EFFECTS OF GAS FLARING ON CASSAVA CROP AT AGGAH-EGBEMA IN OGBA/EGBEMA/NDONI LOCAL GOVERNMENT AREA OF RIVER STATE

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CERTIFICATION

We certify that this work **"EFFECTS OF GAS FLARING ON CASSAVA CROP AT AGGAH-EGBEMA IN OGBA/EGBEMA/NDONI LOCAL GOVERNMENT AREA OF RIVER STATE"** was carried out by **EZEKWE ACHINIKE CHIGOZIE (REG. NO: 20085632828**) in partial fulfilment for the award of the degree of Masters of Science (M.Sc.) in Environmental Technology (Pollution Control Option) in the Department of Environmental Technology of the Federal University of Technology, Owerri.

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DEDICATION

This research work is dedicated to God Almighty for giving me the insight to choose this topic and the good health granted me.

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ABSTRACT

The current research investigated the bioavailability of gas flare pollutant fallouts in crop tissues via the soil repository matrix around the Aggah-Egbema Oil Flow Station in Ogba/Egbema/Ndoni Local Government Area of Rivers State. Three sampling locations were established at 1, 2 and 10 km from the gas flare stack. Ambient air quality for SOx, NOx, COx, H_2S, suspended particulate matter (SPM_{10}), petroleum hydrocarbons, and trace metals (Cd, Cr, Pb, Mn, Va, Zn) were determined with High Volume Sampler and Digital Automatic Gas Monitors according to standard methods. Soil samples were collected with stainless auger, while cassava (*Manihot esculenta*) leaves and tubers were harvested and taken to the laboratory. Air, soil, and crop leaves and tuber samples were analyzed for trace metals concentrations with Varian Spectra AA 600 atomic absorption spectrophotometer. Descriptive statistics was employed in the presentation of ensuing data. The one-way analysis of variance (ANOVA) was used to determine equality in spatial mean variances in the matrices (air, soil, and crop leaves and tubers), while correlation (r) was used to investigate their relationships. The principal components analysis (PCA) was used for data reduction as to remove redundant variables from the data file. Cd, Cr and Pb concentrations varied from 0.010-0.050 (0.023 ± 0.005), 0.010-0.030 (0.014 ± 0.002) and 0.010-0.040 (0.019 ± 0.004) ppm in air samples. However, they ranged from 0.050-1.220 (0.462 ± 0.149), 0.210-0.420 (0.294 ± 0.026) and 0.020-0.080 (0.048 ± 0.008) mg/kg in soil samples. They ranged from 1.440-3.010 (2.099 ± 0.177), 0.710-1.100 (0.892 ± 0.044) and 0.040-1.005 (0.324 ± 0.132) µg/kg in leave samples and 2.300-5.000 (3.476 ± 0.336), 1.200-1.500 (1.342 ± 0.038) and 0.062-1.210 (0.446 ± 0.174) µg/kg in crop tubers. Pb concentrations in air samples correlated at $P<0.05$ with its concentration in crop leaves, even as Mn in soil correlated highly with concentrations in crop leaves and tubers ($P<0.01$). Va in soil correlated with crop tuber concentrations at $P<0.05$. There was significant spatial inequality in mean variances of the parameters measured at $P<0.05$ in air [$F_{(22.49)}>Fcrit_{(3.88)}$], soil [$F_{(28.07)}>Fcrit_{(3.88)}$], cassava leaves [$F_{(13.09)}>Fcrit_{(3.93)}$] and cassava tubers [$F_{(14.68)}>Fcrit_{(3.93)}$]. Five PCs (pH/total N, Cd, Va, Zn, Pb) formed the extracted solution of the original variables and explained about 96% of the variability in the original 25 variables subjected to the PCA.

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background of Study

Crude oil is a complex mixture of mainly hydrocarbons with varying physical, chemical and biological properties. According to Tokolo (1988), about 40% of the world's present energy supply comes from crude oil which is a mixture of many thousands of organic compounds of which more than three-quarters are hydrocarbon (Whittle *et al*., 1988).

Nigeria produces over 2.3million barrels of oil per day from its oilfields in the Niger Delta (Don-Pedro, 2009) and most of this oil comes from deposits containing associated natural gas. About 2 billion standard cubic feet of associated gas is produced everyday (Don-Pedro, 2009) and most of it is flared due to inadequacy in facilities for its utilization.

The environmental impact of gas flaring has since been ignored by governments, who have continued the prolongation of gas flaring phase-out dates since 2008 till date. With increasing production of crude oil since its discovery in 1956, gas flaring activities have also been on the increase.

Gas flaring is a major contributor to the emission of toxic gases and other gaseous pollutants. Like the combustion of other carbonaceous fuels, gas flaring produces oxides of carbon (CO_X), sulphur (SOx) and nitrogen (NOx), water vapour, volatile and non-volatile forms of trace metals (e.g. Pb, Hg, Cd, As, etc) (Oghenejoboh, 2005). Incomplete combustion of the flared gas also produces greenhouse gases (such as methane), other gaseous pollutants (such as CO), and organic elemental participates (such as coke) (Ogwejifor, 2000).

Gas flaring generates heat around flare stacks, a phenomenon that could induce insomnia, especially in the night (since the area is permanently bright red like day light) (Don-Pedro, 2009). Flares are also associated with high sound intensity (Ebuna, 1987). Particulate outfalls from flares contain polynuclear aromatic hydrocarbons (PAHs), acids and trace metals, which could cause lung cancer, cardiovascular and respiratory tract diseases (Agbo, 1997).

Other common effects of gas flaring are reduction in soil moisture content, thereby reducing its fertility, corrosion of house and other engineering structures as the flare pollutants (SOx and NOx) form acids in the presence of rain water. The acidification of rivers and streams could result in reduction in fishery catch and other aquatic biotypes through alteration of pH.

It is sad to note that despite the environmental damages caused by this activity, gas flaring also denies the country huge revenue. Between 1974 and 2004 alone, over 709048 cubic meters of gases were flared in Nigeria alone, totaling a cumulative revenue loss of about US $44,528, 808,000.00 (NES, 2008).

1.2 Justification

The Ebocha gas flare station is one of the major locations operated by the Nigerian Agip Oil Company Limited (NAOC) in the Niger Delta of Nigeria. The station houses gas flare stacks that have been burring for years now. Several researchers have confirmed that flares introduce toxic gases and other pollutants in the environment. The effects of these pollutants could range form air pollution, through soil, water, thermal to noise pollutions. Soil is one of the ecological components that are affected by these pollutions. Plants could thus incorporate these pollutants into their tissues. If these plant tissues are edible, man thus gets affected, especially due to his tertiary consumer positions in the trophic chain. Consumed food could contain elevated levels of these metals resulting from bioaccumulation and 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). Some, such as cancer are transgenic and could thus be transmitted to filial generations.

Unfortunately though, no research has been undertaken to assess the level of possible accumulation of toxic trace metal outfalls from the gas flare station, even as inhabitants are agrarian and their farmland located in the vicinity of the flow station. It is in an attempt to close this gap that the current research was embarked upon.

1.3 Aim and Objectives

The aim of this research is to establish a possible relationship between gas flare pollutant fallouts and their concentrations in crop tissues via soil matrix around the point of pollution. To achieve the aim, the research had the following objectives.

- Determinations of the concentrations of trace metals (and other pollutants) in ambient air, soil and crop (*Manihot esculenta*) samples around the gas flare station.
- Determination of the relationships between trace metals composition in air, soil and crop parts grown around the gas flare station.
- Determination of longitudinal spatial variation in concentrations of the trace metals in air, soil and crop tissues.
- Determination of the pollutant components that contributed significant maximal variabilities in the original variables.

- Establishment of the normality of distribution of the variable components.

1.4 Significance of Study

Findings from this research could be useful in the following areas:

1. Provision of information on the impacts of the gas flare station on soil and food crops of residents of the area.
2. Alert resident food crop consumers on the levels and contributions of toxic metals from gas flaring.
3. Assist policy makers on the need to enforce strict adherence to regulations necessary for the protection of the environment.

1.5 Scope and Delimitation of Study

This study restricts its coverage on gas flare fallouts, with particular interest on the trace metals. It thus measured the concentration of oxides of sulphur (SOx), carbon (COx) and nitrogen (NOx), hydrogen sulphide, and hydrocarbons in ambient air around the gas flare station, trace metals (Cd, Cr, Pb, Mn, Va and Zn), pH, organic carbon, total nitrogen, and nitrate in soils, and trace metals (Cd, Cr, Pb, Mn, Va, and Zn) in cassava crop leaves and tubers. Cassava was chosen since it is the staple food of inhabitants of the study area.

The study was conducted in the vicinity of the Ebocha gas flare station in Ogba/Egbema/Ndoni Local Government Area of Rivers State in the Niger Delta region.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Gas Flaring and the Environment

Oil industry activities all over the world, carry the associate risk of environmental pollution. The Niger Delta area is the hub of the oil and gas industry in Nigeria and this region is encumbered with most of the industry's installations and activities and their concomitant deleterious environmental impact.

In this region, the industry operates over a thousand producing wells, gas plants, a network of thousands of kilometers of pipelines, criss-crossing the delta, carrying crude oil to flow stations, terminals and refines spread across the region (Onosode 2003). Several petroleum services and hydrocarbon dependent industries, including petrochemical, nitrogenous fertilizer and other plants have also sprung up in the Niger Delta region to take advantage of ancillary opportunities created by the oil industry.

During the process of extraction of crude oil at the flow stations, associated gases are vented through open flares, and according to Oghenejoboh (2005), gas flaring is a major contributor to the emission of toxic gases into the atmosphere. Gas flares produce oxides of carbon (COx), sulphure (SOx) and nitrogen (NOx), water vapour, volatile and non-volatile trace elements (such as Pb, Hg, Cd and As) (WHO, 1988). Incomplete combustion of flare gases could also produce greenhouse gases (e.g. CH_4), other pollutants (e.g. CO), and organic elemental particles (e.g. Coke) (Oyekunle, 1999).

The emitted gases and compounds in the atmosphere are deposited on the earth as acid depositions. Acid depositions could either be wet or dry, depending on the state of matter in which it is incorporated and transported (EPA, 2003). Wet depositions are commonly in the forms of acid rain, fog, and snow, while dry depositions are in the forms of acidic gases and particles.

Acid rain refers to a precipitation that has a pH less than 5.6 (the pH of unpolluted water is <5.6) (Cowling, 1982). About half of the acidity in the atmosphere falls back to the earth through deposition. The dry depositions are blown farther away and could be washed by rainstorms. Runoff water adds those acids to the acid rain, thus, making the combination more acidic than the falling rain alone and is introduced both in deeper soils and on the aquatic habitat (US EPA, 2003).

The acidity of rainwater is increased by the presence of particulate matter, which may contain trace metals such as As, Pb, Cd, and Hg that could alter pH (Oghenejoboh, 2005). In the overall, acid deposition causes a cascade of effects or kills individual edaphic or aquatic organisms (depending on the ecosystem), reduce their population, completely eliminate their species and decrease overall biodiversity (Ogwejifor, 2000; US EPA, 2003).

2.2 Trace/Heavy Metals

The term heavy metal refers to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentration (Agarwal, 2009). The term “trace” metals identifies the low concentrations that these elements are required for biological utilizations. However, the two terms could be inter-used. Example of heavy metals include Mercury (Hg), Nickel (Ni), cadmium (Cd), Aluminum (Al), chromium (Cr), lead (Pb), copper (Cu), Arsenic (As), Zinc (Zn), iron (Fe), etc. Heavy metals are natural components of the earth’s crust and cannot be degraded or destroyed. To a small extent they enter our bodies through food, drinking water, and air. As trace elements, some heavy metals (e.g. copper, selenium, zinc) are essential to maintain the metabolism of the human body (Sharma, 2006).

However, at higher concentrations, they can result to poisoning. Heavy metal poisoning could result, for instance, from drinking water contamination (e.g. lead pipes), high ambient air concentrations near emission sources (Oghenejoboh, 2005) or intake via the food chain (Aremu *et al.*, 2010).

Heavy metals are dangerous because they tend to bioaccumulate.

Bioaccumulation means an increase in the concentration of a chemical in a biological, compared to the chemical's concentration in the environment. According to Idodo-Umeh and Ogbeibu, (2010), heavy metal compounds accumulate in living things any time they are taken up and stored faster than they are broken down (metabolized) or excreted.

Increasing urbanization and technological advancement are twin contributors of pollutants, including heavy metals in the environment at high concentrations.

Soil represents the major repository of trace element over geologic time. On a worldwide basis, soil exhibits an average composition close to the crust, but the near surface parent materials from which soils are derived are not uniform and soil forming processes differ markedly from one climatic region to another (accounting for considerable overall variability in trace metals concentration) (Arun*et al.*, 2005).

Trace metals, such as Cd, Cu, Pb, Cr and Hg are important environmental pollutants, particularly in areas with high anthropogenic pressure. Their presence in the atmosphere, soil and water, even in traces, can cause serious problems to all organisms. Heavy metal accumulation in soils is of concern in agriculture production due to the adverse effects on food quality (safety and marketability), crop growth (due to phytotoxicity) and environmental health (soil flora/fauna and terrestrial animals)(Zhuang *et al*., 2009).

The mobilization of heavy metals into the biosphere by human activities 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 rate (Ogbonna *et al*., 2009). Heavy metal bioaccumulation in the food chain can be highly dangerous to human health. These metals enter the human body mainly through two routes namely, inhalation and ingestion; with ingestion being the main route of exposure to these elements in human population (Aremu, *et al*., 2010). Heavy metals in-take by human population through the food chain has been reported in many countries with this problem receiving increasing attention from the public as well as governmental agencies, particularly in developing countries, (Idodo-Umeh and Ogbeibu, 2010).

Agarwal (2009) observed that heavy metals settled after emission from a zinc smelter. Their deposition showed large variation from metal to metal and site to site. The value of iron which was even otherwise, present in high concentration ranged from 6940-1315ppm (on dry weight basis) because the area is rich in iron ores. Zinc concentrations under the influence of zinc smelter emission were highest and varied from 290-1990ppm. Manganese and lead content in soil ranged from 200-590ppm and 10-34.5ppm respectively, and these were followed by copper (10-77ppm)

Aerosols contain different toxic metals which fall on the soil and are retained in the top few centimeters and are subsequently carried down by leaching, presumably due to their interaction with soil colloids (Arun *et al.*, 2005). They are therefore liable to be quite persistent in the soil. Once deposited, metal-containing materials are subject to chemical and microbial modifications. With metal solubility, ultimately approach in the thermodynamic equilibrium with native soil minerals and organic matter, the rate and extent of solubilization are governed by the physicochemical properties of the deposited mineral, soil processes and properties (Graig, 1987).

Particulates arising from fossil fuel combustion, metal smelting operation etc may be expected to be largely insoluble in soil solution. Hydrolyzable metals (for example nickel, cadmium) or metal forming insoluble precipitate with sulphur and phosphorous on entering the soil-soluble form may be expected to be rapidly solubilized at near neutral pH of most soil due to hydrolysis on dilution and subsequent precipitation on, or reaction with particle surface (Graig, 1987).

Certain elements (for example iron) may also form precipitates with sulphur or phosphorus.

Metals with low ionic potential tend to form primarily simple soluble ion while metals with intermediate and high ionic potentials tend to form soluble complex. Common inorganic complex forming ions in the soil solution include CO_3^{2-}, HCO_3^- SO_4^{2-}, HS^-, OH^- and Cl^-. Soil microorganism may play an important role in this process through the production of soluble ligands with high affinity for metals (Arun,*et al*., 2005).

Soil physico-chemical parameters that are most important in influencing the solubility of metals include soil composition (inorganic or organic), pH, type and density of change on soil colloids and reactive surface area (Graig, 1987). These phenomena will be dependent upon soil properties, including metal concentration and form; particles size distribution, quantity and reactivity of hydrous oxides, mineralogy, degree of aeration and microbial activity (Sharma, 2006).

Observation shows that the mobility of heavy metals decrease in soil with inorganic matter, as compared to the soil will decomposed organic matter. This may be due to the high adsorption capacity of the soil organic matter associated with clay particles due to clay-meal soil-organic matter interaction (David and Peter, 1987). The mobility order observed was Ni < Mn Cr < Cu < pb. This trend in the reverse order of their binding capacities with soil organic matter means that there will be decrease in mobility (Sharma, 2006).

Disposal of industrial, as well as domestic sewage sludge and domestic wastes on land is a common practice. One of the major problems with land disposal of sludge is the likely introduction of heavy metal in the soil. In general, sludge solution appears to increase the mobility of trace element in soil. Increase in mobility of trace elements is often attribute to a combination of factors, including complexation by dissolved organic, inorganic ligand, high background concentration of metals and other ions and high ionic strength of amended soil solution.

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).

2.3 Effects of Trace Metals on Soils

Trace metals are considerable environmental concern due to their toxicity and accumulative behaviour (Purves, 1985; Omgbu, 1992). Trace quantities of certain heavy elements are essentially assimilable and accumulate in ecological materials (Nurnberg, 1984) such as soil. According to Kakulu (1985) and Omgbu and

Kokogho (1993), comprehensive studies of trace metals in various Nigerian crude oils have shown them to contain relatively high concentrations of Fe, Cu, Zn, Pb and Hg. Associated gases, when flared could release these pollutants as outfalls on soil (Ademoroti1996; Ogundipe, 2006) and such could exert adverse effects on edaphic variables and biota necessary for soil health (Adesiyan, 2005). The contaminants could further infiltrate ground water aquifers (Ogbonna *et al.,* 2006) and so pose public health hazards (Ogbonna *et al*., 2008). A salient case of public health danger from trace metals poisoning of the environment is the recent lead poisoning reported by the June 26th edition of the Saturday Sun Newspaper; whereby many deaths were recorded (and still counting)(Saturday Sun, 2010).

Contaminated soils could result in decline in crop productivity and sustainability (Hart *et al*., 2005). Trace metals have bioaccumulation potential due to their persistence in the environment. This attribute enables them to get translocated along the food chain, albeit in small doses. Over time they accumulate and magnify across the trophic levels to pose serious health hazards to tertiary consumers such as man (Agbaire and Esiefarienrhe, 2009).

Trace metals absorption is governed by soil characteristics such as pH and organic matter content (Agbogidi *et al.,* 2006). This thus portend that high levels of trace metals in soil may not always indicate similar high concentrations in plants, as the extent of accumulation will depend on the plant and trace metal species under consideration (Hart *et al*., 2005). In an investigation of the uptake of Cd, Cu. Ni and Pb from air and soil by milfoil (*Achillea millefolium*) and barley (*Hordeum Vulgare*) in Denmark, it was concluded that Cu and Pb plant concentrations correlated with aerial deposition but not with soil concentrations. In contrast, Ni and Cd contents in plant correlated with deposition and soil content (Hart *et al*., 2008).

According to Ma *et al*. (1994), Msaky and Calvert (1990) and Fergusson (1990), trace metal accumulation in soils is of concern in agricultural production due to the adverse effects on food quality (safety and marketability), crop growth (due to phytotoxicity), and environmental health (soil/fauna and terrestrial animals). The mobilization of these metals into the biosphere by human activities has become an important process in the geochemical cycling of these pollutants. This is acutely evident in urban areas where various stationary and mobile sources releases large quantities of trace metals into the atmosphere and soil, exceeding the natural emission rates (Nriagu, 1989; Bilos *et al.*, 2001).

2.4 Effects of Trace Metals on Crops

Crops provide nutritional needs of both man and animals. Man in turn also consumes the animals. Some trace metals such as Pb, Zn and Cd, etc are related to environmental problems such as gas flaring, and also have accumulative properties in both soil, plant tissues, and man (Onyedika and Nwosu, 2008). Traces of these metals though can be found naturally in the environment, but industrial activities increase their levels and so lead to pollution (Adediran *et al*., 1990). In the oil rich Niger Delta region of Nigeria, one of the major sources of these trace metals, especially at elevated concentrations is oil and gas activities (Hart, *et al*., 2005).

Trace metals are mainly absorbed through leaves, roots and aerial deposition (Flam, 1978; Onyedika and Nwosu, 2008) and their accumulation by plants greatly influenced by suuplies from soil (Abbdel-Sabour and Mortvedt, 1998; Honma and Hirata, 1978; Haghiri, 1974). However, high levels of trace metals in soil could indicate similar concentrations in plant by accumulation at concentrations causing serious risk to human health when consumed (Vousta *et al*., 1996). More so, constant exposure to very low levels of elements such as Pb, Cd and Hg have been shown to have cumulative effects since there is no homeostatic mechanism which can operate to regulate their toxity (Carter and Fernando, 1979; Yeast and Brewers, 1983).

Recent work (Osu and Odoemelam, 2007) has revealed elevated trace metals concentrations in edible grains grown and marketed, trace metals in crops harvested in some oil producing locations(Hart *et al*., 2005), bioaccumulation of heavy metals in periwinkle and oyster (Fubara and Christian, 2006) and the concentrations of Pb, Zn and Cd in root crops from other mineralized areas and environment (Onyedika and Nwosu, 2008).

The consumption of vegetables and fruits as food offer rapid and least means of providing adequate vitamins supplies, minerals and fibre. In Aggah-Egbema community for example, vegetables used as food include those used in making soup or served as integral parts of the main sources of meal. Each crop species has its nutritive requirements differing from others. Thus, different plants supported by identical solutions will contain varying concentrations of micro- and macro-elements (Akan *et al.*, 2009). According to Ihekeronye and Ngoddy (1985), application of industrial effluent decreases the budding and growth rate of vegetables. Additionally, the excessive application of nitrogen and other inorganic fertilizers and organic manures to these vegetables can accumulate high levels of nitrate and other anions as well as trace metals (Akan *et al.*, 2009). Consequently, their consumption by humans and animals can pose serious health hazards.

Although some heavy metals such as Cu, Zn, Mn and Fe are essential in plant nutrition, many of them do not play any significant role in the plant physiology (Akan *et al.*, 2009). The uptake of these heavy metals by plants, especially leafy vegetables is an avenue of their entry into the human food chain with harmful effects on health (Ihekeronye and Ngoddy, 1985).

2.5 Growth Response of Vegetables to Heavy Metals

Crop plants growing on trace metal contaminated soil can accumulate high concentrations of the elements to cause serious health risk to consumers (Islam *et al*., 2007). According to a study by Long *et al*. (2003) on the effects of Zn on plant growth of three selected vegetable (Chinese cabbage, celery and packchoi), excess Zn in growth media caused toxicity to all three vegetable crops. Toxicity symptoms included chlorosis in young leaves, browning of coralloid roots, and serious inhibition on plant growth, shoot fresh weight progressively decreased with increasing Zn concentrations. Large differences in Zn tolerance were also noted among the three vegetable crops. Celery was more sensitive to higher Zn levels and reduced shoot growth than Chinese cabbage and Pakchio. Shoot fresh weight decreased to approximately 63%, 73% and 36% of the control for Chinese cabbage, pakchoi and celery, respectively when plants were grown at Zn level of 50 mg/L.

Xiong and Wang (2005) showed that seed germination was significantly adversely influenced by Cu ($P<0.001$) in *Brassica Pekinensis*. The 0.5mmol/L Cu treatment remarkably reduced the germination rate, and the LC_{50} (median lethal concentration), calculated as the lethal effect on seed germination, was 0.348 mmol/L. Root and shoot lengths of the young seedlings were also inhibited by Cu, but stimulatory elongation of the shoots occurred with the 0.008mmol/L treatment.

Further investigations by Zhang and Zhou (2005) revealed that the Al-based coagulants at the tested concentrations had a poisonous effect on the germination of vegetable. There were positive curvilinear or linear relationships between the inhibitory rate of seed germination and the concentration of Al in the acidic and neutral conditions, except for the toxic effects of polyaluminum-chloride (PAC) on *Brassica chinensis* in the neutral condition. However, there were obvious differences in root elongation of *B. chinensis* exposed to $AlCl_3$ at various pH levels.

Elevated Cu levels in growth media caused toxicity to all the three vegetables, resulted in chlorosis in new leaves, brown, stunted, coralloid roots, and plant growth was inhibited (Yang *et al.*, 2002). Shoot fresh weight progressively decreased with increasing Cu levels in the nutrient solution. Great differences in Cu tolerance were also noted among the three vegetable crops. Shoot fresh weight of pakchoi, celery and Chinese cabbage decreased to about 33%, 37% and 50% of the control, respectively, when grown with Cu supply of 10mg/L. Those results indicate that celery is more tolerant to the toxicity of Cu than Chinese cabbage or pakchoi grown in nutrient solution, as also observed by Islam *et al.*(2007).

Other studies conducted on vegetables such as celery, Chinese cabbage and winter greens by Ni *et al*. (2002) revealed that no nutrient deficiency or toxicity symptoms caused by Cd were visible on any plant. Biomass productions of root and shoot for Chinese cabbage and winter greens, as well as root, petiole and leaf blade for celery, expressed as shoot fresh weight were not significantly different among the treatments.

2.6 Heavy Metals uptake and Accumulation in Vegetable parts

Plant species and varieties vary in their capacity for heavy metal accumulation. Long *et al*. (2003) showed that zinc uptake and accumulation by shoots and roots varied with Zn levels in growth media and vegetable types. Both shoot and root Zn concentrations increased sharply with increasing Zn concentrations for Chinese cabbage, celery and pakchoi. However, shoots contained over 3-fold less Zn than roots when grown under nutrient solution culture conditions. The three vegetable crops differed greatly in their ability to take up Zn from the growth media and to transport it to the shoots. At an external Zn level of 25 mg/L, shoot Zn concentration of Chinese cabbage was almost 2-fold lower than that of pakchoi or celery. Zinc concentration in the edible part of celery was nearly 2-fold higher than that of the other two species when grown at higher Zn levels (50 mg/L). Moreover, under soil culture conditions, the zinc accumulation coefficient (AF) in shoots increased for pakchoi, but decreased for celery and Chinese cabbage when soil available Zn was raised from 10 to 172 mg/L. However, root Zn AF increased to varied extents, with increasing soil Zn for all the vegetables. Celery showed highest AF in edible parts at low soil Zn (i.e. in control), whereas pakchoi had the higher AF of Zn at higher soil available Zn levels. The AF for zinc in edible parts of the three vegetable crops decreased in the order pakchoi>celery (stem)>Chinese cabbage. Significant positive correlations were noted between shoot Zn and soil available Zn level (long *et al*., 2003). Zn threshold for human health has been established to be 20mg/kg (Chinese Department of Preventive Medicine, 1995).

Ni *et al*. (2002) studied the effect of Cd on the growth of three vegetable crops i.e. Chinese cabbage (*Brassica chinensis* L cv. Zao-Shu 5), winter greens (*B. rosularis* var. Tsen et Leecv. Shang-Hai-Qing), and celery (*Apiumg graveolens* L. var. dulce DC). Their results indicated that the Cd concentration in shoots and roots varied both with different Cd levels and type of vegetable. Generally Cd accumulation in various plant parts in vegetable crops increased with the increasing cadmium concentrations in the growth medium. Root Cd increased more sharply than shoot Cd. Celery contained higher Cd in edible parts than other vegetable species.

Yang *et al*. (2002) studied the response of three vegetables to Cu toxicity and found that Cu levels in both root and shoot increased, but root Cu concentration increased more sharply than shoot with increasing Cu levels in growth media. Cu mainly accumulated in roots while a small fraction (10-20%) of absorbed Cu was transported to shoot. Celery accumulated higher Cu contents both in roots (1557 mg/L) and shoot (166.7 mg/L in leaves).

Copper AFs in the shoots of vegetable species were relatively small when grown at soil addition Cu levels of 200-400 mg/kg and dramatically increased at soil addition Cu levels above 600 mg/kg.

While investigating copper toxicity and bioaccumulation in Chinese cabbage (*Brassica pekinensis*Rupr), Xiong and Wang (2005) found that Cu concentration on the shoots was significantly influenced by Cu treatment ($P<0.001$). Cu concentration increased markedly with an increase in the soil Cu concentration. With a background level of 13.6 Cu (the control, 13.6 mg/kg dry soil), Cu concentration in the shoots was 9.9 mg/kg. With the 0.2 mmol/kg treatment, shoot Cu concentration rose to 42.5 mg/kg. With the 1.0 mmol/kg treatment, shoot Cu concentration was 119.0 mg/kg (1.9mmol/kg). According to the LSD test, shoot Cu concentration in both treatments was significantly higher than that in the control. These facts showed that when Chinese cabbage (cultivar Xiayangbai) plants were exposed to certain levels of Cu pollution, the shoots could accumulate a relatively high amount of Cu.

2.7 Soil Threshold values of potential Dietary Toxicity

Soil threshold for heavy metal toxicity is an important factor affecting soil environment capacity of heavy metal and determining heavy metal cumulative loading limit. For the soil-plant system, the heavy metal toxicity threshold is the highest permissible content in the soil (total or bioavailable concentration) that does not produce any phytotoxicity (i.e. inhibition of plant growth and decrease of yield), or the heavy metal in the edible parts of crops does not exceed the critical dietary heavy metal threshold for human health.

During the recent years, much effort was exerted to calculate the soil thresholds of potential dietary toxicity by different ways. The critical food Cu threshold for human health has been established to be 10 mg/kg (Chinese Department of Preventive Medicine, 1995). Yang *et al*. (2002) reported that from the regression lines between shoot DM yields and Cu concentration in plant tissue or soil, Cu thresholds for phytotoxicity (10% yield reduction) and potential dietary toxicity inedible parts of the vegetable could be calculated. Soil total and available Cu thresholds for potential dietary toxicity in the edible parts of vegetable crops were 5-fold higher than those for phytotoxicity (at 10% yield reduction). Among the three vegetable crops, pakchoi had much lower soil total and available Cu thresholds, as compared with the other two vegetable species.

The critical dietary Zn threshold for human health has been established to be 20 mg/kg (Chinese Department of Preventive Medicine, 1995). Long *et al*. (2003) showed that from the regression equations between shoot yield or Zn concentration and soil total or available Zn, soil Zn thresholds for yield reduction (decreased 10%) and potential dietary toxicity in edible parts of the vegetables could be calculated. The total soil Zn thresholds for shoot dry matter yield reduction were higher for pakchoiand only slightly lower for celery (stem), than that for potential dietary toxicity. Soil available Zn thresholds for Zn potential dietary toxicity were 175.6, 74.9 and 101.0 mg/kg for Chinese cabbage, pakchoi, and celery (stem), respectively. For pakchoi, a higher soil available Zn threshold for yield reduction (10%) (103 mg/kg) was again noted relating to that for potential dietary toxicity(74.9 mg/kg). The lower soil available Zn threshold for Zn potential dietry toxicity for pakchoi than for the other vegetable species is mainly associated with its greater ability to absorb Znfrom the soil and to translocate and accumulate Zn in the shoots. These results indicate that some vegetable species, like pakchoi, may accumulate Zn in the edible part over dietary toxic threshold before yield reduction occurs. Based on the regression equation established in our study and the limit of Cd concentration in vegetable products (0.05 mg/kg fresh weight, GBN 238-84 in China), the threshold of Cd concentration in growth media was evaluated as 0.5 mg/kg of soil extractable Cd for soil. The results indicated that the criteria for extractable Cd content in soil were 0.869, 0.730 and 0.489 mg/kg soil for Chinese cabbage, winter greens and celery, respectively (Ni *et al*., 2002).

2.8 Bioavailability of added Heavy Metal in the Vegetable Garden Soil

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 (Kuo *et al*., 1983). Metals such as Zn exist in soils in various fractions, chemical species or forms including exchangeable, carbonate-bound, oxide-bound, organic matter-bound and crystal lattic metals (Shuman, 1991). Availability of soil Zn to plants differs and may be governed by dynamic equilibrium among these fractions (Kiekens, 1990). The biologically active fractions of Zn in soils mainly consist of its soluble, exchangeable and complexed forms. Many studies showed that DTPA-extractable Zn is correlated well with plant uptake Zn (Arnesen and Singh, 1998; Miner *et al*., 1997). DTPA extractable Zn decreased progressively with incubation, 60-70% of added Zn was still extractable by the DTPA method (Long *et al*., 2003). The results showed that a major portion of the Zn added to the garden soil is phytoavailable, which is in agreement with other studies (Cajuste *et al*., 2000; Darmawa and Wada, 1999).

Total copper in soil includes six pools classified according to their physicochemical behavior. 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; and crystal lattice-bound Cu (Baker, 1990). When added to soil, Cu may react with soil constituents, changes its chemical form, then its availability to plants is also altered. The amount of soil Cu removed by a chemical chelating agent like DTPA or EDTA is considered as the plant available portion (Baker, 1990). 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 (Yang *et al*., 2002).

Although the amount of soil heavy metal removed by a chelating agent like DTPA or EDTA is considered to be the plant-available portion, many results have shown that the concentration of Pb is not well correlated to the amount of plant uptake (Yang and Zhang, 1993). Some results showed that significant and positive correlations existed between shoot Pb and soil NH_4NO_3-extractable Pb levels (Song, 2002).

2.9 Soil-Plant-Man Relations Determining Heavy Metal Toxicity

Soil-to-plant transfer is one of the key components of human exposure to metals through the food chain. Lacatusu *et al*. (1996) studied soil-plant-man relationships in heavy metal polluted areas in Romania and detected significant overclark levels of Cd and Pb from the geogenic abundance viewpoint. Although the polluted soils were neutral to slightly alkaline and well supplied with organic matter, the soluble forms of heavy metals in EDTA-CH_3COONH_4, pH=7.0 represented on average 37% Cd, 17% Cu, 28% Pb and 14% Zn, respectively of their global concentration, exceeding the maximum allowable limits (MAL), for soluble forms, by on average up to 14.8 (Pb), 4.2 (Cd) and 2.1 (Zn) times. The relationship between their contents in plants and in soil (soluble forms) showed significant correlations for Cd, Cu, Pb and Zn. As a result, the contents of these elements in vegetable often exceed those allowable for normal human and animal consumption. In this case, if an adult consumed 2 kg potatoes, 2 kg tomatoes and 1 kg carrots in a week, his/her food would exceed by 12% the MAL for Cd (0.525 mg). The daily maximum allowable rate of ingested Pb (0.430 mg) could be reached by consuming 880 g of vegetables (equal parts of potatoes, tomatoes, carrots and cucumbers). The higher acidity of soils enhances the transfer of large amounts of heavy metals in soluble forms, exceeding MAL on average up to 23.4 (Pb), 2.1 (Cd), 2.8 (Cu) and 2.7 (Zn) times. As a result, the average Pb content in carrots was 10 times higher than the MAL and the Pb accumulation in the lettuce, parsley and garden orach, significantly above the critical contents. At the same time, the Cd content in the analyzed vegetables exceeded by 5 times the MAL, while the Cu and Zn contents were close to critical levels (Lacatusu *et al*., 1996). Ingestion of vegetables containing high concentrations of heavy metals is one of the main ways in which these elements enter the human body. Typical diseases recorded were Pb and Cd intoxication, saturnine encephalopathy, radial nerve paralysis and saturnine colic. The most affected group of inhabitants was children (Lacatusu *et al*., 1996). Estimates form various countries showed that the dietary intake for lead in adults is between 54 mg per day (Dabeca *et al*., 1987) and 412 mg per day (Dick *et al*., 1978), and that of cadmium is between 10 and 30 mg per day (Reilly, 1991). For zinc and copper, the estimated daily intake is from 1 to 3 mg, and 10 to 20 mg, respectively (Fox, 1982). Lacatusu *et al*. (1996) found that their estimations for lead and zinc were above those reported from other countries, whereas the estimations for cadmium were within the range. The levels of copper were observed to be below the estimation. Bahemuka and Mubofu (1999) suggested that a large daily intake of these vegetables is likely to cause a detrimental health hazard to the consumer.

Since the dietary intake of food may constitute a major source of long-term low-level body accumulation of heavy metals, the detrimental impact becomes apparent only after several years of exposure. Regular monitoring of these metals from effluents, sewage, in vegetables and in other food materials is essential for preventing excessive build-up of the metals in the food chain (Bahemuka and Mubofu, 1999).

2.10 Hazardous Effects of Heavy Metals on Human Health

Chronic low-level intakes of heavy metals have damaging effects on human beings and other animals, since there is no good mechanism for their elimination. Metals such as lead, mercury, cadmium and copper are cumulative poisons. These metals cause environmental hazards and are reported to be exceptionally toxic (Ellen *et al*., 1990). Vegetables take up metals by absorbing them from contaminated soils, as well as from deposits on parts of the vegetable exposed to the air from polluted environments (Zurera-Cosano *et al*., 1989).

Metal contamination of garden soil may be widespread in urban areas due to past industrial activity and the use of fossil fuels (Chronopoulos *et al*., 1997; Sanchez-Camazano *et al*., 1994; Sterrett *et al*., 1996; van Lune, 1987; Wong,1996). Heavy metals may enter the human body through inhalation of dust, direct ingestion of soil, and consumption of food plants grown in metal-contaminated soil (Cambra *et al*., 1999; Dudka and Miller, 1999; Hawley, 1985). Potentially toxic metals are also present in commercially produced foodstuffs (DEFRA, 1999). Exposure to potentially toxic metals from dust inhalation or soil ingestion is usually modeled simply as the concentration of contaminant measured in the soil multiplied by the quantity of dust inhaled or soil ingested (Konz *et al*., 1989). This is a conservative approach to estimate dose, because the bioaccessibility of heavy metals adsorbed on ingested soil is not 100% (Ruby et al., 1999). However, predicting 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 physiologic 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 (McKone, 1994).

Lead is toxic element that can be harmful to plants, although plants usually show ability to accumulate large amounts of lead without visible changes in their appearance or yield. In many plants, Pb accumulation can exceed several hundred times the threshold of maximum level permissible for humans (Wierzbicka, 1995). The introduction of Pb into the food chain may affect human health, and thus, studies concerning Pb accumulation in vegetables have increasing importance (Coutate, 1992). Although a maximum Pb limit for human health has been established for edible parts of crops (0.2 mg/kg) (Chinese Department of

Preventive Medicine, 1994), soil Pb threshold for producing safe vegetable are not available.

Knowledge of Zn toxicity in humans is minimal. The most important information reported is its interference with Cu metabolism (Barone *et al.*, 1998; Gyorffy and Chan, 1992). The symptoms that an acute oral Zn dose may provoke include tachycardia, vascular shock, dyspeptic nausea, vomiting, diarrhea, pancreatictis and damage of hepatic parenchyma (Salgueiro *et al.*, 2000). Although maximum Zn tolerance for human health has been established for edible parts of crops (20 mg/kg) (Chinese Department of Preventive Medicine, 1995), soil Zn threshold for producing safe vegetable is not available.

According to Hough *et al.*, (2004) under Part IIA of the Environmental Protection Act 1990, the UK government favors a “suitable for use” approach to redevelopment (DETR, 2000): Land is contaminated only if the current or intended use of a site has the potential to cause an unacceptable health risk to human occupants or to the environment. Under the UK Town and Country Planning Act 1990 (DETR, 2000), this approach requires that land be assessed for redevelopment on a site-specific basis. At present, concentrations of metals in the soil are compared to metals-specific “trigger values” (termed “maximum contaminant levels or maximum contaminant concentrations” in North America). In the past these trigger values were based on total contaminant concentration in the soil (ICRCL, 1987). More recently, the introduction of Contaminated Land Exposure Assessment (CLEA) (DEFRA and Environment Agency, 2002a) in April 2002 has replaced these trigger values with generic soil guidance values (SGVs) (DEFRA and Environment Agency, 2002b). The SGVs are considered a significant improvement on the previous ICRCL values and for Cd at least, soil pH categories are employed where food plants are to be grown. Where a soil exceeds the SGV, it is recommended that a risk assessment or remediation measure be conducted for the site in question (DEFRA and Environment Agency, 2002b). Additionally exceeding of an SGV indicates that some further risk management action be undertaken. However, the use of single trigger values of SGVs for most scenarios may represent a poor indication of the risk associated with a specific site. There is therefore requirement for site-specific risk assessment based on commonly measured geochemical and population parameters (Hough *et al*., 2004).

CHAPTER THREE

3.0 METHODOLOGY

3.1 Study Area

Aggah-Egbema, a town in Ogba/Ebema/Ndoni Local Government Area of Rivers State, Nigeria has a total land area of about 890 km^2 and a population of about 8500 people (NPC, 2006). Egbema within which Aggah-Egbema town is located lies within the coordinates of E 006° 33′57.50” N05°16′0.47” (Fig. 3.1).

The climate of the area is typical of rainforest zone of the tropics and average rainfall is about 200mm. Mean ambient temperature is 28^{0}C while relative humidity is about 88% (SPDC, 2002).

Wet season usually lasts between March and November while the dry season lasts for remaining four months (December-February). The soil is characterized by sandy-loam (SPDC, 2002).

The study area houses an oil flow station operated by the Nigerian Agip Oil Company Limited (NAOC). The flow station has gas flare stacks whose outfalls diffuse across the vast farmlands within (and outside) its vicinity. Residents of the area are predominantly agrarian and grow crops like yam, cassava, cereals and other vegetables. Comparatively minor fraction of the inhabitants is artisans, while few others are civil servants.

3.2 Experimental Design

The research was conducted in two phases-field sampling and laboratory analysis. Air, soil and crop samples were collected during field sampling while chemical analyses were conducted during laboratory analysis.

3.3 Field Sampling

3.3.1 Sampling Locations

Three sampling locations were chosen at 1 km (location 1), 2 km (location 2) and 10 km (location 3) from the gas flare stack.

3.3.2 Air Quality Monitoring

The sampling equipment used includes high volume sampler (HVS) and Digital automatic gas monitors.

1. **High Volume Sampler (HVS)**: The modified EPA gravimetric high volume method was used. This technique involved drawing a known volume of air

through a pre-weighted glass fibre filter (20 X 25cm) by means of heavy duty turbine blower at flow rate of 1.3m^3/min (Lahmann, 1992). This collected suspended particulate matter within the size range of 100-0.1μm diameters. Sampling was made at the three sampling locations.

2. **Digital automatic gas monitors (DAGMs)**. The Crowcon Gasman Air Monitor that had been pre-calibrated using air cylinder standard (SPDC, 2002) was used in the direct detection of COx, NOx, SOx, H_2S and HCs while the Hazdust 10 μm Particulate Monitor was used for the detection of particulate matter (SPM_{10}).

3.3.3. Soil sample collection

Replicate soil samples were collected with stainless soil augers at depth 0-15cm at the three sampling locations. Replicate samples from the respective locations were composited and taken to the laboratory in labeled polythene bags (Aremu *et al.*, 2010).

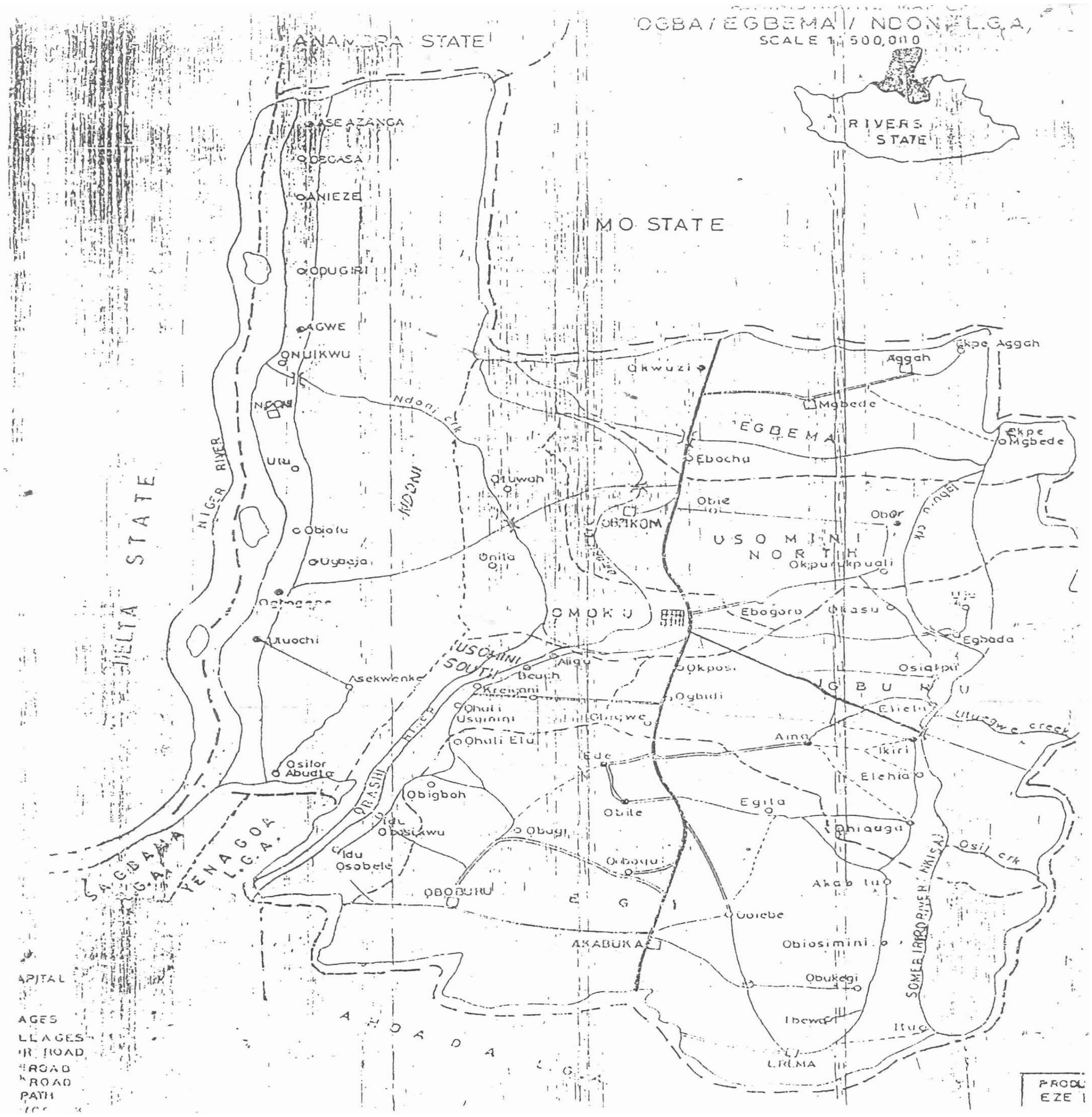

Fig. 3.1. Map of Ogba/Egbema/Ndoni Local Government Area showing the study location

Plate 3.1. Two gas flare stacks at the NAOC Flow station in Aggah-Egbema

3.3.4 Food Crop sample Collection

Leaves and tubers of cassava (*Manihot esculenta*) grown in farms at the three sampling locations were collected. Leaves were collected with stainless steel knife while tubers were harvested from the crop at the outset of harvesting season (October) and taken to laboratory.

3.4 Laboratory analysis

3.4.1 Sample Preparation

Trace metal particles collected with glass fibre filters of the HVS were extracted with concentrated H_2SO_4. Soil and crop parts samples were air dried. After drying, the soils were ground into fine particles using the laboratory mortal and pestle. The fine soil particles were sieved using a 2mm mesh sieve. The finer soil particles were packed in sample bottles and labeled.

Each crop part was oven dried at 105^0C for 2 hours. The dried samples were then ground into powder using Author Thomas milling machine, sieved as in soil samples and appropriately labeled. (Aremu *et al.*,2010).

A portion, (0.5g), of each soil and crop sample was weighed using Metler balance (AE 160) into50ml pyrex glass beakers. Concentrated 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 placed on the heater for about 3 hours (Udo and Ogunwale, 1978) to digest properly.

3.4.2 Sample analysis

The concentrations of Cd, Cr, Pb, Mn, Va and Zn in the four matrices (air, soil, crop leaves and crop tubers) were determined with an atomic absorption spectrophotometer (Varian Spectr AA 600 model).

3.4.3 Determination of other edaphic variables

3.4.3.1 Soil pH

This was measured in 1.25 slurry of soil in water using corning pH meter (model 7) (Jackson, 1964). The pH was determined by dipping the electrode into the 1:25 soil water suspension that had been stirred and allowed to settle for 1 hour.

3.4.3.2 Organic Carbon

Organic carbon was determined by the wet combustion method of Walkey and Black (1934) as modified by Jackson (1964).

10ml of IN potassium dichromate was added to a flask, which contain 1g of soil sample. The mixture was swirled gently to disperse the soil. 20 ml of conc. H_2SO_4 was added with a pipette and the flask swirled more vigorously for 1 minute and then allowed to stand for further 30 minutes. At the end of this period, 100ml of distilled water and 3 drops of 0.025M ferrous indicator were added and titrated with 0.5N ferrous sulphate solution. Percentage organic C was calculated using the titre value.

3.4.3.3 Total Nitrogen

Total N in soil was determined by the Macro Kjeldah's method (Bremner, 1965).

5.0g of sieved soil sample was added into a dry 500ml Macro-kjeldah flask. 20ml of distilled water was added and mixture was swirled for a few minutes before being allowed standing for 30 minutes. To this was added one tablet of mercury catalyst and 10g of potassium tetraoxo-sulphate (VI), followed by 30ml of conc. H_2SO_4. The flask was heated at low temperature and fronting ceased. The heat was then increased until digest cleared. After this, the mixture was boiled for 5 hours.

One hundred ml of distilled water was added to the digest after it had been allowed to cool, and then transferred into a 750ml Macro-Kjeldahl flask, with the soil particles retained in the original digest flask. The soil residue was then washed with 590ml of distilled water four times and the aliquot transferred to the 750 ml flask on each occasion.

Fifty ml of trioxobromate (III) acid (hydrobromic acid) indicator solution was measured into a 500 ml Erlenmeyer flask and placed under the condenser of the distillation apparatus. The 750 ml Kjeldahl flask was then attached to the distillation apparatus and 150 mL of 10N NaOH solution poured through the distillation flask by opening the funnel stop cock. 150 ml of distillate was collected and the ammonia-nitrogen in it determined by titrating with 0.0IN standard HCl, with the end point indicated by a colour change from green to pink. The % nitrogen content of the sample was obtained by calculation.

3.4.3.4 Phosphate-Phosphorus

This was determined by the Bray and Kurtz No. 1 method as modified by Jackson (1964).

The extraction solution was first prepared by adding 15mL IM ammonium fluoride and 25mL of 0.5N HCl to 460ml distilled H_2O. One gram of sieved air-dried soil was weighed into a centrifuge tube and 7ml of the extraction solution added. This was shaken for 1 minute and centrifuged. Two milliliters of the clear supernatant was transferred into a 20mL test tube, followed by the addition of 5ml distilled

H_2O and 2ml of ammonium solution. The contents were mixed. One milliliter was measured in a spectrophotometer at 660nm wavelength. The amount of phosphate in soil sample was determined from the standard curve prepared with phosphate in soil standard solution.

3.4.3.5 Total Hydrocarbon Content (HCs)

The spectrophotometric method was used. 10g of a representative sample was shaken with 20ml of toluene and oil extracted determined by the absorbance of the extract at 420nm in a spectronic 21-D spectrophotometer. Hydrocarbon concentration was then calculated with reference to the standard curve, moisture content and multiplying by the appropriate dilution factor (Concawe, 1972).

3.4.3.6 Nitrate-Nitrogen

This was determined in soil extracts by shaking 5g of a representative soil sample with 50ml of 1N H_2SO_4. Aliquots of this extract were used for nitrate nitrogen concentration according to the phenoldisuphonic acid method. Removal by decomposition with H_2SO_4 was done.

3.5 Statistical Analysis

Descriptive statistics that further employed the use of graphical illustrations were used to present requisite data. The Pearson Product Moment Correlation Coefficient (r) was used to investigate the relationships between the parameters measured. The test of equality in mean variances of the parameters measured in air, soil, cassava leave and tubers was conducted with the one-way analysis of variance (ANOVA). The factor analysis procedure, using the principal components analysis (PCA) method of extraction for data reduction and further structure detection was used to remove highly correlated (redundant) variables from the data file and replacing the entire data file with a smaller number of uncorrelated variables (factors) and to further examine the underlying (latent) relationships between the variables. Factor rotation for the transformation of extracted factors to a new position for interpretation was achieved with the varimax method. The magnitude of the eigenvalues and 75% (0.75) rule for variance contribution were used for factor selection (Manly, 1986)

CHAPTER FOUR

4.0 RESULTS

4.1 Ambient air Quality

Slight variations were observed in the air pollutants measured across the sampling locations (Appendix 1). Carbon (11) oxide (CO), carbon (IV) oxide (CO_2) and nitrogen (IV) oxide (NO_2) varied between 1.000-4.000 (2.444 ± 0.338), 250.000-350.000 (300.556 ± 11.826) and 20.000-35.000 (25.667 ± 1.787) ppm; with ranges of 3.000, 100.000 and 15.000, respectively (Table 4.1).

Minimum and maximum concentrations of suspended particulate matter (SPM), hydrogen sulphide (H_2S), sulphur (IV) oxide (SO_2) and total petroleum hydrocarbons (HCs) were 0.280 and 0.730 (0.456 ± 0.064), 0.100 and 0.700 (0.433 ± 0.082), 3.000 and 11.000 (7.667 ± 0.972) and 255.000 and 343.000 (307.778 ± 9.401) ppm, respectively.

Cd, Cr and Pb ranged from 0.010-0.050 (0.023 ± 0.005), 0.010-0.030 (0.014 ± 0.002) and 0.010-0.040 (0.019 ± 0.004) ppm, respectively.

However, Mn ranged between 0.180 and 0.410 (0.299 ± 0.028) ppm, Va between 0.010 and 0.040 (0.020 ± 0.003) ppm, and Zn between 4.200 and 6.800 (5.822 ± 0.363) ppm, with ranges of 0.230, 0.030 and 2.600, respectively.

Nitrogen (IV) oxide, SO_2 and total petroleum hydrocarbon contents exceeded the Federal Environmental Protection Agency's (FEPA) short-term tolerance limits of 0.085, 0.500 and 5.000 ppm, respectively for ambient air pollutants.Additionally, other than for Va and Zn that are not specified (NS), the other trace metals measured exceeded FEPA's short-term tolerance limits for ambient air pollutants.

4.2 Soil Quality

Table 4.2 reveals that other than phosphors, total petroleum hydrocarbons, Mn and Zn, the other soil variables had narrow ranges. pH, organic C and total N varied from 5.400-7.600 (6.344 ± 0.302), 2.100-6.800 (4.833 ± 0.630) mg/kg and 0.180-0.530 (0.334 ± 0.047) mg/kg, respectively. Phosphorus varied from 15.500-43.900 (30.856 ± 3.874) mg/kg, nitrate (nitrate-N) from 0.100-1.550 (0.598 ± 0.217) mg/kg and HCs from 31.200-95.270 (56.446 ± 7.921) mg/kg (Appendix 2).

Table 4.1. Descriptive statistics of the trace metals concentrations and other pollutants in air samples (ppm)

Parameters	Minimum	Maximum	Range	Mean	SE	FEPA (1991)
CO	1.000	4.000	3.000	2.444	0.338	5.000
CO_2	250.000	350.000	100.000	300.556	11.826	NS
NO_2	20.000	35.000	15.000	25.667	1.787	0.085
SPM	0.280	0.730	0.450	0.456	0.064	0.500
H_2S	0.100	0.700	0.600	0.433	0.082	NS
SO_2	3.000	11.000	8.000	7.667	0.972	0.500
HCs	255.000	343.000	88.000	307.778	9.401	5.000
Cd	0.010	0.050	0.040	0.023	0.005	0.010
Cr	0.010	0.030	0.020	0.014	0.002	0.0015
Pb	0.010	0.040	0.030	0.019	0.004	0.002
Mn	0.180	0.410	0.230	0.299	0.028	0.030
Va	0.010	0.040	0.030	0.020	0.003	NS
Zn	4.200	6.800	2.600	5.822	0.363	NS

SE = standard error, HCs = total petroleum hydrocarbons, SPM = suspended particulate matter, NS = none specified

Table 4.2. Descriptive statistics of the trace metals concentrations (mg/kg) and other edaphic pollutants in soil samples

Parameters	Minimum	Maximum	Range	Mean	SE
pH	5.400	7.600	2.200	6.344	0.302
Organic C	2.100	6.800	4.700	4.833	0.630
Total N	0.180	0.530	0.350	0.334	0.047
Phosphorus	15.500	43.900	28.400	30.856	3.874
Nitrate	0.100	1.550	1.450	0.598	0.217
HCs	31.200	95.270	64.070	56.446	7.921
Cd	0.050	1.220	1.170	0.462	0.149
Cr	0.210	0.420	0.210	0.294	0.026
Pb	0.020	0.080	0.060	0.048	0.008
Mn	0.800	25.200	24.400	13.467	3.326
Va	0.001	0.100	0.099	0.022	0.010
Zn	20.700	62.100	41.400	40.704	4.575

SE = standard error, HCs = total petroleum hydrocarbons

Table 4.3. Descriptive statistics of the trace metals concentrations (µg/kg) in cassava leaves (CL) (*M. esculenta*) samples

Parameters	Minimum	Maximum	Range	Mean	SE
Cd	1.440	3.010	1.570	2.099	0.177
Cr	0.710	1.100	0.390	0.892	0.044
Pb	0.040	1.005	0.965	0.324	0.132
Mn	1.890	31.110	29.220	19.026	4.346
Va	0.020	0.560	0.540	0.220	0.073
Zn	50.700	101.120	50.420	72.117	6.926

SE = standard error

Table 4.4. Descriptive statistics of the trace metals concentrations (µg/kg) in cassava tuber (*M. esculenta*) samples

Parameters	Minimum	Maximum	Range	Mean	SE
Cd	2.300	5.000	2.700	3.476	0.336
Cr	1.200	1.500	0.300	1.342	0.038
Pb	0.062	1.210	1.148	0.446	0.174
Mn	2.220	45.220	43.000	25.494	6.008
Va	0.040	0.650	0.610	0.228	0.084
Zn	69.440	130.460	61.020	91.120	8.038

SE = standard error

Cadmium, Cr and Pb varied between 0.050 and 1.220 (0.462 ± 0.149), 0.210 and 0.420 (0.294 ± 0.026), and 0.020 and 0.080 (0.048 ± 0.008) mg/kg, respectively. Mn, Va and Zn ranged from 0.800-25.200 (13.467 ± 3.326), 0.001-0.100 (0.022 ± 0.010) and 20.700-62.100 (40.704 ± 4.575) mg/kg, respectively.

4.3. Trace Metals Concentrations in Cassava Leaves

Manganese and Zn showed very high ranges in the leave samples (Table 4.3). Cd ranged from 1.440-3.010 (2.099 ± 0.177), Cr from 0.710-1.100 (0.892 ± 0.044), Pb from 0.040-1.005 (0.324 ± 0.132) and Mn from 1.890-31.110 (19.026 ± 4.346) µg/kg (Appendix 3).

However, vanadium ranged between 0.020 and 0.560 (0.220 ± 0.073) µg/g while Zn ranged between 50.700 and 101.120 (72.117 ± 6.926) µg/kg; with ranges of 0.540 and 50.420 respectively.

4.4 Trace Metals Concentrations in Cassava Tubers

Mn and Zn also showed very high concentrations in the tubers sampled (Appendix 4). Cd varied from 1.440-3.010, Cr from 0.710-1.100 and Pb from 0.040-1.005 µg/kg, with mean and standard errors of 2.099 ± 0.177, 0.892 ± 0.044 and 0.324 ± 0.132, respectively (Table 4.4).

Mn, Va and Zn recorded minimum and maximum values of 1.890 and 31.110, 0.020 and 0.560, and 50.700 and 101 120 µg/kg, respectively, with mean values of 19.026 ± 4.346, 0.220 ± 0.072 and 72.117 ± 6.926 µg/kg, respectively.

4.5 Spatial Variation in trace Metals Concentrations

There existed variations in concentrations of the trace metals measured across the sampling locations. Generally, Cd, Cr, Pb and V concentrations were comparatively low across the sampling locations. Generally, the metals concentrations were highest at 2 km (sampling location 2) from the flare stack. In both air, soil, crop leaves, and crop tuber samples, Zn recorded an overall highest concentration. This was followed by Mn concentrations. However, least concentrations of 0.01 ppm were recorded for Cd, Cr and Pb in sampling location 1 (Fig. 4.1), and for Cr, Pb and Va in air samples at locations 3.

In the soil samples, least concentration of 0.01 was recorded for Va in locations 1 and 3 (Fig. 4.2). Least concentrations (0.03, 0.50 and 0.14 µg/kg) were also recorded for Va in sampling locations 1,2 and 3 respectively in cassava leaves (Fig. 4.3), even as least concentrations of 0.05, 0.55 and 0.08 µg/kg were recorded for it in tuber samples at those respective sampling locations (Fig. 4.4).

The test of equality in mean variances of the trace metals concentrations at 1 km (sampling location 1), 2 km (sampling location 2) and 10 km (sampling location 3)distances from the flare stack revealed inequalities in air [F(22.49) > Fcrit(3.88)], soil (F(28.07) > Fcrit(3.88)], cassava leaves (F(13.09) > Fcrit(3.93)], and cassava tubers [F(14.68) > Fcrit (3.93)] samples at $P<0.05$ (Appendixes 10,11,12 and 13).

4.6 Relationships between Metals Concentration in Air, Soil and Crop Plant Parts

Although the trace metals concentrations in air samples did not show significant correlations with those in soil samples (Appendix 5), lead concentration in air samples showed significant correlation with that in leave samples at $P<0.05$ ($r = 0.742$), (Appendix 6).Manganese concentration in the soil samples showed high significant relationship with those in crop leaves ($r = 0.899$) (Appendix 7) as well as those in crop tubers ($r=0.813$) at $P<0.01$ (Appendix 8). Additionally, Va in soil samples correlated with Va in cassava tubers ($r =0.671$) at $P< 0.05$.

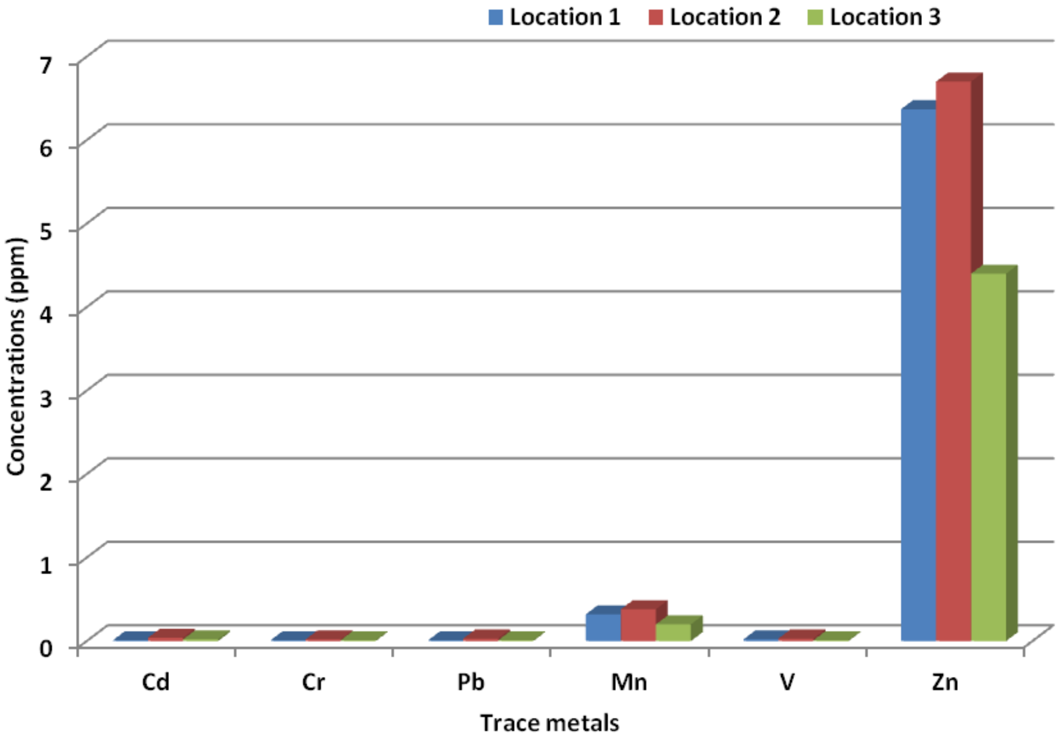

Fig. 4.1. Variation in mean trace metals concentrations in air samples across the sampling locations

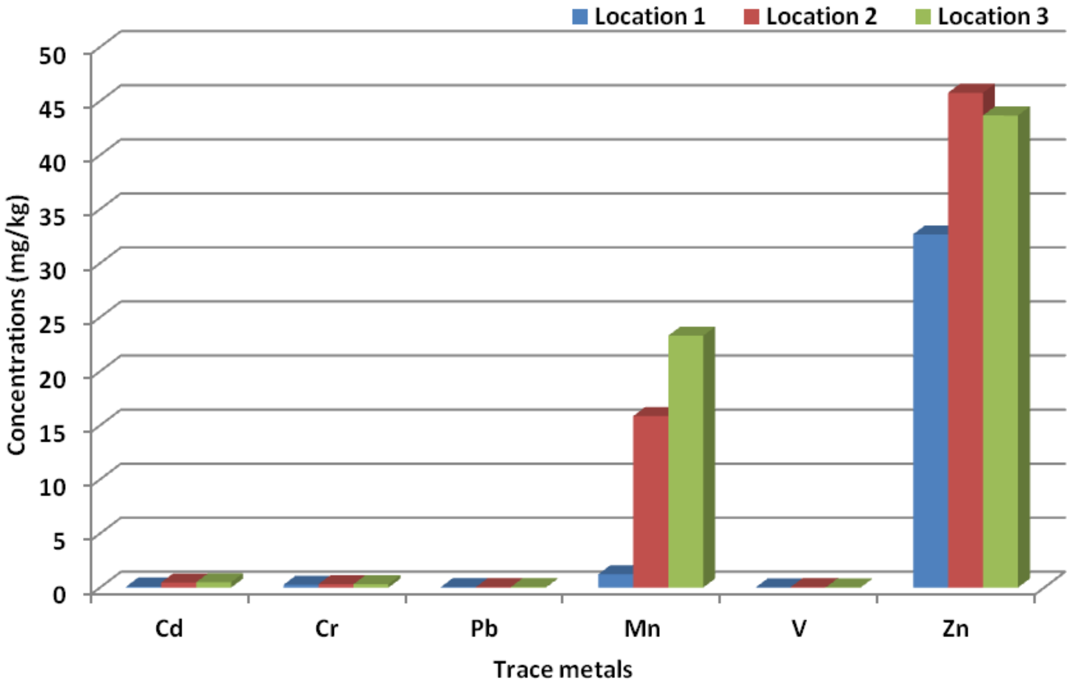

Fig. 4.2. Variation in mean trace metals concentrations in soil samples across the sampling locations

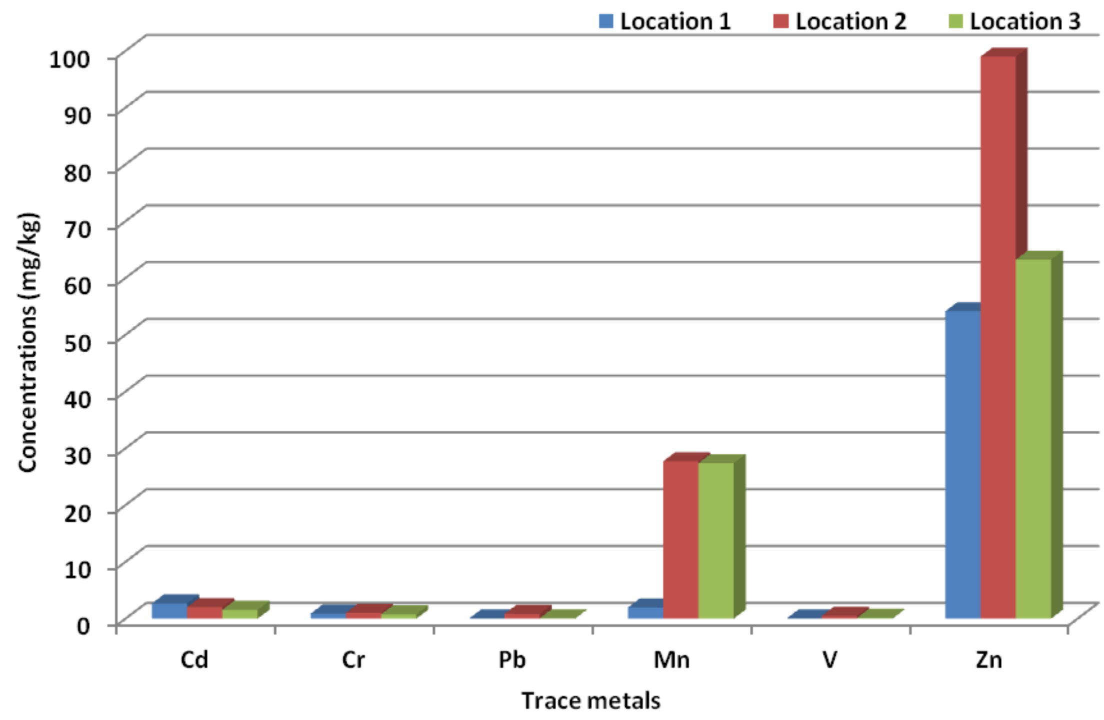

Fig. 4.3. Variation in mean trace metals concentrations in cassava leaves across the sampling locations

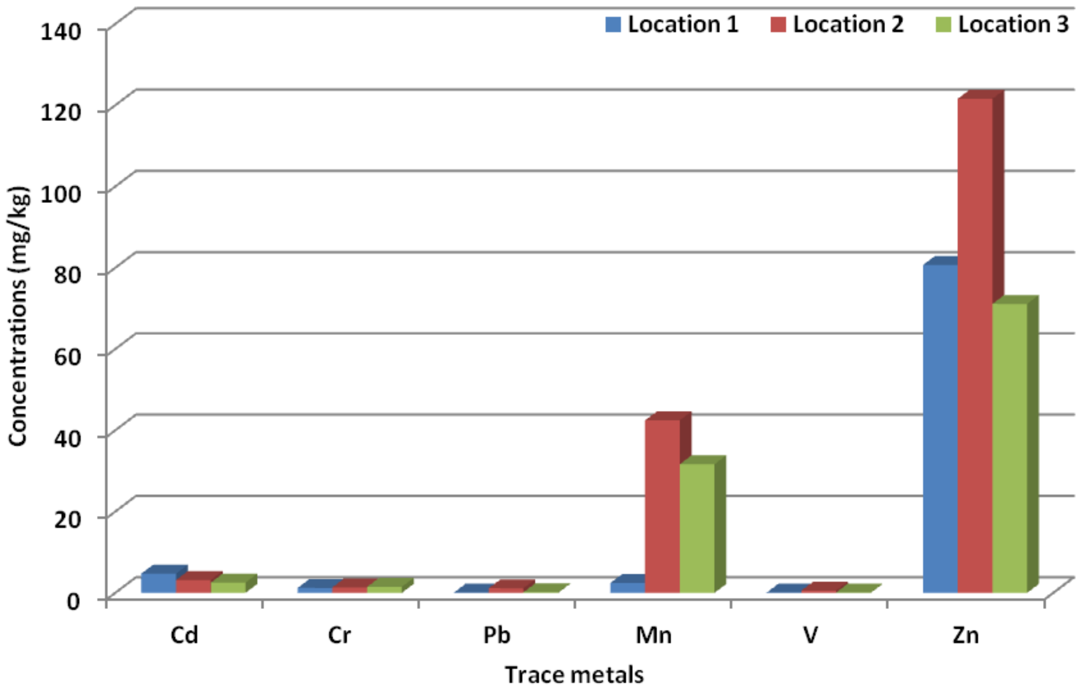

Fig. 4.4. Variation in mean trace metals concentrations in cassava tubers across the sampling locations

Apart from in Cr, the other trace metal pollutants showed high significant correlations between crop leaves (CL) and tubers (CT) at $P<0.01$ (Appendix 9). Cd in leaves correlated with that in CT ($r=0.940$), Pb in CL correlated with that in CT ($r=0.989$), Mn correlated with that in CT ($r=0.933$), Va in CL correlated with Va in CT ($r=0.979$) and Zn in CL correlated with Zn in CT ($r=0.862$).

4.7 Principal Components Analysis (PCA)

The trace metals concentrations measured in air and soil samples were subjected to the PCA as regulators of accumulations in leaves and tubers of the crop. The communalities were all high, indicating that the extracted components represented the variables well (Appendix 14). The first 5 PCs formed the extracted solution. The cumulative percent revealed that the extracted components explained about 96% of the variability in the original 25 variables.

This reduces the complexity of the data set by using these components, with only about 4% loss of information.

The rotation maintained the cumulative percentage of variation explained by the extracted components. The scree plot (Fig.4.5) represents the eigenvalue of each component in the initial solution. The extracted components are on the steep slope, while the components on the shallow slope contributed little (4%) to the solution. The last big drop occurred between the 5th and 6th components.

The first component was most highly correlated with pH/total nitrogen (-0.986) in soil samples, the second component with Cd in air samples (0.947) and the third with Va in soil samples (0.936). However, the fourth and fifth components were most correlated with Zn and Pb concentrations in soil samples (0.922 and 0.949, respectively).

The scatterplot matrix (Fig 4.6) revealed that the extracted components had slightly skewed distribution between PCs 1 and 2 and 3, and normal distributions between PCs 1 and 4 and 5.

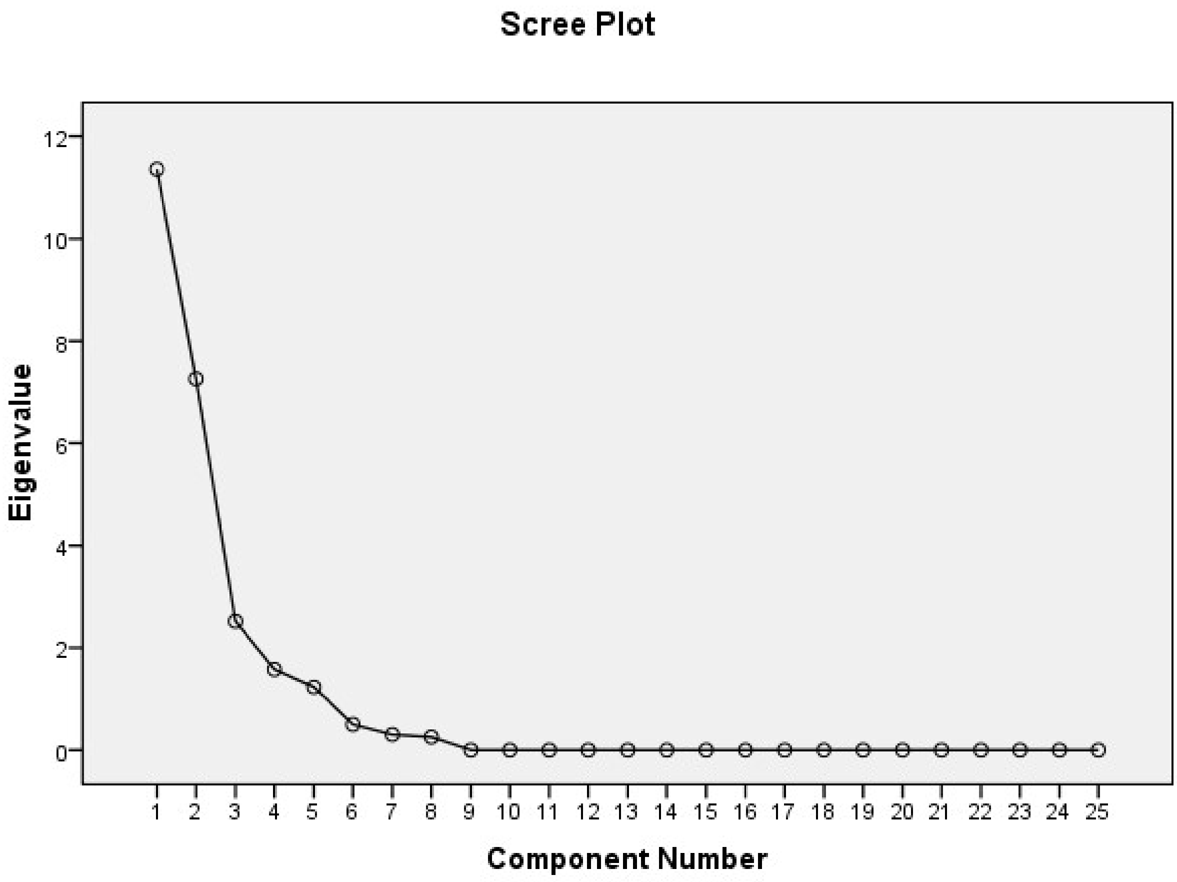

Fig. 4.5. Scree plot of the eigenvalues of components in the initial solution

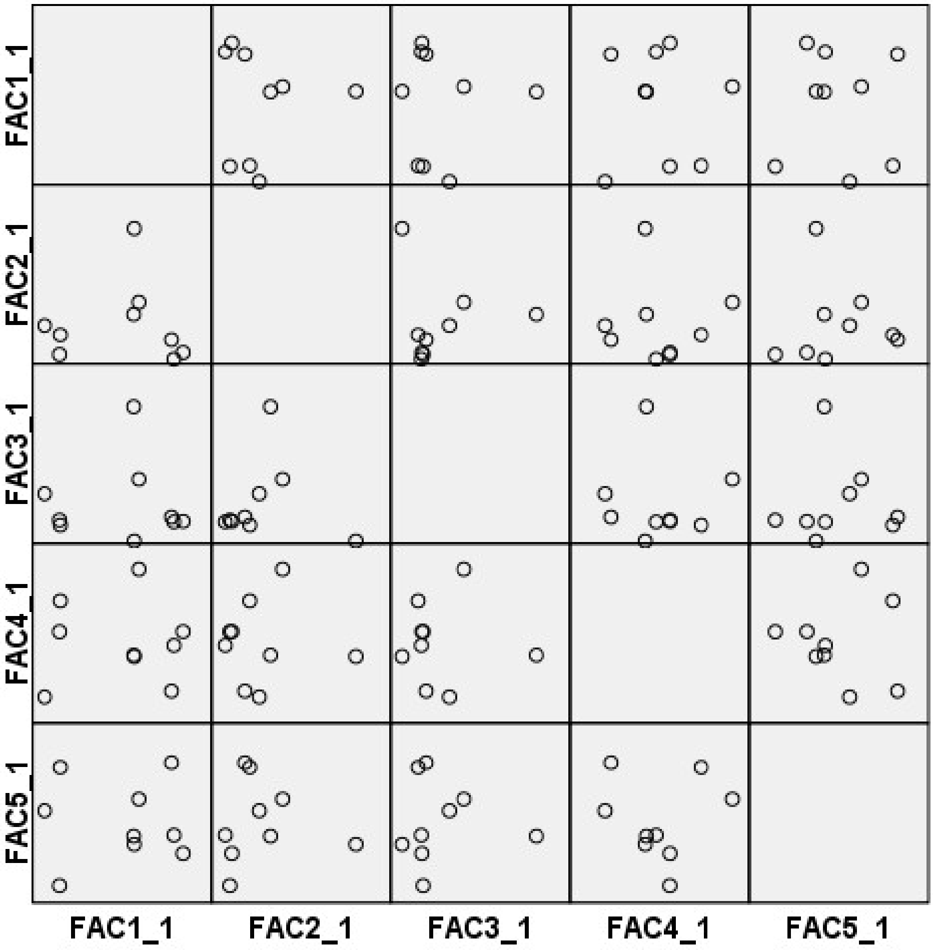

Fig. 4.6. Scatterplot matrix of the extracted components

CHAPTER FIVE

5.0 DISCUSSION, SUMMARY AND CONCLUSION

5.1 Discussion

Air pollution deteriorates ecological condition, and it is the fluctuation in any atmospheric constituent from the value that would have existed without human activity (Tripathi and Gautam, 2007). According to Joshi and Swami, (2007), in recent past, air pollutants, responsible for vegetation injury and crop yield losses, are causing increased concern. The increasing number of industries and automobile vehicles are continuously adding toxic gases and other substances to the environment (Seyyednejab *et al*., 2011). These could include sulphur and nitrogen oxides, carbon (II) oxide and soot particles, as well as smaller quantities of toxic metals, organic molecules and radioactive isotopes (Agbaire and Esiefarienrhe, 2009).

Adverse effects of air pollution on biota and ecosystems have been demonstrated worldwide. The current study analyzed air pollutant fallouts and their contributory effects on soil and subsequent bioavailability in a food crop in a Niger Delta area of Nigeria. Vegetation is thus an effective indicator of the overall impact of air pollution and the effects observed is a time averaged result that is more reliable than the one obtained from direct determination of the pollutant in air over a short period (Rai *et al*., 2010; Joshi and Swami, 2009).

The concentration of the pollutant gasses and trace metals in this study are obviously elevated high above natural ambient levels (FEPA, 1991; SPDC, 2002). However, values recorded in this study are slightly lower than those recorded by Oghenejoboh (2005) in ambient air samples around a gas flare station at Afiesere community in the Niger Delta of Nigeria. This elevation was obviously contributed by the gas flare source point of pollution. This collaborates the works of Ogwejifor (2002) and Oghenejoboh (2005) that gas flare fallouts contribute pollutants to the air.

Polluted air could lead to loses in essential nutmeats as well as contribution of toxic components of crops growth in most agricultural villages. WHO (1987) had identified rainwater containing various metals (such as Cd, Pb and Hg) as a major cause of serious health problems in the lower Niger Delta area. Some of these health problems include anaemia, renal disfunction, lung cancer and other neo-behavioural effects. Other negative effects are corrosion and tarnishing of metals (including building roofs), erosion and soiling of buildings, as well as discoloration and peeling of paints (Harter, 1986; Oghenejoboh, 2005). The negative effects of air pollutants on plants have been reviewed by Seyyednejad*et al*. (2011).

Soil samples in the current study also contained trace metal concentrations that are above natural background levels in Rivers State soils (RSMENR, 2002). Soil represents a major sink for metals released into the environment from a variety of anthropogenic activities (Aremu *et al.,* 2010). These metals are not biodegradable and can undergo global ecological circles in which natural waters serve as the main pathways (Adekola *et al*., 2000). The bioavailability of these pollutants has been observed by several authors (Hart *et al*., 2010).

The pH of the soils closest to the flare stack were acidic, organic carbon very high, total nitrogen moderate, available phosphorus very high and hydrocarbon contents indicating low pollution levels(ENI, 2002).

Mean Zn concentration of the current study was higher than values recorded by Aremu *et al*., (2010) in soil around the derelict Udege mines in Nasarawa State, even as the concentrations of Pb, Cd, Cr and Mn were lower than those recorded in their work.

The consumption of vegetables and other crops offer rapid and least means of providing adequate vitamins supplies, minerals and fibre, as well as energy for the various works. Akan *et al*. (2009) state that food crops could constitute a group of foods which contribute maximally to nitrate and the anions, as well as heavy metal consumption. Their consumption by humans and animals can pose serious health hazards.

Although some trace metals are essential in plant nutrition, many of them do not play any significant role in the plant physiology (Akan *et al*., 2009). The uptake of these trace elements by plants, especially crops plants is an avenue of their entry into the human food chain, with attendant harmful effects on health (Ihekeronye and Ngoddy, 1985; Hart *et al*., 2005; Onyedika and Nwosu, 2008). Values of Zn and Pb in cassava parts (leaves and tubers) in this study were lower than those earlier detected by Hart *et al*., (2005) in some oil prospecting locations in Rivers State.

Values recorded for Cr by Akan *et al*., (2009) (0.54-2.33 µg/kg) were higher than the current study's. However, values of the other trace metals were comparable to their own, except for Zn Mn which were higher in the current study.

Generally, values of the trace metals were higher in the crop tubers than in the leaves. This indicates the greater storage and accumulative potentials of the tubers of the crop than the leaves. Ni *et al.* (2002) and Yang *et al.* (2002) had also observed higher concentrations of trace metals (Cd and Cu) in tuber (root) than in the shoots of vegetable crops.

The observed significant correlation between air and cassava leave samples in Pb concentration indicates the possibility of stomatal diffusion of the pollutant. Seyyednejad *et al*. (2011) observed that air pollution can directly affect plants via leaves or indirectly via soil acidification. When exposed to air borne pollutants, most plants experience physiological changes before exhibiting visible damages to leaves (Liu and Ding, 2008).

However, the correlations in Mn and Va concentrations in soil and crop parts indicate high uptakes of these substances via the roots and subsequent contributory translocation to leaves. The several correlations existing between traces metals in leaves and tubers of the crop indicates the close relatedness of these plant parts. Nutrients and other substances are usually taken up by roots (tuber) and translocated to the leaves via the stem. On the other hand, gaseous exchanges occur in the leaves and are translocated to the other parts of the plant.

The observed spatial variation in the metals concentrations has also been documented by other researchers (Oghenejoboh, 2005; Hart *et al*., 2005; Onyedika and Nwosu, 2008; Zhuang*,* 2010; Aremu *et al*., 2010; Seyyedejad *et al*., 2011). The consistency in highest concentrations in Zn across the sampling locations indicates common pollutant source as well as ecological mobility and bioavailability in biotic tissues.

Pollutant concentrations were generally highest in sampling location 2, 2km from the flare stack and least in sampling location 3, 10 km from the stack for air samples. This confirms the dispersal of aerial materials from point sources of pollution to distances in and around its vicinity. Dispersal of pollutants has been stated to be controlled by wind speed, direction as well as topography, and its concentrations affected by dilution effects over distances by Narayanan (2007).

Accordingly, the pattern of concentrations in soil as repository and crop parts followed fairly the same spatial patterns.

The extracted components explained well the variability in the original variables in air and soil matrices. The components (pH and total nitrogen) are very important edaphic factors necessary for crop growth and productivity. The other components (Cd, Va, Zn and Pb) are pollutants to crops, especially at elevated levels. Their influences are toxic to both flora and fauna.

The normality from the scatterplot matrix between PCs 1, 4 and 5 indicates the influence of pH on the trace metals (Zn and Pb).

5.2 Summary and Conclusion

The concentrations of the pollutant gases and airborne trace metals were higher than natural ambient levels. This elevation was contributed by the gas flare stack in the neighborhood of the study area. These pollutants could pose health hazards to man and animal consumers, as well toxicity to crops.

Soil samples also contained trace metal concentrations above natural background levels in the Niger Delta area. These were most likely contributed by the flare outfalls as soil serves as repository to many forms of pollutants.

Soils very close to the flare stack were acidic, contained high organic carbon, moderate nitrogen, high available phosphorus and high hydrocarbon contents that indicated low petroleum pollution.

The concentrations of the trace metals in the crop parts pose health risk to farmers and consumers. Concentrations were generally higher in tubers than in leaves. This indicates the higher storage capacity of the crop roots than the leaves. Stomata diffusions were observed in airborne Pb pollutant.

Correlations in concentrations of trace metals (Mn and Va) between soil and crop parts indicate high uptake of these pollutants via the roots.

Several correlations were observed in the trace metal concentrations between leaves and tuber parts of the crop. This indicates the parts relatedness and substances translocations across them.

There was observed significant spatial variation in trace metals pollutant levels, indicating the dispersal of aerial materials from point sources of pollution. The pattern of soil and crop parts contaminations followed that of ambient air. Sampling location 2 had the highest concentrations of the pollutants in both air, soil and crop parts, while location 3, the farthest location from the flare stack had experienced dilution in concentrations.

Five PCs were extracted and were most highly correlated with pH/ total nitrogen in soil samples, Cd in air samples, Va in soil samples and Zn and Pb in soil samples. The extracted components explained 96% of the variability in the original 25 variables entered in the PCA; with only 4% loss of information. pH exerted influences on some trace metals through a normal distribution pattern.

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APPENDIXES

Appendix 1. Concentrations of air pollutants (A) at the sampling locations

Parameters (ppm)		Sampling locations		
	Replicates	1	2	3
Carbon (II) oxide	1	3	3	1
	2	2	3	1
	3	3	4	1
Carbon (IV) oxide	1	340	300	260
	2	310	350	265
	3	308	322	250
Nitrogen (IV) oxide	1	22	30	20
	2	24	35	22
	3	20	31	27
Sulphur (IV) oxide	1	10	8	4
	2	11	10	5
	3	9	9	3
SPM	1	0.73	0.37	0.34
	2	0.71	0.28	0.32
	3	0.69	0.31	0.35
H_2S	1	0.60	0.60	0.10
	2	0.50	0.70	0.10
	3	0.40	0.70	0.20
Hydrocarbons (HCs)	1	320	340	280
	2	305	343	295
	3	310	322	255

Cd	**1**	**0.01**	**0.04**	**0.02**
	2	**0.01**	**0.05**	**0.01**
	3	**0.02**	**0.03**	**0.02**
Cr	**1**	**0.01**	**0.02**	**0.01**
	2	**0.01**	**0.03**	**0.01**
	3	**0.01**	**0.02**	**0.01**
Pb	**1**	**0.01**	**0.03**	**0.02**
	2	**0.02**	**0.02**	**0.01**
	3	**0.01**	**0.04**	**0.01**
Mn	**1**	**0.34**	**0.38**	**0.22**
	2	**0.30**	**0.35**	**0.19**
	3	**0.32**	**0.41**	**0.18**
Va	**1**	**0.02**	**0.02**	**0.01**
	2	**0.01**	**0.04**	**0.01**
	3	**0.02**	**0.03**	**0.02**
Zn	**1**	**6.60**	**6.70**	**4.60**
	2	**6.10**	**6.80**	**4.20**
	3	**6.40**	**6.60**	**4.40**

Appendix 2. Concentrations of trace metals and other edaphic factors in soil samples (S) (0-15cm) at the sampling locations

Parameters		**Sampling locations**		
	Replicates	**1**	**2**	**3**
pH	**1**	**5.5**	**6.1**	**7.6**
	2	**5.5**	**6.0**	**7.5**
	3	**5.4**	**6.1**	**7.4**
Organic C (%)	**1**	**2.7**	**5.6**	**6.8**
	2	**2.1**	**5.2**	**6.2**
	3	**2.4**	**6.0**	**6.5**
Total N (%)	**1**	**0.20**	**0.29**	**0.53**
	2	**0.19**	**0.30**	**0.48**
	3	**0.18**	**0.33**	**0.51**
Phosphorus (mg/kg)	**1**	**16.6**	**35.0**	**43.9**
	2	**16.1**	**32.1**	**40.0**
	3	**15.5**	**37.0**	**41.5**
Nitrate (mg/kg)	**1**	**0.13**	**0.20**	**1.43**
	2	**0.11**	**0.25**	**1.55**
	3	**0.10**	**0.21**	**1.40**
HCs (mg/kg)	**1**	**48.50**	**95.27**	**50.41**
	2	**35.21**	**48.20**	**31.20**
	3	**36.52**	**89.00**	**73.70**
Cd (mg/kg)	**1**	**0.10**	**1.22**	**0.50**
	2	**0.11**	**0.10**	**0.65**
	3	**0.05**	**1.10**	**0.33**

Cr (mg/kg)	**1**	**0.21**	**0.33**	**0.40**
	2	**0.25**	**0.42**	**0.22**
	3	**0.31**	**0.21**	**0.30**
Pb (mg/kg)	**1**	**0.03**	**0.06**	**0.08**
	2	**0.04**	**0.02**	**0.02**
	3	**0.08**	**0.05**	**0.05**
Mn (mg/kg)	**1**	**1.70**	**20.00**	**25.20**
	2	**0.80**	**15.40**	**21.00**
	3	**1.20**	**12.20**	**23.70**
Va (mg/kg)	**1**	**0.001**	**0.020**	**0.010**
	2	**0.010**	**0.010**	**0.010**
	3	**0.020**	**0.100**	**0.020**
Zn (mg/l)	**1**	**45.22**	**62.10**	**60.50**
	2	**32.10**	**33.30**	**40.11**
	3	**20.70**	**41.90**	**30.41**

Appendix 3. Concentrations of trace metals in cassava leaves (CL) at the sampling locations

Parameters (mg/kg)		Sampling locations		
	Replicates	1	2	3
Cd	1	2.82	2.01	1.56
	2	3.01	2.00	1.72
	3	2.22	2.11	1.44
Cr	1	0.95	1.03	0.85
	2	0.80	0.97	0.71
	3	0.88	1.10	0.74
Pb	1	0.061	1.005	0.100
	2	0.040	0.820	0.080
	3	0.040	0.700	0.07
Mn	1	2.01	30.05	27.11
	2	1.89	22.00	27.05
	3	2.00	31.11	28.01
Va	1	0.02	0.52	0.14
	2	0.03	0.41	0.10
	3	0.03	0.56	0.17
Zn	1	50.70	101.12	61.18
	2	51.21	98.14	66.10
	3	60.50	97.70	62.40

Appendix 4. Concentrations of trace metals in cassava tubers (CT) at the sampling locations

Parameters (µg/g)		Sampling locations		
	Replicates	1	2	3
Cd	1	4.89	3.25	2.60
	2	5.00	3.11	2.30
	3	4.31	3.16	2.66
Cr	1	1.22	1.40	1.48
	2	1.21	1.35	1.50
	3	1.20	1.31	1.41
Pb	1	0.062	1.203	0.103
	2	0.070	1.210	0.110
	3	0.070	0.990	0.200
Mn	1	2.57	43.23	31.91
	2	2.22	45.22	30.41
	3	2.41	38.88	32.60
Va	1	0.040	0.600	0.080
	2	0.060	0.400	0.090
	3	0.050	0.650	0.080
Zn	1	89.41	121.57	70.25
	2	81.70	130.46	69.44
	3	70.90	112.70	73.65

Appendix 5. Correlations between trace metals in Air and Soil samples

		HCsA	CdA	CrA	PbA	MnA	VA	ZnA	HCsS	CdS	CrS	PbS	MnS	VS	ZnS
HCsA	Pearson Correlation	1	.588	.713*	.470	.870**	.567	.869**	.172	.198	.068	-.259	-.372	.147	.155
	Sig. (2-tailed)		.096	.031	.202	.002	.111	.002	.659	.610	.862	.500	.324	.707	.690
	N	9	9	9	9	9	9	9	9	9	9	9	9	9	9
CdA	Pearson Correlation	.588	1	.933**	.531	.522	.795*	.489	.520	.316	.632	-.013	.306	.243	.170
	Sig. (2-tailed)	.096		.000	.141	.150	.010	.181	.151	.408	.068	.974	.424	.529	.661
	N	9	9	9	9	9	9	9	9	9	9	9	9	9	9
CrA	Pearson Correlation	.713*	.933**	1	.562	.606	.860**	.570	.397	.259	.439	-.310	.157	.292	.098
	Sig. (2-tailed)	.031	.000		.115	.084	.003	.109	.290	.501	.237	.416	.686	.445	.803
	N	9	9	9	9	9	9	9	9	9	9	9	9	9	9
PbA	Pearson Correlation	.470	.531	.562	1	.665	.356	.449	.698*	.732*	.007	.145	.122	.761*	.433
	Sig. (2-tailed)	.202	.141	.115		.051	.347	.226	.037	.025	.986	.711	.755	.017	.244
	N	9	9	9	9	9	9	9	9	9	9	9	9	9	9
MnA	Pearson Correlation	.870**	.522	.606	.665	1	.598	.953**	.425	.275	-.078	-.001	-.484	.475	.106
	Sig. (2-tailed)	.002	.150	.084	.051		.089	.000	.255	.473	.841	.997	.186	.197	.787
	N	9	9	9	9	9	9	9	9	9	9	9	9	9	9
VA	Pearson Correlation	.567	.795*	.860**	.356	.598	1	.608	.361	.011	.284	-.274	-.050	.377	-.221
	Sig. (2-tailed)	.111	.010	.003	.347	.089		.082	.340	.977	.459	.475	.898	.317	.569
	N	9	9	9	9	9	9	9	9	9	9	9	9	9	9
ZnA	Pearson Correlation	.869**	.489	.570	.449	.953**	.608	1	.249	.007	.005	-.048	-.624	.244	-.055
	Sig. (2-tailed)	.002	.181	.109	.226	.000	.082		.519	.986	.991	.902	.073	.527	.889
	N	9	9	9	9	9	9	9	9	9	9	9	9	9	9
HCsS	Pearson Correlation	.172	.520	.397	.698*	.425	.361	.249	1	.761*	.016	.227	.379	.593	.458
	Sig. (2-tailed)	.659	.151	.290	.037	.255	.340	.519		.017	.968	.556	.314	.092	.215
	N	9	9	9	9	9	9	9	9	9	9	9	9	9	9
CdS	Pearson Correlation	.198	.316	.259	.732*	.275	.011	.007	.761*	1	-.153	.152	.498	.590	.639
	Sig. (2-tailed)	.610	.408	.501	.025	.473	.977	.986	.017		.694	.697	.173	.094	.064
	N	9	9	9	9	9	9	9	9	9	9	9	9	9	9

CrS	Pearson Correlation	.068	.632	.439	.007	-.078	.284	.005	.016	-.153	1	.318	.424	-.332	.172
	Sig. (2-tailed)	.862	.068	.237	.986	.841	.459	.991	.968	.694		.405	.255	.383	.658
	N	9	9	9	9	9	9	9	9	9	9	9	9	9	9
PbS	Pearson Correlation	-.259	-.013	-.310	.145	-.001	-.274	-.048	.227	.152	.318	1	.070	.152	.177
	Sig. (2-tailed)	.500	.974	.416	.711	.997	.475	.902	.556	.697	.405		.858	.696	.648
	N	9	9	9	9	9	9	9	9	9	9	9	9	9	9
MnS	Pearson Correlation	-.372	.306	.157	.122	-.484	-.050	-.624	.379	.498	.424	.070	1	.016	.500
	Sig. (2-tailed)	.324	.424	.686	.755	.186	.898	.073	.314	.173	.255	.858		.968	.171
	N	9	9	9	9	9	9	9	9	9	9	9	9	9	9
VS	Pearson Correlation	.147	.243	.292	.761*	.475	.377	.244	.593	.590	-.332	.152	.016	1	-.007
	Sig. (2-tailed)	.707	.529	.445	.017	.197	.317	.527	.092	.094	.383	.696	.968		.986
	N	9	9	9	9	9	9	9	9	9	9	9	9	9	9
ZnS	Pearson Correlation	.155	.170	.098	.433	.106	-.221	-.055	.458	.639	.172	.177	.500	-.007	1
	Sig. (2-tailed)	.690	.661	.803	.244	.787	.569	.889	.215	.064	.658	.648	.171	.986	
	N	9	9	9	9	9	9	9	9	9	9	9	9	9	9

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

Appendix 6. Correlations between trace metals contents in Air and Crop Leaves samples

		CdA	CrA	PbA	MnA	VA	ZnA	CdCL	CrCL	PbCL	MnCL	VCL	ZnCL
CdA	Pearson Correlation	1	.933**	.531	.522	.795*	.489	-.286	.627	.896**	.469	.822**	.893**
	Sig. (2-tailed)		.000	.141	.150	.010	.181	.456	.071	.001	.203	.007	.001
	N	9	9	9	9	9	9	9	9	9	9	9	9
CrA	Pearson Correlation	.933**	1	.562	.606	.860**	.570	-.089	.656	.890**	.383	.808**	.883**
	Sig. (2-tailed)	.000		.115	.084	.003	.109	.819	.055	.001	.308	.008	.002
	N	9	9	9	9	9	9	9	9	9	9	9	9
PbA	Pearson Correlation	.531	.562	1	.665	.356	.449	.029	.759*	.742*	.475	.841**	.736*
	Sig. (2-tailed)	.141	.115		.051	.347	.226	.941	.018	.022	.196	.004	.024
	N	9	9	9	9	9	9	9	9	9	9	9	9
MnA	Pearson Correlation	.522	.606	.665	1	.598	.953**	.520	.927**	.678*	-.146	.583	.579
	Sig. (2-tailed)	.150	.084	.051		.089	.000	.152	.000	.045	.709	.099	.102
	N	9	9	9	9	9	9	9	9	9	9	9	9
VA	Pearson Correlation	.795*	.860**	.356	.598	1	.608	-.042	.646	.669*	.183	.639	.695*
	Sig. (2-tailed)	.010	.003	.347	.089		.082	.914	.060	.049	.638	.064	.038
	N	9	9	9	9	9	9	9	9	9	9	9	9
ZnA	Pearson Correlation	.489	.570	.449	.953**	.608	1	.633	.815**	.567	-.365	.401	.434
	Sig. (2-tailed)	.181	.109	.226	.000	.082		.067	.007	.111	.334	.285	.243
	N	9	9	9	9	9	9	9	9	9	9	9	9
CdCL	Pearson Correlation	-.286	-.089	.029	.520	-.042	.633	1	.234	-.124	-.803**	-.283	-.297

	Sig. (2-tailed)	.456	.819	.941	.152	.914	.067		.544	.752	.009	.461	.438
	N	9	9	9	9	9	9	9	9	9	9	9	9
CrCL	Pearson Correlation	.627	.656	.759*	.927**	.646	.815**	.234	1	.762*	.138	.735*	.696*
	Sig. (2-tailed)	.071	.055	.018	.000	.060	.007	.544		.017	.723	.024	.037
	N	9	9	9	9	9	9	9	9	9	9	9	9
PbCL	Pearson Correlation	.896**	.890**	.742*	.678*	.669*	.567	-.124	.762*	1	.524	.940**	.965**
	Sig. (2-tailed)	.001	.001	.022	.045	.049	.111	.752	.017		.148	.000	.000
	N	9	9	9	9	9	9	9	9	9	9	9	9
MnCL	Pearson Correlation	.469	.383	.475	-.146	.183	-.365	-.803**	.138	.524	1	.698*	.647
	Sig. (2-tailed)	.203	.308	.196	.709	.638	.334	.009	.723	.148		.036	.060
	N	9	9	9	9	9	9	9	9	9	9	9	9
VCL	Pearson Correlation	.822**	.808**	.841**	.583	.639	.401	-.283	.735*	.940**	.698*	1	.967**
	Sig. (2-tailed)	.007	.008	.004	.099	.064	.285	.461	.024	.000	.036		.000
	N	9	9	9	9	9	9	9	9	9	9	9	9
ZnCL	Pearson Correlation	.893**	.883**	.736*	.579	.695*	.434	-.297	.696*	.965**	.647	.967**	1
	Sig. (2-tailed)	.001	.002	.024	.102	.038	.243	.438	.037	.000	.060	.000	
	N	9	9	9	9	9	9	9	9	9	9	9	9

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

Appendix 7. Correlations between trace metal contents in Soil and crop Leaves samples

		CdS	CrS	PbS	MnS	VS	ZnS	CdCL	CrCL	PbCL	MnCL	VCL	ZnCL
CdS	Pearson Correlation	1	-.153	.152	.498	.590	.639	-.349	.447	.614	.749*	.741*	.654
	Sig. (2-tailed)		.694	.697	.173	.094	.064	.357	.228	.079	.020	.022	.056
	N	9	9	9	9	9	9	9	9	9	9	9	9
CrS	Pearson Correlation	-.153	1	.318	.424	-.332	.172	-.441	.053	.312	.240	.206	.299
	Sig. (2-tailed)	.694		.405	.255	.383	.658	.234	.892	.414	.534	.594	.435
	N	9	9	9	9	9	9	9	9	9	9	9	9
PbS	Pearson Correlation	.152	.318	1	.070	.152	.177	-.234	.110	-.109	.010	-.033	-.092
	Sig. (2-tailed)	.697	.405		.858	.696	.648	.545	.778	.780	.980	.933	.813
	N	9	9	9	9	9	9	9	9	9	9	9	9
MnS	Pearson Correlation	.498	.424	.070	1	.016	.500	-.903**	-.191	.254	.899**	.383	.358
	Sig. (2-tailed)	.173	.255	.858		.968	.171	.001	.623	.509	.001	.309	.344
	N	9	9	9	9	9	9	9	9	9	9	9	9
VS	Pearson Correlation	.590	-.332	.152	.016	1	-.007	-.093	.571	.398	.409	.637	.519
	Sig. (2-tailed)	.094	.383	.696	.968		.986	.812	.108	.288	.275	.065	.152
	N	9	9	9	9	9	9	9	9	9	9	9	9
ZnS	Pearson Correlation	.639	.172	.177	.500	-.007	1	-.203	.330	.382	.491	.376	.290
	Sig. (2-tailed)	.064	.658	.648	.171	.986		.600	.386	.311	.180	.319	.449
	N	9	9	9	9	9	9	9	9	9	9	9	9
CdCL	Pearson Correlation	-.349	-.441	-.234	-.903**	-.093	-.203	1	.234	-.124	-.803**	-.283	-.297

	Sig. (2-tailed)	.357	.234	.545	.001	.812	.600		.544	.752	.009	.461	.438
	N	9	9	9	9	9	9	9	9	9	9	9	9
CrCL	Pearson Correlation	.447	.053	.110	-.191	.571	.330	.234	1	.762*	.138	.735*	.696*
	Sig. (2-tailed)	.228	.892	.778	.623	.108	.386	.544		.017	.723	.024	.037
	N	9	9	9	9	9	9	9	9	9	9	9	9
PbCL	Pearson Correlation	.614	.312	-.109	.254	.398	.382	-.124	.762*	1	.524	.940**	.965**
	Sig. (2-tailed)	.079	.414	.780	.509	.288	.311	.752	.017		.148	.000	.000
	N	9	9	9	9	9	9	9	9	9	9	9	9
MnCL	Pearson Correlation	.749*	.240	.010	.899**	.409	.491	-.803**	.138	.524	1	.698*	.647
	Sig. (2-tailed)	.020	.534	.980	.001	.275	.180	.009	.723	.148		.036	.060
	N	9	9	9	9	9	9	9	9	9	9	9	9
VCL	Pearson Correlation	.741*	.206	-.033	.383	.637	.376	-.283	.735*	.940**	.698*	1	.967**
	Sig. (2-tailed)	.022	.594	.933	.309	.065	.319	.461	.024	.000	.036		.000
	N	9	9	9	9	9	9	9	9	9	9	9	9
ZnCL	Pearson Correlation	.654	.299	-.092	.358	.519	.290	-.297	.696*	.965**	.647	.967**	1
	Sig. (2-tailed)	.056	.435	.813	.344	.152	.449	.438	.037	.000	.060	.000	
	N	9	9	9	9	9	9	9	9	9	9	9	9

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

Appendix 8. Correlations between trace metal contents in Soil and Crop Tubers samples

		CdS	CrS	PbS	MnS	VS	ZnS	CdCT	CrCT	PbCT	MnCT	VCT	ZnCT
CdS	Pearson Correlation	1	-.153	.152	.498	.590	.639	-.495	.478	.552	.639	.756*	.376
	Sig. (2-tailed)		.694	.697	.173	.094	.064	.176	.194	.123	.064	.018	.319
	N	9	9	9	9	9	9	9	9	9	9	9	9
CrS	Pearson Correlation	-.153	1	.318	.424	-.332	.172	-.330	.315	.326	.432	.085	.246
	Sig. (2-tailed)	.694		.405	.255	.383	.658	.385	.410	.392	.245	.827	.523
	N	9	9	9	9	9	9	9	9	9	9	9	9
PbS	Pearson Correlation	.152	.318	1	.070	.152	.177	-.004	-.036	-.162	-.113	-.036	-.302
	Sig. (2-tailed)	.697	.405		.858	.696	.648	.991	.927	.677	.773	.927	.429
	N	9	9	9	9	9	9	9	9	9	9	9	9
MnS	Pearson Correlation	.498	.424	.070	1	.016	.500	-.938**	.959**	.254	.813**	.223	.025
	Sig. (2-tailed)	.173	.255	.858		.968	.171	.000	.000	.510	.008	.565	.949
	N	9	9	9	9	9	9	9	9	9	9	9	9
VS	Pearson Correlation	.590	-.332	.152	.016	1	-.007	-.180	-.072	.432	.332	.671*	.328
	Sig. (2-tailed)	.094	.383	.696	.968		.986	.643	.854	.246	.382	.048	.389
	N	9	9	9	9	9	9	9	9	9	9	9	9
ZnS	Pearson Correlation	.639	.172	.177	.500	-.007	1	-.309	.516	.282	.434	.364	.243
	Sig. (2-tailed)	.064	.658	.648	.171	.986		.419	.155	.462	.243	.336	.529
	N	9	9	9	9	9	9	9	9	9	9	9	9
CdCT	Pearson Correlation	-.495	-.330	-.004	-.938**	-.180	-.309	1	-.929**	-.275	-.825**	-.266	-.019

	Sig. (2-tailed)	.176	.385	.991	.000	.643	.419		.000	.474	.006	.489	.961
	N	9	9	9	9	9	9	9	9	9	9	9	9
CrCT	Pearson Correlation	.478	.315	-.036	.959**	-.072	.516	-.929**	1	.136	.728*	.119	-.080
	Sig. (2-tailed)	.194	.410	.927	.000	.854	.155	.000		.726	.026	.760	.837
	N	9	9	9	9	9	9	9	9	9	9	9	9
PbCT	Pearson Correlation	.552	.326	-.162	.254	.432	.282	-.275	.136	1	.751*	.935**	.949**
	Sig. (2-tailed)	.123	.392	.677	.510	.246	.462	.474	.726		.020	.000	.000
	N	9	9	9	9	9	9	9	9	9	9	9	9
MnCT	Pearson Correlation	.639	.432	-.113	.813**	.332	.434	-.825**	.728*	.751*	1	.699*	.565
	Sig. (2-tailed)	.064	.245	.773	.008	.382	.243	.006	.026	.020		.036	.113
	N	9	9	9	9	9	9	9	9	9	9	9	9
VCT	Pearson Correlation	.756*	.085	-.036	.223	.671*	.364	-.266	.119	.935**	.699*	1	.854**
	Sig. (2-tailed)	.018	.827	.927	.565	.048	.336	.489	.760	.000	.036		.003
	N	9	9	9	9	9	9	9	9	9	9	9	9
ZnCT	Pearson Correlation	.376	.246	-.302	.025	.328	.243	-.019	-.080	.949**	.565	.854**	1
	Sig. (2-tailed)	.319	.523	.429	.949	.389	.529	.961	.837	.000	.113	.003	
	N	9	9	9	9	9	9	9	9	9	9	9	9

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

Appendix 9. Correlations between trace metal contents in Crop Leaves and Crop Tuber samples

		CdCT	CrCT	PbCT	MnCT	VCT	ZnCT	CdCL	CrCL	PbCL	MnCL	VCL	ZnCL
CdCT	Pearson Correlation	1	-.929**	-.275	-.825**	-.266	-.019	.940**	.171	-.252	-.910**	-.413	-.426
	Sig. (2-tailed)		.000	.474	.006	.489	.961	.000	.660	.513	.001	.269	.252
	N	9	9	9	9	9	9	9	9	9	9	9	9
CrCT	Pearson Correlation	-.929**	1	.136	.728*	.119	-.080	-.843**	-.299	.150	.837**	.256	.260
	Sig. (2-tailed)	.000		.726	.026	.760	.837	.004	.434	.700	.005	.506	.498
	N	9	9	9	9	9	9	9	9	9	9	9	9
PbCT	Pearson Correlation	-.275	.136	1	.751*	.935**	.949**	-.148	.742*	.989**	.531	.946**	.974**
	Sig. (2-tailed)	.474	.726		.020	.000	.000	.704	.022	.000	.141	.000	.000
	N	9	9	9	9	9	9	9	9	9	9	9	9
MnCT	Pearson Correlation	-.825**	.728*	.751*	1	.699*	.565	-.705*	.296	.729*	.933**	.816**	.817**
	Sig. (2-tailed)	.006	.026	.020		.036	.113	.034	.439	.026	.000	.007	.007
	N	9	9	9	9	9	9	9	9	9	9	9	9
VCT	Pearson Correlation	-.266	.119	.935**	.699*	1	.854**	-.118	.807**	.942**	.580	.979**	.948**
	Sig. (2-tailed)	.489	.760	.000	.036		.003	.762	.009	.000	.102	.000	.000
	N	9	9	9	9	9	9	9	9	9	9	9	9
ZnCT	Pearson Correlation	-.019	-.080	.949**	.565	.854**	1	.121	.798**	.937**	.298	.837**	.862**
	Sig. (2-tailed)	.961	.837	.000	.113	.003		.757	.010	.000	.437	.005	.003
	N	9	9	9	9	9	9	9	9	9	9	9	9
CdCL	Pearson Correlation	.940**	-.843**	-.148	-.705*	-.118	.121	1	.234	-.124	-.803**	-.283	-.297

	Sig. (2-tailed)	.000	.004	.704	.034	.762	.757		.544	.752	.009	.461	.438
	N	9	9	9	9	9	9	9	9	9	9	9	9
CrCL	Pearson Correlation	.171	-.299	.742*	.296	.807**	.798**	.234	1	.762*	.138	.735*	.696*
	Sig. (2-tailed)	.660	.434	.022	.439	.009	.010	.544		.017	.723	.024	.037
	N	9	9	9	9	9	9	9	9	9	9	9	9
PbCL	Pearson Correlation	-.252	.150	.989**	.729*	.942**	.937**	-.124	.762*	1	.524	.940**	.965**
	Sig. (2-tailed)	.513	.700	.000	.026	.000	.000	.752	.017		.148	.000	.000
	N	9	9	9	9	9	9	9	9	9	9	9	9
MnCL	Pearson Correlation	-.910**	.837**	.531	.933**	.580	.298	-.803**	.138	.524	1	.698*	.647
	Sig. (2-tailed)	.001	.005	.141	.000	.102	.437	.009	.723	.148		.036	.060
	N	9	9	9	9	9	9	9	9	9	9	9	9
VCL	Pearson Correlation	-.413	.256	.946**	.816**	.979**	.837**	-.283	.735*	.940**	.698*	1	.967**
	Sig. (2-tailed)	.269	.506	.000	.007	.000	.005	.461	.024	.000	.036		.000
	N	9	9	9	9	9	9	9	9	9	9	9	9
ZnCL	Pearson Correlation	-.426	.260	.974**	.817**	.948**	.862**	-.297	.696*	.965**	.647	.967**	1
	Sig. (2-tailed)	.252	.498	.000	.007	.000	.003	.438	.037	.000	.060	.000	
	N	9	9	9	9	9	9	9	9	9	9	9	9

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

Appendix 10. Test of spatial equality in mean variances of Air Samples

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Column 1	117	5860.78	50.09214	12030.52
Column 2	117	234	2	0.672414

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	135301.9	1	135301.9	22.49187	3.69E-06	3.881853
Within Groups	1395618	232	6015.594			
Total	1530920	233				

Appendix 11. Test of spatial equality in mean variances of Soil Samples

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Column 1	109	1600.721	14.68551	624.2996
Column 2	109	218	2	0.666667

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	8770.263	1	8770.263	28.06636	2.88E-07	3.88487
Within Groups	67496.36	216	312.4831			
Total	76266.62	217				

Appendix 12. Test of spatial equality in mean variances of Cassava Leaves Samples

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Column 1	54	852.096	15.77956	782.7425
Column 2	54	108	2	0.679245

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	5126.656	1	5126.656	13.08786	0.000457	3.930692
Within Groups	41521.35	106	391.7109			
Total	46648.01	107				

Appendix 13. Test of spatial equality in mean variances of Cassava Tubers Samples

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Column 1	54	1098.958	20.35107	1237.719
Column 2	54	108	2	0.679245

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	9092.572	1	9092.572	14.68441	0.000216	3.930692
Within Groups	65635.08	106	619.1989			
Total	74727.66	107				

Appendix 14. Principal Components Analysis (PCA) outputs

Communalities

	Initial	Extraction
CO	1.000	.945
CO2	1.000	.947
NO2	1.000	.920
SPM	1.000	.976
H2S	1.000	.977
SO2	1.000	.963
HCsA	1.000	.930
CdA	1.000	.984
CrA	1.000	.988
PbA	1.000	.863
MnA	1.000	.991
VA	1.000	.950
ZnA	1.000	.996
pH	1.000	.994
OrganicC	1.000	.990
TotalN	1.000	.983
Phosphorus	1.000	.996
Nitrate	1.000	.994
HCsS	1.000	.815
CdS	1.000	.936
CrS	1.000	.982
PbS	1.000	.988
MnS	1.000	.991
VS	1.000	.917
ZnS	1.000	.933

Extraction Method: Principal Component Analysis.

Total Variance Explained

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	11.357	45.430	45.430	11.357	45.430	45.430	10.475	41.902	41.902
2	7.261	29.045	74.475	7.261	29.045	74.475	5.784	23.138	65.040
3	2.518	10.072	84.548	2.518	10.072	84.548	4.096	16.383	81.423
4	1.579	6.316	90.864	1.579	6.316	90.864	2.028	8.111	89.533
5	1.233	4.933	95.796	1.233	4.933	95.796	1.566	6.263	95.796
6	.499	1.996	97.793						
7	.299	1.197	98.990						
8	.252	1.010	100.000						
9	5.497E-16	2.199E-15	100.000						
10	5.040E-16	2.016E-15	100.000						
11	3.797E-16	1.519E-15	100.000						
12	3.111E-16	1.244E-15	100.000						
13	2.106E-16	8.423E-16	100.000						
14	1.926E-16	7.704E-16	100.000						
15	1.154E-16	4.617E-16	100.000						
16	7.400E-17	2.960E-16	100.000						
17	-2.921E-17	-1.168E-16	100.000						
18	-4.041E-17	-1.617E-16	100.000						
19	-7.334E-17	-2.934E-16	100.000						
20	-1.655E-16	-6.622E-16	100.000						
21	-1.816E-16	-7.264E-16	100.000						
22	-2.537E-16	-1.015E-15	100.000						
23	-3.532E-16	-1.413E-15	100.000						
24	-4.209E-16	-1.684E-15	100.000						
25	-5.146E-16	-2.058E-15	100.000						

Extraction Method: Principal Component Analysis.

Component Matrix[a]

	Component				
	1	2	3	4	5
CO	.853	.297	.187	-.129	.279
CO2	.939	.000	-.205	-.063	-.139
NO2	.438	.764	-.302	-.229	.025
SPM	.409	-.867	.199	.133	.017
H2S	.947	.267	.003	-.073	-.057
SO2	.943	-.213	-.025	-.015	-.164
HCsA	.834	.275	-.103	.139	-.359
CdA	.389	.783	-.384	.241	.120
CrA	.522	.729	-.427	-.007	-.055
PbA	.380	.719	.444	.047	-.047
MnA	.915	.301	.221	.103	-.047
VA	.597	.545	-.425	-.193	.282
ZnA	.979	.106	.028	.162	-.012
pH	-.937	.321	-.067	-.080	-.047
OrganicC	-.625	.770	-.023	-.075	-.013
TotalN	-.896	.407	-.069	-.097	.024
Phosphorus	-.676	.730	-.016	-.068	-.023
Nitrate	-.978	.097	-.106	-.124	-.031
HCsS	.137	.766	.433	.048	.138
CdS	-.089	.731	.584	-.002	-.230
CrS	-.117	.344	-.601	.670	.200
PbS	-.166	-.010	.447	.689	.535
MnS	-.724	.662	-.131	.085	-.071
VS	.252	.533	.547	-.379	.355
ZnS	-.211	.471	.337	.460	-.584

Extraction Method: Principal Component Analysis.

a. 5 components extracted.

Rotated Component Matrix[a]

	Component				
	1	2	3	4	5
CO	.657	.403	.564	-.177	.022
CO2	.836	.430	.018	-.026	-.250
NO2	.060	.844	.370	.006	-.258
SPM	.723	-.563	-.299	-.187	.114
H2S	.766	.496	.336	.044	-.173
SO2	.945	.175	.007	-.003	-.196
HCsA	.698	.514	.104	.362	-.194
CdA	.053	.947	.184	.158	.156
CrA	.169	.939	.187	.131	-.160
PbA	.155	.348	.755	.382	.056
MnA	.773	.390	.450	.194	.013
VA	.253	.858	.242	-.279	-.114
ZnA	.882	.408	.207	.083	.038
pH	-.986	-.076	-.032	.125	-.019
OrganicC	-.857	.317	.312	.239	-.015
TotalN	-.986	.006	.044	.087	.004
Phosphorus	-.887	.268	.281	.242	-.010
Nitrate	-.955	-.221	-.172	.012	-.048
HCsS	-.099	.324	.772	.265	.185
CdS	-.253	.080	.744	.559	-.024
CrS	-.229	.657	-.425	.146	.544
PbS	-.044	-.215	.186	.063	.949
MnS	-.896	.286	.091	.307	.065
VS	.030	.117	.936	-.165	-.011
ZnS	-.213	.018	.169	.922	.096

Extraction Method: Principal Component Analysis.

Rotation Method: Varimax with Kaiser Normalization.

a. Rotation converged in 9 iterations.

Component Transformation Matrix

Component	1	2	3	4	5
1	.914	.346	.188	-.049	-.088
2	-.356	.686	.551	.314	.000
3	.122	-.622	.706	.258	.180
4	.133	.096	-.323	.506	.783
5	-.077	.114	.241	-.759	.589

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.

Component Score Coefficient Matrix

	Component				
	1	2	3	4	5
CO	.035	.026	.170	-.185	.076
CO2	.069	.062	-.056	.040	-.119
NO2	-.038	.148	.032	-.088	-.127
SPM	.095	-.109	-.027	.013	.085
H2S	.061	.044	.040	.020	-.070
SO2	.094	-.001	-.037	.080	-.095
HCsA	.083	.052	-.093	.263	-.116
CdA	-.013	.206	-.068	-.004	.146
CrA	-.011	.185	-.065	.017	-.064
PbA	.024	-.032	.167	.119	.030
MnA	.081	.004	.070	.094	.038
VA	-.033	.189	.027	-.258	.004
ZnA	.089	.042	-.003	.062	.069
pH	-.098	.009	-.003	.014	-.059
OrganicC	-.095	.054	.055	.018	-.040
TotalN	-.105	.025	.021	-.031	-.035
Phosphorus	-.095	.046	.049	.025	-.041
Nitrate	-.097	-.005	-.019	-.023	-.076
HCsS	-.010	-.015	.199	.007	.120
CdS	.000	-.099	.173	.233	-.069
CrS	-.012	.237	-.242	.045	.385
PbS	.033	-.025	.086	-.063	.630
MnS	-.085	.072	-.030	.089	.005
VS	-.033	-.067	.345	-.262	.019
ZnS	.051	-.071	-.081	.563	-.025

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.
Component Scores.

Component Score Covariance Matrix

Component	1	2	3	4	5
1	1.000	.000	.000	.000	.000
2	.000	1.000	.000	.000	.000
3	.000	.000	1.000	.000	.000
4	.000	.000	.000	1.000	.000
5	.000	.000	.000	.000	1.000

Extraction Method: Principal Component Analysis.

Rotation Method: Varimax with Kaiser Normalization.

Component Scores.