QUANTIFICATION OF AMBIENT AIR QUALITY IN SELECTED URBAN ATMOSPHERE IN DELTA STATE, NIGERIA

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ABSTRACT

Carbon monoxide (CO), carbon dioxide (CO_2), hydrogen sulfide (H_2S), nitric oxide (NO) and methane (CH_4) were seasonally monitored. The study was carried out in four sites located in Delta state in the Niger Delta floodplain on the coast of Nigeria. Sampling was done during the dry (October 2015 – March 2016) and wet (April – September 2016) season respectively. Air sample collection was carried out daily between 7 – 10am (morning), 12 – 3pm (afternoon) and 4 – 7pm (evening) by use of aeroqual gas detector kit model ASTM D3249-95 – 2011. Results has shown that the dry season concentration (μgm^{-3}) ranged from 4.04 – 8.13 (CO), 17.94 – 14.30 (CO_2), 0.05 – 0.39 (H_2S), 0.04 – 0.14 (NO) and 0.41 – 4.94 (CH_4) in all sample sites. Similarly, the wet season concentration (μgm^{-3}) ranged between 4.20 and 7.94 (CO), 6.90 and 14.50 (CO_2), 0.03 – 0.15 (H_2S), 0.03 and 0.17 (NO) and 0.44 and 4.21 (CH_4) in all sample sites. Observed Poisonous Gaseous Pollutants (PGPs) concentrations are relatively lower than recommended standards and guidelines. Pearson Correlation shows good and high significant relationship between study sites in dry and wet seasons. Further study should be carried out on the environment and human health risk of observed pollutants concentrations.

Keywords: *Air Quality, Gaseous Pollutants and Urban Atmosphere*

INTRODUCTION

Ambient air quality is the condition of pollutants in the atmosphere or outdoor air surrounding us, (NAAQS 2009 and WHO, 2005). Unpolluted air is necessary for the survival and sustaining the delicate balance of aquatic and terrestrial ecosystem, wildlife, vegetation, water and soil, (Seyyednejad, *et. al.*, 2011 and IEA, 2017). The composition of outdoor air varies depending on the elevation above sea level and anthropogenic variables such as the pollution index. Therefore, ambient air quality is directly affected by anthropogenic activities, (Jecobson, 2002). Air pollution is the introduction of harmful substances, smog, carbon monoxide (CO), carbon dioxide (CO_2), hydrogen sulfide (H_2S), nitric oxide (NO), and methane (CH_4) to the atmosphere by natural or anthropogenic means, (Jacob 1999 and Daniel, 2014). This brings about undesirable change or imbalance in the biological physical and chemical characteristics of the atmosphere, which could result to environment and human health risk, (Robert and Robert 2012).

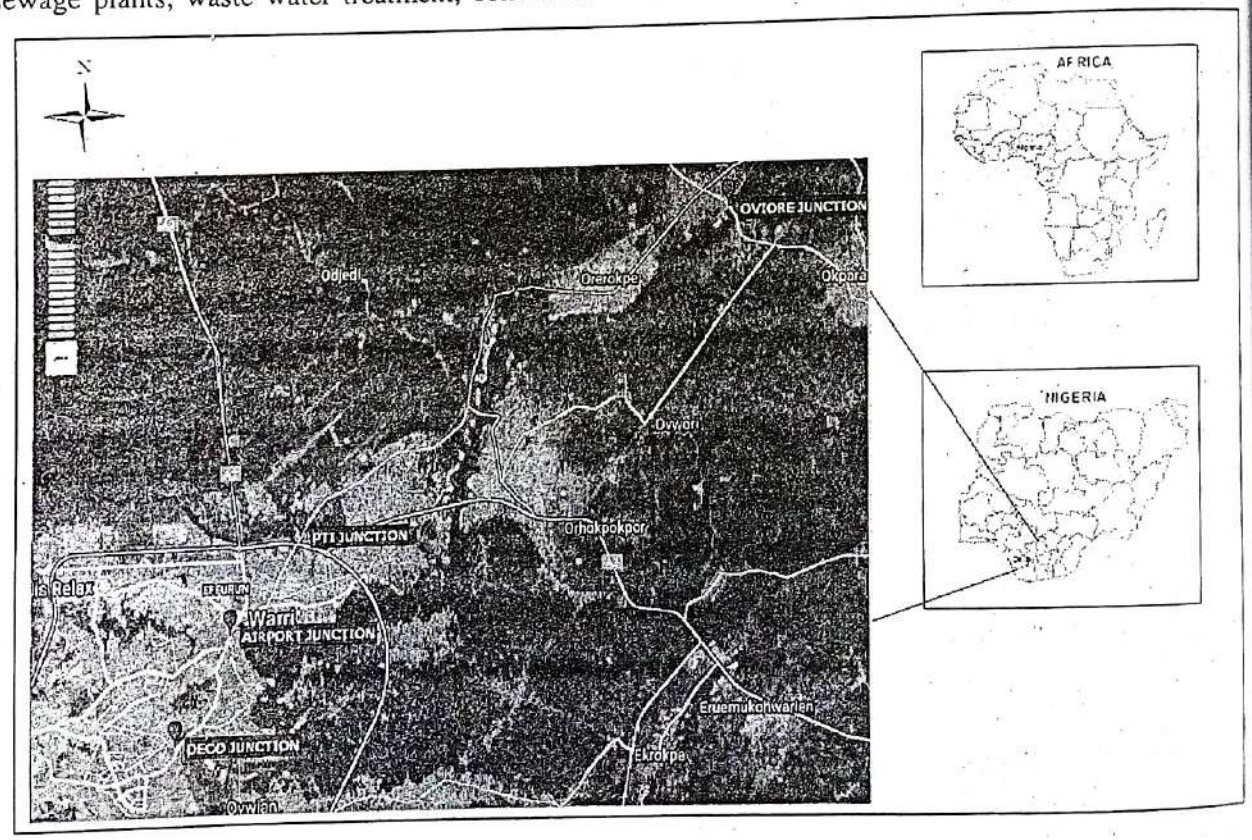
Carbon monoxide is an air pollutant produced by incomplete combustion of carbon-containing fuel, (US.EPA 2017). Anthropogenic sources account for 60 % CO emission from incomplete combustion of carbonaceous materials with greater proportions from exhaust of internal combustion engines, various industrial processes, coal power plants and waste incineration or combustion (outdoor sources), (IEA 2017). Other sources are kerosene, gas stoves, tobacco smoking and space heaters fuelled with oil, gas (indoor sources), (Cullis and Hirschler, 1989). Plants, oceans and oxidation of hydrocarbons biological and non biological sources account for 40 % of CO emission, (US.EPA, 2017).

Carbon dioxide is a gaseous component of atmospheric air (0.037 %), it plays a balancing role in the earth's environment as a vital factor in

life cycle of plants and animals. However, CO_2 is hazardous to environment and human health when its atmospheric concentration exceeds 0.037 %, (US.EPA, 2017). The main anthropogenic sources of CO_2 emission are the combustion of fossil and biomass-based fuels, and industrial processes, such as the production of iron and steel, ammonia, hydrogen and cement, (US.EPA, 2017). Currently, studies have shown that the combined power generation and production industries dominate global CO_2 emissions, accounting for about 60 % of total CO_2 emissions, (US.EPA, 2017). Volcanic eruption, earth's carbon cycle, fermentation of organic compounds and animal and plant respiration processes are natural sources of CO_2, (IEA 2017).

Hydrogen sulfide is a soluble gas in alcohol and water. It can be produced in the presence of sulfate and organic materials under conditions of deficient oxygen, (WHO, 1981 and Steudler and Peterson, 1984). Naturally, atmospheric H_2S occurs around sulfur lakes and springs, in swamp bogs in geothermal active areas and marshes, (Steudler and Peterson, 1984). Anthropogenic H_2S is produced through kraft process in paper and pulp industry, viscose rayon production, sewage plants, waste water treatment, coke oven oil refineries and industrial processes, (Wolfgang, *et. al.*, 1980). The major sinks of H_2S are consumption by bacteria found in soil and oxidation of H_2S by water to elemental sulfur. Photosynthetic bacteria can also oxidize H_2S to sulfate, and sulphur, (WHO, 1981). Atmospheric H_2S can be degraded through oxidation by O_2, O_3 and hydroxyl radicals, (ATSDR, 2016). The effective half-life of H_2S has been estimated to be between 6 and 58 hours, (ATSDR, 2016).

Nitric oxide in ambient air occurs alongside NO_2 hence primarily grouped as NO_X. Nitrogen oxide is a precursor to O_3 (a constituent of photochemical smog), HNO_3 (component of dry and wet acid precipitation) and particulate NO_3 (which affect global climate), (US.EPA 2017). Its atmospheric resident time is 72 hours, (US.EPA 2017). Nitrogen oxide is regarded as a significant pollutant of the lower atmosphere which affects plants and acidifies the pH of fresh water lakes and streams ecosystem with a potential terrestrial and aquatic ecosystem consequences. Anthropogenic (biomass burning and fossil fuel combustion) and natural (lighting, photolytic distribution of nitrogen compounds in upper atmospheric and processes of denitrification by anaerobic bacteria in soils, plants and water) are



the major atmospheric sources of NO, (Godish 1991). Kinetic reactions, deposition to the surface and dissolution in ocean waters are the major atmospheric sinks of NO, (Clark and Tomlin, 1999).).

Methane is a Short- Lived Climate Pollutants (SLCPs) regarded as a green house gas (GHG) and absorbs infrared radiation 25 × more efficiently than CO_2. (US.EPA, 2017). Environmental CH_4 concentration has increased since pre-industrial times, (Wuebbles and Hayhoe, 2002). Methane is released into the atmosphere by both anthropogenic (animal and human wastes, rice paddies, biomass burning, enteric fermentation and landfills) and natural (wetland, termites, wild ruminants, oceans and hydrates) means, (Barns and Edmonds, 1990; Beck, *et. al.*, 1993; Khalil *et. al.*, 1998 and Isaksen, *et. al.*, 2014). The major sinks of CH_4 from the atmosphere is through precipitation, biological uptake and gas-phase oxidation process, (IPCC, 1996).

The exposures to pollutants outside of a built environment are ambient air pollution. Atmospheric air contains emissions from several different sources (fuel and diesel engine fumes, (Rooda-Knape *et. al.*, 1999) industrial, commercial and domestic combustion processes, (William *et. al.*, 2012 and Daniel, 2014), solvent utilization and tobacco smoke) which can be classified as mobile, stationery, direct, indirect, point and area, (Marchwinska-Wyrwal, 2011). Modern industries are the major sources of these pollutants and causes of air pollution, (Riga-Karandinos and Saitanis, 2005 and Faiz 1993).

It has been reported that exposure to ambient air pollution could cause different human adverse health effects, (Tominz, *et al.*, 2004; Downs, *et al.*, 2007; IEA, 2017 and IHME (2017). Results from these studies shows that air pollution harm human health especially with children, the aged or those with existing health challenges as vulnerable targets, (Marchwinska-Wyrwal, 2011). These human health effects linked to ambient air pollution are: mortality and morbidity, cardiovascular, life expectancy, cancer and respiratory diseases, (Defense, 1996; Ricciardi and Guastdisegni, 2003; Moa *et. al.*, 2005; Laden, *et. al.*, 2006; Han and Naeher, 2006; IEA, 2017 and US.EPA, 2017). Evidence from epidemiological study showed that the adverse health risk and effects are dependent on concentration and length of exposure and that long-term exposure have high and persistent cumulative effects than short-term exposures, (Pope, 2007). Due to trans-boundary effect, ambient air pollution has environmental health challenges that affect all humans in the G8 and developing economies, (IEA, 2017). The impact of these health challenges associated with ambient air pollution could be quantified in terms of cost effect on health care, absenteeism and job loss resulting from permanent disability and death, (Ghozikali *et. al.*, 2016). Air pollution sources and characterization have been carried out in several studies (Godish 1997; Cooper and Alley 2011; Abdulkarim *et al.*, 2007; Tawari and Abowei, 2012; Ogukwe *et. al.*, 2014; Confalonieri *et. al.*, 2007; Lopes *et. al.*, 2016; IEA, 2017). However, there is no empirical pollution status of CO, CO_2, H_2S, NO and CH_4 pollution status in the study area. These PGPs and their oxidation products have been identified as human and environment health stressors at elevated atmospheric concentrations. Therefore, this article focuses on monitoring the seasonal variation of these air pollutants in four sites in the Niger Delta in order to quantify the air quality.

MATERIALS AND METHODS

Study Location Description

The study was carried out in four sites located in Delta state. Delta State is situated in the Niger Delta floodplain on the coast of Nigeria. The climate and weather conditions of the study area are of the Niger Delta region with high humidity and temperature, and rain forest zone, Figure I, (Emoyan *et. al.*, 2015). The study area has a human population of about 302,652. The study sites and geographical coordinates are: Petroleum Training Institute Junction (05^0 57533'N and $005^0$80727'E), Deco Junction (05^0 52275'N and $005^0$76567'E), Oviore Junction (05^0 65852' N and $005^0$925386' E) and Airport Junction (05^0 555041'N and $005^0$78130'E). These sites were selected due to industrial (oil servicing and allied industries) and commercial (waterway and inland transportation with indiscriminate open air biomass and waste burning) activities. These sites are classified as: roadside, (residential and commercial area with high traffic), urban (densely populated residential area alongside industrial and commercial activities) and rural (with little commercial activity).

Table 1: Study Area Average Meteorological Data: (Uku and Tamunobereton-Ari, 2013).

Variable	Temp. (^{0}C)	Rainfall (mm)	Wind speed (km/h)	Evaporation (mm)	Humidity (%)	Solar Radiation (mJm-2day-1)
Min.	21.79	-	10	-	50.83	-
Max	30.35	203.03	15	92.76	93.73	8.79

Sampling and Sample Collection

Air sample collection was carried out daily between 7 – 10 am (morning), 12 – 3 pm (afternoon) and 4 – 7 pm (evening) by use of *aeroqual* gas detector kit model ASTM D3249-95 – 2011. Sampling was done during the dry (October 2015 – March 2016) and wet (April – September 2016) season respectively.

Quality Control and Assurance

To ensure reliability of results, the inlet height is 2 – 10 m above ground level, (ii) the sampler was placed 20 m from trees, (iii) distance of the sampler from buildings was more than two times the height of the obstacle above the sampler and (iv) airflow was unrestricted in three of four quadrants, (v) Furnace or incineration equipments were avoided. Due to reconnaissance survey of average 10,000 traffic vehicles per day, the *aeroqual* gas detector kit was placed at distance of 10 meters from road side, (Sengupta, 2003).

Approach to Data Analysis

Descriptive statistical analysis such as: Mean, Pearson Correlation and bar charts were used to transform primary data.

RESULTS AND DISCUSSION

Distribution of Air Pollutants

One hundred and forty-four air samples were collected from sample site A, B. C and D in the morning, afternoon and evening, these samples were quantified for CO, CO_2, H_2S, NO and CH_4 The dry season concentration (μgm^{-3}) ranged from 4.04 – 8.13 (CO), 17.94 – 14.30 (CO_2), 0.05 – 0.39 (H_2S), 0.04 – 0.14 (NO) and 0.41 – 4.94, while the wet season concentration (μgm^{-3}) ranged between 4.20 and 7.94 (CO), 6.90 and 14.50 (CO_2), 0.03 – 0.15 (H_2S), 0.03 and 0.17 (NO) and 0.44 and 4.21 (CH_4) in all sample stations.

The statistical summary of studied air pollutants in dry and wet season in all sample stations are shown in Table 2 and 3, and Figure 2.

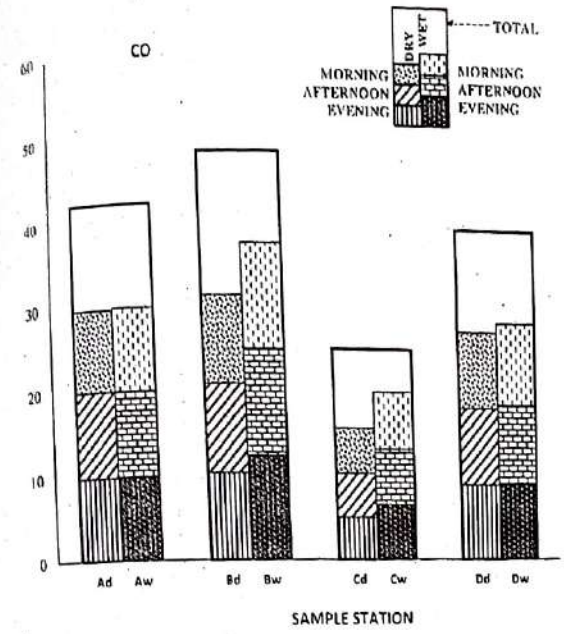
Table 2: Statistical Summary of air Pollutant Concentration in Dry and Wet Season (μgm^{-3})

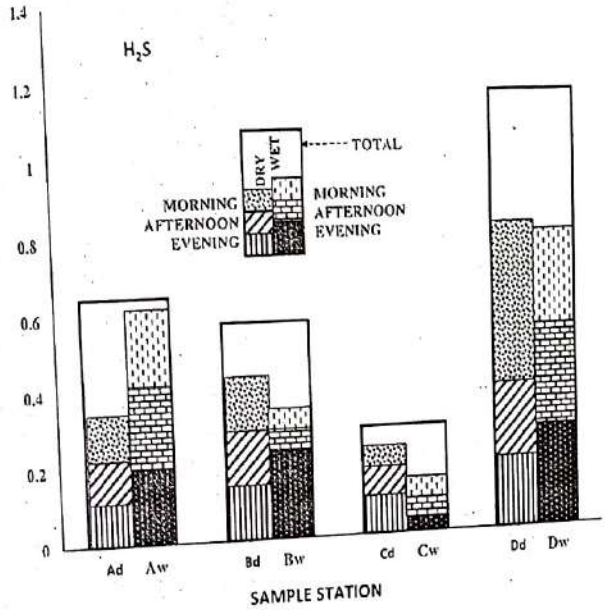
Pollutant	Min.		Max.		X	
	DS	WS	DS	WS	DS	WS
CO	4.04	4.20	8.13	7.74	6.75	6.12
CO_2	7.94	4.20	14.30	14.50	12.02	12.6
H_2S	0.05	0.03	0.39	0.15	0.14	0.14
NO	0.04	0.03	0.14	0.17	0.09	0.08
CH_4	0.41	0.44	4.94	4.21	3.46	3.09

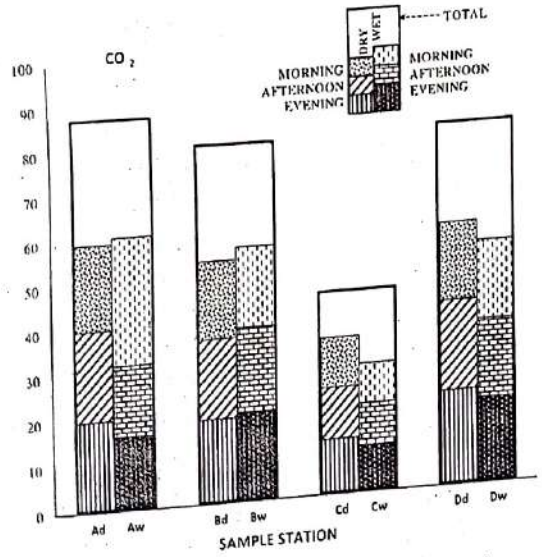
Table 3: Sample Station Statistical Mean of air pollutants in Dry and Wet Season (μgm^{-3}).

Pollutant	CO		CO_2		H_2S		NO		CH_4	
SS	Dry	Wet	Dry	Wet	Dry	Dry	Dry	Wet	Dry	Wet
A	7.70	6.38	13.13	15.39	4.13	4.13	0.10	0.11	4.13	4.04
B	8.12	7.92	12.55	14.38	4.46	4.66	0.07	0.04	4.46	4.16
C	4.08	4.22	7.98	7.06	0.41	0.41	0.04	0.03	0.41	0.47
D	7.08	6.00	13.71	13.71	4.84	4.84	0.14	0.14	4.84	3.67

Where: Min. = Minimum, Max. = Maximum, X = Mean, DS = Dry Season, WS = Wet Season, SS = Sample Site







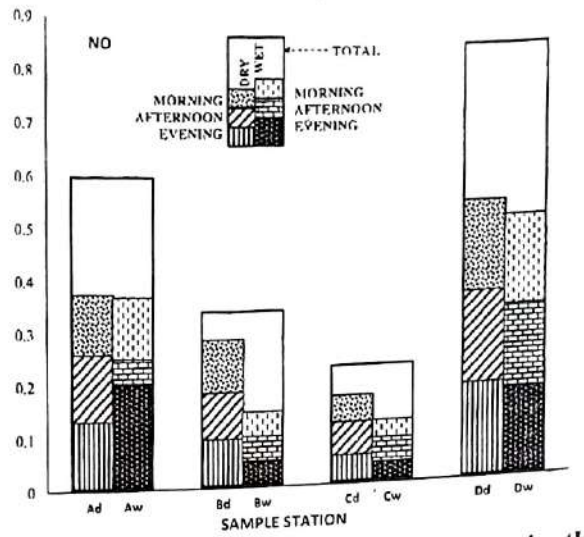
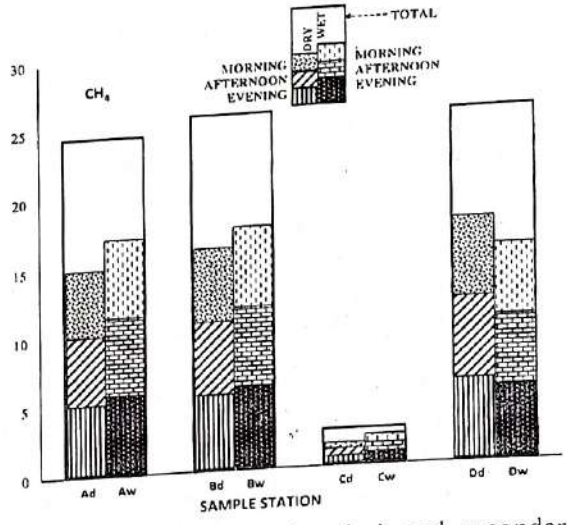


Figure 2: Distribution of Air Pollutants in the Study Area Sites

Results show high concentration of pollutants in all sites except C as shown in Figure 2, and Table 2 and 3. This trend could be related to the multiple sources of these pollutants which may primarily include: emission from re-deposited soils, refinery operations, open solid waste and biomass combustion and incineration, busy urban road, diesel and petrol driven generators and forest fires, (Horsfall and Spiff, 2013 and IEA, 2017). The maximum mean concentration reported in Table 2 and 3 are relatively lower than the primary (provide public health protection for



children, elderly and asthmatics) and secondary (provide public welfare protection against detracted visibility and damaged to crops, vegetation, animals, and buildings) guidelines and

standards listed in National Ambient Air Quality Standards, (NAAQS, 2009).

Meteorological factors such as humidity, temperature, rainfall, wind speed and direction, and solar radiation has been applied in evaluation of the composition, distribution and fate of environment pollutants, (Fisher, 2002; Lan, *et al.*, 2008; Kim and Guldmann 2011; Jayamurugan, 2013; Ogukwe, *et. al.*, 2014; and Zeng and Zhang, 2017). The study area meteorological variables could be responsible for the observed pollutants concentration, Figure 2 showing relatively lower concentrations of pollutants in dry season CO_2, (C and D), H_2S (B and C) NO (A,B,C and D) and CH_4 (D). Similarly these variables could also be responsible for higher concentrations of pollutants CO (A, B.C and D), CO_2, (A and B), H_2S (A) and CH_4 (A, B. and C) during the wet season. Due to high moisture and humidity level, incomplete combustion arising from biomass and solid waste combustion, and forest fire could also be high, (Williams, *et. al.*, 2012). Also, CO is a by-product of incomplete combustion of carbon-containing compounds, (US.EPA, 2017). Sample site A, B, C and D are recipients of emissions from exhaust of petrol and diesel engine combustion hence the concentration level of CO in all sites. Also, high temperature and evaporation tends to exceed precipitation in dry season, (Uko and Tamunobereton-Ari, 2013).

Though rain has scavenging effects on air pollutants out of atmosphere, (Shuklabc, *et. al.*, 2008), the environment and human health implications of the observed wet season values is that, it could form dry or wet acid deposition, Equation 1, 2, 4, 9, 14, 19 and 20, and weathering, corrosion of materials and subsequently contribute to global pollution load of aquatic and terrestrial ecosystem. Similarly, the reaction of O_3 with NO, HO_2^*, and CO (the major O_3 loss pathways in the atmosphere), are potential sources of secondary (CO_2, *OH and NO_2) air pollution precursors, Equation 2, 13 and 15. The significance of observed PGPs concentration in this study is in the tropospheric ozone formation and elimination, photochemical smog formation and production of radicals that are detrimental to environment and human health. Since NO concentrations are much lower than O_3 in background air, reaction 5 does not deplete O_3 either at night or day. However, in urban environment when NO concentrations are high, O_3 can be depleted at night. CO contribute to O_3 and photochemical smog formation and accelerate the oxidation process through the production of hydroperoxy radical (HO^*_2), (Isaksen, *et al.*, 2014).

Table 4: Chemical Reactions for the Atmospheric CO, CO_2, H_2S, NO and CH_4 Adapted in Part from: Jacob, 1999; NAPAP, 2011; Robert and Robert 2012 Horsfall and Spiff, 2013 and Daniel, 2014 Isaksen, *et al.*, 2014

Carbon Monoxide (CO)

$CO\,(g) + {}^*OH\,(aq) \rightarrow CO_2\,(g) + H^*\,(aq)$ (1)

$CO\,(g) + O_3\,(g) \rightarrow O_2\,(g) + CO_2\,(g)$ (2)

$H^*\,(g) + O_2\,(g) + M \rightarrow HO^*_2\,(g) + M$ (3)

Carbon Dioxide (CO_2)

$CO_2\,(g) + H_2O\,(l) \rightarrow H_2CO_3\,(aq)$ (4)

$H_2CO_3\,(aq) + CaCO_3\,(s) \rightarrow 2HCO_3^-\,(aq) + Ca^{2+}\,(aq)$ (5)

Hydrogen Sulphide (H_2S)

$2H_2S\,(g) + 3O_2\,(g) \rightarrow 2SO_2\,(g) + 2H_2O\,(l)$ (6)

$SO_2\,(g) + {}^*OH\,(g) \rightarrow HSO^*_3(aq)$ (7)

$HSO^*_3\,(aq) + O_2(g) \rightarrow SO_3\,(g) + HO^*_2(g)$ (8)

$SO_3\,(g) + H_2O\,(l) \rightarrow H_2SO_4(aq)$ (9)

Nitric Oxide (NO)

$NO\,(g) + HO_2^*\,(g) \rightarrow NO_2\,(g) + {}^*OH\,(g)$ (10)

$NO_2\,(g) + h\nu \rightarrow NO\,(g) + O^*\,(g)$ (11)

$O^*\,(g) + O_2\,(g) + M \rightarrow O_3(g) + M$(12)

$HO_2^*(g) + O_3\,(g) \rightarrow {}^*OH(g) + 2O_2(g)$ (13)

$NO_2\,(g) + {}^*OH\,(g) \rightarrow HNO_3\,(aq)$ (14)

$NO\,(g) + O_3\,(g) \rightarrow O_2(g) + NO_2(g)$ (15)

Methane (CH_4)

$CH_4\,(g) + 8O_2\,(g) \rightarrow CO\,(g) + H_2O\,(l) + 4O_3\,(g) + 2{}^*OH\,(g)$ (16)

$CH_4\,(g) + OH^*(g) + HO^*_2(g) \rightarrow CO\,(g) + H_2\,(g) + 2H_2O\,(l)$ (17)

$CH_4\,(g) + OH^*(g) + CH^*_3(g) \rightarrow H_2O\,(l)$ 18)

$CH^*_3\,(g) + O_2\,(g) + M \rightarrow CH_3O^*_2\,(g) + M$ (19)

$CH_3O^*_2\,(g) + NO(g) \rightarrow CH_2O_2\,(g) + NO_2\,(g)$ (20)

$CH_3O^*_2\,(g) + O_2(g) \rightarrow HCHO^*\,(g) + HO^*_2\,(g)$ (21)

Where:

M = an inert third body (O_2 or N_2)

$h\nu$ = solar energy

It has been reported that wind speed at ground level tends to drop at night (forcing emissions to drop overnight) and rise again during the morning, especially during cloud-free conditions, (Clark and Tomline, 1999; Lan *et. al.*, 2008; Kim and Guldman, 2011 and Isaksen *et. al.*, 2014). The effects of less combustion, boilers and cars on the roads at night, and the effects of increased emissions, and wind speed, and improved dispersion conditions during the day could be responsible for observed pollutants concentrations, Table 2, 3 and Figure 2. Also, traffic pattern has been applied to evaluate air pollution load, (Jo and Park, 2005 and Carslaw and Beevers, 2004). The observed concentration of pollutants in this study, Figure 2 varies from a typical urban pattern characterized with, morning and evening peaks, where direct pollutant emissions from petrol and diesel-powered engines is highest for NO_2, SO_2, CO, (Fugita *et al.*, 2003 and Kim and Guldmann, 2011). This trend could be related to the diverse sources of air pollutants ranging from trans-boundary contribution, biomass and solid waste combustion, forest fire and industrial sources from refinery operations. Also, the relatively observed low concentrations

Table 5: International Ambient Air Quality Standards and Guidelines With Established Dose Effect Relationships of Studied PGPs, (μgm^{-3})

Pollutant	Concentration		Effect	Ref.
	This Study	Standards		
	Dry Wet			
CO	4.04 -8.13 - 4.20 -7.74	10,000 (8 hrs)	chronic toxicological, neurological, neurobehavioral, and cardiovascular effects on human	Cullis and Hirschler, 1989 and US.EPA, 2017
CO_2	7.94 -14.30 - 4.20 -14.50	1.7×10^6	asphyxia	US.EPA, 2017, IEA 2017,
H_2S	0.05 -0.39 - 0.03 -0.15	< 30 40-42 > 42 1.3×10^4 - 2.7×10^4 6.9×10^4 - 1.3×10^5 2.0×10^5 - 3.4×10^5 4.44×10^5 - 7.37×105 7.37×10^5 - 1.39×10^6 1.39×10^6 - 1.39×10^6	Low Medium High Eye Irritation Threshold Severe Eye Damage Loss of Olfactory Sense Pulmonary Oedema With Risk of Death Strong CNS Stimulation, Hyperpnoea Followed by Respiration Arrest Immediate collapse with Paralysis of Respiration	ATSDR, 2016, Steudler and Peterson, 1984; Ronk and White 1985, Jappinen, *et.al.*, 1987 and Anold, 1995 US.EPA, 2017
NO	0.04 -0.14 - 0.03 -0.17	< 140 140-200 > 200	Low Medium High Atmospheric Limit Reversible and Irreversible Lung Effect Reversible Pulmonary Dysfunction	Wolfgang, *et. al.*, 1980 Steudler and Peterson, 1984, EPA, 2017 Godish, 1991 Wuebbles and Hayhoe 1999
CH_4	0.41 - 4.94 - 0.44 -4.21	1.19×10^6 $< 32.7\times10^6$ $< 98.1\times10^6$	Atmospheric Limit $CH_4 - O_2$ Mixture below Combustion $CH_4 - O_2$ Mixture High to Ignite Combustion	IEA, 2017; US.EPA, 2017 Wuebbles and Hayhoe 2002

of these PGPs could be adduced to the concentration and ratio of precursor chemicals/radicals. Also, the intensity of solar radiation resulting from their gas-phase oxidation since the study area is a region rich in shortwave solar radiation, (Kim and Guldmann, 2011; Slanina, *et al.*, 1994; IPCC, 1996; Havey and Huang, 1995; Weubbles and Hayhoe 2002). Also, two trends of high concentration of CO and CO_2 in all sample sites could be observed, Figure 2 and Table 2 and 3. Similarly site A, B. and D recorded high concentration of all pollutants. This could be related to favorable *hv* catalyzed environments, the rate of add-up and elimination of CO and CO_2 is near equilibrium, and CO_2 is a component of natural air. Secondly, sample site C is a rural settlement where PGPs could be converted to secondary pollutants under favorable environmental conditions Equation 1, 2 and 16.

Concentration Variation and Human and Environment Health Effects

Though observed pollutants concentrations in this study, Table 2 and 3 are below recommended standards and limits, Table 4, their human and environment health significance lies on future projection of abundance of complex direct and indirect sources of these PGPs, this complicates and makes emission control measures difficult, (Slanina, et al., 1994; IPCC 1995; Havey and Huang, 1995; Weubbles and Hayhoe 2002).

It has been reported that in the presence of shortwave solar radiation, atmospheric concentrations of NO, NO_2, HO_2^+, CH_4, CO, CO_2, H_2S, alkane, alkenes, aromatics, and multifunctional compounds, mainly from fossil fuel consumption, fuel evaporation and solvent use, there is constant formation of secondary pollutants, Equation. 1-20. Secondary pollution radicals like gaseous hydroperoxyl is involved in various atmospheric reaction cycles that affects stratospheric ozone. Also, hydroperoxyl is present in the troposphere, a reaction by-product of hydrocarbons by the hydroxyl radical and oxidation of carbon monoxide.

Observed pollutants concentration in this study and International Ambient Air Quality Standards and Guidelines, Table 5 are of environment and human health concern. This is due to the fact that the magnitude of these PGPs sources, elimination and toxicity is govern by the constantly changing and advancing energy demand, agricultural practice, human population, economic and living standards, land use pattern, meteorological conditions, transportation system, fate and other anthropogenic and natural factors determined by future scientific advancement. Hence there is need to curtail and reduce the sources and distribution of these pollutants in the study area due to the potential environment and human health effects because what was thought to be environment and human health friendly thirty years ago may no longer subsist, (US.EPA, 2017),

Above allowable atmospheric guideline and standards, epidemiological and clinical evidence has shown different and varied human and environment health effects, CO concentration greater than 10,000 μgm^{-3} has been linked to chronic toxicological, neurological, neurobehavioral, and cardiovascular effects on human, Table 5. The hazardous effects of CO_2 to the environment occur when its concentration in the atmosphere exceeds 0.5 – 1.5 %, this leads to reduction of atmospheric oxygen concentration below 16 % required to sustain human life, i.e. asphyxia. In chronic exposure above environmental concentration of 40 μgm^{-3} H_2S results in severe eye, nose and conjunctional irritation, headache, respiratory and neurological effects and balance problems, (Kangos *et. al.*, 1984). Epidemiological and toxicological study has reported effect on children and adults from exposure to outdoor concentration greater than 140 – 200 μgm^{-3}. However, long-term exposure of NO causes phlegm production, human respiratory effects or physiological and pulmonary dysfunction especially at 3760 $\mu g.m^{-3}$, (Schwartz and Zeglar, 1990). In reaction with textiles and dye, NO could cause fading, yellowing, weaken fabrics or reduce their binding strength for certain dyes. Therefore, uncontrolled NO release in the study area could cause human and environmental effects on both aquatic and terrestrial ecosystems in the presence of Ca and Mg carbonates that could neutralize the acidified wet or dry acidic deposition, (Stuedler and Petersn, 1984). Observed concentration of NO in Table 2, 3 and Figure 2 showed that the study area could experience the formation of secondary pollutant that may have adverse human and environmental consequences, (Isaksen, *et. al.*, 2014). Though

CH_4 has no direct human health effects at atmospheric concentrations of 1.19×10^6 μgm^{-3}, Table 5, long-term exposure to observed concentrations in this study, Table 2 and 3 and Figure 2 could cause headache, dizziness or fatigue, (ATSDR, 2016). With residence time of 365 days in the atmosphere, couple with CH_4 global concentration estimate of $1.19 \times 10^{-6}\mu gm^{-3}$, and approximately 60 % and 40 % from anthropogenic and natural activities respectively, (ATSDR, 2016), uncontrolled anthropogenic release could contribute to pollution load and CH_4 build-up which could displace environmental oxygen, thereby causing asphyxiation hazards, (Wuebbles and Hayhoe, 2002 and US.EPA. 2017). Also CH_4 is a known potential flammable gas when sufficient quantities accumulate within 32×10^{-6} μgm^{-3} and 98×10^{-6} $\mu g.m^{-3}$ boundary, Table 5. Equation 16-21, shows that CH_4 gas-phase atmospheric decomposition produces secondary gaseous compounds ($CH_3^{\cdot}$, OH, CO, and O_3, $CHO^{\cdot}$) of environment and human health concern, (Weubbles and Hayhoe 2002, IPCC, 1990). Depending on NO level, CH_4 atmospheric gas-phase oxidation could either be a production or elimination routes process for $OH^{\cdot}$ and $HO_2^{\cdot}$

Table 6: Pearson Correlation between Study Sites

CO									
Dry	A	B	C	D	Wet	A	B	C	D
A	1.000	**0.996***	-0.479	-0.410	A	1.000	**0.638****	-0.594	-0.993
B		1.000	-0.554	-0.327	B		1.000	0.240	-0.727
C			1.000	-0.605	C			1.000	**0.492****
D				1.000	D				1.000
CO_2									
Dry	A	B	C	D	Wet	A	B	C	D
A	1.000	**0.877***	**0.761***	0.353	A	1.000	-0.995	-0.647	**0.776***
B		1.000	**0.979***	0.759*	B		1.000	**0.569****	-0.834
C			1.000	**0.876***	C			1.000	-0.021
D				1.000	D				1.000
H_2S									
Dry	A	B	C	D	Wet	A	B	C	D
A	1.000	0.000	-0.866	**0.999***	A	1.000	**0.500****	**0.500****	**0.500****
B		1.000	0.000	0.000	B		1.000	-1.000	**0.500****
C			1.000	-0.885	C			1.000	-0.500
D				1.000	D				1.000
NO									
Dry	A	B	C	D	Wet	A	B	C	D
A	1.000	-1.000	**0.500****	0.000	A	1.000	0.000	-0.814	-0.096
B		1.000	-0.500	0.000	B		1.000	0.000	0.000
C			1.000	0.000	C			1.000	-0.500
D				1.000	D				1.000
CH_4									
Dry	A	B	C	D	Dry	A	B	C	D
A	1.000	0.000	**0.904***	**0.645****	A	1.000	1.000*	1.000*	1.000*
B		1.000	-0.427	-0.764	B		1.000	1.000*	1.000*
C			1.000	**0.910***	C			1.000	1.000*
D				1.000	D				1.000

One tailed significance, *p < 0.01;**p < 0.05; significant correlations are in bold phase type.

Table 7: Pearson's Significant Relationship Between Sample Sites

Pollutant	CO	CO_2	H_2S	NO	CH_4
Dry Season	AB	AB, AC, BC, BD, CD	AD	AC	AC, AD, CD
Wet Season	AB	AD, BC	AC, AD, BD	-	AB, AC, AD, BC, BD, CD

(odd-hydrogen), (Thompson *et al.*, 1989). However, the resultant elimination and add-up odd-hydrogen depends on the concentration of hydroxyl, methyl peroxide reaction routes and the elimination rates of intermediate precursors or species. For example, Weubbles and Hayhoe 2002, and IPCC, 1990, has reported that in the reaction sequence for CH_4, CHO^* and CO in polluted and unpolluted environment, the consequence of the complete gas-phase atmospheric oxidation of 1 mole of CH_4 on odd-hydrogen in NOx-rich and NOx-deficient environment is + 0.4 to + 0.5 mole and - 3.5 to – 3.9 mole respectively. Similarly, the change in O_3 for the complete gas-phase atmospheric oxidation of 1 mole of CH_4 on odd-hydrogen is + 3.6 to + 3.8 mole and - 1.7 to – 1.8 mole in NOx-rich and NOx-deficient environment respectively.

Therefore, the add-up and elimination of CH_4 reaction species to the environment is non-linear. Methane has also been linked to various direct and indirect detrimental impacts on global warming, human health, climate and atmospheric chemistry raises concern over its concentration growth rate, (IPCC, 1990; Weubbles and Hayhoe 2002 and IEA, 2017).

Correlation and Source Apportionment

Different correlation analysis has been applied to apportion relationship and possibly sources of pollutants either due to common atmospheric characteristics, by-products, fate or origin, (Rajput and Lakhani, 2010 and Emoyan, *et. al.*, 2015). In this study, Pearson Correlation was applied to determine the relationship between pollutants concentration across sample sites. Pearson Correlation matrix shows a good and high significant correlation between sample sites ranging between 0.5 and 0.999 at $P > 0.05$. This high significance occur seasonally between sample site; AB, AC, AD, BC, BD, and CD, could be related to common source of these pollutants either due to meteorological conditions of the study area or common origin of pollutants.

CONCLUSION

Quantification of air quality of the study area was seasonally investigated for CO, CO_2, H_2S, NO and CH_4 in four sites. We have demonstrated that time, season and meteorological conditions of the study area played significant role in observed concentration of pollutants and are relatively lower than recommended standards and limits. We have also shown that atmospheric photochemistry and oxidation played important role in add-up and elimination of observed pollutants concentration. This could possibly activate chemical interactions of these pollutants and other environmental precursors, and transformations to more harmful secondary by-products with potential effects to environment and human health. We have further established that correlation analysis shows a good and significant relationship among study sites, this indicates that there exist common characteristics of either chemical behavior or sources of these pollutants.

Recommendations

In order to reduce the emission of these pollutants in the study area and its environs, relevant agencies should strictly enact and regulate laws on; improved methods of agricultural practice, domestic and industrial waste management, fossil fuel consumption that emits minimal PGPs as by products, encourage usage of combustion vehicles, machines and equipments with improved technology of fuel and air mixtures, and strict control of industrial emissions especially from large scale fossil fuel combustion equipments. Environment and human health risk of observed pollutants concentration and assessment of other ambient air quality indicators should be carried out in the study area.

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