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**ENVIRONMENTAL DEGRADATION: MORTGAGING OUR
FUTURE FOR TODAY'S GAIN**

By

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ENVIRONMENTAL DEGRADATION: MORTGAGING OUR FUTURE FOR TODAY'S GAIN

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Members of my Immediate and Extended Families
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Great FUNAABITES

1.0 Preamble

It is with joy and deep sense of humility that I stand before you this afternoon to deliver the 55th Inaugural lecture of this great University. Today's event is of special significance as this is the first Inaugural Lecture from the Department of Environmental Management and Toxicology (EMT) and the ninth Inaugural Lecture from the College of Environmental Resources Management. Also, this Inaugural Lecture is the second to be delivered during the tenure of the current Vice Chancellor, Professor Felix Kolawole Salako.

I am therefore immensely grateful to the Almighty God for the grace to stand before this audience today to deliver this lecture. This exercise gives me the opportunity to share with you all, my 34 years of experience in the academia. I joined the Federal University of Technology, Abeokuta (FUTAB) on 1st December, 1983 as an Assistant Lecturer (Analytical Chemistry) in the Department of Chemical Sciences. By His Grace, I survived all the transformations from FUTAB to ULAB (University of Lagos, Abeokuta Campus) to COSTAB (College of Science and Technology, University of Lagos, Abeokuta Campus), and finally to the Federal University of Agriculture, Abeokuta, first as UNAAB and now, FUNAAB.

The administration of the founding Vice Chancellor of the University, Prof. Nurudeen O. Adedipe introduced the Environmental Management and Toxicology (EMT) degree programme into the Nigerian University system in 1989. This University was the first to commence the study of EMT at the undergraduate level in Nigeria with the primary aim of producing highly skilled manpower in all areas of specializations in the field.

It is a great honour therefore for me to present aspects of my contributions to research nationally and internationally to this great audience of scholars and eminent persons. The topic of my lecture is “**Environmental Degradation: Mortgaging Our Future for Today’s Gain**”.

2.0 Introduction

Environment is everything that is around us. It can be living or non-living things. It includes biological, chemical, physical and other natural forces. Living things live in their environment and constantly interact with it and change in response to conditions in their environment. In the environment, there are interactions between animals, plants, soil, water and other living and non-living things (Wikipedia, 2017a). Simply defined, environment refers to the total combination of living things, non-living things, man-made objects and the interaction between them and the conditions surrounding them on earth. Environment can be divided into 4 components: the physical environment, e.g. water, air, soil, housing, wastes, radiation e.t.c; the biological environment e.g. plants, animals, bacteria, viruses, insects, rodents, e.t.c; the social environment e.g. customs, culture, religion e.t.c. and the economic environment e.g. refineries, transportation, marine, telecommunications etc.

Substances introduced into the environment are distributed among the five environmental spheres: hydrosphere (water), atmosphere (air), geosphere (solid earth – soil and rock), biosphere (life) and anthrosphere (the part of the environment made and operated by humans). The anthrosphere is where pollutants are made and from which they are released with profound effects on all other environmental spheres (Manahan, 2013). It is important to consider the anthrosphere as a distinct environmental sphere. If we take a look around our environment, we would observe buildings, roads, airports, factories, power lines and numerous other things constructed and operated by humans as evidence of the existence of the anthrosphere on earth.

Environmental degradation is the deterioration of the environment through depletion of resources such as air, water and soil; the destruction of ecosystems; habitat destruction; the extinction of wildlife and pollution. It is defined as any change or disturbance to the environment perceived to be deleterious or undesirable (Johnson et al., 1997). The United Nations International Strategy for Disaster Reduction defines environmental degradation as "the reduction of the capacity of the environment to meet social and ecological objectives, and needs" (Wikipedia, 2017b). Environmental degradation is of many types. When natural habitats are destroyed or natural resources are depleted, the environment is degraded. Efforts to counteract this problem include environmental protection and environmental resources management.

Pollution, by definition, is the introduction of contaminants into the natural environment that harmfully disrupts it or cause adverse change. While nature sometimes produces its own damaging contaminants – wildfires send up billows of smoke and ash, volcanoes emit noxious gases; humans are responsible for the lion’s share of the pollution plaguing the planet today. Environmental pollution consists of four basic types namely, air, water, soil and noise. Other types are thermal pollution, chemical pollution, etc.

There is a growing body of evidence confirming the contamination of all environmental media, even in the remotest regions of the world, once thought to be pristine. Humans appear to have done

a thorough job of contaminating the Earth's rivers, oceans and atmosphere. Is there anywhere pristine left on the planet? Wherever we go, we seem to have a knack for leaving our rubbish and waste behind. It has been reported that spent oxygen canisters and raw sewage mar the snows of Mount Everest (see Plate 1)! It is only if we know the type and quantity of these contaminants that we can make efforts to protect the environment and its inhabitants.



Plate 1. Collecting rubbish left by climbers on Mount Everest in the Himalayas

The rapid growth in the world population has led to sharp increases in the consumption of energy and resources and in the production of consumer goods and chemicals. This explosive growth has caused environmental challenges such as pollution, urban overcrowding, overuse of arable land and diminishing water resources. The effects of human activities on the environment are complex. As the world's population approaches 8 billion, the strain on the planet's resources is steadily increasing.

In pursuit of economic development, Nigeria and most post-colonial countries veered into industrialization at independence. The focus was on maximum exploitation of natural resources for rapid economic development with scant regard for resource conservation and sustainability. Industrial activities, usually carried out in developing countries with weak legal framework and regulations, led to pollution of water resources, destruction of fauna and flora, health hazards and deterioration of health quality, air and noise pollution. Without pollution control, the waste products from consumption, agriculture, mining, manufacturing, transportation and other human activities, whether they accumulate or disperse, will degrade the environment. This realization stirred worldwide efforts to stem the tide of unacceptable levels of environmental degradation.

Sustainable Development Goals

Sustainable development that is linked to the environment was popularized by the World Commission on Environment and Development (WCED) report of 1987 titled “Our Common Future”. The 1972 Stockholm UN Conference on Human Environment established the nexus between underdevelopment and environmental integrity. Twenty years later, the 1992 UN Conference on Environment and Development (UNCED), also known as the Earth Summit held in Rio de Janeiro, Brazil generated an action plan for sustainable development in the 21st Century, which forms the policy instrument for programmes on environment in various countries.

The term ‘sustainability’ according to Brundtland Commission denotes the development that meets the needs of the present without compromising the ability of future generations to meet their own needs. In other words, sustainability is the basic idea that people should live on this planet in such a way that ‘the needs of the present can be satisfied without jeopardising the ability of future generations to satisfy theirs’. Since Rio, governments, international bodies, organizations, companies, and individual consumers have been urged to develop constructive approaches to the vision of sustainability and to do their fair share. Consequently, environmental awareness is increasing locally and internationally, especially regarding environmental degradation and pollution resulting from anthropogenic activities which have led to threat to human, fauna and flora, biodiversity, ecosystem and indeed environmental sustainability challenges of serious consequences.

Common environmental pollution problems in Nigeria

In addition to environmental threats posed by Nigeria’s natural physical setting, there are a number of threats that are related to human activities which have further amplified the country’s vulnerability to environmental degradation. These include:

- ❖ Population growth
- ❖ Urbanization
- ❖ Solid waste management and urban sewage problems
- ❖ Oil pollution and gas flaring
- ❖ Deforestation and loss of biological diversity
- ❖ Desertification
- ❖ Pollution (Water, Soil, Air, Noise)
- ❖ Climate Change
- ❖ Ozone layer depletion
- ❖ Open cast mining and mining waste land
- ❖ Flooding and soil erosion
- ❖ Wetland destruction
- ❖ Agro-chemical problems (resulting from farming practice)
- ❖ Trans-boundary movement of toxic and hazardous waste

Air Pollution

One of the most profound environmental problems confronting major cities around the world is air pollution and Nigerian cities are not an exception. Polluted air has become an almost inescapable part of urban life throughout the world. According to the World Development Indicators Report for 1997, more than 1.5 billion urban dwellers are exposed to levels of ambient

air pollution that are above the recommended maximum levels (World Bank, 1997). Air pollution is recognized today as a major health risk. Compared to adults, children spend more time outdoors, breathe more rapidly, and inhale more pollutants per pound of body weight. The elderly are more susceptible to air pollution because their immune systems are weakened by age and they often suffer from one or more chronic illnesses. Exposure to the many pollutants in the air (both ambient and household) can cause a range of adverse health effects, from shortness of breath, coughing, chronic bronchitis to heart attacks, stroke and lung cancer. According to the latest available estimates, in 2013, 5.5 million premature deaths worldwide, or 1 in every 10 total deaths, were attributable to air pollution. In 1990, as in 2013, air pollution was the fourth leading fatal health risk worldwide, resulting in 4.8 million premature deaths (WB-IHME, 2016).

Air pollution has three principal man-made sources – energy use, vehicular emissions, and industrial production - all of which tend to expand with economic growth unless adequate pollution abatement measures are put in place (World Bank, 1992). In fact, most outdoor air pollution in urban areas comes from the combustion of fossil fuels in industrial processes, for heating and electricity generations, and by motor vehicles. Electricity generation stations are major sources of pollutant emissions in both developed and developing countries as more than half the world's consumption of coal and one-third of fossil fuel consumption go to electricity generation.

The major pollutants that could be encountered include carbon monoxide (CO), sulphur oxides (SO_x), nitrogen oxides (NO_x), lead, particulate matter and ozone (O₃). Other pollutants include hydrocarbons, most of which come from petrol evaporation and possibly leaks in gas pipes and emissions from petroleum industries. Fine particles or microscopic dust from coal or wood fires and unfiltered diesel engines are rated as one of the most lethal forms of air pollution caused by industry, transport, household heating, cooking and ageing coal or oil-fired power stations. In 2005, the World Health Organisation (WHO) estimated that death rates in cities with higher particle pollution were 15 to 20 percent above those found in cleaner cities. When carbon monoxide, nitrogen dioxide and other primary pollutants (those that are injected directly into the atmosphere) find their way high into the atmosphere, they often get transformed through chemical reactions into secondary pollutants. Some of these pollutants can linger for months. Others, like methane, are less reactive and may circulate the globe for years until they are eventually broken down or find their way to the ground via snow or rain.

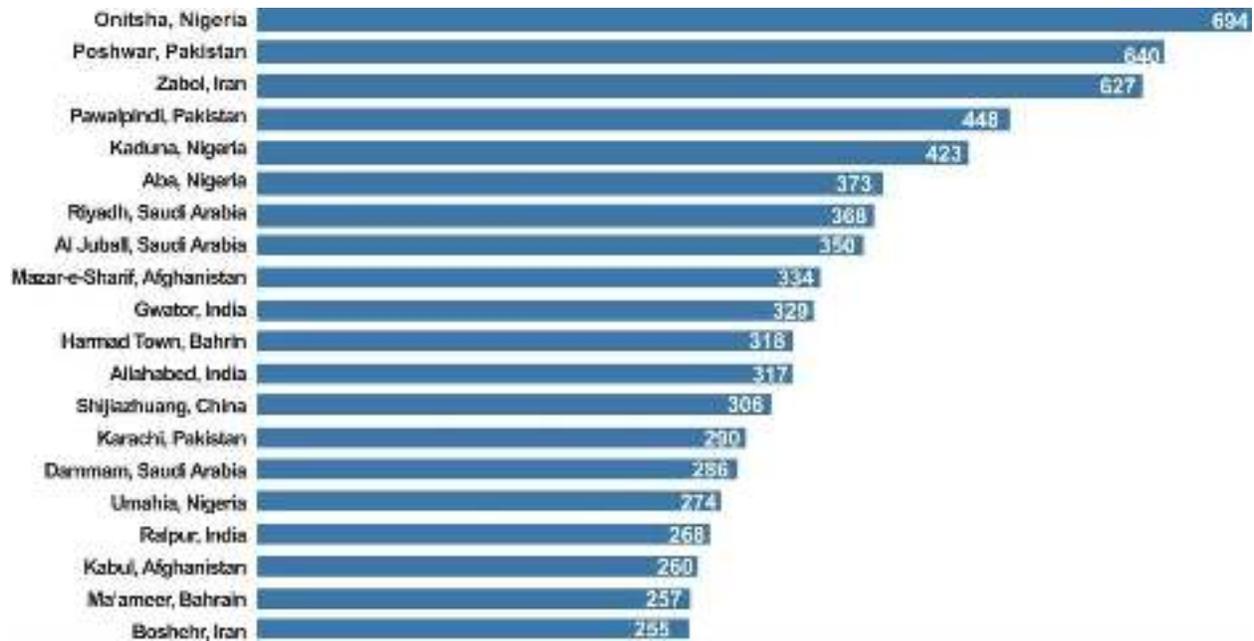
Climate Change

Early this year, the National Aeronautics and Space Administration (NASA) and the National Oceanic and Atmospheric Administration (NOAA) reported that the Earth's 2016 surface temperatures were the warmest since modern record-keeping began in 1880! This makes 2016 the third year in a row to set a new record for global average surface temperatures. The El Niño weather in the Pacific and human emissions of CO₂ have been identified as the causes of the unprecedented warmth.

Scientists believe that gases released from industry and agriculture are adding to the natural greenhouse effect, the way the Earth's atmosphere traps some of the energy from the Sun. Human activities such as burning fossil fuels like coal, oil and natural gas increase the amount of carbon dioxide (CO₂), the main greenhouse gas responsible for global warming. Carbon-absorbing forests

are also being cut down. The concentration of CO₂ in the atmosphere is now higher than at any time in the last 800,000 years (Amos, 2006; Wikipedia, 2017c)

In June 2016, Nigeria was reported to have a city with worst Particulate Matter (PM₁₀) levels in the World by WHO. The latest WHO urban air quality data, collected between 2011 and 2015, reveal that 98% of cities with over 100,000 inhabitants in low and middle-income countries do not meet WHO air quality guidelines. Of the 3,000 cities in the WHO's air quality database, the most polluted at the time of measurement was Onitsha, a fast-growing city in Nigeria, which recorded roughly 30 times more than the WHO's recommended levels of PM₁₀ particles (WHO-UAAP, 2016). Four of the worst cities in the world for air pollution are in Nigeria according to the WHO report. The other three cities named in the WHO report for high PM₁₀ levels are Kaduna, in the north, which came fifth, followed by the cities of Aba in sixth place and Umuahia in 16th position. Last year, the World Bank reported that 94% of the population in Nigeria is exposed to air pollution levels that exceed WHO guidelines (compared to 72% on average in Sub-Saharan Africa in general). The WHO study tracked the growth in the two different sizes of particulate matter, PM₁₀ and PM_{2.5}, per cubic meter of air. Nigeria did not feature in the top 10 for PM_{2.5} levels (Figure 1).



Annual mean of PM₁₀ particulate concentration (µg/m³)

Fig. 1: The 20 most-polluted cities in the world
Source: WHO-UAAP, 2016

The possible contributing factors to the air pollution reported above (see Plate 2) are:

- (a) traffic pollution from old vehicles

- (b) noxious fumes from generators (due to unreliable electricity supplies, many Nigerians rely on generators at home and in the office often in unventilated areas).
- (c) vehicular emissions which go unregulated on the street.
- (d) burning of municipal solid waste
- (e) reliance on using solid fuels for cooking



Plate 2: Vehicular emission and air pollution in Lagos metropolis

Water

Water comprising over 70% of the Earth's surface is undoubtedly the most precious natural resource that exists on our planet. Without this invaluable compound, life on Earth would be non-existent: it is essential, for everything on our planet to grow and prosper. According to the World Development Indicators Report for 1997, 1 billion people live without clean water and 2 billion without sanitation (World Bank, 1997). The scarcity of clean water and pollution of fresh water has, therefore, led to a situation in which only 61% of the households in Nigeria have access to an improved source of drinking water (SFH, 2013), with a much higher proportion among urban households (76%) than among rural households (49%).

Urbanization, intensive agriculture, recreation, and the manufacturing industry are affecting water quality throughout the world. Waste generated by the industries and households are indiscriminately disposed-off into water bodies. This has led to pollution of inland water bodies and coastal waters and subsequently increased water quality parameters such as heavy metals, nutrients and organic matter, soluble ions, oil and grease, and organic chemicals such as pesticides and poly-nuclear aromatic hydrocarbons (PAHs) (Jaji et al., 2007; Taiwo et al., 2012; 2013). Urgent attention is, therefore, necessary to mitigate water pollution problems in Nigeria through monitoring as well as enforcement of relevant standards by industries.

Pollution in the form of organic material enters waterways in many different forms as sewage, as leaves and grass clippings, or as runoff from recently fertilized farms, livestock feedlots and pastures. Some of these organic materials contain nutrients such as nitrates and phosphates. In excess, nutrients over-stimulate the growth of aquatic plants and algae which consequently clogs our waterways, use up dissolved oxygen as they decompose and block light to deeper waters. This, in turn, proves very harmful to aquatic organisms as it affects the respiratory ability of fish and other invertebrates that reside in water. Many types of fish and bottom-dwelling animals cannot survive when levels of dissolved oxygen drop below two to five parts per million. When this occurs, it kills aquatic organisms in large numbers which leads to disruptions in the food chain.

Pathogens are another type of pollutants that are very harmful. They can cause many illnesses that range from typhoid and dysentery to minor respiratory and skin diseases. Pathogens include such organisms as bacteria, viruses, and protozoan. These pollutants enter waterways through untreated sewage, storm drains, septic tanks, runoff from farms, and particularly boats that dump sewage. Though microscopic, these pollutants have a tremendous effect as evidenced by their ability to cause sickness. The United Nations Environment Programme (UNEP) in a report titled “*Snapshot of the World's Water Quality*” which was released on 30th August, 2016 confirmed that pathogen and organic pollution increased in more than 50% of river stretches in Africa, Asia and Latin America (UNEP, 2016). In fact, about 323 million people on the three continents are at risk of infection from diseases caused by pathogens in water (UNEP, 2016). This study by UNEP, therefore, confirms that water pollution has risen across three continents, placing hundreds of millions of people at risk of contracting life-threatening diseases such as cholera and typhoid, UN Environment warns. This is as a result of the increasing amount of wastewater being dumped into our surface waters.

Soil

The soil is a multiphase system in which the hydrosphere, atmosphere, lithosphere, and biosphere exist side by side. It serves as a source of water and nutrients for plants; is a habitat for a large number of organisms, and is an important carbon sink. Harmful soil pollutants can easily enter the human body through plants and animals. Soil contamination or soil pollution is caused by the presence of xenobiotic (human-made) chemicals or other alteration in the natural soil environment. For example, human activity introduces heavy metals (such as cadmium, arsenic, lead and mercury) to our soils through mining, smelting, industry, agriculture, burning fossil fuels, or improper disposal of waste. Contamination may sometimes be correlated with the degree of industrialization and intensity of chemical usage. The concern over soil contamination stems primarily from attendant health risks (see Plate 3).

Soils are the major sinks for environmental contaminants released into the environment by aforementioned anthropogenic activities and unlike organic contaminants which are oxidized to carbon (IV) oxide by microbial action, most metals do not undergo microbial or chemical degradation, and their total concentration in soils persists for a long time after their introduction. Changes in their chemical forms (speciation) and bioavailability are, however, possible. Heavy metal contamination of soil may pose risks and hazards to humans and the ecosystem through: direct ingestion or contact with contaminated soil, the food chain (soil-plant-human or soil-plant-animal-human), drinking of contaminated groundwater, reduction in food quality (safety and

marketability) etc. Consumption of food crops contaminated with heavy metals is a major food chain route for human exposure. Environmental pollution and food safety are two of the most important issues of our time. Soil and water pollution, in particular, have historically impacted on food safety which represents an important threat to human health.

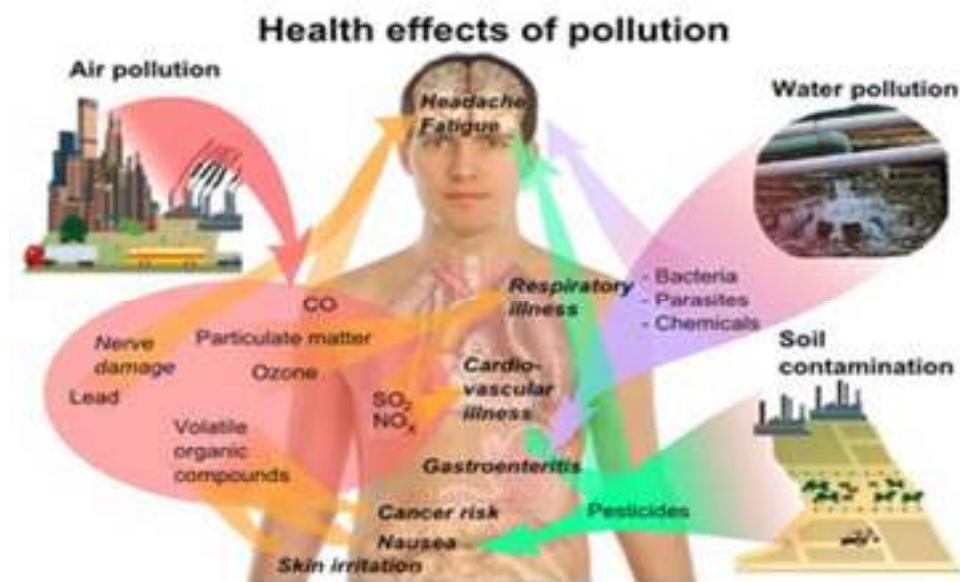


Plate 3: Health effects of pollution.

Most of the materials we use nowadays are impregnated with several chemicals to make them fireproof and meet fire safety regulations. These are classically halogenated compounds such as **polybrominated diphenyl ethers (PBDEs)**. Recently, the food safety authorities in the European Union (EU) banned PBDEs because several studies linked them to hepatic damage and perturbations in metabolism. Chemists, therefore, developed a new kind of fire retardants known as **hexabromocyclododecanes (HBCDs)**. Manufacturers of goods such as plastics, textiles and electronic equipment are increasingly using these compounds. A recent study (Tao et al., 2016) found HBCD in dust, air, sediments, and sewage in areas surrounding electronic waste (or e-waste) processing plants. The presence of HBCDs has also been reported in eggs, while researchers have confirmed human exposure from eating food sourced near the e-waste treatment plants (Tao et al., 2016). These are issues of concern, since these chemicals are potentially toxic, persistent and bioaccumulative. We may be ingesting dangerous amounts of toxic, accumulative chemicals. Unfortunately, the dangers of some of these compounds are not completely defined yet!

3.0 Contribution to Knowledge

The main focus of my research in the past few years had been in the application of Analytical Chemistry in Environmental Management and Toxicology. Specifically, I have studied the levels, forms, mobility and fate of essential trace elements, potentially toxic elements and rare earth

elements in soils, sediments, air, water, plants, food and biological samples. Linked to this is analytical methods development for environmental analysis.

3.1 Method Development

In the early years of my academic career, my research concentrated on the development of novel and improved methods for the analysis of environmental samples.

Automated Methods

One major area of analytical chemistry which attracted a lot of interest in the 1970s and 1980s was the automation of analytical methods which provide analytical data with a minimum operator's intervention. Initially, these systems were designed to fulfill the needs of clinical laboratories, where 30 or more chemical species were routinely determined for diagnostic and screening purposes. This was made possible by the scope of instrumental improvements provided by solid state electronic circuits and the increasing application of digital computers. Automation is a key demand in modern analytical chemistry. Process and quality control requires fast and reliable results in all areas of human activity.

The advantages of automatic analysis over manual methods include the fact that:

- (i) The system can operate reproducibly over long periods and is more precise and accurate than manual methods.
- (ii) Automated instruments are very fast when compared to manual devices.
- (iii) The system increases the analysis rate per day and the cost per analysis is generally reduced.
- (iv) Automatic methods eliminate human error and fatigue, both of which are likely to become more prevalent as the number of samples increases.
- (v) There is high reproducibility of timing sequences.
- (vi) Materials which are toxic and unstable in air can be more conveniently processed.

3.1.1 Development and Application of Automated Method for the Determination of Sulphide

The determination of anions and cations in solution by conversion of the determinant into a volatile molecular species followed by their molecular absorbance measurements in the gas phase has been thoroughly investigated in the past few decades. The gaseous product is carried by a stream of air or nitrogen to a flow-through absorption cell which is positioned in the light path of the spectrometer in the space normally occupied by the flame of the atomic absorption spectrometer. A narrow band of radiation corresponding to an absorption maximum of the evolved compound is passed through the cell and the absorbance signal of the compound is measured. The technique is known as Gas-Phase Molecular Absorption Spectrometry (GPMAS).

Determination of sulphide is important because of its extreme toxicity as hydrogen sulphide and its objectionable odour. There is also considerable interest in its measurement because one of the steps in the accurate determination of total sulphur in soils and plants involves the conversion of the various sulphur compounds in the sample into sulphide by reduction. A variety of analytical techniques have been applied to the determination of sulphide in environmental samples. However,

most of these methods are manual and involve considerable manipulation. They lack speed, simplicity and precision for routine analysis of a large daily throughput of samples.

Arowolo and Cresser (1991a) reported the development and subsequent automation of a new analytical technique of GPMAS for the analysis of sulphide in solution. The method was automated by the interfacing of an automatic sampler, a proportioning pump and a gas-liquid separator to an atomic absorption spectrometer (A Shandon Southern A3600 atomic absorption spectrometer) with a deuterium hollow cathode lamp and an Auto-graph S chart recorder. The spectrometer was modified for a non-flame cold vapour analysis by removing the burner head and replacing it with a 13 cm long, quartz-windowed flow-through absorption cell supported by a holder (Fig. 2).

The method is relatively free from interference with a detection limit for sulphide of $0.06 \mu\text{g ml}^{-1}$ and relative standard deviations of 1.4-3.3% for repeated analyses. The calibration graph is linear up to $100 \mu\text{g ml}^{-1}$ of sulphide. Twenty samples can be analysed in 1 h. The method was applied to the determination of sulphate-sulphur in plants and the results of the analysis are shown in Table 1. The values obtained were in good agreement with those obtained by the Methylene Blue method of Johnson and Nishita (1952).

3.1.2 Automated Determination of Sulphite by GPMAS

Using a similar procedure like the one described above, Arowolo and Cresser (1991b) also developed an automated method for the determination of sulphite in aqueous solution based on measuring the absorbance of sulphur dioxide evolved upon acidification of samples. The proposed method has a detection limit of $0.20 \mu\text{g ml}^{-1}$ and relative standard deviations of 2.3 and 1.8% for 20 and $10 \mu\text{g ml}^{-1}$ of sulphite, respectively. The calibration graph was linear up to $120 \mu\text{g ml}^{-1}$ and samples can be analysed at the rate of 20 per hour. Typical recorder tracing for a series of sulphite standards is shown in Fig. 3. The method was applied to the determination of sulphur dioxide in synthetic samples and in white wines (Table 2) and the results obtained by the proposed method correlated well with those obtained using an official method.

Our study suggested that the technique should be applicable to polluted air and other samples that will readily evolve sulphur dioxide upon acidification. The method is particularly attractive because of its simplicity, reproducibility and speed of analysis. Interferences in the proposed method are few and are readily overcome. The interference effect of nitrite is eliminated by adding sulphamic acid while that of heavy metals such as Mn^{2+} , Cu^{2+} and Fe^{3+} is minimized by the addition of Ethylenediaminetetraacetic acid (EDTA).

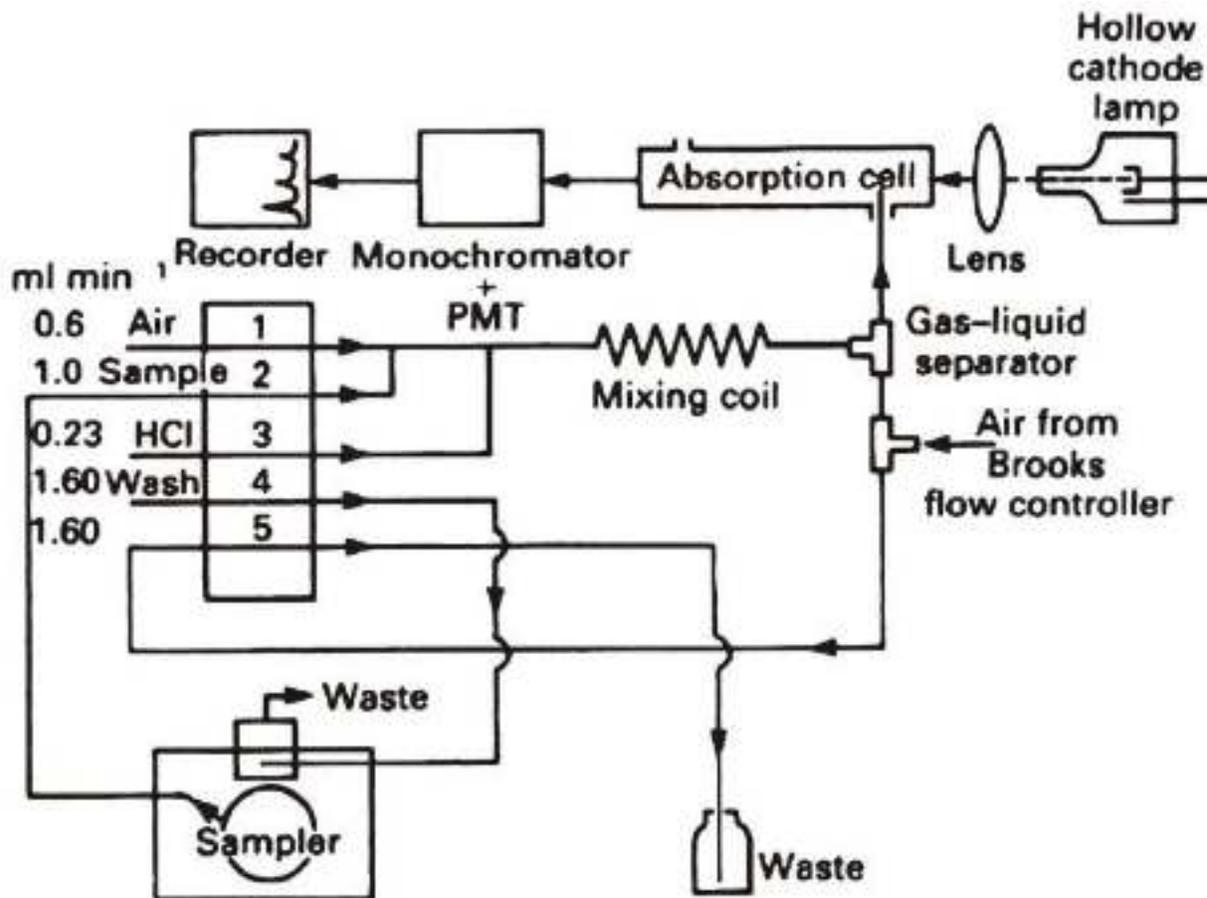


Fig. 2: Schematic diagram of the autoanalyzer-atomic absorption spectrometer system
 Source: Arowolo and Cresser (1991a)

Table 1: Sulphate sulphur in mixed herbage

Sample No.	Concentration found* /mg kg ⁻¹	
	Automated GPMAS	Methylene Blue method
1	765.5	789.4
2	774.5	764.8
3	202.2	198.7
4	266.2	274.8
5	176.1	176.2
6	763.4	751.5

*Mean of duplicate determinations.
 Source: Arowolo and Cresser (1991a)

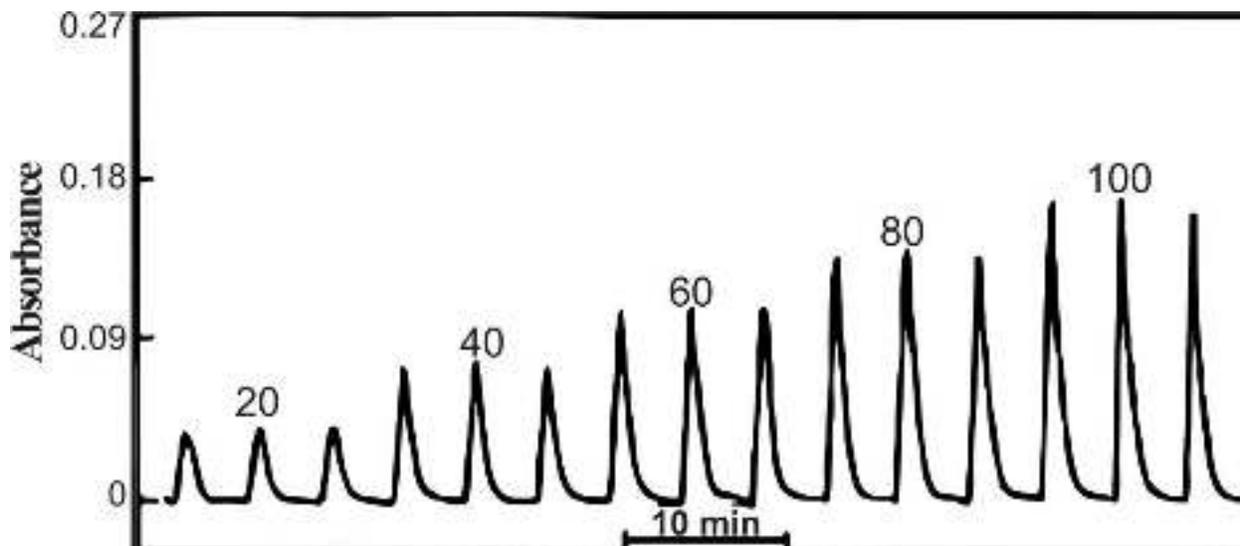


Fig. 3: Typical recorder tracing for a series of sulphite standards. Numbers above peaks denote concentrations in $\mu\text{g ml}^{-1}$
Source: Arowolo and Cresser (1991b)

3.1.3 Automated Determination of Sulphide by Cool Flame Molecular Emission Spectrometry

Many industrial waste waters contain inorganic sulphur compounds such as sulphate and sulphite which may be reduced to sulfide under anaerobic conditions. In a polluted watercourse, sulfide is a toxic nuisance and is a measure of the prevalence of anaerobic conditions. The problems arise from the liberation of hydrogen sulphide, which has an unpleasant odor and is highly toxic. Strict legislation for the control of pollutants in industrial areas, especially with respect to waste waters, has caused heavy workloads in the control laboratories. The need for a higher analysis rate has led to a continuous search for new automated methods which are reliable and sensitive.

The GPMAS technique described above was successfully adopted for cool flame emission spectrometry by Arowolo and Cresser (1992a and 1992b). The technique is based on passing the hydrogen sulphide liberated on acidification of samples with 3 M HCl into a cool, nitrogen-hydrogen diffusion flame and the resulting S_2 molecular emission is measured at 384 nm (Fig. 4). The method, which is automated, has a detection limit of $0.026 \mu\text{g ml}^{-1}$ for sulphide and relative standard deviations of 0.8-2.5% for repeated analyses. Under the optimized conditions, the proposed method is applicable over the concentration range $0.1-8.0 \mu\text{g ml}^{-1}$ of sulphide and twenty samples can be analyzed in 1 h. The method was applied to the determination of sulphide in effluent water samples obtained from a paper factory. The results obtained are shown in Table 3, from which it can be seen that the concentrations of sulfide obtained with both methods are in good agreement. A least square analysis of the data produced the following equation for the straight line:

Y (CFES) = 0.9980 X (MEB) - 0.10 with $r = 0.9992$ ($n = 10$).

Table 2: Determination of sulphur dioxide in synthetic samples

Sample \diamond	Sulphur dioxide* $\mu\text{g ml}^{-1}$		
	Automated GPMAS method	West-Gaeke Method	Difference (%)
1	3.04	3.13	-2.9
2	2.35	2.39	-1.7
3	1.73	1.75	-1.1
4	2.81	2.88	-2.4
5	4.30	4.29	+0.2
6	5.51	5.50	+0.2
7	0.38	0.39	-2.6
8	0.67	0.69	-2.9
9	0.79	0.78	+1.3
10	2.87	2.97	-3.4
11	6.33	6.53	-3.1
12	4.49	4.48	+0.2
14	4.20	4.30	-2.3
15	5.33	5.20	+2.5
16	6.12	6.06	+1.0
		Average:	1.8

*Mean of three values

\diamond Samples 1-6 were prepared from stock sulphite solution. Samples 7-16 were prepared by absorbing sulphur dioxide generated from stock sulphite solution (after acidification) in 0.04 mol dm⁻³ sodium tetrachloromercurate (II) (TCM) solution.

Source: Arowolo and Cresser (1991b)

The accuracy of the new method was confirmed by testing the recovery of sulphide from three different water samples. The results obtained indicate recovery in the range 98-103%. Automated cool-flame emission spectrometric determination of sulphide is a sensitive, reproducible, and versatile method for analyzing ppb amounts of sulphide. Introduction of the determinant in vapor form has the added advantage of avoiding the formation of compounds that are slow to volatilize or decompose in such cool flames when solutions are nebulized. By this approach, the inefficiency of the nebulization process is avoided and the inherently low oxygen content of the diffusion flame permits S₂ molecules to exist for reasonable lengths of time.

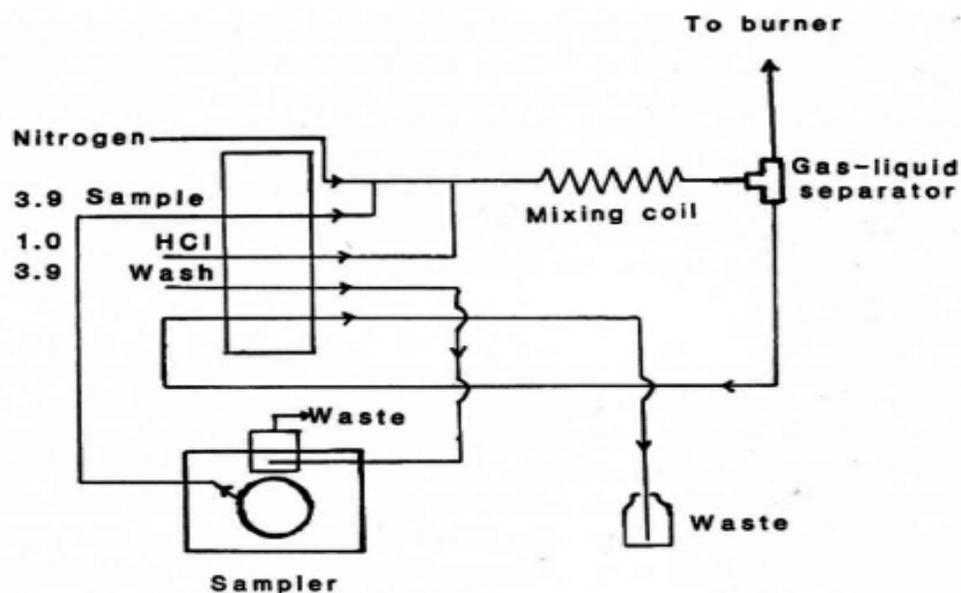


Fig. 4: Schematic diagram of the manifold for the automated cool flame emission spectrometric method for sulphide. Flow rates in ml min⁻¹.
Source: Arowolo and Cresser (1992a)

Table 3: Sulphide content wastewater

Sample No.	Concentration found ^a (µg ml ⁻¹)	
	Automated CFES	Methylene blue method
1	2.13	2.25
2	3.56	3.60
3	2.80	3.00
4	1.10	1.20
5	1.28	1.40
6	6.99	7.20
7	1.00	1.10
8	1.38	1.55
9	1.29	1.35
10	4.86	4.80

^a Mean of three values

Source: Arowolo and Cresser (1992a)

3.1.4 Automated Determination of Sulphite and Sulphur Dioxide by Cool Flame Molecular Emission Spectrometry after Reduction to Hydrogen Sulphide with Sodium Tetrahydroborate III

Arowolo and Cresser (1992b) also developed reported the development of an improved and automated method for the determination of sulphite and sulphur dioxide. The method is based on the reduction of both compounds to hydrogen sulphide with sodium tetrahydroborate (III). The sample which is mixed with NaBH₄ is acidified with 6M hydrochloric acid and carried by a continuous-flow stream into a gas-liquid separator where the evolved hydrogen sulphide is swept by nitrogen into a cool, hydrogen-nitrogen-entrained air flame. The intensity of the blue diatomic S₂ molecular emission generated is measured at 384 nm. The proposed method has a detection limit for sulphite of 0.029 µg/ml and relative standard deviations of 1.2 and 1.5% for 1 and 5 µg/ml, respectively. The calibration graph is linear up to 24 µg/ml sulphite and samples can be analysed at a rate of about 40/hr.

The application of the proposed method to the determination of sulphur dioxide stabilized by various concentrations of sodium tetrachloromercurate (II) (TCM) was investigated in an attempt to establish the optimum TCM concentration that would be suitable for absorbing sulphur dioxide from air. The results indicate that TCM concentrations in the range 2-10 mM did not affect significantly the emission intensity from 5 µg/ml of sulphite while concentrations greater than 0.01 M reduced the emission intensity drastically. Therefore, complete recovery of sulphite occurs from TCM concentrations <0.01 M. When 30 mM was used, the emission intensity from 5 µg/ml sulphite was quenched completely. It was, therefore, decided that the final concentration of TCM in the analyte solution should not exceed 0.01 M. Analysis of atmospheric sulphur dioxide in the vicinity of the University Chemistry laboratory was carried out by both the conventional West-Gaeke method and the proposed method. The results obtained by both methods are in good agreement as shown in Table 4.

The proposed method was also applied to the determination of total SO₂ in wines. The results were compared with those obtained by the standard method recommended by the European Commission which involves the direct titration with iodine after a prior alkaline hydrolysis. The results in Table 5 show reasonable agreement between the two methods. Recovery studies were carried out by analysing aliquots of the treated wine samples spiked with known amounts of the standard solution using the proposed method. The results indicate recovery in the range 95.4-105.4%, with a mean recovery 100.7% and a relative standard deviation of 2.4%.

Table 4: Determination of sulphur dioxide in air

Sample No	Sulphur dioxide/µg/m ⁻³)	
	West-Gaeke Method	CFES Method
1	16.5	16.8
2	15.7	15.6
3	19.9	20.3
4	17.4	17.1
5	14.4	14.6

Source: Arowolo and Cresser (1992b)

Table 5: Comparison between the proposed and the recommended methods for the determination of total sulphite ($\mu\text{g/ml SO}_2$) in wines

Wine		Recommended method*	CFES Method ‡
White	sweet	83.8	81.9
White	sweet	120.3	118.4
White	dry	91.2	88.4
Red		70.4	72.0
Red		105.6	102.1

* Mean of three values

‡ Mean of the value

Source: Arowolo and Cresser (1992b)

3.2 Surface and Groundwater

Assessment of water quality is very important and not only for suitability for human consumption but also in relation to its agricultural, industrial, recreational, commercial uses and its ability to sustain aquatic life. Water quality monitoring is therefore a fundamental tool in the management of freshwater resources. To underpin its importance, WHO, UNEP, United Nations Educational, Scientific and Cultural Organization (UNESCO) and World Meteorological Organization (WMO) launched, in 1977, a water monitoring programme to collect detailed information on the quality of global ground and surface water.

Monitoring can be conducted for the following five major purposes (Taiwo et al., 2012). To

- characterize waters and identify changes or trends in water quality over time;
- identify specific existing or emerging water quality problems;
- gather information to design specific pollution prevention or remediation programs;
- determine whether program goals such as compliance with pollution regulations or implementation of effective pollution control actions are being met; and
- respond to emergencies, such as spills and floods.

3.2.1 Water quality assessment of Ogun River, South West, Nigeria

Water quality data on fresh and marine waters in Nigeria are still sparse and uncoordinated. Calamari and Naeve (1994) reviewed early studies on pollution in the African aquatic environment while Aina and Adedipe (1996) edited the proceedings of a national symposium on water quality monitoring in Nigeria. Physico-chemical and microbiological analyses of surface waters are important in assessing the impact of domestic and industrial activities on such water bodies.

Jaji et al., (2007) carried out a study to establish the water quality status of Ogun River for a period of one year (covering dry season and rainy season) and monitored changes in the quality from its source until it discharges into the Lagos lagoon. Ogun River was chosen as case study because it is abstracted for water supplies in Ogun and Lagos States. At various points along the river (which flows through Oyo, Ogun and Lagos States), people without any easy access to clean water can be

seen using the untreated river water for washing, drinking purposes and irrigation of vegetables. Water samples were collected from thirteen sites and analysed for physico-chemical and bacteriological parameters as well as heavy metals using standard methods.

Generally, the values obtained for turbidity, phosphate, oil and grease, iron and faecal coliform from all the sites in both seasons were above the maximum acceptable limit set by the WHO for drinking water. Similarly, the manganese content from all the sites in the dry season, lead concentrations from three sites in the dry season and cadmium concentrations from some sites in both seasons were above the WHO limit. The values obtained for total dissolved solids, dissolved oxygen and chloride at site M in the dry season and nitrate at site J in the rainy season were also above the WHO limit. The pollution trend between the two seasons varied in relation to parameters. While turbidity, phosphate, oil and grease, faecal coliform and iron showed a remarkable significant effect during the rainy season, manganese and lead were significant during the dry season. The overall picture emerging from the present study (see Tables 6 to 9) indicated that the four sites closest to the river source (sites A, B, C and D) as well as sites G, H and I were of moderate quality and were the least polluted of all the sampling sites. The anthropogenic impact of the urban-industrial areas of Abeokuta and Lagos was clearly evident in sampling sites J, L and M.

Pollution of Ogun river water along its course is evidenced by the high concentrations of pollution indicators, nutrients and trace metals above the acceptable limit. This poses a health risk to several rural communities that rely on the river primarily as their source of domestic water. The study showed a need for continuous pollution monitoring programme of surface waters in Nigeria. More importantly, the study also recommended the need by Federal Government to check the indiscriminate dumping of human waste and solid waste into the rivers in Nigeria.

Table 6: Physico-chemical characteristics of Ogun River sampled over a period of 12 months

Sites	Temperature (°C)	pH	Dissolved oxygen (mg dm ⁻³)
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	-----		-----		-----	
	Rainy	Dry	Rainy	Dry	Rainy	Dry
A	26.7±0.6	28.2±2.5	7.1±0.2	7.2±0.4	7.9±0.7	6.0±0.9
B	26.5±0.9	29.3±2.5	7.4±2.5	7.9±0.8	9.9±2.2	5.2±1.8
C	26.7±0.6	29.0±1.8	7.2±0.2	6.9±0.4	8.6±2.5	5.4±1.5
D	26.3±0.6	29.0±1.7	7.1±0.1	7.1±0.1	8.0±2.5	5.8±1.3
H	26.7±2.1	30.2±0.6	7.3±0.1	7.0±0.4	8.2±1.5	5.3±1.4
I	27.3±1.5	29.8±1.6	7.2±0.2	7.1±0.3	7.9±1.5	5.5±1.0
J	27.7±2.1	30.7±1.4	7.2±0.2	7.4±0.5	5.3±1.0	4.7±1.6
K	27.5±2.6	31.0±1.5	6.9±0.1	7.0±0.1	6.8±0.2	6.3±0.7
L	27.3±2.3	31.8±0.8	6.9±0.1	7.0±0.2	7.0±1.9	5.7±0.7
M	27.3±2.3	31.3±1.3	6.9±0.1	6.3±0.2	67.4±1.2	3.7±1.5
E	25.7±0.3	30.5±2.3	7.1±0.2	6.9±0.1	7.5±0.6	6.5±0.6
F	26.3±1.5	26.8±1.0	6.9±0.2	7.0±0.1	6.6±0.9	5.9±0.1
G	27.7±1.0	30.7±0.8	6.9±0.1	7.1±0.1	8.4±2.3	7.3±1.1
WHO ^a	67.5-8.5				<4.0*	

Source: Jaji et al. (2007)

Table 7: Physico-chemical characteristics of Ogun River sampled over a period of 12 months

Sites	-----		-----		-----	
	Turbidity (NTU)		Total dissolved solids (mg dm ⁻³)		Chloride (mg dm ⁻³)	
	Rainy	Dry	Rainy	Dry	Rainy	Dry
A	46.3±29.5	16.3±7.1	144.7±48.0	202.0±72.4	12.0±4.4	35.0±17.6
B	7.3±3.2	24.0±17.1	62.7±21.0	258.3±148.4	12.3±4.6	20.7±3.5
C	40.0±8.7	10.0±7.2	161.8±94.8	96.7±15.3	12.7±2.1	21.3±10.4
D	32.7±18.6	9.3±7.0	167.0±78.6	162.0±73.4	13.7±3.8	17.3±1.5
H	39.3±24.0	12.0±10.4	153.3±45.1	122.3±30.4	18.7±3.1	26.0±6.0
I	45.3±15.5	10.7±5.7	130.4±23.3	115.7±36.1	14.3±4.0	22.3±4.2
J	57.0±32.1	10.3±5.8	200.3±66.1	146.0±32.0	19.7±6.7	36.7±13.1
K	40.0±10.0	25.3±5.0	160.3±17.3	117.7±10.0	17.0±2.0	29.0±6.9
L	58.0±24.0	19.7±9.8	180.0±20.0	206.7±86.0	18.3±1.5	63.7±49.9
M	61.0±29.5	16.0±1.0	200.0±20.01	3001.03±1097.1	27.7±19.3	2347.7±290.4
E	63.0±27.6	14.0±7.2	166.7±30.6	171.7±51.6	10.7±1.5	27.35±4.2
F	70.0±11.4	27.3±17.1	166.5±22.4	147.7±20.4	14.3±2.5	25.0±5.0
G	24.3±13.8	13.7±8.5	98.0±17.1	99.7±29.5	16.04±1.7	22.0±3.5
WHO ^a	5.0		500		250	

Source: Jaji et al. (2007)

Table 8: Seasonal mean and standard deviation of Pb, Cd and Zn in Ogun River sampled over a period of 12 months

Sites	Lead (mg dm ⁻³)		Cadmium (mg dm ⁻³)		Zinc (mg dm ⁻³)	
	Rainy	Dry	Rainy	Dry	Rainy	Dry
A	0.009±0.008	0.015±0.005	0.003±0.002	0.008±0.001	0.030±0.026	0.087±0.034
B	0.008±0.005	0.044±0.026	0.005±0.003	0.008±0.002	0.041±0.026	0.039±0.029
C	0.045±0.026	0.086±0.080	0.024±0.020	0.005±0.004	0.007±0.006	1.074±1.340
D	0.003±0.002	0.046±0.031	0.012±0.007	0.020±0.002	0.027±0.022	0.147±0.127
H	0.013±0.002	0.019±0.016	0.009±0.002	0.003±0.002	0.036±0.030	0.082±0.006
I	0.006±0.001	0.010±0.003	0.016±0.002	0.002±0.001	0.033±0.024	0.278±0.244
J	0.013±0.010	0.052±0.007	0.015±0.001	0.003±0.002	0.018±0.016	0.081±0.057
K	0.019±0.017	0.075±0.073	0.005±0.000	0.007±0.006	0.010±0.009	0.021±0.020
L	0.043±0.038	0.035±0.031	0.005±0.004	0.006±0.006	0.033±0.024	0.180±0.176
M	0.025±0.023	0.027±0.025	0.010±0.002	0.041±0.012	0.030±0.024	0.044±0.025
E	0.030±0.020	0.000±0.000	0.009±0.001	0.004±0.001	0.136±0.129	0.104±0.077
F	0.000±0.000	0.049±0.020	0.002±0.001	0.005±0.004	0.025±0.205	0.025±0.021
G	0.018±0.031	0.134±0.120	0.005±0.001	0.004±0.001	0.018±0.012	0.074±0.076
WHO ^a	0.05		0.005		5.0	

WHO^a maximum acceptable limit (World Health Organization, (1984)

Source: Jaji et al. (2007)

Table 9: Seasonal mean and standard deviation of Fe, Mn and Cu in Ogun River sampled over a period of 12 months

Site	Iron (mg dm ⁻³)		Manganese (mg dm ⁻³)		Copper (mg dm ⁻³)	
	Rainy	Dry	Rainy	Dry	Rainy	Dry
A	1.9±1.5	2.5±0.5	0.066±0.090	1.889±1.834	0.047±0.016	0.077±0.015
B	3.0±2.7	1.9±1.8	0.208±0.132	0.565±0.5112	0.037±0.012	0.653±0.195
C	2.8±1.4	1.8±0.9	0.083±0.060	0.250±0.214	0.060±0.010	0.060±0.044
D	3.6±0.7	1.4±0.9	0.110±0.081	0.185±0.171	0.027±0.006	0.060±0.010
H	2.9±1.4	1.3±0.7	0.112±0.027	0.091±0.065	0.0176±0.015	0.027±0.012
I	2.7±1.2	1.6±1.0	0.071±0.054	0.134±0.064	0.017±0.006	0.047±0.015
J	3.1±1.2	1.8±1.0	0.182±0.141	0.206±0.113	0.037±0.012	0.073±0.015
K	4.0±1.6	2.6±1.5	0.119±0.051	0.281±0.167	0.007±0.006	0.033±0.006
L	4.7±1.8	2.4±0.2	0.164±0.023	0.179±0.078	0.044±0.006	0.053±0.004
M	4.1±2.4	1.3±0.3	0.1510±0.035	0.269±0.151	0.036±0.006	0.063±0.012
E	4.8±0.7	2.2±0.8	0.590±0.250	0.283±0.249	0.047±0.006	0.037±0.006
F	4.6±2.7	4.1±4.3	0.077±0.047	1.756±1.448	0.040±0.010	0.067±0.015
G	2.2±1.3	2.2±1.5	0.043±0.025	0.127±0.021	0.040±0.010	0.073±0.015
WHO ^a	0.3		0.1		1.0	

WHO^a maximum acceptable limit (World Health Organization, (1984)

Source: Jaji et al. (2007)

3.2.2 Seasonal variation of nitrate in surface and groundwaters of Southwestern Nigeria

Even though nitrate is only one of the environmental parameters related to water quality, its presence in drinking water is of concern because of its toxicity, especially for young children.

Excess in rivers and lakes encourages water plants to flourish and algae to "bloom" (Forman et al., 1985; Addiscott et al., 1991). Currently, there is concern over the increasing concentrations of nitrate present in groundwater aquifers that are used as sources of potable water. In 1984, the WHO introduced guidelines on permissible nitrate-N levels in drinking water (WHO, 1984). However, in many tropical African countries, little or no validated information is available on the magnitude of the nitrate leaching and its effect on the quality of underground water (Adetunji, 1994).

Two surveys of nitrate-N concentrations in surface and groundwater in Ogun and parts of Lagos and Oyo States of south-western Nigeria were conducted between October and December 1997, and between July 2000 and May 2001 (covering both dry and rainy seasons). The study was conducted to ascertain the extent of nitrate-N pollution of the surface/ground water in some parts of the three states. Seventy-two water points (rivers/streams, wells and boreholes) were sampled three times during each of the two seasons (Arowolo, 2005).

Nitrate-N was detected in all the river/stream samples analysed with concentrations ranging from 0.5 to 15.3 mg/L with an average value of 2.7 mg/L for rainy season and 1.0 to 7.7 mg/L with average value 2.4 mg/L (Table 10) for dry season, respectively. A total of 98.5% of the rivers/streams sampling points contained nitrate-N in amounts equal to or less than 10 mg/L while 88.1 % of wells and 97.2% of boreholes had nitrate-N content less than 5 mg/L (Table 11). Nitrate-N concentrations in the sampled wells ranged from 1.4 to 7.4 mg/L with an average value of 2.6 mg/L for rainy season and 1.1 to 6.0 mg/L with average value 2.2 mg/L for dry season, respectively). The sampled boreholes had a lower nitrate-N concentration ranging from 0.1 to 5.2 mg/L and from below the detection limit to 5.0 mg/L during the rainy and dry seasons, respectively (average value 1.8 and 1.6 mg/L respectively). Nitrate-N concentrations in boreholes were below detection limit in 22% of the samples. Generally, for most of the sampling points, nitrate-N concentrations were slightly higher during the rainy season compared with the dry season. The results indicated that nitrate-N concentrations in all the water points (except one) were below the WHO maximum acceptable limit in potable waters (10 mg/L). Therefore, contamination of the surface and groundwater of the study area is not indicated.

The increasing importance of surface/ groundwater sources in many tropical countries suggests that close attention should be paid to nutrient use within the agricultural sector, sewage effluents, land disposal of domestic waste (caused by rapid urbanization), and industrial waste (solid and effluents) because they may result in future contamination of natural water resources. The study, therefore, suggested that there is a need to continue to monitor nitrate concentrations in both surface water and groundwater supplies in order to ensure that it does not rise beyond the WHO safe limit.

Table 10: Distribution of nitrate nitrogen concentrations in the water points studied

Nitrate-nitrogen Content (mg/l)	0-2.5	2.6-5.0	5.1-7.5	7.6-10	10-12.5	>12.5
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<i>Rivers and Streams</i>						
No. of water Point	50	10	2	3	0	1
% of Water Points	75.8	15.2	3.0	4.5	0	1.5
<i>Wells</i>						
No. of Water Points	36	1	5	0	0	0
% of water Points	85.7	2.4	11.9	0	0	0
<i>Boreholes</i>						
No. of Water Points	32 ^a	3	1	0	0	0
% of Water Points	88.9 ^a	8.3	2.8	0	0	0

^a Include samples with nitrate-nitrogen levels below detection limit
Source: Arowolo (2005)

3.2.3 Toxic Elements in groundwater of Lagos and Ogun States, Southwestern Nigeria

Groundwater is an important resource for drinking, washing, bathing, irrigation, and industrial uses. The preference for groundwater to surface water as a source of drinking is based on the fact that groundwater is less susceptible to pollution because it is excluded from the atmosphere (Korfali and Davies, 2005). Drinking water plays a major role in the intake of a number of nutritional and toxic trace elements in humans (Nkono and Asubiojo, 1997). One of the most important environmental issues today is groundwater contamination, and between the wide diversity of contaminants affecting water resources, trace elements are of particular concern because of their high toxicity even at low concentrations. Pollution can impair the use of water and can create hazards to public health through toxicity or the spread of disease. Even though some trace elements are essential to man, essential and non-essential elements at elevated levels can cause morphological abnormalities, reduced growth, increased mortality, and mutagenic effects in humans (Underwood 1971). Toxic elements of great concern in the groundwater are arsenic (As), cadmium (Cd), chromium (Cr), lead (Pb), mercury (Hg), and nickel (Ni).

A good quality drinking water is essential for human survival. However, a large percentage of the populations in most developing countries (Nigeria inclusive) do not have access to potable water. In collaboration with other researchers, the extent of risk arising from consumption of toxic elements in groundwater samples collected from Lagos and Ogun States, Southwest, Nigeria was assessed (Ayedun et. al., 2015). Twelve toxic elements concentrations (As, Mn, Cd, Cr, Pb, Ni, Al, Ti, V, Hg, Li, and Sn) were determined from 170 groundwater samples using inductively coupled plasma-mass spectrometry, and the physicochemical parameters were determined using standard methods.

The results obtained from this study (Tables 11 and 12) revealed that the majority of the groundwater samples were slightly acidic. The chloride concentrations were higher in groundwater samples from Lagos State than from Ogun State. Wells had higher values of the various physico-chemical parameters analyzed in this study than the boreholes. Of the twelve toxic elements, only Mn, Cd, Pb, Ni, and Al have concentrations higher than the WHO recommended limit in drinking water. The average dose of Mn and Al consumed daily from groundwater by an adult in Lagos State is 8.23 and 23.2 ($\mu\text{g}/\text{kg}$ body weight), respectively. Similarly, an adult in Ogun State consumed an average daily dose of 4.48 and 21.57 ($\mu\text{g}/\text{kg}$ body weight) Mn and Al, respectively. A greater threat was posed to children and infants. The relative high concentrations of Mn, Al, and Pb obtained in this study can be attributed to industrial and anthropogenic activities in the study area.

The doses taken were calculated using the average concentrations of toxic elements measured in the groundwater from the study area. The assumption according to U.S. Environmental Protection Agency (USEPA, 2007) was that an adult weighing 70 kg consumes 2 L of water per day, a child weighing 10 kg consumes 1 L of water per day while an infant weighing 5 kg consumes 0.75 L per day. Therefore, for a 70-kg person consuming 2 L day^{-1} of water (containing average concentration of elements recorded) from Lagos State must have consumed 0.006, 0.004, 23.2, 0.401, and 8.23 mg of As, Cd, Al, Pb, and Mn, respectively. Similarly, a person of the same body weight from Ogun State must have consumed 0.008, 0.011, 21.6, 0.192, and 4.48 mg of As, Cd, Al, Pb, and Mn respectively. However, for locations containing highest concentration of these elements, higher amount of the toxic metals will be consumed daily. It is worth noting that despite the lower volume that is expected to be consumed by children (1 L) and infants (0.75 L), the concentration of these elements consumed on the average was much higher than that of the adult. An adult (weighing 70 kg) consuming 2 L per day, must have consumed per week concentration of As, Cd, Al, and Pb from groundwater of Lagos State and Ogun State in excess of provisional tolerable weekly intake (PTWI) set by JECFA (1982). Although there is no PTWI value for Mn, it is clear that the people consuming the water containing highest concentration of all the elements must have consumed per week amounts that exceeded provisional weekly intake.

The risk of cancer for consuming the average values of As, Cd, Pb, and Cr were calculated under the assumption that water is consumed every day during the whole human lifetime. The order for risk of cancer in groundwater from Lagos State was $\text{Pb} > \text{Cd} > \text{As} > \text{Cr}$ while the order in Ogun State groundwater was $\text{Cd} > \text{As} > \text{Pb} > \text{Cr}$. Batayneh, (2010) reported $\text{Cd} > \text{Pb}$ in the assessment of water from the Yarmouk Basin, Jordan for potential health risks which is similar to results obtained from Ogun State.

The results obtained from this study revealed high concentrations of aluminum, lead, and manganese which are a source of concern in the area. The calculation of dosage and cancer risks showed that continuous consumption of most of the groundwater without treatment will put the populace at risk of cancer while the non-cancer hazard index calculation suggests susceptibility to other illnesses like kidney toxicity. It was recommended that sanitation control should be intensified in order to prevent contamination of groundwater with toxic elements and safeguard human health. Treatment of groundwater before consumption was also recommended to avoid

possible adverse cumulative effect. Improved waste disposal methods and regular monitoring of toxic elements in groundwater of the study area should be adopted to safeguard human health.

Table 11: Toxic metals and Physicochemical Parameters in Groundwater Samples Collected from Lagos State.

Parameters	Min	Max	Mean± SD	WHO
pH	4.13	6.10	5.17±1.09	6.50-8.50
Temp (°C)	25.4	32.5	28.4±4.27	NA
EC(μS cm ⁻¹)	28.4	2600	404 ±466	NA
RP(mV)	-12.0	569	134±112	NA
TDS (mg L ⁻¹)	60.0	1560	245±279	250
DO (mg L ⁻¹)	0.530	5.60	2.35±1.15	NA
Depth (m)	2.00	108	17.7±33.8	NA
Cl ⁻¹ (mg L ⁻¹)	18.7	602	201±138.03	250
HCO ₃ ⁻ mgCaCO ₃ L ⁻¹)	24.5	1360	240.68±264.49	NA
NO ₃ ⁻ (mg L ⁻¹)	0.0300	180	7.38±29.33	50.00
NH ₄ ⁺ (mg L ⁻¹)	0.00200	3.10	0.750± 0.92	1.50
PO ₄ ³⁻ (mg L ⁻¹)	0.20	91.8	44.2±29.1	NA
SO ₄ ²⁻ (mg L ⁻¹)	5.58	335	72.6±90.1	250
As (μg L ⁻¹)	0.04	1.11	0.225±0.228	10.0
Mn (μg L ⁻¹)	13.7	1940	288±438	500
Cd (μg L ⁻¹)	0.02	0.59	0.139±0.134	3.00
Cr(μg L ⁻¹)	<0.50	14.6	2.231±3.08	50.0
Pb(μg L ⁻¹)	0.400	200	14.04±43.89	10.0
Ni(μg L ⁻¹)	1.10	52.0	7.121±11.76	20.0
Al(μg L ⁻¹)	24.0	2000	810.7±700	200
Ti(μg L ⁻¹)	1.60	500	41.19±112.7	NA
V(μg L ⁻¹)	0.200	13.8	2.51±3.17	NA
Hg(μg L ⁻¹)	1.40	18.2	5.226±4.99	1.00
Li(μg L ⁻¹)	<1.00	30.0	5.158±7.19	NA
Sn(μg L ⁻¹)	<0.01	0.200	0.121±0.041	NA

Key: NA- Not Available; ND-Not Detected

Source: Ayedun et al. (2015)

Table 12: Toxic metals and Physicochemical Parameters in Groundwater Samples Collected from Ogun State.

Parameters	Min	Max	Mean± SD	WHO
pH	3.60	7.03	5.51±0.740	6.50-8.50

Temp ($^{\circ}\text{C}$)	25.0	33.5	29.9 \pm 1.92	NA
EC($\mu\text{S cm}^{-1}$)	10.0	1400	345 \pm 257	NA
RP(mV)	-26.0	180	81.6 \pm 45	NA
TDS (mg L $^{-1}$)	6.00	840	207 \pm 155	250
DO (mg L $^{-1}$)	0.740	8.19	2.76 \pm 1.59	NA
Depth (m)	3.00	103	45.7 \pm 37.4	NA
Cl $^{-}$ (mg L $^{-1}$)	36.4	565	161 \pm 103	250
HCO $_3^{-}$ mgCaCO $_3$ L $^{-1}$	80.0	820	316 \pm 169	NA
NO $_3^{-}$ (mg L $^{-1}$)	ND	12.1	2.14 \pm 2.44	50.0
NH $_4^{+}$ (mg L $^{-1}$)	ND	2.87	0.170 \pm 0.230	1.50
PO $_4^{3-}$ (mg L $^{-1}$)	0.680	56.0	15.6 \pm 13.7	NA
SO $_4^{2-}$ (mg L $^{-1}$)	1.84	443	113 \pm 115	250
As ($\mu\text{g L}^{-1}$)	<0.03	1.5	0.301 \pm 0.308	10.0
Mn ($\mu\text{g L}^{-1}$)	1.40	1210	156.7 \pm 235.7	500
Cd ($\mu\text{g L}^{-1}$)	<0.01	4.68	0.369 \pm 0.747	3.00
Cr($\mu\text{g L}^{-1}$)	<0.50	13.1	2.049 \pm 2.304	50.0
Pb($\mu\text{g L}^{-1}$)	0.97	62.1	6.722 \pm 11.59	10.0
Ni($\mu\text{g L}^{-1}$)	0.60	52.0	7.582 \pm 10.64	20.0
Al($\mu\text{g L}^{-1}$)	34.0	2000	754.8 \pm 691.5	200
Ti($\mu\text{g L}^{-1}$)	0.60	296	27.05 \pm 53.82	NA
V($\mu\text{g L}^{-1}$)	<0.10	17.2	2.794 \pm 3.64	NA
Hg($\mu\text{g L}^{-1}$)	0.30	23.3	3.94 \pm 4.19	1.00
Li($\mu\text{g L}^{-1}$)	<1.00	22.0	4.608 \pm 5.28	NA
Sn($\mu\text{g L}^{-1}$)	<0.10	80.0	2.649 \pm 11.44	NA

Key: NA- Not Available; ND-Not Detected

Source: Ayedun et al. (2015)

3.2.4 Evaluation of rare earth elements in groundwater of Lagos and Ogun States, Southwest Nigeria

The Rare Earth Elements (REE) consist of fifteen lanthanides (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) which can be divided into two main groups, namely light rare earth elements (LREEs) from La to Eu and heavy rare earth elements (HREEs) from Gd to Lu (Emsley

2001). The former group includes elements with lower atomic numbers, larger ionic radii, higher solubility and alkalinity, whereas the HREEs encompass sparingly soluble elements with higher atomic numbers, smaller ionic radii and lower alkalinity. REEs in our environment are becoming important because of their utilization in permanent magnets, lamp phosphors, superconductors, rechargeable batteries, catalyst, ceramics and other applications. The increase in the consumption of REE in high-tech products and in many other chemical and manufacturing processes is accompanied by increasing amounts of REE released into the environment. Consequently, high technology metals such as the REE have become emerging contaminants in the environment. Not much work has been done on REEs in Africa, so in another collaborative research, we decided to evaluate the level of REEs and the variability of their anomalous behavior in groundwater samples collected from Lagos and Ogun States, Southwest, Nigeria (Ayedun et. al., 2016). REE concentrations were determined in 170 groundwater samples using inductively coupled plasma-mass spectrometry, while the physicochemical parameters were determined using standard methods.

We observed that Lagos State groundwater is enriched with REE [sum REEs range (mean \pm SD)]; [0.314 - 378.9 (49.49 \pm 89.54)] $\mu\text{g/L}$ than Ogun State groundwater [sum REEs range (mean \pm SD)]; [0.245 - 166.9 (22.4 \pm 39.4)] $\mu\text{g/L}$. Boreholes are more enriched with REEs than wells. The only positive correlation ($P < 0.05$) ($R = \text{Pearson}$) recorded in Lagos State groundwater was between sum REEs and redox potential (Eh) ($R = 0.004$). However, there were positive correlations between sum REEs, pH ($R = 0.222$) and SO_4^{2-} ($R = 0.337$) in Ogun State groundwater. Chondrite-normalized plot shows that Lagos groundwater exhibits positive Ce anomaly while Ogun State groundwater does not. The source of REE in Lagos State may be from the ocean and leaching from wastes dumpsites while the source in Ogun State groundwater may be from the rocks.

The results from the present study (Table 13) showed that Lagos groundwater is enriched with light REEs whose source may be from the ocean, chemical and manufacturing processes and leaching from electronic wastes into groundwater. The Lagos groundwater exhibited positive Ce anomaly which shows that Ce^{4+} is mobilized into the groundwater apart from the rock. The Ogun State groundwater is less enriched with REE but exhibited negative Eu anomaly, which suggests the source to be from the rock. The factors controlling REEs in groundwater in Ogun State are pH, and sulphate concentration. Scientists and researchers should intensify efforts on generation of REE toxicity data for animals and by extension humans so that WHO and other regulatory bodies can come up with guideline values in drinking water. This study (Ayedun et al., 2016), is one of the very few published papers on REEs in Africa and has increased our understanding of the fate of REEs in groundwater of the study area.

Table 13: Range and Mean of REE in groundwater samples collected from Lagos and Ogun States

Parameters	Lagos ($\mu\text{g L}^{-1}$)		Ogun ($\mu\text{g L}^{-1}$)		Sun et al., 2011	Kim & Kim, 2011 ($\mu\text{mol L}^{-1}$)
	Range	Mean \pm SD	Range	Mean \pm SD	Range	Range
La ($\mu\text{g L}^{-1}$)	0.067-94.1	10.95 \pm 21.7	0.016-46.8	2.369 \pm 6.38	0.0013-0.0330	0.00212-0.00599
Ce ($\mu\text{g L}^{-1}$)	0.111-63.4	11.86 \pm 16.3	0.048-24.8	3.522 \pm 4.38	0.0011-0.0081	0.000745-0.011450
Dy ($\mu\text{g L}^{-1}$)	0.007-20	2.648 \pm 5.02	0.002-9.13	0.587 \pm 1.275	0.0010-0.0130	0.0000375-0.000699
Er ($\mu\text{g L}^{-1}$)	0.005-11.6	1.427 \pm 2.813	<0.001-5.72	0.35 \pm 0.813	0.0007-0.0085	0.000029-0.000334
Eu ($\mu\text{g L}^{-1}$)	0.009-9.18	0.958 \pm 2.07	<0.002-3.78	0.196 \pm 0.499	0.0028-0.1500	0.000023-0.000252
Pr ($\mu\text{g L}^{-1}$)	0.016-25.6	3.22 \pm 5.9	0.004-9.95	0.653 \pm 1.36	0.0002-0.0017	0.000070-0.001270
Nd ($\mu\text{g L}^{-1}$)	0.067-98	13.19 \pm 23	0.014-37.0	2.78 \pm 5.14	0.0001-0.0089	0.00260-0.00510
Gd ($\mu\text{g L}^{-1}$)	0.012-24.5	3.412 \pm 6.06	0.003-9.85	0.71 \pm 1.37	0.0007-0.0046	0.000055-0.000983
Tb ($\mu\text{g L}^{-1}$)	0.001-3.77	0.511 \pm 0.94	<0.001-1.61	0.11 \pm 0.22	0.0004-0.0038	0.0000069-0.000115
Ho ($\mu\text{g L}^{-1}$)	0.001-3.83	0.492 \pm 0.949	<0.001-1.86	0.114 \pm 0.257	0.0005-0.0018	0.0000082-0.000123
Tm ($\mu\text{g L}^{-1}$)	<0.001-1.62	0.191 \pm 0.389	<0.001-0.827	0.045 \pm 0.112	0.0004-0.0014	NA
Yb ($\mu\text{g L}^{-1}$)	0.004-11.5	1.319 \pm 2.73	<0.001-6.09	0.314 \pm 0.818	0.0001-0.01	NA
Lu ($\mu\text{g L}^{-1}$)	<0.001-1.75	0.197 \pm 0.415	<0.001-0.913	0.046 \pm 0.122	0.0002-0.0019	0.0000077-0.000037
Sm ($\mu\text{g L}^{-1}$)	0.012-10	2.52 \pm 3.53	0.003-8.66	0.661 \pm 1.21	0.0029-0.0150	0.000048-0.001080
Sum REE	0.314 - 378.9	49.49 \pm 89.54	0.245 -166.9	22.4 \pm 39.4	0.0218-0.3158	-

Source: Ayedun et al. (2016)

3.3.0 Distribution and enrichment of metals in sediments of the Ogun River within Abeokuta, South-Western Nigeria

Sediment has been described as a ready sink or reservoir of pollutants, including heavy and trace metals where they concentrate according to the level of pollution. Sediments play a major role in the transport and storage of contaminants, and are frequently used to identify sources of toxicants, determine dispersion pathways, and locate contaminant sinks in water systems. Sediments have been found to record and time-integrate the contaminant status of an

environment and are therefore, also used to measure temporal change and to detect the anthropogenic impacts over time. Accumulated heavy metals or organic pollutants in sediment could be released back into the water with deleterious effects on human health.

Sediments are also important repositories of heavy metals such as Cr, Cu, Zn and Ni, and have the ability to exchange cations with the surrounding aquatic medium. By virtue of their composition, sediments can integrate contaminants over time and are in constant flux with the overlying water column (Yahaya et al., 2012). Bottom sediments are important sources of organic and inorganic matter in streams, freshwaters, estuaries and oceans. Bottom sediments have always contained some level of metals due to the natural pathways of elements in the environment. Therefore, it is not the mere presence of heavy metals in sediments, but their enrichment above natural levels that indicates pollution and threat to the environment.

Olatunde et al. (2014) assessed the distribution and enrichment of selected metals in bottom sediments of Ogun River, within Abeokuta City, south-western Nigeria, using the enrichment factor (EF) and the index of geoaccumulation (*I*_{geo}), two approaches widely used to evaluate the degree of metal contamination or pollution in terrestrial, aquatic and marine environments. This was done to provide information for the proper management of the river. Replicate samples of sediments were collected from 10 sampling sites along the length of the river within the city. Concentrations of Cd, Zn, Cr, Fe, Ni and Pb ranged between 0.03 and 0.66 mg kg⁻¹, 1.75 and 12.63 mg kg⁻¹, 5.19 and 28 mg kg⁻¹, 156 and 750.50 mg kg⁻¹, 17.50 and 60.00 mg kg⁻¹, and 0.73 and 4.5 mg kg⁻¹, respectively, all, with the exception of Fe, being lower than sediment quality guideline values. Sediment pollution assessment was carried out using enrichment factor (EF) and geoaccumulation index (*I*_{geo}). On the average, EF values indicated that Ogun River sediments were moderately contaminated with Cd while *I*_{geo} values suggested that the sediment was moderately polluted with Cd, Zn, Fe, Mn and Pb. Since sediments serve as a reservoir for heavy metals, and their quality can influence the quality of the overlying water, there is a need for continuous analysis of Ogun River sediments to check if their metal content exceeds the accepted regulatory standards.

3.4.0 Fish

3.4.1 Seasonal Variation in Heavy Metal Content of Tongue Sole, *Cynoglossus brownii* and Croaker, *Pseudotolithus typus* from Lagos and Delta States, Nigeria

Tongue sole, *Cynoglossus brownii* and croaker, *Pseudotolithus typus* are among the most commonly available and economically important fish species in Nigeria's maritime states. They contribute significantly to the animal protein intake of the urban population in these states. Compared to other coastal states, Lagos and Delta states are peculiar, with a blossoming shipping and freighting industry especially Lagos state, which doubles as Nigeria's industrial and commercial centre, having the highest number of industries and arguably the largest human population within a state in the country. Over 60% of Nigeria's industries are cited in the state, each discharging its characteristic range of effluents, often containing heavy metals, into the state's terrestrial and aquatic ecosystems.

In 2010 and 2011, we carried out a study (George et. al., 2013) to evaluate seasonal variability in level of some common heavy metal pollutants (cadmium, chromium, lead, copper and zinc) in the

flesh of croaker and sole; compared the levels of these metals in the fish species with international tolerable levels and finally provided information on the quality of the fish species; and possible health challenges inherent in the consumption of fish with high levels of heavy metals.

The study locations were purposively selected, being coastal locations where major industries and crude oil exploration facilities are located; and with a high probability of discharging effluents with high levels of heavy metals. Twelve samples each of both fish species were purchased from landing sites in Makoko (Lagos State) and Koko (Delta State) respectively and transported in ice boxes to the laboratories for subsequent analyses. Twelve samples each of tongue sole and croaker were collected bi-monthly from each sampling location in May, July and September, 2010 (Wet season) and November (2010) and January and March, 2011 (Dry season). Six samples each were analyzed for heavy metal contents using Atomic Absorption Spectrophotometry (AAS) after wet digestion of dried, milled samples of the fish muscles with 1:1 HNO₃: H₂O₂.

Levels of Pb, Cd, Cu, Cr and Zn observed in the Sole and Croaker during the dry season (November – March) at both study locations compared with international tolerable values are shown in Table 14; while those for the wet season (April – October) are presented in Table 15. Table 16 describes variation in metal contents between wet and dry seasons. Generally, significant (P = 0.5) variation was observed between these seasons in Cd, Cu and Cr levels, with Cu and Cr being higher during the dry than wet season; and Cd being higher during the wet than the dry season. Table 17 describes variation in metal content between experimental fish species. Pb and Zn were significantly (P = 0.5) higher in Sole than in Croaker.

Table 14: Heavy metals content of fish samples during the dry season (November – March)

Metals	Metals content (µg/g) of fish samples*				International Standards
	LS	LC	DS	DC	
Pb	0.330±0.31	0.163±0.05	0.149±0.13	0.045±0.05	0.200
Cd	0.097±0.03	0.115±0.09	0.063±0.05	0.029±0.03	0.050
Cu	0.869±0.48	0.990±0.57	0.434±0.22	0.694±0.29	3.280
Cr	1.184±0.60	1.008±0.15	0.826±0.18	1.038±0.12	0.730
Zn	7.612±0.83	6.756±0.83	7.890±0.80	6.168±0.34	30.00

*LS (Lagos State), LC (Lagos Croaker), DS (Delta Sole), DC (Delta Croaker)
Source: George et al. (2013)

Table 15: Heavy metals content of fish samples during the wet season (April – October)

Metals	Metal content (µg/g) of fish samples*				International Standards
	LS	LC	DS	DC	
Pb	0.534±0.62	0.210±0.14	0.527±0.61	0.213±0.27	0.200
Cd	0.373±0.14	0.264±0.15	0.416±0.24	0.307±0.18	0.050

Cu	0.437±0.14	0.442±0.23	0.556±0.15	0.483±0.18	3.280
Cr	0.834±0.32	0.517±0.37	0.983±0.36	0.597±0.44	0.730
Zn	6.764±1.56 ^{ab}	4.783±1.87 ^b	9.343±2.82 ^a	5.724±2.08 ^{ab}	30.00

*LS (Lagos State), LC (Lagos Croaker), DS (Delta Sole), DC (Delta Croaker).
 Rows with different superscripts are significantly (p<0.05) different
 Source: George et al. (2013)

Table 16: Seasonal variation in metal content of Sole and Croaker Fish species

Season	*Metal content (µg/g)				
	Pb	Cd	Cu	Cr	Zn
Wet	0.34±0.11	0.34±0.04 ^a	0.48±0.04 ^b	0.73±0.10 ^b	6.70±0.64
Dry	0.17±0.05	0.08±0.02 ^b	0.75±0.12 ^a	1.01±0.09 ^a	7.11±0.30

* Columns with different superscripts are significantly (p<0.05) different
 Source: George et al. (2013)

Table 17: Variation in metal content between fish species

Season	*Metal content (µg/g)				
	Pb	Cd	Cu	Cr	Zn
Sole	0.41±0.12 ^a	0.26±0.06	0.56±0.06	0.95±0.10	7.92±0.51 ^a
Croaker	0.13±0.04 ^b	0.19±0.04	0.62±0.10	0.76±0.10	5.83±0.44 ^b

* Columns with different superscripts are significantly (p<0.05) different
 Source: George et al. (2013)

As shown in Table 18, observed differences in metal content of Sole and Croaker between Lagos and Delta States were not statistically significant.

Table 18: Variation in metal content of Sole and Croaker Fishes between Lagos and Delta States

Location (States)	*Metal content				
	Pb	Cd	Cu	Cr	Zn

Delta	0.28±0.10	0.23±0.04	0.65±0.11	0.86±0.11	6.38±0.46
Lagos	0.27±0.11	0.23±0.06	0.54±0.05	0.85±0.09	7.37±0.61

Source: George et al. (2013)

Metal contents ($\mu\text{g/g}$, dry weight) for tongue sole in Lagos and Delta States during the wet season (April – October) were: Pb (0.330 and 0.149), Cd (0.097 and 0.063), Cu (0.869 and 0.434), Cr (1.184 and 0.826), Zn (7.612 and 7.890); for croaker: Pb (0.163 and 0.045), Cd (0.115 and 0.029), Cu (0.990 and 0.694), Cr (1.008 and 1.038) and Zn (6.756 and 6.168). For the dry season (November – March) metal contents obtained were: Pb (0.534 and 0.527), Cd (0.373 and 0.410), Cu (0.437 and 0.556), Cr (0.834 and 0.983), Zn (6.764 and 9.343) for sole; and Pb (0.210 and 0.213), Cd (0.264 and 0.307), Cu (0.442 and 0.483), Cr (0.577 and 0.597) and Zn (4.783 and 5.924) for croaker. Significant ($P = 0.05$) variations were observed in metal content between sole and croaker and also between dry and wet seasons notably for Cd, Cr and Cu. Generally, metal concentrations were higher in sole than croaker; and Cadmium content was significantly ($P = 0.05$) higher in fish samples during wet season, while Chromium and Copper were significantly ($P = 0.05$) higher during the dry season. Cd and Cr levels in the test species were found to exceed recommended international tolerable levels.

Trace metal contents of the two economically important fish species evaluated varied with season and among species, with the benthic species studied (Sole) having significant higher levels of Pb and Zn than the pelagic species, Croaker. Cu and Cr levels were significantly higher during the dry season; and Cd level in fish species were significantly higher during the wet season. Cadmium and Chromium contents exceeded international tolerable limits, thus continued consumption of these fish species could expose consumers to serious health risks arising from metal toxicity. A programme of continuous monitoring and control of the physical and chemical characteristics of the components and food products of Nigeria's coastal zone is recommended as a management tool for this important ecological zone.

3.5.0 Soil, Dust, Plants and Vegetation

3.5.1 The chemical forms of lead in roadside dusts of metropolitan Lagos, Nigeria

Of the three materials, soil, sediment and dust, which derive primarily from the Earth's crust, and with which human beings come into contact, dust is the most pervasive. Therefore, dust is an important pathway in human exposure to lead (Fergusson and Kim, 1991). Vehicular dust entrainment rate in Nigeria has been estimated to be 6.5g/vehicle-km for paved roads and 62g/vehicle-km for unpaved roads compared to only 0.1g/vehicle - km for streets in London, England (Akeredolu, 1989). However, dust has largely been ignored as a significant source of heavy metals in the African urban environment unlike in the developed countries where there is a growing awareness of the substantive contribution that dust can make to the levels of trace metals in humans (Evans et al., 1992; Fergusson and Kim, 1991). Young children have been identified as the highest risk group for two reasons. Firstly, young children are more likely to ingest significant quantities of dust than adults, and secondly, young children are usually more susceptible to a given intake of toxin than adults (Evans et al., 1992; Fergusson and Kim, 1991). "Pica" and repetitive

hand or finger sucking are thought to be the two main dust ingestion routes (more or less) unique to children.

It has been recognized for many years that in many applications, a knowledge of the total level of metals present in a sample, although useful, is inadequate (Hill, 1992). This is because the toxicity, mobility and bioavailability of trace metals in soils and dusts are influenced by the physico-chemical form of the metal. For instance, Cr (III) is an essential trace element but Cr (VI) is toxic. In other words, the toxic effect of a metal is determined more by the type of chemical species present than its concentration. Therefore, in many applications, a knowledge of the chemical form of a trace element is becoming increasingly important in addition to its total concentration (Evans et al., 1992; Ure, 1991; Xingfu and Shokohifard, 1989).

In the year 2000, our research team investigated the chemical forms of lead in roadside dusts taken at several locations in the Lagos metropolis. The degree of environmental hazard posed by dust to adults and children residing, schooling or working in and around busy Lagos major highways and byeways was also studied. The city of Lagos was the 22nd largest city in the World with a population of 5.5million in 1991 (The Guardian, 1998). With its 300 industries on 12 industrial estates, Lagos has over 60% of all industrial activities in Nigeria and stands the greatest risk of being irreparably degraded by uncontrolled particulate emissions with concomitant deleterious health effects to man and living resources.

Five fractions namely exchangeable, carbonate, Fe-Mn oxide, organic and residual were identified from the roadside dust samples by using a selective extractant speciation scheme. The Pb in each fraction was determined by flame atomic absorption spectrophotometric technique. The results obtained indicate that Pb in roadside dusts is primarily associated with the Fe/Mn hydrous oxide fraction.

The results of the study (Tables 19 and 20) also indicated that less than 30% of the total Pb in the roadside dust was readily bioavailable. The fraction of lead in the environment is an important factor in the assessment of the potential hazards associated with the metal by providing information on the bio and geo-availability of the metal and, therefore, the potential risk to living things. Obviously, the five-step sequential chemical extraction procedure provides considerable information on the extent and relative rates of release of Pb from dust under progressively more vigorous conditions of chemical attack. From the results obtained, it would appear that lead in roadside dusts of metropolitan Lagos is primarily associated with the iron/manganese hydrous oxide fraction.

The future persistence of lead in roadside dust can be predicted in view of the element's strong association with the less accessible, moderately reducible phase primarily through adsorption and binding to amorphous iron oxides and hydroxides. Therefore, while forthcoming legislation to reduce lead level in petrol or to eliminate anti-knock lead compounds altogether, will undoubtedly cause a substantial and rapid drop in atmospheric lead concentrations, surface soils/dust will remain highly contaminated with lead. This could have severe long-term environmental implications, including the maintenance of elevated levels of "available" lead via slow release from the moderately reducible phase and continuing contributions to the content of street dust, a notable source of lead exposure for young urban children.

This study was followed by the determination of heavy metals content in classroom dust and playground topsoil of some public primary schools in Lagos (Popoola et. al., 2012a; Popoola et. al., 2012b).

Table 19: Mean values for chemical associations of lead in dusts (n=3). Lead levels are in $\mu\text{g g}^{-1}$ of dry sample

Sample Site		Exchangeable	Carbonate	Fe/Mn	Organic	Residual	Total
Mile 12	Mean	4.4	15.3	104.0	1.0	29.9	154.6
	S.D	0.6	0.1	2.8	0.3	0.9	4.3
	%	2.8	9.9	67.3	0.7	19.3	100.0
Yaba Central	Mean	4.0	32.5	108.0	8.0	39.3	191.8
	S.D	0.1	0.6	5.7	5.7	10.5	1.4
	%	2.1	16.9	56.3	4.2	20.5	100.0
Idumota	Mean	3.3	31.3	75.0	22.0	26.0	157.6
	S.D	0.1	0.1	1.4	42.8	2.8	1.4
	%	2.1	19.9	47.6	13.9	16.54	100.0
Mile 2	Mean	2.5	43.5	109.0	30.0	22.0	207.0
	S.D	0.1	0.1	4.2	8.5	11.5	7.1
	%	1.2	21.0	52.7	14.5	10.6	100.0
Oshodi	Mean	3.5	51.9	88.6	12.2	61.0	217.2
	S.D	0.1	1.0	2.1	0.3	4.4	7.1
	%	1.6	23.9	40.8	5.6	28.1	100.0
Ojota	Mean	3.7	19.2	68.0	0.8	13.3	105.0
	S.D	0.3	3.4	2.8	0.6	0.6	7.1
	%	3.5	18.3	64.8	0.8`	12.6	100.0
Ojuelegba	Mean	3.5	15.6	101.0	13.6	6.3	140.0
	S.D	0.3	0.6	26.9	0.6	1.1	28.3
	%	2.5	11.1	72.2	9.7	4.5	100.0
Oyingbo	Mean	4.2	6.3	120.0	1.6	12.9	145.0
	S.D	0.7	0.1	14.1	0.6	8.4	7.1
	%	2.9	4.3	82.8	1.1	8.9	100.0
Tinubu Square	Mean	4.4	15.3	106.0	16.0	10.8	152.5
	S.D	0.6	0.1	14.1	5.7	4.3	3.5
	%	2.9	10.0	69.5	10.5	7.1	100.0
Tafawa Balewa Square	Mean	3.4	10.6	82.0	14.0	12.5	122.5
	S.D	0.2	0.1	5.7	2.8	5.3	3.5
	%	2.8	8.7	66.9	11.4	10.2	100.0

Source: Arowolo et al. (2000)

Table 20: Prediction of percent lead in the sampled roadside dusts of metropolitan Lagos that may be bio-available in the acid conditions of the stomach

Sample Site	Exchangeable	Carbonate ⁺	Overall Total	Percentage Available
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Mile 12	4.4	15.3	154.6	12.7
Yaba Central	4.0	32.5	191.3	19.0
Idumota	3.3	31.3	152.6	22.0
Mile 12	2.5	43.5	207.0	22.2
Oshodi	2.5	51.9	217.2	25.5
Ojota	3.7	19.2	105.0	21.8
Ojuelegba	3.5	15.6	140.0	13.6
Oyingbo	4.2	6.3	145.0	7.2
Tinubu Square	4.4	15.3	152.5	12.9
Tafawa Balewa Square	3.4	10.6	122.5	11.4

⁺In $\mu\text{g g}^{-1}$ dry sample

Source: Arowolo et al. (2000)

3.5.2 A comparison of the elemental contents of the <2 mm and <150 μm particles size fractions of Jamaican soils.

In 2001, I was appointed as Third World Academy of Science (TWAS) Visiting Scientist to the International Centre for Environmental and Nuclear Sciences (ICENS) at The University of the West Indies, (UWI) Kingston, Mona, Jamaica. I visited the Centre three times between 2001 and 2004; spending three months on each visit. ICENS, which operates the only research reactor in the Caribbean region operates internal quality control procedures and has provided Neutron Activation Analysis (NAA) data since 1984 for an array of over 60 chemical elements to a wide range of clients.

ICENS developed a geochemical map of elements in Jamaican soils which aids in the exploration of minerals, detection of contaminated land and provides important information for government planning agencies. The focus of ICENS has been expanded to also include the study of abundances and transfers of inorganic trace elements from soils to people (from the chain bedrock to soil; then to food and finally to humans). One of the projects I carried out during my visit to ICENS was the comparison of the elemental contents of the <2 mm and <150 μm particles size fractions of Jamaican soils (Rattray et al., 2007).

An orientation study conducted earlier by the Centre over a selection of sites from the most important geological, physiographic and climatic features of the island indicated that for most elements examined, the variation in concentration with soil particle size was minimal. The <150 μm particle size fraction was accepted for the preparation of the global geochemical database and in Jamaica, this fraction often occurs as a very large proportion of the total sample and was used for geochemical mapping of the island. By using this fine fraction, sample dilution and equipment wear produced by grinding larger particle size soil fractions, which may contain harder grains of minerals such as quartz that are barren of trace elements, were also reduced.

The soil content of potentially toxic elements in Jamaican soils, especially those over White Limestone that include land used extensively for small farmer crop production has become of

interest due to transfers to the food chain and possible health effects. There have been debates on which particle size, the <2 mm usually used in agriculture or the <150 µm which was used for the geochemical mapping of Jamaica was the more suitable. Large amounts of data continue to be generated both locally and internationally for both fractions (Danley et. al., 1995). This study sets out to clarify whether there are differences between the results obtained for several elements in the two particle sizes in a selection of soil samples. A comparison of the elemental contents of the <2 mm soil particle size fraction normally used for agricultural studies and the <150 µm soil particle size fraction used for geochemical mapping was carried out. Eighty seven (87) samples of Jamaican soil were digested in aqua regia and analysed for Cd, Zn, Co, Mg, Fe, Cu and Pb by Atomic Absorption Spectrometry. Various quality assurance protocols were included in the study and the results in Tables 21 and 22 confirm the accuracy of the results obtained.

A good correlation between the concentrations of all elements except Fe in the two fractions was obtained (Fig. 5 and Table 23). Therefore, the <150 µm fraction of Jamaican soils can be used for both geochemical mapping and agricultural applications for Cd, Zn, Mg, Pb, Cu and Co. The agreement between the data obtained from the analysis of two different soil particle size fractions allows the use of the <150 µm fraction of Jamaican soils for geochemical mapping and agricultural applications, for Cd, Zn, Mg, Pb, Cu and Co but not Fe.

Table 21: Certified Reference Materials (NIST 2709) Aqua Regia Results (n=21)

	Cd	Zn	Mg (%)	Pb	Cu	Co	Fe (%)
Mean	0.32	98	1.4	20.3	33	14	2.9
% RSD	18%	2.7%	4.8%	20%	4%	22%	16%
Certified Value	0.38	106	1.51	18.9	34.6	13.4	3.5
% Recovery	84%	92%	91%	107%	96%	103%	83%

Source: Rattray et al. (2007)

Table 22: Difference between Duplicates for <2 mm and 150 µm Soil Samples

Mean % Difference between Duplicates			
Element	N	<2mm	<150µ
Cd	63	8.4	5.2
Zn	80	3.9	3.1
Mg	76	4.6	4.5

Pb	73	11.7	7.4
Cu	74	4.9	3.2
Co	73	5.2	3.6
Fe	68	13.9	10.4

Source: Rattray et al. (2007)

Table 23: Soil sample results: <2 mm vs <150 µm Data for 7 Metals by AAS

Element	n	Slope	SE Slope	Intercept	SE intercept	r ²
Cd	72	1.03	0.007	-0.22	0.60	0.9965
Mg	87	1.17	0.012	-5.57	1.59	0.9912
Zn	88	0.999	0.016	0.71	4.08	0.9790
Pb	86	1.19	0.037	-7.98	2.09	0.9258
Cu	88	0.873	0.037	4.05	3.36	0.8656
Co	87	0.722	0.034	8.86	1.47	0.8448
Fe	88	0.925	0.083	0.903	0.58	0.5804

Source: Rattray et al. (2007)

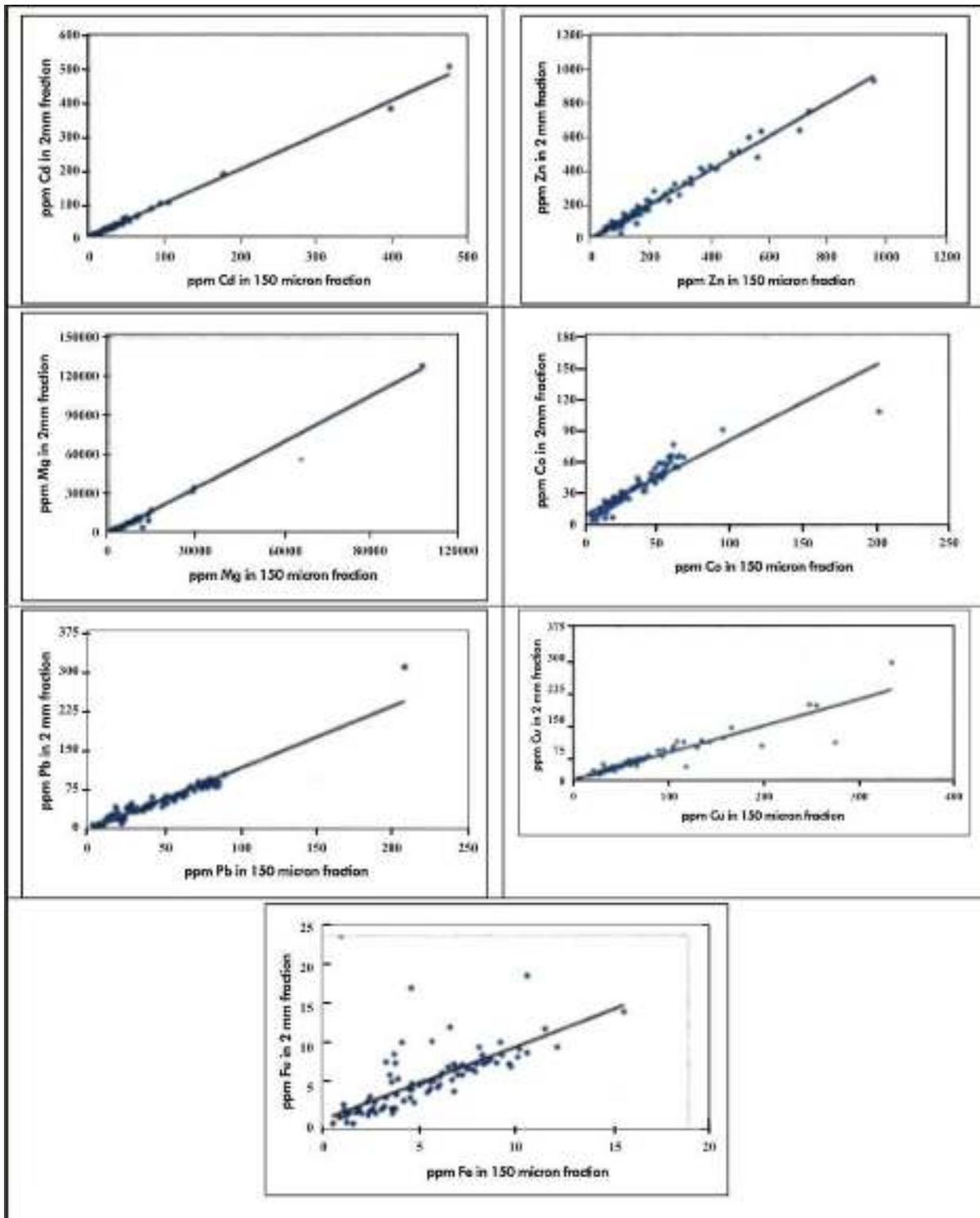


Fig. 5: Elemental content of two particle size fractions of soils by AAS
 Source: Rattray et al. (2007)

3.5.3 Effect of Cement Dust on Soil, Water, Vegetation and Human health in the Neighbourhood of Ewekoro Cement factory, Southwest Nigeria

One of the common environmental polluters throughout the world is the cement industry. The main environmental issues associated with cement production are emissions to air and energy use. The production of cement kiln dust (CKD) and its disposal may have an impact on the environment and human health. Cement production is invariably a dusty operation resulting in the exposure of factory workers to cement dust. The resulting exposure to cement dust has led to impairment of respiration and a prevalence of respiratory symptoms amongst workers (Alakija *et al.*, 1990; Al-Neaimi *et al.*, 2001; Meo *et al.*, 2002) culminating in lung diseases. The severity of the impairment of respiratory function, however, has been shown to depend on years of exposure (Alakija *et al.*, 1990), although there were reports that contradicted this notion (Vestbo and Rasmussen, 1990; Yang *et al.*, 1993; Fell *et al.*, 2003). At a local level the environmental impacts of cement production relate to 'nuisance' issues mainly through emissions of dust, noise and/or vibration as well as visual impact. Dust is commonly connected with many processes involved in the production of cement like crushing and extraction of mined rocks, milling activities, kiln operations etc. The dust can have numerous adverse effects on employees' health.

Air pollution affects the surrounding community and water bodies as the dust settles and can be washed into nearby waterways. The periodic discharge of dust from the kiln stack creates a serious effluent problem in the form of fine particles. Local prevailing winds blow these generated dusts to the adjoining villages. Downwind residents have expressed concerns about subsequent health and environmental effects of Cement plant production activities in various parts of the world (Downwinders, 2005). The extent of dust pollution varies from place to place.

Added to the health and environmental effects of cement production is the effect of liquid waste/effluent generated by the quarry, press house and milling operations on soil, water quality and vegetation around the factory, while the generation of noise from quarry, cement and raw mills, due to its effects on human health, also presents an environmental issue worthy of close observations.

The impacts of cement dust from Ewekoro factory on soil, water, vegetation and human health were studied in the vicinity of the cement factory for two years (Agbede, 2010). Sample plots of 25m x 25m were established at 0.5 km from the factory up to Lapeleke village, a distance of 3 km. Soil samples at 0-15 cm were taken from completely randomized block design plots and analyzed for pH, CEC, OM, Alkalinity, Available P and heavy metal levels using standard methods. Water samples were collected from five sites along Akinbo River and analyzed for eighteen physicochemical parameters. Woody plants in the study area were enumerated and their heights measured while leaves of cassava (*Manihot esculenta*) and sugar cane (*Saccharum officinarum*) were randomly selected for chlorophyll content determination and leaf preponderance. Medical records of common ailments among the factory workers and the neighbouring villagers were collected for the period 2003-2006. All the results were compared with similar results from a control site 22 km away at Obada Oko.

Results showed that mean soil pH (7.49 ± 0.29) and OM ($2.7 \pm 0.96\%$) at the study site were significantly higher than at the control site (6.59 ± 0.59 and $1.31 \pm 0.29\%$ respectively). Available P ($16.44 \pm 5.16 \text{ mg kg}^{-1}$) was significantly higher in the vicinity of the factory than at the control site

and gradually reduced from 23.32 to 9.93 mg/kg across the plots compared with the control site (5.65 ± 0.49 mg/kg). Soil alkalinity (mean $6.16 \pm 5.87\%$) was significantly higher up to 1.5 km from the factory compared to control site ($1.88 \pm 0.88\%$). Exchangeable cations (46.98 ± 24.08 cmolkg⁻¹) decreased significantly with increasing distance from the factory (control site: 7.03 ± 2.74 cmolkg⁻¹). A 668%, 328% & 291% rise in CEC, Alkalinity and Phosphorus values respectively in the study site over the control site is due to the fact that exchangeable cations, CaCO₃ and Phosphorus are major components of the raw materials used in cement manufacture.

Heavy metals have significantly higher concentrations at the study site (Cr 71.79 ± 28.36 ; Cu 9.96 ± 4.52 ; Fe 16614.86 ± 1000.62 & Zn 73.64 ± 60.73 mgkg⁻¹) than at the control site. These values were, however, lower than similar results obtained from developed countries. Cement dust and soil properties influenced pH of Akinbo River which was significantly higher near the factory locations (7.34 ± 0.25) than for the upstream point (6.51 ± 0.54) and control site (6.56 ± 0.41). Mean electrical conductivity and hardness for the river water at the study site were 380.37 ± 79.30 μ Scm⁻¹ and 234.50 ± 62.59 mgL⁻¹ respectively; values were significantly higher after the point where the factory effluents emptied into Akinbo River when compared with the upstream (EC 122.51 ± 48.39 μ Scm⁻¹, Hardness 81.50 ± 47.40 mgL⁻¹) and control site (EC 40.5 ± 23.35 μ Scm⁻¹, Hardness 25.5 ± 9.15 mgL⁻¹). Water temperature, total dissolved solids, total suspended solids, total solids, dissolved oxygen and heavy metals did not show any significant difference with distance from the factory and the control site.

The increase in leaf abundance for cassava (36 to 125) and sugarcane (11 to 14), chlorophyll contents for cassava (2.53 to 4.42 mg/g) and sugarcane (1.44 to 2.88 mg/g), woody species density, tree height and basal areas with increasing distance from the factory was significant up to a distance of 3 km ($P \leq 0.05$). The incidences of dust-induced ailments like upper respiratory tract infections, arthritis, dermatitis, carbuncle and eye infections were higher significantly among the factory workers compared with the neighbouring villagers and the inhabitants of the control site. The results obtained in this study indicated that dust deposition affected the environment up to a distance of 3 km from the factory site. There is, therefore, a need for a continuous pollution-monitoring programme of cement industries in Nigeria.

3.6.0 Monitoring and Modelling of Ambient Air Quality in Lagos, Nigeria

The relationship between urban air quality and health came to the fore in the early and mid-twentieth century when a series of severe pollution episodes resulted in demonstrable negative health effects. In another research study, Oyediran assessed the ambient air quality due to the impact of heavy traffic, high population density and industrial activities in Lagos Metropolis and use appropriate air quality model to recommend management options (Oyediran, 2014). A preliminary assessment of gases and particulate matter along kerbsides and ambient environment was carried out between July 2005 and June 2006. Further studies were carried out between May 2007 and April 2008 and emission studies were completed in 2009 in the following several sampling stations: Ikeja, CMS, Maryland, Oshodi, Imota and University of Lagos (Plates 4 and 5).



Plate 4: Airmetrics samplers for particulate mounted at Oshodi, Lagos.
Source: Oyediran (2014)



Plate 5: Airmetrics sampler mounted at Ikeja, Lagos

Source: Oyediran (2014)

The results showed that traffic jam was high in the city with emission of high concentration of the gases and suspended particulate matter on the kerbside. Bus-stops and road intersections were worse hit because of the traffic jam around these areas. In 2005/2006, the maximum concentration of various pollutants monitored was carbon monoxide, 110 ppm; hydrocarbons, 962 ppm; nitrogen dioxide, 4.0 ppm; sulphur dioxide, 1.2 ppm and particulate matter, 2260 $\mu\text{g}/\text{m}^3$. During the 2007/2008 monitoring period, the maximum concentration of various pollutants monitored was Carbon monoxide, 4.75 ppm; hydrocarbons (as BTEX), 120.9 ppb; Nitrogen dioxide, 94.8 ppb; Sulphur dioxide, 48.8 ppb and particulate matter (as TSP), 1500 $\mu\text{g}/\text{m}^3$. Old rickety diesel-powered vehicles, which are the principal sources of particulate matter in the city were in common use. Although the mean ambient concentration of most of the gases was within the National and International standards sometimes with corresponding low composite air quality index, the standard exceedance was quite high and this portends great danger for the residents, most of whom have their houses very close to major roads and intersections or trade by roadsides and in traffic.

From the study, particulate matter was identified to be the most prevailing air pollutant and its occurrence and effect were exacerbated by annual harmattan and unpaved/road network in the city. Although low concentrations of most of the other pollutants were obtained, their cumulative impact was significant as depicted by their violation of health standards (Standard Exceedance Index). The model was able to provide different options for managing ambient air quality in the metropolis and if implemented, the city would become healthier.

3.7.0 Lead, Zinc and Copper levels in tree barks as indicator of atmospheric pollution

The combustion of fossil fuels and automobile exhaust emission in certain areas are the primary sources of the atmospheric metallic burden (Williamson, 1973; Nriagu, 1992; Biney et al., 1994). For example, many reports have shown that environmental lead loadings are related to traffic volume and that lead levels in soils and vegetation rise as average daily traffic (ADT) increases (Wheeler and Rolfe, 1979; Kapu et al., 1989). A report by Nriagu has also confirmed automobiles as a dominant source of air pollution in many cities of Africa (Nriagu, 1992). This is because the lead contents of gasoline sold in African countries are among the highest in the world; typical concentrations of lead in regular fuel fall in the range of 0.5-1.0 g/l (Alliance, 1994; Nriagu et al., 1996).

Trace levels of some toxic metals have been shown to be hazardous when ingested by humans through inhalation or along the food chain. They are known to have a deleterious effect on humans, most especially children (Osibanjo and Ajayi, 1980; Nriagu, 1992). Heavy metal pollution is a potential health problem in Africa, where a significant population rely on the ingestion of medicinal herbs made from tree barks, leaves, etc., to cure various ailments. Furthermore, the plucking and eating of raw fruits without washing and food hawkers displaying their food-stuff openly and unwrapped alongside heavy traffic road are common sights in most cities in Africa; therefore, the amount of heavy metals ingested in one form or the other can be frightening if quantified, particularly over a long-time interval. The use of vegetation monitors provides the cheapest and simplest indicator for monitoring trace metal levels in the atmosphere; however, trees are preferable to grasses, shrubs, mosses, and food crops (Barnes et al., 1976; Hammpp and Holl, 1974; Osibanjo and Ajayi, 1980; Tanka and Ichikuni, 1982; Walkenhorst et al., 1993; Kuik and Wolterbeek, 1994) because they are widely distributed and remain in a fixed position over a considerable period of time, thus enabling analysis of trends over time intervals. Our study investigated the levels of trace heavy metals in tree barks located near roads in Abeokuta as indicator of atmospheric pollution.

Seven different species of trees with different bark features (degree of roughness) were sampled from 31 locations in Abeokuta. The locations were selected to represent areas of different traffic density. A suitable place remote from traffic (S22) off Layi Balogun Avenue, Ibara Housing Estate served as an unpolluted reference point. Trees of about the same age situated close to the highway (about 5 m) were selected and the barks were carefully removed with a stainless steel penknife at an average height of about 2.0m above the ground (Barnes et al., 1976). Each sample was ashed in triplicate to test the reproducibility of the method used. The samples were analyzed using the Buck Scientific Model 210 Atomic Absorption Spectrophotometer. Standard addition technique (which tends to compensate for variation caused by physical and chemical interferences in the sample solution) was employed in this study.

The Pb and Zn contents, 1.9-159.8 and 16.5-659.1 µg/g, dry weight respectively, correlate with traffic volume, indicating pollution from anthropogenic sources. The results obtained for Cu, 4.2-20.7 µg/g, dry weight, though lower, were still significant but did not show any correlation with traffic density (see Tables 24 -26). The study also confirmed the suitability of *Azadirachta indica* (Dogonyaro-a very popular local tree) as a suitable bio-indicator of aerial fallout of heavy metals particularly in areas where *Terminalia catapa* and Rain Trees (*Samanea saman*) were not readily available. The Dogonyaro is a very popular local tree of immense value to the indigenes. The tree barks and leaves are traditionally soaked in water and the concoction made, used in the treatment of malaria. The study also confirmed that the medicine made from the barks of trees, particularly those that have rough barks, may be an important route for heavy metals into the food chain. The level of metallic pollutants reported in this study is low compared to levels reported in developed countries. This is due to the highly industrialized nature and heavy traffic volume in the other areas. It is important that the level of metals in the environment should be continuously monitored to know the state of the environment.

Table 24: Average concentration of lead, copper and zinc at city high traffic and low traffic density sites for Nigerian *Azadirachta indica* (Dogonyaro)

Sample No	Location	Bark Features	Lead* Mean**	SD	Copper* Mean**	S.D	Zinc* Mean**	S.D
S ₁ ⁺	Lagos Road (MIDGAL)	Rough, Hard and thick	44.7	3.25	7.3	0.91	575.5	14.46
S ₂	Lagos Road, near L/S feeds	-do-	159.8	6.15	20.7	0.25	659.1	12.70
S ₂₇	Alabata Junction, Ibadan Road	“	98.5	1.62	8.1	0.46	68.4	6.17
S ₃₁	Tejumola Plaza, Adatan	“	35.3	0.84	6.9	0.16	107.5	2.20
S ₃₂	Kugba Road, Elega	“	55.7	1.73	6.5	0.75	141.8	2.67
S ₃	Neuro-Psychiatric Hospital, Aro (near the Fence)	“	42.2	0.87	9.8	0.43	168.6	2.68
S ₄	Neuro-Psychiatric Hospital, Aro (inside – near the Ward)	“	18.0	0.66	9.0	1.26	41.7	0.72
S ₁₅	NUD Road (beside Atilab Pharmacy)	“	13.4	0.43	7.2	0.24	66.5	1.58
S ₅	N/Psy (near maintenance yard)	“	9.7	0.51	8.4	1.05	48.1	2.69
S ₂₀	Oke-Ilewo (round about)	“	9.6	0.46	5.1	0.15	40.1	0.14
S ₂₂ ⁺⁺	Layi-Balogun Av., Ibara	“	1.9	0.33	4.7	0.67	32.9	3.32

*= Dry weight of µg/g sample ** = Mean of three replicate analysis S.D = Standard deviation

+ = Sample from Lagos Road (MIDGAL)

++ = Unpolluted reference point

Source: Odukoya et al. (2000)

Table 25: Statistical measurement of lead, copper and zinc contents of bark of Nigerian *Azadirachta Indica* ((Dogonyaro) collected from two areas of different traffic density levels

Area	Pb	Cu	Zn
High traffic density sites (6 samples)			
Mean ($\mu\text{g g}^{-1}$)	72.7	9.9	286.8
Range ($\mu\text{g g}^{-1}$)	35.3-159.8	6.5-20.7	68.4-659.1
Standard error of the mean (S.E.M)	19.7	2.2	105.9
Low traffic density sites (5 samples)			
Mean ($\mu\text{g g}^{-1}$)	10.5	6.9	45.9
Range ($\mu\text{g g}^{-1}$)	1.9-18.0	4.7-9.0	32.9-66.5
Standard error of the mean (S.E.M)	2.6	0.86	5.7
t-value	2.84	1.17	2.05

The t-value with 9 degrees of freedoms 1.83 at 90% confidence level

Source: Odukoya et al. (2000)

Table 26: Correlation coefficients between metals in Nigerian *Azadirachta indica*((Dogonyaro)

Element	High traffic density area			Low traffic density area		
	Pb	Cu	Zn	Pb	Cu	Zn
Pb	-	0.8704	0.5025	-	0.7891	0.4758
Cu	-	-	0.6684	-	-	0.4045
Zn	-	-	-	-	-	-

Source: Odukoya et al. (2000)

3.7.1 Lead Contamination in Cocoa and Cocoa Products: Isotopic Evidence of Global Contamination

Lead contamination in candies is a long standing problem that has evolved with time in the developed world. Since the middle of the 19th century, various measures including regulations and public education were implemented to minimize the contamination of candies from such sources (Nriagu 1985). Specific focus on the source of lead in cocoa, the principal material used to make chocolate, began during the late 1970s. Despite subsequent marked reduction in the release of lead into the environment, due primarily to removal of lead from gasoline (Nriagu 1990), recent market-basket surveys still indicate continued lead contamination in some foods, notably manufactured cocoa and chocolate products. For example, in the 2000 U.S. Food and Drug Administration

(FDA) Total Diet Survey (TDS), the average lead content for milk chocolate candy bars (27 ng/g) was the fourth highest reported for all food items (FDA 2000). Onianwa et al., (1999) found the average lead content of cocoa powders sold in Nigeria to be 310 ng/ g with a range of 80-880 ng/g. The latter measurements are consistent with reports of elevated levels of lead in cocoa by the Cocoa Producer's Alliance (COPAL), which is based in Nigeria. COPAL is the supplier of 75% of all cocoa beans to the world market (COPAL 2004a). The sources of lead in Nigerian cocoa products, which have become a concern, may conceivably include lead from local soils and rocks where the cocoa plant is grown; farming practices (e.g., the application of fertilizers, lead-containing pesticides, composts and other soil additives); atmospherically deposited lead; handling and processing of cocoa beans after harvesting (including drying in open air, transportation, and storage); grinding and manufacturing processes (wear and tear of lead-soldered machine parts); mixtures and additives to final products; and packaging and wrapping material. The presence of relatively high concentrations in a consumer product that is heavily marketed to children is a special concern, because children are particularly susceptible to lead poisoning (Silbergeld 1997).

Unfortunately, the contribution of different natural and industrial leads in cocoa beans, cocoa, and chocolate products has not been resolved. To the best of our knowledge, there has been no systematic auditing of the sources of lead during the manufacture of chocolate products-from the harvesting of cocoa beans to the finished products. In 2002, our research team with the support of a small research grant from Prof. Nriagu set out to determine the concentration and isotopic composition of lead in cocoa beans and soils from cocoa plantations of Nigeria to establish the baseline lead concentration of the beans and determine the relative contribution of soil lead to that concentration. Our other objective was to determine the contribution of other lead sources in cocoa bean products, cocoa, and chocolates, again using lead concentration and stable isotopic composition analyses.

Our research team collected cocoa bean and soil samples in November and December 2002 from six farms in the three highest cocoa-producing states in Nigeria (Ondo, Osun, and Ogun), which were identified from statistics presented in the Central Bank of Nigeria Annual Reports (CBN 2002). Soil samples were collected at four depths in the soil profile: 0-10 cm, 0-20 cm, 35-50 cm, and 85-100 cm. At each farm, six separate samples were taken from the first and third profiles, and three samples were taken from the other profiles. Ripe cocoa bean samples were taken from each farm, as well as a sample of cocoa beans that had been fermented and dried in their shells, ready for export. To create representative samples for each Nigerian farm, we made composites for each soil profile, both types of cocoa beans and the shells corresponding to the ripe cocoa beans collected. This process yielded homogenized composites of at least four soil, two cocoa bean, and two cocoa bean shell samples per farm for analysis. In addition to the Nigerian samples, cocoa beans from other countries and finished chocolate products including processed cocoa were collected for analysis (Rankin et al., 2005).

Lead concentrations in the samples were analyzed using a Finnegan MAT Element high-resolution magnetic sector inductively coupled plasma mass spectrometer (HR-ICPMS) (Thermo Electron Corporation, Waltham, MA). In addition to the concentration measurements made with the HR-ICPMS, we made preliminary isotopic measurements from instrumental scans of all stable lead isotopes (^{204}Pb , ^{206}Pb , ^{207}Pb , and ^{208}Pb). Fractionation corrections were derived from concurrent analyses of SRM 981 (NIST; common lead standard reference material).

As shown in Table 27, lead concentrations in cocoa beans ranged from < 0.103 to 1.78 ng/g, with an average concentration of 0.512 ng/g (Rankin et al., 2005). This average was comparable with the lowest reported concentrations of lead in food (Flegal et al. 1990; Tahvonen and Kurnpulinen 1995). Moreover, that average is considered to be conservatively high because it uses the detection limit (0.103 ng/g) for three samples with lead concentrations below that limit and includes the relatively high (order-of-magnitude) concentration of another sample (Kango Village Farm; sample taken directly from husk) that appears to have been contaminated when compared with the concentrations of the other 11 samples. Therefore, we assumed that the average lead concentration of cocoa beans from the Nigerian farms is < 0.5 ng/g and may well be < 0.1 ng/g. Although, the lead content of cocoa beans is as low as or lower than those of hundreds of different foods in the United States and elsewhere, lead concentrations of manufactured cocoa are among the highest of all foods. A comparison of lead concentrations in the analyzed source material and the finished products is shown in Figure 6.

Table 27: Lead concentration (ng/g) of cocoa beans taken directly from husk and after being fermented and dried at Nigerian farms.

State	Farm	Directly from husk		Fermented and dried	
		(Pb)	% RSD	(Pb)	% RSD
Ogun	Oke Osun, Ibese, Kango Village	0.846	9.81	0.839	7.73
		1.78	62.4	0.941	3.83
Ondo	Igbo Eleruku, Ita Ogbolu Ase Igbo	0.213	5.16	0.182	4.45
		-	-	<DL	7.06
Osun	Idi Obi I Aba Arawense, Modakeke	0.313	8.30	<DL	10.1
		<DL	8.06	0.211	9.51

Source: Rankin et al. (2005)

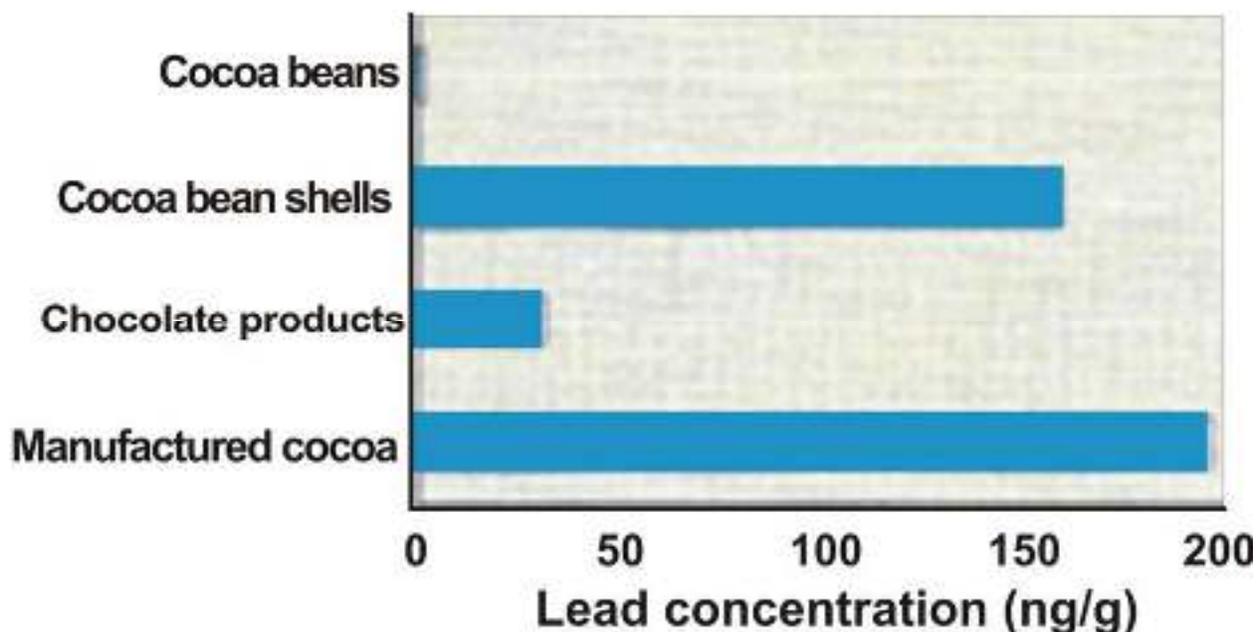


Fig. 6: A comparison of average lead concentrations (ng/g) for analyzed cocoa beans, cocoa bean shells, chocolate products and manufactured cocoa

Source: Rankin et al. (2005)

Table 28: Lead Isotopic ratios and concentrations (ng/g) of manufactured cocoa

Sample	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{208}\text{Pb}/^{207}\text{Pb}$	(Pb)	% RSD
Baking chocolate 1A	1.149(4)	2.428(4)	251	11.8
Baking chocolate 1B	1.148(2)	2.425(9)	241	0.75 ^a
Baking chocolate 1C	1.150(5) ^b	2.426(8) ^b	263	0.75 ^a
Baking chocolate 2A	1.160(6)	2.429(5)	188	6.93
Baking chocolate 2B	1.160(1)	2.423(1)	200	0.4 ^a
Baking chocolate 2C	-	-	181	0.5 ^a
Cocoa powder 1A	1.158(3)	2.431(11)	188	5.17
Cocoa powder 1B	-	-	186	0.8 ^a
Cocoa powder 1C	-	-	183	0.7 ^a
Cocoa powder 2	1.183(3)	2.467(1)	147	28.2

Source: Rankin et al. (2005)

Possible origins of lead contaminant in both the manufactured cocoa and chocolate products are identified by their lead isotopic ratios, which are also shown in Tables 28 and 29. A comparison of the lead isotopic ratios for chocolate products and manufactured cocoa with the ratios of the world's industrial aerosols, as compiled by Bollhofer and Rosman (2000, 2001, 2002) shows that isotopic compositions of all of the chocolate products overlap with those of lead aerosols measured by Bollhofer and Rosman (2000, 2001, 2002), but the isotopic compositions of manufactured

cocoa and chocolate products are variable. Consequently, there is no single, identifiable source of contaminant lead in either processed cocoa or chocolate products, which is consistent with reports of geographic differences of lead concentrations in cocoa powder (Mounicou et al. 2003).

One of those sources may be cocoa bean shells, which have been shown to be very efficient in removing lead from solutions (Meunier et al. 2003a, 2003b, 2003c, 2004). Meunier et. al., (2003a, 2003b) showed extraneous lead adsorption onto cocoa bean shells of up to 17,000 $\mu\text{g/g}$, or approximately 35 million times greater than our conservatively high calculation of the average lead concentration in cocoa beans. The shells can thus be regarded as an excellent protective shield against intrusion of lead into the bean from external sources before the beans are harvested. Furthermore, the removal of lead results in an increase in solution pH (removal of protons) and the release of calcium, magnesium, potassium, and sodium from the cocoa shells (Meunier et al. 2003c). The modification of ion balance may result in the transfer of lead from the bean to the shell, a decontamination process. Due to their capacity to scavenge lead, the shells may become a source of contamination after the beans are harvested.

That potential is indicated by the high lead concentrations of cocoa bean shells listed in Table 30. The average of our measurements of lead in cocoa bean shells (160 ng/g) is approximately 320-fold greater than the average values of lead measured in Nigerian cocoa beans (Figure 6). The disparity between lead levels in the cocoa beans and shells is consistent with the literature on lead contamination in foods, which have shown that contamination is greatest on plant surfaces that are subject to the direct deposition of industrial lead aerosols. This potential source of contamination is further evidenced by the absence of a measurable increase in lead concentration between the beans sampled directly after removal from the husk of the plant and those that had been fermented in banana and plantain leaves and sun-dried (Oke Osun Farm; directly from husk, 0.846 ng/g ; fermented and dried, 0.839 ng/g).

Table 29: Lead isotopic ratios and concentrations (ng/g) of chocolate products

Sample	(Pb)	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{208}\text{Pb}/^{207}\text{Pb}$
Bittersweet chocolate 1	69.8	1.1712(2)	2.4282(1)
Bittersweet chocolate 2	29.4	1.1797(1)	2.4357(1)
Chocolate Candy 1	23.0	1.2029(1)	2.4542(1)
Chocolate Candy 2	27.9	-	-
Chocolate Candy 3	18.7	1.1716(1)	2.4242(2)
Chocolate Candy 4	20.0	-	-
Chocolate Candy 5	11.9	-	-
Chocolate pudding 1	14.8	-	-
Chocolate Pudding 2	15.9	-	-
Dark Chocolate 1	49.6	1.1768(1)	2.4276(1)
Dark Chocolate 2	40.9	1.1774(1)	2.4271(1)
Dark Chocolate 3	57.6	1.1688(1)	2.4252(1)
Dark Chocolate 4	29.4	1.1992(3)	2.4405(2)
Dark Chocolate 5	26.0	-	-

Dark Chocolate 6	35.1	1.1866(1)	2.4400(1)
Milk Chocolate 1	23.4	1.1617(1)	2.4201(1)
Milk Chocolate 2	14.9	1.1619(8)	2.4163(5)
Semisweet Chocolate 1	42.1	1.1720(1)	2.4294(1)
Semisweet Chocolate 2	41.7	1.1826(1)	2.4330(1)
Semisweet Chocolate 3	31.1	1.1638(1)	2.4198(1)
Semisweet Chocolate 4	56.1	1.1836(11)	2.4456(12)
Semisweet Chocolate 5	36.2	1.1766(1)	2.4275(1)
Semisweet Chocolate 6	-	1.1820(5)	2.4376(4)

No. in parentheses are the error (2σ) recorded from TIMS counting statistics. Isotopic ratios were obtained at the University of California, Santa Cruz, and concentrations were determined at WCAS

Source: Rankin et al. (2005)

Table 30: Lead concentration (ng/g) and isotopic compositions of cocoa bean shells from Nigerian Farms

State	Farm	Sample	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{208}\text{Pb}/^{207}\text{Pb}$ (Pb)	% RSD	
Ogun	Oke Osun, Ibese	Shell 1	1.155(5)	2.434(9)	61	1.92
		Shell 2	1.156(5)	2.412(8)	72	0.28
	Kango Village	Shell 1	1.158(5)	2.439(9)	74	0.75
		Shell 2	1.156(5)	2.438(9)	82	0.24
Ondo	Igbo Eleruku, Ita Ogbolu	Shell 1	1.1566(1) ^a	2.4336(2) ^a	417	0.46
		Shell 2	1.153(5)	2.425(9)	409	0.22
	Ase Igbo	Shell 1	1.158(5)	2.436(9)	73	0.46
		Shell 2	1.158(5)	2.431(9)	144	0.29
Osun	Idi Obi I	Shell 1	1.156(5)	2.428(9)	185	0.22
		Shell 2	1.155(5)	2.432(9)	132	0.26
	Aba Arawense Modakeke	Shell 1	1.155(5)	2.434(9)	120	0.24
		Shell 2	1.156(5)	2.429(9)	157	0.18

% RSD, percent relative standard deviation. Except where noted, numbers in parentheses are the internal error (2σ) calculated from the average relative deviation from concurrent analyses of SRM 981 on the HR-ICPMS. The percent relative deviation is reported as the internal error (σ) from the HR-ICPMS counting statistics.

^aIsotopic compositions and the error (2σ) are from TIMS analysis.

Source: Rankin et al. (2005)

The presence of contaminant lead in bean shells from the cocoa farms is substantiated by the concentrations we observed in the various soil profile composites of this study (Table 31). The average lead concentration was 14.2 $\mu\text{g/g}$, which is consistent with the survey of Chukwuma (1997), who reported the lowest lead value measured in Nigerian soils as 10 $\mu\text{g/g}$. The lead isotopic ratios of the soil profiles, listed in Table 32 are variable, indicating that multiple sources (e.g., historically different sources of TEL, pesticides, fertilizers, machinery) are responsible for the contamination observed. Although the isotopic area encompassed by the soil profiles overlaps the lead isotopic compositions of the cocoa bean shells and may be a source of current contamination, the similarities in the isotopic compositions of cocoa bean shells are indicative of a single predominant source of lead contamination at the cocoa farms. In light of the numerous published reports on the predominance of gasoline emissions as a source of lead contamination in Nigeria, this source is tentatively attributed to TEL, although we were not able to obtain samples of Nigerian gasoline for isotopic composition analysis in the United States for this study.

Table 31: Lead concentrations ($\mu\text{g/g}$) of soil profile composites from Nigerian Farms

State	Farm	0-10 cm		0-20 cm		35-50 cm		80-100 cm	
		(Pb)	% RSD	(Pb)	% RSD	(Pb)	% RSD	(Pb)	% RSD
Ogun	Oke Osun, Ibese	3.54	2.4	3.00	0.7	2.94	0.6	3.46	0.7
	Kango Village	17.0	0.5	21.5	0.4	40.6	0.5	29.8	0.4
Ondo	Igbo Eleruku, Ita Ogbolu	11.2	2.2	12.1	1.2	12.6	0.4	-	-
	Ase Igbo	30.8	0.6	17.4	0.7	25.5	0.7	17.7	0.4
Osun	Idi Obi I	10.8	2.3	11.7	0.4	10.6	0.4	14.9	0.4
	Aba Arawense, Modakeke	7.55	1.3	6.86	2.4	6.25	0.5	8.21	0.4

% RSD, percent relative standard deviation reported as the internal error (σ) from HR-ICPMS counting statistics

Table 32: Lead isotopic compositions of soil profile composites from Nigerian Farms

State	Farm	0-10 cm		0-20 cm		35-50 cm		80-100 cm	
		$^{206}\text{Pb}/^{207}\text{Pb}$	$^{208}\text{Pb}/^{207}\text{Pb}$	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{208}\text{Pb}/^{207}\text{Pb}$	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{208}\text{Pb}/^{207}\text{Pb}$	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{208}\text{Pb}/^{207}\text{Pb}$
Ogun	Oke Osun	1.168(5) ^a	2.469(9) ^a	1.1226(1) ^b	2.6942(2) ^b	1.1953(1) ^b	2.4988(1) ^b	1.1959(1) ^b	2.4972(1) ^b
	Kango Village	1.130(5) ^a	2.760(10) ^a	-	-	1.1237(1) ^b	2.7179(2) ^b	1.1259(1) ^b	2.6860(1) ^b
Ondo	Igbo Eleruku, I	1.138(5) ^a	2.493(9) ^a	1.141(5) ^a	2.492(9) ^a	-	-	-	-
	Ase Igbo	1.2558(1) ^b	2.6417(2) ^b	1.161(5) ^a	2.428(9) ^a	1.2561(1) ^b	2.6269(2) ^b	1.2493(1) ^b	2.6248(4) ^b
Osun	Idi Obi I	1.1922(1) ^b	2.4911(6) ^b	-	-	1.1983(1) ^b	2.3329(1) ^b	1.1671(1) ^b	2.4527(1) ^b

	Aba Arawense	1.203 (5) ^a	2.479 (9) ^a	1.200 (5) ^a	2.482 (9) ^a	-	-	-	-
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^a Numbers in parentheses are the internal error (2σ) calculated from the average relative standard deviation from concurrent SRM 981 analyses on the HR-ICPMS.

^b Numbers in parentheses are the internal error (2σ) from the TIMS counting statistics.

Source: Rankin et al. (2005)

In summary, chocolate products and manufactured cocoa contain relatively high levels of contaminant lead compared with the baseline value for Nigerian cocoa beans used to make those products. Isotopic composition analyses of the products indicate multiple sources of contamination of industrial origin, which is consistent with the observation that there are numerous sources of lead contamination during the production of cocoa that have yet to be identified (COPAL 2004a, 2004b). Similar lead isotopic composition in contaminated cocoa bean shells from Nigeria, together with the high ability of cocoa bean shells to adsorb lead, suggest that contamination during cocoa processing at each farm may be responsible for some of the contamination in cocoa products: we propose that the on-going use of leaded gasoline in Nigeria contributes to that contamination. However, the low lead concentration in cocoa beans compared with those of manufactured cocoa and chocolate products indicates that most lead contamination in those products occurs after the beans are harvested and dried, during the shipping of those beans and/or the manufacturing of cocoa and chocolate products.

One source of contamination of the finished products is tentatively attributed to atmospheric emissions of leaded gasoline, which is still being used in Nigeria. Owing to high capacity of cocoa bean shells to adsorb lead, contamination from leaded gasoline emissions may occur during the fermentation and sun-drying of unshelled beans at cocoa farms.

3.8.0 Biological Samples

3.8.1 Lead levels in blood and urine of some residents of Abeokuta, Nigeria

Lead, the most ubiquitous toxic metal, is detectable in practically all phases of the inert environment and in all biologic systems (ATSDR 1997, Elinder et al. 1988). As a result of its toxicity to most living things and since there is no demonstrated biological need for lead, the major issue regarding lead is at what dose does it become toxic. The levels of lead considered safe have shifted dramatically downward over the years (USEPA 1991); bringing into question whether there is any threshold for humans and other animals.

Evaluation of human exposure to lead can be carried out by determining the levels in biological fluids such as blood and urine (Cuellar and Kamper 1986; Elinder et al., 1988). The concentration of lead in blood reflects a dynamic equilibrium between exposure, absorption, distribution and elimination of lead. Blood lead is therefore, a widely-used index for measuring recent exposure. Data on baseline levels of lead in human blood and urine in Nigerian population are sparse in the literature. Ademuyiwa et al., (2002) reported the determination of lead in blood and urine of university students, petrol station attendants and pregnant women (all of whom are residents in Abeokuta) by a spectrophotometric method in order to assess human exposure to lead.

A mean blood lead level of 16.27 ± 2.65 $\mu\text{g/dl}$ was found for male university students while the female students had a mean blood lead level of 15.19 ± 2.36 $\mu\text{g/dl}$. The male petrol station attendants had a mean blood lead level of 42.40 ± 2.41 $\mu\text{g/dl}$ whereas their female counterparts had 34.95 ± 4.25 $\mu\text{g/dl}$. The highest mean blood lead concentration (54.52 ± 4.38 $\mu\text{g/dl}$) was observed in the pregnant women in their third trimester of pregnancy. The urinary excretion of lead followed the same pattern as that of blood. The study provides additional data pointing to the prevalence of elevated blood lead levels in urban areas.

3.8.2 Lead levels in carious teeth of residents in three Nigerian cities.

The evaluation of human exposure to lead can be carried out by monitoring lead concentrations in the environment. The blood lead level reflects a dynamic equilibrium between exposure, absorption, distribution and elimination of lead. Lead in blood is, therefore, thought to be the best indicator of recent prolonged exposure. Lead in the body is rapidly transported through the blood to bones and teeth where it is stored. Lead undergoes bioaccumulation in bone and teeth throughout life. It is estimated that about 90% of the body burden of Pb is retained in these media after long time exposure. However, lead in bones is moveable and subject to loss during the re-modelling process. Therefore, out of these two major reservoirs for lead in the body, the teeth may be considered to be better assessment as an index of environmental pollution and as indicator of the body burden of lead.

Analysis of teeth has now become common in prospective and retrospective studies of lead exposures and also in relating exposure to human health. The lead levels in teeth have the advantage of reflecting the cumulative lead burden over a given period. The aim of this study was to determine the lead level in carious teeth of some adult inhabitants of Lagos, Ibadan and Abeokuta, Nigeria in order to provide a reliable data for the assessment of the extent of environmental pollution (Arowolo and Bamgbose, 2004).

A total of three hundred and six samples of teeth extracted from men and women living in Lagos, Ibadan and Abeokuta, aged 14 to 70 years were collected from Dental Centres in these cities. Most of the teeth donors were permanent residents in these cities. The subjects were randomly selected

and people who had been or still were occupationally exposed to lead were excluded from the study. For each donor, age, sex and other relevant information were recorded. The teeth samples were stored in refrigerator at -5°C immediately after collection until needed for analysis.

Lead determination was carried out with a Buck Scientific 200A model flame atomic absorption spectrophotometer with air-acetylene flame. Quality control procedures were incorporated to monitor and maintain reproducibility of the procedure. Repeated measurements of a typical tooth in solution (Precision) yielded a mean of $6.51\ \mu\text{g/g}$, $n=10$, SD of $0.638\ \mu\text{g/g}$ and coefficient of variation 9.80%.

The average lead levels in the teeth of male and female living in the three cities, Lagos, Ibadan and Abeokuta, were classified according to donor's age and are presented in Table 33. The concentrations ranged from 1.91 to 26.80 for Lagos; 2.05 to 21.6 for Ibadan and 1.95 to 18.08 μg per gram dry root for Abeokuta. The results showed a significant increase in lead level with increase in donor's age. The regression coefficients obtained readily confirm that the lead levels are age-dependent which is a direct evidence for the accumulation of Pb in teeth. Similar results have been obtained by several workers.

The results obtained indicated the intensity of lead contamination in the three cities. However; our data were from teeth roots, where the lead level is higher than anywhere else in the tooth (Bercovitz et. al., 1993). A gradual increase in the level of lead contamination by various forms including automobiles and industries polluting air and water has been observed in the past few decades in Nigeria (Nriagu 1992; Odukoya et al., 2000; Adetunji et. al., 2001). The high standard deviations observed in the age range groups could be attributed to non-classification of social habit, e.g. smoking and drinking habits which could influence lead intake from several sources. For example, blood lead levels were reported to increase with the consumption of wine. A similar increase was observed for beer drinkers and smokers although not statistically significant. The results in Table 34 showed that lead level in teeth is not affected by gender since no significant difference in lead accumulation in teeth of adult male and female within the same age group has been demonstrated except at the old age group of 51-60 years. Therefore, there were no sex specific differences. This was supported by other similar studies using carious teeth.

No significant difference exists between the lead level in teeth of residents of the three cities – Lagos, Ibadan and Abeokuta. Lagos is an industrial and metropolitan city, with high population density; Ibadan has a few industries and was the third largest city in Africa a few decades ago. It also has a high population density while Abeokuta is the smallest of the three cities covered in this study. It is, therefore, surprising that no significant difference existed between the results of lead in teeth from the three cities. The explanation may be attributed to the short distances between these cities. Today people are very mobile and do not always work in their vicinity. Even if they live for many years within the same domicile, they do not reflect their particular environment because of their mobility. We assumed that the daily mobility of the residents, the short distances among the three cities, and the common food condiments may have a greater effect on the lead level in teeth than do difference in environmental pollution.

The results obtained in the study were low (in most cases) when compared to the levels reported in the literature by several workers as compared in Table 35. These can readily be attributed to the

level of development and the high motorization rate in such countries. However, the present data indicate a bio-magnification effect of Pb in the teeth of adults of Lagos, Ibadan and Abeokuta, Nigeria.

Although, it would be unreliable in our conclusions based on such a small sample set particularly when the population of Nigeria is considered, it would seem on the balance of probability that the results obtained in this study confirm that Nigerians are exposed to lead. The amount of lead in teeth denotes the amount of absorption into the body and serves as index of pollution. The donor's age can be considered as the period of lead accumulation. The pathways of lead exposure in the three cities are not different from what one would expect in many urban areas of Nigeria.

Table 33: Lead level in teeth (dry root) of urban residents classified according to age groups

Age Range	Lagos		Ibadan		Abeokuta	
	Average Lead level	N	Average Lead Level	n	Average Lead Level	N
14-20	4.50 ±2.71a	27	4.24±2.38a	24	4.07±2.14a	13
21-30	5.42±2.91a	28	5.24±2.76a	34	5.01±3.01a	19
31-40	6.04±4.07a	27	6.25±3.98a	27	5.84±3.46a	33
41-50	9.25±5.28b	14	8.82±4.76b	11	8.70±4.51b	18
51-60	14.07±6.09c	11	12.61±5.89c	5	11.92±5.61c	8
61-70	19.11±7.63d	5	14.43±6.87c	4		
r*	0.83		0.90		0.87	

Source: Arowolo and Bamgbose (2004)

Table 34: Lead level in teeth (dry root) of donors classified according to sex and age

Age Group	Male	Female
14-20	4.90 ±2.58	3.48±2.32
21-30	5.04±3.02	5.76±2.79
31-40	6.95±4.38	5.85±3.88
41-50	9.16±6.05	8.90±4.12
51-60	15.06±8.18	11.62±6.57

Source: Arowolo and Bamgbose (2004)

There is, therefore, a clear and urgent need for the Nigerian Government to commence the implementation of a programme of planned phase out of leaded gasoline in the country. This is important because lead pollution is known to play a major role in urban areas as a result of

automobiles. The latter accounts for most (about 90%) of lead pollution in urban areas of Nigeria. In addition, the removal of lead from gasoline has been associated with reduced exposure and lowered blood lead levels in the general population of many countries.

Table 35: Lead level in teeth ($\mu\text{g g}^{-1}$) and motorization rate in some countries

Country	Subjects age (years)	Lead level (Average/Range)	Motorization rate	Remarks (Ref)
Northern Ireland	3-10	2.4 - 38.6	-	Whole teeth (Gil et. al., 1996)
England (Sheffield)	40-72	26.6 \pm 12.4 112.5 \pm 52.9	383	Dentine Pulp (Bercovitz et. al., 1993)
France (Strasbourg)	32-65	45.3 \pm 15.8	516	Inner root dentine (Frank et. al., 1990)
Finland	Adults	53.5 \pm 7.8	412	Whole dry dentine Lappalainen and Knuuttila (1979)
USA (Philadelphia)	Children	51.1 \pm 10.9	801	Whole Teeth Needleman et. al., 1972
South Africa	6-12	26.5 - 74.5	182	Dentine, range between urban and rural regions (Grober et. al., 1995)
Mexico City	12-29	24.1 \pm 9.3	-	Root inner dentine (Frank et. al., 1990)
Israel	31-40	6.41 \pm 3.80	189	Whole roots (Bercovitz et. al., 1993)
Nigeria Lagos Ibadan Abeokuta	31-40	6.04 \pm 4.01		Whole roots
		6.25 \pm 3.98		Whole roots (present study)
		5.84 \pm 3.46		

Source: Arowolo and Bamgbose (2004)

3.8.3 Lead poisoning associated with malaria in children of urban areas of Nigeria

One of the most prevalent and neglected diseases in Nigeria and most of the Sub-Saharan African countries probably is lead poisoning which has affected a large fraction of the childhood population because of the growing multiplicity of potential exposure routes. This point is illustrated by the fact that only three studies of childhood lead poisoning with limited sample sizes have been conducted in Nigeria (Nriagu et al., 1996; Pfitzner et al., 2000; Wright et al., 2005). The three studies were conducted in two medium cities (Jos and Kaduna) in northern Nigeria and, thus far, there has been no investigation of childhood lead poisoning in any of the major cities in the country. Therefore, a research team headed by Prof. Jerome Nriagu examined the inter-city and trans-cultural differences in lead exposure of the pediatric population in three of the largest metropolitan areas of Nigeria (Nriagu et al., 2008).

The disabilities created by lead poisoning (impaired mental and physical development, poor school performance, anemia, under-nutrition, infertility) represent a significant social, financial and health burden on the affected individuals, their families and communities (ATSDR, 1999; United Nations, 2005). Lead poisoning is the sixth most important contributor to the global burden of diseases measured in disability adjusted life years (DALYs), with Sub-Saharan African countries being predominantly responsible for the global DALYs (Pruss-Ustun and Corvalan, 2006). What has generally not received much attention in the scientific literature is the fact that lead poisoning can moderate the susceptibility of a child to parasitic diseases, including infections from vector-borne, food-borne, water-borne or soil-transmitted pathogens and that its overall contribution to the global DALYs may be considerably higher (Ogunseitan and Smith, 2001). In many urban areas of Nigeria, poverty, poor housing, high population densities and unsafe or inadequate living conditions, combined with inadequate sanitation and environmental pollution promote not only the spread of some communicable diseases but also can increase the children's vulnerability to lead. Co-incident lead poisoning and parasite infection among young children remain an unexplored public health problem in African countries. The objectives of our study were to (a) determine the prevalence of elevated blood lead levels (EBLLs) of children in three cities of Nigeria with different levels of industrial pollution; (b) identify the environmental, social and behavioral risk factors for the EBLLs in the children; and (c) explore the association between malaria and EBLLs in the study population. Although many parasitic diseases are endemic in Nigeria, *Plasmodium* infections (specifically malaria) are the most deadly (Snow and Marsh, 1998), hence the focus of this study.

The study involved 653 children aged 2–9 years (average, 3.7 years). The mean blood lead level (BLL) for the children was 8.9 ± 4.8 mg/dL, the median value was 7.8 mg/dL, and the range was 1–52 mg/dL (Fig. 13). About 25% of the children had BLL greater than 10 mg/dL. There were important differences in BLLs across the three cities, with the average value in Ibadan (9.9 ± 5.2 mg/dL) and Nnewi (8.3 ± 3.5 mg/dL) being higher than that in Port Harcourt (4.7 ± 2.2 mg/dL). Significant positive associations were found between BLL and a child's town of residence ($p < 0.001$), age of the child ($p = 0.004$), length of time the child played outside ($p < 0.001$), presence of pets in a child's home ($p = 0.023$), but negatively with educational level of caregiver ($p < 0.001$). The study was one of the first to find a significant negative association between BLL and malaria in a pediatric population, and this association remained significant after controlling for confounding diseases and symptoms. The shared environmental and socio-demographic risks factors for lead exposure and *Plasmodium* (most common malaria parasite) infection in urban areas

of Nigeria were investigated along with possible ways that lead exposure may influence the host response to infection with malarial parasites.

Our result still needs to be confirmed by other studies. The message from this study is on the need for improved understanding of the moderating effects of lead exposure on communicable diseases endemic in the study area. In addition to the well-known psycho-somatic effects of chronic lead poisoning, pre-school lead exposure is increasingly being linked to criminal behavior later in life—another critical public health problem in Nigeria. For instance, recent studies by Nevin (2000, 2007) showed a very strong association between preschool blood lead and subsequent crime rate trends (including burglary, murder and other violent crimes) over several decades in the USA, Britain, Canada, France, Australia, Finland, Italy, West Germany, and New Zealand.

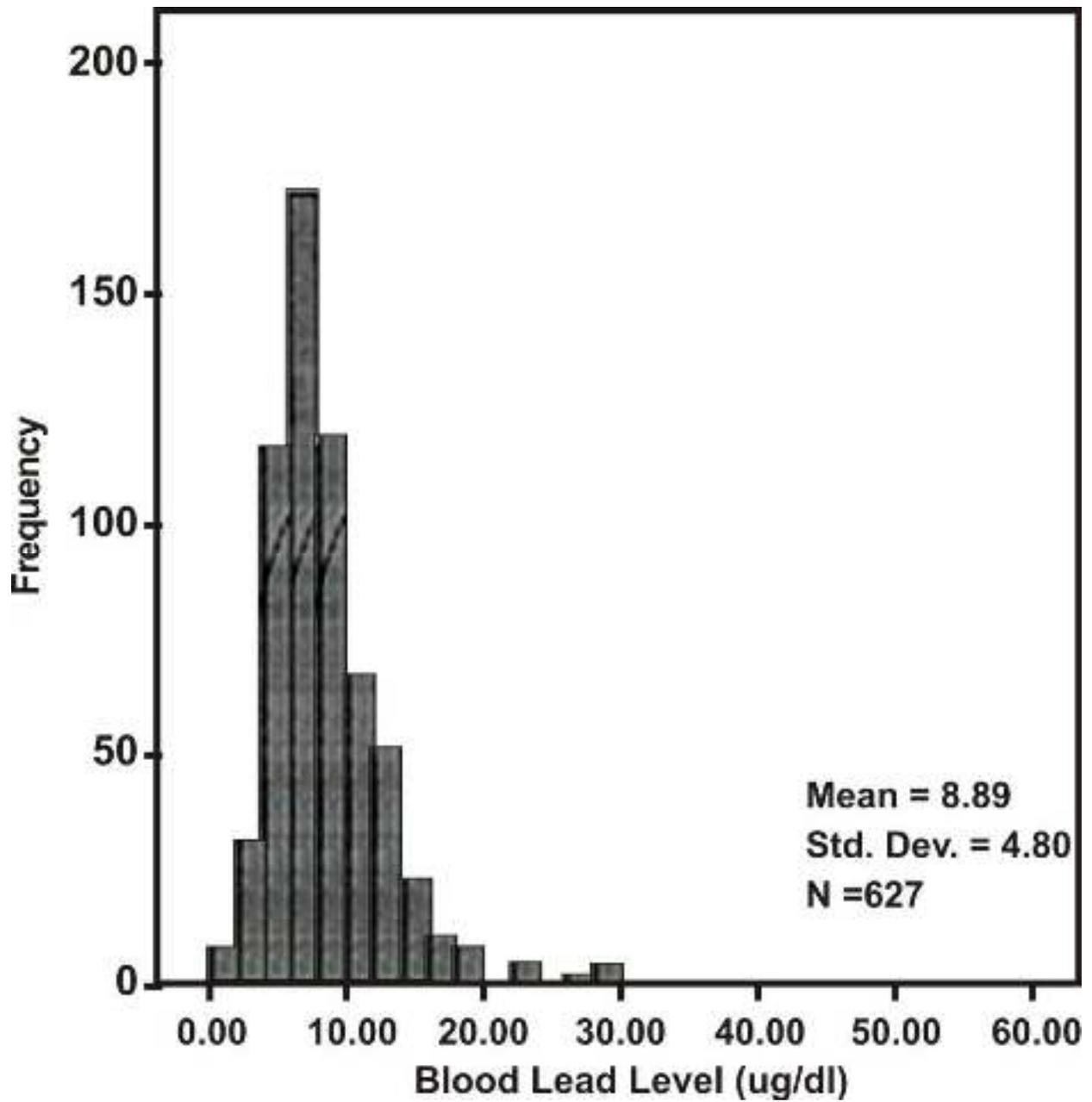


Fig. 7: Histogram of blood level in children
Source: Nriagu et al. (2008)

3.10 Current Research

In 2014, our research team won a four million naira grant from the Lagos State Government to conduct research on **Profiling and Mapping of Endocrine Disrupting Chemicals in Soil, Leachate, Groundwater, Plants and Air from Landfill sites of Lagos State: A Case Study for Policy Formulation on Establishment of Future Dumpsites**

The question most people asked us is “why are we interested in dumpsites? Our simple answer is “Remember the Love Canal episode in US?” Love Canal is a U.S. neighbourhood built on a chemical dumping ground from the 1940s and 50s in New York State. The site contained chemicals and toxins dating from the Second World War. That canal was later capped, and homes and a school were built on top of it. Later, snow melt from an unusually harsh winter in 1977 seeped into the buried 16-acre canal and forced chemical waste into groundwater and to the surface, oozing into yards and basements. Residents began complaining of miscarriages, urinary and kidney problems and mental disabilities in their children. Some residents also suffered from birth defects and cancer. Unfortunately, people unknowingly lived and died while residing atop the toxic waste dump. The problem was uncovered in the 1970s and the homes were demolished. In 1978, President Jimmy Carter declared the site a federal emergency area (Plate 6).

Over 800 families were relocated and the Environmental Protection Agency sued Hooker's parent company then Occidental Petroleum, for \$129 million. The Environmental Protection Agency cleaned up 21 tons of toxic chemicals on the 16 acre site. With Love Canal getting national attention, President Jimmy Carter in 1978 issued a disaster declaration that eventually led to evacuation and compensation for more than 900 families. The crisis also led to federal Superfund legislation to clean up the nation’s abandoned waste sites. Quite simply, Love Canal is one of the most appalling environmental tragedies in American history. However, it cannot be regarded as an isolated event. It could happen again, anywhere in the world unless we move expeditiously to prevent it. Landfills can of course be an environmentally acceptable method of hazardous waste disposal, assuming they are properly sited, managed and regulated.

Dumpsites spread pollutants across our atmosphere and our oceans; and damage our health and environment. Dumpsites are a major cause of greenhouse gases and soil pollutants leach into our food streams.



Plate 6: Barrels block a road near a buried chemical dump in an uninhabitable area of Niagara Falls. Photo: AP Photo/Carolyn Thompson

Dumpsites in Lagos State

1. Olusosun -----active since 19th Nov 1992
2. Souls 1----- not active since 5th October 2006
3. Souls 2----- active since 20 July 2006
4. Souls 3----- active since 4th July 2008
5. Abule Egba-----not active since 7th July 2008
6. Ewu elepe----- active since 14th Nov 2008
7. Owutu-----not active since 10 Dec 2008
8. Epe----- active since 12th Feb 2009
9. Ogombo----- not active since 14th March 2009
10. Anthony Village not active since 20th Nov 1992
11. Isolo----- not active since 1995
12. Makoko----- not active since 1983
13. Adeniji Adele----- not active since 1983

14. Agunlejika-----not active since 1990
15. Omole.----- not active since 1991
16. Billings way----- not active since 1997

Endocrine Disrupting Chemicals (EDCs) are exogenous chemicals that interfere with the production, release, transport, binding, action, or elimination of natural hormones responsible for the maintenance of homeostasis and regulation of developmental processes (Scrippo et al., 2004; Hjelemborg et al., 2006; Gelbke et al., 2007). Specifically, EDCs interfere with the body's endocrine system and produce adverse developmental, reproductive, neurological and immune effects in both humans and wildlife. Several million tons of both biodegradable and non-biodegradable wastes (domestic, industrial and hospital) are usually disposed-off at designated landfills or dumpsites.

Lagos State Waste Management Authority (LAWMA) already has a plan to close Olusosun dumpsite and turn it into an Ecology Park. Our fear is that in say, 50 years' time, we hope the Executive Governor will not convert the proposed Ecology Park to a housing estate! And with no plan for potable water, residents will dig boreholes and wells!! Another Love Canal in the making!! That was why we applied for the research grant with the overall objectives of assessing the availability, distribution and source apportionment of EDCs due to dumpsite location within the Lagos metropolis. At the end of the project, we also plan to produce a policy document that will guide and control future establishment of new landfill sites in the State.

Our research team includes three foreign members. They are Prof. Yingxin Yu of the University of Shanghai, China, Prof. Xiang Meng of the Tongji University, China and Prof. W. Goessler of the University of Graz, Austria. Our research study is focused on Olusosun, Abule Egba, Igando, Epe and Ikorodu Dumpsites. Heavy metals determination in plants, soils, sediments, groundwater, surface water and leachate samples, were analysed at the Institute for Analytical Chemistry, University of Graz, Austria using microwave digestion system and Inductively Coupled Plasma - Mass Spectrometer (ICP-MS). Analysis of the phthalate esters and Polybrominated flame retardants were carried out at Tongji University, China. Interpretation of the results obtained in the study is in progress.

4.0 Conclusion and Recommendations

Mr. Vice-Chancellor Sir, in the course of this lecture, I have attempted to explain some challenges facing the Nigerian environment. We seemed to be "living in inaction" in Nigeria. The exponential growth in population, energy consumption and vehicular traffic predispose our environment to rapid deterioration of the air quality.

There is an urgent need for Governments to pay close attention to the problems of environmental degradation in Nigeria. Pollution continues to pose a significant threat to the environment, quality of life and health of the urban population in Nigeria. In order to improve public health, governments must implement policies to reduce pollution. There is also the need for Governments to strengthen regulatory infrastructure, enforcement and compliance monitoring in environmental management and protection for sustainable development.

Considering the threats and the extent of degradation to which the Nigerian environment is being subjected, substantial resources are required for control, monitoring and remediation in the sector. In order to successfully combat the myriad of environmental problems that currently bedevil our nation, government at the three tiers must rise to the occasion and ensure that certain critical issues are tackled immediately

Many of the man-made threats to our environment are fuelled by ignorance and non-challant attitude of the populace. We have not educated our people enough to convince them to turn away from bad environmental management practices such as illegal felling of trees, indiscriminate lighting of fire, poor refuse disposal habits, etc. Environmental issues are part of daily living; therefore, their knowledge or awareness must be reduced to messages and languages understood by all. Therefore, we need to embark on an aggressive advocacy programme that will bring the populace on board as major stakeholders in the protection of our environment.

It is of utmost importance that we do everything possible to ensure the preservation of a healthy environment, not only in our own interest but also in the interest of generations that will come after us and to whom, ideally, we should bequeath a legacy of a clean, habitable and safe environment. Since we are all stakeholders in the global village, the time is now for all of us to join the struggle for a healthy environment.

We (Government and People) must all imbibe good environmental management practice. To this end, I wish to recommend as follows:

Federal and State Governments

1. The Federal and State Governments must ensure that the country's infrastructure meets the modern era of 2017 and beyond. In this regard, uninterrupted power supply, potable water for all and railway system must be developed. This will go a long way to protect the environment.
2. The Federal and State Governments must ensure adequate funding for the management and protection of the environment. Judicious application of the funds allocated and funds secured from donor agencies must be ensured. Transparent management of and accountability for donor funds will encourage such donors to do more.
3. Nigeria should adopt a National Strategy for Sustainable Development that identifies key principles and priorities, sets short and long-term goals, align legal and policy tools to those goals and creates a process and timetable for achieving them.
4. Increased public awareness is essential. There is an urgent need for greater public education so that the populace fully understands the importance of halting pollution. Make environmental education, like mathematics, part of standard education curriculum.
5. The use of alternative, less polluting, energy sources should be considered. Adoption of environmentally – friendly options such as solar energy, wind and ocean currents should be considered. More countries of the world are investing in renewable energy.

6. Solid and liquid waste management especially municipal waste in the country must be drastically improved.
7. Updating of environmental laws. Environmental laws existing in the country are generally obsolete and need to be updated and made more relevant to current conditions and economic reality.
8. There is an urgent need for drastic improvement in the enforcement strategies of the myriads of environmental laws, statutes and guidelines in the country. The existing environmental laws should be effectively enforced.
9. Nigeria should consider banning the use of plastic bags in the country. More than 40 other countries in the world have banned, partly banned or taxed single use plastic bags, including China, France, Rwanda, Kenya and Italy. Habib El-Habr, an expert on marine litter working with the UNEP in Kenya said “If we continue like this, by 2050, we will have more plastic in the ocean than fish”.

Things we can do

There are many things all of us can do to reduce contaminants in our environment. These include:

- Plant trees and encourage others to plant trees in houses and along road sides. We should also plant grass, trees and shrubs in bare areas to reduce and absorb runoff, reduce erosion, and improve habitat. Trees absorb and store carbon dioxide from the atmosphere and filter out air pollution. During warmer days, trees provide cool air.
- Prevent or reduce pollution in order to improve public health.
- Reduce waste, dispose waste properly and recycle plastic, glass and paper.
- Organize environmental education (neighbourhood campaigns) on the importance and the need for a healthy and safe environment.
- Support local action and community participation. Organize neighbourhood clean-ups.
- Keep trash out of storm drains, where it will clog up the drain or end up in the nearest stream or lake.
- We should drive less and save energy on the road by walking, cycling (avoiding short journeys by car), using a car pool or sharing a car or travel by public transport (all produce fewer emissions than those emitted by a single person in a car).
- We must keep our vehicles well-maintained. A poorly maintained engine both creates more air pollution and uses more fuel. Replace oil and air filters regularly, and keep tyres properly inflated.

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