THE LEVELS OF HEAVY METALS AND OTHER POLLUTANTS IN AIR AND SOILS AROUND AGBADA II FLOW STATION IN IGWURUTA, RIVERS STATE

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CERTIFICATION

This is to certify that this work **"The levels of heavy metals in air and soils around Agbada II Flow Station in Igwuruta, Rivers State."** was carried out by **Eloy, Linda M. (Reg No 20114774298)** in the Department of Environmental Technlology, Federal University of Technology, Owerri (FUTO).

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DEDICATION

This research work is dedicated to Almighty God for his immense love and faithfulness in my academic pursuit and to my wonderful parents, Mr. and Mrs. Ogbonnia Eloy for their support and encouragement throughout the course of this study.

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ABSTRACT

The levels of heavy metals and other pollutants in ambient air and soils of Agbada II Flow Station in Igwuruta, Rivers State were investigated. Four sampling stations (SS A-D) located 500m apart in the downwind direction and a control located 2km in the upwind direction from the gas flare stack were monitored between September and November, 2012. High Volume Sampler (HVS) was used in the collection of suspended particulates for heavy metals analysis with Atomic Absorption Spectroscopy (AAS) while calibrated Digital Automatic Gas Monitors (DAGMs) were used to determine the levels of CO, NOx, SOx, H_2S, O_3, Volatile Organic Compounds (VOCs) and smoke *in situ*. Suspended Particulate Matter (PM_{10}) was determined using a Hazdust 10µm Particulate Monitor. Wind speed, Ambient Temperature, Wind Turbulence, Pressure, Sun Radiation, Wind Direction, Relative Humidity (RH) and Precipitation were measured with a hand-held Testrel 4500 Weather Tracker. The descriptive statistics, Pearson correlation (r), the one way ANOVA and post-hoc means plots were used for analysis. The air pollutant parameters varied as follows: CO 1.20–3.00 (2.01± 0.13), SOx 0.00–0.01 (0.008±0.001), SPM 70.00–90.20 (82.04±1.75), Pb 0.01–0.80 (0.38±0.07), Ni 40.00–80.20(65.41±3.68) and Cd 0.00- 0.30 (0.05±0.022) ppm. The heavy metals in soil varied as follows: Pb 6.30–25.05 (13.35±3.25), Ni 7.18–14.60(11.69±1.32), Cd 2.70-9.40 (6.70±1.10) ppm while the meteorological parameters varied as follows: Wind speed 0.20–0.30 (0.23±0.013) m/s, ambient temperature 27.20–29.20 (28.25± 0.188) ^{O}C, and RH 70.00–90.00 (77.33±1.720) %. There was significant spatial difference in mean levels of the ambient air quality parameters (Sig. F=0.000) at P<0.05 and SPM contributed the difference, even as there were no significant correlations between the levels of heavy metals in ambient air and soil matrices. The mean levels of Ni, Co and Fe varied significantly between the seasons (Sig. t=0.025, 0.028 and 0.038 respectively). Results indicate that none of the recorded parameters exceeded the DPR maximum permissible limits.

CHAPTER ONE

1.0 INTRODUCTION

1.1. Background of Study

Air pollution from human activities can be said to have originated with the discovery of fire (Nathanson, 2009). Even today, most air contaminants originate from combustion processes; both mobile and stationary sources (Nathanson, 2009). Nigeria is a nation highly endowed with natural resources among which are oil and gas. Gas flaring has been an integral part of the operation associated with the exploration of crude oil since the inception of the petroleum industry in Nigeria (Kuranga, 2002).

In the Niger Delta Region of Nigeria, this activity has been in existence since 1956 when crude oil was first discovered in the region and its effects are obvious. Gas flaring is a major contributor to the emission of toxic gases, as well as other pollutants. Its products include oxides of carbon (CO_x), nitrogen (NO_x), sulphur (SO_x), photochemical oxidants (mainly Ozone - O_3),Volatile Organic Compounds (VOCs)– precursor to photochemical oxidants, Suspended Particulate Matter (SPM_{10}), heavy metals (such as Cu ,Ni, Co, Fe, Hg, Cd, Pb, Cr, Zn, Mn), organic matter such as Polynuclear Aromatic Hydrocarbons(PAHs), acid aerosols (e.g. SO_4^{2-},$N0_3^-$) (Oghenejoboh, 2005). Incomplete combustion of flared gases can bring

about emission of gaseous pollutants such as methane (CH_4), Carbon (ii) oxide (CO), particulates (such as coke). These gases make up the greenhouse gases (Ogwejiofor, 2000).

Today, as petroleum exploration and exploitation intensifies, gas flaring is now associated with every oil producing community in the Niger Delta region (Chijioke, 2002).

Various ecological and human disasters which have continuously occurred over the last three decades implicate gas flaring by oil companies as a major contributor to environmental degradation and pollution of various magnitudes (Avwiri and Ebeniro, 1996).

Gas flaring is known to have many adverse effects, including those on human health, building facades and other exposed materials, vegetation, agricultural crops, animals, aquatic and terrestrial ecosystems and the climate as a whole. The adverse health effects of man's exposure to increased ambient levels of oxides of carbon, especially CO, include its reaction with hemoglobin, causing a reduction in oxygen–carrying capacity of the blood. Quite low levels of CO have been shown experimentally to induce myocardial ischaemia in subjects with Coronary Artery Diseases (CAD) (Wickramatillake *et al*., 1998). Sulphur (iv) oxide (SO_2) irritates the mucous membranes of the eye and the upper airways. Its reaction with water

vapour produces H_2SO_4, a component of acid rain. The inhalation of the acidic ion ($S0_4^{2-}$) into the lungs has a damaging effect on the lungs (Oreyomi, 2005). Oxides of Nitrogen (NO_X) tend to aggravate respiratory diseases, and slight increases in respiratory illness. Decreases in pulmonary functions have also been associated with concentration of NO_2 of about 0.10ppm (Davis and Masten, 2004).

Volatile Organic Compounds (VOCs) present in the air can have direct harmful effects on the receptors causing ailments such as cancer and/or mutagenic effect (Oreyomi, 2005). Particulate outfalls from flares contain Polynuclear Aromatic Hydrocarbons (PAHs), acid aerosols and trace metals which contribute immensely to cardiovascular and respiratory tract diseases (Agbo, 1997).

Aside the above effects, the damages caused by gas flaring activities also require a huge amount of revenue for its replacement. For instance, between 1974 and 2004, over 709048 cubic meters of gases were flared in Nigeria alone resulting to a cumulative loss of approximately US $44, 528, 808,000.00 (NES, 2008) .

However, it is difficult for public health experts to correlate or match up specific air pollutants with specific diseases with absolute certainty, though Nathanson (2009) states that some general conclusions can be drawn from available data, particularly data obtained during air pollution episodes.

1.2. Geology of the Study Area

Generally, Rivers State lies on the recent coastal plain of the eastern Niger Delta. Its surface geology consists of alluvial sediments. The formation is generally water bearing, hence it serves as the main source of portable groundwater in the area (Etu-Ejeofor, 1997). The aquifers are usually recharged through surface precipitation and in some cases through surface drainage.

1.3. Climate and Vegetation

The area is essentially dry land with poor drainage, being low-lying with much surface water and as a result subjected to occasional flooding during the wet season. According to PEAH-1 District HSE case (SPDC-2005-0056915) revision 10, mean ambient temperatures range between 23 and 35^0 C with annual rainfall of 3800mm. Rainfall is usually adequate for all year round crop production while its relative humidity is high throughout the year and decreases slightly in the dry season (Salawu, 1999). The area is generally characterized by lengthy and heavy rainy seasons and very short dry seasons. Temperatures throughout the year are relatively constant, showing little variation throughout the course of the year.

Agbada II Flow Station is located on the plain land rainforest belt of Nigeria. However, there are naturally occurring vegetations around the surroundings, a part

of which has given way to various agricultural activities such as banana and palm trees plantations.

1.4. Economic Activities

Igwuruta community is slightly metropolitan, although communal life of the inhabitants seems intact with commercial trading and farming as the major occupations. Generally, the agricultural policy of the state government is anchored on food production.

1.5. Justification

The Agbada gas Flare Station in Igwuruta, Rivers State is one of the major locations operated by the Shell Petroleum Development Company (SPDC) of Nigeria Limited in the Niger Delta region of Nigeria. The station encompasses gas flare stacks that have been burning for years now. It has been confirmed by many researchers that through gas flaring, a good number of toxic gases as well as other pollutants are being introduced into the atmosphere. The effects of these pollutants range from air pollution, through soil, water, thermal to noise pollutions.

Plants on the other hand could incorporate these pollutants into their tissues and man can easily be exposed when these plant tissues are being consumed owing to

his position in the trophic chain (Nathanson, 2009). Consumed food however, could contain high concentrations of metals, thus resulting to bioaccumulation. Bioaccumulation is also of ecological concern in organisms on the lower levels of the trophic chain.

When contaminated organisms are consumed by a second organism that can neither metabolize nor excrete the substance, the concentration of that substance will build to even higher levels in the second organism and this effect is magnified at each successive trophic level (biomagnification). Several diseases associated with trace metals bioavailability in human systems such as neurological dysfunctions and carcinogenicity have been noted (Islam, *et al*., 2007, Akan *et al*., 2009).

Since environmental protection or management entails routine monitoring of pollutant outfalls from especially source points of pollution (such as Agbada II Flow Station), this research was therefore an attempt towards surveillance monitoring requirements for a sustainable development.

1.6. Statement of problem

Heavy metal concentration in air and soil is an issue of concern in agricultural production due to its adverse impacts on food quality, crop growth as well as environmental health. Heavy metals, due to their persistent nature in the environment tend to accumulate and magnify across the trophic levels to pose serious health hazards to man (Agbaire and Esiefarienrhe, 2009). This is a matter of serious concern since farming is the main source of livelihood of the local residents of Igwuruta community.

1.7. Aim and Objectives

This study was aimed at establishing possible presence and levels of air pollutants station and further establishment of possible relationships between these pollutants in air and soil matrices.

Objectives

- Determination of the presence and levels of ambient air pollutants around a Gas Flow Station.
- Determination of the presence and levels of ambient air pollutants in soils around a Gas Flow Station.
- Determination of meteorological variables of the study area.

- Establishment of possible relationship between trace metals composition in air and soil around a Gas Flow Station.
- Determination of spatial variations in levels of pollutants in air and soil matrices around the Flow Station.
- Comparison of levels of pollutants in ambient air with the regulatory standard.

1.8. Scope and Delimitation of Study

The study restricts its coverage on gas flare fallouts with special reference to the trace metals (As, Pb, Cu, Ni, Co, Zn, Hg, Fe, Cd, Mn). Measurements were conducted to determine the concentrations of the oxides of Sulphur (SOx), Nitrogen (NO_x) and Carbon (CO_x) as well as hydrogen Sulphide (H_2S) in ambient air around the Gas Flow Station. The levels of the heavy metals in soils around the Flow Station were determined. The following meteorological data were also determined in the study area: Wind speed, ambient temperature, pressure, wind turbulence, sun radiation, wind direction, relative humidity and precipitation.

The study was conducted within the vicinity of the Agbada II Oil Flow Station belonging to the SPDC, in Igwuruta, Rivers State.

1.9. Significance of the Study

Results from this study could serve in the:

- Provision of valuable information that could assist policy makers and planners in making informed decisions on the management and improvement of the environment.
- Generation of data on the impacts of gas flaring of air and soils of residents of the study area.
- Determination of the current and future need for pollution control at current or projected levels of air quality.
- Establishment of compliance with regulatory standards necessary for environmental protection.

CHAPTER 2

2.0 LITERATURE REVIEW

2.1. Gas Flaring and the Environment

Nigeria is by far the number one flarer of natural gas on the planet both absolutely and proportionally; accounting for about 28 percent of the total amount of gas flared globally (Abiodun, 2004), the quantity of gas flared in Nigeria being equivalent to the total annual power generation in the sub Saharan Africa according to "World Bank" (World Bank report, 2004; Akpan, 2009). The Energetic Solution Conference (ESC, 2004) estimates that the Niger Delta region has about 123 gas flaring sites. In other words, the largest proportion of these flare sites are located in this region. Here in the region, the industry operates over a thousand producing wells, gas plants and a network of thousands of kilometers of pipelines. (Onosode, 2003).

Much of the natural gas extracted in oil wells in the Niger Delta is immediately flared into the environment at a rate that approximates 70 million/m^3 per day. This is equivalent to 40% of African natural gas consumption and forms the single largest source of greenhouse gas emissions on the planet. (Moffat and Linden, 1995).

According to Oghenejoboh (2005), gas flaring has been seen to be the major source of toxic gases emission into the atmosphere. The activity releases oxides of carbon (CO_x), sulphur (SO_x) and nitrogen (NO_x), heavy metals (such as Hg, Cd, As, Pb, Ni and Co) and water vapour. Oluwole *et al*., (1998) in a comprehensive air quality assessment of the Niger Delta observed that the levels of concentration of volatile oxides of carbon , nitrogen , sulphur and the total particulates exceeded existing Federal Environmental Protection Agency's (FEPA, 1991) Standards.

When these gases being flared are incompletely combusted, toxic products such as methane (CH_4), carbon (ii) oxide (CO) as well as organic elemental particulates (such as coke) are usually emitted. (Oyekunle, 1999).

These gases often emitted in the atmosphere are usually deposited as acids. Acidic depositions into the atmosphere could be in wet or dry forms, owing to the state of matter in which it is incorporated and transported (EPA, 2005).While wet depositions are commonly in the forms of acid rain, fog and snow, dry depositions are usually in the forms of acidic gases and particles. Dissolved SO_2, NO_2 in mists, fogs and rain which are major environmental problems in industrialized nations, the gases are released to the atmosphere as exhaust gases from industries (Awosika, 1995).

Generally, the term acid deposition is used to describe the overall effect of both wet and dry precipitation at ground level when acidic materials have reached the surface environment. It is the long term accumulation of acid deposition, rather than individual rainfall that has significant effect on the environment (Ogbuigwe, 1998).

Rainwater is naturally acidic even in regions far removed from human activity because atmospheric carbon (iv) oxide (CO_2) reacts with water vapour (H_2O) to form carbonic acid (H_2CO_3). As a result, a pH of approximately 5.6 is considered to represent background rainwater acidity in a pristine environment. Thus, acid rain is usually defined to be precipitation with a pH less than 5.6 (Cowing, 2002).

Dissolved gases in rainfall may include O_2, N_2, CO_2, SO_2, NO, NO_2 etc. NO_2 and SO_2 are primarily responsible for acid rain as shown in the following reactions below:

$$O_3 \rightarrow O_2 + O^{\cdot}$$

$$O^{\cdot} + H_2O \rightarrow 2OH^-$$

$$OH^- + NO_2 \rightarrow HNO_3$$

$$2OH^- + SO_2 \rightarrow H_2SO_4$$

The purity of water deteriorates rapidly as the falling rain or snow accumulates these dissolved chemicals and particulates from the atmosphere. This “scrubbing”

action is the major mechanism by which our atmosphere is purged of materials that otherwise could accumulate to deadly concentrations and these concentrations of chemical constituents in precipitation may account for a substantial fraction of impurities in a stream, exerting a profound influence on the composition of many surface waters and groundwater. (Ahiarakwem, 2004).

Acid deposition however, tend to lower the pH of lakes and rivers and most aquatic ecosystems are disrupted as the pH drops, which consequently leads to drastic reduction in phytoplankton population. It also leads to loss of biodiversity, with forest and economic crops being destroyed (Uyigue and Agho, 2007). Accumulation of toxic metals in the food chain can also be caused by acid deposition.

2.2. Heavy Metals and the Environment.

Heavy metals can be referred to as any metallic chemical element having a relatively high density, atomic number greater than 20, which is toxic at low concentrations. They are also called trace metals and are used in identifying the low concentrations that these elements are required for in biological activities. (Agarwal, 2009).These two terms (trace and heavy metals) are often times inter-used. Heavy metals may include: mercury (Hg), cadmium (Cd), arsenic (As), aluminium (Al), nickel (Ni), copper (Cu), zinc (Zn), iron (Fe), cobalt (Co) etc.

They are natural components of the earth's crust which can neither be degraded nor destroyed. They are important environmental pollutants particularly in areas with high anthropogenic pressure (Bilos *et al*., 2001). As trace elements, some heavy metals such as copper, selenium and iron are essential to life and play irreplaceable roles such as in the functioning of critical enzyme system (Sharma, 2006).

Exposure to heavy metals can occur through a variety of routes. They may be inhaled as dust or fume (tiny particulate matter such as lead oxide particles). Some metals can be vaporized (such as mercury), while some may be ingested involuntarily through food or drink. The amount that is actually absorbed from the digestive tract can vary widely, depending on the chemical form of the metal, the age and nutritional status of the individual. Once a metal is absorbed, it distributes in tissues and organs. Consequently, these metals whenever taken tend to persist in some storage sites like the liver, bones and kidneys for decades (Ogbeibu, 2010).

However, at higher concentrations, these metals can result to poisoning. For instance, lead and mercury may be toxic even at trace levels of exposure. Even those metals that are essential have the potential to turn harmful at very high levels of exposure, a reflection of a very basic tenet of toxicology--"the dose makes the poison" (Ellen *et al*., 1990).

Increasing urbanization and technological advancement are two major contributors of pollutants, including heavy metals in the environment at high concentrations (Ruby *et al.*, 1999).

Heavy metal concentration in soils is of concern in agricultural production due to its adverse impacts on food quality, crop growth (due to phytotoxicity) as well as environmental health (soil flora/fauna and terrestrial animals) (Msaky and Calvert,1990).

The mobilization of heavy metals into the biosphere by human activity has become an important process in the geochemical cycling of these metals. This is acutely evident in urban areas where various stationary and mobile sources release large quantities of heavy metals into the atmosphere and soil, exceeding the natural emission rates (Nriagu, 1989; Bilos *et al*., 2001).

2.3. Effects of Trace Metals on Soils

The accumulation of heavy metals in soils is of great concern in agricultural production due to the adverse effects on food quality, crop growth and environmental health. Flaring of associated gases may bring about the emission of pollutants that are composed of heavy metals such as Cu, Fe, Zn, Pb and Hg which in turn are deposited into the soil as outfalls (Ademoroti,1996).These contaminants

could further infiltrate ground water aquifers thereby posing public health hazards (Ogbonna *et al*.,2006).

Contaminated soil could result in decline in crop productivity and sustainability (Hart *et al*., 2005).Trace metals, due to their persistent nature in the environment tend to accumulate and magnify across the trophic levels to pose serious health hazards to tertiary consumers such as man (Agbaire and Esiefarienrhe, 2009). Aerosols contain different toxic metals which fall on the soil and are being retained in the top few centimeters and as well subsequently carried down by leaching, probably due to their interaction with soil colloids (Arun *et al*., 2005).They are therefore liable to be quite persistent in the soil.

Observation shows that the mobility of heavy metals decrease in soil with inorganic matter as compared to the soil will decompose organic matter. This may be due to high adsorption capacity of the soil organic matter associated with clay particles due to clay- meal soil- organic matter interaction. (David and Peter, 1989)

The increasing order of heavy metals mobility is as follows: Ni < Mn < Cr < Cu < Pb. The bioavailability and mobility of metals in soil system are functions of the metal species in soil solution and the distribution of metals in the soil solid component (Zhuang *et al*., 2009).

However, exposure to potentially toxic metals from soil ingestion is usually modeled simply as the concentration of a contaminant measured in the soil multiplied by the quantity of soil ingested. (Konz *et al*., 1989). This is a conservative approach to estimate doze because the bio-accessibility of heavy metals adsorbed on ingested soil is not 100% (Ruby *et al*., 1999).

Generally, the prediction of exposure to potentially toxic metals from consumption of food crops is more complicated because uptake of metals by plants depends on soil properties and plant's physiological factors. This leads to much larger uncertainties associated with estimating potential doses through food chains compared to the uncertainties associated with other exposure pathways such as soil ingestion and dust inhalation.

2.4. Effects of Heavy Metals on Crops

The problem of soil contamination may be of great importance for crops grown in the vicinity of heavy industrialized sites. Heavy metal pollution is an issue of global importance which although associated particularly to intensely industrialized areas, has become highly typical for farmland. Its impact on soils influences crop yield and quality. In such surroundings, the uptake of metals by plants depends on the bioavailability of metals (Teklic *et al*., 2008). The bio-available fraction of heavy metals is an issue of particular concern from ecological,

toxicological and health standpoints, due to possible penetration into most environmental segments, including food chains (Kucharski *et al*., 2005).

The fact that the level of heavy metals in the agriculture ecosystem largely depends on the pH and type of the soil, type of plant as well as the quantity and quality of organic matter in the soil is well established (Suruchi, 2011).

Heavy metals like Cd, Cu, Ni, Pb and Zn may affect the status of plants differently. Some of them are essential elements for cellular metabolism (Cu, Zn, and Ni). For instance, Cu reduces or stops transcription process and ribonucleic acid (RNA) synthesis, while some are non essential (Cd and Pb). Cu and Zn are constituents of many enzymes and other proteins. The requirement of plants for Ni appears to be mainly related to its role in forming the active metallocentre of urease (Gratao *et al*., 2005; Page and Feller, 2005).The excessive application of Nitrogen and other inorganic fertilizers and manure to food crops such as vegetables can result in accumulation of high levels of nitrate and other anions as well as trace metals (Akan *et al*., 2009).The intake of these food crops tend to pose serious health hazards.

However, the routes of absorption of the trace metals from the soil are mainly through the leaves, roots and aerial deposition while their accumulation by plants

are greatly influenced by the amount being supplied by the soil (Abbdel and Mortvedt, 1998).

The redistribution of metals within plants is metal specific. The elevation of non – essential metals like Pb, Cd and micronutrients such as Zn, Cu and Ni may be the cause of several negative aspects of oxidative stress (Zengin and Munzuroglu, 2005).Therefore, the effectiveness of a plant's antioxidant defense may be crucial for elucidating its tolerance mechanisms to heavy metals, which are common contaminants of soil.

2.5. Heavy Metals Uptake and Accumulation in Vegetables

Heavy metals are very harmful because of their non-biodegradable nature, long biological half-lives and their potential to accumulate in different body parts. Most of the heavy metals are extremely toxic because of their solubility in water (Chen, *et al.*, 2005; Singh *et al.*, 2004).

Food and water are the main sources of our essential metals; these are also the media through which we are exposed to various toxic metals. Heavy metals are easily accumulated in the edible parts of leafy vegetables, as compared to grain or fruit crops (Mapanda *et al.*, 2005).

Due to rapid urbanization, the demand for food crops is rising day by day and vegetables can be grown in small fields with intensive use of inputs within shorter period. Its cultivation is gaining popularity and fetching profitability in peri-urban areas of mega cities. This is a matter of serious concern since vegetables, particularly leafy ones, being prolific accumulators of heavy metals provide an easy entry into food chain to these dreaded metals. The excessive intake of these elements from the soil can lead to the contamination of the harvested crops as well as the decline of crop yield due to the inhibition of metabolic processes (Sander *et al.,* 1987; Singh and Aggarwal, 2006).

Vegetable crop plants have high ability to accumulate metals from the environment, which may pose risks to human health when they are grown on or near contaminated lands and consumed. Metal accumulation in plant depends on plant species, growth stages, types of soil and metals, soil conditions, weather and environment (Asami, 1981; Chang *et al*., 1984; Khairiah *et al*., 2004). Thus, accumulation of heavy metals in the edible parts of vegetables represents a direct pathway for their incorporation into the human food chain (Florijin, 1993). The health risk will depend upon the chemical composition of the waste material, its physical characteristics, types of vegetables cultivated and the consumption rate (Cobb *et al*., 2000).

According to a field trial conducted at the Research Farm, Indian Agricultural Research Institute during *Rabi* season of 2005 to 2006 where 16 different vegetable crops comprising of root vegetables (radish and carrot), tuber and bulb vegetables (potato and onion), leafy vegetables (spinach, amaranthus, fenugreek, mustard and Cabbage), fruit vegetables (okra, brinjal, Tomato, Soya bean, Pea and Cluster bean) and others (cauliflower) were grown in a field pre-contaminated with copper, zinc, lead, cadmium and nickel at 20 kg/ha by incorporating their salts into the soil. Results revealed that the total as well as available level of almost all the heavy metals in soil increased markedly following their application in soil. However, their availability percent was very low (0.84 to 17%) in the soil even after their application. Meanwhile the accumulation of metals by these vegetables has been described as their content or concentration in different parts on the basis of their amount per unit dry weight of tissues (µg/g dry weight). Amongst the heavy metals the availability was recorded to be highest for cadmium (17%) followed by copper (11%) and the lowest was registered for nickel (0.84%).

The leaves contained maximum zinc followed by roots, stem and fruits. Average accumulation recorded in leaf, root, stem and fruit were 68, 62, 60 and 53µg/g respectively.

Among the various plant parts, roots showed highest accumulation of copper followed by stem, leaf and fruits. Regarding lead accumulation in different

vegetables and their different plant parts, highest content of lead was recorded in crop leaves followed by stem, roots and fruits. Generally the root and leafy vegetables showed higher distribution of metals to the edible parts whereas fruit type vegetables exhibited least transport of metals to fruits.

2.6. Soil Threshold values of Potential Dietary Toxicity

Soil threshold for heavy metal toxicity is an important factor affecting the tendency of the soil to accumulate heavy metals and determines their cumulative loading limits.

For soil-plant system, heavy metal toxicity threshold is the highest permissible content in the soil that does not pose any phytotoxic effects of heavy metals in the edible parts of the crops and ensures that they do not exceed food hygiene standards. Agronomic practices such as fertilizer, water management and crop rotation system can affect bioavailability and crop accumulation of heavy metals, thus influencing the thresholds for assessing dietary toxicity of heavy metals in the food chain. The soil threshold for potential dietary toxicity can be affected by the following factors: soil type which includes soil pH, organic matter content, clay mineral and a host of chemical and biochemical properties and crop species or

cultivars regulated by genetic basis for heavy metal transport and accumulation in plants.

The contamination of the human food chains by heavy metals is not directly affected by plants' total uptake but rather by the concentration in those parts that are directly consumed. The external morphology of vegetables however cannot guarantee safety from contamination (Bieleski and Launchli, 1983).

According to Alloway and Ayres (1993) and Lee *et al*., (1996), sensitivity of organisms to heavy metal toxicity depends on heavy metal accumulation rate in plants, intake rate (in animals) and age of consuming organism amongst other factors. The consumer council of Zimbabwe's total dietary study estimated a leafy vegetable consumption rate for low-income urban dwellers to be 66.7-79.8kg person^{-1}yr^{-1} or 183-219 person^{-1}day^{-1}(Vhurumuku, 2000).

According to the research carried out by them to determine the concentrations of Cu, Zn, Cd, Ni, Cr and Pb in *Brassica juncea* and *B.napus* leaves from gardens irrigated with waste water from Mukuvisi River and partially treated sewage effluent at Pension farm in Harare and the estimation of their intake rates by people consuming the vegetables, the concentrations of heavy metals (mg kg^{-1} dry weight) in vegetable leaves ranged from 1.0-3.4 for Cu, 18-201 for Zn, 0.7-2.4 for Cd, 2.5-6.3 for Ni, 0.7-5.4 for Pb and 1.5-6.6 for Cr. Bio-concentration factors in

the range of 0.04-3 were obtained, with Zn and Cd having the highest concentration factors of 1.6 and 3. Estimated intakes rates of heavy metals from consumption of the vegetables in mg day-1 ranged from 0.04-0.05 for Cu, 0.6-3.3 for Zn, 0.02-0.04 for Cd, 0.05-0.1 for Ni, 0.05-0.09 for Pb and 0.05-0.1 for Cr. Cadmium intake rates were above their recommended Minimum Risk Levels (MRLs) at both sites, while Cu, Ni, Cr and Pb had daily intakes above 40 % of their MRLs. Potential health risks, particularly from Cd intake, existed for the daily consumers of the leafy vegetables at both Mukuvisi and Pension sites.

The total concentrations of heavy metals in the soils from which the vegetables were sampled at the Mukuvisi and Pension sites were below the maximum permissible limits (MAFF, 1993). Soil pH (in water) was higher in Mukuvisi gardens (6.1-7.8) than in Pension gardens (5.1-6.3), while the concentrations of all heavy metals tested were lower at the Mukuvisi site than at the Pension site.

The concentrations of Cd in plant tissues exceeded the permissible limit of 2 mg However; Cr concentrations at both sites did not exceed the tolerable limit of 23 mg kg^{-1} (Weigert, 1991). The mean bio-concentration factors (CFs) of the selected heavy metals at the Pension and Mukuvisi sites, calculated as the concentration of the heavy metals in leaves relative to concentration in soil, ranged from 0.04-3.0 depending on the element. The order was: CFCd>CFZn>CFNi>CFPb>CFCu

>CFCr at Mukuvisi and CFZn>CFCd>CFNi>CFPb>CFCu>CFCr at Pension. The proportions of studied heavy metals in vegetable leaves, expressed as a percentage fraction of their added total concentration in the leaves were in the order: Zn>Cr>Ni>Cu>Cd>Pb for vegetables at the Mukuvisi site and Zn>Ni>Pb>Cu>Cr>Cd for vegetables at the Pension site. Zinc made the highest fractions of 48-75 % (Mukuvisi) and 88-92 % (Pension). Therefore no evidence of phytotoxicity of Cu and Zn in the vegetables could be found from the concentrations of Cu and Zn in the vegetable leaves at both Pension and Mukuvisi sites.

2.7. Bioavailability of Heavy Metal in the Garden Soil

Vegetables play an important role in the human diet, and production in suburban areas has increased as population has become more urbanized. Heavy metal pollution in soils has increased in these areas because of increased disposal of municipal and industrial solid and liquid wastes to the soils and precipitation of pollutants from air on the soils (Bradatan and Editura, 2007). Retention of heavy metals by soil has also been stated to depend on factors such as the nature of the inorganic and organic constituents, the nature of metals, the composition of soil solution, and pH (Davidescu, 1998). Heavy metal accumulation in soils is of

concern in agricultural production due to adverse effects on food quality (safety and marketability), crop growth (due to phytotoxicity), and environmental health (soil flora/fauna and terrestrial animals) (Editura, 1986). Metal accumulation in vegetables may pose a direct threat to human health.

Total soil metals can be used to estimate the degree of soil exposure to heavy metal pollution, although this is not generally well correlated with metal mobility and bioavailability (Schwartz and Stewart, 2001). Plant availability, however, is better correlated with most extractable forms of Cu rather than total Cu concentration across a range of soil conditions (Wager and Kim, 1996). Total Cu in soils includes six 'pools' classified according to their physical–chemical behaviour. The pools are soluble ions and inorganic and organic complexes in soil solution; exchangeable Cu; stable organic complexes in humus; Cu adsorbed by hydrous oxides of Mn, Fe and Al; Cu adsorbed on the clay–humus colloidal complex; (Korrick and Sparrow, 1999) and the crystal lattice-bound Cu. When added to soil, Cu may react with soil constituent, changes its chemical form, and then its availability to plants is also altered. The amount of soil Cu removed by a chelating agent like Diethylenetriamine Pentaacetic Acid (DTPA) or Ethylenediamine Tetraacetic Acid (EDTA) is considered as the plant-available portion. The DTPA

extractable Cu decreased with incubation time, especially in the first 8 weeks. After 12-week incubation, 60% of added Cu was not extractable by DTPA.

These may have resulted from transformation of the added soluble Cu fraction to slowly available fractions of Cu in the soil.

Excess Cu in growth media caused toxicity to all the three vegetable crops, resulted in chlorosis in new leaves, brown, stunted, coralloid roots, and plant growth was inhibited. Shoot fresh weight (FW) progressively decreased as the Cu in nutrient solution increased. Great differences in Cu tolerance were also noted among the three vegetable crops. Shoot fresh weight of celery, pakchoi and Chinese cabbage decreased to about 33%, 37% and 50% of the control, respectively, when grown with the Cu supply of 10 mg L^{-1}. Shoot growth of pakchoi decreased sharply at higher Cu supply levels, and its FW reduced to 90% of the control at Cu supply over 20 mg L^{-1}

Shoot growth between celery and Chinese cabbage was similar when external Cu levels were over 20 mg L^{-1}. The results indicate that celery is more tolerant to Cu toxicity than Chinese cabbage and pakchoi when grown under nutrient solution.

Significant negative correlations occur between shoot (or stem for celery) biomass and soil available or total Cu. Shoot biomass of the three vegetable species was negatively and closely correlated with total soil Cu or soil available Cu, with the correlation coefficients being 0.95–0.99**. The critical soil available Cu

concentrations at 10% reduction of dry matter yield were 50.6, 57.6, and 70.7 mg kg^{-1} for Chinese cabbage, pakchoi, and celery (stem), respectively. These results indicate that Chinese cabbage and pakchoi are less tolerant to Cu toxicity than celery when plants were grown in the soil, which showed a similar trend as those grown in nutrient solution.

2.8. Effects of Heavy Metals on Human Health

Heavy metals have been extensively studied and their effects on human health regularly reviewed by the World Health Organization (WHO). Metals occur naturally in the earth's crust, and their contents in the environment can vary between different regions resulting in spatial variations of background concentrations. The distribution of metals in the environment is governed by the properties of the metal and influences of environmental factors (Khlifi and Hamza-Chaffai, 2010). Of the 92 naturally occurring elements, approximately 30 metals and metalloids are potentially toxic to humans. Heavy metals enter the environment by natural and anthropogenic means. Such sources include: natural weathering of the earth’s crust, mining, soil erosion, industrial discharge, urban runoff, sewage effluents, pest or disease control agents applied to plants, air pollution fallout, and a number of others (Ming-Ho, 2005). Although some

individuals are primarily exposed to these contaminants in the workplace, for most people the main route of exposure to these toxic elements is through the diet (food and water).

Chronic exposure of humans to heavy metals can cause adverse effects and its toxicity and the resulting threat have been traced to be a function of concentration. (Mendez-Armenta, 2008)

Therefore, there has been increasing concern, mainly in the developed world, about exposures, intakes and absorption of heavy metals by humans.

Populations are increasingly demanding a cleaner environment in general, and reductions in the amounts of contaminants reaching people as a result of increasing human activities is desired (European Commission, 2006; Figueroa, 2008).

Lead, cadmium, mercury, and arsenic are widely dispersed in the environment. These elements have no beneficial effects in humans, and there is no known homeostasis mechanism for them (Draghici *et al*., 2010; Vieira *et al*., 2011). They are generally considered the most toxic to humans and animals; the adverse human health effects associated with exposure to them, even at low concentrations, are diverse and include, but are not limited to, neurotoxic and carcinogenic actions (ATSDR, 2003a, 2003b, 2007, 2008; Castro-González and Méndez-Armenta, 2008; Jomova and Valko, 2011;Tokar *et al*. ,2011).

Lead as a toxicologically relevant element has been brought into the environment by man in extreme amounts, despite its low geochemical mobility and has been distributed worldwide (Oehlenschläger, 2002). Lead, like many other contaminants, is ubiquitous and can be found occurring as metallic lead, inorganic ions and salts (Harrison, 2001).

Food is one of the major sources of lead exposure; the others are air (mainly lead dust originating from petrol) and drinking water. Plant food may be contaminated with lead through its uptake from ambient air and soil; animals may then ingest the lead contaminated vegetation. In humans, lead ingestion may arise from eating lead contaminated vegetation or animal foods. Another source of ingestion is through the use of lead-containing vessels and it has been observed that in humans, about 20 to 50% of inhaled, and 5 to 15% of ingested inorganic lead is absorbed. In contrast, about 80% of inhaled organic lead is absorbed, and ingested organic lead is absorbed readily (Ming-Ho, 2005). Once found in the blood stream, lead is primarily distributed among blood, soft tissue, and mineralizing tissue (Ming-Ho, 2005). The bones and teeth of adults contain more than 95% of the total body burden of lead. Children are particularly sensitive to this metal because of their more rapid growth rate and metabolism, with critical effects in the developing nervous system (ATSDR, 2007; Castro-González and Méndez-Armenta, 2008). Cadmium is naturally present in the environment: in air, soils, sediments and even

in unpolluted seawater. Cadmium is emitted to air by mines, metal smelters and industries using cadmium compounds for alloys, batteries, pigments and in plastics, although many countries have stringent controls in place on such emissions (Harrison, 2001).

Food products account for most of the human exposure burden to cadmium (ExtoxNet, 2003). In food, only inorganic cadmium salts are present. Organic cadmium compounds are very unstable. In contrast to lead and mercury ions, cadmium ions are readily absorbed by plants. They are equally distributed over the plant. Cadmium is taken up through the roots of plants to edible leaves, fruits and seeds. Cadmium also accumulates in animal milk and fatty tissues (Figueroa, 2008). Therefore, people are exposed to cadmium when consuming plant- and animal-based foods. Seafood, such as molluscs and crustaceans, can also be a source of cadmium (Castro-González and Méndez-Armenta, 2008; WHO 2004; WHO 2006).

Cadmium accumulates in the human body affecting negatively several organs: liver, kidney, lung, bones, placenta, brain and the central nervous system (Castro-González and Méndez- Armenta, 2008). Other damages that have been observed include reproductive, and development toxicity, hepatic, haematological and immunological effects (Apostoli and Catalani, 2011; ATSDR, 2008).

Mercury is one of the most toxic heavy metals in the environment (Castro-González and Méndez-Armenta, 2008). Exposure to high levels of metallic, inorganic, or organic mercury can permanently damage the brain, kidneys, and developing fetus (ATSDR, 2003b).

The toxicity of mercury depends on its chemical form (ionic < metallic <organic) (Clarkson, 2006). Up to 90% of most organic mercury compounds are absorbed from food (Reilly, 2007).

When deposited in soil, organic mercury compounds are slowly broken down into inorganic compounds; conversely, inorganic mercury can be converted by microorganisms in soil and water into the organic compound; methyl mercury, which is then bio-concentrated up the food chain. Mercury can be detected in most foods and beverages, at levels of < 1 to 50 μg/kg (Reilly, 2007). Higher levels are often found in marine foods. Organic mercury compounds easily pass across biomembranes and are lipophilic. Therefore elevated mercury concentrations are mainly found in liver of lean species and in fatty fish species. Methyl mercury has a tendency to accumulate with fish age and with increasing trophic level. This leads to higher mercury concentrations in old fatty predatory species like tuna, halibut, redfish, shark, and swordfish (Oehlenschläger, 2002). In the year 2003, the JECFA revised its risk assessment on methyl mercury in fish and adopted a lower PTWI of 1.6 μg/kg body weight/week to replace the previous PTWI of 3.3 μg/kg

b.w./week of total mercury for the general population (Castro-González and Méndez-Armenta, 2008; JECFA, 2004). This risk assessment was based on two major epidemiology studies which investigated the relationship between maternal exposure to mercury through high consumption of contaminated fish and seafood and impaired neurodevelopment in their children (Castro-González and Méndez-Armenta, 2008; Grandjean *et al*., 1997; Murata *et al*., 2007).

Arsenic is a metalloid. It is rarely found as a free element in the natural environment, but more commonly as a component of sulphur-containing ores in which it occurs as metal arsenides. Arsenic is quite widely distributed in natural waters and is often associated with geological sources, but in some locations anthropogenic inputs, such as the use of arsenical insecticides and the combustion of fossil fuels, can be extremely important additional sources. Arsenic occurs in natural waters in oxidation states III and V, in the form of arsenous acid (H_3AsO_3) and its salts, and arsenic acid (H_3AsO_5) and its salts, respectively (Sawyer *et al.*, 2003).

The toxic effects of arsenic depend specially on oxidation state and chemical species, among others. Inorganic arsenic is considered carcinogenic and is related mainly to lung, kidney, bladder, and skin disorders (ATSDR, 2003a). The toxicity of arsenic in its inorganic form has been known for decades under the following

forms: acute toxicity, sub chronic toxicity, genetic toxicity, developmental and reproductive toxicity (Chakraborti *et al*., 2004), immuno-toxicity (Sakurai *et al.*, 2004), biochemical and cellular toxicity, and chronic toxicity (Mudhoo *et al*., 2011; Schwarzenegger et al., 2004). Drinking water is one of the primary routes of exposure of inorganic arsenic (Mudhoo *et al*., 2011; National Research Council, 2001).

Ingestion of groundwater with elevated arsenic concentrations and the associated human health effects are prevalent in several regions across the world. Arsenic toxicity and chronic arsenicosis is of an alarming magnitude particularly in South Asia and is a major environmental health disaster (Bhattacharya *et al*., 2007; Chakraborti *et al.*, 2004; Kapaj *et al*., 2006).

Chronic arsenic ingestion from drinking water has been found to cause carcinogenic and non carcinogenic health effects in humans (ATSDR, 2003a; Mudhoo *et al.,* 2011; USEPA 2008, 2010a, 2010b). The growing awareness of arsenic-related health problems has led to a rethinking of the acceptable concentration in drinking water (Sawyer *et al*., 2003). Following a thorough review and in order to maximize health risk reduction, the USEPA in 2001 decided to reduce the drinking water maximum contaminant limit (MCL) to 0.010 mg/L, which is now the same as the WHO guidelines (USEPA, 2005a).

The adverse effects of arsenic in groundwater used for irrigation water on crops and aquatic ecosystems are also of major concern. The fate of arsenic in agricultural soils is less characterized compared to groundwater. In foods, the major source of arsenic is mainly fish and seafood. The organic arsenic in food and seafood appears to be much less toxic than the inorganic forms (Uneyama *et al*., 2007). The presence of arsenic in fish has been detected in several species such as; sardine, chub mackerel, horse mackerel (Vieira *et al*., 2011) blue fish, carp, mullet tuna, and salmon (Castro-González and Méndez-Armenta, 2008). Results show that arsenic concentration is low in most fish, being always its highest concentration in muscle (Vieira *et al*., 2011).

Generally, the Joint FAO/WHO Expert Committee on Food Additives (JECFA) established a provisional tolerable weekly intake (PTWI) for lead, cadmium, mercury and arsenic as 0.025, 0.007, 0.0033 and 0.015mg/kg body weights respectively (JECFA, 2004). Similarly, the provisional guidelines for lead, cadmium, mercury and arsenic in drinking water were established by WHO as 0.01, 0.003, 0.002 and 0.010mg/L respectively (WHO, 2004).

In response to the risks associated with these heavy metals, many developed countries over the last 25 years have implemented regulatory actions that have effectively decreased actual exposures of the general population.

CHAPTER THREE

3.0. RESEARCH METHODOLOGY

3.1. Study Area

Agbada II Flow Station which belongs to the Shell Petroleum Development Company Nigeria Limited (SPDC) was commissioned in February 1993 and designed to receive both high and low pressure gases. The station is located between Eneka and Igwuruta communities in Ikwerre Local Government Area, within the Oil Mining License (OML) 17 concession areas in Rivers State.

Geographically, Agbada II Flow Station is located between longitude 7° 0′-7°10 ′E and latitude 4° 31′ 4° 40′ N in Rivers State of Nigeria (Gobo *et al*., 2009) and is routed through two suction lines to the gas compression station. Agbada II Flow Station is bounded on the north by Igwuruta town, on the south by Eneka town, on the east by Eneka- Igwuruta road and on the west by the Airport road (Fig. 3.1). The facility is composed of three different flare parts with two vertical and one horizontal flare points. It can be accessible either by land through a tarred road from Eneka axis or air (through the airport road).The facility is well fenced with an entrance gate in front and surrounded by farm lands.

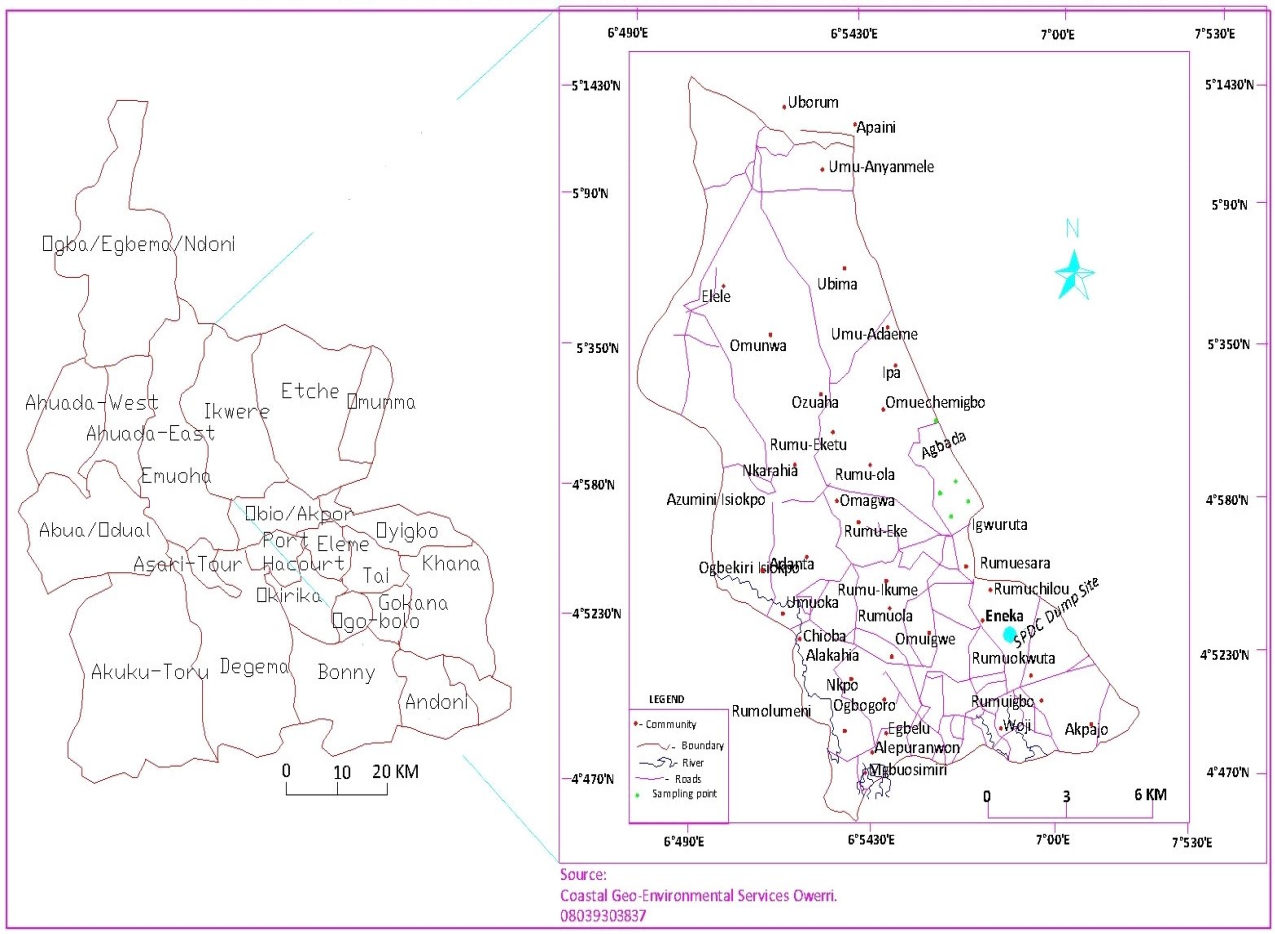

FIG.3.1 Map of Rivers State showing Agbada II Flow Station.

3.2. Field Sampling

3.2.1. Sampling Locations

Four sampling locations sited 500m apart in the prevailing wind direction from the gas flare stack and a control sited 2Km in the upwind direction were chosen.

3.2.2. Air Quality Monitoring

3.2.2.1. *In situ* Determination of Ambient Air Quality parameters

The sampling equipment used includes the Digital Automatic Gas Monitors (DAGMs) and the High Volume Sampler (HVS).

- **Digital Automatic Gas Monitor (DAGM)**: The Crowcon Gasman Air Monitor that had been pre-calibrated using air cylinder standard (SPDC, 2002) and was used in the direct detection of CO_x, NO_x, SO_x and H_2S, whereas the Hazdust 10µm Particulate Monitor was used for the detecting of suspended particulate matter (SPM_{10}). This was done in replicates for 3 months (September, October and November 2012).

- **High Volume Sampler (HVS):** The modified EPA gravimetric high volume method was used. A known volume of air was drawn through a pre-

weighted glass fibre filter (20 x 25cm) with the aid of a heavy turbine blower at flow the rate of 1.3m^3/min. This collected suspended particulate matter within the size range of 100-0.1µm diameters. Sampling was made at the five sampling locations in replicates.

3.2.3. Meteorological parameters

A hand-held Testrel 4500 Weather Tracker, a high precision *in-situ* weather monitoring equipment, was used to determine the following meteorological data: wind speed, ambient temperature, pressure, wind turbulence, sun radiation, wind direction, relative humidity and precipitation. Measurement was made at the five sampling locations and readings were read off the Liquid Crystal Display (LCD) screen of the equipment each time.

3.2.4. Soil Sample Collection

Replicated soil samples were collected using stainless soil augers at depths 0-15cm from the five sampling stations, composited and labeled in polyethylene bags and thereafter taken to the laboratory for analysis (Aremu *et al*., 2010).

3.3 Laboratory Analysis

3.3.1. Sample preparation

Trace metal particles collected with glass fibre filters of the HVS were extracted with conc. H_2SO_4 **.** The soil samples were allowed to dry under atmospheric oxygen (air) and ground into fine particles using the laboratory mortar and pestle. Ground samples were sieving using a 2mm mesh sieve and the finer soil particles carefully packaged and labeled in sample bottles.

A portion (0.5g) of soil sample was weighed with a Metler balance (AE 160) and poured into a 50ml pyrex glass beakers, and 5ml solution of conc. HCl, HNO_3, $HClO_4$ and HF were added in that order to each of the samples in 5ml applications. The beakers containing each of the samples were heated for approximately 3hr for proper digestion.

3.3.2. Heavy Metals Analysis

The concentrations of the heavy metals (Cd, Ni, Cr, Pb, Co, Mn, Va As Fe and Zn) in the two matrices (air and soil) were determined using the Varian Spectra AA 600 Atomic Absorption Spectrophotometer (AAS).

3.4. Statistical analysis

Univariate and Multivariate analysis were used in the organization of data. Descriptive statistics was used to explore mean, standard error, range, etc of ambient air quality parameters. The student's t-test was used to explore seasonal variations in levels of the ambient air quality parameters while the Pearson Correlation (r) was used to establish possible relationships between the presence of heavy metals in air and soil matrices. The one -way analysis of variance (ANOVA) was used to explore spatial variations in levels of the parameters while the structure of group means was detected with the post – hoc means plot at the 95% confidence limit. Variation plots were used to represent data graphically.

CHAPTER FOUR

4.0 RESULTS

4.1. Ambient Air Quality Parameters around Agbada II Gas Flow Station

The levels of ambient air quality parameters including heavy metals and meteorological data are presented in Appendixes 1-3. The levels of Suspended Particulate Matter (SPM_{10}) (range = 20.20 ppm), Ni (range = 40.20 ppm), air pressure (range = 200 PSI) and Relative Humidity (RH) (range = 20.00 %) varied widely while the other parameters had narrow variations.

CO, SO_X, SPM and Volatile Organic Compounds (VOC) varied from 1.20 – 3.00 (2.01± 0.13), 0.00 – 0.01 (0.008 ± 0.001), 70.00 – 90.20 (82.04 ± 1.75) and 0.00 – 0.01 (0.002 ± 0.001) ppm respectively (Table 4.1). As, Pb and Ni varied as follows: 1.00 – 3.00 (1.60 ± 0.16), 0.01 – 0.80 (0.38 ± 0.07) and 40.00 – 80.20 (65.41 ± 3.68) ppm respectively. Co, Fe and Cd varied as follows: 0.00 – 0.40 (0.12 ± 0.035), 0.00 – 0.50 (0.10 ± 0.041) and 0.00 – 0.30 (0.05 ± 0.022) ppm respectively.

The meteorological variables varied as follows: Wind speed 0.20 – 0.30 (0.23 ± 0.013) m/s, ambient temperature 27.20 – 29.20 (28.25 ± 0.188) ^{o}C, Pressure 1000.00 – 1200.00 (1056.20 ± 14.89) Psi and Relative Humidity 70.00 – 90.00 (77.33 ± 1.720) %.

Table 4.1. Descriptive statistics of ambient air quality parameters

Parameters	Minimum	Maximum	Range	Mean	SE
CO (ppm)	**1.20**	**3.00**	**1.80**	**2.01**	**0.13**
SOx (ppm)	**0.00**	**0.01**	**0.01**	**0.08**	**0.001**
SPM (ppm)	**70.00**	**90.20**	**20.20**	**82.04**	**1.748**
VOC (ppm)	**0.00**	**0.01**	**0.01**	**0.002**	**0.001**
As (ppm)	**1.00**	**3.00**	**2.00**	**1.600**	**0.164**
Pb (ppm)	**0.01**	**0.80**	**0.79**	**0.376**	**0.068**
Ni (ppm)	**40.00**	**80.20**	**40.20**	**65.41**	**3.677**
Co (ppm)	**0.00**	**0.40**	**0.40**	**0.08**	**0.02**
Fe (ppm)	**0.00**	**0.50**	**0.50**	**0.10**	**0.041**
Cd (ppm)	**0.00**	**0.30**	**0.30**	**0.05**	**0.022**
Wind Speed (m/s)	**0.20**	**0.30**	**0.10**	**0.23**	**0.013**
Ambient Temp (°C)	**27.20**	**29.20**	**2.00**	**28.25**	**0.188**
Pressure (psi)	**1000.00**	**1200.00**	**200.00**	**1056.20**	**14.89**
Relative Humidity (%)	**70.00**	**90.00**	**20.00**	**77.33**	**1.720**

SE=standard error of means, VOC=Volatile Organic compounds, SPM= Suspended Particulate Matter.

4.2. Spatial Variations in Ambient Air Quality Parameters

The levels of the ambient air quality parameters also showed spatial variations. Minimum levels of the VOC and SO_X (0.00 ppm each) were recorded in sampling stations (SS) A, B, D & Control, and SSC respectively while their maximum levels (0.01 ppm each) were recorded in SSC and SSA, B, D & Control (Fig 4.1).

However, the level of ozone (O_3) across the five Sampling Stations (SS) was constant (0.00ppm). The minimum level of CO (1.20 ppm) was recorded in the control station (SS Control). Similarly, SPM recorded its minimum value of 70.00 ppm in SS Control. CO recorded its maximum value of 2.40ppm at SS A and SPM (80.20ppm) at SS B SS D (Appendix 1).

For the heavy metals, Cd and Fe recorded their minimum levels of 0.00 ppm each at SS D, SS Control and SS Control respectively while their maximum values of 0.30 and 0.50 ppm were recorded in SS C and SS B respectively. Co recorded its minimum value of 0.20 ppm in SS A, SS B and SS Control while Pb recorded its minimum value of 0.01ppm in SS D and SS Control. Their respective maximum values of 0.40 and 0.80 ppm were each recorded in SS C. On the other hand, As and Ni recorded their minimum levels of 1.20 and 70.00 ppm in SS Control while their maximum levels of 2.30 and 80.20 ppm were recorded at SS A and SS B &

SS D respectively. However, the levels of Cu, Hg and Mn did not vary across the sampling locations (Appendix 2).

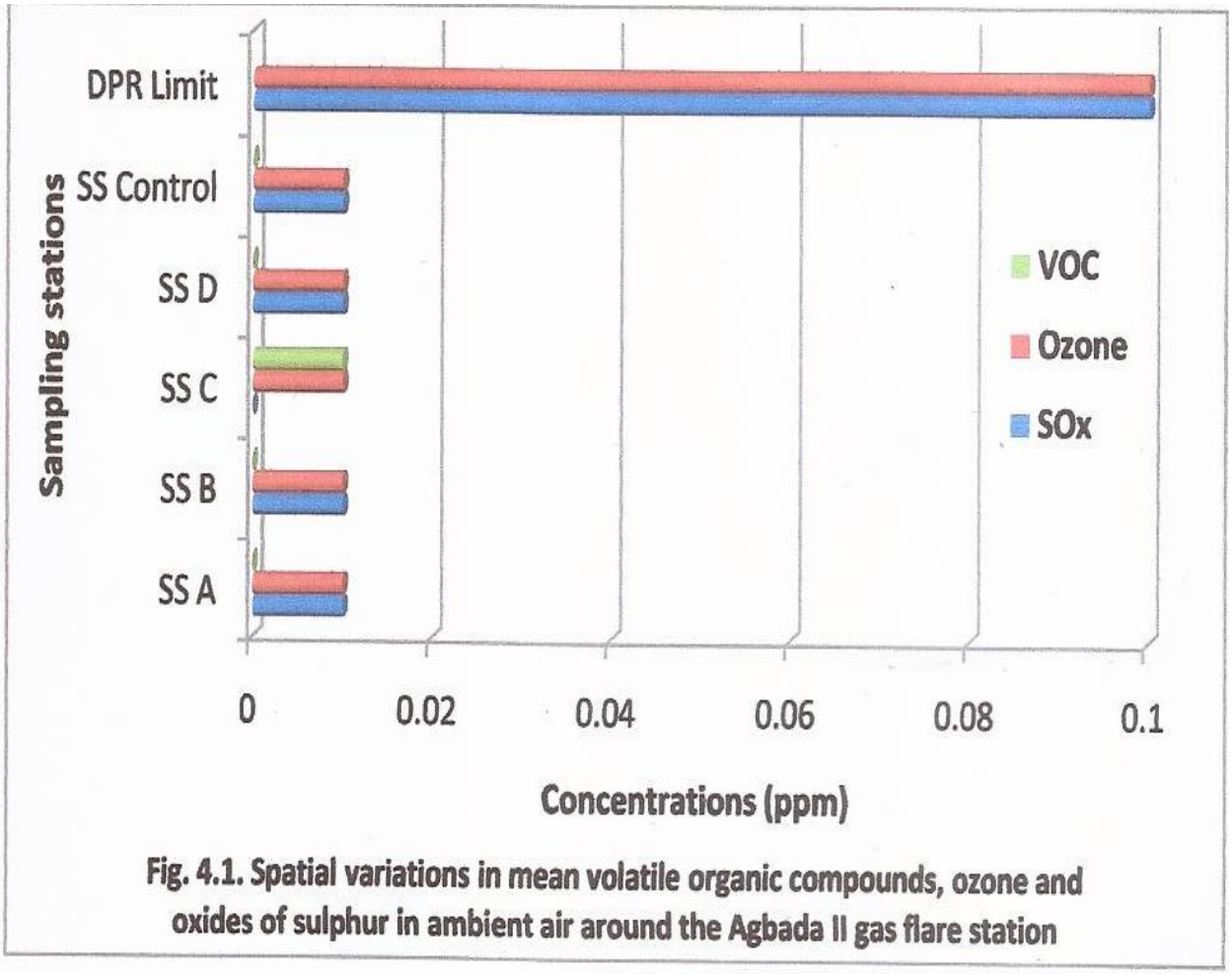

Fig. 4.1. Spatial variations in mean volatile organic compounds, ozone and oxides of sulphur in ambient air around the Agbada II gas flare station

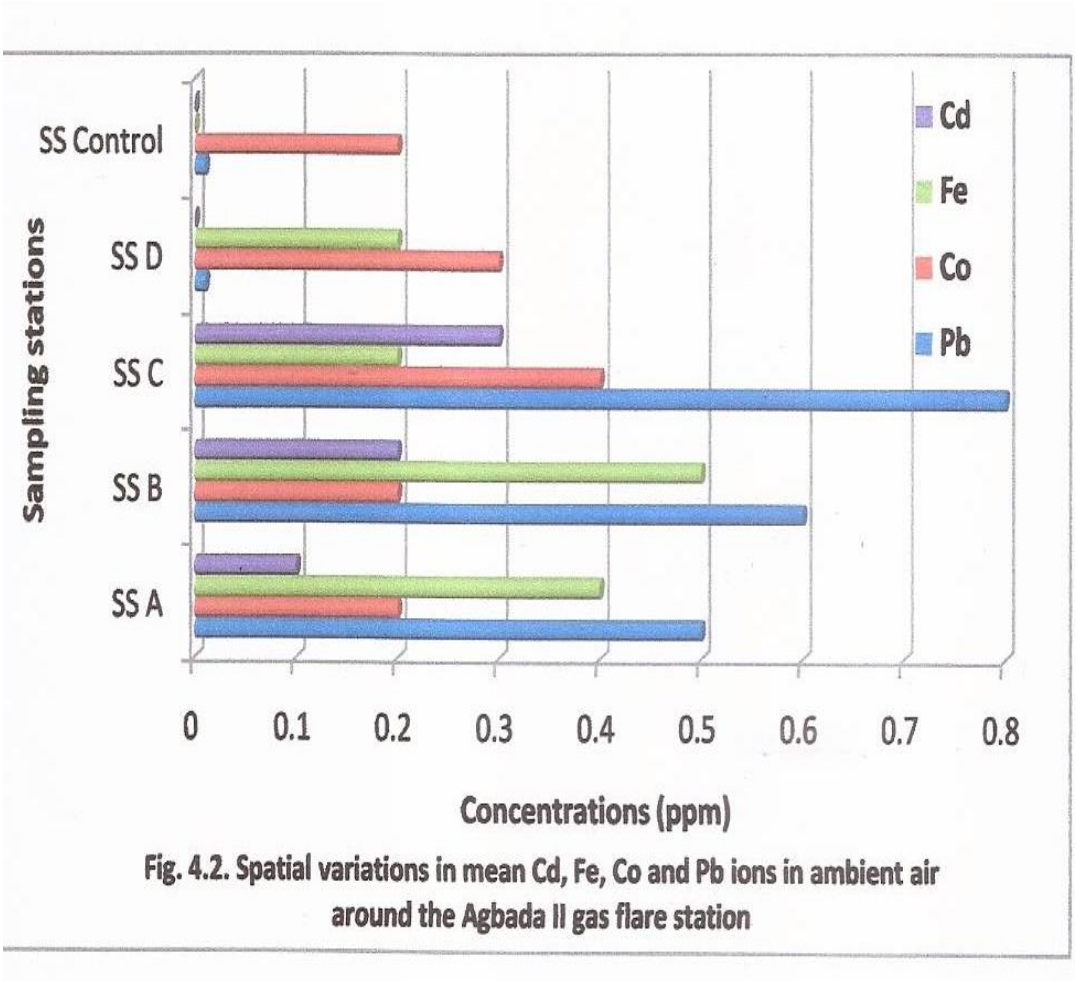

Fig. 4.2. Spatial variations in mean Cd, Fe, Co and Pb ions in ambient air around the Agbada II gas flare station

The one-way analysis of variance (ANOVA) test revealed that there were significant differences in mean values of the ambient air quality parameters across the sampling stations (Sig.F = 0.000) at P<0.005 (Appendix 4). A pos-hoc structure of group means was used to plot the graph of the mean levels of the ambient air quality parameters in ppm across the four Sampling Stations (SS A – SS D) against their mean levels in the control station (SS Control) where SS Control was utilized as predictor variable.

In Fig 4.3, a graph of the mean levels of CO, SO_x NO_x, SPM, VOC, Ozone and H_2S in SS A (2.40, 0. 01, 0.00, 80.00, 0.00 and 0.001ppm respectively) was plotted against their mean levels of 1.20, 0.01, 0.00, 70.00,0.00 and 0.001 ppm respectively in SS Control. Similarly, In Fig 4.4, the mean levels of CO, SO_x NO_x, SPM, VOC, Ozone and H_2S in SS B (2.00, 0. 01, 0.00, 80.20, 0.00, 0.01 and 0.001ppm respectively) was plotted against their respective mean levels in the SS Control; 1.20, 0.01, 0.00, 70.00,0.00 and 0.001 ppm.

In Fig 4.5, the mean levels of 2.20, 0.00, 0.00, 75.00, 0.01, 0.01 and 0.001ppm for CO, SO_x NO_x, SPM, VOC, Ozone and H_2S respectively in SS C were plotted against their mean levels of 1.20, 0.01, 0.00, 70.00,0.00, 0.01 and 0.001 ppm in the SS Control. In Fig 4.6, the means plot of CO, SO_x NO_x, SPM, VOC, Ozone and H_2S between SS D and SS Control was plotted using the values of 2.30, 0. 01,

0.00, 80.20, 0.00, 0.01, 0.001ppm for SS D and 1.20, 0.01, 0.00, 70.00, 0.00 and 0.001 ppm for SS Control. However, in all the sampling stations, SPM contributed the observed difference.

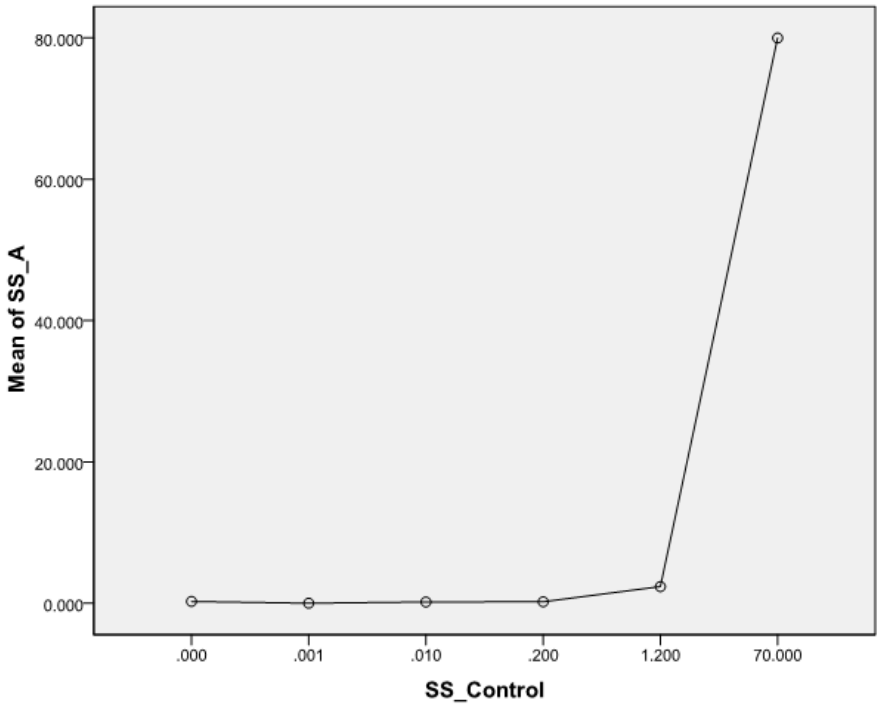

Fig 4.3. Means plot in ambient air quality parameters between SS control and SS A

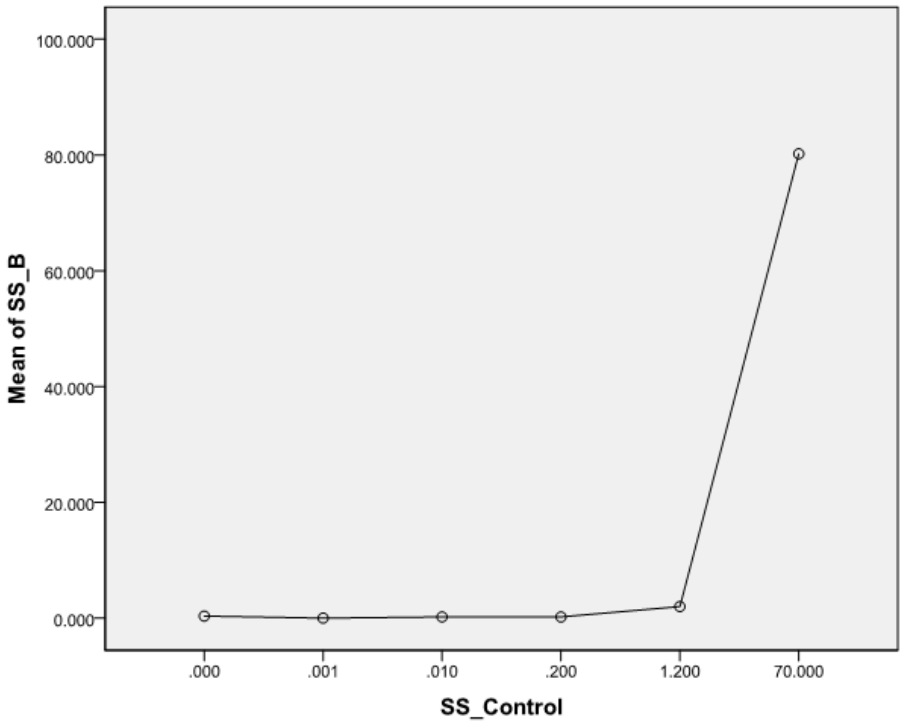

Fig 4.4. Means plot in ambient air quality parameters between SS control and SS B

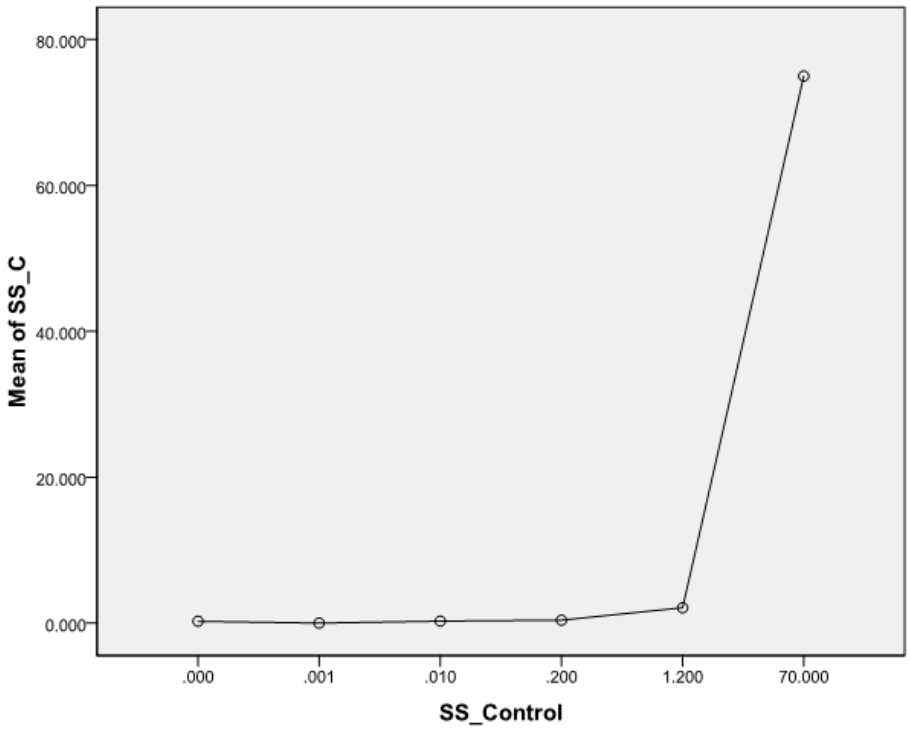

Fig 4.5. Means plot in ambient air quality parameters between SS control and SS C

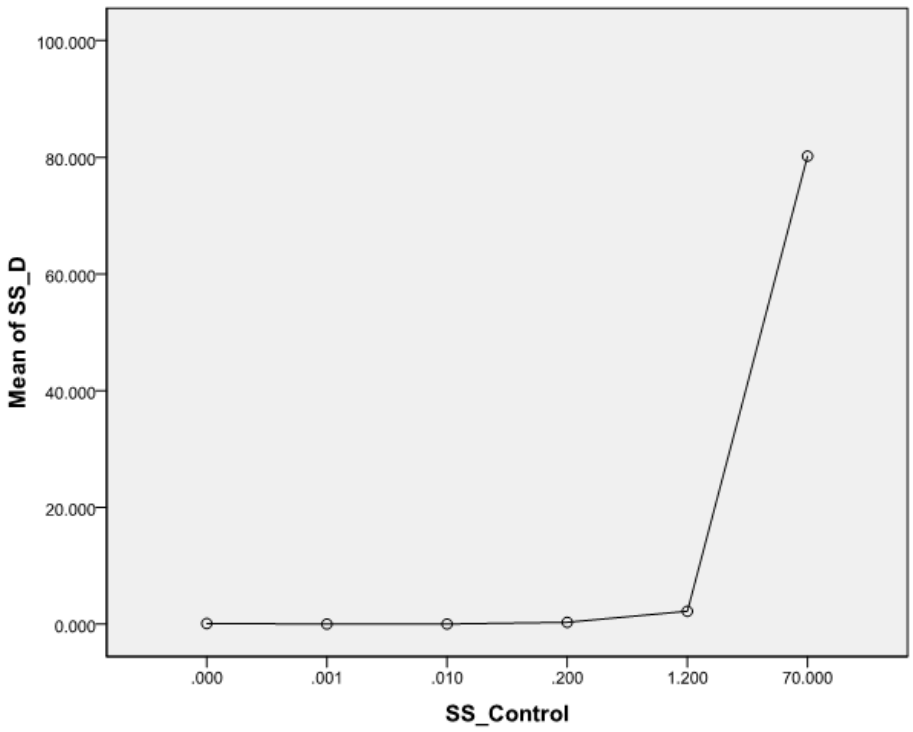

Fig 4.6. Means plot in ambient air quality parameters between SS control and SS D

4.3. Seasonal Variations in Ambient Air Quality Parameters

The output of a pair-wise comparison in mean levels of the ambient air quality parameters between the wet and dry season is shown in Table 4.2 where Significant correlation (Sig r) and Significant difference (Sig t) are feasible at $P<0.05$.

The mean levels of CO in the wet and dry seasons were 2.02 ± 0.22 ppm and 1.94 ± 0.21ppm respectively. However, their mean levels between the two seasons did not correlate (Sig r = 0.172) or differ significantly (Sig. t = 0.642). On the other hand, the mean levels of SPM and As in the wet season were 77.08 ± 2.03 ppm and 1.92 ± 0.19 ppm and in the dry season; 82.00 ± 2.55 ppm and 1.44 ± 0.39 ppm respectively. Their mean values neither correlated (Sig r = 0.344 and 0.629) nor differed significantly (Sig t = 0.093 and 0.277) between the seasons. Similarly, Pb recorded the mean value of 0.38 ± 0. 16 ppm in the wet season and 0.34 ± 0.09 ppm in the dry season and did not correlate (Sig r = 0.457) nor differ significantly (Sig t = 0.787). However the mean values of Fe between the two seasons (0.26 ± 0.09 and 0.22 ± 0.010 ppm) correlated (Sig r = 0.026) and differed significantly (Sig t = 0.038). The mean values of Ni and Co (77.08 ± 2.03 and 0.26 ± 0.04 ppm) in wet season and (59.08 ± 6.00 and 0.04 ± 0.03 ppm) in dry season did not correlate (Sig r = 0 .326 and 0.582) but differed significantly (Sig t = 0.025 and

0.028). In the wet season, the mean level of Cd was 0.12 ± 0.058 ppm and 0.01 ± 0.006 ppm in the dry season. The mean levels of Cd however, did neither correlate (Sig r = 0.559) nor differ significantly (Sig t = 0.122) between the seasons.

Table 4.2. Pair–wise comparison in levels of the ambient air quality parameters between the seasons (P<0.05)

Pairs	Mean	SE	r	Sig r	t	Sig t
CO Wet	2.02	0.22	0.718	0.172	0.502	0.642
CO Dry	1.94	0.21				
SPM Wet	77.08	2.03	0.543	0.344	-2.200	0.093
SPM Dry	82.00	2.55				
As Wet	1.92	0.19	0.296	0.629	1.259	0.277
As Dry	1.44	0.39				
Pb Wet	0.38	0.16	0.441	0.457	0.289	0.787
Pb Dry	0.34	0.09				
Ni Wet	77.08	2.03	0.561	0.326	3.497	0.025
Ni Dry	59.08	6.00				
Co Wet	0.26	0.04	-0.335	0.582	3.354	0.028
Co Dry	0.04	0.03				
Fe Wet	0.26	0.09	0.922	0.026	3.056	0.038
Fe Dry	0.22	0.010				
Cd Wet	0.12	0.058	0.559	0.327	1.954	0.122
Cd Dry	0.01	0.006				

SE = Standard error of mean, r = Pearson correlation

4.4. Levels of heavy metals in soils

The levels of heavy metals in soil samples are presented in Appendix 5. The levels of Pb (range = 18.75 ppm), Cu (range = 40.42 ppm) and Mn (range=20.00 ppm) varied widely whereas As, Cd, Ni, Zn and Fe had narrow variations.Pb and As varied from 6.30–25.05 (13.35±3.25) and 0.00 – 8.20 (3.44±1.67) ppm respectively Cd and Cu varied from 2.70–9.40 (6.70±1.10) and 20.38–60.80 (39.04±6.47) ppm respectively (Table 4.3). The values of Ni and Zinc varied from 7.18–14.60 (11.69 ±1.32) ppm and 10.28–20.20 (16.25±1.69) ppm respectively. Fe and Mn varied from 20.50–25.40 (22.48±1.08) ppm and 40.80– 60.80 (50.46 ± 3.17) ppm respectively.

However, the minimum levels of Pb (6.30 ppm) and As (0.00 ppm) were recorded at SS Control & SS D and SS Control respectively while their maximum values of 25.05 and 8.20 ppm were recorded at SS Control. Minimum values of 2.70 and 20.38 ppm for Cd and Cu respectively were each recorded at SS Control and their maximum values of 9.40 and 60.80 ppm were each recorded in SS A (Appendix 5). Ni, Zn, and Mn with the minimum values of 7.18, 10.28, and 40.80 ppm respectively were each recorded at SS Control for Ni, Zn while the minimum value for Fe (20.50 ppm) was recorded at SS A. However, maximum values of 14.60, 20.20, 25.40 and 60.80 ppm for Ni, Zn, Fe and Mn were recorded in SS B, SS A, SS D and SS C respectively.

Table 4.3. Descriptive statistics of heavy metals in soils around Agbada II Flow Station.

Parameters	Minimum	Maximum	Range	Mean	SE
Pb (ppm)	**6.30**	**25.05**	**18.75**	**13.35**	**3.25**
As (ppm)	**0.00**	**8.20**	**8.20**	**3.44**	**1.67**
Cd (ppm)	**2.70**	**9.40**	**6.70**	**5.68**	**1.10**
Cu (ppm)	**20.38**	**60.80**	**40.42**	**39.04**	**6.47**
Ni (ppm)	**7.18**	**14.60**	**7.42**	**11.69**	**1.32**
Zn (ppm)	**10.28**	**20.20**	**9.92**	**16.25**	**1.69**
Fe (ppm)	**20.50**	**25.40**	**4.90**	**22.48**	**1.08**
Mn (ppm)	**40.80**	**60.80**	**20.00**	**50.46**	**3.17**

SE =Standard error of mean

4.5. Relationships in levels of heavy metals in ambient air and soils

There were no significant correlations between the levels of heavy metals in ambient air and soil matrices at both the 95% and 99% confidence levels (Table 4.4).

Table 4.4. Correlation (r) matrix in the levels of heavy metals in air and soil

	Pb_{air}	As_{air}	Cd_{air}	Ni_{air}	Fe_{air}
Pb_soil	0.417				
As_soil		0.610			
Cd_soil			0.377		
Ni_soil				0.660	
Fe_soil					0.578

CHAPTER FIVE

5.0. DISCUSSION AND CONCLUSION

5.1. Discussion

The levels of heavy metals in ambient air can vary between different regions resulting in spatial variations of background concentrations and this distribution is usually governed by the properties of the metals and influences of environmental factors (Khlifi and Hamza-Chaffai, 2010). The mobilization of heavy metals into the biosphere by human activity has become an important process in the geochemical cycling of these metals (Nriagu, 1989). The toxicity of ingested heavy metals has been an important issue for decades (LeCoultre, 2001), even as chronic exposure of humans to them can cause adverse effects and its toxicity and the resulting threat has been traced to be a function of concentration (Mendez-Armenta, 2008). Therefore, there has been an increasing concern about exposures, intakes and absorption of heavy metals by humans; hence populations are increasingly demanding a cleaner environment in general and reductions in the amounts of contaminants reaching people as a result of increasing human activities (Figueroa, 2008).

The levels of SPM_{10}, Ni, air pressure and relative humidity (RH) varied widely, indicating that there were high levels of the parameters in ambient air though not

exceeding the acceptable limits. The high levels of SPM_{10} and Ni could be attributed to low precipitation during the study period. This is because high precipitation helps in washing pollutant particles thereby helping to minimize particulate matter and other pollutants emitted into the atmosphere. On the other hand, the narrow variation observed in other pollutants in the ambient air is an indication that a good gas flare reduction technique may have been used by the operators of the facility. The ambient temperature was warm (27.20-29.20^{0}C) while a range of 70-90% for relative humidity was maintained throughout the study period. Humans are sensitive to humid air because the human body uses evaporative cooling as the primary mechanism to regulate temperature (Perry and Green, 1997). High humidity causes condensation on windows or windowsills and obvious mold growth or a mildew odor. The relatively stable atmospheric temperature accounts for the low level wind speed. This is because air tends to move from an area with high atmospheric temperature to area of low atmospheric temperature which then causes wind movement. Consequently, the low wind speed could cause the polluted air not to rise high above earth's surface causing rapid cooling of the ground, thus, increasing the ground level concentration of pollutants in this layer. With strong wind conditions, there is greater dispersion and relatively low ground level concentrations of pollutants.

The mean concentrations of the heavy metals were generally low when compared to DPR acceptable standards. Ni was the most abundant heavy metal in the study. Since the concentrations of Ni are usually inversely proportional to the particle size, Ni from combustion processes most effectively enters the deep regions of the lung and then into the blood stream. Cancer, acute health effects (such as irritation and allergic sensitization), chronic non cancer and cancer health effects are all the resultant effects of long-term exposure to Nickel (Obianjunwa *et al*., 2001).

The study also revealed spatial variation in mean levels of the ambient air quality parameters measured across the sampling stations. The level of VOC was highest in SS C and that of SOx in SS A, B and C. The high levels could be attributed to proximity to gas flare stack. This is expected since any area near petroleum activities usually has higher levels of pollutants (Woodward and Riley, 1983). Accordingly, the level of Ni at SS B and SS D indicates the proximity of these sampling stations to the gas flare stack. However, the levels of Cu, Hg and Mn did not vary across the sampling stations. Ozone did not also vary across the sampling stations and this could be attributed to the very low concentration of NO_2 which is a precursor to ozone formation.

The observed significant differences in levels of Fe, Ni and Co between the wet and dry seasons indicate that the seasons affected the availability of these pollutant

species during the study period in the area. This could be attributed to higher availability in ambient air during periods of low precipitation (dry season) and low availability during periods of high precipitation (wet season).

The absence of significant correlations between the levels of heavy metals in ambient air and soil matrices indicate that their sources in soil was not from the gas flare outfalls but from geogenic origins. Heavy metals in soils have been documented to originate from rocks.

5.2. Conclusion

The contributions of heavy metals and other pollutants in ambient air and soils from the Agbada II Oil Flow Station were minimal, with both spatial and seasonal variations in their levels.

5.3. Recommendations

- A strong technological basis should be developed to harness Nigeria's gas potentials.
- Water analysis should be carried out regularly on the area to ascertain the portability of the community's drinking water.

- The company should take care of the community's basic needs and pay huge attention in terms of compensation and medical care.
- The gas should be liquefied and bottled for domestic and industrial purposes.
- Residential areas should be situated at a minimum distance of 1km from the gas flare stack so as to reduce the detrimental effects of pollutant gases as well as heavy metals on the inhabitants of Igwuruta community.

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LIST OF APPENDICES

APPENDIX 1. Ambient Air Quality Parameters around Gas Flare Station in Agbada II Flow Station

Sampling Stations	CO (ppm)	SOx (ppm)	NOx (ppm)	SPM (ppm)	VOC (ppm)	H_2S (ppm)	Ozone (ppm)	Smoke Density
SS A	2.40	0.01	0.00	80.00	0.00	0.001	0.01	low
SS B	2.00	0.01	0.00	80.20	0.00	0.001	0.01	Low
SS C	2.20	0.00	0.00	75.00	0.01	0.001	0.01	Low
SS D	2.30	0.01	0.00	80.20	0.00	0.001	0.01	Low
SS Control	1.20	0.01	0.00	70.00	0.00	0.001	0.01	Low
DPR Limit	10	0.1	0.06	250	NA	0.008	0.1	NA

APPENDIX 2. Levels of Heavy Metals in ambient air around Gas Flare Station at Agbada II Flowstation

Sampling Stations	As (ppm)	Pb (ppm)	Cu (ppm)	Ni (ppm)	C0 (ppm)	zn (ppm)	Hg (ppm)	Fe (ppm)	Cd (ppm)	Mn (ppm)
SS A	2.30	0.50	0.00	80.00	0.20	0.001	0.00	0.40	0.10	0.00
SS B	2.00	0.60	0.00	80.20	0.20	0.001	0.00	0.50	0.20	0.00
SS C	2.00	0.80	0.00	75.00	0.40	0.001	0.00	0.20	0.30	0.00
SS D	2.10	0.01	0.00	80.20	0.30	0.001	0.00	0.20	0.00	0.00
SS Control	1.20	0.01	0.00	70.00	0.20	0.001	0.00	0.00	0.00	0.00

APPENDIX 3. Meteorological variables of the study area

Sampling Stations	Wind speed (m/s)	Ambient Temp (^{o}C)	Pressure (PSI)	Wind Turbulence	Sun Radiation	Wind Direction	Relative Humidity (%)	Precipitation
SS A	0.2	29.2	1090	LOW	SUNNY	NS	75	Low
SS B	0.3	29.0	1060	LOW	SUNNY	NS	73	Low
SS C	0.3	29.0	1120	LOW	SUNNY	NS	70	Low
SS D	0.2	29.0	1004	LOW	SUNNY	NS	70	Low
SS Control	0.3	27.2	1003	LOW	SUNNY	NS	70	LOW

APPENDIX 4. Pair wise Comparison in Levels of ambient Air Quality Parameter between the Wet and Dry Seasons using Student's t-test (P<0.05)

Paired Samples Statistics

		Mean	N	Std. Deviation	Std. Error Mean
Pair 1	CO_Wet	2.0200	5	.48166	.21541
	CO_Dry	1.9400	5	.46690	.20881
Pair 2	SOx_Wet	.0080[a]	5	.00447	.00200
	SOx_Dry	.0080[a]	5	.00447	.00200
Pair 3	SPM_Wet	77.0800	5	4.54004	2.03037
	SPM_Dry	82.0000	5	5.70088	2.54951
Pair 4	VOC_Wet	.0020[a]	5	.00447	.00200
	VOC_Dry	.0020[a]	5	.00447	.00200
Pair 5	As_Wet	1.9200	5	.42071	.18815
	As_Dry	1.4400	5	.87636	.39192
Pair 6	Pb_Wet	.3840	5	.35809	.16014
	Pb_Dry	.3420	5	.20327	.09091
Pair 7	Ni_Wet	77.0800	5	4.54004	2.03037
	Ni_Dry	59.0800	5	13.42431	6.00353
Pair 8	Cobalt_Wet	.2600	5	.08944	.04000
	Cobalt_Dry	.0420	5	.08843	.03955
Pair 9	Fe_Wet	.2600	5	.19494	.08718
	Fe_Dry	.0220	5	.02280	.01020
Pair 10	Cd_Wet	.1200	5	.13038	.05831
	Cd_Dry	.0120	5	.01304	.00583

a. The correlation and t cannot be computed because the standard error of the difference is 0.

APPENDIX 5. Levels of heavy metals in soils around the Gas Flare at Agbada II Flow Station

Heavy Metals (mg/kg)	Sampling Stations (SS)				
	A	B	C	D	Control
Pb	25.05	15.16	10.24	10.02	6.30
Hg	ND	ND	ND	ND	ND
As	8.20	6.40	2.60	ND	ND
Cd	9.40	5.60	6.10	4.60	2.70
Cu	60.80	38.50	40.10	35.40	20.38
Ni	10.40	14.60	13.42	12.84	7.18
Zn	20.20	15.45	18.52	16.82	10.28
Co	ND	ND	ND	ND	ND
Fe	20.50	24.80	20.80	25.40	20.90
Mn	50.50	50.00	60.80	50.22	40.80

APPENDIX 6. Test of Homogeneity in mean variance (One-way ANOVA)

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
SS_A	Between Groups	10517.124	5	2103.425	60078.780	.000
	Within Groups	.210	6	.035		
	Total	10517.334	11			
SS_B	Between Groups	10578.317	5	2115.663	45815.619	.000
	Within Groups	.277	6	.046		
	Total	10578.594	11			
SS_C	Between Groups	9233.611	5	1846.722	24821.535	.000
	Within Groups	.446	6	.074		
	Total	9234.057	11			
SS_D	Between Groups	10595.981	5	2119.196	317879.434	.000
	Within Groups	.040	6	.007		
	Total	10596.021	11			