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Analysis of Environmental Pollutants by Atomic Absorption Spectrophotometry

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1. Introduction

Environmental pollution as a result of man's increasing activities such as burning of fossil fuels and automobile exhaust emission has increased considerably in the past century due mainly to significant increases in economic activities and industrialization. Burning of fossil fuels and petroleum industry activities have been identified as primary sources of atmospheric metallic burden leading to environmental pollution. Several studies have shown that heavy metals such as lead, cadmium, nickel, manganese and chromium amongst others are responsible for certain diseases (Hughes, 1996). In general, heavy metals are systemic toxins with specific neurotoxic, nephrotoxic, fetotoxic and teratogenic effects. Heavy metals can directly influence behavior by impairing mental and neurological function, influencing neurotransmitter production and utilization, and altering numerous metabolic body processes. Systems in which toxic metal elements can induce impairment and dysfunction include the blood and cardiovascular, eliminative pathways (colon, liver, kidneys, skin), endocrine (hormonal), energy production pathways, enzymatic, gastrointestinal, immune, nervous (central and peripheral), reproductive and urinary that have lethal effects on man and animals. These diseases include abdominal pain, chronic bronchitis, kidney disease, pulmonary edema (accumulation of fluid in the lungs), cancer of the lung and nasal sinus ulcers, convulsions, liver damage and even death (Hughes, 1996).

Heavy metals get into the environment: water, soil, air and land through activities like intense agriculture, power generation, industrial discharges, seepage of municipal landfills, septic tank effluents e.t.c. Many authors have reported high levels of heavy metal ions in the soil, rivers and groundwater in different areas of Nigeria (Ibeto & Okoye, 2010a). To save the environment from further deterioration and also maintain sound public health, a strategy can be effectively utilized which is the use of organic materials such as municipal solid waste, agricultural waste and industrial waste to produce biogas. Biogas is a suitable alternative fuel which burns with similar properties to natural gas. Unlike natural gas, it is clean and has no undesirable effects on the environment. It is a mixture of gases consisting

of around 60 to 70% of methane produced by the process of anaerobic digestion in a digester. The effluent of this process is a residue rich in the essential inorganic elements needed for healthy plant growth known as bio fertilizer, which when applied to the soil enriches it with no detrimental effects on the environment. Many authors have also reported the utilization of various wastes found in the environment, ranging from animal wastes, plant wastes to leaf litters and food wastes (Ofoefule et al., 2010; Uzodinma et al., 2011). It is also recommended that other alternative fuels such as bioethanol, which are becoming increasingly important not only because of the diminishing petroleum reserves, but also because of the environmental consequences of exhaust gases from petroleum fueled engines be made available for use in Nigeria. Good quality biodiesel fuel which is derived from triglycerides has attracted considerable attention during the past decade as a renewable, biodegradable and non-toxic fuel producing less particulate matter, hydrocarbons, aromatics, carbon-monoxide and soot emissions when burnt in the engines. Its production, marketing and use should therefore be highly encouraged as is the case in Europe, America and some other parts of the world.

Several spectroscopic methods have been used to monitor the levels of heavy metals in man, fossil fuels and environment. They include; flame atomic absorption spectrometry (AAS), atomic emission spectroscopy (AES), graphite furnace atomic absorption spectrometry (GFAAS), inductively coupled plasma-atomic emission spectroscopy (ICP/AES), inductively coupled plasma mass spectrometry (ICP/MS), x-ray fluorescence spectroscopy (XRFS), isotope dilution mass spectrometry (IDMS), electrothermal atomic absorption spectrometry (ETAAS) e.t.c. Also other spectroscopic methods have been used for analysis of the quality composition of the alternative fuels such as biodiesel. These include Nuclear magnetic resonance spectroscopy (NMR), Near infrared spectroscopy (NIR), inductively coupled plasma optical emission spectrometry (ICP-OES) e.t.c.

2. Sources of heavy metal pollution of the environment

2.1 Lead

Lead is a common industrial metal that has become widespread in air, water, soil and food. It is a naturally occurring metal that has been used in many industrial activities and therefore many occupations may involve exposure to it such as auto-mechanic, painting, printing, welding e.t.c putting the workers at risk of potential high exposure. In the atmosphere, lead exists primarily in the form of $PbSO_4$ and $PbCO_3$. Lead in paints and automobile exhausts are still recognized for its toxicity (Hughes, 1996). Episodes of poisoning from occasional causes such as imperfectly glazed ceramics (Matte et al., 1994), the use of medicines which may contain as much as 60% lead available from Asian healers and cosmetic preparations, may affect any age group and cases may present as acute emergencies (Bayly et al., 1995). The main source of adult exposure is food, air inhalation accounts for 30% and water of 10% (John et al., 1991).

Some individuals and families may be exposed to additional lead in their homes. This is particularly true of older homes that contain lead based paint. In an attempt to reduce the amount of exposure due to deteriorating leaded paint, the paint is commonly removed from homes by burning, scraping or sanding. These activities have been found to result to at least temporarily, in higher levels of exposure for families residing in those homes. Special

population at risk of high exposure to tetra ethyl lead produced by reacting chloroethane with a sodium-lead alloy, includes workers at hazardous sites and those involved in the manufacturing and dispensing of tetraethyl lead (Gerbeding, 2005a). The production process is illustrated with the equation below.



Individuals living near sites where lead was produced or sites where lead was disposed and also hazardous waste sites where lead has been detected in some environmental media also may be at risk for exposure (Hazdat, 2005).

2.2 Cadmium

The principal form of cadmium in air is cadmium oxide, although some cadmium salts, such as cadmium chloride, can enter the air, especially during incineration. Environmental discharge of cadmium due to the use of petroleum products, combustion of fossil fuels (petroleum and coal) and municipal refuse contribute to airborne cadmium pollution (De Rosa et al., 2003) and possibly introduce high concentrations of this potential reproductive toxicant into the environment. This may be particularly true for Nigeria where refuse are burnt without control. In addition, humans may be unwittingly exposed to cadmium via contaminated food or paper (Wu et al., 1995) cosmetics and herbal folk remedies (Lockitch, 1993). All these factors put Nigerian population at high risk of cadmium toxicity (Okoye, 1994).

The greatest potential for above average exposure of the general population to cadmium is from smoking which may double the exposure of a typical individual. Smokers with additional exposure are at highest risk (Elinder, 1985). Soil distribution of urban waste and sludges is also responsible for significant increase in cadmium content of most food crops (WHO, 1996). Persons who have cadmium-containing plumbing, consume contaminated drinking water or ingest grains or vegetables grown in soils treated with municipal sludge or phosphate fertilizer may have increased cadmium exposure (Elinder, 1985). Persons who consume large quantities of sun flower kernels can be exposed to higher levels of cadmium. Reeves & Vanderpool (1997) identified specific groups of men who were likely to consume sunflower kernels. The groups included: basket ball and soft ball players, delivery and long distance divers and line workers in sunflower kernel processing plants.

2.3 Nickel

A person may be exposed to nickel by breathing air, drinking water, or smoking tobacco containing nickel. Skin contact with soil, bath or shower water, or metals containing nickel, as well as metals plated with nickel can also result in exposure. Coins contain nickel. Some jewellery are plated with nickel or made from nickel alloys (Gerbeding, 2005b). Exposure of an unborn child to nickel is through the transfer of nickel from the mother's blood to fetal blood. Likewise, nursing infants are exposed to nickel through the mother to breast milk. However, the concentration of nickel in breast milk is either similar or less than the concentration of nickel in infant formulas and cow's milk. Children may also be exposed to nickel by eating soil. Normally, the exact form of nickel one is exposed to is not known. It could be in form of nickel sulphate, nickel oxide, nickel silicate, iron-nickel oxides, nickel subsulfide or metallic nickel (Gerbeding, 2005b).

Patients may be exposed to nickel in artificial body parts made from nickel-containing alloys which are used in patients in joint prostheses, sutures, clips, and screws for fractured bones. Corrosion of these implants may lead to elevated nickel levels in the surrounding tissue and to the release of nickel into extracellular fluid. Serum albumin solutions used for intravenous infusion fluids have been reported to contain as much as 222 µg nickel/L, but are very rarely encountered. Dialysis fluid has been reported to contain as much as 0.82 µg nickel/L. Studies of nickel in serum pre- and post-dialysis show between 0 and 33% increases in nickel concentrations in patients (IARC, 1990).

2.4 Manganese

Populations living in the vicinity of ferromanganese or iron and steel manufacturing facilities, coal-fired power plants, or hazardous waste sites are exposed to elevated manganese particulate matter in air or water, although this exposure is likely to be much lower than in the workplace (Koplan, 2000a). Manganese is eliminated from the body primarily through the bile. Interruption of the manufacture or flow of bile can impair the body's ability to clear manganese. Several studies have shown that adults and children as well as experimental animals with cholestatic liver disorders have increased manganese levels in their blood and brain and are at risk from potentially increased exposure to manganese due to their decreased homeostatic control of the compound (Devenyi et al., 1994). In addition to oral diets, people on partial and total parenteral nutrition may be exposed to increased amounts of manganese. Forbes & Forbes (1997) found that of 32 patients receiving home parenteral nutrition due to digestive problems, 31 had elevated serum manganese levels (0.5–2.4 mg/L compared to normal range of 0.275–0.825 mg/L).

In comparison to other groups within the general population, persons living close to high density traffic areas, automotive workers, and taxi drivers may be exposed to higher concentrations of manganese arising from the combustion of methylcyclopentadienyl manganese tricarbonyl (MMT). MMT is actually a fuel additive developed in the 1950s to increase the octane level of gasoline and thus improve the antiknock properties of the fuel. Farmers, people employed as pesticide sprayers, home gardeners, and those involved in the manufacture and distribution of maneb and mancozeb may also be exposed to higher concentrations of these pesticides than the general public. People who ingest fruits and vegetables that have been treated with these pesticides and that contain higher-than-usual residues of the compounds (due to incomplete washing or over-application) may be exposed to increased concentrations of the pesticides. It is possible that medical workers may be exposed to higher concentrations of mangafodipir than the general population, although exposure routes other than intravenous are not expected to pose a significant risk (Koplan, 2000a). Manganese in the environment is in the form of their oxides or carbonates e.g MnO_2 , MnCO_3 e.t.c.

2.5 Chromium

Blue prints, primer paints, household chemicals and cleaners, cements, diesel engines utilizing anti-corrosive agents, upholstery dyes, leather tanning processes, welding fumes, battery, rubber, dye, candles, printers and matches are occupational and environmental sources of chromium (Koplan, 2000b). In addition to individuals who are occupationally exposed to chromium, there are several groups within the general population that have

potentially high exposures (higher than background levels) to chromium. These populations include individuals living in proximity to sites where chromium was produced or sites where chromium was disposed. Persons using chromium picolinate as a dietary supplement will also be exposed to higher levels of chromium than those not ingesting this product (Anderson, 1998). People may also be exposed to higher levels of chromium if they use tobacco products, since tobacco contains chromium. Workers in industries that use chromium are one segment of the population that is especially at high risk to chromium exposure. Occupational exposure from chromate production, stainless steel welding, chromium plating, and ferrochrome and chrome pigment production is especially significant since the exposure from these industries is to chromium (VI) (EPA 1984a).

Persons using contaminated water for showering and bathing activities may also be exposed via inhalation to potentially high levels of chromium(VI) in airborne aerosols. Elevated levels of chromium in blood, serum, urine, and other tissues and organs have also been observed in patients with cobalt-chromium knee and hip arthroplasts (Koplan, 2000b). Chromium in the environment can exist in many forms e.g chromium trioxide, potassium dichromate, sodium dichromate, potassium chromate, sodium chromate or ammonium dichromate e.t.c.

3. Environmental pollution

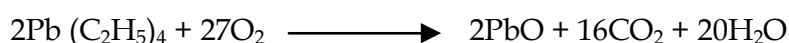
3.1 Fossil fuels combustion

The major sources of heavy metal pollution in urban areas of Africa are anthropogenic while contamination from natural sources predominates in rural areas. Anthropogenic sources of pollution include those associated with fossil fuel i.e. the non-renewable energy resources of coal, petroleum or natural gas (or any fuel derived from them) combustion, mining and metal processing (Nriagu, 1996). Fossil fuel consumption in Nigeria has risen ten-fold in the last two decades and consumption by urban households accounts for a large percentage, a trend which is expected to continue in the future. In a survey on urban household energy use patterns in Nigeria with respect to fuel preferences, sources and reliability of energy supply, it was found that kerosene, fuel wood, charcoal and electricity are the major fuels for urban use in Nigeria. Dependence on biomass fuels is rapidly giving way to the use of fossil fuels. Pollution problems associated with incidents of oil spills around automobile repair workshop resulting in metal contamination have been the subjects of many reports (Onianwa et al., 2001). Lead, cadmium, nickel, manganese and chromium are associated with automobile related pollution. They are often used as minor additives to gasoline and various auto-lubrication and are released during combustion and spillage (Lytle et al., 1995).

It is estimated that 8.5 million kg of nickel are emitted into the atmosphere from natural sources such as windblown dust and vegetation each year. Five times that quantity is estimated to come from anthropogenic sources (Nriagu & Pacyna, 1988) and the burning of residual and fuel oil is responsible for 62% of anthropogenic emissions. Chromium is released into the atmosphere mainly by anthropogenic stationary point sources including industrial, commercial and residential fuel combustion via the combustion of natural gas, oil, and coal. It has been estimated that emissions from the metal industry ranged from 35% to 86% of the total chromium and emissions from fuel combustion ranged from 11% to 65% of the total chromium. The main sources of manganese release to the air are industrial

emissions, combustion of fossil fuels and re-entrainment of manganese-containing soils (EPA, 1987). High concentration of cadmium is released by human activities such as mining smelting operations and fossil fuel combustion. Coal, wood and oil combustion can all contribute cadmium to the atmosphere. It has been suggested that coal and oil used in classical thermal power plants are responsible for 50% of the total cadmium emitted to the atmosphere (Thornton, 1992). Anthropogenic sources of lead also include the mining and smelting of ore, manufacture of lead-containing products, combustion of coal and oil most notably leaded gasoline that may still be used in some countries including Nigeria. It is important to note that land is the ultimate repository for lead, and lead released to air and water ultimately is deposited in soil or sediment. For example, lead released to the air from leaded gasoline or in stack gas from smelters and power plants will settle on soil, sediment, foliage or other surfaces (Gerbeding, 2005a).

Atmospheric lead emissions in Nigeria have been estimated to be 2800 metric tonnes per year with most (90%) derived from automobile tail pipe (Nriagu et al., 1997). Lead in the form of tetra-ethyl lead $\text{Pb}(\text{C}_2\text{H}_5)_4$ is the most common additive to petrol to raise its octane number. Upon combustion in the petrol engine, the organic lead is oxidized to lead oxide according to the following reaction:



The lead oxide (PbO) formed, reacts with the halogen carriers (the co-additives) to form particles of lead halides- PbCl_2 , PbBrCl , PbBr_2 - which escape into the air through the vehicle exhaust pipes. By this, about 80% of lead in petrol escapes through the exhaust pipe as particles while 15-30% of this amount is air borne. Human beings, animal and vegetation are the ultimate recipients of the particulate (Ademoroti, 1996).

The lead level in Nigeria's super grade petrol is in the range 210-520 mg/L (Ademoroti, 1986). Automobile exhausts are also believed to account for more than 80% of the air pollution in some urban centres in Nigeria. The highest level of lead occurs in super grade gasoline with a concentration range of 600 to 800 mg/L (with a mean of 70 $\mu\text{g}/\text{mL}$) and aviation gas with a concentration of 915 $\mu\text{g}/\text{mL}$ (Shy, 1990), which is much higher than permissible levels in some other countries. The comparable maximum levels in United States and Britain (UK) are 200 $\mu\text{g}/\text{mL}$ and 500 $\mu\text{g}/\text{mL}$, respectively (Osibanjo & Ajaiyi, 1989). Automobiles in Nigeria may still be using leaded gasoline. Many cars are poorly maintained and characteristically emit blue plumes of bad odour and unburnt hydrocarbons (Baumbach et al., 1995), implying that a higher percentage of the lead in gasoline is emitted to the atmosphere.

Gasoline sold in most African countries contains 0.5-0.8g/L lead. In urban and rural areas and near mining centers, average lead concentrations are up to 0.5-3.0 $\mu\text{g}/\text{m}^3$ in the atmosphere and >1000 $\mu\text{g}/\text{g}$ in dust and soils (Nriagu et al., 1996). In Nigeria, the level of lead in petrol is estimated at 0.7g/L. The national consumption of petrol in the country is estimated at 20 million litres per day with about 150 people per car. It is therefore predicted that at least 15 tonnes of lead is emitted into the environment through combustion of fossil fuel (Agbo, 1997). The annual motor gasoline consumption in 2000 was 56 litres per person. In 2005, Nigerian National Petroleum Corporation (NNPC) recorded domestic consumption of Premium Motor Spirit (Petrol) as 9,572,014,330 litres, while 2,361,480,530,000 litres of Automotive Gas Oil (Diesel) were equally recorded. Therefore, an average car in Nigeria

uses over 1800 liters of petrol per year. The number of cars in Nigeria is assumed to be 3.27 million and fuel consumption for an average Nigerian car is 9.0 km L^{-1} (Ajao & Anurigwo, 2002). In 2006, 9.13 billion Litres of gasoline were consumed in Nigeria. Presently, Nigeria's daily fuel consumption stands at 30 million litres per day (Energy ministry, 2008). As reported by Agbo, 1997, the level of lead in petrol used in Nigeria is estimated at 0.7g/L . This probably is still the case as the use of leaded petrol may still be obtainable in Nigeria even though several countries have banned its use (United Nations, 2006). It is therefore predicted that if it is so, at least $21,000\text{kg}$ of lead is emitted into the environment through combustion of petrol. Infact, Bayford & Co Ltd brought leaded petrol back to the UK market in 2000, primarily to service the needs of the classic car owners. As the only government approved supplier of leaded fuel in the UK, following the decision of the major oil companies to withdraw the product, Bayford remains committed to do all it can to make leaded fuel as widely available as possible and presently supplies over 36 petrol stations in the UK and still advertising for more supplies (Jonathan, 2008).

3.2 Indiscriminate disposal of waste

Anthropogenic sources of environmental pollution include those associated with industrial effluents, solid waste disposal and fertilizers (Nriagu, 1996). Heavy metals may enter soil and aquatic environments via sewage sludge application, mine waste, industrial waste disposal, atmospheric deposition and application of fertilizers and pesticides (Adaikpoh, et al., 2005). In Nigeria, recent reports indicate that the major contaminants found in drinking water especially from wells are heavy metals. These heavy metals find their way into the soil and groundwater through activities like intense agriculture, power generation, industrial discharges, seepage of municipal landfills, septic tank effluents, to mention a few. Infact, many authors have reported high levels of heavy metal ions in the soil, rivers and groundwater in different areas of Nigeria (Okuo et al., 2007). Indiscriminate disposal of toxic wastes therefore poses a great threat to human health.

4. Highlighted spectroscopic methods for heavy metals determination

4.1 Lead

Several analytical methods are available to analyze the level of lead in biological samples like blood. The most common methods employed are flame atomic absorption spectrometry (AAS). GFAAS and Anode stripping voltametry (ASV) are the methods of choice for the analysis of lead. In order to produce reliable results, background correction, such as Zeeman background correction that minimizes the impact of the absorbance of molecular species, must be applied. Limits of detection for lead using AAS are on the order of $\mu\text{g/mL}$ (ppm) for flame AAS measurements, while flameless AAS measurements can detect blood lead levels at about 1ng/mL (Flegel & Smith, 1995). Inductively coupled plasma mass spectrometry (ICP-MS) is also a very powerful tool for trace analysis of lead and other heavy metals. ICP/MS not only can detect very low concentrations of lead but can also identify and quantify the lead isotopes present. Other specialized methods for lead analysis are X-ray fluorescence spectroscopy (XRFS), neutron activation analysis (NAA), differential pulse anode stripping voltametry, and isotope dilution mass spectrometry (IDMS). The most reliable method for the determination of lead at low concentrations is IDMS but due to the technical expertise required and high cost of the equipment, this method is not commonly used (Gerbeding, 2005a).

The primary methods of analyzing for lead in environmental samples are AAS, GFAAS, ASV, ICP/AES and XRFS. Less commonly employed techniques include ICP/MS, gas chromatography/photoionization detector (GC/PID), isotope dilution mass spectrometry (IDMS), electron probe X-ray microanalysis (EPXMA) and laser microprobe mass analysis (LAMMA). Chromatography (GC, HPLC) in conjunction with ICP/MS can also permit the separation and quantification of organometallic and inorganic forms of lead. Various methods have been used to analyze for particulate lead in air. The primary methods, AAS, GFAAS, and ICP/AES are sensitive to levels in the low $\mu\text{g}/\text{m}^3$ range (0.1–20 $\mu\text{g}/\text{m}^3$). Chelation/extraction can also be used to recover lead from aqueous matrices. GC/AAS has been used to determine organic lead, present as various alkyl lead species, in water. XRFS has been shown to permit speciation of inorganic and organic forms of lead in soil for source elucidation (Gerbeding, 2005a).

4.2 Cadmium

The most common analytical procedures for measuring cadmium concentrations in biological samples use the methods of atomic absorption spectroscopy (AAS) and atomic emission spectroscopy (AES). Methods of AAS commonly used for cadmium measurement are flame atomic absorption spectroscopy (FAAS) and graphite furnace (or electrothermal) atomic absorption spectroscopy (GFAAS or ETAAS). A method for the direct determination of cadmium in solid biological matrices by slurry sampling ETAAS has been described (Taylor et al., 2000).

Analysis for cadmium in environmental samples is usually accomplished by AAS or AES techniques, with samples prepared by digestion with nitric acid. Since cadmium in air is usually associated with particulate matter, standard methods involve collection of air samples on glass fiber or membrane filters, acid extraction of the filters, and analysis by AAS. Electrothermal inductively coupled plasma mass spectrometry (ETV-ICP-MS) has also been used to analyze size classified atmospheric particles for cadmium. The accuracy of the analysis of cadmium in acid digested atmospheric samples, measured by ACSV, was evaluated and compared with graphite furnace atomic absorption spectrometry (GFAAS) and inductively coupled plasma mass spectrometry (ICP-MS) (Koplan, 1999). Sediment and soil samples have been analyzed for cadmium using the methods of laser-excited atomic fluorescence spectroscopy in a graphite furnace (LEAFS), GFAAS and ETAAS preparation of the samples is generally accomplished by treatment with HCl and HNO₃.

Electrothermal vaporization isotope dilution inductively coupled plasma mass spectrometry (ETV-ID-ICP-MS) has been utilized for the analysis of cadmium in fish samples. Radiochemical neutron activation analysis (RNAA), differential pulse anodic stripping voltametry (ASV) and the calorimetric dithizone method may also be employed. The AAS techniques appear to be most sensitive, with cadmium recoveries ranging from 94 to 109% (Koplan, 1999).

4.3 Nickel

Analytical methods used in the determination of nickel in biological materials are the same as those used for environmental samples. Nickel is normally present at very low levels in biological samples. Atomic absorption spectrometry (AAS) and inductively coupled plasma-

atomic emission spectroscopy (ICP-AES), with or without preconcentration or separation steps, are the most common methods. These methods have been adopted in standard procedures by EPA and the International Union of Pure and Applied Chemistry. Direct aspiration into a flame and atomization in an electrically heated graphite furnace or carbon rod are the two variants of atomic absorption. The latter is sometimes referred to as electrothermal AAS (ETAAS). Typical detection limits for ETAAS are $<0.4 \mu\text{g/L}$, while the limit for flame AAS and ICP-AES is $3.0 \mu\text{g/L}$ (Todorovska et al., 2002). Good precision was obtained with flame AAS after preconcentration and separation, electrothermal AAS, and ICP-AES. Inductively coupled plasma mass spectrometry (ICP-MS) techniques have been used to quantify nickel in urine with detection sensitivities down to approximately $1 \mu\text{g/L}$. Voltammetric techniques are becoming increasingly important for nickel determinations since such techniques have extraordinary sensitivity as well as good precision and accuracy. Direct measurement of nickel in urine in the presence of other trace metals (e.g., cadmium, cobalt, and lead) was demonstrated using adsorption differential pulse cathodic stripping voltammetry at a detection limit of $0.027 \mu\text{g/L}$ (Gerbeding, 2005b).

The most common methods used to detect nickel in environmental samples are AAS, either flame or graphite furnace, ICP-AES, or ICP-MS. Nickel can also be analyzed in ambient and marine water using stabilized temperature graphite furnace atomic absorption (STGFAA) detection techniques as described in EPA methods 1639 and 200.12 respectively, which give limits of detection for nickel concentrations ranging between 0.65 and $1.8 \mu\text{g/L}$ and recoveries of $>92\%$. Two other EPA standard test methods, 200.10 and 200.13, also use preconcentration techniques in conjunction with ICP-MS or graphite furnace AAS detection techniques, respectively, for analysis of nickel in marine water. One method uses activated charcoal to preconcentrate nickel in natural waters, followed by elution with 20% nitric acid and analysis by inductively coupled plasma-optical emission spectrometry (ICP-OES). This method achieved a detection limit of 82 ng/L (Gerbeding, 2005b).

4.4 Manganese

Flame atomic absorption analysis is the most straightforward and widely used method for determining manganese. In this method, a solution containing manganese is introduced into a flame, and the concentration of manganese is determined from the intensity of the colour at 279.5 nm . Furnace atomic absorption analysis is often used for very low analyte levels and inductively coupled plasma atomic emission analysis is frequently employed for multianalyte analyses that include manganese. Simple methods for the direct determination of Mn in whole blood by ETAAS have been described. Methods for measuring manganese therefore include spectrophotometry, mass spectrometry, neutron activation analysis and X-ray fluorimetry (Koplan, 2000a).

Atomic absorption spectrometry has been the most widely used analytical technique to determine manganese levels in a broad range of foods, as well as other environmental and biological samples. Tinggi et al., (1997) carried out a wet digestion technique using a 12:2 (v/v) nitric:sulfuric acid mixture for their determination, and for food samples with low levels of manganese, they found that the more sensitive graphite furnace atomic absorption analysis was required. Because manganese is often found at very low levels in many foods, its measurement requires methods with similarly low detection limits; these researchers

identified detection limits of 0.15 mg/kg (ppm) and 1.10 µg/kg (ppb) for flame and graphite furnace atomic absorption spectrometry respectively (Tinggi et al. 1997).

A number of analytical methods for quantifying MMT in gasoline have been described including simple determination of total elemental manganese by atomic absorption and gas chromatography followed by flame-ionization detection (FID). In a certain method, in which MMT is detected in gasoline by gas chromatography coupled with flame photometric detection (FPD); the chemiluminescence of manganese is measured to determine MMT levels in a method that uses simple, inexpensive, and commercially available instrumentation (Koplan, 2000a).

4.5 Chromium

Prior to 1978, numerous erroneous results were reported for the chromium level in urine using electrothermal atomic absorption spectrometry (ETAAS) because of the inability of conventional atomic absorption spectrometry systems to correct for the high nonspecific background absorption. The use of GC-MS and ETAAS to determine ^{53}Cr and total Cr in biological fluids in order to investigate the distribution of Cr in lactating women following oral administration of a stable ^{53}Cr tracer have been reported. The authors detected ^{53}Cr in blood within 2 h of administration. They noted, however, that blood Cr changes in response to oral administration were variable and they considered that blood Cr was not tightly regulated. Similarly, the reported serum and plasma chromium concentrations of normal subjects have varied more than 5,000-fold since the early 1950s (Taylor et al., 2000).

The four most frequently used methods for determining low levels of chromium in biological samples are neutron activation analysis (NAA), mass spectrometry (MS), graphite spark atomic emission spectrometry (AES), and graphite furnace atomic absorption spectrometry (GFAAS). Of these four methods, only the GFAAS is readily available in conventional laboratories, and this method is capable of determining chromium levels in biological samples when an appropriate background correction method is used. The three commonly used methods that have the best sensitivity for chromium detection in air are GFAAS, instrumental neutron activation analysis (INAA), and graphite spark atomic emission spectrometry. Measurements of low levels of chromium concentrations in water have been made by specialized methods, such as inductively coupled plasma mass spectrometry (ICP-MS), capillary column gas chromatography of chelated chromium with electron capture detection (ECD), and electrothermal vaporization inductively coupled plasma mass spectrometry (Koplan, 2000b).

4.6 Biofuels

There are different spectrophotometric techniques for analysis of contaminants in biofuels. Simultaneous detection of the absorption spectrum and refractive index ratio with a spectrophotometer for monitoring contaminants in bioethanol has been carried out by Kontturi et al., 2011. Inductively Coupled Plasma Atomic Emission Spectrometry and optical emission spectral analysis with inductively coupled plasma (ICP-OES) have also been used to analyze biodiesel samples for trace metals (ASTM, 2007; ECS, 2006). An ICP-MS instrument fitted with an octopole reaction system (ORS) was used to directly measure the inorganic contents of several biofuel materials. Following sample preparation by simple

dilution in kerosene, the biofuels were analysed directly. The ORS effectively removed matrix- and plasma-based spectral interferences to enable measurement of all important analytes, including sulfur, at levels below those possible by ICP-OES. A range of commonly produced biofuels was analysed, and spike recovery and long-term stability data was acquired. Also, suitably configured ICP-MS has been shown to be a fast and very sensitive technique for the elemental analysis of biofuels (Woods & Fryer, 2007).

A flow system designed with solenoid micro-pumps is proposed for fast and greener spectrophotometric determination of free glycerol in biodiesel. Glycerol was extracted from samples without using organic solvents. The determination involves glycerol oxidation by periodate, yielding formaldehyde followed by formation of the colored (3,5-diacetyl-1,4-dihydrolutidine) product upon reaction with acetylacetone. The coefficient of variation, sampling rate and detection limit were estimated as 1.5% (20.0 mg L⁻¹ glycerol, $n = 10$), 34 h⁻¹, and 1.0 mg L⁻¹ (99.7% confidence level), respectively. A linear response was observed from 5 to 50 mg L⁻¹, with reagent consumption estimated as 345 µg of KIO₄ and 15 mg of acetylacetone per determination. The procedure was successfully applied to the analysis of biodiesel samples and the results agreed with the batch reference method at the 95% confidence level (Sidnei & Fábio, 2010).

5. Review of heavy metals in the environment using atomic absorption spectrophotometry

The negative effect on air quality will be unavoidable, if solid wastes are incinerated under uncontrolled conditions or left to biologically decompose in open areas, because waste gas will be given off to the atmosphere. Besides, heavy metals and hazardous organic pathogens are disseminated with organic wastes. Effluents from point sources change the characteristics of the receiving environment and its suitability for maintaining its living communities and their ecological structure. Some metals when discharged into natural waters at increased concentration in sewage, industrial effluent or from mining and refining operations can have severe toxicological effects on aquatic environment and humans. Nigeria has a population of over 120 million. Degradation of water quality is most severe in the four states that contain 80 percent of the nations industries; Lagos, Rivers, Kano and Kaduna States, with the highest level of emission of 8000 tones of hazardous waste per year from Lagos State (Alamu, 2005).

5.1 Heavy metals in soils

In a study of soil samples of refuse dumps in Awka (Anambra State, Nigeria) the lead level (2467mg/kg) exceeded the limits set by the US Environmental Protection Agency. This study suggests that the refuse dumps in Awka may increase the level of environmental heavy metals in Nigeria (Nduka et al., 2006). Concentrations of cadmium, chromium, manganese, nickel and lead were determined in surface sediments of the Lagos Lagoon, Nigeria. The results revealed largely anthropogenic heavy metal enrichment and implicated urban and industrial waste and runoff water transporting metals from land - derived wastes as the sources of the enrichment. Okoye (1991) also reported that urban and industrial wastes discharged into the Lagos lagoon have had a significant impact on the ecosystem following the relative enrichment in the Lagoon fish with lead.

Several attempts have been made to assess the impact of the use of fossil fuels on the environment. Results obtained from the study on heavy metals (chromium, lead, cadmium, and nickel) concentrations and oil pollution in Warri area revealed that the concentrations of the heavy metals considered were higher in the oil-spilled sites relative to the control sites. Similarly, when compared with the European Community standards, the concentration is said to be quite significant. The results indicate the contribution of the oil industry to heavy metals contamination in the Niger-Delta area of Nigeria and that the operations of the oil industry in this study area have not been sufficiently accompanied by adequate environmental protection. To safeguard agricultural land in the area and hence human health, there is an urgent need for government to address the incidence of oil spills in this area (Essoka et al., 2006).

Concentrations of lead, cadmium, nickel, chromium and manganese were determined to assess the impact of automobiles on heavy metal contamination of roadside soil. The lead levels in polluted sites varied from 70 to $280.5\mu\text{g g}^{-1}$ and it rapidly decreased with depth. Similarly, mean concentrations of cadmium, nickel, chromium, and manganese were significantly higher at polluted sites and followed a decreasing trend with increase in depth. Correlation coefficients between heavy metals and traffic density were positively significant except for nickel. Profile samples showed that lead, cadmium, manganese were largely concentrated in the top 5cm confirming airborne contamination (Ramakrishnaiah & Somashekar, 2002).

In a study of the effect of traffic density on heavy metal content of soil and vegetation along roadsides in Osun State Nigeria, the concentration of the heavy metals decreased with increasing soil depth and horizontal distance from the road. Metal contamination correlated positively with traffic volume. Concentrations of lead, cadmium and nickel along the low traffic density were lower than the high traffic density (Amusan et al., 2003). Reclamation of auto repair workshop areas for residential and agricultural purposes makes high the risk assessment of heavy metal contamination (Ayodele et al., 2007). The levels of lead, cadmium and nickel were determined in the roadside topsoil in Osogbo, Nigeria, with the view to determining the effect of traffic density and vehicular contribution to the soil heavy metal burden. The levels of the metals at the high density roads were significantly higher than the corresponding levels at the medium and low traffic density roads. The average levels of lead, cadmium, and nickel in all road locations at a distance of 5m from the roads were 68.74 ± 34.82 , 0.60 ± 0.31 and $8.38\pm 2.40\text{mg/kg}$ respectively. Lead and cadmium were of average levels of 92.07 ± 21.25 and $0.76\pm 0.35\text{ mg/kg}$ respectively at a distance of 5m from the road at high traffic density roads, while the levels of nickel averaged $9.65\pm 2.61\text{mg/kg}$ respectively. There was a rapid decrease in the level of the metals with distance, with the metal levels at a distance of 50m from the road almost reaching the natural background levels of the metals at the control sites (Fakayode & Olu-Owolabi, 2003a). The levels of the metals were also determined at the four major motor parks and at the seven mechanic workshop settlements. The levels of the metals at the motor parks and mechanic workshops were far above the levels at the control sites. The levels of lead, cadmium and nickel at the motor parks were 519 ± 73.0 , 3.6 ± 0.8 , and $7.3\pm 4.6\text{ mg/kg}$ respectively, with the levels of lead, cadmium and nickel at the mechanic workshops averaging 729.57 ± 110.93 , 4.59 ± 1.01 and $30.21\pm 9.40\text{mg/kg}$ respectively (Fakayode & Olu-Owolabi, 2003a).

5.2 Heavy metals in food

Heavy metals have been analyzed and found to be in considerable quantities in Food in Nigeria. In the assessment of heavy metal levels in fish species of Lagos Lagoon, lead levels in the fishes were beyond W.H.O. acceptable limit of 1 ppm with a concentration range of 10.81-152.42 ppm (Akan and Abiola, 2008). Also, 86% and 84% of the 50 beverages (canned and non-canned respectively) obtained in Nigeria failed to meet the US EPA criteria for acceptable lead and cadmium levels in consumer products. 79.3% of the non-canned beverages showed lead levels that exceeded the US EPA's maximum contaminant level (MCL) of 0.015 mg/dm³, 100% of the canned beverages had lead levels that were greater than the MCL. The range of the lead in the canned beverages was 0.002–0.0073 and 0.001–0.092 mg/dm³ for the non-canned beverages. The cadmium levels ranged from 0.003–0.081 mg/dm³ for the canned and 0.006–0.071 mg/dm³ for non-canned beverages. About 85.71% of the canned beverages had cadmium levels that exceeded the maximum contaminant level (MCL) of 0.005 mg/dm³ set by US EPA while 82.7% non-canned beverages had cadmium levels exceeding the MCL (Maduabuchi et al., 2006). In addition, Fakayode and Olu-Owolabi (2003b), reported that concentrations of lead and cadmium 0.59 mg/kg and 0.07 mg/kg respectively in chicken eggs in Ibadan were comparatively greater than levels found in other countries e.g lead concentrations of 0.048 ppm and 0.489 ppm obtained in China and India respectively and cadmium concentrations of 0.01 ppm and 0.004 ppm obtained in Canada and finland respectively.

Some reported works have also shown that planted crops and vegetations along major roads where there was high traffic volume contained high levels of lead content due to automobile exhaust. For instance, cadmium levels (0.12 ± 0.03 – 0.28 ± 0.03 ppm) and nickel levels (3.02 ± 0.14 – 6.50 ± 0.25 ppm) of staple foods (yam, cassava, cocoyam and maize) from oil-producing areas of Rivers and Bayelsa States of Nigeria were higher than those of non-oil producing areas (Abakaliki). Because of this high trace metal level, the staple foods from oil-producing areas examined are likely to be the major source of exogenous contamination of these metals in the populace (Akaninwor et al., 2005).

The concentration of cadmium has been found to be higher in some Nigerian foods as compared to those of some other countries as shown in Table 1.

5.3 Heavy metals in water

Groundwater and soil samples from 16 locations near petrol stations (PS) and mechanic workshops (MW) around Calabar, Nigeria, were analyzed for heavy metals and hydrocarbons to determine their concentrations and assess the impact of the PS and MW on groundwater in the area. Results show that mean concentrations of cadmium, chromium, manganese, nickel, and lead in groundwater are higher than the maximum admissible concentration (Nganje et al., 2007).

Results from the evaluation of ground water quality characteristics near two waste sites in Ibadan and Lagos revealed that some of the ground-water quality constituents determined exceeded the World Health Organization (WHO) standards for drinking water irrespective of source of pollution. Some of the ground-water samples were poor in quality in terms of cadmium, chromium, lead and nickel recorded (Ikem et al., 2002). The levels of heavy metals (cadmium, chromium, nickel, and lead) were analysed in the River Ijana (Ekpa-

Warri, Nigeria). Generally, excessive levels of the parameters of pollution above W.H.O. standards recommended for surface waters were observed (Emoyan et al., 2005). The possible sources of these parameters of pollution are diverse: originating from anthropogenic/ natural and point sources. Coal contains diverse amounts of trace elements in their overall composition. Certain trace elements such as lead, cadmium and chromium if present in high amount could preclude the coal from being used in environmentally sensitive situations. Ekulu River is the largest body of inland waters in Enugu Urban, which is of considerable importance industrially, culturally, and in agriculture. Ekulu coal mine is located by the bank of the Ekulu river. The coal mine station discharges its effluents directly into River Ekulu. Enugu coal mine occurs in the area where River Ekulu takes its source. Metal concentrations were generally higher in the coal samples than in the sediments. The metals (manganese, chromium, cadmium, nickel, and lead) analysed for were present throughout the period monitored in both the sediment and coal samples with some variations. Mean concentrations of Mn (0.256-0.389mg/kg) and Cr (0.214-0.267mg/kg) were high relative to concentrations of Cd (0.036-0.043mg/kg), Ni (0.064-0.067mg/kg) and Pb (0.013-0.017mg/kg). The presence of toxic metals in the area is established, calling for the assessment of their impact on the health of human and aquatic lives around the area (Adaikpoh et al., 2005). Other industrial effluents also contribute to the level of the heavy metals such as lead in the environment as reported by (Ayodele et al., 1996).

Commodity	Greece	Japan and China	Nigeria	European Countries
Rice	0.006	0.070	0.060	0.010
Cereal – other	0.002	0.023	0.075	0.016
Roots and tubers	0.022	0.015	0.103	0.025
Soya bean	–	0.041	0.200	0.021
Pulses – other	0.004	0.019	0.140	0.019
Sugars and honey	–	0.003	0.015	0.004
Groundnuts – shelled	–	–	0.370	0.050
Oilseeds – other	–	0.021	0.100	0.119
Vegetable oils – other	0.002	0.001	0.127	0.002
Stimulants – other	–	0.017	0.160	0.006
Spices	–	0.005	0.191	0.055
Leafy vegetables	0.054	0.025	0.155	0.034
Vegetables – other	0.024	0.020	0.343	0.013
Fish and other seafood – other	0.034	0.035	0.207	0.014
Eggs	0.001	0.003	0.500	0.003
Fruits	0.009	0.006	0.067	0.004
Milks	0.001	0.004	0.006	0.001
Milk products	0.004	0.004	0.375	0.005
Poultry meat	0.013	0.005	0.110	0.002
Meats – other	0.027	0.006	0.083	0.006

Source: Moriyama et al., (2002)

Table 1. Average concentrations of cadmium in foods (mg/kg)

Several works have been done to access the impact of improper waste management on the environment. The elevated level of heavy metal in the Niger Delta aquatic environment as a result of industrial discharges from refining operations has been elaborated by Spiff & Horsfall, (2004). Therefore it can be said that there is unregulated discharge of untreated effluents into natural receptors by industries in Nigeria. Samples of industrial effluents from Sharada industrial area Kano Nigeria were assessed for heavy metals. The study showed that about 60% of the industries discharge effluents with heavy metal concentration higher than 0.30 mg/L. Lead and chromium ions were the most prevalent with values above the minimum tolerable limit. The presence of these metal ions could pose a serious public health hazard. It is therefore recommended that these effluents be adequately treated before discharge. Table 2 shows the nickel content in naturally occurring waters.

WATER TYPE	LOCATION	CONCENTRATION RANGE (µg/L)
River water	Poland	2-75
	Germany-Rhine	8.9-24
	USA	0-71
Lake water	Poland-Lakes of Wielkopolska National Park *	2-11
	Poland-Lakes of the Golanieckie stream	1-8
Underground water	Poland-Poznzn	0.5-20
	Poland-Pozan voivodship	1-30
	Poland-Szczecin	1-15
Drinking water	USA	0.5-7
	Poland-Pozcan	0-5

Source: Barańkiewicz and Siepak (1999)

Table 2. Content of nickel in naturally occurring waters

6. Reports of research works done on heavy metals analysis in Nigerian environment

6.1 Blood

6.1.1 Methodology

3 ml of blood were collected directly from the select population comprised of 60 children, 114 women (pregnant, nursing mothers, others) and 66 men. This was carried out by venous puncture by a qualified nurse under contamination controlled conditions using pyrogen-free sterile disposable syringes and placed into 5 ml capacity EDTA plastic bottles containing K₃EDTA as anticoagulant. Each sample (3 ml) was transferred into 100 ml conical flasks. The EDTA bottle was rinsed with a little nitric acid and transferred into 100ml conical flask. Perchloric acid and nitric acid which were of analytical grade was added in the ratio 1:3 as follows: 2 ml perchloric acid and 6 ml nitric acid. The conical flask was covered with an evaporating dish and the mixture digested at low temperature using a thermostated Bitinett hot plate until a clear solution was obtained. The digest was made up to 20 ml with deionized water in a 20 ml standard flask (Rahman et al., 2006). The sample solutions were then analyzed for lead, cadmium, nickel, manganese and chromium using a GBC atomic absorption spectrophotometer, model A6600 AVANTA PM.

6.1.2 Results

As shown in Table 3, lead was detected in 235 of the 240 samples (97.92 %), the concentration range was from 0.039-0.881 ppm. Cadmium was detected in 205(85.42 %) samples, the concentration range was from 0.007-0.293 ppm. Nickel was detected in 137(57.08 %) samples while in 103(42.92 %) of the samples, the concentration range was from 0.007-0.849 ppm. Manganese was detected in 203(84.58 %) samples, the concentration range was from 0.006-0.861 ppm. Chromium was detected in 113(47.08 %) samples, the concentration range was from 0.006-0.829 ppm. Comparing the concentrations obtained from this study with the WHO (1996) guideline for heavy metals in blood, all the detectable samples had concentrations higher than the permissible levels stipulated for all the heavy metals except for 5 that were within the range stipulated for manganese i.e 0.008–0.012 ppm and 24 that were within the stipulated range for lead i.e 0.05-0.15 ppm. Thus there is a clear indication of high concentrations of the heavy metals in the general population in Nigeria especially the Southeast (Ibeto & Okoye, 2009; 2010a; 2010b).

Group		Heavy metal				
		Lead	Cadmium	Nickel	Manganese	Chromium
Men	N	66	65	40	63	26
	Mean ± sd	0.394 ± 0.126	0.093 ± 0.048	0.122 ± 0.079	0.119 ± 0.075	0.305 ± 0.228
	Range	0.07 - 0.76	0.01 - 0.21	0.01 - 0.33	0.01- 0.40	0.01- 0.83
Pregnant women/ Nursing mothers	N	56	48	31	52	35
	Mean ± sd	0.288 ± 0.198	0.099 ± 0.064	0.096 ± 0.061	0.088 ± 0.040	0.201 ± 0.150
	Range	0.04 - 0.72	0.01 - 0.28	0.01 0.21	0.01 - 0.21	0.01 - 0.57
Other women	N	54	50	20	53	28
	Mean ± sd	0.328 ± 0.121	0.080 ± 0.046	0.096 ± 0.067	0.121 ± 0.059	0.214 ± 0.167
	Range	0.12 - 0.67	0.01 - 0.29	0.01 - 0.25	0.02 - 0.31	0.01 - 0.67
Children	N	59	42	46	35	24
	Mean ± sd	0.488 ± 0.153	0.088 ± 0.056	0.411 ± 0.240	0.091 ± 0.147	0.267 ± 0.228
	Range	0.12 - 0.88	0.01 - 0.23	0.01 - 0.85	0.01 - 0.86	0.01 - 0.68
WHO guideline		0.05-0.15	0.0003-0.0012	0.001-0.005	0.008-0.012	<0.005

Source: Ibeto & Okoye, 2009; 2010a; 2010b

Table 3. Concentrations (ppm) of heavy metals in blood of different categories of the urban population in Enugu State Nigeria

However certain measures can be taken to reduce the effects of these heavy metals in the body. All of the currently available methods to obviate the toxic effects of the heavy metals

are mainly by chelation. The chelating agents bind to the heavy metals, enhance its excretion by facilitating their transfer from soft tissues to where it can be excreted. Some of the standard chelating agents currently in use are meso-2,3- dimercaptosuccinic acid for cadmium, triethylenetetramine and cyclam (1,4,8,11-tetraazacyclotetradecane) for nickel, and ethylenediamine tetraacetic acid for lead, manganese and chromium. Also, through specific dietary supplementation, for example, sufficient iron or calcium stores, as opposed to a deficiency in these or other minerals, may reduce the heavy metals absorption, and thus reduce potential toxicity (Koplan, 2000a).

6.2 Fruit juices

6.2.1 Methodology

100ml of each of ten different brands of fruit juice was measured into a 200ml conical flask and heated till the volume reduced to 10ml. Perchloric acid and nitric acid was then added in a ratio of 1:2 with perchloric acid being 6ml and the nitric acid 12ml. The solution was then digested at low heat until a clear solution was obtained. It was then allowed to cool and made up to 25ml with distilled water using a standard flask. Heavy metals were then determined by atomic absorption spectrophotometry using Alpha 4 Serial no 4200 with air acetylene flame.

6.2.2 Results

As shown in Table 4, all the samples except one of guava brands contained lower concentration of copper than the 5ppm permissible limit set for the metal. All samples had concentrations of zinc well below the 5ppm maximum permissible level. The iron concentrations were below the limit of 15ppm in all the samples except for the pineapple brand, which showed a concentration of 50ppm. This could be due to many reasons such as the fact that the fruit juice brand was acidic and the fruit acids could pick up the metal from the equipment during processing or storage. As minerals are soil and species dependent, the fruit acids might also have picked up iron and other metals from the soil during growth. Iron could also be added for fortification.

Cadmium was more wide spread, occurring in seven brands with a range of 0.16 to 0.38ppm. Lead occurred in four brands with range 0.11 to 0.33 ppm. Only the foreign made apple juice brand with the lead content of 0.33ppm exceeded the maximum permissible level of 0.3ppm by FAO/W.H.O. The limit for cadmium was not stipulated but compared with the limit set for lead (since they are both non-nutritive elements), the foreign made guava brand and the pineapple brand may be considered to be high in cadmium (Okoye & Ibeto, 2009).

6.3 Soil

6.3.1 Methodology

Soil samples were collected from twenty different locations in three Local Government Areas in Enugu State. Soil samples were collected in duplicates at a dept of 15-20cm and transferred into a pre-washed polyethylene nylon bag to avoid contamination. Soil samples were dried at 105°C and sieved with 100mesh (152µm BS Screen 410). The samples were

prepared for analysis by cold extraction. 1g of the dried soil sample was weighed into a labeled 100ml conical flask and 20ml of mixture of conc. HCl and conc. HNO₃ (1:1) were added and well shaken. The solution was kept overnight after which it was filtered through a whatman No 1 filter paper formerly leached by pouring cupious quantity of dilute HNO₃ on the filter paper while in the funnel. The clear solution obtained was made up to 50ml using a standard flask and transferred into a plastic bottle (Okoye, 2001). The sample solutions were analysed at various wavelengths for each metal using Buck Scientific Atomic Absorption Spectrophotometer 205.

SAMPLES	MEAN CONCENTRATIONS (mg/l) OF PARAMETERS				
	Cr	Mn	Ni	Cd	Pb
Lime	0.06	0.11	0.08	<0.002	<0.004
Mango	<0.002	0.67	<0.05	0.17	<0.004
Orange	<0.002	0.19	0.13	<0.002	0.11
Guava	<0.002	0.42	0.13	0.27	<0.004
Guava*	<0.002	0.67	0.03	0.37	<0.004
Black Currant	0.03	0.24	<0.05	0.16	0.13
Mixed fruit	<0.002	0.42	<0.05	<0.002	<0.004
Apple	<0.002	0.19	<0.05	0.26	0.33
Apple	<0.002	0.14	0.03	0.25	<0.004
Pine-apple	0.09	6.96	0.15	0.38	0.20

Source: Okoye & Ibeto, 2009

Table 4. Concentrations (ppm) of metals in fruit juice samples

6.3.2 Results

The ranges of concentrations were: Pb(30.3-235), Cr(9.0-15.5) and Cd(5.5-42.25) ppm in Igbo-Eze North. Pb (0.2-100), Cr(9.5-10.8) and Cd(0.51-44.8) ppm in Nsukka and Pb(14.8-165) and Cd(0.43-5.0) ppm in Udi. The order of abundance in the soil follow the order Pb>Cd> Cr. Compared with the work done in an automobile spare parts market the values for chromium and cadmium were relatively high. Compared with the Indian standard for heavy metals in soils, some of the samples exceeded the stipulated range of 3-6ppm for cadmium, indicating considerable cadmium contamination of some of the sampling points. However, the variations in the mean concentration of each metal in the three Local Government Areas were not significant (P>0.05) (Okoye & Ibeto, 2008).

6.4 Water

6.4.1 Methodology

Samples were collected from 17 different locations in Southeast Nigeria at various occasions covering the dry and wet seasons. In collecting samples from rivers, lakes and streams, the polyethylene sampling containers were dipped just below the surface to minimize the

contamination of the water sample by surface films. For borehole samples, the mouth of the tap was cleaned with cotton wool and was left to run to waste for several minutes before collection while for spring water, samples were collected at different outlets of the spring. All the samples were collected with 2 L polyethylene cans which were leached with a 1:1 HCl and water and rinsed with distilled-de-ionized water (Okoye et al., 2010).

The samples were concentrated by evaporating 500 mL of water sample to about 100 mL followed by addition of 1 mL conc HCl and digesting until volume was about 15-20 mL. This was later made up to mark with distilled-de-ionized water in a 25 mL standard flask and later transferred into an acid-leached polyethylene bottle prior to analysis. Trace metals were determined with AAS (ALPHA Series 4200 CHEM TECH ANALYTICAL Ltd, UK) equipped with air-acetylene flame.

6.4.2 Results

The metal analysis gave values (mg/L) with ranges as follows: Pb (nd-13.5); Cd (nd-0.60); Ni (nd-0.075) and Cr (nd-0.10). Less than 40% had high levels of lead and cadmium which are indicative of the impact of indiscriminate discharge of untreated industrial effluents, domestic waste and inputs from other human activities on the pollution of the environment by trace metals. Concentrations of lead and cadmium in five locations were higher than the WHO limits of 0.01 mg/L and 0.003 mg/L respectively. Water containing high levels of lead and cadmium is not fit for drinking purposes. This study has created awareness concerning the risk of drinking from the identified water sources which have high concentrations of lead and cadmium (Okoye et al., 2010).

6.5 Chicken

6.5.1 Methodology

The samples of the liver, gizzards, muscles of chickens and also their feed were prepared by wet digestion. 10ml of nitric acid and 5ml of perchloric acid were added to 1g of each finely ground sample into different 100ml conical flasks covered with watch glasses for overnight predigestion. It was then heated on a hot plate until a clear solution was obtained. The contents were cooled and transferred to a 25ml standard flask and made up to mark with deionised water. These were then transferred to sample bottles until clear solutions were obtained. Each digested sample was transferred to prewashed sample bottles (Ibeto & Okoye, 2010a).

The sample solutions were then analyzed for the heavy metals: lead, cadmium, copper and zinc at required wavelength using a GBC atomic absorption spectrophotometer, model no A6600 AVANTA PM.

6.5.2 Results

The concentrations in ug/g of the heavy metals were in the range of 1.78 - 15.32, 9.7 - 147.07, 15.82 - 47.79 and 0.03 - 2.29 for cadmium, lead, copper and zinc respectively. Concentrations of cadmium were higher than the permissible limit of 0.5 ppm set by FAO/WHO and concentrations of lead were above the permissible limit of 1 ppm set by Australia New Zealand Food Authority. The high concentrations of the toxic metals obtained show a

certain level of pollution of the environment. However, the low concentration of the essential metals in the feed shows there was no addition of nutritive supplements to the feed (Okoye et al., 2011).

7. Conclusion

Atomic absorption spectrophotometry was used to determine the heavy metal content of various samples from the environment and also human blood. The heavy metal content of the environmental samples indicated a certain level of heavy metal pollution in the Nigerian environment which can be attributed to fossil fuels combustion and indiscriminate disposal of wastes. This is also reflected in the level of heavy metals in the blood of the select population which on accumulation in the human system has led to low level of life expectancy globally. It is therefore recommended that utilization of alternative fuels be aggressively pursued and integrated into the energy mix of countries globally. These fuels include biogas, biodiesel and bioethanol and are becoming increasingly important not only because of the diminishing petroleum reserves but also because of the environmental consequences of exhaust gases from petroleum fuelled engines.

8. References

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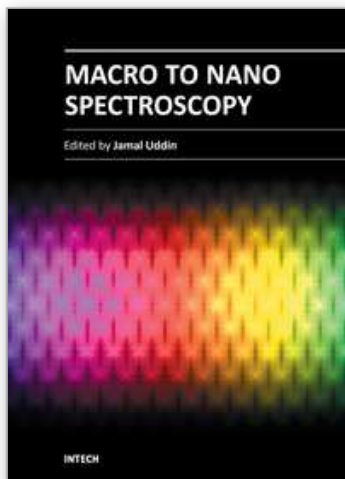
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