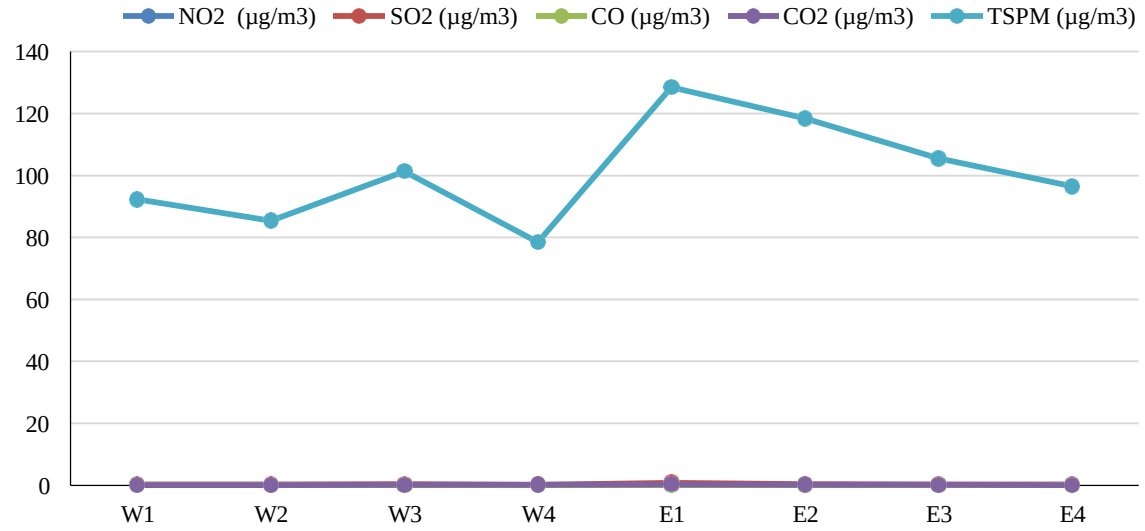

Figure 9. (b) Trends of the air pollutants during dry season.

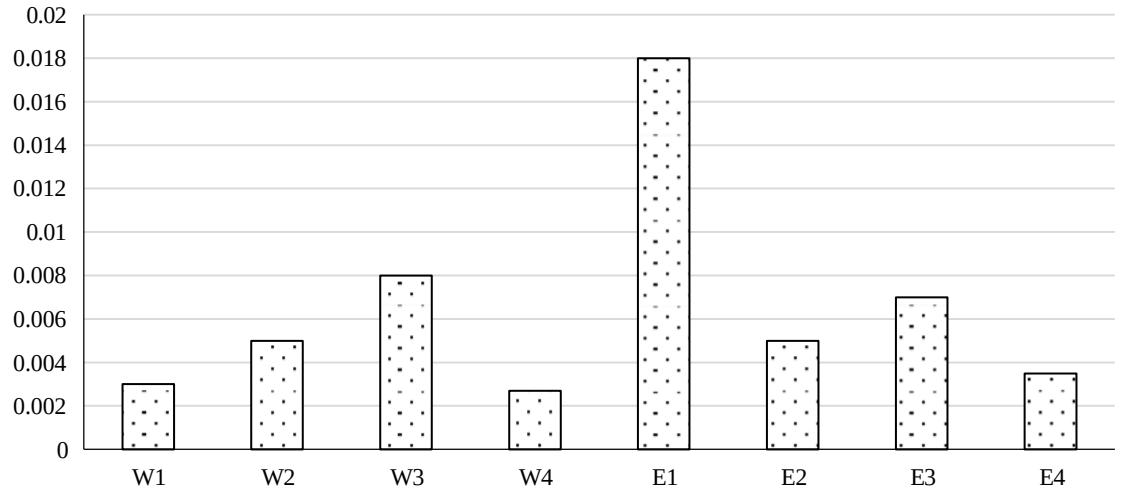

Figure 10. (a) NO_2 ($\mu g/m^3$).

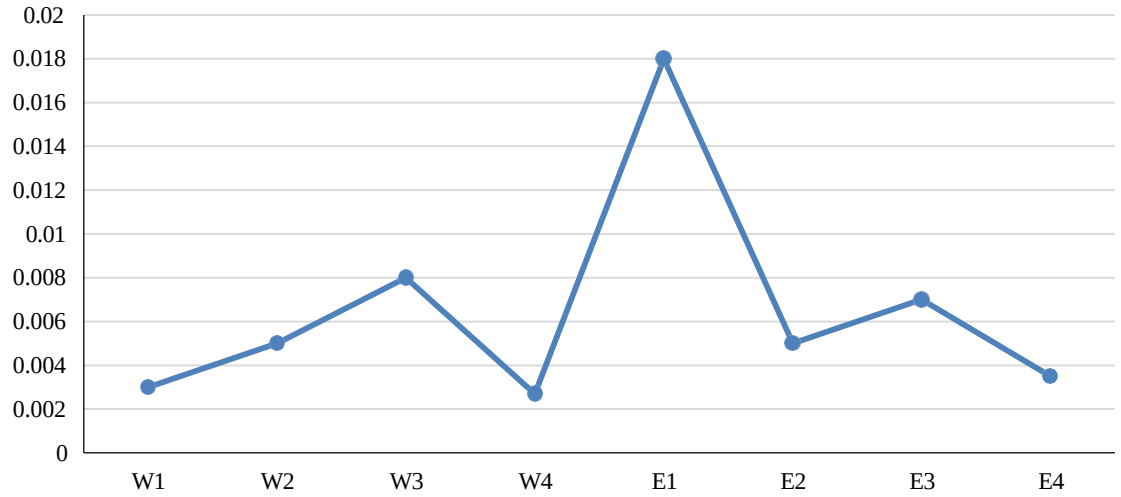

Figure 10. (b) NO_2 ($\mu g/m^3$).

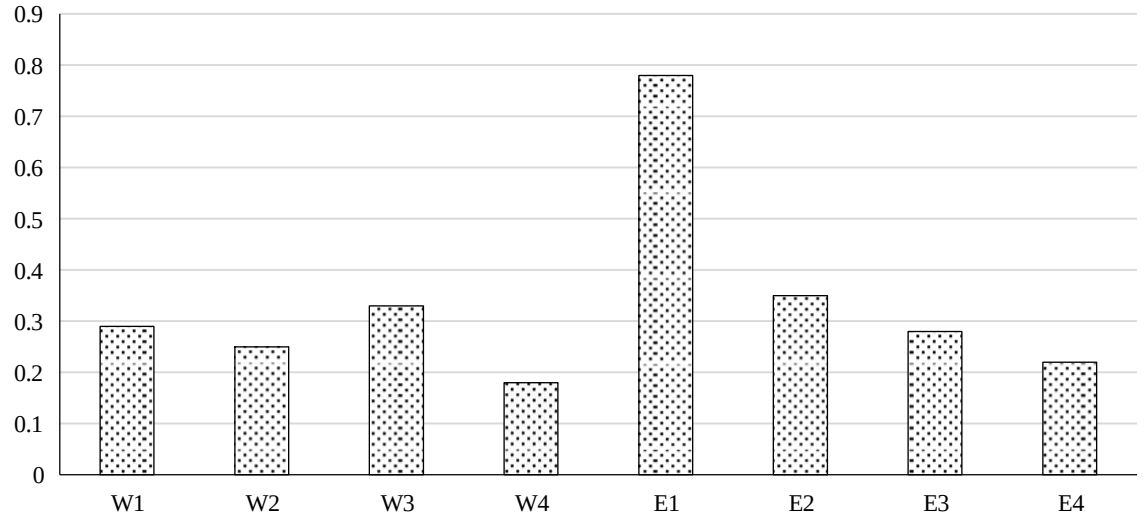

Figure 11. (a) SO_2 (µg/m^3).

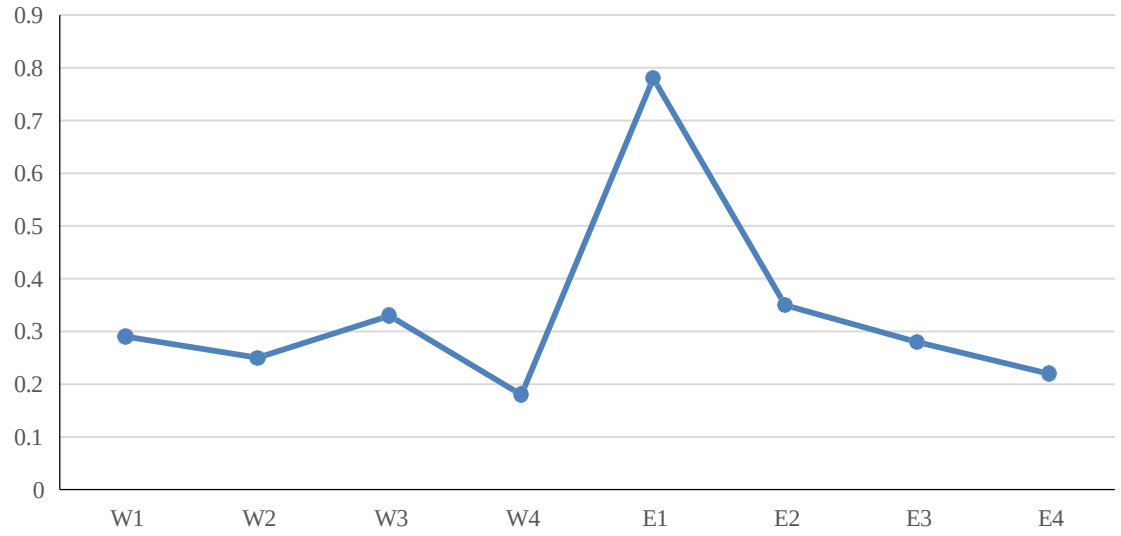

Figure 11. (b) SO_2 (µg/m^3)

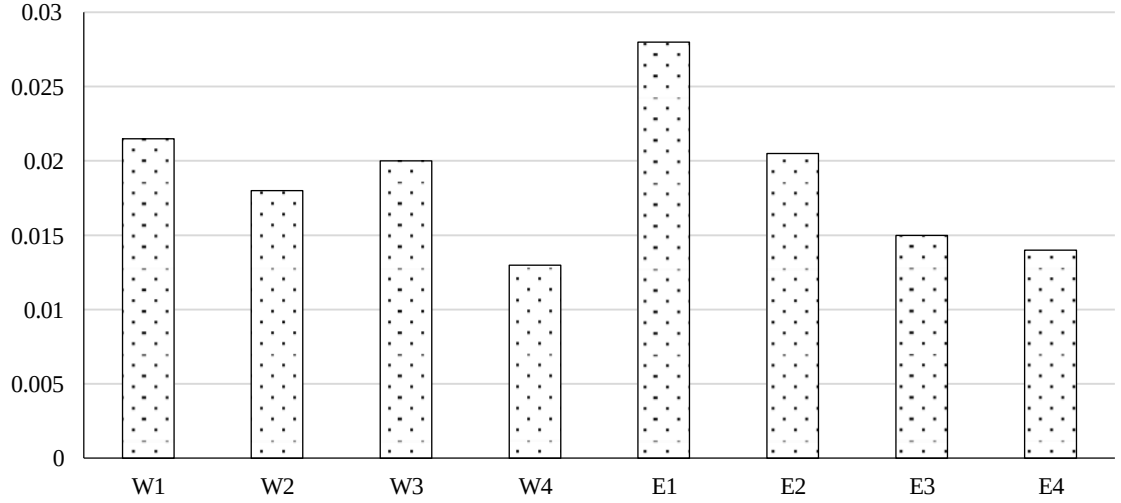

Figure 12. (a) CO (µg/m^3).

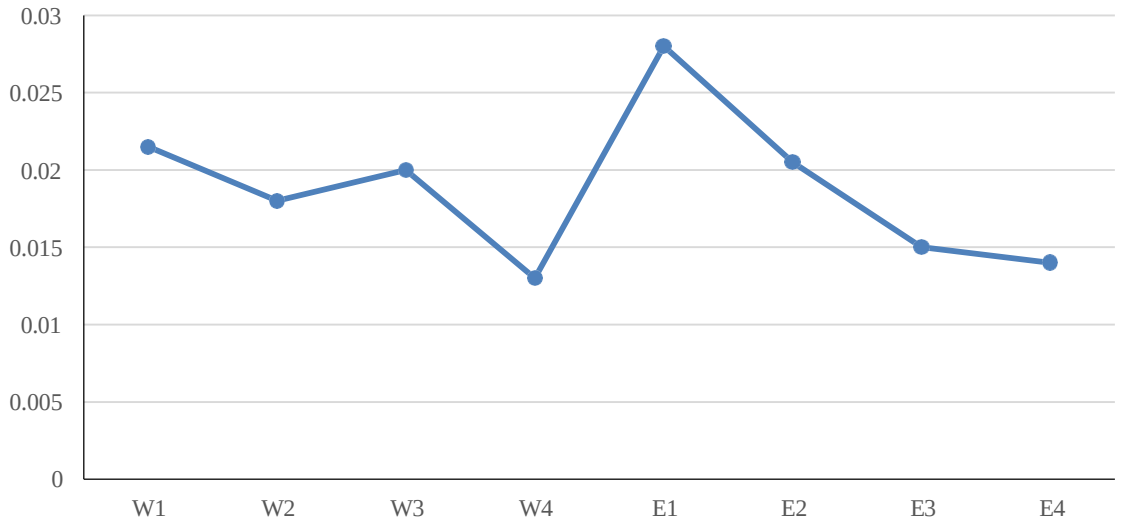

Figure 12. (b) CO (µg/m^3).

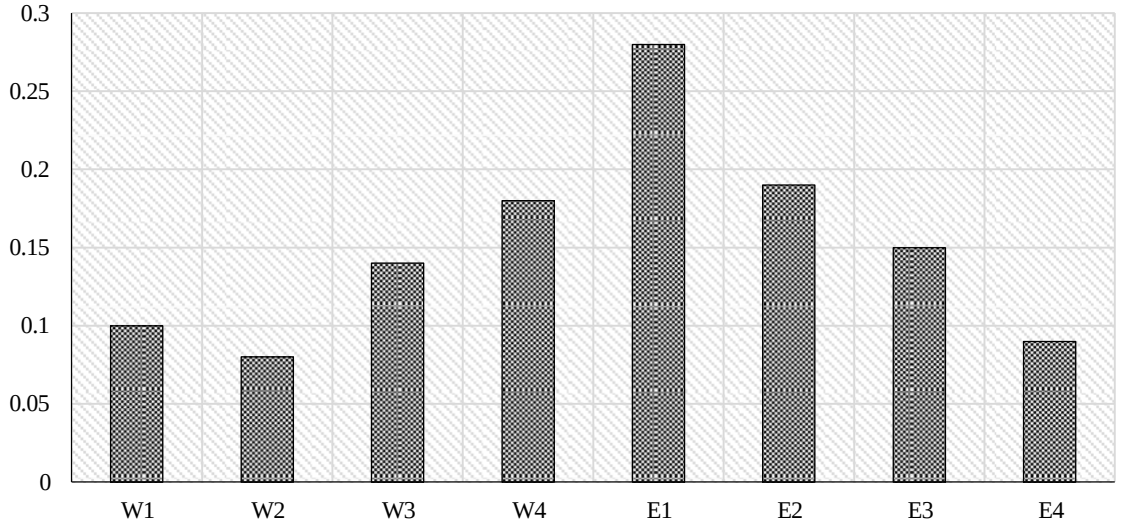

Figure 13. (a) CO_2 (µg/m^3).

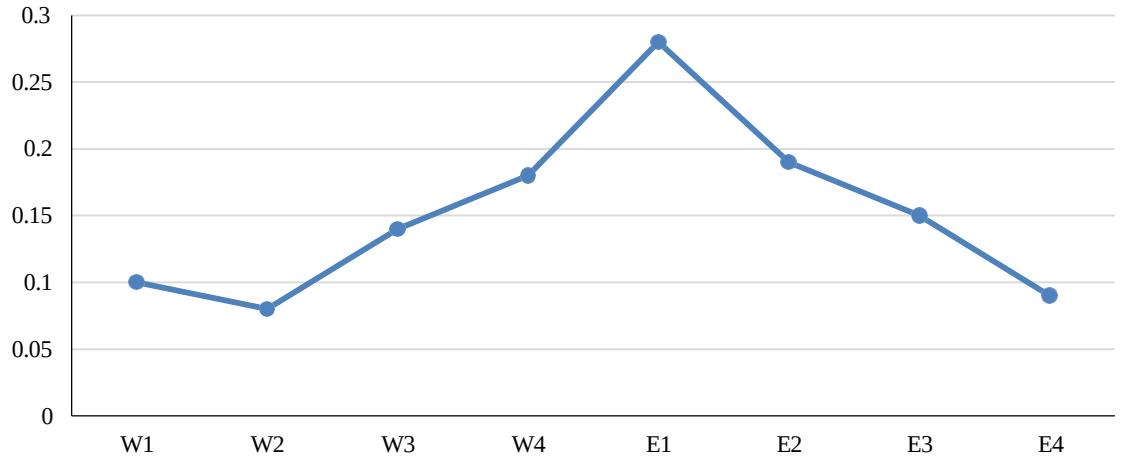

Figure 13. (b) CO_2 (µg/m^3).

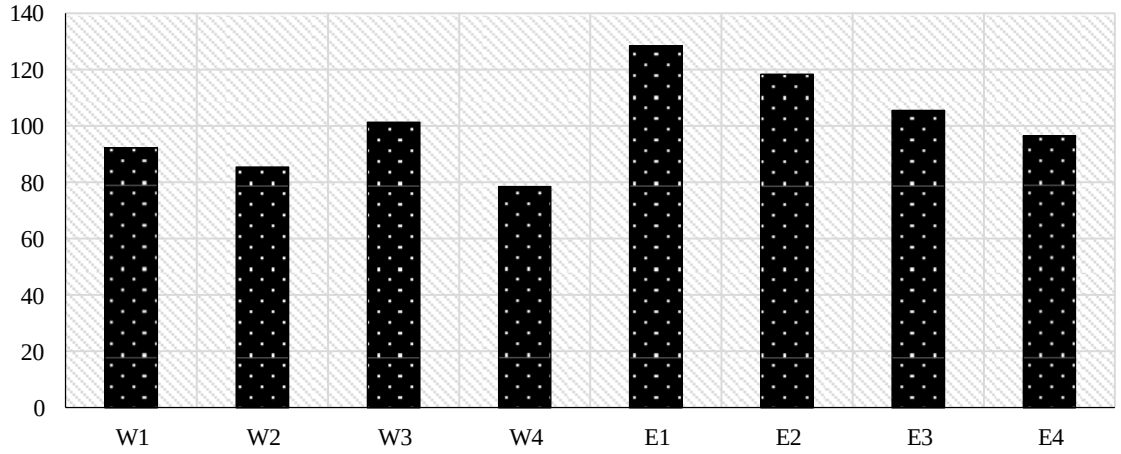

Figure 14. (a) TSPM (µg/m^3).

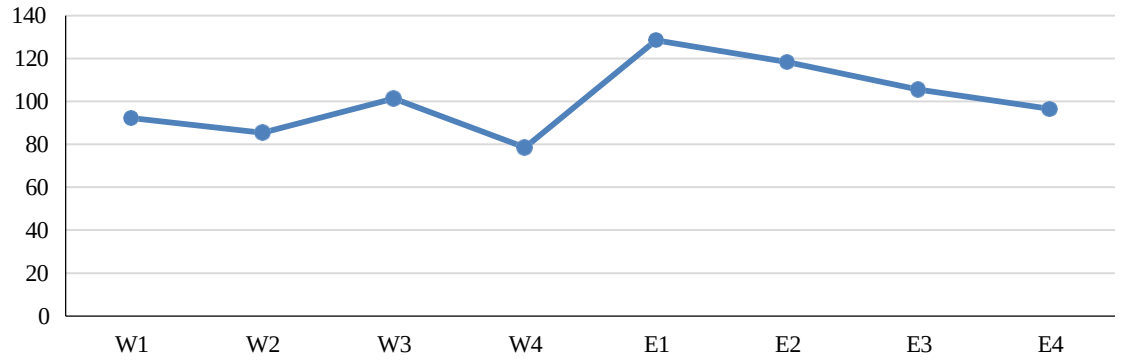

Figure 14. (b) TSPM (µg/m^3).

Plots of the Results of the Pollutants for the Rain Season

Figure 14a shows the mean values of TSM over the period of dry season and Figure 14b shows the trend of TSM over the period.

Figures 15a and 15b shows the mean values and trends of the pollutants of NO_2, SO_2, CO, CO_2 and TSM over the period of dry season respectively.

Figures 16a and 16b shows the mean values and trends of NO_2 over the period of rainy season respectively.

Figures 17a and 17b shows the mean values and trends of SO_2 over the period of rainy season respectively.

Figures 18a and 18b shows the mean values and trends of CO over the period of rainy season respectively.

Figure 19a shows the mean values of CO_2 during the period of rainy season while Figure 19b shows the trends of CO_2 during the rainy season.

Figures 20a and 20b shows the mean values and trends of suspended particulate matter (TSM) during the period of rainy season respectively.

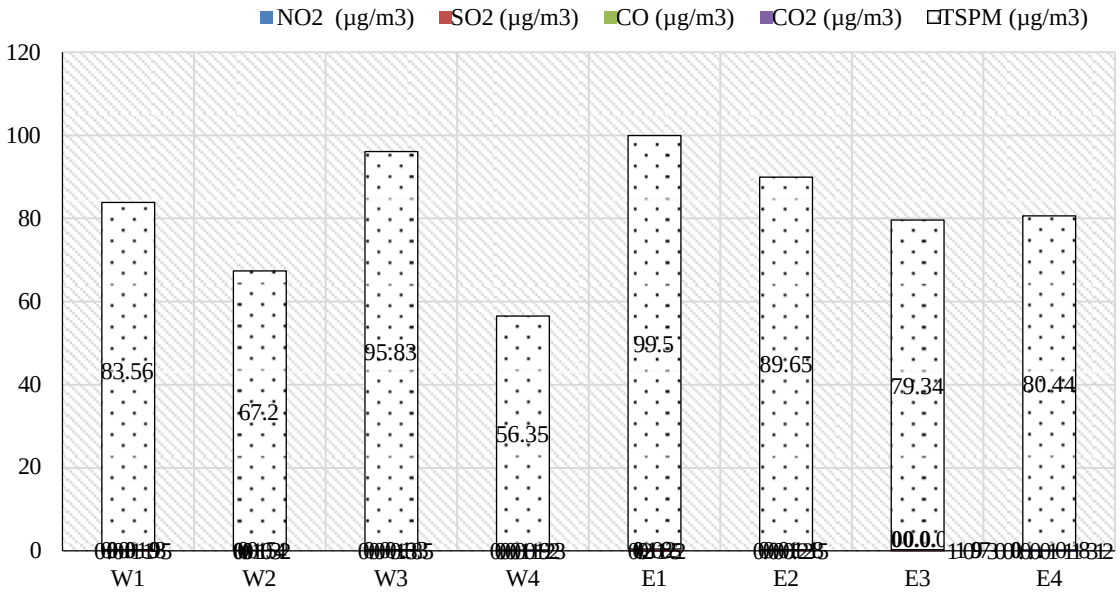

Figure15. (a) Mean values of the air pollutants for the rain season in Effurun and Warri.

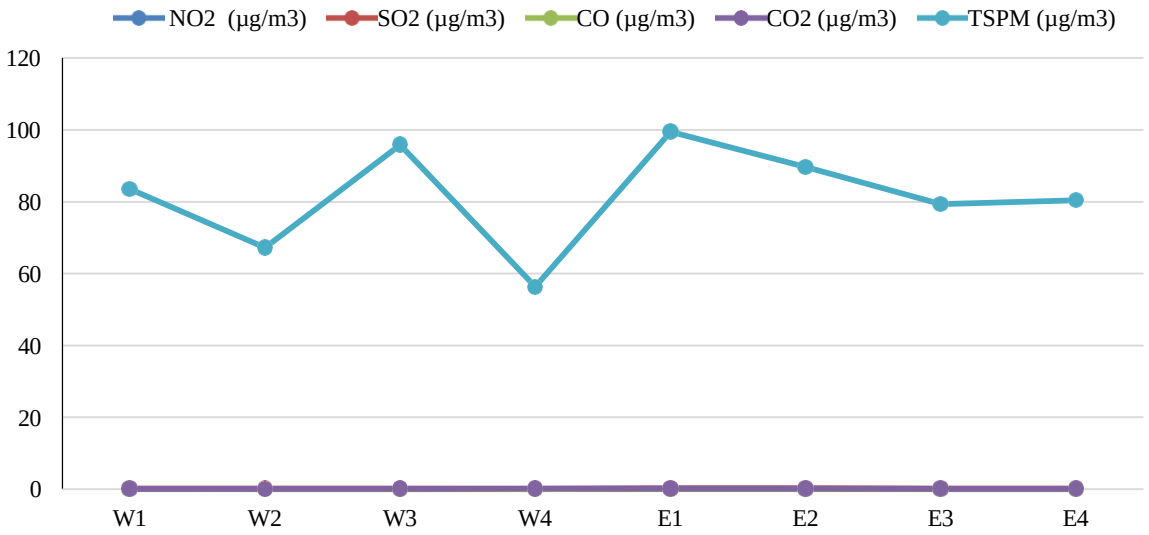

Figure 15. (b) Trends of the Air Pollutants for the Rain Season in Effurun and Warri.

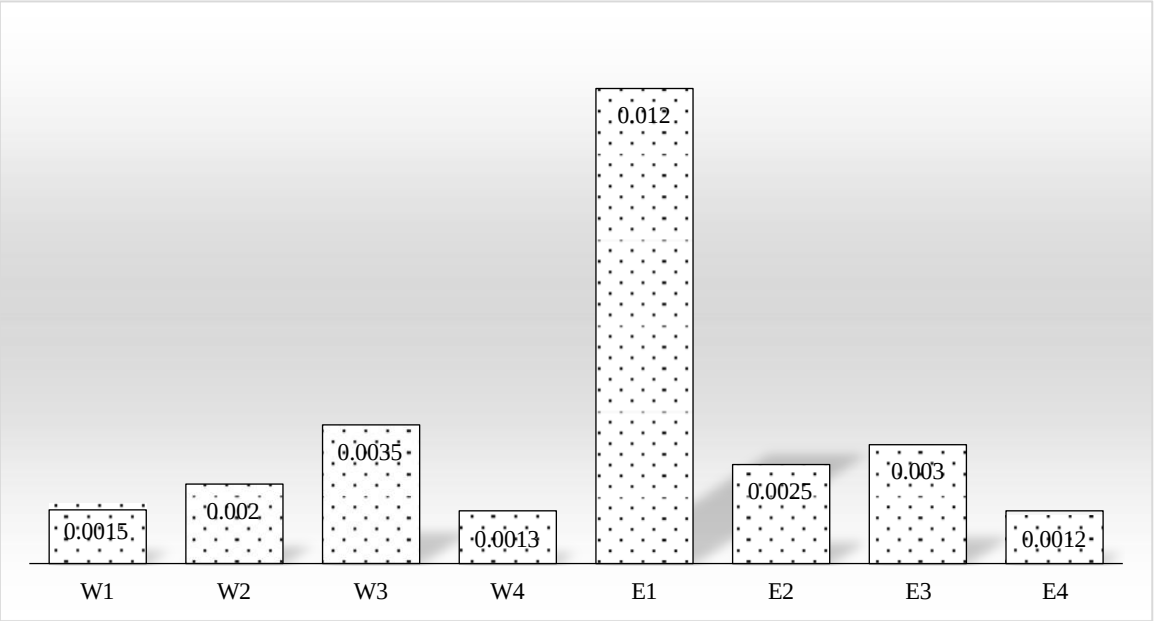

Figure 16. (a) NO_2 (µg/m_3).

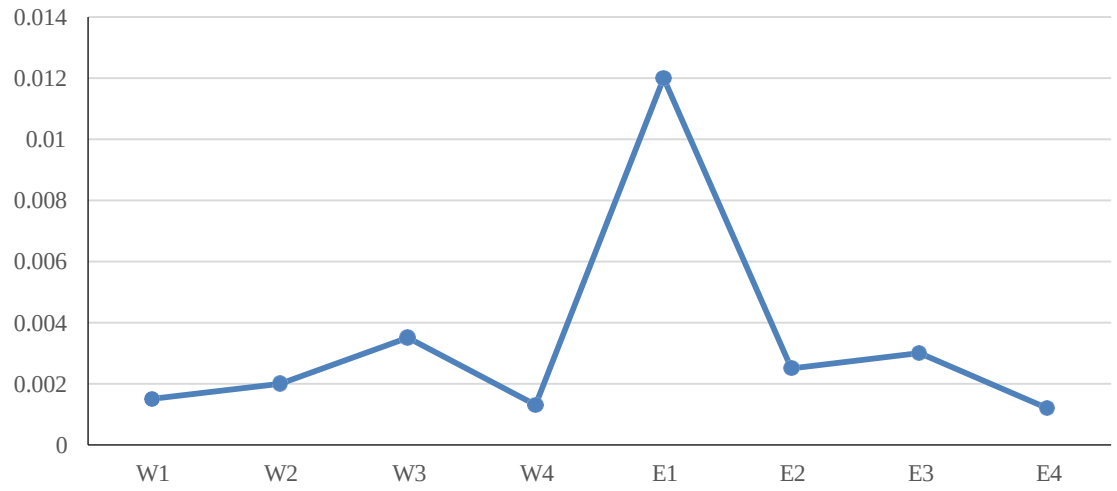

Figure 16. (b) NO_2 (µg/m^3).

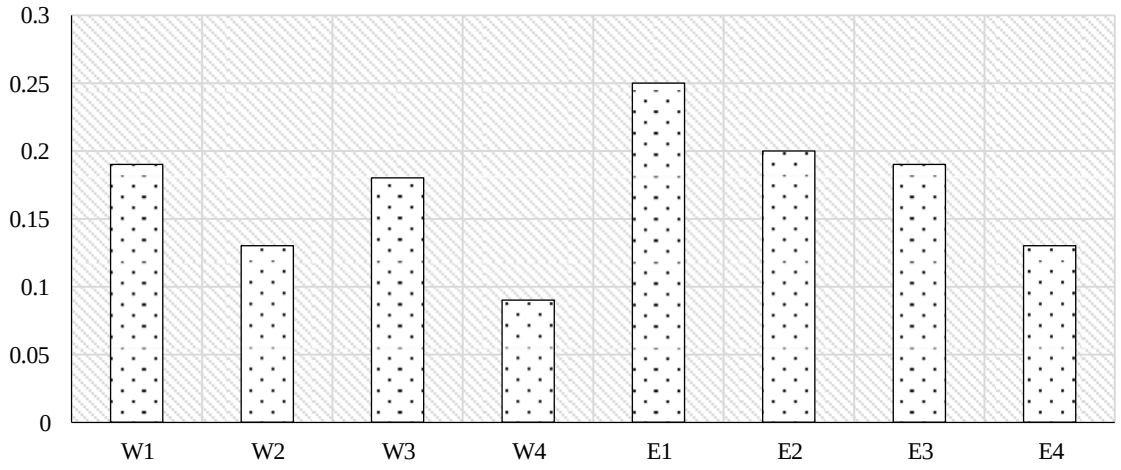

Figure 17. (a) SO_2 (µg/m^3).

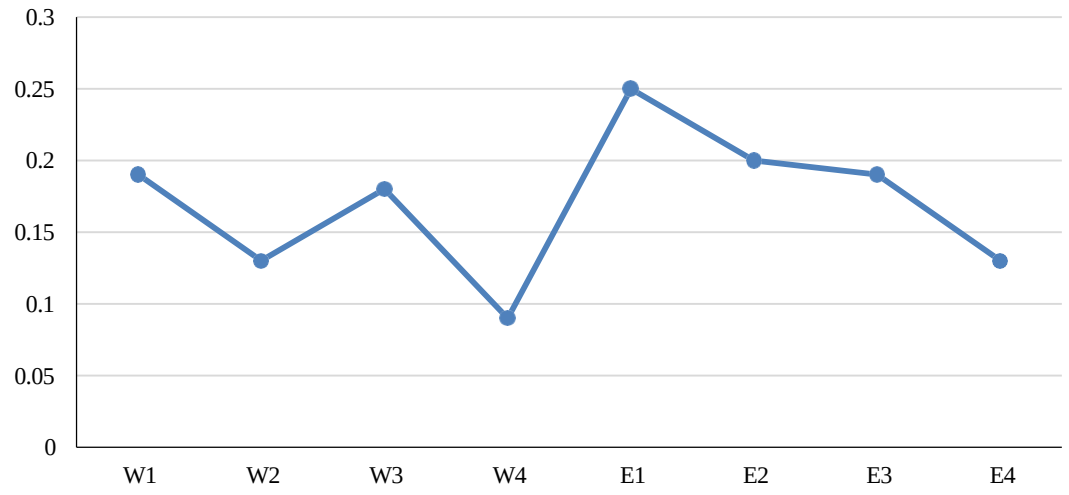

Figure 17. (b) SO_2 (µg/m^3).

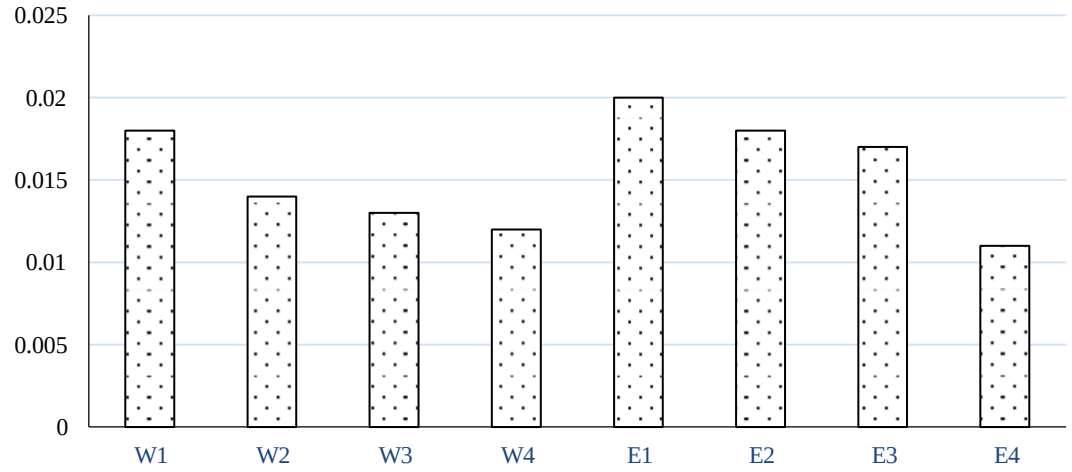

Figure 18. (a) CO_2 (µg/m^3).

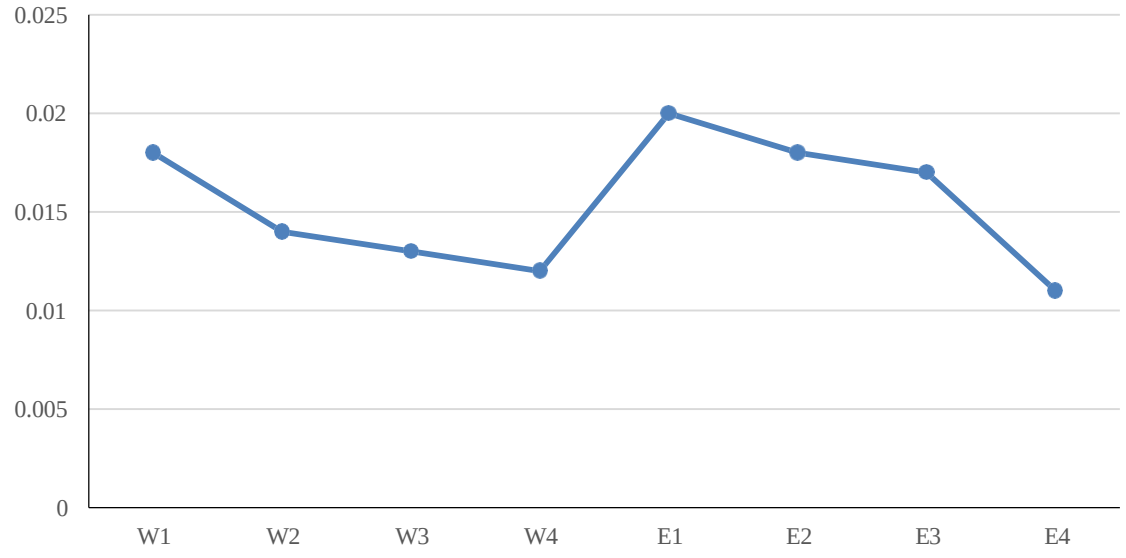

Figure 18. (b) CO (µg/m^3).

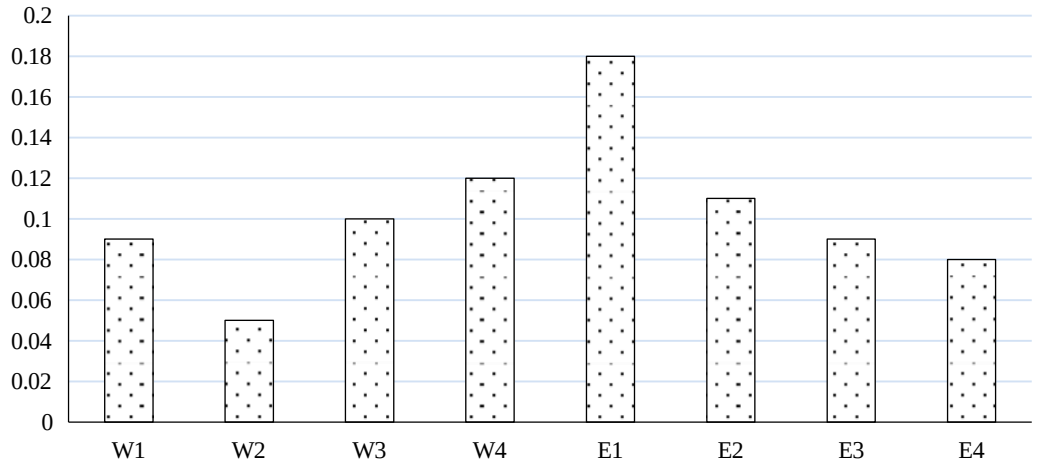

Figure 19. (a) CO_2 (µg/m^3).

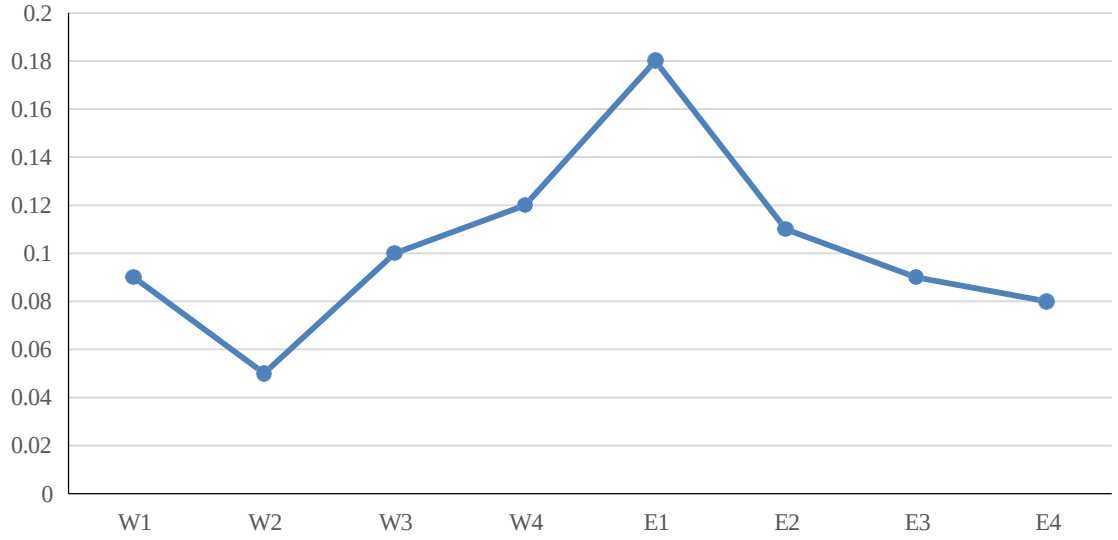

Figure 19. (b) CO_2 (µg/m^3).

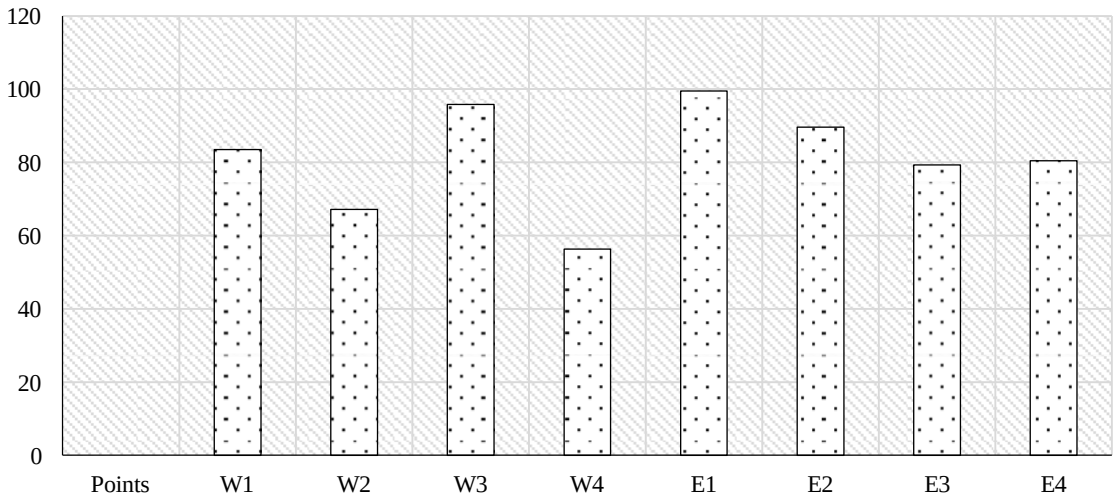

Figure 20. (a) TSPM (µg/m^3).

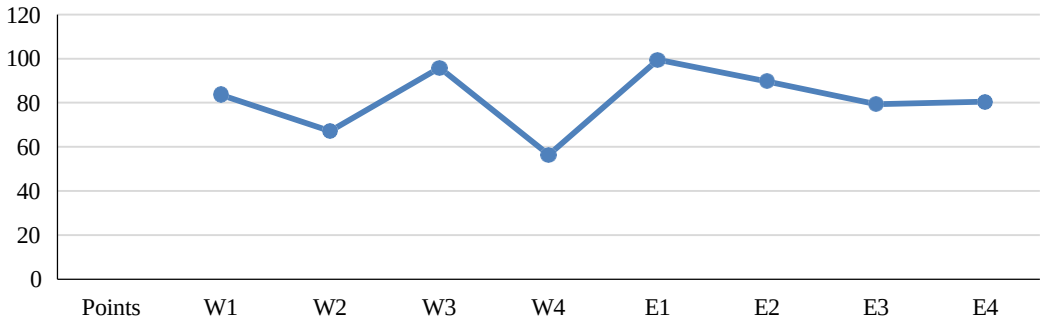

Figure 20. (b) TSPM (µg/m^3).

The annual mean values of physicochemical parameters shows that rain water is slightly acidic as can be seen from the mean pH value of 6.04.

Chloride has the highest mean value of 21.79 mg/l of all the anions analysed. Arsenic is completely not detected, this may be the detection limits of arsenic by the method used (i.e 0.3).

For the heavy metals Lead (Pb) has the highest annual mean concentration of 0.036 mg/l with annual mean concentration of mercury (Hg) of 0.0015mg/l the least.

The results of the rain water samples both of the dry and wet season shows that the pH of the rain water is generally acidic. While it is slightly acidic during the months of the rainy season. It is however more acidic during the months of the dry season, this may be due to dusts, sooths, particulate matter ad vehicular emissions which disperse into the atmosphere during the dry season as the humidity is expected to be during the dry season as the humidity is expected to high due to dry weather.

In January, the month with the least amount of precipitation, the pH value is at its most acidic. This can be the effect of increased pollution and dry deposition brought on by the dry weather.

The pH value slightly increases from the value of 5.3 in January to a peak of 6.82 in October the least month of heavy rainfall and begins to fall as from the month of November which is the beginning of the dry season.

Where the rain water to be used for portability is then means it falls below WHO standard of 6.5 – 8.5.

In figure 4.2a where the monthly mean values of the physicochemical parameters is displayed, rainfall for the month of March has the highest value of chloride 32.75mg/L, Nitrates 3.75mg/L and Carbonate 1.0 mg/L. The rainfall for the month of February has the highest concentration of sulphate 6.70 mg/L

The trend is that there is gradual increase of the chloride concentration from January (16.25 mg/L) to March (32.7 mg/L) before a steady fall in concentration from April (25.25 mg/L) to September (21.5 mg/L) after which the chloride concentration finally falls to a value of 17.55 mg/L in December.

There was also a decrease in the concentration of sulphate (6.3 mg/L) from January to 2.8 mg/L in August before a rise again in September (3.5 mg/L) to 6.35 mg/L in December.

The concentration of nitrates increases from January (3.45 mg/l) to March (3.75 mg/L) before falling in April (3.5 mg/L) to October (0.9 mg/L) and then rises again in November (2.78 mg/L).

Carbonates concentration increases steadily from January (0.9 mg/L) to 1.0 mg/L in March before falling in April from 0.95 mg/L to 0.40 mg/L in October probably the month of highest rainfall. The concentration then rises in the month of November to 0.58 mg/l.

In Figure 5a, the month of February and June has the highest concentration of Lead (Pb) of 0.06 mg/L while it was below the instrument diction limit of 0.01 mg/L in the month of May, July, and October. The high concentration in June may be due to the environmental pollution as there were lots of activities then that might impart the rain water.

As rightly indicated before the concentration of Arsenic (As) in all the rain water samples was below the instrument detection limit of 0.3 mg/L for the method used in determination of Arsenic (As).

Zinc has the highest concentration of 0.008 mg/l in the month of February and had also the least concentration of 0.019 mg/L in the month of August.

The concentration of Iron (Fe) ranges from 0.01 mg/l in the month of June and July to 0.025 mg/l in the months of February, April and December. The concentration of Iron (Fe) in the months of August to October is below the instrument's detection limit of 0.06 mg/L for the method used in the determination of Iron (Fe).

Cadmium (Cd) has a concentration range from 0.002 mg/l in March and November to 0.01 mg/l in September and November. Cadmium was not detected in July and October, as the concentration of Cadmium in those two months was below the instrument detection limit of 0.002 mg/L.

Mercury (Hg) was not detected in the rainfall of the months of July to October as the concentration of mercury was below the instrument's detection limit of 0.001 mg/L. However, the concentration of Mercury in the rainfall ranges from 0.001 mg /l in the month of March and June to 0.0025 mg/L in January.

The concentration of Copper (Cu) in the rainfall ranges from 0.001 mg/L in September to 0.006 mg/L in April.

The trend of the heavy metals was that there was a decrease in concentration of Cadmium (Cd) in January from 0.003 mg/l to 0.002 mg/l in April to not been detected in July.

There was an increase in the concentration of Iron (Fe) 0.02 mg/l in January to 0.03 mg/l in March before a fall in April (0.025 mg/l) to not been detected in August to October i.e (0.006 mg/l).

There were rises and falls in the concentration of Lead (Pb) throughout the season. There was an increase in the concentration of Copper (Cu) from January (0.0028 mg/L) to 0.0031 mg/L in February before a fall to a concentration of 0.003 mg/L in March. There were subsequent rise and fall in the concentration of Copper (Cu) in remaining part of the months for the period.

There was a sharp increase in the concentration of Zinc (Zn) 0.0056 mg/L in the month of January to 0.008 mg/L in February before it fell to 0.0075 mg/L in March. There was a subsequent fall in concentration of Zinc (Zn) from March (0.0075 mg/L) to 0.0019 mg/L in August. There was a rise in concentration of Zinc from September to October i.e. 0.0025 mg/L – 0.0031 mg/L. There was a decrease in concentration of Mercury (Hg) from 0.0025 mg/L in January to 0.001 mg/L in March

before a rise of 0.0018 mg/L in April to 0.002 mg/L in May.

There was no detection of Mercury (Hg) in the months of July – October as the concentration was below the instruments' and methods' of detection limits of 0.001 mg/L.

Concentration of CO_2 for the period is 0.08 $\mu g/m^3$ at point W_2 during the same period.

Total Suspended Particulate Matter (TSPM) concentration is highest at point E_1 which is 128.50 $\mu g/m^3$ and it is lowest at point W_4 (78.10 $\mu g/m^3$) as there is less vehicular and human traffic here.

Plots in figure 12a and 12b represents the mean concentration of the air pollutants analyzed during the rainy season (March – October).

Sampling Point E_1 has the highest mean concentrations for all the air pollutants i.e. 0.0012 $\mu g/m^3$ for NO_2, 0.25 $\mu g/m^3$ for SO_2, 0.020 $\mu g/m^3$ for CO, 0.18 $\mu g/m^3$ for CO_2 and 99.50 $\mu g/m^3$ for TSPM. This may be due to the proximity of the point E_1 to the WRPC and PPMC which is about 2 km array. There are lots of activities involving fuel transfer refining of crude oil, loading of tanker and transferring of petroleum products. All these activities might have adverse effect on the quality of air around the point E_1.

The concentration of NO_2 ranges from 0.0012 $\mu g/m^3$ in point E_4 which is the least to 0.012 $\mu g/m^3$ in point E_1 which is the highest during the rainy season, this agrees with [18]. SO_2 has a concentration of 0.25 $\mu g/m^3$ at point E_1 which is the highest during the rainy season and a concentration of 0.09 $\mu g/m^3$ at point W_4 during the same period.

The concentration of 0.020 $\mu g/m^3$ for CO is highest at points E_1 while 0.011 $\mu g/m^3$ of CO is the lowest concentration at point E_4. There is slight variation of concentration of CO at various sampling points.

CO_2 has a concentration of 0.18 $\mu g/m^3$ at point E_1 which is the highest and a concentration of 0.05 $\mu g/m^3$ at point W_2 and this represent the lowest concentration of CO_2 at any sampling points.

The concentration of TSPM was 99.50 $\mu g/m^3$ at point E_1 and this represents the highest concentration at all point during the rainy season. The least concentration of TSPM of 56.35 $\mu g/m^3$ was at point W_4.

The seasonal trends of the concentration of the air pollutants considered was such that it was higher in the dry season than the rainy season. This might be due to the fact that during the dry season there are lots of pollution and due to the dry weather there might be with or no hindrance in the transportation of this pollutants. The factor of rain fall might also play a major role in reduction of concentration during the rainy season as some of these pollutants might be dissolved in the rain of washed away by the rain.

It was also observed that the concentrations of the pollutants are lowest (at least for some of the pollutants) as points E_4 and W_4. This was so because both points have less vehicular movement and human activities here is also less.

CONCLUSION

One significant environmental health danger is air pollution. The global burden of disease from heart disease, lung cancer, and respiratory infections won't be as high if air pollution is low.

Variation is part of life and it can be observed at every point of human endeavour. Also,

considering the available data, the values vary as time varies which calls for test of significant variation among the parameters present in the sample of rain water collected. The variation if significant can be attributed to seasonal effect such as rainy season and dry season. It is a known fact that volume of rain water during the rainy season is significantly higher than that of dry season which can also affect the minerals present as rain can be attributed to some atmospheric factors and the weather condition of a location. Industrial areas are bound to have acidic rain water due to carbon emission in the area and nature of rain water in forest region can be observed to be better in terms of presence of harmful minerals.

The spatial variability of all the pollutants considered for both the dry and rainy season remains the same pattern.

The fact that the concentration levels were greater during the dry season indicates that the season had a significant impact on the variability of the contaminants.

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