CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND

The pollution of water bodies has continued to be a contemporary issue with investigation of the source, nature and level of these pollutants continuously engaging researchers globally. Water pollution mostly facilitated by increasing population and industrialization of the water bodies' catchments sometimes induce debilitating environmental and health implications that may result in socio-economical impacts on the affected community (Withers and Jarvie, 2008). Pollutant input into surface waters could be through natural or anthropogenic sources via point and non-point (diffuse) discharges. While natural pollution sources such as weathering of soil parent materials, atmospheric depositions among others, are mostly low except in cases of natural disasters, anthropogenic pollution have steadily increased over the years due to a sustained level of industrialization and unsustainable exploitation of mineral resources and industrial and agricultural practises. Uneven distribution of population around few locations has also contributed to the upscale in anthropogenic sources of pollution. Coastal settlements, which have been estimated to host nearly half the world's population (Paerl et al., 2006), with large swath of coastal waters such as Lagos, Nigeria constantly receive pollutants from numerous sources including industrial, domestic and agricultural discharges, atmospheric depositions, and urban runoff (Gelinas and Schmit, 1998; Li-ging et al., 2007). While point source discharges could be effectively managed and controlled, diffuse inputs such as atmospheric depositions and runoffs which are characterised by numerous entry points are usually difficult to control.

1.2 URBAN RUNOFF AND ROADSIDE SOILS

Runoff (also called stormwater) could be described as a water movement which flows over exposed surfaces when the soil is infiltrated to full capacity. Runoff is a major component of the water cycle and is occasioned by precipitation such as rainfall, snow melt or other sources which results into excess water beyond the absorbing capacity of the soil. In the urban areas, runoff is a permanent feature due to the mostly impervious nature of the surfaces and serves as an important surface water pollution mechanism through which pollutants are introduced into water systems. Highway runoff picks up chemical, physical and biological pollutants (e.g. plant debris, automotive fluids, used oil, paint, fertilizers and pesticides) from the impervious surfaces like streets, bridges, highway, parking lots, and driveways and carries them to the recipient surface water. Urban runoffs including highway runoff have been recognised as a major source of pollution to receiving waters (Driscoll *et al.*, 1990; Davies *et al.*, 2001; Wei *et al.*, 2010). During intervening dry period between precipitations, pollutants are deposited on roadside soils which serve as a temporary sink for these pollutants before they are mobilized by runoff into the recipient water body. The urban roadside soils tend to be highly disturbed due to the intense human activities in the surroundings and are often exogenous i.e. transported from elsewhere (Craul, 1999; Wong *et al.*, 2006). Thus, they serve as transfer mechanism for pollutants sourced from immediate and remote catchments of the highways and are therefore important components of the surface water pollution by runoffs from the highways and streets.

1.3 ROADSIDE SOIL, HIGHWAY RUNOFF AND POLLUTANT LOAD

Increasing urbanisation has often led to the development of complex highway systems to facilitate transportation. These systems are potential sources of a wide variety of possible pollutants accumulating on the highway surfaces, median areas and adjoining right-of-way as a result of highway use, maintenance, natural contributions and pollution fallout to surrounding environment especially surface and subsurface waters (Gupta *et al.*, 1981, US-FHWA, 1996). The impervious surfaces of the highways and associated hard shoulders, gutter and pavement areas, can lead to extensive modification of the hydrological cycle with larger volume of pollutant bearing rainfall-runoff conveyed over shorter periods of time at increased flow rates to adjacent receiving waters (UK-IHT 2001; Brezonik and Stadelmann, 2002). Characterized as a non-point source pollution (Vase and Chew, 2004), highway runoff derives its pollutant loads from various sources as shown in Figure 1.1.

The contributions from sources including atmospheric fallout, windblown particulates and vehicle-displaced particles continuously accumulate on the impervious highway surfaces and adjoining areas eventually becoming roadside soil and sediment which serve as local sink for more pollutants' build up (Jartun *et al.*, 2003; Andersson *et al.*, 2004).



Figure 1.1: Pathway of Urban Highway Pollutants through Highway Runoff (Adapted: UK IHT, 2001).

Since the impervious areas of a typical highway environment often constitute 60-100% of the total area (Lu and Weng, 2006), these pollutants are easily washed off the highway and carried to streams, lagoons, rivers, lakes or any of such receiving water bodies during rainfall (Lee *et al.*, 2011). As carrier for a variety of elements ranging from nutrients to potentially toxic metals, pesticides among other water degrading pollutants (Zhang and Zhang, 2010), highway runoffs have the potential of negatively affecting the receiving environment exerting an acute and chronic impact on the receiving soil or water-based ecosystem (Li-qing, *et al.*, 2007; Opher, *et al.*, 2009). Thus, highway or road runoff pollution problems are more difficult to control than steady-state point discharges because of the intermittent nature of rainfall and the consequent runoff, the large variety of pollutant source types, and the variable nature of source loadings (Li *et al.*, 2007).

1.4 NATURE OF POLLUTANTS FROM HIGHWAY RUNOFF AND ROADSIDE SOIL

The nature and sources of pollutants from highway runoff and roadside soils are as tabulated in Table 1.1. These pollutants could broadly be classified into sediments, organics, potentially toxic metals (PTMs) and nutrients.

1.4.1 Roadside Sediment

This is made up of particles derived from rocks, biological materials, or chemical precipitates transported by, suspended in, or deposited in flowing water. This is the most widely spread pollutant in rivers and streams affecting the aquatic habitats and other uses of the water. Highways instigate sediment transport by runoff into recipient waters due to the reduced infiltration of the impervious highway surfaces. Rapid concentration of flow with minimal flow resistance along relatively high slopes of roadside drainage structures combine to increase velocities, volumes and peaks of runoff and in the process increase the potential for erosion and increased entrainment of sediment (US-ASTM 1997; Bent *et al.*, 2000). Roadside sediment also serves as the matrix for particle bound pollutants such as organics, potentially toxic metals (PTMs) and nutrients thus facilitating their movement into the receiving water bodies (Pereira *et al.*, 2007; Yisa, 2010). The level of sediment transport by highway and urban runoffs is controlled by precipitation and the availability of erodible and (or) transportable sediments (Bent *et al.*, 2000).

1.4.2 Organic Pollutants

Compounds such as semivolatile organic compounds (SVOCs), volatile organic compounds (VOCs) and other organic compounds are present in runoff and roadside soil samples. These solvent-extractable compounds can be determined by techniques such as gas chromatography-mass spectrophotometry (GC-MS) and high performance liquid chromatography (HPLC). Examples of SVOCs include phthalates, phenols, and polycyclic aromatic hydrocarbons (PAHs). Sources of these compounds in the highway environment include fuels and additives, paints, vehicular exhaust among others. As a result of their hydrophobic nature, SVOCs may accumulate to concentrations that will adversely affect

aquatic organisms and their predators including man (Furlong, et al., 1995; Lopes and Dionne, 1998).

Nature	Primary Sources					
Particulates	Pavement wears, vehicles, atmosphere, sediment disturbance					
Anionic Nutrients (P and N)	Atmosphere, sediments, roadside fertilizer use					
PTMs: Pb, Zn, Fe, Cu, Cd, Cr, Mn, Ni e.t.c.	Leaded fuel, tyre wear, lubricating oil and grease, motor oil, bearing wear, autobody rust, atmospheric fallout, brake lining wear, asphalt paving					
Bromide	Exhaust					
Cyanide	Anticake compound used to keep deicing salt granular					
Sodium, Calcium	Deicing salts, grease					
Chloride	Deicing salts					
Sulphate	Roadway beds, fuel, deicing salts					
Petroleum	Spills, leaks, blow-by motor lubricants, antifreeze, hydraulic fluids, asphalt, surface leachate					
PCBs, pesticides	Spraying of highway right of ways, atmospheric deposition, PCB catalyst in synthetic tyres.					
Pathogen bacteria	Soil litter, bird droppings, trucks hauling farm produce and domestic waste.					
Rubber	Tyre wear					

 Table 1.1: The Nature and Sources of Pollutants in Roadside Soils and Runoff

Source: Kobringer, 1984

1.4.3 Potentially Toxic Metals (PTMs)

Potentially toxic metal (PTM) is an acronym used to define a metal which at low or trace concentration have adverse effects on humans, aquatic biota and their dependants and/or the environment or a metal which though essential for biochemical processes, may be deleterious

to body system if present in high concentration. Such is likely through gradual bioaccumulation in the body. These PTMs include lead, arsenic, nickel, zinc and copper among others. Thus PTMs are of particular interest in runoff studies due to their toxicity, ubiquitousness, and the fact that metals cannot be chemically transformed, metabolised or destroyed (Davies et al., 2001). They constitute the most widely studied pollutant in urban runoff and roadside soils due to the potentials of vehicle related activities as major sources of the metals' input to recipient water systems. These metals are released during different operations of road transport such as combustion, component wear, fluid leakage and corrosion of the metals with the major PTMs in roadside environment being lead, copper and zinc (Akbar et al., 2006; Dolan et al., 2006). PTMs are also contributed from atmospheric depositions onto the impervious highway environment from fluxes originating from proximate or remote industrial emission, refuse burning and other associated sources (Nriagu et al., 1996). Upon emission, they tend to adhere to particulate matter to form fine particulates and dust which remain transient in ambient air until they are deposited on land or water (Vesper and White, 2003; Wong et al., 2006). The general impervious nature of the highway environment enables the accumulation of the metal bearing particulates which are eventually transported to the recipient environment by runoff. There is a general agreement that these metals decrease in concentration with depth and distance from the road (Turer and Maynard, 2003). Table 1.2 shows some PTMs contributed by vehicular sources to the highway environment.

1.4.4 Anionic Nutrients

Nutrients such as phosphorus, nitrogen, silicates and carbon are constantly being discharged into water bodies through runoff. These discharges are greatly enhanced by increasing urbanisation and high imperviousness of the catchments. Excessive inputs of these nutrients especially anionic phosphate and nitrate species into water lead to eutrophication which is signified by excessive algae bloom in the recipient water. While nutrients bearing runoffs from agricultural soils have been a subject of various studies (Sharpely *et al.*, 2002; Davis *et al.*, 2005), potential input of phosphate and nitrates from urban roadside soils have often been overlooked. The biological enrichment of surface waters stemming from anthropogenic inputs of nutrients has been described as one of the most common sources of surface water

Source	Metals										
	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn	V	Pt
Gasoline											
Exhaust											
Motor oil & grease											
Antifreeze											
Undercoating											
Brake linings											
Rubber/tyre											
Asphalt & bitumen											
Auto Paints											
Diesel oil											
Engine wear											
Catalytic Converters											

Table 1.2: Some PTMs derived from Vehicular and other Highway Sources

Adapted from Sansalone et al. (1997)

impairment which limits the use of water for drinking, recreation and commerce (Howarth *et al.*, 2000; Shikagi *et al.*, 2006). The impervious highway environment enables a semicontinuous supply of rapidly mobilized nutrients into recipient waters throughout the year due to the very limited or totally absent infiltration capacity of the surfaces (Withers and Jarvie, 2008). Some sources of anionic nutrients mobilised in urban runoff include atmospheric deposition, industrial and vehicular particulate emissions, animal excreta and lubricants. Phosphorus compounds such as 2-ethylhexyl dihydrogen phosphate is used in many anti-wear and friction-reducer compounds in engine and gear oils, metalworking compositions and various industrial and automotive lubricating oils, greases and specialties (Xu and Spike, 2007). Tricresyl phosphate, another compound of phosphorus is used as an additive gasoline to scavenge for tetraethyl lead (Solbu *et al.*, 2007). Although the P in these organic compounds along with others of biological origin are not readily bioavailable unlike some of the inorganic P compounds, their degradation mechanisms such as biodegradation, hydrolysis, and photodegradation which are also hastened by the chugging agitation of runoff water eventually result in the release of the P to the recipient water. While the sum total of each nutrient makes up the total nutrient, the bioavailable fraction however is the composite fraction that can pass through a 0.45 μ m filter. This fraction could be readily absorbed and utilized by plants and other aquatic organisms. Sources of nitrogen as nitrates in the highway environment include vehicular emissions, atmospheric deposition and nitrogen fixation by bacteria.



Tricresyl phosphate

Nutrients in surface waters are operationally described as either total dissolved or bioavailable fractions. The total phosphorus concentration is made up of the inorganic and organic species which could exist as particulates or dissolved fractions.

1.5 FACTORS INFLUENCING LEVELS OF POLLUTANTS IN HIGHWAY RUNOFF AND ROADSIDE SOILS

Several factors influence the level of pollutants from the highway environments with some identified as having major influence on pollutant constituents and concentrations. Atmospheric deposition, traffic characteristics and surrounding land use have been identified as the dominant variables among the listed factors.

1.5.1 Atmospheric Deposition

Atmospheric deposition is defined as the solid, liquid, and gaseous materials, often pollutants, which settle out from the atmosphere onto surfaces by gravitational pull (Bricker and Rice, 1993). Atmospheric deposition could occur as dry atmospheric fallout (dustfall) of pollutant bearing particulates or as wet precipitation aided deposition involving rain, sleet or snow (Figure 1.2). Fine particulates usually have several pollutants associated with them such as nitrogen, phosphorus, metals and a variety of organic compounds sourced from vehicle exhaust emissions, industrial stack emissions, and generators among other sources (US-FHWA, 1996). The deposition chemistry and processes involved in atmospheric deposition can contribute significant amounts of pollutants to roadside soils and highway runoff due to the retention capacity of the mostly impervious highway surfaces and their catchments which allow for a longer residence time of the deposited pollutants unlike depositions on bare soil surfaces and surface water whose residual constituents could initiate a chemical transformation of the deposited pollutants to harmless derivatives. Thus, the atmospheric fluxes onto urban impervious surfaces significantly contribute to the contamination of runoff and roadside soils (Garnaud et al., 1999). Most materials delivered to the road surfaces which consequently appear in highway runoff could be considered to be from either ambient atmospheric deposition or traffic or from both (Colman et al., 2001). Dry depositions of pollutants such as nutrients and PTMs are usually greater than levels obtained during wet deposition with most in particulate forms (Colman and Friesz, 2001). The level of pollutants during atmospheric depositions are mostly determined by the antecedent dry period (ADP), intensity of the precipitation and its duration (Turer et al., 2001).

1.5.2 Traffic Characteristics

Vehicles contribute pollutants directly or indirectly to the highway environment. The wear of vehicular parts, leakages of oils and emission from the exhaust of vehicles input pollutants directly onto the highway roads (Barret *et al.*, 1993). Indirectly, vehicles can transport pollutants which adhered to solid materials onto the highways from remote sources especially through their tyres during rainy seasons. The volume, average speed and frequency of brake application among others contribute to the concentration of pollutants in the



Figure 1.2: A Schematic overview of Tropospheric Chemistry (Courtesy: Monks *et al.*, 2009)

highway runoffs. For example, each time the brakes are applied and the semi-metallic brake pads squeeze against the wheel rotors, tiny amounts of metal dust, often copper but sometimes also zinc and lead, are deposited along the road (Nixon and Saphores, 2007). Thus, with higher number of vehicles undergoing this process, more PTMs get deposited on the road surface and eventually to the recipient environment. The level or concentration of pollutants in roadside soils and highway runoffs have been positively correlated with the volume of traffic plying the highway which is mostly measured as average daily traffic (ADT) or vehicles during a storm (VDS) and thus serves as an important factor for estimating the pollutants' concentration (Lee *et al.*, 2011). Urban highways with ADT greater than 30,000 per day could produce 2 to 5 times the pollutant levels present in highway runoff than rural highways due to the higher number of vehicles plying a typical urban road (US-FHWA, 1996). However, the ADT may be less influential in determining the concentration of pollutants from site to site during a rainfall event as rainfall duration and intensity at the

different sites may have influenced the observed concentrations more than the ADT. Nevertheless, ADT remains a vital variable in predicting pollutant concentrations and is used in many studies to formulate pollutants load estimates based on the differing ADT values for different settlements (US-FHWA, 1996).

1.5.3 Degree of Imperviousness of Catchments and Surrounding Land Use

Diffuse pollutants' input into recipient water is greatly enhanced by the level of the imperviousness of the catchment area of the water body (US FHWA, 1996). As urban settlements gradually get built up, the rate of surface evaporation and sub-surface infiltration reduces with a consequence increase in generated surface runoff. Thus, large amount of pollutant bearing water are moved into recipient water within a short time. Aquatic ecosystems become impaired when as little as 10-15% of catchment area is occupied by impervious surfaces (Withers and Jarvie, 2008; Jartun et al., 2008). The surrounding land use also influences the concentration of pollutants accumulated on the highway surfaces, for instance, an urban highway located within an area of high industrial activities will tend to accumulate more pollutants than a highway near residential or administrative land use structures. Also, the retention and movement of pollutants vary on different types of road surfaces. In other words, mobilisation of pollutants on asphalted road surface is different from a concrete one leading to differences in the level of pollutants from these surfaces. The rigidness of concrete surfaces confers an ability to retain its shape and consequently drain water with little frictional resistance to water flow leading to increased highway runoff rates unlike asphalt surfaces which is flexible and subject to deformation in shape when heavily used leading to rougher surfaces, more friction and more possible accumulation of pollutants (Driscoll et al., 1990).

Other factors which influence the level of pollutants in roadside soils and highway runoffs include the age and condition of vehicles, accidental spills, maintenance practices such as street sweeping, line painting and roadside vegetation control and beautification, and law and regulations bothering on litter disposal and vehicle emissions (Gupta *et al.*, 1981).

1.6 THE FIRST FLUSH PHENOMENON

First flush implies a greater discharge rate of pollutant concentration in the early part of a highway runoff flow as compared with later parts of the event (Sansalone and Cristina, 2004). It is a characteristic of pollutant emissions from impervious features such as roads and highways (Kang *et al.*, 2008). High mass loadings of pollutants are discharged from the store of accumulated pollutants on the impervious surface into the recipient environment at the initial stage of the wet precipitation induced runoff event but as the runoff event continues, the pollutants' concentrations gradually decline over time (Figure 1.3) at a rate depending on the intensity and duration of the precipitation (Lee *et al.*, 2011). The first 20 – 25% of the runoff volume could be regarded as the first flush (Vorreiter and Hickey, 1994; Deletic 1998). It has been suggested that the first flush includes the "half-inch rule" where about 90% of pollutants are transported in the first half inch of runoff (The Center for Watershed Protection, 1994).



Figure 1.3: A First Flush Concentration Gradient Curve

Under a given condition for the rainfall duration and initial available pollutant mass at the highway watershed, the magnitude of the first flush effect can be estimated using only three

parameters, which are time of concentration, watershed length and rainfall duration (Kang *et al.*, 2008)

1.7 MOBILIZATION OF POLLUTANTS FROM ROADSIDE SOILS AND HIGHWAY RUNOFF TO RECIPIENT ENVIRONMENT

Pollutants in roadside soils and highway runoff are present mainly as dissolved and particulate bound species. In roadside soils, pollutants may exist as vapour in the pores of the soils, adsorbed species on mineral or organic surfaces, dissolved species in soil water, and/or as non-aqueous phase liquids (Singer and Munns, 1999). While dissolved forms of the pollutants such as metals and nutrients are very mobile and readily bioavailable for uptake and assimilation by biotic components of the environment, the adsorbed particulate forms are not readily available and may not pose immediate risks associated with such pollutants, though they can go into dissolved forms at adverse conditions thus they remain as a potential source of bioavailable pollutants in the system (Zhang and Zhang, 2010). Although, some fauna are capable of ingesting or inhaling particulate materials including contaminants, nevertheless, toxic response to the ingested contaminants still generally requires its bioavailability in a solubilised form before absorption by biological tissues (Triana and Laperche, 1999).

The metals and nutrients as well as other pollutants in the highway environment are partitioned among the various physical, chemical and biological components or phases of the highway runoff and the recipient water (Breault and Grenato, 2000). This partitioning or transfer process among the phases is usually multi-directional with a dynamic interchange of the pollutants between the phases. For example, dissolved PTMs or nutrients could be precipitated and adsorbed on particulates at conditions which favour such processes thus the PTMs are made unavailable for assimilation and vice versa. The partitioning of the pollutants which influences their movement or mobility from the highway environment into the recipient water is effected by conditions such as pH, ionic strength, temperature, suspended sediments (organic matter), oxidation-reduction potential, among others (Bricker, 1999). Partitioning has implications not only for washoff or transfer of pollutants by highway runoff but can also indicate which physicochemical mechanisms will be most effective for immobilisation of the dissolved and particulate-bound pollutants (Sansalone and Buchberger,

1997). The dynamics of the partitioning of PTMs in highway runoff and recipient water could be divided into four phases as summarised in Figure 1.4.



Figure 1.4: The Phases of Runoff/Recipient Water Systems and Conditions which Favour Partitioning in each Phase (Source: Breault and Granato, 2000)

At high pH (8 - 14), the reaction of equation 1.1 predominates

$$O_2 + 2H_2O(I) + 4e^- \longrightarrow 4 OH^-(aq.)$$
 - Equation 1.1

This condition favours high level of particulate organic matter concentrations resulting in suspended sediment loads. This implies that the metal or nutrient pollutants tend to be more

adsorbed on particulate organic matter and thus are less bioavailable. The complex so formed exists as suspended sediments and less mobile than the dissolved species but nevertheless could still be moved into the recipient water by the high hydraulic energy of the highway runoff water depending on the drag or friction of the highway and intensity of the precipitation. The negatively charged ions formed combine with the metal ion (Equation 1.2) to go into solution as soluble metal hydroxides (Equation 1.3).

$$M(s) \longrightarrow M^{2+}(aq.) + 2e^{-} \qquad (M = Zn, Pb, Cu,..) - Equation 1.2$$
$$M^{2+}(aq.) + 2OH^{-}(aq.) \longrightarrow M(OH)_{2}(aq.) - Equation 1.3$$

At low pH of 0 - 6, the reaction of Equation 1.4 predominates. The electrons released by the ionized pollutants in the medium (as represented in Equation 1.2) reduce the protons in the water to form free hydrogen gas

$$2H^+$$
 (aq.) + $2e^- \longrightarrow H_2(g)$ - Equation 1.4

Released electrons in the medium are in turn taken up by the reaction of Equation 1.1 and the process continues as long as there are PTM pollutants being oxidised in the medium. The concentration of the suspended organic matter and suspended sediment loads are lower under this condition but the dissolved organic matter (DOM) concentrations are higher. The DOM molecules generally consist of a small representative of the total organic matter of a soil which are soluble (Zsolnay, 2003). They are active materials in terrestrial and aquatic systems and play crucial roles in substance transport through environmental media by acting as carrier for a variety of pollutants ranging from nutrients to PTMs. In transporting these pollutants, the PTMs and nutrients bind to the phenolic-OH and carboxylic acid groups of the DOM (Figure 1.5). The DOM-pollutant complex so formed can then easily move to streams and ground waters through the runoff movement and leaching (Zhang and Zhang, 2010).



Figure 1.5: The Metal Binding Fraction: (A) Cutin-Lignin-Tannin Complex and (B) Condensed Flavonoid Tannin Organic Matter (Courtesy: Leenheer *et al.*, 1998)

While the soil pH and ionic strength determine the solubility of the organic matter, presence of oxides of Al and Fe and clay minerals determine the partitioning (sorption/desorption) equilibrium of the pollutants in the dissolved and particulate phases of the organic matter in the system (Benke *et al.*, 1999). Potentially toxic metals such as Cd, Cu, and Zn have low affinity for organic matter and are therefore very mobile and tend to have relative higher concentrations in highway runoff in contrast to Pb which has higher affinity for organic matter and therefore is present more in the particulate phase and consequently less mobile than Zn. The relationship between the distribution of pollutants in the dissolved phase and the particulate phase are represented by the Equations 1.5 and 1.6 (US FHWA, 1996; Sansalone and Buchberger, 1997).

$$f_d = \frac{C_d}{C_T} = \frac{1}{1 + m K_p}$$

- Equation 1.5

- Equation 1.6

 f_d = Fraction of pollutant in dissolved form C_d = Dissolved pollutant concentration (µg L⁻¹) C_T = Total pollutant concentration (µg L⁻¹) K_P = Partition coefficient m = Solids concentration (kg L⁻¹) f_P = Fraction of pollutant in particulate form. C_P = Particulate pollutant concentration (µg L⁻¹)

 $f_{\rho} = \frac{C_{\rho}}{C_{T}} = \frac{m K_{\rho}}{1 + m K_{\rho}}$

The fraction of pollutants in the dissolved and particulate phases depends on ratio of the dissolved phase concentration to the total concentration and the particulate phase concentration to the total concentration respectively.

The partition coefficient, K_p , between particulate bound pollutant mass and dissolved mass is determined by Equation 1.7.

$$K_p = \frac{C_p}{C_d}$$
 - Equation 1.7

 C_d = Dissolved metal (µg L⁻¹) C_p = Particulate bound metal (µg L⁻¹)

In the recipient water, a combination of high pH and organic matter concentrations coupled with low hydraulic energy (Figure 1.4) of the water system results in the pollutants settling as bottom sediments and gradually become the "store" or sink of the pollutants which could be re-dissolved when conditions favour solubilisation.

1.8 IMPACTS OF PTMS AND NUTRIENTS IN ROADSIDE SOILS AND HIGHWAY RUNOFF ON RECIPIENT WATER

The diffuse nature of highway runoff coupled with the nature and characteristics of the road, the runoff event, the geographic location of the study area with respect to its climatic variables and the receiving water eco-system make pollutants in highway runoff likely able to exert an acute or chronic impact on the recipient water (Opher *et al.*, 2009). Toxicity has been detected in over 90 percent of samples obtained from road derived runoffs as a result of the presence of pollutants (Kayhanian *et al.*, 2008). The impervious nature of urban highways and its catchments further increases the degree of impacts exertable by highway runoffs as more pollutants are washed directly into the recipient water as a result of the higher volume of water and the increased flow from the concretised road surface. Among these pollutants, potentially toxic metals (PTMs) and nutrients have attracted the most attention due to impacts such as metal toxicity, eutrophication, and hypoxia which they induce in the runoff receiving water body (Lee and Bang, 2000; Taylor *et al.*, 2005). Other effects such as sedimentation and organic compounds pollution of the receiving water have also been identified as highway runoff induce-able impacts.

1.8.1 PTMs Toxicity and Impacts

The likely exposure to PTMs toxicity from highway roadside soils and runoff take place via two routes; direct inhalation of PTMs bearing fine particulates from road dust especially during windy conditions or local turbulence generated by moving traffic. Highway maintenance workers, commercial bus workers, roadside traders and to a lesser extent, commuters are most susceptible to this route of exposure.

The other route of exposure to PTMs from highways sources is through highway runoff. The accumulated PTMs on the highway surface are mobilized by the highway runoff to the proximate recipient water directly or indirectly through drainage ducts. The PTMs are them assimilated by the aquatic flora and fauna in the receiving water. The levels of the PTMs subsequently increase through the food chain until humans are exposed to them via their food and water. Though the PTMs are significant contaminants, their toxicity is dependent on their

concentration and existing chemical species at the time of exposure e.g free ion and labile complexes of the metals are more toxic and bioavilable to aquatic organisms and plants than the neutral metals (Almas *et al.*, 2006; Wei *et al.*, 2010). In other words, the toxicity of the metals is a function of their intrinsic solubility and relative dissolution rates thus the equilibrium solubility of a given metal cum pollutant and its dissolution kinetics profoundly affect the bioavailability and chemical lability of its constituent ions (Traina and Laperche, 1999). Oyeyiola *et al.* (2011) reported that some of the most mobile and bioavailable PTMa in the Lagos Lagoon sediment include Cd, Pb and Zn.

For a given solid (i.e. particulate or organic matter bearing pollutant), a general dissolution reaction can be represented by Equations 1.8 - 1.10 below (Mota and Goncalves, 1996; Triana and Laperche, 1999).

$$M_x L_y$$
 (s) $\xrightarrow{H_2O} x M^{y+}$ (aq.) + $y L^{x-}$ (aq.) - Equation 1.8

At equilibrium, the equilibrium constant, K, is as expressed by Equation 1.8 and the solubility product, K_{sp} , represented by Equation 1.9

$$K = \frac{[M^{y+}]^x [L^{x-}]^y}{[M_x L_y]} - \text{Equation 1.9}$$

$$K_{sp} = [M^{y+}]^x [L^{x-}]^y$$

M = metal

L = ligand

[] = activity or concentration K_{sp} = solubility constant

The toxicity of the pollutant PTM (M) is directly proportional to the concentration of the free metal ion, M^{y+} , irrespective of whether M^{y+} or its other hydrolytic or complex species is the most toxic form of M. Thus, the least toxic form of M will have the smallest aqueous equilibrium activity of M^{y+} and the most toxic solid will be that which supports the largest aqueous equilibrium activity of the metal ion (Traina and Laperche, 1999). This *solubility*

- Equation 1.10

product model of contaminant availability has some limitations such as the side reactions in the environment which may make equilibrium difficult and involvement of the ligand in other competing reaction amid various environmental factors regulating the prevailing species of the pollutant in the medium. The different types of PTM species in the receiving environment as outlined by Mota and Goncalves (1996) are described below.

1.8.1.1 Free metal ions (e.g. Cu^{2+} , Pb^{2+}) which are very toxic to living organisms at certain levels probably because they form complexes with ligands at the membrane surfaces.

1.8.1.2 Inorganic complexes (e.g. $Pb(NO_3)_2$, $CuCl_2$) whose availability can be explained by the *solubility product* model as shown in Equation 1.10.

1.8.1.3 Metal-organic compounds with low molecular weight (e.g. metal-OOC-alkyl complex, metal-S-alkyl complex) which could be formed by the reaction of organic exudates (released by some bioorganisms such as algae) in the presence of PTMs. This probably results in minimising the toxic effects of some PTMs in natural environments. PTMs like Pb and Hg when complexed to alkyl groups from car exhaust form very toxic alkylated-PTM compounds which when emitted as aerosol could be absorbed directly into the bloodstream through the lungs.

1.8.1.4 Metal-organic macromolecule complexes (e.g. Metal-lipid and metal-humic acid polymers). These compounds tend to reduce toxicity since they cannot easily pass through biological membranes due to their size.

1.8.1.5 Highly dispersed colloidal metal species such as MnO_2 , $Fe(OH)_3$ and Cu_2S which are not very soluble in natural waters.

1.8.1.6 Adsorbed metal species on colloids, particulate matter, and sediments. Clay minerals such as kaolinite and illite possess predominantly surface negative charges which can bind with metals at the pH of most natural ecosystems. This potentially decreases the availability of the PTM ions. Nevertheless, the adsorbed metals can still be released when the complex formed is re-dissolved at adverse conditions such as during acid rain precipitation

Potentially toxic metals (PTMs) in roadside soils derived sediment and highway runoff bioaccumulate in marine organisms especially in species at the highway watersheds of the road or highway. Copper, lead and zinc are the most reported as they are major constituent materials of various vehicle components. While Zn is predominantly present in the dissolved phase in highway runoff, Pb is mostly particulate bound (Sansalone and Buchberger, 1997). Concentrations of these metals have been found to be higher in species such as green algae, purple sea urchins, green toads and molluscs in highway runoff receiving environment than those of the control (Karouna-Renier and Sparling, 2001; Kayhanian et al., 2008; Dorchin and Shanas, 2010). The presence of these metals in these organisms, which are parts of the food chain, places highway runoff as a potential source of PTMs exposure in humans. The effects of PTMs in humans has been well documented and of the three priority PTMs in highway runoff studies, Pb remains the most studied due to its use in wide number of products such as leaded paints and fuel and also because of its toxicological effects on humans. The exposure to Pb contamination and attendant effects on humans especially children have prompted the formation of various bodies including the UNEP/WHO's Global Alliance to Eliminate Lead in Paints (GAELP) who are concerned with preventing and minimizing the exposure of Pb in children and in occupational environments respectively (WHO, 2013).

1.8.2 Eutrophication of Recipient Water

Urban runoffs including highway runoff are one of the sources of input of anionic nutrients into coastal waters (Paul and Meyer, 2001). Nutrients from highway runoff and atmospheric deposition could contribute substantially to the growth of algae, plankton and aquatic plants which serve as food for fish. Excess inputs of nutrients induce algae bloom and wild vegetation growths which choke up the aquatic system and use up large amount of oxygen in the water body during the eventual decomposition of the plants (Estela and Cerda, 2005). The typical nutrient utilising reaction in such an environment is as expressed in Equation 1.11:

 $106CO_2 + 16NO_3 + HPO_4^2 + 122H_2O + 18H^+ \longrightarrow C_{106}H_{263}O_{110}N_{16}P + 138O_2$

- Equation 1.11

This decomposition accompanied by the oxygen deficiency invariably lead to other consequences such as anoxia, fish and invertebrate kill, loss of habitat for resident organisms and general deterioration of water quality (Malin et al., 2006). The balance of phosphorus and nitrogen (existing as anionic phosphate and nitrate in aqueous environment) plays a crucial role in this dynamics. The concentration and nature of phosphorus and nitrate highway runoff changes little from the source of mobilisation, such as the highway surfaces, to the recipient water unlike nutrients from agricultural runoff which though could contain more dissolved phosphorus and nitrogen at source, undergoes changes in concentration and even nature before it reaches the receiving water. This is primarily due to the impervious nature of urban highway catchments and higher hydraulic energy of the highway runoff which allow for little or no infiltration of the runoff water and its borne pollutants in comparison to agricultural runoff which in passing through open or bare field soils, results in loss of some of the nutrients through leaching and adsorption on soil particles. Higher concentrations of impervious runoff phosphorus over pervious runoff nutrients concentration had been observed with the latter having lower average total phosphorus (TP) concentrations and higher proportion in dissolved form in the drained runoff as compared to surface runoff which reflects the greater opportunity for adsorption of soluble reactive phosphorus and filtering of suspended solids and particulate phosphorus through the soil (Haygarth et al., 1998; Wither and Jarvie, 2008). The implication of this semi continuous mobilisation of anionic nutrients and sedimentation from highway catchments into coastal estuaries and waters such as the Lagos Lagoon is a dramatic increase in primary production and phytoplankton biomass, promoting an excess accumulation of organic matter or eutrophication which in turn affect nutrients cycling, water quality, and the general health of the water ecosystem (Nixon, 1995; Conley, 1999; Paerl et al., 2006).

Eutrophication has been the primary causative factor for increased algal bloom, reduced water clarity, expanded hypoxia and decreased fish diversity of coastal waters such as the Lagos Lagoon. Hypoxia is exacerbated by the choked and eutrophied fresh water overlaying the denser salt water with dead phytoplankton sinking to the stratified bottom water (Figure 1.6). The progressive sedimentation and addition of dead organic matter also ensure a continuous supply of nutrients to the upper water layer by upwelling. A direct effect of sustained nutrient enrichment of the creek and river water networks and coastal lagoon

systems in Lagos, Nigeria is the intractable menace of water hyacinth (*Eichorrnia crassipes*) proliferation (Adewolu *et al.*, 2009) as shown in Figures 1.7 and 1.8.



Figure 1.6: A Diagram showing the Input of Nutrients from various Watersheds into the Recipient Water with its attendant Impacts (Adapted from Paerl *et al.* (2006))



Figure 1.7: A Typical Eutrophied Creek in Metropolitan Lagos, Nigeria.



Figure 1.8: Mass of Floating Water Hyacinth Plants on the Lagos Lagoon overlooking the Third Mainland Bridge.

Eutrophication is mainly controlled by the balance or ratio of nitrogen, phosphorus and silicon in surface water. This relative availability of algae, plant and bacterial growth in a water system is defined by the concept of "limiting nutrient" in the system. A limiting nutrient is the nutrient that controls the ultimate primary or net productivity of an ecosystem (Correll, 1999). Although phosphorus has long been held to be the limiting nutrient in most aquatic systems (Morais et al., 2005; Monbet et al., 2009), recent researches have also pinpointed nitrogen as a nutrient limiting eutrophication partly due to the remarkable increase of nitrogen pollution in recent decades as a result of increased combustion of fossil fuels and the use of reactive N fertilizers among other factors (Howarth and Marino, 2006). However, the Redfield ratio (Redfield, 1958) could be used to determine which of the nutrient is limiting in an aquatic system which is based on the notion that algae, under reasonable good growth conditions, will have an elemental composition with relatively defined atomic ratios (Correll, 1999). The ratio of N:P is around 16:1 in most waterbodies. A natural water system which has a Redfield ratio of nitrogen to P greater than 16 could be referred to as being "phosphorus limiting". In other words, a system may be phosphorus limited or become so when nitrogen concentrations are high and N:P>16:1. In such cases, excess phosphorus will trigger eutrophic conditions. The recommended level of total phosphorus in estuaries and coastal ecosystems to avoid algal blooms is 0.01 to 0.1 mg L^{-1} and 0.1 to 1.0 mg L^{-1} of nitrogen (a 10:1 ratio of N:P) (Osmond et al., 1994).

Although, bioavailable phosphorus also called soluble reactive phosphorus, operationally defined as the phosphate species that can pass through 0.45 μ m pore sized filter, is the form by phosphorus available for direct assimilation by P utilising organisms, the total phosphorus which is the sum total of the phosphorus species present in the water system including organically bound phosphorus and total nitrogen is used to determine this N:P ratio. This is based on the fact that organically bound nutrient species though not immediately bioavailable, serve as reservoir of phosphorus and nitrogen as they could still be broken down at extreme conditions and thus re-dissolved in the water body.

1.8.3 Coastal Water Hypoxia

Hypoxia is one of the extreme consequences of eutrophication. The proliferated algae bloom and phytoplankton mass eventually die out due to insufficient oxygen and the general unsustainable conditions in the eutrophied aquatic system. The decaying process of the organic matter consumes a large amount of oxygen in a reverse reaction of the eutrophication process (Equation 1.12).

$$C_{106}H_{263}O_{110}N_{16}P + 138O_2 \longrightarrow 106CO_2 + 16NO_3^{-1} + HPO_4^{-2} + 122H_2O + 18H^{+}$$

- Equation 1.12

This leads to a lack of oxygen in the affected swath of water which results in mass fish and invertebrate kills and migration of resident species, enhanced susceptibility to diseases and disruption of the systems food chain (*Malin et al.*, 2006). Hypoxia is increasingly becoming a major problem in coastal water around the world. Though, industrial and domestic nutrient rich effluent discharges into surface waters in addition to other oxidizable substances in the effluent is a major contributor in this regard, urban runoffs have also been identified as major contributors due to the numerous pollutants they could mobilize into recipient waters within a short period. The rapid development of coastal settlements, as seen in Nigeria as well as other countries in the West African sub-region, has led to mostly geometric increases in the resident human populations. This has been identified as a major driver of the increased nutrient enrichment of numerous coastal lagoons in the sub-region and being a tropical region which receives an average of 0.9 - 0.9 m per year of rainfall, experiences sustained pollutants movement by urban runoffs (Nixon *et al.*, 2007). The Lagos Lagoon has been showing symptoms consistent with nutrient enrichment in recent years with Alo *et al.* (2010) reporting that there are large swaths of hypoxic regions within the Lagoon.

Hypoxia has seen to the drastic reduction in the catch of fishes by fishermen who ply their trade along the coastal region as continuously being related by local fishermen on the Lagos Lagoon. Thus, they have to move farther off coast to improve on their catch which ultimately exposes them to myriads of sea dangers. Hypoxic waters are characterised by low level of dissolved oxygen, high levels of biochemical oxygen demand (BOD), and chemical oxygen demand (COD) among other pollution indication indices.

1.8.4 Impacts of Highway Derived Sedimentation

Highway derived sediments can be a mix of materials including pavement dust and particles; atmospheric dust, natural soils, traction sand and cinders; vehicle rest particles; tyre dust and particles; trash; and plant and leaf materials (Bent *et al.*, 2000). These materials usually accumulate beside the curbs or verges of roads and easily moved, depending on the hydraulic power of the water, and are transported to recipient waters through the watersheds of the roads during rainfall. The materials transported could be described as bed-material load which settles rapidly onto the bottom layer of the receiving water and suspended load which remain suspended in the water. Aside the physical impacts such as decreasing water depth and the gradual covering up of bottom dwelling flora, sedimentation also results to chemical pollution of the recipient water through the gradual release of the constituent components, depending on the parent material of the sediments e.g. a transferred rusted vehicle bits will gradually release its constituent metals under the corrosive bottom environment of the recipient water. In the long run, sedimentation results into loss of habitat of resident organisms and general destruction of the aesthetics of the water.

In metropolitan Lagos, sedimentation of the Lagos Lagoon as well as its numerous catchment creeks, rivers and streams has continued to be a major problem with government agencies allocating huge resources for yearly dredging and sediment evacuation of these water bodies to minimize the attendant seasonal flooding in the city. These sedimentation problems is mostly instigated by the fact that most inner roads and streets adjoining the highways in the city have remained un-tarred or without any concrete cover thus soils are gradually moved from these roads onto the highways by vehicle tyres and wind movements. These soil particles accumulate by the side kerbs of the highways and easily moved by the hydraulic force of the highway runoff into the watersheds of the water bodies. This continuous sedimentation of the Lagos Lagoon tributary water systems along with other pollution pressures may have virtually wiped out all economically important aquatic species like fishes and crabs resident in the canals, creeks and rivers in Lagos.

1.9 DETERMINATION OF POTENTIALLY TOXIC METALS AND ANIONIC NUTRIENTS IN HIGHWAY RUNOFF AND ROADSIDE SOILS

Different methods have been used for the determination of PTMs and nutrients in environmental media over the years. These methods are as discussed below.

1.9.1 PTM Determination

Most of the methods used for PTM determinations are based on atomic spectrometry (AS) with the flame technique being the most commonly used though this is gradually being supplanted by the inductively coupled plasma techniques (ICP-OES and ICP-MS) (de-la-Guardia, 1996) because of their suitable for multi-element determinations, including nonmetals such as phosphorus, and their higher sensitivities. The ICP instruments are however of much higher set-up cost. Other methods for elemental analysis include voltammetric techniques such as anodic stripping voltammetry (ASV) and square wave voltammetry (SWV). While the voltammetric techniques are more sensitive with detection level of up to 10⁻⁹ mol L⁻¹ (Buffle and Tercier-Waeber, 2005), they can only be used for single element determinations unlike the ICP techniques. Determination of mercury is best done by the cold vapour technique because it can exist as vapour at room temperature without any inordinate treatment of the metal. PTMs such as arsenic, antimony and selenium are better determined by the hydride generation methods. This is due to the fact that their compounds are difficult to reduce to their gaseous states and therefore could not be determined directly by AAS. The hydrides of these metals, formed on reduction with sodium borohydride, are volatile and could subsequently be dissociated to give a gaseous state of the element by the flame technique and thus be quantified (Mendham et al., 2000).

The flame atomic spectrophotometric techniques include atomic absorption spectrophotometry (AAS), flame emission spectroscopy (FES) and atomic fluorescence spectroscopy (AFS). These techniques involve the excitation of atoms of the metal being determined by aspirating its solution into a flame produced by a mixture of fuel and oxidant such as acetylene/air or acetylene/nitrous oxide to achieve a suitable temperature. While some of the atoms of the metals may be raised to an energy level sufficiently high enough to permit

the emission of radiation characteristic of the metal (a basis for the FES), a larger number of the gaseous atoms, however, remain in the ground state, capable of absorbing radiant energy of their own specific wavelength when passed through the flame containing the atoms (Mendham *et al.*, 2000). The extent of the absorption of the wavelength which is proportional to the concentration of the atoms present in the aspirated solution serves as the principle for the AAS technique. When the energy absorbed by free atoms is re-emitted, it becomes atomic fluorescence spectroscopy (AFS) (Figure 1.9).



Figure 1.9: Schematic Illustration of Atomic Spectroscopic Techniques (Adapted from Mendham *et al.*, 2000)

A critical factor in these techniques is the ratio of ground state to excited state atoms as expressed in Equation 1.13 below.

$$\frac{N_1}{N_0} = \left(\frac{g_1}{g_0}\right) e^{-\Delta E/kT}$$
 - Equation 1.13

- N_1 = number of atoms in the excited state
- N_0 = number of atoms in the ground state
- g_1/g_0 = ratio of statistical weights for ground and excited states
- ΔE = energy of excitation (*hv*)
- k = Boltzmann constant
- T = temperature in kelvins

This ratio depends on the energy of excitation (hv) and the temperature (T) of the flame. Thus, higher ratios are obtained by a lower energy (hv) and higher temperature.

Among the three techniques mentioned above, the most commonly used is the atomic absorption spectroscopy (AAS) because it is less prone to inter-element interferences. At optimum conditions (i.e. at higher temperature and lower excitation energy) only a small fraction of the atoms are excited thus resulting in under-estimation of the concentration of the metal in the sample if FES or AFS is used. This is because they both involve emission of energy by excited atoms coupled with the fact that the absorption spectra of most elements are simple in character compared with their emission spectra. Therefore, AAS is usually the technique of preference in flame atomic spectroscopy.

The atomic spectroscopy instrumentation (Figure 1.10) includes the nebuliser-burner, usually a premix or laminar flow burner, which converts the test solution into gaseous atoms (as mist or aerosols) by Venturi effect of a jet of air blowing across the top of the capillary through which the test solution is passed. The aerosol produced subsequently mixes with the carrier/oxidant gas and flows to the burner head, passes into the flame (of about 10-12 cm in length for most fuel gas-oxidant combination and 5 cm for nitrous oxide-acetylene) and are atomised. The atomised analytes are then exposed to selected resonance radiation from the hollow cathode lamp produced by passing all the absorbed lines emitted from the lamp through a monochromator (in form of a prism or grating).



Figure 1.10: Schematic Diagram of a Double Beam Atomic Absorption spectrophotometer (Courtesy: Expertmind, 2013)

The resulting emissions from the flame are then passed to a detector after modulation in order to isolate the measurement arising from the resonance line source and those from the effects of flame emission. The resonance line source emission can be modulated using a mechanical chopper device. The signals from the detector are subsequently passed to the recorder or read-out systems such as meters, chart recorders and digital displays (Mendham et al., 2002). Despite the wide use of this technique in the determination of PTMs, there are still identified limitations as a result of the general mechanics of the operations of its different components or interferences which could be spectral or chemical in nature. Some of the former limitations include low percentage of nebulised test solution eventually reaching the flame, restriction to the number of elements being determined to one per cycle of operation of the instrument since this is determined by the resonance lamp source, and matrix effects. The latter set of limitations include overlap between the frequencies of the resonance line of interest and lines emitted by some other elements, incomplete dissociation of the analyte compound, formation of refractory compounds in the flame among others. Though there are various ways that these limitations could be minimised or corrected (Skoog et al., 2004), the introduction and use of the plasma techniques have solved most of these challenges.

The ICP techniques or plasma emission spectroscopy is based on the use of plasma as an atomisation source. Plasma could be defined as a cloud of highly ionised gas, composed of ions, electrons and neutral particles with about 1% of the total atom in the gas (usually argon) being ionised. The gas is ionised by the influence of strong magnetic field by either of three ways; through a direct current to give the direct current plasma (DCP); by radio frequency to give inductively coupled plasma (ICP) or by microwave-frequency. Of the three ionization modes, the ICP offers the greatest in terms of sensitivity and freedom from interference though the DCP is simpler and of lower average cost. Two main features or advantages of the plasma technique over the flame technique is its high heating temperature (7000 – 15000K) and production of spectra for large number of elements which makes the plasma source suitable for multi-element determinations simultaneously. The inductively coupled plasma total rate of 11 - 17 L min⁻¹. The argon stream carries the sample in the form of an aerosol through the central tube.





Page - 32

The outer tube contains a water-cooled induction coil powered by a radiofrequency (RF) generator (typically 1-5 kW at 27 MHz or 41 MHz) which produces an oscillating current in an induction coil that wraps around the tubes. The induction coil creates an oscillating magnetic field which in turn sets up an oscillating current in the ions and electrons of the support gas. These ions and electrons transfer energy to other atoms in the support gas by collisions to create plasma of very high temperature (Tissue, 2000; Skoog *et al.*, 2004). The plasma ionizes and subsequently excites the ions of the analyte(s) in the extreme temperature. When the excited electrons in these ions fall back to lower energy levels, they emit light. The wavelengths of light emitted by a particular element serve as the "fingerprint" for that element. Therefore elements are identified by the characteristic wavelengths of light emitted by the sample. The amount of light emitted by each element gives an indication of the concentration of the element in the sample. The detectors are usually charge-coupled devices (CCD).

The success of ICP led to its being coupled with mass spectrometer as ICP-MS. This instrument combines the high ionization potential of the ICP with the high sensitivity of mass spectrophotometer. The ions generated from the ICP operating at room temperature are passed through specialized interface cones called sampler and skimmer into the vacuum environment of the MS (Figure 1.12) which separates them based on their charge to mass ratios. The use of ICP-MS has greatly improved the quantification of PTMs in environmental media as trace levels of these metals could now be easily determined. For example, the limit of detection for Pb by flame AAS, ICP-AES/OES and ICP-MS are 5, 1 and 0.007 ng mL⁻¹ respectively (Skoog *et al.*, 2004) respectively which underlines the usefulness of ICP-MS in modern analytical determinations.



Figure 1.12: Schematic Diagram of ICP-AES and ICP-MS (Courtesy: US Department of Energy, 2013)

1.9.2 Anionic Nutrients Determination

The nutrients, phosphorus and nitrogen, are mainly determined in their anionic forms as phosphate and nitrite/nitrate by colorimetric methods which offer some advantages such as increased sensitivity and lower instrumentation costs over the ICP procedures. The phosphorus species in environmental media and their operational determination is as outlined in Figure 1.13. The sum of the 0.2 or 0.45 µm membrane filterable dissolved P species (bioavailable or molybdenum reactive P) and membrane filtered residual (often called particulate P) form the total mass of phosphorus in the system. While the dissolved fraction contains inorganic and organic compounds such as orthophosphate; inositol phosphate; sugar phosphate and condensed phosphate, the particulate fraction comprises material of biological origin (animal, plant, and bacterial), weathering products (primary and secondary minerals)

and authigenic minerals from direct precipitation of inorganic phosphorus (Robards *et al.*, 1994; McKelvie *et al.*, 1995; Gimbert *et al.*, 2007).



Figure 1.13: A Flowchart of Operational Phosphorus Species and their Determination in Environmental Samples (Courtesy: Worsfold *et al.*, 2005)

The determination of any of the species of interest (either as the dissolved fraction or the particulate fraction after suitable digestion process to convert them to dissolved forms), is mainly carried out by colorimetric protocols based on the "molybdenum blue method" whereby phosphate reacts with an acidified molybdate reagent to yield a phosphomolybdate heteropolyacid or 12-molybdophosphoric acid (Zhang *et al.*, 1999). The heteropolyacid upon reduction with ascorbic acid or tin (II) chloride produces a blue colour, the intensity of which is proportional to the amount of orthophosphate ion incorporated into the complex (Ciavatta,

et al., 1990; Murphy and Riley, 1962; Sjosten, and Blomqvist, 1996). The equations for the reactions are as given in Equations 1.14 and 1.15.

$$PO_4^{3-} + 12MoO_4^{2-} + 27H^{+} \longrightarrow H_3PO_4(MoO_3)_{12} + 12H_2O$$
 - Equation 1.14

$$H_3PO_4(MoO_3)_{12}$$
 + Reducing Agent $\rightarrow PSb_2Mo_{10}O_{40}^{3-}$ - Equation 1.15

The rate of formation of the phosphomolybdenumantimonyl complex is dependent on conditions such as the reaction temperature and the ratio of proton to molybdate ([H⁺]:[Mo]) in the reacting mixture. A temperature range of $1 - 95^{\circ}$ C and a ratio range of 37 - 206[H⁺]:[Mo] have been reported in past studies (Zhang et al., 1999). However, most studies suggested an optimum temperature of $30 - 40^{\circ}$ C and a ratio of about 70 (Drummond and Maher, 1995). Additional challenges with the molybdenum blue chemistry are the competitive interferences from related species particularly silicates and arsenates in water via the formation of silicomolybdenum and arsenomolybdenum complexes respectively which absorb around the same wavelength used for the phosphomolybdenum detection. The silicomolybdenum blue complex formation is favoured at high reaction temperature (40 - 65) $^{\circ}$ C) and has a broad absorbance at a wavelength of 790 nm which overlaps the 710 – 880 nm range of the phosphomolybdenum (Peat et al., 1997; Gimbert et al., 2007) thus leading to an overestimation of the phosphate signals. This is sometime the case when the total dissolved phosphorus determination (after digestion) is observed to be lower than the concentration of the phosphate alone (without digestion). Silicate interference can be corrected by using lower reaction temperatures; using lower reaction pH to make the reacting solutions more acidic and using masking agents such as tartaric acids before the formation of the blue complexes (Freeman et al., 1990; Yaqoob et al., 2004). It can also be eliminated by digestion (as in the case of total phosphorus determination), through which the dissolved organic phosphorus is oxidized to inorganic phosphate, as the elevated temperature and pressure result in the polymerisation of the silicate in the acidic solution and make it non-reactive to molybdate reagent during subsequent phosphate analysis. Arsenate interference could be eliminated by
the addition of thiosulphate which reduces arsenate to arsenite (Equation 1.16) and therefore does not react with molybdate (Zhang *et al.*, 1999).

$$4HAsO_4^{2-} + S_2O_3^{2-} + H_2O + 6H^+ \longrightarrow 4H_3AsO_3 + 2SO_4^{2-}$$

Equation 1.16

Determination of total phosphorus in soil is carried out by rigorous digestion in acidic medium to ensure the complete release of the phosphorus from their organic linkages and conversion to phosphate which could then be determined by the molybdenum blue chemistry as shown in Equation 1.14.

Bioavailable phosphorus in soil is determined by extraction with a suitable extractant such as water, sodium bicarbonate also called the Olsen P or by the Mehlich 3 or Bray protocols (Olsen *et al.*, 1954; Mehlich, 1984; Haney *et al.*, 2006) depending on the nature of the soil. While Mehlich 3 is a multinutrient extractant capable of extracting a number of nutrients with the exception of ammonium and nitrate, Olsen extractant was developed primarily for extracting phosphorus. The digest or extract so obtained is then analysed by the molybdenum blue chemistry to obtain the phosphate concentration.

In using the molybdenum blue chemistry for the determination of phosphorus in environmental media. the instrumentation employed is basically the UV/Vis spectrophotometer via the manual method i.e. the reagents (sulphuric acid, ammonium molybdate, antimonyl tartarate and ascorbic acid) are manually mixed in a specific ratio before being added to the sample to be determined. The reacting mixture is then left for about 10 minutes to achieve a steady state and maximum colour development. This process could be time consuming especially when large numbers of samples are to be analysed and also fraught with various quality assurance and control issues. In order to eliminate or at best reduce these issues, the continuous flow techniques were introduced to phosphate determinations using same molybdenum blue chemistry but through a different sample handling fully automatic and semi-automatic approach. This had helped in addressing most of the quality assurance issues in the manual protocol. Also, other methods of determination for phosphorus in environmental media include techniques such as induction coupled plasma techniques, gravimetric and volumetric analyses (Estela and Cerda, 2005).

Nitrate (NO₃⁻) is one of the most universally determined anions in natural water and drinking water because it can promote eutrophication and is toxic to fetuses and young of livestock and humans at concentrations that exceed about 10 mg L⁻¹ (U.S. EPA, 1995). The key step in the determination of NO₃⁻ is its reduction to NO₂⁻. The water sample (or water or KCl extract of soil sample) is passed through a cadmium coated copperized bed through which the nitrate is converted to nitrite (Equation 1.7). The acidic reaction of the nitrite formed and sulphanilamide produced a diazo compound which couples with α -naphthylethylenediamine (NED) to form a pink coloured azo dye (Equation 1.18) detectable at 540 nm (Griess, 1879; Moorcroft, *et al.*, 2001).

$$NO_{3}(aq.) + Cd(s) + 2H^{+}(aq.) \longrightarrow NO_{2}(aq.) + Cd^{2+}(aq.) + H_{2}O(l)$$
 - Equation 1.17



- Equation 1.18

Despite the long predominance of the Cd coated copperized bed as the reducing agents of choice for colorimetric nitrate determinations in water, cadmium reactors pose health risks to analysts and waste stream processors, increase waste stream disposal costs are difficult to prepare and activate (in flow through systems) (Patton and Kryskalla, 2011). The concerns on the risks of the cadmium have prompted reported modifications and alternatives for the reduction process such as reduction of nitrate to nitrite with trivalent vanadium (Miranda,

2001), use of nitrate-reductase-based nitrate assays (Campbell *et al.*, 2006) among others. Nevertheless, the fact that the copperized bed reduction is fast and simple to use still makes it the preferred choice for nitrate determination especially in continuous flow system.

1.10 THE USE OF CONTINUOUS FLOW SYSTEMS FOR ENVIRONMENTAL MONITORING OF POLLUTANTS

In monitoring environmental indices, the collection of a large number of samples is sometimes required (Casey and Smith, 1985) especially if the medium is subject to temporal and spatial variation as in non-point sources such as runoff. To overcome these challenges, scientists have over the years been motivated to develop newer techniques and instrumentations designed for adequate and real-time monitoring of these indices with "fieldability" being the ultimate attraction (Toda and Dasgupta, 2008). While some indices such as pH and conductivity can routinely be monitored in-situ, others are still mostly determined by reagent based assays as "beaker chemistry" in the laboratory (Ruzicka, 2008). Flow analytical chemical methods were generally introduced to automate, in a simple and practical way, the steps of an analytical methodology by handling sample and reagents within a fluidic flowing stream. These determinations, which not only depend on the applied chemistry but also on the dynamic processes within the system being used, has been found to be more precise with higher sample throughput and less prone to contamination than manual procedures (Estela and Cerda, 2005). The progression of manual to automated systems of continuous flow analysis is as shown in Figure 1.14. The first application of flow measurement was through air segmented continuous flow analysis (ASCFA) which found wide applications in environmental, agricultural and industrial analyses.



Figure 1.14: Schematic Representation of the Evolution of Continuous Flow Analysis

Subsequent efforts have led to the developments of flow injection analysis (FIA), sequential injection analysis (SIA), bead injection analysis (BIA) as well as other new approaches such as multicommuted flow injection analysis (MCFIA), all injection analysis (AIA), multisyringe flow injection analysis (MSFIA)(Figure 1.15). Emphasis has also been on the construction of μ FIA or micro-total analysis (μ TAS) systems and techniques (Ruzicka and Hansen, 1975; Rochas *et al.*, 2002; Miro *et al.*, 2002; Lapa *et al.*, 2002). The manifold configurations of some of these systems as presented by Estela and Cerda (2005) are shown in Figure 1.15.



Figure 1.15: Schematic Illustration of Continuous Flow Manifolds for Determination of Chemical Parameters: (A) segmented flow analysis (SFA), (B) flow injection analysis (FIA), (C) sequential injection analysis (SIA), (D) multicommutation flow analysis (MCFIA), (E) multisyringe flow analysis (MSFIA), (F)multipumped flow analysis (MPFA), and (G) all injection analysis (AIA): (a) sample and reagent loading; (b) mixing by circulation; (c) to detector and washing of line. S, sample; R, reagent; CA, carrier; A, air; D, detector; IV, injection valve; HC, holding coil; RC, reaction coil; B, debubbler; MV, multiposition valve; SV, solenoid valve; SP, syringe pump; MP, multisyringe pump; PP, peristaltic pump; St, stopper; W, waste; P1 and P2, micropums; C, control interface; x,confluence point; V1–V6, six way valves; L1–L7, Teflon tubes; R1–R3, reagents (Courtesy: Estela and Cerda, 2005).

1.10.1 Air Segmented Continuous Flow Analysis (ASCFA)

Air segmented continuous flow analysis, ASCFA (Figure 1.16) was developed by L. T. Skegg in 1966 was the first generation of continuous flow system where sample solutions were drawn into a system of flow channels by a peristaltic pump, metered and mixed with reagents on the way to detector, while being heated, filtered or extracted (Ruzicka, 2008).



Figure 1.16: Schematic Representation of the Air Segmented Continuous Flow Analysis

(ASCFA) Technique (Courtesy: Ruzicka, 2008)

The main feature of the ASCFA design is the air segmentation incorporated into the flowing stream which divides it into separate segments using numerous air bubbles. The segmentation makes the flowing stream to have a semblance of moving "beakers" containing the reacting mixture and prevents carry over within the train of samples during transport to detector. It also facilitates homogenous mixing within each segments vide the friction with the walls of the tubing thus providing time for the reaction to reach equilibrium. The use of ASCFA has grown in bounds since its introduction into the field of chemical analysis with air bubbles viewed as an essential component of continuous flow analytical system. Most importantly, the system has evolved into units capable of multi-analytes determinations especially for nutrients (Haney *et al.*, 2006). Nevertheless, ASCFA still has some limitations which include

restriction of sampling frequency based on the size of the air bubble, pulsating flowing stream which could distort the response signal output and the need to de-bubble the flowing stream before it reaches the detector because air bubble causes a jump in the output signal.

1.10.2 Flow Injection Analysis (FIA)

The concept of flow injection analysis, FIA (Figure 1.17) was introduced by Ruzicka and Hansen (1975). It involves the injection of a small, fixed volume of liquid sample into an unsegmented, liquid carrier flowing through a narrow bore tube or conduit under laminar flow conditions with the sample progressively dispersing into the carrier substance by convection and through radial and axial diffusion. Depending on the chemistry, reagents may be added and mixed with the flowing stream to produce a detectable species that can be sensed by one of numerous flow-through detectors. The height of the peak shaped signal (Figure 1.17) when extrapolated against a calibrated standard solutions graph gives the concentration of the analyte (McKelvie, 2008). The shape of the signal is characteristic of a given flow injection system and reflects the convention-diffusion process to which the bolus has been subjected. The transient profile is controlled by system parameters such as flow rates, reactor dimensions and sample volume (Gine et al., 1992). A flow injection analysis system primarily consists of a propulsion device used to deliver the carrier and reagent through the conduit, usually a peristaltic pump, gas pressurized reservoirs, constant head reservoirs among others. Other components are the injection valve capable of metering definite volume of solutions into the flowing stream and the detector. The kind of detector is determined by the type of analysis to be done. However, spectrophotometers are the most commonly used detectors since most of the applications are based on wet chemistry.



Figure 1.17: A Flow Injection Analysis (FIA) System (Adapted from Ruzicka, 2009)

FIA is built on three cornerstones which include firstly, the injection or insertion of a discrete, well-defined volume of sample solution into the carrier stream made up of an inert substance (e.g. water) or a reagent with additional reagents being subsequently added if necessary. Secondly, the manipulation of the injected sample zone from the point of injection to detection point to allow for a reproducible and precisely timed analysis, and thirdly, the creation of a concentration gradient of the injected sample, providing a transient, but strictly reproducible readout of the recorded signal (Hansen and Miro, 2007).

1.10.2.1 Sample Injection

The sample injection defines the volume of the analyte and its initial geometry in the tubular channel. The injected sample (pink) forms a moving zone that reacts with the reagent in the carrier stream (blue) to form a product which gradually disperses towards the detector (yellow) (Figure 1.18).

		Flow Thitingh Datastor
-> -		
	Reagent	
*	Reagent	

Figure 1.18: Formation of Sample Zone on Injection in FIA (Courtesy Ruzicka, 2009)

Increase in injection volume, S_{ν} leads to decrease in dispersion of the analyte sample and as S_{ν} increases, the detector response increases until it eventually reaches a maximum value corresponding to the minimum dispersion case. The relationship between dispersion and injection volume can be expressed by Equation 1.19 (McKelvie, 2008).

- Equation 1.19

$$\frac{1}{D} = 1 - e^{-kSv}$$

D - dispersion
K - constant

 S_v – injection volume

D

If $S_{1/2}$ is the sample volume needed for 50% dilution of the original sample zone concentration i.e. D = 2, it has been shown that

$$S_{1/2} = \frac{\ln 2}{k} - \text{Equation 1.20}$$

Invariably, since steady-state (D=1) conditions are not a necessity for a successful FIA measurement, injection volume greater than $2S_{1/2}$ are rarely required. Therefore, varying the injection volume has been a convenient way of selecting the dispersion of injected sample in a FIA manifold.

1.10.2.2 Sample Dispersion

The dispersion of the injected sample and hence its degree of dilution is expressed by the dispersion coefficient (D) Equation 1.21 (Ruzicka and Hansen, 1975).

$$D = \frac{C^o}{C^{\max}} - \text{Equation 1.21}$$

 C^{o} = Original concentration

 C^{max} = Maximum concentration of the sample zone after undergoing all the dispersive processes and passing through the detector.

Dispersion is proportional to the radius of the conduit through which the injected zone travels (Valcarel and Luque de Castro, 1987). As the injected zone moves downstream it disperses, forming a concentration gradient that can be taken as a continuum of concentration segments of individual concentrations with the segment situated at the peak apex (C^{max}) being the one on which peak height measurement and calibration is based (Ruzicka, 2009). Dispersion in flow injection analysis could be grouped into three main categories. These include limited dispersion (1<D<3) which are useful in detection systems where minimal sample dilution is desirable such as ion-selective electrodes and atomic spectroscopy; medium dispersion (3<D<10) used when significant sample and reagent mixing is required as in spectrophotometric detection; large dispersion (D>10) used when extensive dilution of sample and reagent are needed (McKelvie, 2008). Nevertheless, for FIA systems, medium dispersion is recommended because sample and reagent mixing is important to promote the degree of colour formation. Other variables that influence dispersion in a FIA system include geometry of the manifold, length of the tubing used (D = k \sqrt{L} , where L is the length of the conduit or tube, and flow rate. In multiple line flow injection systems, dispersion is also affected by dilution effect of each of the contributing input streams of reagents i.e. for a carrier stream, Q_c, and contributing reagent streams R₁, R₂,.....Rn, the dilution factor is given as shown in Equation 1.22.

Dilution factor =
$$\frac{Q_c + Q_{R_1} + Q_{R_2}....+ Q_{R_N}}{Q_c}$$
 - Equation 1.22

Dispersion increases as flow rate increases to a maximum value at about 4 mL min⁻¹ and thereafter decreases at 4 - 8 mL min⁻¹ (Li and Ma, 1995). However, flow rate may have no effect if other manifold variables are held constant (Karlberg and Pacey, 1989)

1.10.2.3 Reproducible Timing

Reproducible timing is a key catalyst of the high success recorded by FIA since its inception. It refers to the precise timing of the manipulation to which the injected sample zone is subjected in the system, from the point of injection to the point of detection (i.e. the so-called controlled, or rather controllable, dispersion) (Hansen and Miro, 2007). Since the flow of the moving stream is controlled by a propelling device, the timing or residence time of each cycle of analysis is highly reproducible unlike in manual procedures that are subject to various variables including those by the analyst.

These three cornerstones have made FIA a versatile analytical tool that could be used for the automation of virtually all wet chemical analyses. The second generation of flow injection analysis called sequential injection analysis (SIA) took this success a further step through the incorporation of computer controlled system based on the use of multi-positional valve from the ports of which individual, precisely metered zones of sample and reagents are aspirated sequentially by means of a syringe pump and stacked in a holding coil and then subsequently, under dispersion within each other, are forwarded to a suitable detector (Hansen and Miro, 2007). The use of sequential injection analysis (SIA) in the determination of phosphorus has become more successful than other subsequent generations of flow injection analysis practically due to the substitution of the injection valve (as used in FIA) with a selection valve which enables the introduction of sample and reagents sequentially into the holding coil such that they are impelled through the reactor coil towards the detector by a piston (Estella and Cerda, 2005). The SIA improved savings on reagents and reduced the volume of waste generated compared to the FIA. Recent generation of continuous flow systems such as the lab-on-valve system and bead injection and other adapted variant have further enabled the downscaling of flow injection analysis. Continuous flow analyses have found wide application in the determination of physico-chemical parameters such as dissolved oxygen, DO (Sakai *et al.*, 2001), biochemical oxygen demand, BOD (Preininger and *et al.*, 1991), chemical oxygen demand, COD (Balconi *et al.*, 1992) and other water quality indices (Miro *et al.*, 2004a); base metals and potentially toxic metals through various hyphenated techniques (Miro *et al.*, 2004b) and much more extensively for nutrient determinations (Estela and Cerda, 2005 and Miro *et al.*, 2002) since their analyses are mostly by wet chemistry thus likely pose lesser challenges in converting the manual procedures to a FIA manifold based systems.

1.11 THE LAGOS METROPOLIS

The Lagos Metropolis is part of the territorial land mass referred to as Lagos State with a low-lying coastal region of about 180 km coastline on the most southwestern part of Nigeria. It possesses the characteristics of an uncompleted delta formation for upstream rivers such as Ogun, Oshun and Yewa Rivers from neighbouring and upland States to discharge through a network of freshwater creeks and lagoons into the Atlantic Ocean (Akinsanya and Ogunbambi, 2010). The largest of these lagoons is the Lagos Lagoon. The Lagos Lagoon covers an area of >6000 km² and is the main pollutant sink for metropolitan Lagos as it receives unregulated and mostly untreated industrial and domestic effluents, sewage dumping and various other diffuse discharges. Lagos has a littoral type of climate with highest mean monthly and annual rainfall amounting to 450 mm and 1850 mm respectively.

The strategic economical, industrial and political role of Lagos in Nigeria makes it a hub of diverse activities which in turn requires supporting infrastructures among which is a good road network. As at 2006, Lagos has a road network density of about 0.4 kilometres per 1000 population (against a population density of 2,520 people per km²) which is far higher than the national average density of 152 people per km²) (Ogunleye and Awomosu, 2010). This road network density is quite low in comparison to other major cities around the world. The network's efficiency is similarly low, with a limited number of primary corridors carrying the bulk of the traffic. Inadequately designed interchanges, where they exist at all, provide only partial access to the primary network and many tertiary roads play the roles of secondary ones (LAMATA, 2014). As a result, these tertiary roads or highways experience daily high traffic volume.

The lack of intra city mass transit system over the years has resulted in a chaotic public transportation system which is mainly driven mainly by private individual ownership. The buses used were rickety and sometimes smoky but in recent years, the creation of agencies such as Lagos Metropolitan Area Transport Authority (LAMATA), Lagos State Traffic Management Agency (LASTMA) and the strengthening of the Vehicle Inspection Department have brought some order into the system. Nevertheless, rapid urbanisation combined with poorly executed developmental plans have given rise to numerous transportation problems such as traffic congestion, increasing rates of traffic related emission and atmospheric pollution among others (LAMATA, 2014). The fact that most roads in Lagos are bridged to transverse the numerous canals and creeks in the metropolis also introduce the possibility of surface water pollution from runoffs on these roads since there are no consideration for runoff water treatment when these roads were constructed.



Figure 1.19: An Aerial View of the Lagos Metropolis

1.12 STATEMENT OF PROBLEM

Although extensive studies have been conducted on agricultural runoffs, only limited studies on runoffs have been conducted or are being conducted predominantly or exclusively on roadway or highway runoffs (Buckler and Granato, 1999; Kayhanian, *et al.*, 2008). Hall and Anderson (1988) and Karouna-Renier and Sparling (2001) reported that the most common contaminants in urban highway runoff include heavy metals, petroleum hydrocarbons, pesticides, sediments and nutrients. Similarly, Pitt *et al.* (1995) and Marsalek *et al.* (1999) also reported that road runoffs contained pollutants with greater toxicity than other runoff types.

The Lagos Lagoon serves as the main pollutant sink of the emerging mega city of Lagos, the industrial and commercial hub of Nigeria with an estimated population of 15 million people. Thus, Lagos Lagoon receives discharges from point and non-point (diffuse) sources which contain a diverse range of pollutants such as potentially toxic metals, PTMs (Okoye, 1991; Oyeyiola *et al.*, 2011; Olayinka and Alo, 2004); polyaromatic hydrocarbons, PAHs and polychlorinated biphenyl, PCB (Adeyemi, *et al.*, 2008; Oluseyi *et al.*, 2012; Alani *et al.*, 2012a); bioaccumulative and toxic (PBT) micropollutants (Alani *et al.* 2012b); anionic nutrients, chiefly phosphorus and nitrate (Ebiare and Zejiao, 2010) among others. While point discharges including direct pumping of industrial effluents and dumping of sewage along the course of the Lagoon have been identified as the sources of anionic nutrients and PTMs in the Lagoon (Adebayo *et al.*, 2007; Ebiare and Zejiao, 2010), input from runoffs especially highway runoff have largely remained un-investigated.

There is a dearth of any reliable data on the levels of the PTMs and the anionic nutrients such as phosphates and nitrates discharged into the Lagos Lagoon from highway runoff and the contribution of these nutrients to the pollutant level and sedimentary pool of the Lagoon. Also, in view of the annual infestation of *Eichhornia crassipes* (water hyacinth) and other aquatic weeds on the Lagos Lagoon, the need to understand the biogeochemical cycle of the anionic nutrients has become a challenge towards possible ameliorative and control strategies aimed at eradicating the weeds (Adewolu *et al.*, 2009).

In Lagos, as in most Nigerian towns and cities, many roads are un-tarred and roadside soils and sediment are therefore a permanent feature and a significant vector for pollutant transport to catchments, particularly during runoff events in the rainy season. PTMs and anionic nutrients can be transported in different phases during these runoff events into the receiving environment. Considering the fact that Lagos has a relatively high number of highways and bridges which directly or indirectly channel highway runoff into the Lagos Lagoon, the need to investigate and correctly assess the contribution of these contaminants to the pollution level of the Lagos Lagoon has since become an imperative. Currently, there is no researched study on highway runoff input into the Lagos Lagoon.

Studies on anionic nutrient species and their role in water pollution in Nigeria especially of the Lagos Lagoon's annual water hyacinth infestation have been sparse. Studies so far on anionic nutrients distribution in Nigerian water bodies have been based on the open vessel classical methods. These are fraught with quality control and quality assurance challenges. These challenges include inconsistent reaction time for analyte determinations and exposure of reaction to contaminants as a result of the wholly manure handling of reagents. Thus data which are sometimes not reproducible are obtained. Therefore, there is a need to examine the semi-automatic continuous flow methods of analysis for anionic nutrient studies in highway runoff and roadside soils since these techniques have proven to be highly sensitive, more reliable and robust with high sample throughput (Omaka et al., 2007). Studies on runoffs could sometime require the collection of large number of samples especially when the variability of pollutant with respect to storm duration needs to be investigated. In such an instance, analytical tool with high sample throughput like the continuous flow techniques is desirable. The potential for in situ measurements also makes continuous flow technique aa attractive analytical tool for highway runoff studies since real time data collection will afford for larger number of determination and further reduce potential risks of contamination during sample transport to the laboratory.

1.13 AIMS AND OBJECTIVES OF THE STUDY

This study sought to evaluate the levels and dynamics of PTMs and anionic nutrients distribution in highway runoff and roadside soils and also to evaluate their impacts on the receiving Lagos Lagoon catchments. The specific objectives of the study included:

- i. Investigation of the water quality of highway runoff from some selected major highways in the Lagos metropolis.
- Determination of the levels of some potentially toxic metals (PTMs) in atmospheric fallout, runoff and roadside soils from selected major highways in the Lagos metropolis and their possible effects on the Lagos Lagoon.
- iii. Determination of the seasonal concentration of total and bioavailable phosphorus and nitrates in roadside soil among other nutrients in the Lagos Lagoon sediment and its implication on the eutrophication process of the Lagoon.
- iv. Development, optimisation and validation of a customised flow injection analysis system for the determination of phosphorus in runoff water and roadside soils.

1.14 SCOPE/LIMITATION OF STUDY

The scope of the study includes:

- The collection of samples and determination of the physico-chemical parameters, PTMs and anionic nutrients concentrations of highway runoff samples obtained during the first 10 to 20 minutes of the commencement of rainfall at the designated sites on the three identified highways; A, Mile2–Oshodi Highway (Lagos Mainland);
 B, Mile2-Wharf Highway (Lagos Mainland); and C, Ijora-Marina- Ahmadu Bello Road (Lagos Mainland to Lagos Island).
- ii. Collection and determination of the physico-chemical parameters, PTMs' concentration and anionic nutrients concentrations of roadside soil samples from the designated sites on the highways during the rainy and dry seasons.
- iii. Collection and determination of the PTM and anionic nutrient concentrations of sediment samples at selected highway watersheds on the Lagos Lagoon.

- iv. Determination of the PTMs using atomic absorption spectroscopy (AAS) and induction coupled plasma techniques (ICP-OES and ICP-MS). The determination of the anionic nutrients using air segmented continuous flow analysis (ASCFA) and a customised and optimised flow injection analysis (FIA) system.
- v. The development of a customised and optimised flow injection analysis system (FIA) for phosphate determination in highway runoff and roadside soil samples.

The limitations encountered in the study include:

- i. The unpredictability of rainfall which made highway runoff samples difficult to collect and the first flush samples even more difficult to obtain. Although, this could have been solved by the deployment of passive runoff samplers, which however were not readily available and if deployed could easily have been vandalised.
- ii. Inability to simultaneously collect highway runoff samples at all the designated sites since sampling was carried out manually.

1.15 SIGNIFICANCE OF STUDY

In view of the need to continuously monitor and devise control measures for chemical inputs into surface water to sustain their economic potential, the study was designed to provide detailed data on the water quality of Lagos metropolis highway runoffs and the likely impact of these runoffs and roadside soils on the Lagos Lagoon. Specifically, the study was tailored to determine the levels of PTMs and phosphorus concentration in roadside soils and their possible contribution to the sedimentary pollutant pool of the Lagos Lagoon.

The study was conceptualised to provide details on the possible contribution of roadside soils to the phosphorus cycle, an often neglected part of the phosphorus biogeochemical cycle. More importantly, the study will for the first time, develop an optimised FIA system for the determination of phosphorus in runoff geared towards the improvement of analytical chemistry skills on the use of flow injection analysis (FIA) for the continuous monitoring of phosphorus and nitrates in the Lagos Lagoon thus providing a better understanding of the eutrophication process of the Lagoon.

1.16 RESEARCH QUESTIONS AND PRESENT STUDY

The study will attempt to answer the following research questions;

- i. What is the water quality of runoff from Lagos highways?
- ii. What are the seasonal concentrations of PTMs and anionic nutrients in the highway environment in Lagos metropolis?
- iii. Is there any relationship between the nature and levels of PTMs and selected anionic nutrients in the runoff, roadside soils and the Lagos Lagoon sediment?
- iv. Are roadside soils a potential contributor to the nutrient pool of the Lagos Lagoon?
- v. Can Flow Injection Analysis (FIA) be used for the determination of phosphorus in runoff and roadside soils?

1.17 OPERATIONAL DEFINITION OF TERMS

Air segmented continuous flow analysis (ASCFA): A first generation of continuous flow analysis whereby bubbles are used to segment the flowing stream of reagents and samples to improve mixing.

Algal bloom: A rapid increase or accumulation in the population of algae in an aquatic system which is usually instigated by nutrient enrichment of the water body.

Atmospheric deposition: The solid, liquid, and gaseous materials deposited processes under gravity. It could be divided into two categories – wet deposition (rain, sleet, and snow) and dry deposition also called atmospheric fallout or settleable particulates and aerosols.

Bioavailable pollutant: Pollutant determined after filtering a sample through 0.20 or 0.45 μ m filter. It is equated to the fraction of pollutant that could be directly assimilated by plants.

Eutrophication: An increase in the concentration of nutrients such as nitrogen and phosphorus in a water body which invariably leads to an uncontrollable growth in algal and other vegetative growth.

Extractant: A liquid chemical used for removing or separating a substance from its liquid or solid matrix. It serves as a means of separating hazardous contaminants from soils, sludges, and sediments.

First flush: The delivery of a disproportionately large concentration of constituents or pollutants during the early part of the runoff event.

Flow Injection Analysis (FIA): A continuous flow technique which is ideally suited to rapid automated analysis of liquid samples. It is based on three principles of reproducible timing, defined sample injection and controlled dispersion.

Hypoxia: Depletion of the concentration of dissolved oxygen in the water column from what can be near 9 mg L^{-1} (roughly the maximum solubility of oxygen in estuarine water on an average summer day), to below 2 mg L^{-1} which profoundly affect the health of an ecosystem and cause physiological stress, and even death, to associated aquatic organisms.

Inductively coupled plasma-mass spectrometry: A mass spectrometer in hyphenation with an inductively coupled plasma capable of detecting metals and several non-metals at very low concentrations through the ionization of the sample by plasma heating and subsequent separation to ions by the mass spectrometer. **Limiting nutrient**: A nutrient, whose concentration in the environment of an organism, determines the growth and productivity of that organism.

Manifold: The assemblage of flow tubing, mixing coils, injection valve, detection device and other necessary device in a given configuration used in a flow injection analysis system.

Potentially toxic metals (PTMs): A term used to describe metals which are likely to induce toxicity or biochemical disruptions. This phrase is used in lieu of terms such as "heavy metal", "toxic metals" and "trace metals" which could be ambiguous in certain context (Duffus, 2002).

Reference material: A material for which component values have been certified by a technically valid procedure and is accompanied by or traceable to a certificate or other documentation issued by a certifying body (Worsfold *et al.*, 2005).

Runoff: A water flow that occurs from rain, snow melt, or other sources when the soil is water saturated or over an impervious surface eventually merging with a larger water body. A runoff could be a nonpoint source of pollution if it picks up pollutants along its course.

Total phosphorus: Aggregate sum of organic and inorganic phosphorus fractions in a sample. It is usually determined after the oxidation of the sample using strong oxidising agents.

CHAPTER TWO

LITERATURE REVIEW

2.1 ENVIRONMENTAL IMPACTS OF URBAN RUNOFFS AND ROADSIDE SOILS

Increasing industrialization and human activities coupled with an increasing level of imperviousness of urban areas have continued to generate pollutants that contribute to the degrading quality of urban runoff water (Joshi and Balasubramanian 2010). Pollutants from impervious surfaces such as rooftops and roads are transported by diffuse mechanisms into the receiving environment. Such runoffs arrive in the recipient water bodies without passing through any treatment plants (Crabtree et al., 2006; Lee et al., 2011; Terzakis et al., 2008). The negative impacts of such runoffs on surface water quality due to the toxic pollutant loads in the runoff have been investigated and reported by Wei et al., (2010) and Lee et al., (2011). Runoffs carry large pollutant loads, exerting a great influence on the receiving environment, mostly water bodies (Characklis and Wiesner, 1997) and thus enable important diffusion mechanisms for such toxic pollutants (Jartun et al., 2008). The US-EPA (1998) has identified urban runoff as one of the leading causes of degradation in the quality of receiving waters (Boxall and Maltby 1995; Perdikaki and Mason 1999; US-EPA 1998; USGS 1998) with grave implication to the aquatic organisms in such waters especially at the watershed of the roads (Karouna-Renier and Sparling, 2001; Lee et al., 2004; Dorchin and Shanas, 2010). The US FHWA (1996) had reported that diffuse pollutants' inputs into receiving water are greatly enhanced by the level of the imperviousness of the catchment area of the water body.

2.2 POLLUTANTS IN HIGHWAY RUNOFF AND ROADSIDE SOIL

Davies *et al.* (2001) reported that the sources of pollutants in highway runoff are numerous, resulting in the introduction of a diverse range of pollutants to the highway environment. As reported by Patel (2004) and based on the identified variables by Gupta *et al.* (1981) these sources could broadly be classified into different categories thus; temporary (e.g. road maintenance policies such as sweeping, de-icing, chemical based vegetation control, age and

condition of vehicles etc); permanent (e.g. traffic intensity, percent pervious and imperviousness of catchment area, surrounding land usage); seasonal (e.g. climatic conditions including precipitation, atmospheric deposition, wind intensity etc); accidental or acute effects (e.g. hazardous chemical spillage); and chronic effects (e.g. tyre wear).

Some of the contaminants from highway runoff include potentially toxic metals such as zinc (Zn), lead (Pb), cadmium (Cd), copper (Cu), nickel (Ni), chromium (Cr), Manganese (Mn), iron (Fe), vanadium (V) among others (Sansalone and Buchberger, 1997; Al-Chalabi and Hawker, 2000; Adachia and Tainosho, 2004; Turer 2005; Abayomi *et al.*, 2006; Westerlund and Viklander, 2006; Khan *et al.*, 2011); ionic species such as sodium (Na⁺), potassium (K⁺), calcium (Ca²⁺), ammonia (NH₄⁺), phosphorous (P), nitrate (NO₃⁻), chloride (Cl⁻) etc (Mangani *et al.*, 2005; Withers and Jarvie 2008); organics such as polycyclic aromatic hydrocarbons (PAH), volatile organic compounds (VOCs), polychlorinated biphenyls (PCBs) (Colwill *et al.*, 1984; Hewitt and Rashed, 1990; Chebbo *et al.*, 2001; Rossini *et al.*, 2005; Jartun *et al.*, 2008;); and sediment including total suspended solids (Horowitz, 1995; Maltby *et al.*, 1995; US-EPA, 2000; Li *et al.*, 2005; Kayhanian *et al.*, 2007). Alo *et al.* (2007) reported that Zn, Pb, Cu, Cd and Cr are present in the highway runoff from a major highway in Lagos, Nigeria. These pollutants described as road-derived sediments (RDS) by Rijkenberg and Depree (2010) have been found to have originated from a complex mixture of anthropogenic and natural materials (Robertson *et al.*, 2003; Tuccillo, 2006).

Various workers have identified vehicular activities and its variables such as average daily traffic, ADT (Yousef, 1985) and cumulative vehicles during rain event (Chui *et al.*, 1982) as the main contributor of these pollutants to the highway environment and eventually their introduction to the roadside soils and surface waters (Driscoll *et al.*, 1990; Barrett *et al.*, 1995; Barrett *et al.*, 1998; Drapper *et al.*, 2000; van Bohemen and Janssen Van-De-Laak, 2003; Lee *et al.*, 2005; Dorchin, 2007; Robertson and Taylor 2007; Dorchin and Shanas 2010). Antecedent dry period and rainfall intensity were identified by Alo *et al.* (2007) as the factors which affected the concentrations of PTMs observed from highway runoff of Ikorodu road in Lagos, Nigeria. Christensen and Guinn (1979) had shown that a 15cm wide and 65cm diameter tyre contributes about 3.0 mg of Zn (as well as other metals) to road surfaces and their immediate environments on the assumption that 1cm of the vulcanized rubber material is worn off for every 32,000 km drive. This assertion was also reinforced by

Callender and Rice (2000) who stated that a significant amount of zinc is released onto the road surfaces from the ZnO components of tyres through wear and abrasion.

In a study of the contribution of brake pads to levels of PTMs in runoff from Santa Clara valley, USA, Armstrong (1994) revealed that as high as 15% Cu, 5.1% Zn and 2.2% Pb wt/wt are released from brake pads. Legret and Pagotto (1999) and von Uexkull *et al.*, (2005) had also highlighted the contribution of vehicle brake pads to the levels of PTMs in highway runoff.

Garnauld *et al.*, (1999) reported that wet and dry atmospheric depositions onto impervious urban surfaces significantly contribute to the contamination of urban runoff and also play an important role in the geochemical cycle of these pollutants and contamination of the receiving ecosystems. However, Harned (1988) posited that dry deposition provides a substantial mechanism for removing pollutants from atmosphere and represents a larger deposition flux of many contaminants than wet depositions (Colman *et al.*, 2001). Gupta *et al* (1981) identified solids, nutrients, potentially toxic metals, and organics as pollutants that may be contributed to highway surfaces by dry deposition from background and pollution sources. Olayinka and Alo (2001) reported Pb concentration of up to 6000 μ g g⁻¹ in street dust (which is derived mainly from dry depositions) from Nigerian roads.

Wu *et al.* (1998) in a study in North Carolina reported that up to 20% TSS, 70-90% nutrient (N and P) loadings and 10-50% of other constituents in highway runoff and roadside soil could originate from atmospheric depositions (UK-IHT 2001) with anthropogenic activity suggested as the major source of the nutrient depositions (Bergametti *et al.*, 1992; Tsukuda *et al.*, 2005). Lee *et al.* (2011) concluded that the most common non-point pollutants from highway (apart from PTMs) are sediments and nutrients. While sediment is derived from road dust and organic matter debris aggregated to other contaminants, nutrients especially phosphate and nitrates are derived from litters, animal droppings, fuel additives which contains compounds such as tricresyl phosphate and other organically bound phosphorus. Lee and Bang (2000) and Taylor *et al.* (2005) have highlighted the contribution of runoff to the eutrophication of receiving waters. Davis *et al.* (2001) also pinpointed road runoff as a major contributor of suspended sediments and associated contaminants to urban storm water.

2.3 MOBILISATION AND PARTITIONING OF POLLUTANTS IN RUNOFF, ROADSIDE SOIL AND RECEIVING WATER

Sansalone and Buchberger (1997) observed that pollutants such as PTMs, nutrients and solids are transported directly from the highway environment by lateral pavement sheet flow of runoff. While dissolved nutrients and metals are easily mobilised into the target water for quick assimilation by biota, Ashworth and Alloway (2008) informed that others adsorbed on dissolved and suspended organic matter are less mobile but could also be transported to receiving water via physical mobilization during runoff events (Zhang and Zhang, 2010) such as wind-blown dust (Turer, 2005) or by splash and particulate transport (Backstrom et al., 2003). Shaheen (1975) opined that concrete surface can yield high levels of Pb and Zn compared to an asphalt surface (Ellis and Revit, 1981). Lee et al. (2005) concluded that the mobility and bioavailability of these pollutants are a function of their partitioning within the various phases of the rain event. Breault and Grenado (2000) also highlighted some factors determining the partitioning of pollutants mobilized and transported from the highway, through drainage systems, and eventually into receiving waters and aquatic biota. These factors according to Benke et al. (1999) and Bricker (1999) include pH, ionic strength, temperature, hardness (base cations), anions, suspended sediment, redox potential amongst others. Nevertheless, Kalbitz and Wennrich (1998), Akerblom et al. (2008) and Ashworth and Alloway (2008) identified dissolved organic matter (DOM), which consists of the refractory organic substances, humic and fulvic acids derived from plants and animal degradation and account for a small proportion of the total organic matter, as the main carrier of pollutants ranging from nutrients to toxics such as PTMs and nutrients.

Petterson *et al.* (1993) clarified that these pollutants bind strongly and specifically to the functional groups, mainly carboxyl, carbonyl, and phenolic OH groups, of the DOM molecules. The DOM-pollutant complexes so formed can then easily move to streams and other water sources through surface transport such as runoff or via leaching. While Jordan *et al.* (1997) and Impellitteri *et al.* (2002) reported that Pb and Cu form strong complexes with DOM resulting in a slower mobilization through the partitioned phases, Yin *et al.* (2002) suggested that Zn has a lesser tendency to form complexes with DOM and thus are easily

mobilized into the receiving water. Joshi and Balasubramania (2010) put the rate of mobilization of the three principal PTMs in runoff studies as Zn>Cu>Pb.

Yu et al. (2006) and Gao et al. (2009) while discussing the mobilisation of P in receiving water stated that the rainfall characteristics, slope of the terrain, soil type and antecedent moisture status determine the contact time with which the nutrient is mobilised (Yang *et al.*, 2010). The subsequent mobilisation of nitrogen and phosphorus from soil to surface runoff was described by Hooda et al, (2000) who reported that the impact of raindrop on the soil surface produces a thin soil-water inter-phase where turbulent mixing takes place with release of anionic nutrient by dispersion and diffusion into overland flow. Phosphorus as dissolved P in runoff originates mainly from the desorption of P in the surface soil during wet periods (Ng-Kee-Kwong et al., 2001). In the receiving water, Berkheiser et al. (1980), Bostrom (1984), De Montigny and Prairie (1993) and Redshaw et al. (1990) listed temperature, pH, reduction of Fe³⁺ to Fe²⁺ among other factors controlling the release of phosphorus in the water phase (Perkins and Underwood, 2000). Hart et al. (2004) and Quinton et al. (2001) highlighted the influence of transport factors and erosion on phosphorus movement in runoff with an increase in particulate phosphorus observed with increasing runoff and erosion induced by greater rainfall intensities (Shigaki et al., 2007). Sharpley (1985) reported an increased of runoff P from soils in Oklahoma and Texas with increase of rainfall from 2.7 to 14.2m. Davidson et al., (1994) concluded that the toxicity and biotransformation of pollutants' depend on the degree of their distribution in dissolved and particulate phase which also determine their level of environmental mobility.

2.4 ENVIRONMENTAL EFFECTS AND TOXICITY OF HIGHWAY RUNOFF AND ROADSIDE SOIL

Withers and Jarvie (2008) posited that aquatic ecosystems become impaired when as little as 10-15% of catchment area is occupied by impervious surfaces and depending on the nature and characteristics of the road, the intensity of the runoff event and the receiving water body or ecosystem, Opher *et al.* (2009) and Helmreich *et al.*, (2010) argued that pollutants in highway runoff may exert an acute or chronic impact on the receiving environment. While Forman and Alexander (1998) and Beasly and Kneale (2002) observed that among the many constituents of road runoff, heavy metals are of major concern due to their persistence and

bioaccumulation in living tissues, resulting in higher concentrations at top levels of the food chain. Turner *et al.* (2002), Monbet *et al.* (2009) and Dodds (2006) have pinpointed nutrients from runoff, especially around agricultural intensive areas, as effecting greater impact on the receiving water resources through eutrophication.

Erel (1998) found that roadside soils serve as sink for pollutants with toxics being able to bind strongly to the soil once trapped, and calculated a residence time in the soil to be greater than 100 years for some of these pollutants (Turer and Maynard, 2003). Flegal et al. (2005) in reviewing the long-term trends in metal contamination of US San Francisco Bay, indicated that leaded fuel was the primary source of Pb in the bay sediment. Also, Li (2006) confirmed elevated lead level in Canadian roadside soil well after the phase-out of leaded automotive fuels (McKenzie et al., 2009). Dilek and Maynard (2003) stated that contaminated roadside soil and highway runoff may constitute a health hazard if the metals are transferred to other reservoirs such as a water system as they serve as a significant unsuspected source of contamination in the waters. Sutherland et al. (2000) and Sutherland and Tolosa (2001) have shown in studies conducted in Manoa Basin, Hawaii that Cu, Pb and Zn have significant anthropogenic enrichments and that the contaminated soil particles can be washed into proximate water bodies (Turer and Maynard 2003). This situation was said to progressively impact negatively on the water body (Li-qing et al, 2007). Though Bhatia and Choudhri (1991) and Ubogu and Essoka (2006) showed that any effect on the receiving environment is inversely proportional to its distance and depth from the road surface, Turer et al. (2001) concluded that the pollutants can still be sufficiently mobilized with the aid of organic matter during rainfall events.

Dorchin and Shanas (2010) reported that metals' lethal effect on fish has been observed as far as 8 km downstream from a runoff outlet. The toxicity of highway runoff on aquatic organisms was highlighted by Birdsall *et al.* (1986) where high concentration of Pb was reported in tadpoles exposed to highway runoff in eastern US. Also, Blaustein and Kiesecker (2002) showed that the combination of polycyclic aromatic hydrocarbons (PAHs) in runoff with sunlight UV-A radiation were extremely toxic to tadpoles. Lee *at al.* (2004) reported similar toxicity on the DNA of shrimp grass in the highway runoff sediment receiving estuary of the Gulf coast of United States.

2.5 DETERMINATION OF PTMS AND ANIONIC NUTRIENTS IN HIGHWAY RUNOFF AND ROADSIDE SOILS

Determination of PTMs and nutrients in runoff and roadside soils samples has mainly been determined by flame atomic absorption spectrophotometry, inductively coupled plasma spectrometry (ICP), and colorimetric procedures respectively. While ICP could be used for multi-element analysis including metals and non-metals such as phosphorus, colorimetric procedures are usually used for the determination of anionic nutrients such as phosphate and nitrate. The instrumentation used for the determination of PTMs has been gradually shifting from flame techniques to ICP due to the latter's higher sensitivity.

Determination of phosphorus which is traditionally carried out using colorimetric procedures are now being done by ICP. The possibility that P concentrations in extracts, digests, and water samples might be different when measured with inductively coupled plasma spectrometry (ICP) as compared to colorimetric procedures has been debated since the introduction of ICP instrumentation. The ability of ICP to measure several elements simultaneously has increased interest in multi-element extracts for routine soil testing and likely reduced the use of the colorimetric approach. However, colorimetric procedures offer some advantages, such as increased sensitivity and lower instrumentation costs, and it is unlikely that ICP will completely displace colorimetric procedures. The commonly held belief is that ICP would measure greater P concentrations than colorimetric procedures because the high temperature environment of the plasma would allow the measurement of organic P compounds or other soluble P complexes that would not be measured colorimetrically though some reports suggest that this may not be so (Pierzyski, 2005). For example, while Jacoby (2005) discovered that colorimetric P was 55% of the P determined by ICP, Wolf et al. (2005) and Choate (2004) reported that extracts of manures contained about 7% and 13% more P by colorimetric determinations than by ICP methods.

Pittman *et al.* (2005) compared ICP and colorimetric P determination in Mehlich 3 extracts of 6400 soil samples from Oklahoma and found a significant correlation between the two methods with the difference between the two methods greater when considering only soils with <60 mg kg⁻¹ M3 extractable P. The results indicate that P concentrations determined colorimetrically will be 80 to 90% of those determined by ICP. The difference between the two methods was proportionally larger when the extractable P concentration in the soil sample was low (<20 mg kg⁻¹) (Pierzynski *et al.*, 2005).

Mallarino (2003) also found P greater with ICP measurement compared to the colorimetric approach. Differences were large as indicated by a larger intercept and smaller slope (0.779), and the differences were also proportionally larger at low P values. Sikora *et al.* (2005) found the slopes of correlations between ICP and colorimetric P determination in M3 extracts of Kentucky soils were much closer to 1 (1.02 and 0.968 for two data sets) as compared to the results of Pittman *et al.* (2005) and Mallarino (2003). All in all, more reports seem to agree that in P determination, ICP gives better results than those reporting the reverse in favour of colorimetry.

2.6 DETERMINATION OF PHOSPHORUS BY FLOW INJECTION ANALYSIS (FIA)

Flow analysis chemical methods were first introduced in mid nineties (Trojanovic, 2000) and were aimed to mechanize and automate, in simple and practical way, the steps of analytical methodology by confining the handling and reactions of chemical solutions within flowing systems incorporated with a detector (Ruzicka, 1991; Estela and Cerda, 2005). The first generation of these techniques is the segmented flow analysis which involves the inclusion of air bubbles into the flowing stream to enhance the mixing of the flowing fluid in the conduit (Skeegs, 1957). Flow injection analysis proposed by Ruzicka and Hansen (1975) using the Murphy and Riley's molybdenum blue method has proven to be hugely popular and successful in the determination of phosphorus. It involves the injection of a fixed volume of liquid phosphate containing sample into an un-segmented carrier stream of reagents flowing through a narrow tube or conduit to produce the reactive or detectable species measurable by the flow-through detection device placed downstream of the flow (Kolev and McKelvie, 2008). The advantages of flow injection include its high reproducibility of results, relative simplicity and high sample throughput and low reagent consumption (Valcarel and Casro, 1987; Benson *et al.*, 1996).

2.6.1 Optimisation of Flow Injection Analysis Manifold.

Over the years, the sensitivity of this technique and method have been improved by the optimization of the operating pH, reaction temperature, reagents' concentration, especially

the [H+]/[Mo] ratio, and the use of different manifold designs, and modification of the detector design (Valcarel and Casro, 1987; Drummond and Maher, 1995; Zhang *et al.*, 1999). In optimizing a four channel FIA manifold for phosphorus determination in water of the Tamar Estuary, UK, Omaka *et al.* (2007) used a [H+]/[Mo] ratio of 70 at a reaction temperature of 30°C to achieve a practical limit of detection of 2 μ g L⁻¹ P.

Drummond and Maher (1995) in optimising the conditions of automation of the Murphy and Riley method using flow-injection analysis reported that optimum colour formation occured at $[H^+]/[MoO_4^{2^-}]$ ratios between 50 and 80 at all pH values investigated (0.36 - 1.06). The maximum rate of formation occurs at a $[H^+]/[MoO_4^{2^-}]$ ratio of 70 within a pH range of 0.57 - 4.88 when an antimony concentration > 0.06 mM and ascorbic acid concentration > 0.009 M in the final solution are used. Full colour development occurs within 0.8 - 1 min. The results of the study indicated that by suitable selection of reagent conditions, rapid chromophore development can be achieved.

Grudpan *et al.* (2002) suggested the use of a manifold which had molybdate reagent and ascorbic acid streams pre-merged before the injection of the phosphate sample as opposed to a manifold which had the sample introduced into the molybdate stream before being merged with the reducing ascorbic acid reagent stream. In using the former manifold with the premixed stream of molybdate and ascorbic acid, the reactive intermediate of the reduced form of molybdate was readily available and yielded the molybdenum blue faster on injecting the phosphate solution in contrast to the latter manifold which resulted in the formation of a yellow phosphomolybdate that was not as reactive on reduction with the ascorbic acid (Grudpan *et al.*, 2002).

Specific reaction conditions for automated continuous flow analysis of phosphate were optimized with the aim of minimizing coating and silicate interference by Zhang *et al.*, (1999) while ensuring that sensitivity was maintained. It was reported that the use of Sb in the reagent increases sensitivity and gives absorbances with little temperature dependence. Coating was minimized by using a final solution of pH>0.5. At final pH of 0.78 there was maximum interference from silicate in the sample. It was recommended that for an optimal reaction condition with minimal silicate interference, the use of Sb, a final solution pH of

1.00, room temperature for the reaction and a $[H^+]/[MoO_4^{2-}]$ ratio of 70 should be used (Zhang *et al.* 1999).

2.6.2 Continuous Flow Techniques for Phosphorus Determination

Although, a simple two-channel flow injection system is suitable enough for the determination of phosphorus in water and solid matrix extracts, subsequent generation of FIA such as sequential injection analysis (SIA), lab on valve (LOV), bead injection (BI) (Hansen and Miro, 2007) among other variants of the techniques have also been used to determine phosphate in order to improve on the sensitivity of the FIA method and/or to capture the particulate or organically bound P species that may not have been part of the P determined by the simple manifold systems. Some of the applications of flow injection analysis and its other variants are as presented below.

In eliminating the Schlieren or refractive index (RI) effect in the determination of dissolved reactive phosphorus in estuarine waters, Auflistch *et al.* (1997) used a simple reverse flow injection (FI) manifold with a spectrophotometric detector. Schlieren effect occurs because of the differences in RI between the injected sample zone and the carrier stream which gives rise to a lensing effect that is superimposed on the blank response and causes significant error in quantification. Acidic molybdate was injected into a sulphuric acid carrier stream of the same refractive index and sequentially merged with sample and reductant (ascorbic acid). Reduction of phosphomolybdate to phosphomolybdenum blue was carried out in a coil thermostated at 60 °C. The system was able to determine dissolved reactive phosphorus successfully in estuarine waters with salinities ranging from 0 to 30‰ using calibration standards prepared in deionized water, with a detection limit of 2 μ g L⁻¹ PO₄–P ($r^2 = 0.9998$).

The suitability of FIA for in situ measurement was demonstrated by Lyddy-Meaney, Worsfold *et al.* (2002) in designing and validating a compact flow injection analysis system for surface mapping of phosphate in marine waters of Port Phillip Bay, south eastern Australia. The computer controlled portable system employed gas pressure for reagent propulsion and computer controlled miniature solenoid valves for precise injection of multiple reagents into a flowing stream of filtered sample. A multi-reflection flow cell with a

solid state LED photometer was used to detect filterable reactive phosphate (0.2 μ m) as phosphomolybdenum blue. The system was used to carry out 225 phosphate analyses per hour, exhibiting a detection limit of 0.15 μ M, reproducibility of 1.95 % RSD (n= 9) and a linear response of r² = 0.9992).

In driving the limit of detection further down, a flow injection system with a long path length liquid waveguide capillary cell and solid-state spectrophotmetric detection to determine nanomolar concentrations of phosphate in natural waters was reported by Gimbert, Worsfold *et al.* (2007). A flow injection manifold incorporating a 1m liquid waveguide capillary cell and a miniature fibre-optic spectrometer was used. A limit of detection (blank + 3 S.D.) of 10 nM was obtained using the molybdenum blue chemistry with tin(II) chloride reduction. The sensitivity of the flow injection manifold was improved by 100-fold compared with a conventional 1 cm flow cell. The response was measured at 710 nm and background corrected by subtracting the absorbance at 447 nm. Interference from silicate was effectively masked by the addition of 0.1% (m/v) tartaric acid and results obtained using the system were in good agreement (p = 0.05) with a air segmented continuous flow analyser reference method for freshwater samples containing 1 µM phosphate.

Also using a liquid waveguide long pathlength cell which was connected to a charge coupled device (CCD) spectrophotometer, Neves *et al.* (2008) reported improved sensitivity in a flow injection procedure based on the vanadomolybdate method for the determination of dissolved reactive phosphorus in water samples. Calibration of the system was linear up to 500 μ g L⁻¹ P, with a detection limit of 17 μ g L⁻¹ P and a quantification limit of 56 μ g L⁻¹ P. An injection throughput of 60 determinations h⁻¹ and repeatability (R.S.D.) of 2.2% were achieved.

Grudpan *et al.* (2002) used a microprocessor controlled stopped flow injection analysis technique to simultaneously determine phosphate and silicate using molybdenum blue chemistry. The system was made up of a laboratory-made semi automatic stopped-FI Analyzer with LED-based photometer. The stopped flow mode used enabled kinetic information to be gained about the phosphate-molybdate-ascorbic acid reaction and was suitably validated with a standard method.

A sequential injection analysis that was used to also determine phosphate and silicate simultaneously was reported by Galhardo and Masini (2000). The system was used as a combination of sandwiching the sample zone between reagent zones and flow reversal through an auxiliary reaction coil in a single line. While determining phosphate, the interference of silicate was eliminated by using a reagent composed of 5 mmol L^{-1} ammonium molybdate in 0.2 mol L^{-1} nitric acid, and the interference from phosphate was avoided by adding a 10% (w/v) oxalic acid solution to the reaction zone where the molybdophosphoric and molybdosilicic acids were previously formed, in order to destroy the molybdophosphoric acid while silicate was being determined. The method has a phosphate sampling frequency of 75 h⁻¹, with a linear dynamic range between 0.2 and 7mg L⁻¹ and a detection limit of 0.1 mg L⁻¹ PO₄³⁻ - P.

2.6.3 Application of On-line Sample Treatment in Flow Injection Systems

While the traditional manual techniques and procedures suitable for the determination of nutrients in solid matrices such as roadside soils can still be used in flow based determinations by first extracting the nutrient as total or leachable component with a suitable acid (digestion) or extractant before injecting into the flow based system, the introduction of on-line capabilities for filtration/dialysis, digestion, pre-concentration among other sample treatment procedures have made continuous flow techniques much more attractive for environmental applications. For example, on-line filtration using the 0.2 or 0.45 μ m pore sized filter is particularly useful for determining the bioavaialble or dissolved fraction of nutrients as well as PTMs and also in reducing the time needed for sample treatment and minimizing the risk of contamination in trace analyte determination (Worsfold *et al.*, 2008). On line UV-photo oxidation is a technique that has been widely used for digesting environmental samples on-line, thus eliminating the rigorous and contamination liable manual procedures.

The UV-photo oxidation approach was used by Tue-Ngeun, Worsfold *et al.* (2005) in a proposed flow injection system for rapid sequential determination of dissolved reactive and organic phosphate. The on-line UV photo oxidation was used to digest dissolved organic phosphate (DOP) with detection of the phosphate produced as phosphomolybdenum blue at

690 nm after reduction of phosphomolybdate with tin(II) chloride. With two injections performed in the analysis of each sample: the first of sample solution alone enabled DRP determination, while the second in addition with alkaline peroxydisulphate solutions, under the photo-oxidation conditions used, converted DOP to DRP. The DOP content was evaluated from the difference of the two injections. The digestion efficiency for DOP, evaluated using a range of model organic P compounds of varying stability was greater than 97%. Calibrations were linear over the range of 0.01 – 6.00 mg L⁻¹ P for DRP and DRP + DOP graphs, with a detection limit (3 S.D.) of 0.01 mg L⁻¹ P for both species. Relative standard deviations were 0.3% (n = 11, 0.50 mg L⁻¹ P) for the DRP determination and 1.0% (n = 11, 0.50 mg L⁻¹ P) for the DRP + DOP determination. Injection throughput of 22 h⁻¹ was achieved.

With respect to solid matrices, Peat *et al.* (1997) presented a rapid method suitable for the determination of dissolved organic phosphorus (DOP) in soil leachates and runoff using a flow injection (FI) manifold incorporating an in-line PTFE reaction coil wrapped around a low power UV lamp and based on the spectrophotometric determination of dissolved reactive phosphorus (DRP) and mineralised DOP at 690 nm after reduction of phosphomolybdate to molybdenum blue with tin(II) chloride. A linear range of 0 - 1.5 mg L⁻¹ PO³⁻-P , with a detection limit (3 s) of 7 μ g L⁻¹ and a sample throughput of 40 per hour was obtained. Tolerance to potential matrix interferences in soil pore waters, particularly Al(III), Si(IV), Fe(II) and Fe(III), was achieved using a combination of on-line sample pre-treatment by a strong acid ion exchange column, low photoreactor pH and acid induced control of the kinetics of the molybdenum blue reaction.

Tiyapongpattana *et al.* (2004) demonstrated the applicability of continuous flow extraction procedure for the fractionation of phosphorus. Distribution and mobility of phosphorus in soil and sediment was studied using the extraction scheme of Hieltjes and Lijklema in three certified reference materials (CRMs). The extraction was based on a continuous flow technique and was carried out in a closed chamber through which extractants are passed sequentially. A number of fractions were collected for each reagent for subsequent colorimetric determination. The reported results compared well with those obtained from a batch extraction scheme.

Despite the variable chemical composition of the Hieltjes-Lijklema (HL) extraction procedure, a single Flow Injection set-up was assembled by Buanuam et al. (2006) with no need for either manifold re-configuration or modification of chemical composition of reagents using sequential injection micro-column extraction (SI-MCE) and based on the implementation of a soil-containing micro-cartridge as external reactor in a sequential injection network. The on-line fractionation method capitalised on the accurate metering and sequential exposure of the various extractants to the solid sample by application of programmable flow as precisely coordinated by a syringe pump. Three different soil phase associations for phosphorus, that is, exchangeable, Al- and Fe-bound, and Ca-bound fractions, were elucidated by accommodation in the flow manifold of the three steps of the Hieltjes-Lijklema scheme involving the use of NH₄Cl, NaOH and HCl, respectively, as sequential leaching reagents. The precise timing and versatility of SI for tailoring various operational extraction modes were utilized for investigating the extractability and the extent of phosphorus re-distribution for variable partitioning times. Automatic spectrophotometric determination of soluble reactive phosphorus in the soil extracts was performed by a flow injection (FI) analyser based on the molybdenum blue chemistry. The 3S.D. detection limit was 0.02 mg L^{-1} P, while the linear dynamic range extended up to 20 mg L^{-1} P regardless of the extracting media.

Using the same Hieltjes–Lijklema extraction scheme, Buanuam et al. (2007) proposed a fully automated flow-through microcolumn fractionation system with on-line post-extraction derivatization for monitoring orthophosphate in solid samples of environmental relevance. The system was based on dynamic sequential extraction using HL for fractionation of phosphorus associated with different geological phases, and on-line processing of the extracts via the molybdenum blue reaction by exploiting multisyringe flow injection as the interface between the solid containing micro-column and the flow-through detector. The flow assembly was reported to have some advantages over the batch method such as shortening of the operational times from days to hours, highly temporal resolution of the leaching process, capability for immediate decision for stopping or proceeding with ongoing extraction and accurate determination of the various orthophosphate pools by minimization of the hydrolysis of extracted organic phosphorus and condensed inorganic phosphates within the time frame of the assay.

The flexibility and limitless manifold configurations of flow injection analysis systems coupled with the ease of hyphenation with detectors and other techniques have made FIA and its variants veritable tools of modern analytical methods for the determination of analytes of interest in various environmental matrices. The fact that a flow injection system could range from simple one channel system to complex multi-cummutated system gives the analyst the option to satisfy his needs based on the resources, materials or consumables available. Thus, different modifications and additions to existing systems still throw up novel ideas. While some are designed as on-line analytical tools (fully automatic) others could still be semiautomatic with some steps carried out manually. For example, Jakmunee and Junsomboon (2009) reported a new extraction procedure based on an off-line extraction column for extracting available phosphorus from soils. The column was fabricated from a plastic syringe fitted at the bottom with a cotton wool and a piece of filter paper to support a soil sample. An aliquot (50 mL) of an extracting solution (0.05M HCl + 0.0125 M H₂SO₄) was used to extract the sample under gravity and the eluate collected in a polyethylene bottle. The extract was then analyzed for phosphorus contents by a simple flow injection amperometric system, employing a set of three-way solenoid valves as an injection valve. The method was based on the electrochemical reduction of 12-molybdophosphate which is produced on-line by the reaction of orthophosphate with acidic molybdate and the electrical current produced was directly proportional to the concentration of phosphate in range of $0.1 - 10.0 \text{ mg L}^{-1} \text{ PO}_{4}\text{-P}$, with a detection limit of 0.02 mg L^{-1} and sample throughput of 35 h⁻¹. Relative standard deviation (n=11) of 5 mg L^{-1} PO₄-P (0.5%) was achieved for the system. Amperometric detection system does not suffer from the interferences that are encountered in the photometric method such as coloured substances, colloids, metal ions, silicate and refractive index effect (Schlieren effect) (Patey et al., 2008).

CHAPTER THREE

METHODOLGY

3.1 STUDY AREA AND SAMPLING METHODS

The study was conducted on three major highways in Lagos, the commercial hub of Nigeria. Study locations were (A) Mile2–Oshodi Highway (representative of an inland road with mixed industrial and residential influences), (B) Mile2-Wharf Highway (representative of an inland-coastal road with industrial and commercial land use) and (C) Ijora-Marina- Ahmadu Bello Road (representative of a coastal road with mainly commercial/administrative land use). Seven accessible sites on the Lagos Lagoon system receiving highway runoffs and roadside soils' leachates and sediment during rain events were also sampled (Figure 3.1 and Table 3.1). The characteristic features of the different highways and the sampling locations used ind this study are as shown in Tables 3.2 and 3.3.

Mile 2-Oshodi	Mile 2-Wharf	Ijora-Marina-	Lagos Lagoon
Highway	Highway	Ahmadu Bello Road	
(A)	(B)	(C)	(L)
A1 Mile 2 North	B1 Mile 2 South	C1 Ijora Olopa	L1 off Akoka
A2 Itire	B2 Berger	C2 CMS*	L2 off Oko-Baba
A3 Ijesha	B3 NPA	C3 Bonny Camp	L3 off Iddo
A4 Isolo	B4 Liverpool	C4 Bar Beach	L4 Ijora
A5 Oshodi*	B5 Wharf		L5 Leventis
	B6 Emergent		L6 Cowry Creek
	B7 Receiving Water		L7 Falomo

Table 3.1: Sampling	g Locations o	of the Runoff	f and Roadside	Soils Study
---------------------	---------------	---------------	----------------	--------------------

* - Sites of atmospheric fallout samples collection

All the locations used had asphalt surfaces with street sweeping being the major maintenance routine on the roads. There were no runoff treatment structures along the highways. Location C had watersheds which directly discharge runoff into the Lagos Lagoon. Location B also discharges highway runoff directly into the Lagos Lagoon at sites B3 to B5.
Characteristics	Attributes						
	Α	В	С				
Average Daily Traffic	\approx 50,000	$\approx 40,000$	$\approx 60,000$				
(ADT)							
Approximate Road	8.2	7.1	4				
Length (km)							
Drainage Type	Both sided and	Single median sub-	Sub-surface				
	open.	surface.					
Lanes	3+3	3+3	2+2				
Land Use	Industrial,	Sea port	Administrative,				
	Commercial,	operations,	Commercial.				
	Administrative,	Industrial,					
	Residential.	Administrative.					
Maintenance Regime	sweeping.	sweeping	street sweeping				
Road Shoulder Type	Flush	Flush	Curbed				
Road Surface Type	Asphalt	Asphalt	Asphalt				
Runoff Treatment	None	None	None				
Topography	Flat	Flat	Flat				
Estimated Distance to	$\approx 1 \text{km}$	Contiguous at	Contiguous at all				
the Lagos Lagoon		sampling locations	the sampling				
		B3 and B5	locations				

Table 3.2: Characteristics of the Highway Locations used in the Study

Atmospheric fallout (at two sites only as indicated in Table 3.1), runoff and roadside soil samples were collected from the different sites at these highway locations. Lagos Lagoon sediment samples were also obtained from the Lagoon catchments as outlined in Table 2. Sampling was conducted during the wet season (May – September) and dry season (December – January) between 2005 and 2009. The sampling was carried out as outlined in Sections 3.1.1 - 3.1.3.

3.1.1 Atmospheric Deposition Sampling

Dry atmospheric depositions were collected into plastic bowls placed 3 metres above the ground. Each bowl, placed at Oshodi (A5) and CMS (C2), were filled with 500 mL 10% (v/v) nitric acid solution (Garnaud, *et al.*, 1999). The bowls were left at the sampling locations for 48 hours after which their contents were transferred into acid prewashed and distilled water rinsed polyethylene bottles. The bowls were then rinsed with distilled water, filled with 500 mL 10% nitric acid solution and returned to their stands. A total of seven samples were

retrieved from each locations used. Some samples were discarded due to noticeable contamination especially from bird droppings.

Sampling Site	Geo-Referenced Location	Features
A1 Mile 2 North	N 06° 27' 44.9'' E 03° 18' 58.9''	Administrative buildings, highly trafficked, little pedestrian
A2 Itire	N 06° 30' 21.0'' E 03° 19' 24.4''	Administrative and industrial buildings, highly trafficked, little pedestrian influence
A3 Ijesha	N 06° 29' 30.1'' E 03° 19' 22.6''	Administrative and residential buildings, highly trafficked and little pedestrian influence
A4 Isolo	N 06° 31' 53.3'' E 03° 20' 09.7''	Industrial and administrative buildings, highly trafficked, little pedestrian influence
A5 Oshodi*	N 06° 33' 06.2'' E 03° 20' 29.2''	Commercial activities, bus parks, highly trafficked, very high pedestrian influence
B1 Mile 2 South	N 06° 27' 26.2'' E 03° 19' 13.8''	Schools, administrative buildings, highly trafficked, little pedestrian influence
B2 Berger	N 06° 26' 41.3'' E 03° 19' 13.1''	Commercial activities, highly trafficked (especially by heavy vehicles), high pedestrian influence
B3 NPA	N 06° 26' 05.9'' E 03° 20' 24.5''	Commercial activities, highly trafficked (especially by heavy vehicles), high pedestrian influence
B4 Liverpool	N 06° 26' 10.6'' E 03° 21' 07.9''	Highly trafficked (especially by heavy vehicles), low pedestrian influence
B5 Wharf	N 06° 26' 14.8'' E 03° 21' 47.5''	Commercial activities, highly trafficked (especially by heavy vehicles), high pedestrian influence
B6 Emergent	N 06° 26' 06.5'' E 03° 20' 52.0''	Situated at the channel conveying runoff from the highway to the Lagoon.
B7 Receiving Water	N 06° 26' 07.2'' E 03° 20' 51.5''	A runoff watershed at Liverpool. Nearby sand dredging activities
C1 Ijora Olopa	N 06° 28' 09.7'' E 03° 22' 24.5''	Located at the ascent point of Carter Bridge. Surrounding administrative buildings. Highly trafficked

Table 3.3 Geo-referenced Position and Features of Sampling Sites used in this Study

C3 Bonny Camp	N 06° 26' 20.4''	Administrative buildings, high
	E 03° 24' 21 8''	traffic (mostly light vehicle), little
	2.00 2.1 2110	pedestrian influence
C4 Bar Beach	N 06° 25' 18 4''	Administrative buildings, high
	E 03° 24' 51.8''	traffic (mostly light vehicle). little
		pedestrian influence
L1 off Akoka	N 06° 30' 46.7"	On the Lagoon. Receives runoff
	E 03° 24' 21.0"	and roadside soils (from street
		sweeping) from the Third Mainland
		Bridge
L2 off Oko-Baba	N 06° 29' 31.2"	On the Lagoon. Receives runoff
	E 03° 23' 57.0"	and roadside soil from the Third
		Mainland Bridge. Possible
		influence from nearby Saw Mill.
L3 off Iddo	N 06° 28' 10.5"	On the Lagoon. Possible influence
	E 03° 23' 06.1"	from the nearby Iddo sewage
		discharge point.
L4 Ijora	N 06° 27' 53.6"	Watershed of sampling Location C
	E 03° 22' 50.0"	on the Lagoon
L5 Leventis	N 06° 27' 00.7"	On the Lagoon. Situated at the
	E 03° 10' 10.8"	opposite bank of Marina-Ahmadu
		Bello road.
L6 Cowry Creek	N 06° 26' 29.7"	Watershed of Marina-Ahmadu
-	E 03° 24' 15.8"	Bello highway on the Lagoon.
		Mostly characterised by fast and
		high tides
L7 Falomo	N 06° 26' 21.7"	On the Lagoon. Downstream of L6.
	E 03° 25' 34.9"	Administrative buildings

3.1.2 Highway Runoff Sampling

Runoff samples were collected directly from the lateral sheet flow of runoff water from the road directly into acid pre-washed 2-L polyethylene bottles. The polyethylene bottles were placed at the tip of the drainage ducts at an angle which allowed runoff water to fill them up. Samples were collected manually with emphasis on first flush samples (collected within the first 30 minutes of rainfall). Eleven first flush events were captured during the sampling period.



Figure 3.1: Map of Lagos Showing the Highway Runoff, Roadside Soils and Lagos Lagoon Sediment Sampling Locations in 2005 - 2009.

3.1.3 Roadside Soil and Sediment Sampling

Roadside soil samples were collected using a plastic scoop into polyethylene bags previously rinsed with 2% (v/v) hydrochloric acid and distilled water. Wet season roadside soil samples were sampled at each designated sites alongside the runoff samples. Four dry season roadside soils sampling events were carried out at the designated sites. The Lagos Lagoon sediment samples were obtained using a home-made grab sampler. Collected sediment samples were also bagged in dilute HCl pre-rinsed polyethylene bags.

3.2 SAMPLE PREPARATION AND QUALITY CONTROL

Runoff and atmospheric fallout samples were analysed for their physico-chemical parameters immediately on getting to the laboratory. Atmospheric fallout and runoff samples meant for PTM determination were preserved with concentrated nitric acid in separated polyethylene bottles. Samples meant for phosphate determination was preserved with concentrated sulphuric acid. Samples were always refrigerated during the period of analyses. All analyte determinations were carried out within the holding time of the various parameters (APHA, 1995). Roadside soils and sediment samples were air-dried, sieved through a 2 mm mesh into dilute HCl pre-rinsed polyethylene bags and stored for subsequent analyses. All glassware used for the analyses were soaked in 10% hydrochloric acid (v/v) acid bath for 48 hours after which they were rinsed with distilled water and then soaked in milli-Q waters, dried and stored in polyethylene bags before use.

3.3 PHYSICO-CHEMICAL ANALYSIS

The physico-chemical analysis of the runoff and roadside soil samples were carried out as outlined below:

3.3.1 pH

The pH metre (Mettler Toledo Seven Easy brand) was calibrated with pH buffers 4.01, 7.00 and 10.01 (Mettler Toledo). Afterwards, 20 mL of each runoff sample was placed in a 50 mL beaker and the electrode of the pH metre dipped into it. The reading observed was then

recorded.

A mixture of soil and 0.01M CaCl₂ in ratio 1:2 (McLean, 1982) was prepared by weighing 5 g of the soil sample into a 50 mL beaker and adding 10 mL of the CaCl₂ solution to it. The resulting mixture was adequately stirred and allowed to stand for 10 minutes, after which the pH metre electrode was dipped into the upper liquid layer of the mixture. The pH value was then recorded for the soil sample (Watson and Brown, 1998).

3.3.2 Conductivity

The conductivity of the runoff samples was determined with a Mettler Toledo pH/conductivity metre. The conductivity cell was rinsed and soaked in conductivity water and thereafter rinsed with a portion of the sample to be measured before each measurement. (APHA, 1995).

3.3.3 Total Solids

Ten millilitre of the sample was measured into a dried pre-weighed evaporating dish and heated at 105°C to complete dryness in an oven. The dish was then re-weighed after cooling for several times until a constant weight was obtained. The weight differential between the pre-weighed dish and the heated and cooled dish plus its content was subsequently used to calculate the total solids (APHA, 1995).

Total solids (mg L⁻¹) =
$$\frac{Wx1000,000}{V}$$

W = (Weight of heated and cooled dish + sample) – Weight of dried dish (g) V = volume of sample (mL)

3.3.4 Total Dissolved Solids

Ten millilitre (10 mL) of filtered runoff sample was measured into a dried pre-weighed evaporating dish. The dish and its content were then heated to complete dryness at 105^oC. The dish was subsequently cooled in a desiccator after two hours and re-weighed to obtain

the mass of the dried residue. This process was repeated until a constant weight was obtained (APHA, 1995). The TDS was calculated thus:

Total dissolved solids (mg L⁻¹) = $\frac{Wx1000,000}{V}$

W = (Weight of heated and cooled dish + filtered sample) – Weight of dried dish (g) V = volume of sample (mL)

3.3.5 Dissolved Oxygen (DO)

The DO of the sample was determined by the Winkler method (APHA, 1995). Each sample was poured in a dissolved oxygen bottle and filled to the brim. One millilitre (1 mL) each of 0.54 M MnSO₄.H₂O (manganese sulphate) and alkali-iodide-azide (NaOH-KI-NaN₃) solutions was added in turn. The precipitate generated was dissolved with concentrated tetraoxosulphate (VI) acid. Fifty millilitre (50 mL) of the resulting was mixture titrated against standardized 0.0125 M NaS₂O₃ (sodium thiosulphate) solution to a colourless end point using starch indicator. The DO value was calculated using the expression below:

Dissolved oxygen
$$(mg L^{-1}) = \frac{V \times M \times 16,000}{\frac{V2}{V1}(V1-2)}$$

(Ademoroti, 1996)

V = volume of NaS₂O₃ used (mL) V₁ = volume of DO bottle (mL) V₂ = volume of aliquot used for titration (mL) M = molarity of NaS₂O₃

3.3.6 Chemical Oxygen Demand (COD)

The COD was determined by the open reflux method (APHA, 1995). Twenty five milliliter (25 mL) of the sample was put into a refluxing flask and 0.5 g HgSO₄ added. Sulphuric acid reagent, made up silver sulphate (4.4 g) dissolved in 1.0 L of concentrated sulphuric acid, was then added. The resulting mixture was cooled to room temperature and 12.5 mL of 0.125 M potassium dichromate solution was subsequently added. The flask was attached to a

condenser and more sulphuric acid reagent was added. The mixture was gently swirled to ensure proper mixing and allowed to cool. It was thereafter heated at 60 °C on a heating mantle under reflux for two hours after which it was cooled, diluted and titrated against standardized ferrous ammonium sulphate solution to a reddish brown end point using ferroin indicator. A blank was also similarly treated as stated above. The COD was calculated thus:

COD (mg L⁻¹) =
$$\frac{(V_a - V_b)xMx16,000}{V_c}$$

 V_a = volume of ferrous ammonium sulphate solution used for blank V_b = volume of ferrous ammonium sulphate solution used for sample V_c = volume of sample used M = molarity of ferrous ammonium sulphate solution

3.3.7 Acidity

The acidity of the samples was determined by titrimetric method (APHA, 1995). Fifty millilitre (50 mL) of the sample was titrated against a standardized 0.1 M NaOH solution to a pink end point using phenolphthalein solution as the indicator. The acidity was calculated thus:

Acidity (mg L⁻¹ CaCO₃₎ =
$$\frac{V_1 x M x 50,000}{V_2}$$

M = Molarity of Standardized NaOH Solution $V_1 =$ Volume of NaOH Solution used (ml) $V_2 =$ Volume of Sample used (ml)

3.3.8 Alkanility

The alkalinity was determined by titrating 50 mL of the sample against a standardized hydrochloric acid solution using phenolphthalein and a mixed indicator made up of methyl red and bromocresol green to a pink end point (APHA, 1995). The alkalinity was then calculated thus:

Alkalinity (mg L⁻¹ CaCO₃₎ =
$$\frac{V_{1x}Mx50,000}{V_{2}}$$

$$\begin{split} M &= \text{molarity of standardized HCl solution} \\ V_1 &= \text{volume of HCl solution used (mL)} \\ V_2 &= \text{volume of sample used (mL)} \end{split}$$

3.3.9 Hardness

This was determined by titrimetry (APHA, 1995). Fifty milliter (50 mL), to which 4 mL ammonium hydroxide-ammonium chloride buffer had been added, was titrated against standardized solution of 0.01 M EDTA (ethylenediaminetetraacetic acid) to a blue end point using Solochrome black indicator. The hardness was then calculated thus:

Hardness (mg L⁻¹ CaCO₃) = $\frac{V_1 x M x 100,000}{V_2}$

M = molarity of standardized EDTA Solution V_1 = volume of EDTA solution used (mL) V_2 = volume of sample used (mL)

3.3.10 Chloride

Chloride was determined by the mercuric nitrate method (APHA, 1995). The sample (50 mL) was measured into a conical flask and seven drops of s-diphenylcarbazone indicator added to give a purple coloured solution. Several drops of 0.1 M HNO_3 solution were then added until a permanent yellow coloured solution was obtained after which more of the 0.1 M HNO_3 solution was added. The resulting mixture was then titrated with a standardized solution of $0.0242 \text{ M Hg}(NO_3)_2$ to a purple end point. The chloride concentration was calculated thus:

Chloride (mg L⁻¹) =
$$\frac{(V_1 - V_2)xMx35,450}{V_3}$$

 V_1 = volume of standardized Hg(NO₃)₂ used (mL) V_2 = volume of Hg(NO₃)₂ used for blank (mL) V_3 = volume of sample (mL) M= molarity of Hg(NO₃)₂

3.3.11 Total Organic Carbon and Total Organic Matter

The total organic carbon and total organic matter of the roadside soil samples were determined by titrimetric method (Walkley and Black, 1934). One gram (1 g) of each soil sample was weighed into an Erlenmeyer flask and 10 mL of 0.17 M K₂Cr₂O₇ solution and 20 mL concentrated H₂SO₄ were added in tandem. The mixture was adequately mixed by gently swirling the flask and was left to stand for 30 minutes after which distilled water was then added, followed by 10 drops of ferroin indicator. This was titrated to a reddish brown end point with a standardized 0.5 M Fe(NH₄)₂(SO₄)₂.6H₂O solution. A blank was also titrated to same end point. The total organic carbon and total organic matter were calculated thus:

 $TOC (\%) = \frac{(B-S)X M X 0.3}{Mass of sample}$

Total organic matter = % TOC X 1.72

B = volume of Fe²⁺ solution used to titrate blank (mL) S = volume of Fe²⁺ solution used to titrate sample (mL) M = molarity of Fe(NH₄)₂(SO₄)₂.6H₂O

3.4 POTENTIALLY TOXIC METAL (PTM) DETERMINATION

3.4.1 Atmospheric Fallout and Highway Runoff Samples

One hundred millilitre (100 mL) of each sample was measured in an Erlenmeyer flask and 15 mL concentrated nitric acid added. The mixture was placed on hot plate and heated at 60 °C to near dryness. Five millilitre (5 mL) of concentrated nitric acid was thereafter added and the heating continued until a colourless solution was obtained. The volume of the sample was then reduced to about 10 mL and cooled to room temperature. This digest was transferred into a 50 mL volumetric flask, made to mark with distilled water and filtered with Whatman filter paper into an acid washed polyethylene bottle. The concentrations of Cd, Cr, Cu, Ni, Pb and Zn in the sample were subsequently determined using Flame Atomic Absorption Spectrophotometer AAS (Perkin Elmer Aanalyst 200 spectrophotometer model) with a airacetylene, oxidant-fuel combination. The air and gas flow were set at 10.00 and 2.50 L min⁻¹ respectively. Standard solutions were prepared from 1000 mg L⁻¹ stock solutions (Romil, Cambridge, UK) of the metals for every determination after each sampling.

3.4.2 Roadside Soil and Lagoon Sediment Samples

Two grams each of the dried, sieved sample was separately weighed into 50 mL beakers and 15 mL aqua regia (3:1 v/v concentrated HCl:HNO₃, Sigma Aldrich, Analar grade) was added (Crosland et al., 1995). Each beaker was covered with a watch glass and placed on a hot plate at 50 °C for 60 min. and then 100 °C for 5 hours. During the course of the heating, a further 10 mL of aqua regia was added. When the volume of the mixture in the beakers had reduced to about 5 mL, the resulting digests were cooled and transferred into acid washed (10% m/v HCl) 25 mL volumetric flasks and made up to volume with Milli-Q water. The digest solutions were then filtered through Whatman[®] hardened ashless filters into acid pre-washed plastic tubes. Acid blanks and reference materials - SO-2 (Canada Center for Mineral and Energy Technology) and SRM 2711 (National Institute of Standards and Energy, USA) were analysed with each batch of digested samples. Standard solutions of the PTMs determined were prepared from stock standard solutions. The concentration of the PTMs were determined using Inductively Coupled Plasma - Optical Emission Spectrophotometer, ICP-OES [Varian 727-ES model] (Figure 3.2) for Cr, Cu, Ni, Pb and Zn, and Inductively Coupled Plasma – Mass Spectrophotometer, ICP-MS [Thermo X Series model] (Figure 3.3) for Cd, Pd, Pt and V.



Figure 3.2: Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) Instrument



Figure 3.3: Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) Instrument

3.5 ANIONIC NUTRIENT DETERMINATION USING CONTINUOUS FLOW TECHNIQUES

3.5.1 Total Phosphorus by Air Segmented Continuous Flow Analysis (ASCFA)

The total phosphorus concentration of the samples was determined by air segmented continuous flow analysis (SEOES, 2009). Between 80 and 400 µL (depending on the suspected P level in the samples) of the roadside soil and sediment samples digests (as obtained in section 3.4.2 above) were made up to volume in 25 mL volumetric flasks. The diluted digests were injected into an air segmented continuous flow analyser (Skalar SAN⁺, Skalar Analytical BV, The Netherlands) operated in an ISO 9000:2001 accredited environment through an auto sampler as shown in the manifold represented in Figure 3.4. The phosphorus concentration in each sample was determined in triplicate. Detection was based on a modified spectrophotometric molybdenum blue method (Murphy and Riley 1962) by Skalar (2009). The molybdate stream consisted of an acidified solution of 0.55 mM potassium antimony tartrate [K(SbO)C₄H₄O₆.5H₂O], 0.018 M ammonium molybdate [(NH₄)₆Mo₇O₂₄.4H₂O] and 64.4 mL sulphuric acid made up to mark in a 1-L standard flask. Two millilitre (2 mL) of FFD-6 solution, an anionic surfactant (Skalar Chemical BV, The Netherlands) was added to resulting solution. FFD-6 is made up of 55% water and 45% mono- and didodecyl disulphanated diphenyloxide sodium salt (Lurling, 2006)]. The ascorbic acid stream consisted of 11 g ascorbic acid $[C_6H_8O_6]$ and 60 mL acetone $[C_3H_6O]$ made up to 1000 mL in a standard flask with Milli-Q water. Two millilitre (2 mL) of FFD-6 was also added to the prepared ascorbic acid solution. The milli-Q water used for the preparation of the reagents was first degassed by passing argon gas into the water for about 30 minutes.

Three millilitre (3 mL) of each diluted sample digests was automatically injected into the carrier stream at a flow rate of 1.40 mL min⁻¹. Air bubbles were then introduced into the stream and subsequently mixed with the merged streams of ascorbic acid solution (0.42 mL min⁻¹) and ammonium molybdate solution (0.42 mL min⁻¹). The resulting solution was heated at 40°C and debubbled before it passed through the detector. The signals from the absorbance of the phosphomolybedenum blue complex formed were recorded as counts per second (Figure 3.5). Aqueous phosphorus standards in the range of 20 – 240 mg L⁻¹ were prepared daily from potassium dihydrogen phosphate, KH₂PO₄ (Sigma Aldrich, Analar Grade) to

calibrate the instrument.



Figure 3.4: Air Segmented Continuous Flow Analysis, ASCFA (Skalar SAN⁺) Manifold for Phosphate Determination



Figure 3.5: Signal Output of Concentration of Phosphate in Roadside Soil Samples by Air Segmented Continuous Flow Analysis, ASCFA (Skalar SAN⁺)

3.5.2 Bioavailable Phosphorus by Air Segmented Continuous Flow Analysis

The bio-available phosphorus fraction was determined by extracting about 2.5 g of each roadside soil and sediment sample with 40 mL of 0.5 M NaHCO₃ (Olsen *et al.*, 1954). Each mixture was shaken for 30 min on a reciprocating shaker and the supernatant filtered through a 0.45 μ m cellulose acetate membrane. One millitre (1 mL) of each filtrate was diluted to 25 mL with Milli-Q water to give final concentrations within the linear range of the air segmented flow analyser. The phosphorus concentration was determined as outlined in 3.5.1.

3.5.3 Bioavailable Nitrate by Air Segmented Continuous Flow Analysis

The bio-available nitrate was determined by extracting the samples with KCl solution (Haney *et al.*, 2006). Four grams (4 g) of each sample was placed in a 50 mL plastic tube and 40 mL 2 M KCl solution added. The mixture was shaken for 30 minutes and the supernatant filtered through a 0.45 μ m cellulose acetate membrane filter. The filtered samples were afterwards

analysed for their NO₂⁻/NO₃⁻-N levels by the cadmium reduction method using the air segmented continuous flow analyser. The nitrate was determined by the cadmium reduction method through the complete reduction of nitrate to nitrite (Equation 1.17) via copper coated cadmium column as shown in Figure 3.6. The buffer solution stream used in the manifold was prepared by dissolving 50 g of ammonium chloride (NH₄Cl) in 800 mL Milli-Q water. The pH of the resulting solution was then adjusted to 8.2 with ammonium solution and the volume made up to 1 L with Milli-Q water. Three millilitre (3 mL) of Brij 35 (30%) (Skalar Art.Nr. 13900; Skalar Chemical BV, The Netherlands), a nutrient free surfactant, was then added. The colour reagent, made up of 150 mL o-phosphoric acid, H₃PO₄ (85%), 10 g sulphanilamide, C₆H₈N₂O₂S and 0.5 g α -napthylethylene di-amine dihydrochloride, [C₁₂H₁₆Cl₂N₂] was diluted to mark in a 1000 mL standard flask (Skalar, 2009b).

Three mL (3 mL) of the sample was injected into the carrier stream pumped at a flow rate of 0.10 mL min^{-1} . This stream subsequently merged with the buffer solution stream moving at a flow rate of 1.40 mL min⁻¹. The resulting solution was made to pass through the cadmium coated copper column, debubbled and merged with the colour reagent stream (0.42 mL min⁻¹). The pink coloured complex produced was measured at 540 nm and the absorbance recorded as count per minutes. The instrument was calibrated with 0.1, 0.2, 0.5, 1.0 and 2.0 mg L⁻¹ standard nitrate solutions.



Figure 3.6: ASCFA (Skalar SAN⁺) Manifold for Nitrite/Nitrate Determination

3.5.4 Simultaneous Determination of Phosphate and Nitrate in Roadside Soils Samples using Multi-Anionic Nutrients (H³A) Extractant.

Some selected samples from the roadside soil and sediment samples representing different sampled periods and locations were extracted with a multi-nutrient extracting solution, H³A. The H³A solution was made up of 0.02 M lithium citrate (99%, Sigma-Aldrich Co., USA); 0.004 M oxalic acid (99.5%, BDH AnalaR, BDH England; 0.004M malic acid (98%, Alfa Aesar, England); 0.0024 M citric acid (99.7%, BDH AnalaR, BDH England); 0.002 M EDTA (99.5%, BDH AnalaR, BDH England) and 0.001 M diethylenetriaminepentaacetic acid (98%, Alfa Aesar, England) in 1 Litre Milli-Q water.

Four grams of each selected sample was weighed into a 50 mL polyethylene centrifuge tube and 40 mL of the H^3A solution was added. The mixture was shaken for 30 minutes, centrifuged at 3000 rpm for 8 minutes and filtered through Whatman[®] 0.45 µm cellulose acetate membrane filter. The filtrates were simultaneously analysed for their PO₄³-P and NO₂⁻/NO₃⁻-N concentration on different channels of the air segmented continuous flow analyser as outlined in sections 3.5.1 and 3.5.3 above.

3.6 OPTIMISATION OF A CUSTOMISED FLOW INJECTION ANALYSIS (FIA) SYSTEM

A FIA system modified from the manifold used by Omaka *et al.* (2007) was configured to have a four channelled streams made up of the sample and carrier streams controlled by one peristaltic pump and the molybdate and ascorbic acid streams controlled by another pump (Figure 3.7). The peristaltic pumps were Gilson MINIPULS 3 (Villier le Bel, France) fourchannel pumps. The sample and carrier streams were linked to an injector (Rheodyne 6-port switching valve) that discharged to a single stream. The molybdate and ascorbic acid streams were joined by a T-piece connector (3 Way 0.8mm PTFE Valve "T" Connector, Omnifit UK) to form an emergent stream which passed through a mixing coil to merge with the carrier stream at a second T-piece mixing junction. The resulting stream then passes through a reaction coil, in a temperature regulated water bath maintained at 40° C and subsequently to the detector D. The signal obtained was processed by the recorder and the output shown as an absorbance. The detector used was a Philips PU 8620 UV/VIS/NIR spectrophotometer (Cambridge, England) with a 30 µL flow cell that was linked to a computer for data



Figure 3.7: Manifold A; Optimised Flow Injection Analysis Manifold for Phosphorus Determination.

S-sample (110 μ L); Mo-molybdate (0.012M);AA-ascorbic acid (0.28M); MC-mixing coil; RC-reaction coil-90 cm; flow rate-0.13 mL min⁻¹.

processing using purposely built software from LabVIEWTM, UK. Polytetrafluoroethylene, PFTE (0.75mm i.d.) and red/red polyvinyl chloride, PVC, pump tubings (Elkay Laboratory, UK) were used for the manifold. The injection volume, reaction temperature, reaction coil length, flow rate, molybdate concentration and ascorbic acid concentration were subsequently optimised.

3.6.1 Optimisation of the Injection Volume

The effect of injection volume on the sensitivity of the FIA system was carried out by varying the sample volume loop of the injector at 25, 62.5, 110 and 250 μ L. All the other experimental conditions were kept constant as stated below:

Temperature:	40°C
H ₂ SO ₄ Concentration:	0.9 M
Ammonium molybdate concentration:	0.0129 M
Reaction coil length:	MC = RC = 70cm.
Ascorbic acid concentration:	46 g dm^{-3}
Flow rate:	0.17 mL min ⁻¹

Standard phosphate solutions of 125, 250, 500 and 1000 μ g L⁻¹ –P were then injected into the system in pentuplicates.

3.6.2 Optimisation of the Reaction Temperature

Using the adopted injection volume of 110 μ L, the temperature was varied between 30 and 50°C with the upper limit being constrained by the need to balance the operationally desirable temperature and the temperature at which silicate and arsenate are likely to interfere with the reaction through the formation of arsenomolybdenum and silicomolybdenum complexes which also absorb at the same wavelength as the phosphomolybdenum complex. Attempts to carry out analyses at 60°C were thwarted by high baseline absorbance and unstable signal outputs. The conditions during the optimisation of the reaction temperature were:

Injection volume	110 µL
H ₂ SO ₄ Concentration:	0.9 M
Ammonium molybdate concentration:	0.0129 M
Reaction coil length:	MC = RC = 70cm.
Ascorbic acid concentration:	46 g dm ⁻³
Flow rate:	0.17 mL min^{-1}

3.6.3 Optimisation of Ammonium Molybdate Concentration

The following experimental conditions were used for the optimisation of the concentration of ammonium molydate. Varied ammonium molybdate concentration range of 0.006 - 0.015M which correspond to concentrations of 0.0042 - 0.105 M molybdate were studied.

Injection volume:	110 µL
Temperature:	40 °C
H ₂ SO ₄ Concentration:	0.9 M
Reaction coil length:	MC = RC = 70 cm.
Ascorbic acid concentration:	46 g dm^{-3}
Flow rate:	0.17 mL min^{-1} .

3.6.4 Optimisation of Length of Reaction Coil

Reaction coil (RC) lengths of 30, 70, 90 and 120 cm were used while keeping MC coil length constant at 70 cm

Injection volume	110 µL
Temperature:	40 °C
H ₂ SO ₄ Concentration:	0.9 M
Ammonium molybdate concentration:	0.012 M
Ascorbic acid concentration:	46 g dm^{-3}
Flow rate:	0.17 mL min ⁻¹

3.6.5 Optimisation of the Ascorbic Acid Concentration

In optimising the manifold, the concentration of the ascorbic acid was varied between 0.22 and 0.34 M.

Injection volume	110 µL
Temperature:	40 °C
H ₂ SO ₄ concentration:	0.9 M

Ammonium molybdate concentration:	0.012 M
Reaction coil length:	90 cm
Flow rate:	0.17 mL min ⁻¹ .

3.6.6 Optimisation of the Flow Rate of Reagents

The effect of the flow rate of the manifold on the sensitivity was studied by systematically varying the flow rate within the range 0.12 - 0.35 mL min⁻¹. All the other experimental conditions were as previously optimised.

Injection volume	110 μL
Temperature:	40 °C
H ₂ SO ₄ concentration:	0. 9 M
Ammonium molybdate concentration:	0.012 M
Reaction coil length:	90 cm
Ascorbic acid concentration:	50 mg L ⁻¹ (0.28 M, adopted after optimisation of
	ascorbic acid concentration)

The customised and optimised flow injection system was then used to run standard phosphate solutions of concentrations of 25, 50, 100 and 250 μ g L⁻¹ P in pentuplicates.

While retaining the optimised conditions (tempearture, 40° C; flow rate, 0.13 mL min⁻¹; reaction coil length, 90 cm: ascorbic acid concentration, 0.28 M and ammonium molybdate concentration, 0.012 M), the sulphuric acid concentration was systematically varied to give different acid to molybdate reagents ratios ([H⁺]:[MoO₄²⁻]) of 42.9, 53.5, 64.3, 76.2 and 85.7 and a measured pH values of 1.53, 1.43, 1.34, 1.28 and 1.12 respectively. The runs of the different molybdate reagents produced no peaks or signals. Varying the concentration of the potassium antimonyl tartarate also produced no observable difference.

3.6.7 Effects of Change of Manifold on the Sensitivity of the FIA System

Using the same optimised conditions, different manifolds (Figures 3.8 - 3.10) were used to

investigate the effect of the change of manifold on the sensitivity of the method. Firstly, Manifold B as proposed by Omaka *et al.* (2006) without its thiosulphate stream (Figure 3.8) was used for a run of the 250 μ g L⁻¹ PO₄³⁻ - P standard. The manifold was then reconfigured to form Manifold C (Figure 3.9). The system was based on the model of Grudpan *et al.* (2002) whereby the standard phosphate solution was injected directly into the molybdate stream. A delay coil (DC) was also introduced to increase the reaction time and increase the degree of molybdenum blue complex formation. Absorbances of standard phosphate solutions were then determined on the system. A Milli-Q stream was next incorporated into the system to give manifold D (Figure 3.10). This served as an on-line sample dilution to investigate the possibility of reducing the high background level noticed from results obtained from Manifold C to a tolerable level. Absorbances of standard phosphate solutions were also determined using this manifold.



Figure 3.8: Manifold B with a Premixed Sample and Molybdate Stream

S-sample (110µL); Mo-molybdate (0.012M);AA-ascorbic acid (0.28M); MC-mixing coil; RC-reaction coil-90 cm; Flow rate-0.13 mL min⁻¹.



Figure 3.9: Manifold C with the Sample Directly Injected into the Molybdate Stream and Delay Coil to Enhance Colour DevelopIment.

S-sample (110 μ L); Mo-molybdate (0.012M);AA-ascorbic acid (0.28M); MC-mixing coil; RC-reaction coil-90 cm; Flow rate-0.13 mL min⁻¹.



Figure 3.10: Manifold D with an Online Sample Dilution (as Modified from Manifold C) S-sample (110µL); Mo-molybdate (0.012M);AA-ascorbic acid (0.28M); MC-mixing coil; RC-reaction coil-90 cm; DC-delay coil; Flow rate-0.13 mL min⁻¹.

3.7 DETERMINATION OF TOTAL PHOSPHORUS BY INDUCTIVELY COUPLED PLASMA – OPTICAL EMISSION SPECTROMETER (ICP-OES)

The total phosphorus concentration in the roadside soil, sediment, and reference material digests as obtained in section 3.4.2 was also determined using ICP-OES [Varian 727-ES] (Crosland, *et al.*, 1995). The instrument was calibrated with standard phosphorus solutions of concentrations 1.0, 2.0, 5.0, 7.0 and 10.0 mg L⁻¹ prepared from 10,000 mg L⁻¹ stock standard solution (Fisher Scientific, UK).

3.8 DETERMINATION OF PHOSPHATE CONCENTRATION IN THE WATER COLUMN OF LAGOS LAGOON USING FLOW INJECTION ANALYSIS.

The FIA system (Figure 3.11) subsequently set up in the Department of Chemistry, University of Lagos was employed in the determination of the total and bioavailable phosphate concentration in the Lagos Lagoon water column. Water samples from different strata (top, middle and bottom) at nine locations of the Lagos Lagoon were used for this part of the study.

A customised and optimised flow injection system was used for the determination of the phosphate concentration in the collected samples. The system consisted of a three channelled manifold controlled by one peristaltic pump. The channels included the carrier stream of distilled water; the premixed tetraoxosulphate (VI) acid solution (0.90 M), potassium antimonyl tartrate (0.15 μ M) and ammonium molybdate stream (0.0129 M); and the ascorbic acid (0.46 M) stream. Sample volumes of 200 μ L were injected via the sample loop of the injection valve (I) into the carrier stream with a syringe. A reaction temperature of 40°C and flow rates of 0.22 mL min⁻¹ (for the carrier stream) and 0.14 mL min⁻¹ (for the molybdate and ascorbic acid streams) were optimally determined for the system. The mixing coil (MC) and reaction coil (RC) lengths were 70 cm each. The water samples were analysed in triplicate.



Figure 3.11: Flow Injection Manifold used for the Determination of Phosphate in the Water Column of the Lagos Lagoon.

AA- Ascorbic acid; C – Carrier (distilled water); D – Detector; Mo – Molybdate reagent; MC – Mixing coil; P – Peristaltic pump; R – Recorder; RC – Reaction coil.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 PHYSICO-CHEMICAL PARAMETERS OF HIGHWAY RUNOFF AND ROADSIDE SOIL SAMPLES

The results of the physico-chemical analysis of the runoff samples from the selected highways are shown in Tables 4.1, 4.2 and 4.3. The samples had a circum-neutral pH range of 6.20 - 7.25 with mean values of 6.48 ± 0.18 , 6.39 ± 0.19 and 6.87 ± 0.38 for locations A, B and C respectively.

The runoff had generally low dissolved oxygen levels at all the locations with mean concentrations of 3.20 ± 1.37 , 3.60 ± 1.32 and 4.50 ± 1.33 mg L⁻¹ O₂ for the respective sampling locations. The mean chemical oxygen demand (COD) levels were 248 ± 122 , 135 ± 71 and 198 ± 106 mg L⁻¹ respectively which were considerably higher than the 10.0 mg L⁻¹ O₂ observed for the rain water control. Location B had the highest mean level of total solids with a concentration of 1672 ± 3600 mg L⁻¹. The mean concentrations of total dissolved solids were 126 ± 34 , 145 ± 57 and 375 ± 335 for the respective study locations. The chloride levels in the samples from this location had a range of 11 - 325 mg L⁻¹. Location C had the highest mean chloride level among the study locations with a concentration of 175 ± 127 mg L⁻¹. The mean concentration ranges of the acidity and alkalinity of the runoff samples were 8.2 - 18.5 mg L⁻¹ and 24.5 - 109.5 mg L⁻¹.

Mean concentration of total dissolved phosphorus in the samples ranged from 0.06 to 0.11 mg L⁻¹ at location A, 0.05 - 0.62 mg L⁻¹ at location B and 0.23 - 1.76 mg L⁻¹ at location C with the highest level obtained at C2. On the average, the selected highways contributed 0.11 \pm 0.04, 0.34 \pm 0.26 and 0.67 \pm 0.75 mg L⁻¹ dissolved phosphorus in the runoff samples to the receiving water system respectively from the studied highways A, B and C.

The mean total organic matter of the roadside soils was 1.65 ± 0.66 , 0.99 ± 0.48 and 1.81 ± 1.31 % respectively for the A, B and C study locations with corresponding mean pH values of 7.30 ± 0.25 , 6.75 ± 0.15 and 6.73 ± 0.31 respectively (Tables 4.1 - 4.3). The chlorides concentration at Location B with a mean value of 689 ± 339 was relatively higher than those

of the other locations.

Parameter	A1	A2	A3	A4	A5	Overall Mean	Control
					(n=18)		
Runoff							
Temperature, °C	26.0	25.0	25.5	25.5	26.5	25.7 ± 0.6	22.0 ± 0.5
рН	6.79	6.38	6.36	6.47	6.41	6.48 ± 0.18	6.48 ± 0.11
Conductivity, µS/cm ³	184	76	291	160	159	174 ± 77	33 ± 0
Total Solids, mg L ⁻¹	1342	290	722	257	726	667 ± 439	10 ± 0
Dissolved Solids, mg L ⁻¹	104	107	106	129	185	126 ± 34	10 ± 0
Dissolved Oxygen, mg L ⁻¹	5.01	4.21	2.14	2.87	1.82	3.20 ± 1.37	7.70 ± 0.21
COD, mg L ⁻¹	364	98	221	177	382	248 ± 122	10 ± 2
Acidity, mg L ⁻¹	10.4	13.8	25.9	18.6	19.6	17.6 ± 5.9	1.2 ± 3.2
Alkalinity, mg L ⁻¹	65.2	109.5	49.5	70.5	75.6	74.1 ± 22.1	10.1 ± 1.2
Hardness, mg L ⁻¹	75.3	63.6	117.4	105.7	109.7	94.3 ± 23.5	2 ± 0
Chlorides, mg L ⁻¹	25	11	35	35	39	29 ± 11	7 ± 2
$PO_4^{3-}, mg L^{-1}$	0.06	0.11	0.08	0.11	0.17	0.11 ± 0.04	BDL
	Roadsi	de Soils					
pH	7.42	6.93	7.34	7.60	7.22	7.30 ± 0.25	6.81 ± 0.73
Total Org. Carbon, %	0.50	1.47	0.85	1.20	0.74	0.95 ± 0.38	0.25 ± 0.12
Total Org. Matter, %	0.87	2.54	1.47	2.08	1.28	1.65 ± 0.66	0.43 ± 0.41
Chlorides, mg Kg ⁻¹	337	321	333	361	420	354 ± 39	10 ± 12

 Table 4.1: Results of Physico-chemical Analysis of Runoff and Roadside Soils Samples from Location A.

BDL-below detection limit

Runoff Parameters	B1	B2	B3	B4	B5	B6	B7	Overall Mean (n=12)	Control
Temperature, ^O C	24.5	24.5	26.5	25.0	25.5	25.1	25.1	25.1 ± 0.7	22.0 ± 0.5
рН	6.54	6.37	6.18	6.5	6.58	6.48	6.07	6.39 ± 0.19	6.48 ± 0.11
Conductivity, µS/cm ³	323	383	683	613	570	553	$1.5 \ge 10^5$	521 ± 139	33 ± 0
Total Solids, mg L ⁻¹	208	140	435	323	409	356	9833	1672 ± 3600	10 ± 0
Dissolved Solids, mg L ⁻¹	93	50	201	167	210	151	145	145 ± 57	10 ± 0
Dissolved Oxygen, mg L ⁻¹	4.91	3.63	3.7	4.79	4.14	1.01	3.12	3.60 ± 1.32	7.70 ± 0.21
COD, mg L ⁻¹	98	35	153	97	201	226	BDL	135 ± 72	10 ± 2
Acidity, mg L ⁻¹	4.6	5.8	8.2	6.4	8.9	14.8	18.5	9.6 ± 5.1	1.2 ± 3.2
Alkalinity, mg L ⁻¹	24.5	30.2	27.3	27.2	32.5	54.2	106.5	43.2 ± 29.6	10.1 ± 1.2
Hardness, mg L ⁻¹	45.0	19.6	34.3	33.3	42.1	49.9	1333	223.5 ± 489.8	2.0 ± 0.1
Chlorides, mg L ⁻¹	21	42	214	190	56	277	BDL	133 ± 107	7 ± 2
$PO_4^{3-}, mg L^{-1}$	0.05	0.15	0.09	0.57	0.62	0.53	0.68	0.34 ± 0.26	BDL
		Road	lside soil						
pH	6.57	6.60	6.74	7.02	6.70	6.86	6.76	6.75 ± 0.15	6.81 ± 0.73
Total Organic Carbon, %	0.33	0.75	0.93	0.56	0.83	0.45	0.17	0.57 ± 0.28	0.25 ± 0.12
Total Organic Matter, %	0.57	1.30	1.61	0.97	1.44	0.78	0.29	0.99 ± 0.48	0.43 ± 0.41
Chlorides, mg Kg ⁻¹	542	552	543	450	998	416	1324	689 ± 339	10 ± 12

 Table 4.2: Results of Physico-chemical Analysis of Runoff and Roadside Soils Samples from Location B.

Parameter	C1	C2	C3	C4	Overall Mean	Control
					(n=12)	
	Runoff					
Temperature, ^O C	25.7	25.5	24.0	25.0	25.0 ± 0.8	22.0 ± 0.5
рН	6.35	6.79	7.07	7.22	6.87 ± 0.38	6.48 ± 0.11
Conductivity, µS/cm ³	103	319	76	478	244 ± 190	33 ± 0
Total Solids, mg L ⁻¹	369	1587	421	234	653 ± 628	10 ± 0
Dissolved Solids, mg L ⁻¹	123	862	325	191	375 ± 335	10 ± 0
Dissolved Oxygen, mg L ⁻¹	4.8	2.6	4.9	5.7	4.50 ± 1.33	7.70 ± 0.21
COD, mg L ⁻¹	89	341	159	203	198 ± 106	10 ± 2
Acidity, mg L ⁻¹	18.3	20.1	8.4	8.2	13.8 ± 6.3	1.2 ± 3.2
Alkalinity, mg L ⁻¹	32.4	24.7	54.3	68.5	45.0 ± 20.1	10.1 ± 1.2
Hardness, mg L ⁻¹	20.3	74.8	49.3	112.8	64.3 ± 39.3	1.96 ± 0.1
Chlorides, mg L ⁻¹	78	234	62	325	175 ± 127	7 ± 2
$PO_4^{3-}, mg L^{-1}$	0.23	1.76	0.15	0.53	0.67 ± 0.75	BDL
Re	Roadside Soil					
pH	6.98	6.42	6.51	7.02	6.73 ± 0.31	6.81 ± 0.73
Total Organic Carbon, %	0.82	2.13	0.85	0.48	1.07 ± 0.73	0.25 ± 0.12
Total Organic Matter, %	1.44	3.68	1.47	0.63	1.81 ± 1.31	0.43 ± 0.41
Chlorides, mg Kg ⁻¹	157	371	125	432	271 ± 153	10 ± 12

 Table 4.3: Results of Physico-chemical Analysis of Runoff and Roadside Soils Samples from Location C.

Although the pH values obtained in the samples from the highway runoff sampling sites were fairly stable over a narrow range, levels of pollution indicating parameters such as the dissolved oxygen (DO) and chemical oxygen demand (COD) among others, showed that the runoff water quality was low. Mean DO values of 3.20, 3.60 and 4.50 mg L⁻¹ obtained for the respective sampling locations were less than the 7.70 mg L^{-1} obtained for the control rain water sample and the 6.80 mg L^{-1} regulatory DO value for aquatic water (FMoE, 1991). Sites A5, C2, B3 which had DO levels less than 4.0 mg L⁻¹ are points of high anthropogenic influences such as traffic and commercial activities. Site B6 which had a DO value of 1.01 mg L^{-1} is one of the several points along the lower part of the Location B highway where runoff water from the sub-surface drainage is directly discharged to the Lagoon. It is an open channel and therefore subject to anthropogenic influences such as various forms of solid wastes. This may have accounted for the 3.14 mg L^{-1} observed for site B7 on the Lagoon which the channel drains into. The high COD values (in contrast to the 10 mg L^{-1} in the control sample) obtained for all the sites indicate that highway runoffs are capable of mobilizing oxidizable organic compounds common in the highway environment into the receiving water. Along with solids, COD has been identified as a dominant pollution indication parameter of highway runoff (Lee et al., 2011) especially during the first flush event. Sites A1, A5 and C2, the identified major transport hubs in this study all had COD values greater than 300 mg L⁻¹. Levels of the total solids in the runoff sample also showed higher concentration at these sites relative to other sites used in the study.

The acidity, alkalinity and hardness levels of the runoff water were higher than those of the control thus showing the potential of highway runoff in mobilising accumulated pollutant on the road surfaces to the receiving water. The fact that the observed concentrations of these parameters at the three study locations were not significantly different suggests that the increase in their concentration with respect to the observed levels in the control was due to a common source. The levels of alkalinity observed at the different sites showed that runoff from the study area were greater than 20 mg L⁻¹ and therefore has buffering capacity (Godfrey *et al.*, 1996). The hardness levels showed that runoff from Locations A with a mean hardness of 94 ± 24 mg L⁻¹ was moderately hard (61 - 120 mg L⁻¹) (USGS, 2013). Samples from Locations B and C were soft (≤ 60 mg L⁻¹) except at sites B7, the receiving Lagoon water, and at sites C2 and C4 which were also moderately hard. While the higher concentration at C2 could be adduced to anthropogenic activities, C4 on the other hand (though with a lesser traffic volume than C2) was more open to the sea and likely to receive calcium and magnesium salts from this source. The lower chloride concentrations obtained at the A sites was

due to the inland location of the road unlike the B and C locations which are closer to the Lagos Lagoon and thus are influenced by the salty water. Sites B3, B4, B6, C1 and C4 which are closer to the Lagoon showed higher chloride concentrations than the others.

The concentrations of dissolved phosphorus observed in the highway runoff samples from all the sites at the three locations were all higher than the 0.01 mg L⁻¹ maximum level in surface water above which algae bloom could occur. Vehicular activities may be ascribed to the higher levels observed in contrast to the concentration of the control samples which were below detection limit although some sites like A1 and B3 which are heavily trafficked unexpectedly showed lower concentrations than some sites which were not traffic hubs. The comparative high concentration of 1.76 mg L⁻¹ observed for site C2 could be attributed to the fact that vehicles are more stationary and spend more time at this location than at the other identified transport hubs. Also, the higher concentration of chloride at sites on Location C could have resulted in higher phosphate concentration in the highway runoff water since availability of salts such as CaCl₂ and NH₄Cl which are common in brackish environment leads to more bioavailability of phosphorus (Yuanrong, *et al.*, 2012).

The pH values of the roadside soils were not significantly different from those of the runoff at the sampled locations with identical circumneutral pH range. Expectedly, sites with the highest organic load concentrations at the three highway study locations were A2, B3 and C2 (Tables 4.1 - 4.3). The total organic carbon concentrations at these sites were higher than the respective sampling location means. This could be due to the fact that engine oil spillages and lubricant drops, which are rich in organics, are common sights at busy vehicle terminals and bus stops in Lagos and thus serve as sources of organic carbon at such sites.

The concentrations of the pollutanion indicating parameters determined showed that the runoff waters from the studied highways are capable of impacting the receiving Lagos Lagoon water.

4.2 POTENTIALLY TOXIC METALS (PTMS) IN HIGHWAY RUNOFF

Results of the PTM concentrations in the highway runoff samples are as shown in Table 4.4. Mean concentration range of PTMs in the runoff samples from location A (Oshodi – Mile 2 Expressway) were $0.000 \pm 0.003 - 0.170 \pm 0.067$ mg L⁻¹ Cu, $0.083 \pm 0.037 - 0.737 \pm 0.381$ mg L⁻¹ Pb and 0.173

 \pm 0.103 – 0.838 \pm 0.167 mg L⁻¹ Zn. Zinc had the highest location mean concentration of 0.427 \pm 0.260. Location mean concentrations of Cu and Pb were 0.274 \pm 0.266 mg L⁻¹ and 0.064 \pm 0.063 mg L⁻¹ respectively. Similarly, Zn also had the highest concentration in the runoff samples from locations B (Mile 2 – Wharf Expressway) and C (Ahmadu Bello-Marina road) with range of 0.057 \pm 0.23 – 0.544 \pm 0.484 and 0.438 \pm 0.132 – 2.029 \pm 0.626 mg L⁻¹ respectively. Location mean concentrations were 0.264 \pm 0.172 mg L⁻¹ Zn, 0.224 \pm 0.138 mg L⁻¹ Pb and 0.027 \pm 0.020 mg L⁻¹ Cu at location B and 1.131 \pm 0.782 Zn, 0.523 \pm 0.433 Pb and 0.246 \pm 0.153 Cu at location C.

The highest concentration of 2.029 mg L⁻¹ Zn was observed in the runoff samples from C1 at a site just off the foot of one of the bridges linking Mainland Lagos to the Island. Sites A1 (Mile 2), A5 (Oshodi), B3 (NPA) and C2 (CMS) had higher concentrations of the PTMs relative to other sampled sites in the study. These sites are transport hubs with higher vehicular residence time. Lower concentrations of the PTMs were observed at sites A2, B2 and B7.

Location	Zn	Pb	Cu
	Mean \pm SD (mg L ⁻¹)	Mean \pm SD (mg L ⁻¹)	Mean \pm SD (mg L ⁻¹)
A1	0.838 ± 0.167	0.737 ± 0.381	0.170 ± 0.067
A2	0.173 ± 0.103	0.083 ± 0.037	0.002 ± 0.003
A3	0.353 ± 0.125	0.117 ± 0.037	0.042 ± 0.025
A4	0.267 ± 0.215	0.194 ± 0.110	0.039 ± 0.054
A5	0.505 ± 0.035	0.241 ± 0.067	0.068 ± 0.002
A Mean	0.427±0.260	0274±0.266	0.064±0.063
B1	0.308 ± 0.211	0.248 ± 0.235	0.014 ± 0.010
B2	0.057 ± 0.023	0.096 ± 0.008	0.003 ± 0.000
B3	0.544 ± 0.484	0.504 ± 0.293	0.064 ± 0.076
B4	0.190 ± 0.051	0.146 ± 0.045	0.019 ± 0.004
B5	0.302 ± 0.112	0.123 ± 0.014	0.025 ± 0.008
B6	0.372 ± 0.420	0.263 ± 0.236	0.037 ± 0.043
B7	0.074 ± 0.105	0.188 ± 0.054	0.028 ± 0.026
B Mean	0.264±0.172	0.224±0.138	0.027±0.020
C1	2.029 ± 0.626	0.457 ± 0.075	0.294 ± 0.029
C2	1.541 ± 0.134	1.153 ± 0.484	0.440 ± 0.100
C3	0.517 ± 0.284	0.263 ± 0.047	0.151 ± 0.161
C4	0.438 ± 0.132	0.219 ± 0.095	0.100 ± 0.018
C Mean	1.131±0.782	0.523±0.433	0.246±0.153
Ctrl	0.000 ± 0.000	0.09 ± 0.013	0.000 ± 0.000

 Table 4.4: Concentration of PTMs in Highway Runoff from the Sampled Location
Overall Mean	0.532 ± 0.534	0.314 ± 0.283	0.093 ± 0.120
		1	_ 1

Detection Limits for Perkin Elmer AAnalyst 200- Cd=0.002 mg L⁻¹; Cr=0.020 mg L⁻¹; Cu=0.010 mg L⁻¹; Ni=0.020 mg L⁻¹; Pb=0.050 mg L⁻¹; Zn=0.020 mg L⁻¹.

Analysis of the results obtained for the three prominent PTMs (Cu, Pb and Zn) in the highway runoff samples showed that sites with elevated concentrations such as A1 (Mile 2), A5 (Oshodi), B3 (NPA), and C2 (CMS) (Figure 4.1) were generally those with higher vehicular and other anthropogenic activities. Site A1 is a major traffic interchange point of two busy highways (the Lagos - Badagry and the Apapa - Oshodi highways), thus it receives PTM inputs from vehicular activities. Site A5 and C2 are major bus terminals in the Lagos metropolis and also experience a high volume of traffic. Site B3 is located at the entrance of the Lagos main port.



Figure 4.1: Mean Concentration of PTMs in the Runoff Samples

The observed higher level of Zn with a concentration of 2.03 mg L^{-1} at C1 (Figure 4.1) in comparison to other sites may be attributed to the ascending terrain of this site which requires more application of tyre friction which invariably leads to more wear and deposition of the tyre materials.

Sorme and Lagerkvist (2002) and Davies *et al.* (2001) reported that tyres were the most significant of roadway associated Zn, responsible for about 25% of the Zn in urban runoff. The trend in concentration of the metals in the runoff samples was Zn>Pb>Cu>Cr>Ni>Cd. This could be adduced to the influence of vehicles, commercial activities and other anthropogenic sources around the studied areas (Garnaud *et al.*, 1999). McKenzie *et al.* (2009) estimated that though tyres are also a source of Pb and Cu, they provide lesser mass contributions to the total loads of lead and copper in runoff than zinc's.

4.3. POTENTIALLY TOXIC METALS (PTMS) IN ATMOSPHERIC FALLOUT SAMPLES

The results of the PTMs in the atmospheric fallout samples collected at the two study locations and a control location are as shown in Table 4.5. With mean concentrations of 0.93 ± 0.60 and 0.86 ± 0.44 mg L⁻¹ at the Oshodi and Marina stations respectively, Zn had the highest concentration among the PTM determined in the atmospheric fallout. Mean concentrations of the PTMs determined at the two sampling stations (Oshodi and Marina) showed the same trend with a calculated paired t-test value (t_{calc.}) of 1.87 at 95% confidence limit. Cadmium had the lowest mean concentration with a range of 0.01 - 0.01 mg L⁻¹ at both locations. Mean concentrations of the other determined metals respectively for the Oshodi and Marina sampling station were Pb, 0.24 ± 0.18 and 0.13 ± 0.56 mg L⁻¹; Cu, 0.28 ± 0.30 and 0.30 ± 0.35 mg L⁻¹; Cr, 0.11 ± 0.08 and 0.11 ± 0.04 mg L⁻¹; Ni, 0.24 ± 0.30 and 0.09 ± 0.05 mg L⁻¹ respectively. Mean concentrations of the metals were slightly higher at the Oshodi station than those obtained for the Marina station except for Cu which was higher at the Marina site (Figure 4.2). The mean concentration trend for the metals was Zn > Cu > Pb > Cr > Ni > Cd. The trend is in tandem with that observed in the highway runoff samples for Zn, Cu and Pb.

PTM	Oshodi [Mean (mg L ⁻¹)]	Marina [Mean (mg L ⁻¹)]	Control [Mean (mg L ⁻¹)]	Study Mean [Mean (mg L ⁻¹)]
Cu	0.275 ± 0.303	0.300 ± 0.348	BDL	0.293
Cd	0.009 ± 0.006	0.006 ± 0.008	BDL	0.007
Cr	0.106 ± 0.079	0.096 ± 0.037	BDL	0.094
Ni	0.240 ± 0.296	0.089 ± 0.045	BDL	0.208
Pb	0.241 ± 0.184	0.133 ± 0.055	BDL	0.186
Zn	0.930 ± 0.595	0.864 ± 0.435	BDL	0.796

 Table 4.5: Mean Concentration of PTMs in Atmospheric Fallout around Sampled Location

BDL-Below Detection Limit; Detection Limits for Perkin Elmer AAnalyst 200- Cd=0.002 mg L⁻¹; Cr=0.020 mg L⁻¹; Cu=0.010 mg L⁻¹; Ni=0.020 mg L⁻¹; Pb=0.050 mg L⁻¹; Zn=0.020 mg L⁻¹.

The presence, concentration and trend of PTMs such as Cu, Pb and Zn in the atmospheric fallout samples from the Oshodi and Marina sampling stations could be linked to the intense traffic activities around these locations as both stations were close to major bus terminals. These metals are non-crustal elements and therefore are mobilized onto the highway environment through mostly local deposition fluxes occasioned by transport activities. The correlation of the results of the PTMs at both stations suggests this common source of the metals. Furthermore, it has been demonstrated that PTMs from aerial deposition are highly soluble in a wide range of natural waters and therefore more bioavailable than PTMs from eroded soil particles (Gelinas and Schmit, 1998). Zinc and copper are more prevalent because of their wide use in tyres and brake pads which wear out and end up as particulates that eventually settle on road and adjoining area surfaces. Concentrations of the metals in the atmospheric fallout Control samples (samples collected within the premises of the University of Lagos) were below detection limit for the PTMs determined (Table 4.5).





Page 111

4.4 POTENTIALLY TOXIC METALS (PTMS) IN ROADSIDE SOILS AND LAGOON SEDIMENTS

4.4.1 Method Validation

The results of the validation carried out on the reference soil materials are presented in Table 4.6. The evaluation of the method performance demonstrated good agreement between the experimental values obtained and the certified values especially for the SRM 2711 reference material. The absolute difference between the measured value and the certified value (Δ_m) were lower than the expanded uncertainty of difference between results and certified values (U_{Δ}) of the PTMs determined in the reference material which implies the suitability of the method used for the determination of the PTMs in the samples (Linsinger, 2005). The recoveries obtained for Zn, Pb and Cu from the SRM 2711 materials were 91%, 94% and 86% respectively. The validation results for the SO-2 reference material also showed good recovery for Cu (89%) and Pb (93%). However, recovery obtained for Zn was just 58% but with good method performance evaluation (i.e $U_{\Delta} < \Delta m$).

РТМ	Reference Material	Experimental Value ± SD, mg kg ⁻¹	Certified Value ± SD, mg kg ⁻¹	Recovery, %	$\Delta_{\rm m}$	Expanded Uncertainty U _Δ , mg kg ⁻¹
Cu	SO-2	6.21 ± 0.01	7.0 ± 1	89	0.62	1.00
	SRM 2711	97.94 ± 0.01	114 ± 2	86	13.32	2.00
Pb	SO-2	19.55 ± 0.05	21 ± 4	93	0.90	4.00
	SRM 2711	1098 ± 0	1162 ± 0	94	33.26	0.17
Zn	SO-2	71.99 ± 0.01	124 ± 5	58	49.99	5.00
	SRM 2711	319.8 ± 0.0	350.4 ± 4.8	91	21.66	4.80

SO-2, Canada Center for Mineral and Energy Technology; SRM 2711, National Institute of Standards and Energy, USA.

4.4.2 PTMs in Roadside Soil Samples

Results of the PTMs in the roadside soil samples collected during the wet and dry seasons are as shown in Tables 4.7 and 4.8 respectively. Mean concentration range of Pb from the roadside soils were $23 \pm 1 - 208 \pm 6$ mg kg⁻¹ for the wet season and $14 \pm 0 - 368 \pm 24.49$ mg kg⁻¹ for the dry season. Copper concentration ranged from $3.3 \pm 0.0 - 230.2 \pm 11.7$ mg kg⁻¹ in the wet season. The level of Zn obtained ranged from $63 \pm 0 - 338 \pm 2$ and $53 \pm 0 - 518 \pm 15$ mg kg⁻¹ for the wet and dry seasons respectively. Platinum which presence is mainly from the catalytic converter of vehicle engine and thus serves as a good fingerprint of highway derived PTMs had a concentration range of BDL $- 86.45 \pm 0.01$ in the wet season and BDL $- 77.08 \pm 0.01 \mu \text{g kg}^{-1}$ in the dry season. Respective mean concentrations of other PTMs for the wet and dry seasons in the study are 0.55 ± 0.25 and 0.55 ± 0.28 mg kg⁻¹ Cd; 22.47 ± 15.43 and 21.44 ± 11.49 mg kg⁻¹ Cr; 9.04 ± 7.28 and 9.04 ± 4.24 mg kg⁻¹ Ni; and 9.25 ± 2.97 and 8.30 ± 3.61 mg kg⁻¹ V respectively.

Mean concentrations of the PTMs in the roadside soil samples on seasonal basis showed variability between the sampled locations and seasons (Figures 4.3 to 4.10). Dry season concentrations were higher in most of the sites at all the locations except for some sites on Location A which showed higher concentrations during the wet seasons. The highest mean concentration of Pb was observed during the dry season site A2 with a mean concentration $368 \pm 25 \text{ mg kg}^{-1}$ (Figure 4.9). Other sites with comparative higher concentration of Pb were A3, B2, B3, B5 and C1. All the sampled sites had concentrations above the reported 19.0 mg kg⁻¹ background level for Pb in soil (Breault and Grenato, 2000).

In comparison to other locations, mean concentrations of Cu were higher at sites A3, A4 and C1 with concentrations of 192.5 ± 0.9 , 141.5 ± 4 and 230.2 ± 11.7 mg kg⁻¹ respectively (Figure 4.5). These concentrations were all observed in the rainy season samples. Most sampled sites on Location B had mean Cu concentrations lower than the reported 25.00 mg kg⁻¹ background Cu level in soil in the wet season samples except at sites B3 and B5 with concentrations of 36.46 ± 0.53 and 31.49 ± 67.07 mg kg⁻¹ respectively. Mean dry season Cu concentrations were all above background level except at sites B2, C1 and C2.

Site A5 on Location A had the Zn highest level among all the sampled sites with a mean concentration of 517.7 ± 15.4 mg kg⁻¹. All sites on Locations A and B had higher dry season Zn concentrations than the observed concentrations for the wet season except sites A2 and B2 (Figure

4.7). All sites on location C had higher wet season Zn concentrations relative to the dry seasons' with the exception of site C4. Ninety-nine percent of the sites had mean concentrations above the 60.0 mg kg^{-1} background Zn level in soil as reported by Breault and Grenato (2000) in both the wet and dry seasons.

Location/Site	Cd	Cr	Cu	Ni	Pb	Zn	\mathbf{V}	Pt				
				$(mg kg^{-1})$				$(\mu g k g^{-1})$				
			L	ocation A								
A1	0.79 ± 0.02	23.23±0.08	84.9±1.3	8.81 ± 0.08	161 ±3	169±6	10.25 ± 0.72	9.72 ± 0.00				
A2	0.89 ± 0.01	76.97 ± 4.39	47.4 ± 0.4	34.68 ± 2.21	208 ± 6	338±2	15.83 ± 0.35	41.67 ± 0.01				
A3	0.57 ± 0.01	24.79±0.16	192.5±0.9	13.76 ± 0.32	62±0	187 ± 0	13.27±0.65	11.81 ± 0.00				
A4	0.59 ± 0.01	25.36±0.19	141.5 ± 3.9	8.64 ± 0.04	199±8	182 ± 4	12.26 ± 1.46	25.69 ± 0.01				
A5	0.50 ± 0.01	22.84 ± 0.09	85.3±110.3	7.47 ± 0.05	82±2	176±1	11.52 ± 0.98	29.17 ± 0.00				
A Mean±SD	0.67±0.16	34.64±23.69	110.3±57	14.67±11.44	142±67	210±71	12.62 ± 2.10	23.61±13.16				
Location B												
B1	0.38 ± 0.00	10.34±0.16	$8.8 {\pm} 0.1$	3.58 ± 0.09	41±0	78±1	5.11 ± 0.42	32.29±0.00				
B2	0.67 ± 001	24.04 ± 0.50	24.4 ± 0.2	9.21±0.31	130±4	178 ± 2	7.99 ± 0.48	BDL				
B3	1.15 ± 0.06	21.41±0.13	36.5±0.5	8.40 ± 0.12	208±1	160±0	7.34±0.21	BDL				
B4	0.45 ± 0.00	15.26 ± 0.11	23.9±0.4	5.47 ± 0.06	96±1	138±0	8.14 ± 0.72	BDL				
B5	0.50 ± 0.00	23.63±0.55	31.5±0.7	8.88 ± 0.15	101±2	140±3	9.08 ± 0.85	40.62 ± 0.01				
B6	0.46 ± 0.01	16.97±0.22	15.2±0.2	5.62 ± 0.16	36±0	83±1	5.44 ± 0.49	50.00 ± 0.01				
B7	0.14 ± 0.00	11.00±0.39	3.3±0.0	3.88 ± 0.20	23±1	146±12	5.84 ± 0.25	BDL				
B Mean±SD	0.54±0.31	17.52±5.69	20.5±12.0	6.44±2.37	91±7	132±38	6.99±1.53	17.56±22.49				
			L	ocation C								
C1	0.62 ± 0.01	19.75±0.09	230.2±10.3	5.49 ± 0.44	178 ± 2	142 ± 2	7.45 ± 0.32	86.45 ± 0.01				
C2	0.57 ± 0.01	18.96±0.19	73.7±0.2	8.15±0.15	64±1	150±1	11.15 ± 1.41	27.08 ± 0.00				
C3	0.28 ± 0.01	12.99±0.10	22.3±0.8	7.60 ± 0.03	26±0	63±0	8.45±0.17	10.42 ± 0.00				
C4	0.27 ± 0.01	11.90 ± 0.04	15.9±0.4	5.02 ± 0.04	44 ± 0	93±1	8.69±1.25	18.75 ± 0.00				
C Mean±SD	0.44±0.19	15.90±4.03	85.5±99	6.57±1.54	78±68	112±41	8.93±1.57	35.68±34.53				
Overall PTM												
Mean±SD	0.55±0.25	22.47±15.43	64.8±68.1	9.04±7.28	129±93	152±63	9.25±2.97	23.60±21.94				

 Table 4.7: Concentration of PTMs in Roadside Soil Samples during the Wet Season

BDL-below detection limit

Location/Sites	Cd	Cr	Cu	Ni	Pb	Zn	V	Pt				
				$(mg kg^{-1})$				$(\mu g k g^{-1})$				
]	Location A								
A1	0.33 ± 0.00	11.23 ± 0.14	25.5 ± 0.8	3.58 ± 0.02	34±0	257±1	5.38±0.19	8.33±0.00				
A2	0.68 ± 0.00	19.08 ± 0.08	40.3±0.5	7.00 ± 0.06	368±24	223±0	7.84 ± 0.19	BDL				
A3	0.66 ± 0.01	19.06±0.13	34.3±0.4	10.13±0.09	115±2	245±0.9	7.92 ± 0.33	BDL				
A4	$0.54{\pm}0.00$	22.86 ± 0.02	30.7±0.3	15.08 ± 0.40	102±1	194±3	$7.20{\pm}1.13$	BDL				
A5	0.92 ± 0.02	29.41±0.26	58.7±1.9	12.67±0.18	308±5	518±2	10.26 ± 0.07	BDL				
A Mean±SD	0.70±0.20	20.33±6.61	37.9±12.8	9.69±4.55	185±144	287±131	7.72±1.75	1.67±3.73				
Location B												
B1	$0.54{\pm}0.00$	19.93 ± 0.04	46.5 ± 1.1	7.49 ± 0.03	132±1	161±1	9.09 ± 0.58	45.83 ± 0.01				
B2	0.53 ± 0.00	39.97 ± 0.61	22.1±0.4	15.29±0.66	53±2	139±0	11.66 ± 1.00	43.75 ± 0.01				
B3	1.06 ± 0.03	32.46 ± 0.06	$62.4{\pm}1.0$	9.89 ± 0.06	186±4	284±1	13.62±0.56	77.08 ± 0.02				
B4	0.85 ± 0.01	41.86 ± 1.06	73.2±0.3	14.38 ± 0.05	156±0	267±1	14.23 ± 2.63	14.58 ± 0.00				
B5	0.72 ± 0.00	34.81 ± 0.02	67.1±1.1	11.15 ± 0.08	141±3	250±1	11.94±0.34	6.25 ± 0.00				
B Mean±SD	0.74±0.23	33.81±10.82	54.2±18.6	11.64±3.76	134±9	220±97	12.11±3.51	35.50±28.18				
				Location C								
C1	0.29 ± 0.00	10.32 ± 0.11	11.7 ± 0.1	11.43±0.19	30±1	83±1	6.04 ± 0.43	41.67 ± 0.01				
C2	0.21 ± 0.00	12.67 ± 0.10	13.0±0.5	3.41 ± 0.04	14 ± 0	83±0	$7.76{\pm}1.08$	31.25 ± 0.01				
C3	0.10 ± 0.00	4.55 ± 0.05	47.3±3.5	1.82 ± 0.03	29±1	53±2	2.63 ± 0.04	BDL				
C4	0.55 ± 0.02	16.09 ± 0.09	37.0±1.0	9.78 ± 0.04	36±1	133±1	8.79±0.03	BDL				
C Mean±SD	0.29±0.19	10.91±4.86	27.3±17.7	6.61±4.71	27±9	90±36	6.31±2.70	18.23±21.47				
Overall PTMs'			••• • ••• •									
Mean±SD	0.55±0.28	21.44±11.49	38.5±19.3	9.04±4.24	125±9	202±109	8.30±3.61	19.20±23.77				

Table 4.8: Concentration of PTMs Roadside Soil Samples in the Dry Sease	on
---	----

BDL-below detection limit

Analysis of the results of the PTMs obtained in the roadside soils showed the same PTMs' concentration trend as observed for the highway runoff samples and atmospheric deposition samples i.e. Zn>Pb>Cu. This may be an indication that the same variables may likely have influenced the inputs of these metals into the three studied environmental media. In addition, because the roadside soils serve as a temporary sink for these PTMs, they gradually accumulate until the next rainfall when they are mobilised as dissolved or particulate fraction to the recipient water thus the higher concentrations in the roadside soils. Factors such as traffic intensity, level of rainfall, catchment area land use, length of antecedent rainfall and the capture of first flush samples largely account for the general variability observed in the concentrations of the PTMs during the dry and wet seasons studied. Although, it might have been expected that concentrations of the PTMs should be higher in the dry season than the wet season, this was not the case for all the metals determined. Lead and vanadium had fractionally higher overall mean concentrations of 106% and 104% increase during the wet season than in the dry season. Analysis of variance (ANOVA) (p>0.005) of the sampled sites' concentrations obtained during these seasons for the metals showed no significant difference. Also, Cu and Pt had higher overall mean concentrations in the wet season than in the dry season with 159% and 126% increase respectively. Cadmium, nickel and zinc were higher during the dry season than in the wet season with 103%, 105% and 137% increase respectively. Further analysis of the results showed that sites A1 and C2, which are busier in terms of traffic, had higher concentrations in the wet seasons for all the metals except for Zn at A1 and platinum at C1 which were higher in the dry season. Site A3 which also showed comparative higher PTM concentrations than some of the sampled sites also had more metals in the wet season than in the dry season except for Cd and Zn which were higher in the dry season. The observed higher mean concentration of metals in the wet season over that of the dry season could be as a result of spray from traffic during the wet season which can wash the under-carriage of automobiles. As reported by Barret (2008), this process of vehicular under-carriage wet season "wash" results in an increase in metal constituents during the wet season.

Overall mean concentrations of Cd, Cr and V changed little during the two seasons though variability was shown when the results were compared on site to site basis (Figures 4.3, 4.4 and 4.8 respectively). The metals were nevertheless higher than their background levels in soil which showed that they were enriched in the roadside soils. Sites A1, A3 and C2, had higher concentrations of these metals during the wet season than in the dry season as also seen for Pb and Cu indicating additional sources of roadside soil enrichment. The source of Cd enrichment in the roadside soils was attributed to Cd plated brake parts, especially rotors which could contain up to

62.1% Cd (McKenzie et al., 2009).

The mean concentrations obtained for Zn, Pb and Cu were 253%, 547% and 260% higher than the respective background levels in the dry season and 105%, 358% and 272% respectively in the wet season. The lower percentage difference in the mean concentration of for Zn during the wet season compared to the background concentration is due to the relatively higher solubility of Zn which makes it more mobile and easily transported from the impervious road surface unlike Pb which is more strongly associated with organic matter and thus are less mobile than zinc in runoff. However, Pb and similar particulate-bound PTMs could still be mobilised from the impervious environment to the recipient water body as suspension in the highway runoff water (Deletic *et al.* (2000); Jartun *et al.*, 2008). Wei *et al.* (2010) while reporting concentration ranges of $0.025 - 0.12 \text{ mg L}^{-1}$ Pb and $0.1 - 1.2 \text{ mg L}^{-1}$ Zn in runoff from roads in Xiamen city, China said most PTMs in runoff exist as labile complex species which may be adsorbed onto surfaces of suspended particles and could easily be released when the pH decreases.

The preponderance of Zn in all the sampled media in this study could be attributed to the abrasion of vehicle tyres and which could also be exacerbated by the wide use of second-hand tyres in Nigeria. Christensen and Guinn (1979) had shown that a 15 cm wide and 65 cm diameter tyre contributes about 3.0 mg of Zn (as well as other metals) to road surfaces and their immediate environments. This assertion was also reinforced by Callender and Rice (2000) who stated that a significant amount of zinc is released onto the road surfaces from the ZnO component of tyres through wear and abrasion. The mean concentrations of 104 and 69 mg kg⁻¹ Pb for wet and dry seasons respectively in this study were much higher than that reported by Ubogu and Essoka in 2006 from the Kaduna-Zaria expressway which average was 3 mg kg⁻¹. The concentrations obtained for lead also appear to contradict the assertion by relevant Nigerian government agencies that leaded petrol is no longer being imported into Nigeria, especially when smuggled and mostly uncertified fuel still find their way into the market. Concentrations indicated in this study were also higher than the $11 - 70 \text{ mg kg}^{-1}$ range reported by Turer *et al.* (2001) in Cincinnati, US. The source of copper in roadside soils is mainly from the contributions from brake pads. Armstrong (1994) in a runoff study of Santa Clara valley, USA revealed that as high as 15% Cu, 5.1% Zn and 2.2% Pb wt/wt were released from brake pads. Akbar et al. (2006) while reporting concentrations of 176 ± 5 mg kg⁻¹ Zn, 232 \pm 12 mg kg⁻¹ Pb and 87.3 \pm mg kg⁻¹ Cu in soils of northern England stressed that roadside soils are a rich source of PTMs in the environment.

Sites A1, A5, B3 and C2 mostly had higher PTM concentrations compared to the other sites while

comparatively lower concentrations of the PTMs were observed at sites A2, B2 and B7.

Pearson correlation analysis showed parallel relationships between the PTMs determined in the roadside soils especially for Cu, Pb and Zn (Table 4.9). The high correlation between the results of the PTMs in the roadside soils could be attributed to the dominant role of vehicular activities as their major source. Duncan multiple range test (DMRT) homogeneous subset for the metals and the sampling locations showed that the sampling location A (Mile 2 – Oshodi highway) had the highest mean concentration of the PTMs followed mostly by the B sampling location (Mile 2 – Wharf highway) (Table 4.10). This is due to the higher traffic volume on Location A as it is a major road which connects Mainland Lagos to the densely populated suburbs and outskirt settlements of Lagos and is also bothered by substantial number of industrial catchments. The traffic volume on Location B is mainly due to the activities at the main ports of Lagos characterised by heavy vehicles. Location C is mostly characterised by commercial and residential land use catchments thus experience less of the heavy vehicles associated with the other two locations though a substantial number of cars and small buses ply the road.



Figure 4.3: Concentration of Cadmium (Cd) in Roadside Soils during the Wet and Dry Seasons



Figure 4.4: Concentration of Chromium (Cr) in Roadside Soils during the Wet and Dry

Seasons.



Page 120



Figure 4.5: Concentration of Copper (Cu) in Roadside Soils during the Wet and Dry Seasons

Figure 4.6: Concentration of Nickel (Ni) in Roadside Soils during the Wet and Dry Seasons.



Figure 4.7: Concentration of Zinc (Zn) in Roadside Soils during the Wet and Dry Seasons



Figure 4.8: Concentration of Vanadium (V) in Roadside Soils during the Wet and Dry

Page 122

Seasons



Figure 4.9: Concentration of Lead (Pb) in Roadside Soils during the Wet and Dry Seasons



Page 123

Figure 4.10: Concentration of Platinum (Pt) in Roadside Soils during the Wet and Dry

Seasons

		Cd	Cr	Cu	Ni	Pb	Zn	Pt	V
Cd	PC	1.000	0.386**	0.086	0.076	0.367**	0.607^{**}	0.412**	0.194*
	Sig. (2-tailed)		0.000	0.117	0.165	0.000	0.000	0.000	0.040
Cr	PC	0.386**	1.000	0.082	0.542^{**}	0.182^{**}	0.340^{**}	0.390^{**}	0.429^{**}
	Sig. (2-tailed)	0.000		0.135	0.000	0.001	0.000	0.000	0.000
Cu	PC	0.086	0.082	1.000	-0.017	0.420^{**}	0.196**	-0.014	-0.054
	Sig. (2-tailed)	0.117	0.135		0.763	0.000	0.000	0.801	0.573
Ni	PC	0.076	0.542^{**}	-0.017	1.000	0.008	0.063	0.076	0.279^{**}
	Sig. (2-tailed)	0.165	0.000	0.763		0.887	0.251	0.164	0.003
Pb	PC	0.367^{**}	0.182^{**}	0.420^{**}	0.008	1.000	0.521^{**}	0.221^{**}	-0.093
	Sig. (2-tailed)	0.000	0.001	0.000	0.887		0.000	0.000	0.329
Zn	PC	0.607^{**}	0.340^{**}	0.196***	0.063	0.521^{**}	1.000	0.363^{**}	-0.005
	Sig. (2-tailed)	0.000	0.000	0.000	0.251	0.000		0.000	0.957
Pt	PC	0.412^{**}	0.390^{**}	-0.014	0.076	0.221^{**}	0.363**	1.000	0.167
	Sig. (2-tailed)	0.000	0.000	0.801	0.164	0.000	0.000		0.078
V	PC	0.194^{*}	0.429^{**}	-0.054	0.279^{**}	-0.093	-0.005	0.167	1.000
	Sig. (2-tailed)	0.040	0.000	0.573	0.003	0.329	0.957	0.078	

Table 4.9: Pearson Correlation Table for the PTMs Determined in Roadside Soil Samples

PC – Pearson Correlation; **- Correlation is significant at the 0.01 level (2-tailed); *- Correlation is significant at the 0.05 level (2-tailed).

Table 4.10: Multiple	Comparison	for	the	PTMs	Determined	in	Roadside	Soils	and	Lagos
Lagoon Sediment Sam	ples									

Sampling	Sampling								
Location	Location	Cd	Cr	Cu	Ni	Pb	Pt	Zn	V
Mile2-	Mile2-Wharf	0.000	0.001	0.000	0.057*	0.000	0.000	0.001	0.000
Oshodi	Ijora - Ah.Bello	0.000	0.000	0.030	0.032	0.000	0.000	0.000	0.000
	Lagos Lagoon	0.000	0.423*	0.000	0.000	0.000	0.000	0.000	0.000
Mile2-	Mile2-Oshodi	0.000	0.001	0.000	0.057*	0.000	0.000	0.001	0.000
Wharf	Ijora - Ah.Bello	0.000	0.000	0.011	0.632*	0.002	0.000	0.000	0.507*
	Lagos Lagoon	0.000	0.001	0.316*	0.000	0.000	0.000	0.000	0.000
Ijora-	Mile2-Oshodi	0.000	0.000	0.030	0.032	0.000	0.000	0.000	0.000
Ah. Bello	Mile2-Wharf	0.000	0.000	0.011	0.632*	0.002	0.000	0.000	0.507*
	Lagos Lagoon	0.117*	0.000	0.004	0.000	0.018	0.007	0.010	0.000
Lagos	Mile2-Oshodi	0.000	0.423*	0.000	0.000	0.000	0.000	0.000	0.000
Lagoon	Mile2-Wharf	0.000	0.001	0.316*	0.000	0.000	0.000	0.000	0.000
	Ijora -Ah.Bello	0.117*	0.000	0.004	0.000	0.018	0.007	0.010	0.000

4.4.3 PTMs in the Lagos Lagoon Water Column and Sediment Samples

Concentrations of PTMs in the water column and sediment samples of the Lagos Lagoon are shown in Table 4.11 and Figure 4.11. The observed range of the metals were $0 - 0.101 \text{ mg L}^{-1}$ Cu, $0 - 0.235 \text{ mg L}^{-1}$ Pb and $0 - 1.570 \text{ mg L}^{-1}$ Zn with mean concentrations of 0.038 ± 0.045 , 0.084 ± 0.093 and $0.650 \pm 0.641 \text{ mg L}^{-1}$ respectively. Levels of the metals were higher at the highway watersheds than the other sampled stations on the Lagoon.

In the sediment samples, mean concentration of the PTMs were 13.1 ± 9.4 mg kg⁻¹ Cu, 22.7 ± 12.7 mg kg⁻¹ Pb, 65 ± 52 mg kg⁻¹ Zn and $1.64 \pm 1.46 \ \mu$ g kg⁻¹ Pt (Table 4.11 and Figure 4.12). Also mean concentrations observed for Cd, Cr, Ni and V were 0.85 ± 0.68 , 27.20 ± 13.71 , 11.87 ± 6.27 and 21.54 ± 11.83 mg kg⁻¹ respectively (Table 4.11 and Figure 4.13). Trend observed for the PTMs in the highway runoff and roadside soils samples were also shown in the sampled Lagoon water and sediments i.e. Zn>Pb>Cu>Cr>Ni>V>Cd>Pt. Higher concentrations of the PTMs were observed at locations L1, L3, L4 and L7 which were mostly the watersheds (except for L1) of the study Location C (Ijora-Ahmadu Bello Road) into the Lagoon relative to other sampled sites on the Lagoon.

Sampling											
Site		<u>Cu</u>	<u>Pb</u>		2	<u>En</u>	Cd	<u>Cr</u>	Ni	$\underline{\mathbf{V}}$	<u>Pt</u>
	Sediment	Water	Sediment	Water	Sediment Water		Sediment	Sediment	Sediment	Sediment	Sediment
	(mg kg ⁻¹)	(mg L ⁻¹)	(mg kg ⁻¹)	(mg L ⁻¹)	(mg kg ⁻¹)	$(mg L^{-1})$	(mg kg ⁻¹)	(µg kg ⁻¹)			
L1	16.6	0.010	33.4	0.034	89	0.821	0.60	44.39	18.03	36.99	4.50
L2	12.8	0.076	22.6	0.162	76	0.731	1.02	30.57	16.12	27.79	2.49
L3	30.4	0.082	39.8	0.134	161	1.574	1.79	38.19	18.15	33.56	1.65
L4	10.5	0.101	25.0	0.235	20	1.320	1.71	33.94	12.43	16.78	1.18
L5	2.8	BDL	6.6	BDL	16	0.009	0.18	10.09	4.15	8.72	0.41
L6	3.0	BDL	5.7	BDL	24	BDL	0.17	8.30	2.92	6.41	0.42
L7	15.8	BDL	26.0	0.02	66	0.098	0.50	24.94	11.27	20.42	0.85
Mean ± SD	13.1±9.4	0.038±0.046	22.7±12.7	0.084±0.093	65±52	0.650±0.641	0.86±0.68	27.20±13.71	11.87±6.27	21.52±11.83	1.64±1.46

 Table 4.11: Concentration of PTMs in the Sediment and Water Column of the Lagos Lagoon

The PTMs in the water column of the Lagoon (Figure 4.11) showed that watersheds of the sampled highways i.e. L1, L3, L4 and L7 on the Lagoon were selectively PTMs enriched in contrast to sampled sites which do not directly receive highway runoff and roadside soil derived sediments. Comparative higher concentrations of the metals were observed at these locations. Site L1 though located outside the catchment of the sampled highways, directly receives roadside soils and road derived sediment which are dumped into the Lagoon from a drainage duct on the Third Mainland Bridge by the highway managers or road sweepers. Site L3 and L4 receives highway runoff and road derived sediment from site C1 catchments on Location C. Sites L6 and L7 also receive inputs from C3 catchments.

Concentrations of Zn, Pb and Cu were the highest in the sediment obtained from site L3 (Figure 4.12). A noticeable comparative higher Zn concentration of 160.8 mg kg⁻¹ was observed at this site. This is consistent with the higher concentrations of Zn in the highway runoff and roadside soil samples from site C1. Although other sources of Zn apart from highway derived inputs may not be ruled out at this site, the corresponding higher concentrations of copper and lead at this site also suggest a possible highway origin and most importantly, concentration of platinum was also comparatively higher at this site than sites L4 and L5 which were not direct watersheds of the highway (Figure 4.12). Platinum is widely used in catalytic converters of vehicular engines to convert harmful combustion by-product gases to less harmful ones that could be released into the atmosphere (Chauhan, 2010) but the platinum metals of these converters end up being released along with the gases overtime and thus serve as a good fingerprint for identifying the vehicular influence on environmental media (Helmers, 1996). Therefore the comparative higher concentration of Pt in the sediment from this site strongly indicates possible influence of the the adjoining highway on the levels of PTMs observed in the Lagoon. Site L1 had the highest sediment concentration of Pt among the sampled sites and also higher levels of Zn, Cu and Pb than other sites with the exception of site L3 which could directly be adduced to the dumping of swept roadside soils at this site. Site L5 which had the lowest concentrations of PTMs in the Lagoon sediment was on the opposite bank of the sampled watersheds thus was less influenced by the highway derived sediments. Comparative lower concentrations were also recorded at L6 (Cowry creek) despite being close to a highway watershed at C3. This could be attributed to the strength of the water current of the recipient Lagos Lagoon water, of about 0.21 m s⁻¹ (Vijverberg *et al.*, 2012), at this site which is always strong all year round and thus would have made continuous sedimentary accumulation of road derived sediment impossible. Site L7 which was downstream of L6 and also close to a watershed of a busy adjoining road showed higher concentrations of the PTMs than those observed at L6. Concentrations of Cd, Cr, Ni and V (Figure 4.13) were also higher at L1, L2, L3 and L7 than those of the other sampled sites on the Lagoon. Enrichment of nickel and vanadium in environmental samples could be tied down to anthropogenic sources such as the burning of fossil fuel (Hope 1996) and leacheate from poorly surfaced asphalted (bitumen coated) roads. Though inputs of these metals from road runoffs exclusively from asphalted road has been reported to be less than 5 μ g L⁻¹, their concentrations could become significant if inclusive of additional sources such as vehicular emission and crank case oil leakages (Wess *et al.*, 2004). The site concentration trends confirm the highway origin of Ni and V in this study as earlier established for Zn, Pb, Cu and Pt. As observed in the concentrations of the other PTMs determined, mean concentrations of Cd and Cr in the Lagoon sediment were higher than their respective mean in the roadside soil from the contiguous Location C and more so at the L1, L3 and L7 which could only suggest a gradual buildup of the PTMs from the highway roadside soils into the Lagoon sediment. Sutherland (2000) and Sutherland and Tolosa (2000) had associated Pb in studies on the bed sediments from urban streams in Hawaii, US to the pollution from highway with traffic as the main source (Jartun *et al.*, 2008).

The Duncan multiple range test showed a significant variation between the total concentrations of the PTM in the roadside samples obtained from the different locations and those of the Lagos Lagoon (Table 4.12).



Figure 4.11: Concentration of some PTMs in the Water Column of the Lagos Lagoon



Figure 4.12: Concentration of Cu, Pb, Zn and Pt (µg kg⁻¹) in the Sediments of Lagos Lagoon



Figure 4.13: Concentration of Cd, Cr, Ni and V in the Sediments of the Lagos Lagoon

4.4.4 Comparison of the PTM Concentrations in this Study with Results in Literature

Comparison of the results obtained for the runoff samples and rain-water control and available concentration limits for the determined PTMs in surface water with aquatic lifes (FMenv, 1991) showed that the observed concentrations in the highway runoff samples were higher (Table 4.12). This clearly suggests that the highway runoff from these roads can only have a negative impact on the water qualities of the Lagos Lagoon.

Table 4.12: Comparison of PTM Concentrations in this Study, Control Samples and WaterStandard/Soil Background Levels.

PTM	Atmospheric Fallout (mg	2 L ⁻¹)	Highwa	y Runoff	$f(mg L^{-1})$	Roadside Soils (mg kg ⁻¹)			
	This study	Ctrl ¹	This Study	Ctrl ²	Aquatic Water Std.*	This Study	Ctrl ³	Bkgrd Level**	
Cd	0.01 ± 0.01	BDL	0.005 ± 0.01	BDL	0.0002-0.0018	W 0.55 ± 0.57	$0.22\pm\ 0.01$	NA	
Cr	0.10 ± 0.06	BDL	0.02 ± 0.01	BDL	0.02	D 0.57 ± 0.27 W 22.5 ± 22.5	14.1 ± 0.1	NA	

						$^{\rm D}$ 22.4 ± 11.6		
Cu	0.27 ± 0.31	BDL	0.09 ± 0.12	BDL	0.002-0.004	$^{W}64.8 \pm 68.1$	5.24 ± 0.01	25
						$^{\rm D}$ 40.7 \pm 19.5		
Ni	0.17 ± 0.22	BDL	0.03 ± 0.01	BDL	0.025-0.150	$^{W}9.04 \pm 9.51$	4.72 ± 0.02	NA
						$^{\rm D}$ 7.28 \pm 4.36		
Pb	0.19 ± 0.15	BDL	0.31 ± 0.28	0.009	0.0017	W 129 \pm 93	9 ± 0	19
						$^{\rm D}$ 121 ± 107		
Pt	-	-	-	-	NA	$^{\rm W}0.02\pm0.02$	BDL	0.01
						$^{\rm D}$ 0.02 \pm 0.02		
Zn	0.89 ± 0.51	BDL	0.53 ± 0.51	BDL	0.03	W 152 ± 63	9 ± 0	60
						$^{\rm D}207 \pm 117$		
V	-	-	-	-	NA	$^{\mathrm{W}}$ 9.24 \pm 2.97	1.58 ± 0.54	NA
						D 8.88 ± 3.22		

¹-Atm. Fallout Ctrl; ²-Highway Runoff control; ³-Roadside soil control; NA-Not Available; BDL-Below Detection Limit; *Limts of PTMs for water with aquatic life FMEnv (1991); ** Breault and Granato (2000); ^W – Wet Season; ^D – Dry Season.

All the metals determined in the roadside soils were above background PTMs levels in soil as reported by Breault and Granato (2000) and also exceeded the concentration observed for the control sample (Table 4.12).

While there are no published data on highway runoff study from Nigerian roads and urban centres, comparison of the results obtained from this study with other similar studies around the world showed that concentration of Pb obtained were higher than those reported by Mangani *et al.* (2005) in runoff from a highway in Central Italy and Kayhanian *et al.* (2008) in studies carried out on three highways in Los Angeles, USA (Table 4.13). This may also show the inability of Nigeria in meeting up with existing regulations on the phasing out of leaded petrol. The concentrations of Zn and Cu were not significantly different in these reported studies.

Table 4.13: Comparison of PTM Results in this Stu	dy with Similar Stu	udies on Runoff and
Roadside Soils		

PTM	This Study	(Turer <i>et al.</i> , 2001)	(Akbar <i>et al.</i> , 2006)	(Mangani <i>et al.</i> , 2005)	(Kayhanian <i>et al.</i> , 2008)
		Runoff	$(mg L^{-1})$		
Zn	0.074 - 0.838	-	-	0.347 - 0.393	0.007 - 1.830
Pb	0.009 - 0.737	-	-	0.003 - 0.027	0.002 - 0.072
Cu	0.002 - 0.170	-	-	0.018 - 0.012	0.004 -0.560
		Roadside So	oils (mg kg ⁻¹)		
Zn	151.45 ± 206.93	25 - 279	174.6 ± 4.9	87.91 - 437.54	-

Pb	103.77 ± 121.70	11 - 70	232 ± 12.7	46.11 - 101.59	-
Cu	64.83 ± 40.70	3 - 17	87.3 ± 3.0	1.40 - 4.69	-

4.5 ANIONIC NUTRIENTS

4.5.1 Reference Materials and Calibration of Method

The recovery obtained for the reference materials used in the air segmented continuous flow analysis (ASCFA) phosphorus determination were 95.3% and 93.3% for SO-2 and SRM 2711 respectively with calculated expanded uncertainties (U_{Δ} ; k = 2) of 242 and 74 mg kg⁻¹ respectively (Table 4.14). The differences between the certified values and the measured values (Δ_m ; Table 4.8) were lower than the expanded uncertainties, U_{Δ} which shows that there was no significant difference between the certified and measured values (Linsinger, 2005) and thereby affirmed the suitability of the method used.

The calibration graph obtained from the plot of absorbance and concentrations of standard phosphate solutions had a gradient of 14.5 counts / μ g L⁻¹ P, a 0.0 intercept and a correlation coefficient (r) of 0.9991 (Figure 4.14). The limit of detection (blank + 3 S.D. of the blank) was 3.7 μ g P L⁻¹.

	Reference Material		
	SO-2 $(n = 6)$	SRM 2711 (n = 6)	
Experimental value ± 2 S.D. (mg Kg ⁻¹)	2860 ± 332	802 ± 64	
Certified Value ± 2 S.D. (mg Kg ⁻¹)	3000 ± 200	860 ± 70	
Recovery (%)	95.3	93.3	
$\Delta_{\rm m} ({\rm mg}\;{\rm Kg}^{-1})$	140	58	
Expanded Uncertainty U $_{\Delta}$, (mg Kg ⁻¹)	242	74	

Table 4.14: Validation Analysis of Total Phosphorus in Reference Material

SO-2, Canada Center for Mineral and Energy Technology; SRM 2711, National Institute of Standards and Energy, USA.



Figure 4.14: Calibration Graph of Standard Phosphate Solutions used in the ASCFA Determination of Phosphorus

4.5.2 Total Phosphorus in Roadside Soils

Results of the mean total concentrations in the roadside soils using ASCFA are presented in Table 4.15. The mean concentration range for total phosphorus for the different sampling locations were $73 \pm 20 - 622 \pm 514 \text{ mg kg}^{-1}$ for the wet season and $170 \pm 10 - 1320 \pm 480 \text{ mg kg}^{-1}$ for the dry season. The highest concentrations were observed at location A3 ($622 \pm 514 \text{ mg kg}^{-1}$) and C2 ($1320 \pm 480 \text{ mg kg}^{-1}$). Sites B3 and B4, which are in proximity to the Lagos port, had more total phosphorus than other sampled sites at Location B for both seasons with concentrations of 248 ± 189 and $250 \pm 50 \text{ mg kg}^{-1}$ respectively for the wet season and $535 \pm 16 \text{ mg kg}^{-1}$ and $389 \pm 92 \text{ mg kg}^{-1}$ for the dry season. No samples were available for sites B6 and B7 during the dry season as these were runoff ducts and contained no soil.

Sample site	Wet Season	Dry Season (n=6)	
	$[Mean \pm S.D. (mg kg^{-1})]$		
	Location A		
A1 (n = 18)	196 ± 87	170 ± 10	
A2 $(n = 6)$	304 ± 14	321 ± 49	
A3 (n = 15)	622 ± 514	262 ± 10	
A4 (n = 18)	270 ± 180	266 ± 40	
A5 (n = 18)	342 ± 225	386 ± 17	
A (mean±SD)	347 ± 163	281 ± 80	
	Location B		
B1 (n = 12)	134 ± 46	302 ± 22	
B2 (n = 12)	208 ± 170	197 ± 21	
B3 (n = 12)	248 ± 189	535 ± 16	
B4 (n = 12)	250 ± 50	389 ± 92	
B5 (n = 12)	224 ± 170	329 ± 96	
B6 (n = 12)	226 ± 63	NAS	
B7 (n = 12)	73 ± 20	NAS	
B (mean±SD)	195 ± 66	350 ± 124	
	Location C		
C1 (n = 12)	419 ± 588	714 ± 181	
C2 (n = 9)	505 ± 214	1320 ± 480	
C3 (n = 12)	215 ± 126	264 ± 82	
C4 (n = 12)	325 ± 65	219 ± 117	
C (mean±SD)	393 ± 86	629 ± 512	
Overall mean±SD	285 ± 279	424 ± 629	

Table 4.15: Mean Concentration of	of Total Phosphorus using Air	Segmented Continuous
Flow Analysis.		

Generally, the concentrations measured during the wet season had higher temporal variability (as indicated by their higher standard deviations) than those measured during the dry season (Table 4.15). This may be due to the widely variable length and intensity of rainfall events prior to and during each sampling. Samples collected at the beginning of the wet season also indicated higher total phosphorus concentrations compared with samples collected later due to flushing of the system after the dry season (Sansalone and Cristina, 2004). There was no significant difference (P>0.05) between the observed concentrations for the wet and dry seasons at most of the sampling locations except for site A3 (which had the highest wet season concentration for any site and also the highest temporal variability as reflected by its standard deviation) and sites B3, C1 and C2 for which the dry season concentrations were significantly higher (Table 4.15). Similarly for the wet season, locations A3, C1 and C2 were significantly higher. The paired t-test for the three roadside soil locations had t-values of 0.88 (< than tabulated value of 2.78 at P=0.05) for location A; 2.85 (> the tabulated t value of 2.78 at P=0.05) for location B and 1.15 (< the tabulated 4.54 at P=0.05) for location C. Therefore, only the second location (B) could be said to show a significant difference in the observed concentrations for the two seasons. Site A3 is bordered to the west by an industrial estate (one of many in Lagos) and to the east by a densely populated neighbourhood. Traffic density at this location was about 4,210 vehicles per hour with a significant percentage being heavy duty trucks, articulated vehicles and commuter buses. Site B3 is in close proximity to the port of Lagos and site C2 is the site of a major bus and ferry terminus linking mainland Lagos with the surrounding islands. Since sites B3 and C2 are major traffic hubs, a direct link between traffic density and higher total phosphorus concentration in roadside soils is evident particularly during the dry season. Further analysis of the dry season data showed that the P concentration for sites B3, C1 and C2 were significantly higher than the other sites. Similarly for the wet season, sites A3, C1 and C2 were significantly higher, which reinforces the view that a major source of phosphorus loading in the Lagos Lagoon is the mobilisation of roadside soil in close proximity to transport hubs.

4.5.3 Bioavailable Phosphorus in Roadside Soils

The results obtained for sodium bicarbonate (Olsen-P) extractable phosphorus (also defined as

bioavailable phosphorus) are as presented in Table 4.16. The concentrations for bioavailable phosphorus also showed greater variability in the wet season compared with the dry season. Another feature of the data is the consistently lower inter-site variability for the wet season data compared with the dry season, particularly for the Mile 2 – Wharf Highway locations (B1 – B7), suggesting a more consistent bioavailable phosphorus fraction in the solid phase that is not leached by interaction with rainwater but is leached by the standard Olsen P protocol. The mean concentration ranges of bioavailable phosphorus for the different sampling locations were 2.57 ± $0.64 - 9.40 \pm 5.10 \text{ mg kg}^{-1}$ for the wet season and $4.75 \pm 0.70 - 21.98 \pm 0.86 \text{ mg kg}^{-1}$ for the dry season. On a site by site basis the dry season values were consistently significantly higher than the wet season values.

Sampling Location	Wet Season	Dry Season
	[Mean \pm S.I	D. $(mg kg^{-1})]$
	Location A	
A1 (n=18)	3.56 ± 2.16	12.55 ± 1.10
A2 (n=6)	3.76 ± 0.44	17.34 ± 0.34
A3 (n=18)	7.94 ± 3.58	13.61 ± 3.58
A4 (n=18)	6.43 ± 8.04	12.79 ± 8.04
A5 (n=18)	4.72 ± 1.20	21.98 ± 0.86
A (mean)	$\textbf{5.28} \pm \textbf{1.87}$	15.7 ± 4.03
	Location B	
B1 (n=12)	4.72 ± 0.76	11.73 ± 0.43
B2 (n=12)	4.09 ± 0.74	11.41 ± 0.73
B3 (n=12	5.47 ± 2.40	16.27 ± 0.34
B4 (n=12)	4.18 ± 1.58	11.11 ± 0.21
B5 (n=12)	4.99 ± 5.70	8.32 ± 0.57
B6 (n=12)	5.33 ± 3.26	NAS
B7 (n=12)	2.57 ± 0.64	NAS
B (mean)	$\textbf{4.48} \pm \textbf{0.99}$	11.9 ± 4.12
	Location C	
C1 (n = 12)	4.60 ± 2.20	4.75 ± 0.70
C2 (n = 12)	6.80 ± 3.50	10.70 ± 0.41
C3 (n = 12)	4.20 ± 2.70	10.88 ± 0.25
C4 (n = 12)	9.40 ± 5.10	18.16 ± 0.10
C (mean)	6.25 ± 2.39	9.73 ± 5.71
Overall mean	5.17 ± 3.47	13.0 ± 8.7

 Table 4.16: Mean Concentration of Bioavailable Phosphorus using Air Segmented

 Continuous Flow Analysis

NAS - No Available Sample in the Dry Season

The bioavailable fraction of the total phosphorus in the roadside soils ranged from 1.01 - 3.52 % of total phosphorus for the wet season (with a mean of 2.06 ± 0.75 %) and 0.81 - 8.29 % for the dry season (with a mean of $4.32 \pm 2.22\%$) (Table 4.17). The percentage was higher in the samples from the B sampling location during the wet season than the other two locations with a mean of 2.49 \pm 0.73 %. Location A had the highest during the dry season with a value of 5.69 \pm 1.00 %. The dry season bioavailable fraction of the total was consistently higher with higher variability (as shown by the standard deviation) in the dry season for the various sites than the wet season. The wet season data also showed the consistent bioavailable fraction that is residual in the wet season roadside soil that is not leached by the Olsen protocol.

Sampling Location	Wet Season	Dry Season
	(%)	(%)
	Location A	
A1	1.82	7.39
A2	1.23	5.39
A3	1.28	5.19
A4	2.38	4.80
A5	1.38	5.70
A Mean	1.62 ± 0.49	5.69 ± 1.00
	Location B	
B1	3.52	3.89
B2	1.96	5.80
B3	2.21	3.04
B4	1.67	2.85
B5	2.23	2.53
B6	2.36	-
B7	3.51	-
B Mean	$\textbf{2.49} \pm \textbf{0.73}$	3.62 ± 1.32
	Location C	
C1	1.01	0.66
C2	2.01	0.81
C3	1.54	4.12
C4	2.89	8.29
C Mean	$\boldsymbol{1.86 \pm 0.79}$	3.47 ± 3.59
Overall Mean	2.06 ± 0.75	4.32 ± 2.22

Table 4.17: Percentage of Bioavailable Phosphorus in Roadside Soils from the Sampled Highways.

```
Page
```

These results obtained for bioavailable phosphorus showed greater variability in the wet season compared with the dry season for the same reasons as those given above for total phosphorus. The higher concentrations obtained in the dry season over the wet season samples at all the locations indicate a build up process for the leachable P in the wet season prior to rainfall events. Another feature of the data is the consistently lower inter-site variability for the wet season data compared with the dry season, particularly for the sites on Location B, suggesting a more consistent bioavailable phosphorus fraction in the solid phase that is not leached by interaction with rainwater but leached by the standard Olsen P protocol. This is also reflected in the data of percentage bioavailable P as shown in Table 4.17. More consistent percentages were obtained during the wet season in contrast to those of the dry season. Hooda et al. (2002) reported that raindrop impact on the soil produces a thin soil zone of about 10 mm undergoing turbulent mixing which facilitates the desorption of nutrients as dissolved phosphorus and nitrate. This process is even more efficient on impermeable hard surfaces such as the highways whose surfaces act as an opposing force to the runoff and provide some friction to the moving particulates. As a result of the imperviousness of the highways (which means there is little infiltration) it could be taken that concentrations of bioavailable P determined in this study end up in the recipient Lagos Lagoon. This represents a semi-continuous supply of rapidly-mobilized P throughout the year (Withers and Jarvie, 2008).



Figure 4.15: Correlation of Bioavailable Phosphorus and Total Phosphorus in the Roadside Soils Samples during the Wet Season.

The concentrations observed for the bioavailable phosphorus for the road samples during the wet season showed a similar trend with those of the total phosphorus albeit as a weak correlation as shown in Figure 4.15. There was no correlation between the bioavailable and the total P during the dry season.

4.5.4 Bioavailable Nitrate (NO₃⁻) in the Roadside Soils

The calibration graph prepared for the bioavailable nitrate determination by the air segmented continuous flow analysis is shown in Figure 4.16. The graph gave a correlation coefficient $R^2 = 0.9999$.



Figure 4.16: Calibration Graph of the Standard Solutions used in the ASCFA Determination of Nitrate (NO₃⁻)

The concentrations of bioavailable NO_3^- in the roadside samples ranged from $0.53 \pm 0.64 - 12.35 \pm 32.88$ mg kg⁻¹ for the wet season and $0.39 \pm 0.08 - 21.35 \pm 0.50$ mg kg⁻¹ for the dry season (Table 4.18). While most of the observed NO_3^- concentrations for the dry season were comparatively higher than those of the wet season, those for sites A3, B2 and all sites on Location C were lower during the dry season. The NO_3^- concentrations during the wet and dry seasons had paired t-values of $0.22 (<2.77_{tab})$, $1.74 (<2.77_{tab})$ and $2.61 (<3.18_{tab})$ for the three different sampled locations A, B and C at 95% confidence limit, an indication that the set of data are not significantly different. The ANOVA values calculated for the wet and dry seasons had F values of 3.56 and 1.77 respectively. These are lower than the tabulated 95% confidence limit values of 3.68 and 3.81 respectively which also suggest that there are no significant differences in the concentrations observed for the wet season samples indicate that concentration of mobilizable NO_3^- (determined as bioavailable nitrate in this study) varies during each sampled event.

Table 4.18: Concentration of NO₂⁻/NO₃⁻ in the Roadside Soils Samples

Page 140

Sampling Location	Wet Season	Dry Season
	Mean (n=8) (mg kg ⁻¹)	Mean (n=4) (mg kg ⁻¹)
	Location A	
A1	0.97 ± 0.28	2.70 ± 0.06
A2	1.04 ± 0.08	11.50±0.22
A3	12.35 ± 32.88	0.88 ± 0.02
A4	0.93 ± 0.46	1.56 ± 0.02
A5	0.97±0.11	3.48±0.08
	Location B	
B1	1.83±0.10	9.62±0.12
B2	3.30 ± 2.72	2.61±0.06
B3	0.53±0.64	2.55±0.10
B4	0.90 ± 0.94	21.35±0.50
B5	1.08 ± 0.84	4.01±0.22
B6	$0.84{\pm}1.04$	*
B7	$1.34{\pm}1.04$	*
	Location C	
C1	2.29 ± 2.58	0.39 ± 0.08
C2	5.88 ± 4.28	1.66±0.06
C3	4.08 ± 4.10	0.65 ± 0.06
C4	$11.44{\pm}15.88$	5.95±0.10

*- No Available Sample

Concentrations of NO^{3-} in the roadside soil samples were relatively higher in the dry season than the wet season due to the "wash-out" effect of the runoff on the roadside soils in contrast to the continuous deposition in the dry season. Sites A2, B1 and B4 which recorded higher levels during the dry season were identified traffic hubs and therefore were exposed to more nitrogen input sources, chief of which are the exhaust of vehicles. The relatively higher variability in the wet seasons' samples could be linked to the usual variation in the factors such as rainfall intensity, traffic volume and antecedent dry period among others. Nevertheless, the slightly similar concentrations of the bioavailable nitrate showed that an average concentration of 2.5 mg kg⁻¹ NO₃⁻ could be mobilized from roadside soils into recipient. This, in addition to other species of nitrogen inclusive of those from particulate sources, which were not covered in this study, showed that roadside soils could serve as a significant source of nitrogen to receiving water. Park *et al.* (2010) stated that roadside soil have higher nitrogen concentration than interior soil irrespective of the age of the soil. The higher concentration of NO₃⁻ in the wet season over the dry season at all sites on Location C may be due to the relatively higher chloride levels in the runoff during the collection of the wet samples. The relative contributions of nitrate to total inorganic N of soils increased significantly as a result of road salt input resulting in increased leaching of NO_3^- to local recipient water (Scott *et al.*, 2008). Higher concentration of road salts has been shown to increase soil pH in the environment, which alters key microbial N transformations with higher soil pH (6-8) known to benefit nitrifying bacteria causing an increase in nitrification rates (Zhu and Carreiro, 2004; Green *et al.*, 2008) although the dynamics of pH changes is more complex when other pollutants are present in roadside soil.

4.5.5 Nitrogen: Phosphorus Ratio in the Roadside Soils

The nitrogen to phosphorus ratio (N:P) in the wet season roadside soil samples ranged from 0.10 -1.56 and 0.06 - 1.92 in the dry season (Table 4.19). The season mean for the locations were 0.48 ± 0.37 and 0.43 ± 0.46 for the wet and dry seasons respectively. Location C with a value of 0.67 ± 0.30 had the highest mean N:P ratio during the wet season and Location B with a ratio of 0.72 ± 0.72 was highest for the dry season. Paired t-test for the two seasons showed that the set of values were not significantly different. Sites with comparative higher concentrations of available nitrates also showed higher N:P ratio greater than the mean seasonal ratio. These sites include A3, B2 and all sites on Location C (> than 0.48 mean of the wet season) and A2, B1, B4 and B5 (> than 0.43 mean of the wet season). The ratio observed at all the locations indicates that nitrogen is the limiting nutrient of the mobilizable nutrients in the roadside soil.

Table 4.19: Bioavailable Nitrogen: Phosphoru	s Ratio (a	as Nitrate to	Phosphate)	in the
Roadside Soils				

Sampling Location	Wet	Dry
	N:P Ratio	N:P Ratio
	Location A	
A1	0.27	0.22
A2	0.28	0.66
A3	1.56	0.06

A4	0.14	0.12					
A5	0.21	0.16					
A Mean	0.49 ± 0.60	0.24 ± 0.24					
Location B							
B1	0.39	0.82					
B2	0.81	0.23					
B3	0.10	0.16					
B4	0.22	1.92					
B5	0.22	0.48					
B Mean	0.34 ± 0.28	$\boldsymbol{0.72 \pm 0.72}$					
Location C							
C1	0.50	0.08					
C2	0.86	0.16					
C3	0.98	0.06					
C4	1.22	0.33					
C Mean	0.67 ± 0.30	0.25 ± 0.31					
Overall Mean	0.48 ± 0.37	0.43 ± 0.46					

The bioavailable N:P ratios as shown in Table 4.18 suggest that nitrogen is the limiting nutrient in the roadside soils. Phosphorus is said to be limiting if the N:P ratio is higher than 16:1 known as the Redfield ratios (Redfield, 1958; Stelzer and Lamberti, 2001). Howarth and Marino (2006) argued that N and not P is mainly the nutrient responsible for coastal water eutrophication thus it is the limiting nutrient. Location C had the highest mean N:P ratio among the sampled locations in the wet season due to the relatively higher nitrate concentration in the wet samples. Location B had the highest mean ratio in the dry season due to higher nitrate concentration in the dry season samples relative to other sites.

4.5.6 Anionic Nutrients in the Lagos Lagoon Sediment Samples.

Total and bioavailable phosphorus concentrations of the Lagoon sediment samples showed that mean concentrations for all sites within the sampling location were 468 ± 387 mg kg⁻¹ total phosphorus and 10.4 ± 6.2 mg kg⁻¹ bioavailable phosphorus (4.0 ± 4.8 % bioavailable; decreasing to 2.3 ± 1.5 % if site L5 is excluded) (Table 4.20). Site L3 had the highest total and bioavailable P concentrations of 1204 ± 172 and 20.9 ± 0.62 mg kg⁻¹ respectively, with the total phosphorus concentration significantly different from all other sites. This may due to its proximity to the sewage discharge point at Iddo. The lowest total phosphorus concentration (65.9 ± 31.8 mg kg⁻¹)

was observed at site L5 though it also had the highest bioavailable phosphorus fraction (14.4 %) due to the comparative high concentration 9.48 mg kg⁻¹ of Olsen leachable phosphorus in the samples. Sites L2 (619.2 \pm 33.4 mg kg⁻¹) and L7 (637.2 \pm 4.2) also had concentrations above the mean total P concentrations for the Lagoon sediment. Similarly, sites L3 and L7 had more bioavailable P concentrations than the mean concentration for the Lagoon sediment. The location mean of the dissolved phosphorus in the water column of the Lagoon was 1.27 \pm 1.16 mg L⁻¹ with all the sampled sites having concentrations higher than the maximum 0.01 mg L⁻¹ level for surface water.

Site L1 with a mean nitrate concentration of $11.24 \pm 0.38 \text{ mg kg}^{-1}$ was highest in the Lagoon sediment samples (Table 4.20). This concentration was 229% higher than the location mean of 4.90 \pm 4.47 mg kg⁻¹. Sites L4 and L6 were also 134% and 201% higher than the location mean. The lowest concentration was observed at site L3 where a value of 0.71 \pm 0.08 mg kg⁻¹ was recorded. Sites L1 and L4 directly receive runoff and roadside soils sediment. The highest nitrogen to phosphorus ratio (2.45) was obtained at site L1. All the sites showed a sediment bioavailable NO₃⁻ :PO₄³⁻ ratios lower than 16.0.

Sampling Site	Water Column (mg L ⁻¹)	Total PO4 ³⁻ -P (Mean±SD) mg kg ⁻¹	Bioavailable PO4 ³⁻ -P (Mean±SD) mg kg ⁻¹	Percent Bioavailable P (%)	NO3 ⁻ (Mean±SD) mg kg ⁻¹	NO ₃ ⁻ :PO ₄ ³⁻ Ratio
L1	0.91	326.6 ± 15.2	4.65 ± 0.76	1.42	11.24 ± 0.38	2.45
L2	1.26	619.3 ± 33.4	7.45 ± 0.26	1.20	0.92 ± 0.06	0.12
L3	3.83	1203.9 ± 171.6	20.94 ± 0.62	1.74	0.71 ± 0.08	0.03
L4	0.68	253.5 ± 100.8	4.52 ± 0.52	1.78	6.56 ± 0.12	1.45
L5	0.62	65.9 ± 31.8	9.48 ± 0.84	14.38	4.43 ± 0.12	0.47
L6	0.45	174.5 ± 96.0	8.90 ± 0.78	5.10	9.85 ± 0.32	1.11
L7	1.15	637.2 ± 4.2	17.03 ± 0.28	2.67	0.56 ± 0.08	0.03
Mean	1.27 ± 1.16	468 ± 387	10.4 ± 6.2	4.0 ± 4.8	4.90 ± 4.47	0.81 ± 0.91

 Table 4.20: Mean Concentrations of Anionic Nutrients in the Lagos Lagoon Water and

 Sediment Samples.

The results of the nutrient concentration for the Lagos Lagoon water column and sediment confirm (Table 4.20) that the Lagoon is hypereutrophic (DRP concentration > 0.01 mg L⁻¹) with spatial variability in dissolved reactive phosphorus (DRP) across the sampled site. Site L3 had the highest DRP concentration in the Lagoon water with a level of 3.83 mg L⁻¹. This was also
reflected in the sediment samples from this site which had the highest concentration of total and bioavailable P. Though L3 receives input from site C1 catchments, the elevated levels of P in the water column and sediment may have been more as a result of the influence of the proximate sewage discharge area at Iddo rather than highway sources. Nevertheless, sites L1, L4, L6 and L7 which receive inputs directly from the highway catchments all had water column DRP concentrations higher than the identified threshold of 0.01 mg L^{-1} . In the Lagoon sediment, the higher concentration recorded at site L3 was more likely due to the reason stated above even though the site served as watershed to proximate catchments around sites C1 and C2. Sites L2 and L7 with concentrations above the mean total P value for the Lagoon sediments are direct watersheds of the Location C highway catchments and thus receive runoff bearing sediments from the highway during rainfalls. The lower concentrations at sites L5 and L6 which were lower than concentrations observed at other sampled sites was due to the fact that L5 was not a watershed of the highway and more remote from the influence area of the road as it was on the opposite of the sampled sites of the recipient water unlike the other locations which are adjacent to the road. Site L6 comparative lower concentration could be ascribed to the strong water current here which made a continuous accumulation of sediment difficult. Mau (2001) reported that fine P bearing particles are transported farther from an agitated area of recipient water to calmer areas where they settle out of the water column as sediment. The factors responsible for the total P were also responsible for relatively higher concentrations of bioavailable concentration in the sediment samples at sites L3 and L7. However, the comparative higher concentration obtained at L5 could be as a result of the Port activities on its side of the Lagoon since the location was closer to various jetties on that side of the recipient water. The mean percent bioavailable P values obtained for the Lagoon sediment (4.0 ± 4.8) in this study showed a potential for sediment to water column P movement in the recipient Lagoon water.

The Pearson correlation of the water column and sediment P concentration gave value of 0.9354 which indicates that a strong interaction exists between the sediment and water column of the Lagos Lagoon. The higher concentrations of total P observed at L2 and L7 showed that there is a possible build up of P from the road catchments in the Lagoon sediment. Site L1 also showed higher concentration indicative of possible contributions from roadside soil. The site directly receives swept roadside soils from the highway thus enriched with highway sourced pollutants. The nitrate concentrations of the sediment samples showed that nitrogen is limited with ratios obtained for all the sampled location less than the 16.0 Redfield threshold for phosphorus limitation. Sites L1, L4 and L6 which are highway watersheds had higher concentrations than

the mean NO_3^- level of the Lagoon sediment. This is indicative of the transport influence in the sediment sample. However site L5 also had a comparative mean concentration higher than some runoff influenced sites such as L2, L3 and L6. This may also be adduced to its proximity to the jetties on the opposite bank of the highway watersheds and thus had inputs from other sources outside the highway source.

4.5.7 Phosphate and Nitrate Concentration in Roadside Soils Samples using Multi-Anionic Nutrients Extractant (H³A).

The $H^{3}A$ extractant developed by Haney *et al.* (2006) was designed to mimic plant organic exudates which stimulate the availability of nutrients especially phosphorus in soil solution. Thus the use of the $H^{3}A$ was intended to further assess the level of bioavailable phosphorus and nitrate that could additionally be mobilized from the roadside soils and sediment samples.

The results of the bioavailable phosphorus and nitrate concentrations in selected samples of the roadside soils using the H³A extractant are presented in Figures 4.17 and 4.18 respectively. Extracted phosphorus in the samples had a range of $23.3 - 58.0 \text{ mg kg}^{-1}$. Although the trends of the phosphorus concentrations in the samples were mostly similar for both extractants, there were significant increases in the concentrations of the H³A-extractable P over the NaHCO₃-extractable P in all the samples analysed. Percentage increases of 166 to 846% were observed in comparison to the concentration extracted with the bicarbonate method. The concentration range of the bicarbonate extractable P in the respective selected samples was $4.7 - 16.3 \text{ mg kg}^{-1}$. A Pearson correlation coefficient of 0.3578 was calculated for the set of concentrations showing a weak relationship.

With the exception of site B3, the H^3A extracted NO_3^- also had higher concentrations than those of the traditional KCl extract though the differences were not as significant as noticed for the P (Figure 4.19). The concentration range of NO_3^- in the samples using the H^3A extractant was 1.4 – 18.1 mg kg⁻¹. This range was not significantly different (P>0.05) from the 1.2 - 21.3 mg kg⁻¹ obtained using the KCl extractant. A correlation coefficient of 0.9639 was obtained for the two sets of concentrations showing a strong relationship.



Figure 4.17: Concentration of Bioavailable Phosphorus in Selected Roadside Soils using the H³A Extractant.

The results obtained showed that higher levels of bioavailable phosphorus could still be mobilized from the roadside soils and Lagoon sediment into the recipient Lagoon water on the basis of the H³A extractant than with the Olsen (1954) bicarbonate method. In all the selected samples, levels of phosphorus extracted by the H³A cocktail of reagents were between x2 to x9 the levels extracted by the biocarbonate extractant. Nitrate concentrations in the sample were also higher than those obtained by the use of the KCl extractant. This was primarily due to the presence of citric, malic and oxalic acids which mimic the exudates release by plants to solubilise soil solutions and cause the release of nutrients needed. The concentrations obtained thus showed that potential of roadside soils to contribute nutrients to the recipient environment could be higher than thought.



Figure 4.18: Concentration of Nitrate in Selected Roadside Soils using the H³A Extractant.

4.6 OPTIMISATION OF FLOW INJECTION ANALYSIS (FIA) SYSTEM AND ITS USE IN THE DETERMINATION OF TOTAL PHOSPHORUS

The customised and optimised FIA manifold developed in this study and used for total phosphorus determination was demonstrated for the first time to be suitable for roadside soil and dissolved phosphorus determination based on the molybdenum blue-ascorbic acid reduction method. This is very important because the robustness, high reproducibility and field deploy-ability potential of the FIA technique make it suitable for nutrient studies in environmental media with high variability such as runoff and extensive surface water (Worsfold *et al.*, 2005). The results of the optimisation process are as discussed below.

4.6.1 Optimisation of the Injection Volume

The results of the optimisation of the injection volume of the customised FIA system is presented as plot of the absorbance against the concentrations of the standard solutions used for the varied volumes (Figure 4.19). The absorbance peaks of the standard solutions showed an increasing sensitivity with increased injection volume (Appendix 1, Figures 1a-1d)). Correlation coefficients of 0.9591, 0.9687, 0.9861 and 0.9864 were obtained for the injected 25, 62.5, 110

and 250 μ L standard phosphate solutions respectively. The 110 μ L volume was adopted for the system to achieve the twin objective of adequate sensitivity and moderate volume.

The result of the optimisation of the injection volume showed that increased sensitivity of the FIA system could be achieved by increase in the injection volume and online dilution of the sample can be achieved by reducing the injected volume. Higher injection volume invariably means that more phosphate species are available for the formation of the phosphomolybdenum blue complex within each run cycle of the system which translates to less dispersion and a more improved signal or sensitivity. Nevertheless, the need to achieve the twin aim of improved sensitivity and use of moderate volume necessitates striking a balance between the volume of sample injected and sensitivity of the system. Thus, the 110 μ L (0.11 mL) injection volume was adopted in this study. This volume gave a correlation coefficient of 0.9861 for the standard phosphate solutions with good reproducibility for the triplicate runs of each standard solution. The use of this smaller sampling volume improves the sampling frequency though dispersion of the sample in the FIA manifold is also increased (van der Linden, 1982; Bysouth and Tyson, 1992; McKelvie, 2008).



Figure 4.19: Calibration Graphs showing the Effect of Injection Volume on the

Absorbance of a Series of Standard Phosphate Solutions.

4.6.2 Optimisation of the Reaction Temperature

For the reaction temperature the absorbance varied within the temperature range used (Appendix 2, Figures 2a-2c). Formation of the molybdenum blue complex was stable at 30°C with a slower response of the signal though the peaks of the signals were fairly reproducible with a mean absorbance of 0.020 ± 0.018 (Figure 4.20). The observed absorbance at 40°C had a mean value of 0.030 ± 0.033 with steady baseline. At 50°C, the formation of the molybdenum complex became more intense with multiple peaks signals and unstable baseline. Gradual coating of the internal walls of the tubing was also noticed. The mean absorbance at this temperature was 0.085 ± 0.074 with higher variability of the signal compared to the lower temperatures used. Thus, 40° C was adopted as the optimal temperature for subsequent studies.



Figure 4.20: Effects of Temperature on the Absorbance of 250 μ g L⁻¹ PO₄⁻³-P Standard Solution.

The formation of phosphoantimonylmolybdenum blue complex through the reaction of the

phosphate and antimonylmolybdenum has been investigated with a reported increase in the rate of colour formation with increasing temperature. Though a widely varied temperature range of 1 -95°C (Sjosten and Blomvist, 1997) has been used in these studies, however at the upper end of this temperature range, interference of silicate becomes more pronounced which like arsenate also forms a similar blue complex with the molybdate (Linge and Oldham, 2001) and thus leads to overestimation of the phosphate (Neal et al., 2000). The presence of arsenate is often much lower in water except in cases of arsenic pollution and if present in samples for phosphate analysis could be masked by the addition of thiosulphate to reduce the arsenate to arsenite which is non-reactive to molybdate (Omaka et al., 2007). While in open vessel batch method, the reaction is recommended to be left for about 10 minutes at room temperature to allow for colour development, it has been argued that analyses of cold solutions with low concentrations of phosphate might easily result in under-estimation of the true concentration which could be a significant source of error (Sjosten and Blomvist, 1997). In FIA, the reaction needs not get to a steady state (which the batch methods strive to achieve by allowing for a longer reaction time) but should be reproducible at a transient state of the reaction which corresponds only to a fraction of the steady state to enable high sample throughput. Thus, the need for a temperature regulated environment incorporated into the manifold design to hasten the colour development is highly desirable. The 40°C optimum temperature adopted in this study had stable and reproducible signals with no evidence of silicate interference.

4.6.3 Optimisation of the Molybdate Concentration

The response of the system increased with increasing molybdate concentration. The absorbance obtained for the 0.006 M molybdate concentration was low at a mean of 0.007 \pm 0.004 indicating that much reduction of the phosphorus did not take place. There was rapid colour development in the manifold tubing resulting in the coating of the internal walls of the tubings. At the highest concentration of 0.015 M molybdate which translate to a lower [H⁺] / [MoO₄⁻²] ratio, the response observed were multiple peaks shaped signal with a mean absorbance of 0.098 \pm 0.010 (Appendix 3, Figures 3a-3d). An optimal concentration of 0.012 M molybdate was therefore adopted as it had the lowest standard deviation and did not show any evidence of self reduction (Figure 4.21).



Figure 4.21: Effects of Molybdate Concentrations on the Absorbance of 250 μ g L⁻¹ PO₄⁻³-P Standard Solution.

One of the most important factors in the determination of phosphate by the Murphy and Riley (1962) method is the $[H^+]$: $[MoO_4^{-2}]$ ratio determined from the sulphuric acid and molybdate concentrations. A ratio range of 37 - 206 and pH as low as 0.2 have been previously used (Zhang et al., 1999). At a low ratio i.e. low acidity, high pH or high molybdate concentration, there is an appreciable self reduction of the molybdate existing as Mo(VI) dimers, the state at which it tends to react in high acidic medium even in the absence of phosphorus which normally results in rapid coating of the internal walls of the manifold tubes by the molybdenum blue complex. At ratios higher than 80 which translate to higher acidity, low pH or lower molybdate concentration, the rate of colour formation decrease rapidly leading to underestimation of sample concentration. Since high concentrations of molybdate are needed to maintain a constant ratio of $[H^+]$: $[MoO_4^{-2}]$ at low pH values (Zhang et al., 1999), polymerisation of the molybdate may occur at such concentration and thus hinder the molybdenum complex formation due to a lack of molybdenum dimmer (Huang and Zhang, 2008). At the 0.015 M molybdate concentration used in this study, which translate to a lower $[H^+]$: $[MoO_4^{-2}]$ ratio, the signals were shown as multiple peaked values with evidence of rapid colour development in the manifold tubings which could be attributed more to the auto-reduction of the molybdate at this concentration. The absorbance obtained for

the 0.006 M was low indicating that little reduction of the phosphorus took place probably due to lack of the molybdenum dimer in the highly acidic environment. The 0.012 M molybdate concentration was therefore adopted as it had the lowest standard deviation and did not show any evidence of self reduction.

4.6.4 Optimisation of the Length of Reaction Coil

The results obtained showed that there was an increase in the absorbance of the phosphate solution injected as the coil length was increased. Mean absorbance for the coil lengths used were 0.027 ± 0.002 , 0.028 ± 0.003 , 0.032 ± 0.001 and 0.049 ± 0.001 for the 30, 70, 90 and 120 cm coils respectively (Figure 4.22). Peak signal distortions was observed for the 120cm coil though it produced the highest absorbance which was attributed to the build up of the phosphomolybdate blue in the internal walls of the reaction coil. The 90 cm coil was adopted for use as the peak outputs were more replicable and without any outcropping (Appendix 4, Figures 4a-4c).





Standard Solution.

The formation of the phosphoantimonylmolybdenum though now hastened by the temperature regulated environment could still be enhanced by adequate mixing of the sample and reagents. For this reason, coiled tubes and other mixing devices (reactors) are incorporated into the manifold. These reactors with varying lengths promote radial mixing of the merged solutions and delay the time it takes for the resulting mixture to reach the detector thereby enhancing the response or sensitivity of the system (Mckelvie, 2008). Although the 120 cm coil length produced the highest absorbance, there was some peak signal distortions observed for this length thus it was not suitable for use. The peak signal distortions could be attributed to the build up of the phosphoantimonylmolybdenum blue complex in the internal walls of the reaction coil.

4.6.5 Optimisation of the Ascorbic Acid Concentration

There was little difference in the mean absorbance for the different concentrations of ascorbic acid used which ranged from 0.051 M - 0.096 M except for the 0.31 M concentration which had a mean absorbance of 0.096 ± 0.010 . However the peaks output at this concentration had some side outcroppings (Appendix 5, Figures 5a-5d) and attempts to reproduce this observation was not succesful. Subsequently, the 0.28 M ascorbic acid concentration was adopted for the system (Figure 4.23).



Figure 4.23: Effects of Ascorbic Acid Concentration on the Absorbance of 250 μ g L⁻¹ PO₄⁻³-P Standard Solution.

For the Murphy and Riley (1962) method ascorbic acid acts as the reducing agent for the the phosphomolybdate. This product appears as a yellow solution and reacts with the ascorbic acid to form the reduced molybdenum blue compex. Depending on the manifold design adopted, this reaction impacts upon the sensitivity of the system. Using a manifold with premixed stream of molybdate and ascorbic acid yields a faster reaction than a manifold having the phosphate first in the molybdate stream, before being merged with the ascorbic acid (Grudpan et al., 2002). Nevertheless, in most studies, the sample was premixed with the molybdate before merging with the reductant. Irrespective of the approach adopted, the common practise is to have an excess concentration of the ascorbic acid for the reduction process. Though in systems where there is inadequate pre-mixing of the sample with the carrier stream, the reduction of Mo(VI) to Mo(V)by the ascorbic acid along with the Schlieren effect could induce high blank signal and large errors in quantification (McKelvie et al., 1997). The result obtained showed that there was little difference in the mean absorbance for the different concentrations except for 0.31 M ascorbic acid solution. However, the peak output for this concentration had some side distortions and attempts to reproduce the signals were not successful. Subsequently, the 0.28 M ascorbic acid concentration was adopted for the system.

4.6.6 **Optimisation of the Flow Rate**

The absorbance of the standard phosphate solution increased as the flow rate was decreased (Figure 24). The faster rates of 0.24, 0.27 and 0.35 mL min⁻¹ with relative standard deviations (RSD) of 5.2, 5.4 and 5.6% respectively were more reproducible than the slower rates of 0.12, 0.13 and 0.17 mL min⁻¹ with RSD of 8.4, 26.7 and 14.4 respectively (Appendix 6, Figures 6a-6d). The slowest run rate of 0.12 mL min⁻¹ gave a mean absorbance of 0.184 but a low sample throughput of about nine samples per hour. The flow rate of 0.13 mL min⁻¹ which gave a sample throughput of twelve per hour was subsequently adopted for the system.

The dispersion of reagents in the carrier stream is the most important physical phenomenon of a FIA system. This impacts on reproducibility and determines the sample throughput of the system. The dispersion of a FIA system can be improved through the manipulation of the flow parameters and geometric dimensions of the flow conduits. Dispersion diminishes with a decrease in flow rate which in turn leads to an increase in the retention or residence time of the sample and the chance for the reaction to reach completion or equilibrium prior to detection, hence higher peak signal or sensitivity (Ruzicka and Hansen, 1981). The results obtained showed that as the flow rate is decreased, the absorbance decreased though the faster rates of 0.24, 0.27 and 0.35 mL min⁻¹ with relative standard deviations (RSD) of 5.2, 5.4 and 5.6% respectively seem to be more reproducible than the slower ones of 0.12, 0.13 and 0.17 with RSD of 8.4, 26.7 and 14.4% respectively. The lowest run rate of 0.12 ml min⁻¹ gave a mean absorbance of 0.184 but a low sample throughput of about nine samples per hour. The 0.13 mL min⁻¹ flow rate was adopted for the system runs which gave a sample throughput of twelve. The linearity of the graph of standard phosphate solutions run through the optimised manifold showed that the customised and optimised system was suitable for the determination of dissolved reactive phosphorus despite the fact that the $[H^+]$: $[MoO_4^{-2}]$ ratio of the system was 21.4 which was below most reported range of 40 - 70.



Figure 4.24: Effects of Flow Rates on the Absorbance of 250 μ g L⁻¹ PO₄⁻³-P Standard Solution.

4.6.7 Calibration of the Optimised FIA System

The results of the standard solutions' calibration runs (n=5) carried out on the optimised system had a correlation coefficient of 0.9983 with a limit of detection of 0.018 μ g L⁻¹ (Blank + 3SD of Blank). The blank consistently showed no signal (Figure 4.25). The [H⁺]:[MoO₄²⁻] ratio for the manifold was 21.4 with a [H⁺] of 1.8 M and a pH of 1.02.



Figure 4.25: Calibration Graph of Standard PO_4^{3-} - P solutions (n=5) at Optimised Conditions.

4.6.8 Effect of Manifold Change on the Sensitivity of the FIA System

There was no substantial increase in the absorbance observed for the injected standard PO_4^{3-} -P concentration using Manifold B in comparison to the optimised Manifold (Figure 4.26). Much improved signals were obtained for Manifold C especially at higher concentrations of the standard solutions used but it was observed that there were signals for the blank (Figure 4.27). These high blank signals may be due to the differences in the refractive index of the sample solution and the molybdate reagent since the sample was directly injected into the reagent or due to the fact that the blank consisting of pre-mixed solutions of molybdate reagent and ascorbic acid (which usually produced a yellow molybdate complex) absorbed some of the incident light. The limit of detection calculated for this manifold was 5.0 µg L⁻¹. The calibration graph obtained from the data had a non-linear range for both the uncorrected (inclusive of the blank absorbance values) and the corrected (with blank absorbance deducted from the absorbance of the standard solutions' absorbance) plots for the 0 - 75 µg L⁻¹ standard PO₄³⁻ - P solutions used. Manifold D also gave similar results as observed for Manifold C i.e. blank signals though absorbance obtained from Manifold D were lower than those for manifold C. This is primarily due to the online dilution introduced into the manifold which though did not correct the blank signal,

reduced the level. However, the calibration curves obtained for both manifolds C and D were non-linear parabola curves as shown in Figures 4.27 and 4.28.



Figure 4.26: Calibration Graph of Standard Phosphorus Solutions using Manifold B (Uncorrected and Corrected) at 0.13mL min⁻¹.



Figure 4.27: Calibration Curve of Standard Phosphorus Solutions using Manifold C (Uncorrected and Corrected) at 0.13mL min⁻¹.



Figure 4.28: Calibration Graph of Standard Phosphorus Solutions using Manifold D

(Uncorrected and Corrected) at 0.13ml min⁻¹.

Though the optimised manifold as obtained in Section 3.6 was suitable for the determination of phosphorus in roadside soil and the Lagoon sediment, the sensitivity of the system was still comparatively higher than that of Omaka *et al.* (2006) which had a limit of detection of 2 μ g L⁻¹ thus the effort to optimise the manifold configuration. The change of manifold configurations (as discussed in Section 3.6.7 and as shown in Figures 3.7 to 3.9) gave higher absorbance signals but also threw up other issues such as initial negative peaks and high blank values which reduced the sensitivity of the system. This occurrence known as Refractive Index (Schlieren) effect is probably due to the poor mixing of the sample and molybdate stream since it was injected directly into the molybdate stream. Under lamina flow conditions which the moving stream of FIA operates, when samples are injected into a carrier or reagent stream directly, the difference in the refractive index of the two solutions leads to a lensing effect in which the sample zone acts as a dispersing and collecting lens (Ausflitsch et al., 1997). This usually results in large errors of quantification especially at low analyte concentration (McKelvie et al., 1997) and explains why comparatively high blank values were recorded for the standard phosphate runs of manifold B. The corrected values (absorbance of standard phosphate solutions minus absorbance of blank) and uncorrected values both gave a linear relationship with the standard phosphate concentrations used albeit with a detection limit of 5.0 μ g L⁻¹ (Blank ± 3SD) which is higher than the optimised manifold. Wolfgang and McKelvie (2008) suggested the use of improved mixing devices such as knotted coils, mixing chamber among other strategies to minimize Schlieren effect in FIA systems. Manifolds C and D also gave high blank reading for the same reason but with a non linear relationship and even higher limit of detection of 12.0 µg L⁻¹ though the manifolds could still be used for samples suspected to have concentrations above 0.01 mg L⁻ ¹. The optimised manifold A was therefore adopted and used for the determination of phosphorus in the roadside soils and sediment samples' extract as its well premixed ascorbic acid and molybdate streams result in the formation of a readily available reactive intermediate of the reduced form of molybdate which reacts with the phosphate sample in the carrier stream to form the phosphoantimonylmolybdenum blue. Grudpan et al. (2002) described this approach as being more preferable than injecting the sample into the molybdate stream directly before being merged with the ascorbic acid (as outlined for manifolds B, C and D) because the resulting yellow product formed between the injected phosphate solution and the molybdate produces a phosphomolybdate product which slower reduce vellow is even to to phosphoantimonylmolybdenum blue.

4.7 TOTAL PHOSPHORUS IN ROADSIDE SOILS AND LAGOON SEDIMENT SAMPLES USING THE OPTIMISED FIA SYSTEM AND COMPARISON WITH RESULTS FROM ICP-OES AND ASCFA TECHNIQUES

Results of the concentration of total phosphorus in the roadside soils and sediment samples using the customised and optimised flow injection analysis (FIA) system and the results of the total phosphorus determination using induction coupled plasma-optical emission spectroscopy (ICP-OES) (as discussed in Section 4.4.2) in comparison with the results obtained using the air segmented continuous flow analysis (ASCFA) are shown in Figures 4.29 – 4.31. The comparison showed a parallel relationship among the three techniques used in this study for the total phosphorus determination in roadside soil samples and the Lagos Lagoon sediment samples. The Pearson correlation matrix for the thechniques shown in Table 4.21 gave strong correlation between all the techniques used for the total phosphorus concentration in the samples. Also, paired t-test (at 95% confidence limit) gave no significant difference between any two pair of the techniques for the sampled locations and seasons.



Figure 4.29: Comparative Concentration of Total P in Roadside Soils (Wet Season) using

different Techniques.



Figure 4.30: Comparative Concentration of Total P in Roadside Soils (dry season) using different Techniques.



Figure 4.31: Comparative Concentration of Total P in the Lagos Lagoon Sediments using different Techniques.

Table 4.21: Pearson's Correlation Matrix for Total Phosphorus	Concentration obtained
from the Different Techniques used in this Study.	

Technique	Correlation			
	ASCFA	FIA	ICP-OES	
	Wet Season Roadside soils			
ASCFA		0.992	0.862	
FIA	0.992		0.896	
ICP-OES	0.862	0.896		
	Dry Season Roadside soils			
ASCFA		0.957	0.994	
FIA	0.957		0.695	
ICP-OES	0.994	0.695		
	Lagoon Sediments			
ASCFA		0.996	0.979	
FIA	0.996		0.993	
ICP-OES	0.979	0.993		

The results of the determination of the total phosphorus in the roadside soils (wet and dry seasons) and sediment samples using the optimised FIA system in comparison to the results of the total P determination using ICP-OES and the air segmented continuous flow analyser

(ASCFA) showed strong agreement in the three techniques. The Pearson correlation coefficients of the concentrations obtained were above 0.800 for the matched techniques except for the FIA and ICP-OES results for the dry season roadside soil samples which had a coefficient of 0.695, with the ICP-OES results slightly lower (but not significantly different, P>0.05) than the results of the FIA technique. Although Nathan *et al.* (2002) suggested that determination of phosphorus using ICP gives better result than colorimetric methods since the high temperatures of the ICP would be able to breakdown most of the organically bound P that will not be measured by the colorimetric methods, nevertheless, some reports of higher sensitivity of colorimetric methods over ICP in the determination of P have been reported (Choate, 2004; Wolf *et al.*, 2005).

In this present study, the roadside soils and sediment samples analysed have already been rigorously digested to ensure the release of the organically bound P thus increasing the sensitivity of the colorimetric methods since most of the P have now been converted to the detectable phosphate specie for the Murphy and Riley method. Also the slightly higher sensitivity of the ASCFA and FIA methods reported in this study could be due to the possibility of using smaller diluted volume of samples which could enhance the sensitivity of the colorimetric method. Nevertheless, the fact that there are no statistical significant differences in the results obtained for the same sets of samples using the three methods affirmed that the customized and optimized FIA system was suitable for the determination of P in roadside soils and sediment samples as well as in water samples.

4.8: PHOSPHATE CONCENTRATION IN THE WATER COLUMN OF THE LAGOS LAGOON USING FLOW INJECTION ANALYSIS.

The results of the phosphate concentrations in the different strata of the water of Lagos lagoon are as presented in Table 4.22. Mean total phosphorus concentration range in the top, middle and bottom strata were $0.054 - 0.600 \text{ mg L}^{-1}$, $0.041 - 0.961 \text{ mg L}^{-1}$ and $0.058 - 1.710 \text{ mg L}^{-1}$ respectively. Iddo and Ogudu with concentrations of 0.600 and 0.513 mg L⁻¹ had higher levels compared to other locations at the top strata of the water. Concentrations at the bottom stratum were higher than those of the other strata at most of the locations. Mean concentrations of total phosphorus in the water were 0.198 ± 0.208 , 0.192 ± 0.291 and 0.339

 \pm 0.537 mg L⁻¹ respectively.

Mean location concentrations of bioavailable phosphorus at the different strata were 0.210 ± 0.275 , 0.120 ± 0.121 and $0.134 \pm 0.135 \text{ mg L}^{-1}$ at the top, middle and bottom respectively. Sites with higher total phosphorus levels also showed higher bioavailable phosphorus levels with concentration ranges of 0.046 - 0.910, 0.046 - 0.453 and $0.048 - 0.492 \text{ mg L}^{-1}$ for the top, middle and bottom strata. All the observed concentrations were higher than the 0.01 mg L⁻¹ upper limit of phosphorus in water bodies.

These results of phosphate concentrations in the different strata of the Lagos Lagoon suggest that there is a strong interaction between the sedimentary phosphorus reserve and the level obtained in the intervening water column (Filippelli, 2002). This explains the higher concentrations observed at the bottom stratum of the Lagoon at most of the sampled locations even though the analysis of variance of the concentrations showed that there was no significant difference in the concentrations between the stratums. The higher levels obtained at Iddo and Ogudu were due to anthropogenic influences from sewage disposal and runoff from the impervious catchments areas including highway runoff at the Iddo end and domestic and industrial effluents at the Ogudu end. The spatial distribution of the phosphate concentrations showed that the Lagoon is eutrophic since the observed concentrations were higher than the 0.01 mg L^{-1} threshold phosphate concentration for surface water.

Sampling Site	Total PO_4^{3-} - P (mg L ⁻¹)		
	Тор	Middle	Bottom
Cowry Creek	0.082 ± 0.065	0.041 ± 0.043	0.093 ± 0.109
Falomo	0.054 ± 0.066	0.101 ± 0.098	0.115 ± 0.101
Marina (CMS)	0.067 ± 0.067	0.061 ± 0.071	0.074 ± 0.078
Iddo	0.600 ± 0.942	0.133 ± 0.105	0.058 ± 0.065
Makoko	0.076 ± 0.073	0.060 ± 0.069	0.071 ± 0.086
Akoka	0.105 ± 0.088	0.191 ± 0.207	0.239 ± 0.173
Oworo	0.105 ± 0.088	0.093 ± 0.061	0.139 ± 0.123
Ogudu	0.513 ± 0.753	0.961 ± 1.435	1.710 ± 1.795
Ketu	0.177 ± 0.101	0.091 ± 0.112	0.556 ± 0.549
Радо			

 Table 4.22: Concentration of Phosphorus in Different Strata of the Lagos

Lagoon using Flow Injection Analysis (FIA).

Location Mean	0.198 ± 0.208	0.192 ± 0.291	$\textbf{0.339} \pm \textbf{0.537}$	
	Bioavailable PO ₄ ³⁻ - P (mg L ⁻¹)			
	Тор	Middle	Bottom	
Cowry Creek	0.062 ± 0.048	0.071 ± 0.064	0.063 ± 0.048	
Falomo	0.046 ± 0.028	0.046 ± 0.019	0.048 ± 0.018	
Marina (CMS)	0.048 ± 0.018	0.049 ± 0.019	0.051 ± 0.062	
Iddo	0.058 ± 0.036	0.067 ± 0.043	0.068 ± 0.042	
Makoko	0.085 ± 0.047	0.078 ± 0.039	0.109 ± 0.082	
Akoka	0.080 ± 0.038	0.064 ± 0.047	0.065 ± 0.052	
Oworo	0.910 ± 0.086	0.103 ± 0.081	0.102 ± 0.082	
Ogudu	0.450 ± 0.544	0.453 ± 0.596	0.492 ± 0.634	
Ketu	0.147 ± 0.146	0.151 ± 0.149	0.213 ± 0.195	
Location Mean	$\textbf{0.210} \pm \textbf{0.275}$	$\textbf{0.120} \pm \textbf{0.121}$	$\textbf{0.134} \pm \textbf{0.135}$	

4.9 RELATIONSHIP BETWEEN LEAD AND PHOSPHORUS IN THE ROADSIDE SOILS

The results obtained from this study showed that the mobilization of some PTMs (such as lead) and phosphorus from the roadside soils to the recipient water body was synergistic. This relationship as presented in Figures 4.32 and 4.33 showed that there was a parallel relationship between the concentration of lead (Pb) and total phosphorus of the roadside soils in both the dry and wet seasons. This is significant in understanding dynamics of phosphorus availability in the roadside soils in the presence of the PTMs and possible roadside soil PTM pollution containment strategy. Cotter-Howells (1996) suggested that the halides of Pb from vehicular emissions in the presence of phosphorus in roadside soils eventually converts to insoluble Pb phosphate compounds such as pyromorphite (Pb₃(PO₄)₃Cl and plumbogummite (PbAl₃(PO₄)₂(OH)₅.H₂O. The stability and low solubility of these compounds makes it effective in reducing the bioavailability of PTMs in the recipient water (Hettiarachchi *et al.*, 2000; Jiang *et al.*, 2010).



Figure 4.32: Concentration of Pb and P in Roadside Soils during the Wet Season



Page 168 Figure 4.33: Concentration of Pb and P in Roadside Soils during the Dry Season

CHAPTER FIVE

CONCLUSION

5.1 SUMMARY OF FINDINGS

The study has demonstrated for the first time in Nigeria that highway runoffs from major roads in the Lagos metropolis are of low water qualities and are capable of impacting the receiving Lagos Lagoon into which these runoffs are directly channelled without any pre-treatment structures.

The study established a pattern for the type and level of some potentially toxic metals (PTMs) in atmospheric depositions (Sheet *et al.* 2001), highway runoffs and roadside soils from selected highways in the Lagos metropolis and also in sediment samples of the Lagos Lagoon. The presence of the PTMs in these environmental media signifies the influence of highway sources

on the PTMs' pollution of the Lagos Lagoon (Abayomi, *et al.*, 2006; Alo, *et al.*, 2007). The presence of rare metals like platinum at these locations is an indication of their vehicular sources since Pt is attributed to catalytic emissions (Helmers, 1996). These PTMs apart from serving as a source of danger to road users and residents (Olayinka and Alo, 2001; Osuntogun and Koku, 2007) eventually accumulate in the Lagoon sediment (Oyeyiola *et al.*, 2011) and its resident aquatic organisms. Higher levels of the PTMs which were observed in the sediment samples from the watersheds of the highway bordering the Lagos Lagoon confirm that highway runoffs are major contributor of PTMs to the Lagos Lagoon. This is in contrast to lower levels obtained at a remote sampled site (L5) (control) on the Lagoon which does not directly receive highway runoff and road derived sediment.

The phosphorus concentrations in roadside soils from the sampling campaign support the conclusion that mobilisation of soils in close proximity to transport hubs is a major source of phosphorus load in the hypereutrophic Lagos Lagoon (Abayomi *et al*, 2011). Concentrations of both total phosphorus and bioavailable phosphorus were generally higher and less variable in the dry season than the wet season. This correlated with increased leaching during intense periodic rain events. The results also show a small but consistent fraction of bioavailable phosphorus that is extracted by the bicarbonate extraction but is resistant to leaching by rainwater. This along with the mobilize-able particulate phosphorus contributes to the phosphorus pool of the Lagos Lagoon system and hence influences the annual intractable eutrophication process of the Lagoon.

Thus, highway roadside soils could now be considered as one of the sources of phosphorus inputs into the Lagos Lagoon and ultimately as a component of the local biogeochemical phosphorus cycle. Gupta *et al.* (1981b) and FHWA (1996) have outlined the various factors which influence the nature and extent of pollutants on a highway system. While traffic characteristics, highway maintenance policies, and surrounding land use determine the nature of pollutants introduced onto the roads, climatic factors such as intensity and duration of rainfall, strength of prevailing wind among others determine to a great extent the magnitude of the pollutants that could be mobilised to the receiving environment. The fact that Nigeria, and Lagos in particular lies on the equatorial region where there is heavy rainfall for a substantial period of the year makes the mobilization of accumulated PTMs and anionic nutrients on the highway environment into the receiving water bodies such as the Lagos Lagoon easier.

The customised and optimised FIA manifold used for the phosphorus determination was

demonstrated to be suitable for roadside soils, sediment samples and dissolved phosphorus determination based on the molybdenum blue ascorbic acid reduction method as it compared well with other techniques such as the air segmented continuous flow analysis (ASCFA) and induction coupled plasma optical emission spectroscopy (ICP-OES) analytical techniques. This is very important because the robustness, high reproducibility and field deployable potential of the FIA technique makes it suitable for anionic nutrient studies in environmental media with high variability such as runoff and surface water as it reduces the need for sample storage (Worsfold, *et al.*, 2005). The sampling scheme was designed to investigate a number of contrasting locations and the results suggest that future campaigns should target locations adjacent to key transport hubs and point sources such as sewage discharges.

Also, the fact that phosphorus has a synergistic relationship with some PTMs especially Pb as presented in this study further indicates that the presence and mobilization of anionic nutrient to the Lagos Lagoon could also increase the potential for PTMs introduction into the water body through mostly the soluble and insoluble particulate fractions in the highway runoffs and roadside soils.

5.2 CONTRIBUTION TO KNOWLEDGE

This research study has been able to contribute the following to the body of existing knowledge:

- i. It has demonstrated for the first time that highway runoffs from major roads in the Lagos metropolis are capable of negatively impacting the water qualities of the Lagos Lagoon.
- ii. The study clearly showed the relationship between the nature of PTMs and anionic nutrients from highway runoffs and roadside soils and established their concentrations and spatial distribution in the sediment of the Lagos Lagoon.
- iii. The study established the seasonal variation (during the wet and dry seasons) of the

concentrations of PTMs and anionic nutrients in roadside soils of highways in the Lagos metropolis.

iv. The thesis is the first Nigerian study on continuous flow analysis (ASCFA and FIA) of roadside soils in Nigeria and also demonstrated for the first time the suitability of FIA for determination of phosphorus in runoffs and roadside soils.

REFERENCES

- Abayomi, A. A., Olayinka, K. O., Osuntogun, B. and Alo, B. I. (2006). Urban highway runoff in Nigeria II: Effects of sheet flow on roadside soils in Lagos metropolis. *Journal of Scientific Research and Development*, 10, 51-60.
- Abayomi A., Nimmo M., Williams, C., Olayinka K. O., Osuntogun, B., Alo, B. and Worsfold, P.
 J. (2011). The contribution of roadside soil to Phosphorus loading in the eutrophic Lagos
 Lagoon, Nigeria. *Journal of Environmental Monitoring*, 13, 1884-1889.
- Adachi, K. and Tainosho, Y. (2004). Characterization of heavy metal particles embedded in tire dust. *Environment International*, 30, 1009-1017.

- Adebayo, O. T., Balogun, A. M. and Olubiyi, O. A. (2007). Chemical Analysis of some industrial effluents that discharge into the Lagos Lagoon, Nigeria. *Research Journal of Environmental Sciences*, 1(4), 196-199.
- Ademoroti, C. M. A. (1996). Standard methods for water and effluents analysis. Mareh Prints and Consultancy, Benin, Nigeria. Pp 46.
- Adewolu, M. A., Akintola, S. L., Jimoh, A. A., Owodeinde, F. G., Whenu, O. O. and Fakoya, K.
 A. (2009). Environmental threats to the development of aquaculture in Lagos state.
 Nigeria. *European Journal of Scientific Research*, 34(3), 337-347.
- Adeyemi, D., Ukpo, G., Anyakora, C. and Unyimadu, J. P. (2008). Organochlorine pesticide residues in fish samples from Lagos Lagoon, Nigeria. American Journal of Environmental Sciences, 4(6), 649-653.
- Akbar, K. F., Hale, W. H. G., Headley, A. D. and Athar, M. (2006). Heavy metal contamination of roadside soils of Northern England. *Soil and Water Resources*, 1(4), 158-163.
- Akerblom, S., Meili, M., Bringmark, L., Johansson, K., Kleja, D. B. and Bergvist, B. (2008). Partitioning of Hg between solid and dissolved organic matter in the humus layer of boreal forests. *Water, Air, and Soil Pollution*, 189(1-4), 239-252.
- Akinsanya M. and Ogunbambi A. (2010). Stormwater drainage and flood control. State of the Environment Report, 2010, Edited by Ogunleye, M. and Alo, B. Published by Ministry of the Environment, Lagos State / Beachland Resources Limited. P 2.
- Alani, R. A., Drouillard, K. G., Olayinka, K. O., and Alo, B. I. (2012a). Bioaccumulation of polyaromatic hydrocarbons (PAHs) in fish and invertebrates of Lagos Lagoon. *Journal of Emerging Trends in Engineering and Applied Sciences, (JETAS)*, 3(2), 287 - 296.
- Alani, R. A., Drouillard, K. G., Olayinka, K. O., and Alo, B. I. (2012b). Modeling and risk assessment of persistent, bioaccumulative and toxic (PBT) organic micropollutants in the Lagos Lagoon. *Proceedings of the 35th Annual International Conference, Workshop &*

Exhibition of Chemical Society of Nigeria held in Owerri, Imo State, Nigeria. Page 358 - 362.

- Al-Chalabi, A. S. and Hawker, D. (2000). Distribution of vehicular lead in roadside soils of major roads of Brisbane, Australia. *Water, Air, and Soil Pollution*, 118, 299 310.
- Almas, A. R., Lombnaes, P., Sogn, T. A. and Mulder, J. (2006). Speciation of Cd and Zn in contaminated soils assessed by DGT-DIFS, and WHAM/Model VI in relation to uptake by spinach and ryegrass. *Chemosphere*, 62(10), 1647 - 1655.
- Alo, B. I., Abayomi, A. A., Osuntogun, B. A. and Olayinka, K. O. (2007). Urban highway runoff in Nigeria I: Heavy metals in sheet flow from the main expressway in Lagos metropolis. *Journal of Applied Sciences*, 7(19), 2800-2805.
- Alo B., Orgu B. and Abayomi, A. (2010). Low sub-surface harmattan season hypoxia events in the Lagos Lagoon. *European Journal of Scientific Research*, 40(2), 270 286
- American-Chemistry-Council-Petroleum-Additives-Panel (2003). Test plan for phosphoric acid, mono (2-ethylhexyl) ester, compound with tert-dodecanamine. High Production Volume (HPV) Challenge Program US Environmental Protection Agency.
- Andersson, M., Ottesen, R. T. and Volden, T. (2004). Building materials as a source of PCB pollution in Bergen, Norway. *Science of the Total Environment*, 325, 169 144.
- APHA (1995). Standard Methods for the Examination of Water and Wastewater, American Public Health Association, Washinton, DC.
- Armstrong, L. (1994). Contribution of heavy metals to storm water from automotive disc brake pad wear. Santa Clara Valley Non-point Source Pollution Control Program.
- Ashworth, D. J. and Alloway, B. J. (2008). Influence of dissolved organic matter on the solubility of heavy metals in sewage-sludge-amended soils. *Communications in Soil Science and Plant Analysis*, 39(3-4), 538-550.

- Ausflitsch, S., Peat, D. M. W., McKelvie, I. D. and Worsfold, P. J. (1997). Determination of dissolved reactive phosphorus in Estuarine waters using reversed flow injection manifold. *The Analyst*, 122, 1477 - 1480.
- Backstrom, M., Nilsson, U., Hakansson, K., Allard, B. and Karlsson, S. (2003). Speciation of heavy metals in road runoff and roadside total deposition. *Water, Air, and Soil Pollution*, 147, 343 - 366.
- Balconi, M. L., Borgarello, M., Ferraroli, R. and Realini, F. (1992). Chemical oxygen demand determination in well and river waters by flow injection analysis using microwave oven during the oxidation step. *Analytica Chimica Acta*, 261, 295 - 299.
- Barret, M. E. (2008). Effects of permeable friction course on highway runoff. *Journal of Irrigation and Drainage Engineering*, 134, 646-651.
- Barret, M. E., Zuber, R. D., Collins, E. R., Malina, J. F., Charbeneau, R. J. and Ward, G. H. (1993). A review and evaluation of literature pertaining to the quantity and control of pollution from highway runoff and construction Center for Research in in Water Resources, Bureau of Engineering Research, University of Texas, Austin, TX.
- Barrett, M. E., Jr, L. B. I., Malina, F. M. and Charbeneau, R. J. (1998). Characterization of highway runoff in Austin, Texas area. *Journal of Environmental Engineering*, 124, 131-137.
- Barrett, M. E., Zuber, R. D. and III, E. R. C. (1995). A review and evaluation of literature pertaining to the quantity and control of pollution from highway runoff and construction. 95-5, 1-180, Bureau of Engineering Research, the University of Texas at Austin, J.J. Pickle Researcg Campus, Austin, Texas.
- Beasley, G. and Kneale, P. (2002). Reviewing the impact of metals and PAHs on macroinvertebrates in urban watercourses. *Progress in Physical Geography*, 26, 236-270.

- Benke, M. B., Mermut, A. R. and Shariatmadari, H. (1999). Retention of dissolved organic carbon from vinnase by tropical soil, kaolinite, and Fe-oxides. *Geoderma*, 91(1), 47 63.
- Benson, R. L., Truong, Y. B., McKelvie, I. D. and Hart, B. T. (1996). Monitoring of dissolved reactive phosphorus in wastewaters by flow injection analysis. Part 1. Method development and validation. *Water Research*, 30(9), 1959 - 1964.
- Bent, G. C., Gray, J. R., Smith, K. P. and Glysson, G. D. (2000). A synopsis of technical issues for monitoring sediment in highway and urban runoff. Open-File Report 00-497. Norhborough, Massachusetts, US Geological Survey.
- Bergametti, G., Remoudaki, E., Losno, R., Steiner, E., Chatenet, B. and Baut-Menard, P. (1992). Source, transport and deposition of atmospheric phosphorus over the North-western Mediterranean. *Journal of Atmospheric Chemistry*, 14, 501 - 513.
- Berkheiser, V. E., Street, J. J., Sao, P. S. C. and Yuan, T. L. (1980). Partitioning of inorganic orthophosphate in soil water sysyems, Agricultural Experiment Station, University of Florida, Gainsville, US.
- Bhatia, I. and Choudhri, G. N. (1991). Impact of automobile effusion on plant and soil. International Journal of Ecology and Environmental Science, 17, 121 - 127.
- Birdsall, C. W., Cue, C. E. and Anderson, A. (1986). Lead concentrations in bullfrog *Rana* catesbeiana and green frog *R. clamitans* tadpoles inhabiting highway drainages. *Environmental Pollution*, 40, 233 - 247.
- Blaustein, A. R. and Kiesecker, J. M. (2002). Complexity in conservation: lessons from global decline of amphibian populations. *Ecology Letters*, 5, 597 608.

Bostrom, B. (1984). Potential mobility of phosphorus in different types of lake sediment. *Internationale Revue der gesamten Hydrobiologie und Hydrographie*, 69, 457 - 475.

- Boxall, A. B. A. and Maltby, L. (1995). The characterization and toxicity of sediment contaminated with road runoff. *Water Research*, 29(9), 2043 2050.
- Breault, R. F. and Grenato, G. E. (2000). A synopsis of technical issues of concern for monitoring trace elements in highway and urban runoff. Open-File Report 00-422; US Federal Highway Administration, Northborough, Massachusetts.
- Brezonik, B. L. and Stadelmann, T. H. (2002). Analysis and predictive models of stormwater runoff volumes, loads, and pollutant concentrations from watersheds in the Twin Cities metropolitan arae, Minnesota, USA. *Water Research*, 36, 1743 - 1757.
- Bricker, O. P. (1999). An overview of the factors involved in evaluating the geochemical effects of highway runoff on the environment. Open-File Report 98-630. US Federal Highway Authority, Massachusetts.
- Bricker, O. P. and Rice, K. C. (1993). Acid rain. Annual Review of Earth and Planetary Sciences, 21, 151 174.
- Buanuam J., Miro M., Hansen H. E., Shiowatana J. (2006). On-line dynamic fractionation and automatic determination of inorganic phosphorus in environmental solid substrates exploiting sequential injection microcolumn extraction and flow injection analysis. *Analytica Chimica Acta*, 570, 224 – 231.
- Buanuam, J., Miro, M., Hansen, H., Shiowatana, J, Estela, M., Cerd, V. (2007). A multisyringe flow-through sequential extraction system for on-line monitoring of orthophosphate in soils and sediments. *Talanta*, 71, 1710 – 1719.
- Buckler, D. R. and Granato, G. E. (1999). Assessing biological effects from highway-runoff constituents. Northborough, MA, US Geological Survey: 46.
- Bysouth, S. R. and Tyson, J. F. (1992). Simple model of flow-injection sample transport for prediction of peak heights. *Analytica Chimica Acta*, 261, 549 556.

- Callender, E. and Rice, K. C. (2000). The urban environmental gradient: anthropogenic influences on the spatial and temporal distributions of lead and zinc in sediments. *Environmental Science and Technology*, 34(2), 232 238.
- Campbell, W. H., Pengfei, S. and Barbier, G. G. (2006). Nitrate reductase for nitrate analysis in water. *Environmental Chemistry Letters* 4: 69 73.
- Carolli, S. (1996). Element speciation in bioinorganic chemistry. Analytical Chemistry and Its Applications, John Wiley & Sons, New York, USA.

Casey H. and Smith, S. (1985). Application of flow injection analysis to water pollution studies. *Trend in Analytical Chemistry*, 4(10), 256 - 258.

- Characklis, G. W. and Wiesner, M. R. (1997). Particles, metals, and water quality in runoff from large urban watershed. *Journal of Environmental Engineering*, 128(8), 753 759.
- Chauhan, S. (2010). Catalytic converters for propane oxidation. *Journal of Natural and Environmental Sciences*, 1(2), 91 - 95.
- Chebbo, G., Gromaire, M., Ahyerre, M. and Garnaud, S. (2001). Production and transport of urban wet weather pollution in combined sewer systems: the marais experimental catchment in paris. *Urban Water*, 3(1-2), 3 15.
- Choate, J. (2004). Phosphorus availability in biosolids-amended soils. Corvallis, Oregun, Oregun State University, US. M.S.
- Christensen, E. R. and Guinn, V. P. (1979). Zinc from automobile tyres in urban runoff. *Journal* of the Environmental Engineering Division, ASCE, 105, 165 168.
- Chui, T., Mar, B. and Horner, R. (1982). Pollutant loading model for higway runoff. *Journal of Environmental Engineering, ASCE,* 108(6), 1193 - 1210.

Ciavatta, C., Antisari, L. V. and Sequi, P. (1990). Interference of soluble silica in the

determination of orthophosphate- phosphorus. *Journal of Environmental Quality*, 19, 761 - 764.

- Colman, J. A., Rice, K. C. and Willoughby, T. C. (2001). Methodology and significance of studies of atmospheric deposition in highway runoff. Open-File Report 01-259, US Geological Survey, Northborough, Massachusetts.
- Colman, J.A. and Friesz, P.J. (2001). Hydrology and trophic ecology of Walden Pond, Concord, Massachusetts: U.S. Geological Survey Water-Resources Investigations Report 01-4153, 1 sheet.
- Colwill, G. M., Peters, C. J. and Perry, R. (1984). Water quality of motorway runoff. Transport and road research laboratory supplementary report, Transport and Road Research laboratory, Crowthorne, UK.
- Conley, D. J. (1999). Biogeochemical nutrients cycles and nutrient management strategies. *Hydrobiologia*, 419, 87 - 96.
- Correll, D. L. (1999). Phosphorus: A rate limiting nutrient in surface waters. *Poultry Science*, 78, 674 682.
- Crabtree, B., Moy, F., Whitehead, M. and Roe, A. (2006). Monitoring pollutants in highway runoff. *Water and Environment Journal*, 20, 287 294.
- Craul, P. J. (1999). Urban Soils: Application and Practices, John Wiley and Sons, Inc, New York.
- Crosland, A. R., Zhao, F. J., McGrath, S. P. and Lane, P. W. (1995). Comparison of aqua regia digestion with sodium carbonate fusion for the determination of total phosphorus in soils by inductively coupled plasma atomic emission spectroscopy (ICP). *Communications in Soil Science and Plant Analysis*, 26, 1357 - 1368.

Davidson, C. M., Thomas, R. P., McVey, S. E., Perala, R., Littlejohn, D. and Ure, A. M. (1994).

Evaluation of sequential extraction procedure for the speciation of heavy metals in sediments. *Analytica Chimica Acta*, 291, 277 - 286.

- Davies, A. P., Shokouhian, M. and Ni, S. (2001). Loading estimates of lead, copper, cadmium, and zinc in urban runoff from specific sources. *Chemosphere*, 44, 997 1009.
- Davis, R. L., Zhang, H., Schroder, J. L., Wang, J. J., Payton, M. E. and Zazulak, A. (2005). Soil characteristics and phosphorus level effect on phosphorus loss in runoff. *Journal of Environmental Quality*, 34, 1640 - 1650.
- de-la-Guardia, M. (1996). Nonchromatographic methods of element speciation by atomic spectrometry: Element speciation in bioinorganic chemistry; Ed. Sergio Carolli; Vol. 135, John Wiley & Sons, Inc., New York, USA. P 97.
- De-Montigny, C. and Prairie, Y. (1993). The relative importance of biological and chemical processes in the release of phosphorus from a highly organic sediment. *Hydrobiologia*, 253, 141 150.
- Deletic, A. (1998). The first flush load of urban surface runoff. Water Research, 32, 2462 2470.
- Deletic, A., Ashley, R. and Rest, D. (2000). Modeling input of fine granular sediment into drainage systems via gully-pots. *Water Research*, 34(15), 3836 3844.
- Dodds, W. K. (2006). Eutrophication and trophic state in rivers and streams. *Limnology and Oceanography*, 51(1, part 2), 671 680.
- Dolan, L. M. J., Van-Bohemen, H., Whelan, P., Akbar, K. F., O'Malley, V., O'Leary, G. and Keizer, P. J. (2006). Heavy metal contaminated of roadside soils of Northern England. *Soil & Water Research*, 4, 158 - 163.
- Dorchin, A. (2007). Road runoff and their effects on biological systems, Department of Evolutionary and Environmental Biology, Faculty of Sciences and Science Education,
Haifa University, Mt. Carmel (Unpublished M. Sc. Thesis).

- Dorchin, A. and Shanas, U. (2010). Assessment of pollution in road runoff using a *Bufo viridis* biological assay. *Environmental Pollution*, 158, 3626 3633.
- Drapper, D., Tomlinson, R. and Williams, P. (2000). Pollutants concentrations in road runoff: southeast Queensland case study. *Journal of Environmental Engineering*, 126, 313 320.
- Driscoll, E. D., Shelley, P. E. and Strecker, E. W. (1990). Pollutant loading and impacts from stormwater runoff. Analytical investigation and research report, vol. III. FHWA-RD-88-008, Federal Highway Administration, USA.
- Drummond, L. and Maher, W. (1995). Determination of phosphorus in aqueous solution via formation of phosphoantimonylmolybdenum blue complex: re-examination of optimum conditions for the analysis of phosphate. *Anal. Chim. Acta* 302: 69-74.
- Duffus, J. H. (2002). "Heavy metals A meaningless term? *Pure and Applied Chemistry*, 74(5), 793 807.
- Ebiare, E. and Zejiao, L. (2010). Water quality minitoring in Nigeria: case study of Nigeria's industrial cities. *Journal of American Science*, 6(4), 22 28.
- Ellis, J. B. and Revitt, M. (1981). Incidence of heavy metals in street surface sediments: solubility and grain size studies. *Water, Air, and Soil Pollution,* 17, 87 100.
- Erel, Y. (1998). Mechanisms and velocities of anthropogenic Pb migration in Mediterranean soils. *Environmental Research*, 78, 112 - 117.
- Estela, J. M. and Cerda, V. (2005). Flow analysis techniques for phosphorus: an overview. *Talanta*, 66, 307 - 331.
- Expertsmind (2013). Double Beam Atomic Absorption Spectrophotometer. Expertsmind IT Educational Pvt. Ltd. URL: http://www.expertsmind.com/topic/atomic-absorption-

spectrophotometer/double-beam-atomic-absorption-spectrophotometer-914072.aspx; Accessed on 20th March, 2013.

- Filippelli, G. M. (2002). The global phosphorus cycle. *Reviews in Mineralogy and Geochemistry*, 48, 391 425.
- Flegal, A. R., Conaway, C. H., Scelfo, G. M., Hibdon, S. A. and Sanudo-Wilhelmy, S. A. (2005). A review of factors influencing measurements of decadal variations in metal contamination San Francisco Bay, California. *Ecotoxicology*, 14, 645 - 660.
- FMenv (1991). National Guidelines and Standards for Water Quality in Nigeria. Federal Ministry Environment, Federal Republic of Nigeria.
- Forman, R. T. T. and Alexander, L. E. (1998). Roads and their major ecological effects. *Annual Review of Ecology and Systematics*, 29, 207 231.
- Freeman, P. R., McKelvie, I. D., Hart, B. T. and Cardwell, T. J. (1990). A flow injection analysis method for the determination of low levels of phosphorus in natural waters. *Analytical Chimical Acta*, (234), 409 - 416.
- Furlong, E. T., Vaught, G. G., Merten, L. M., Foreman, W. T. and Gates, P. M. (1995). Methods of analysis by the U.S. Geological Survey National Water Quality Laboratorydetermination of semivolatile organic compounds in bottom sediment by solvent extraction, gel permeation chromatographic fractionation, and capillary-column gas chromatography/mass spectrometry. Open-File Report 95-719, US Geological Survey.
- Galhardo C. X. and Masini J. C. (2000). Spectrophotometric determination of phosphate and silicate by sequential injection using molybdenum blue chemistry. *Anaytica Chimica Acta*, 417, 191 200.
- Gao, Y., Zhu, B., Zhou, P., Tang, J. L., Wang, T. and Miao, C. Y. (2009). Effects of vegetation cover on phosphorus loss from hillslope cropland of purple soil under simulated rainfall: A case study of China. *Nutrient Cycling in Agroecosystem*, 85, 263 273.

- Garnaud, S., Mouchel, J.-M., Chebbo, G. and Thevenot, D. R. (1999). Heavy metal concentrations in dry and wet atmospheric deposits in Paris district: comparison with urban runoff. *The Science of the Total Environment*, 235, 235 245.
- Gelinas, Y. and Schmit, J. (1998). Estimation of the bulk atmospheric deposition of major and trace elements to a rural watershed. *Atmospheric Environment*, 39(9), 1473 1483.
- Gimbert, L. J., Haygarth, P. M. and Worsfold, P. J. (2007). Determination of nanomolar concentrations of phosphate in natural waters using flow injection with a long path length liquid waveguide capillary cell and solid-state spectrophotometric detection. *Talanta*, 71, 1624 - 1628.
- Giné M.F., Tuon R. L., Krug F. J., Arruda M. A. Z. (1992). Experimental fluctuations of flowinjection signals. Analytica Chimica Acta, 261(1-2), 533 - 538.
- Godfrey, P. J., Mattson, M. D., Walk, M.-F., Kerr, P. A., Zajicek, O. T. and III, A. R. (1996).The Massachusetts acid rain monitoring project: Ten years of monitoring Massachusetts lakes and streams with volunteers, University of Massachusetts Water Resources Research Centre.
- Green, S. M., Machin, R. and Cresser, M. S. (2008). Effect of long-term changes in soil chemistry induced by road salt applications on N-transformations in roadside soils. *Environmental Pollution*, 152, 20 - 31.
- Griess, P. (1879). Bemerkungen zu der Abhandlung der HH. Weselky und Benedikt Ueber einige Azoverbindungen. Berichte der Deutschen chemischen Gesellschaft, 12(1), 426 428.
- Grudpan, K., Ampan, P., Udnan, Y., Jayasvati, S., Lapanantnoppakhun, S., Jakmunee, J., Christian, G. D. and Ruzicka, J. (2002). Stopped-flow injection simultaneous determination of phosphate and silicate using molybdenum blue. *Talanta*, 58, 1319 -1326.

- Gupta, M. K., Agnew, R. W. and Kobringer, N. P. (1981). Constituents of highway runoff, Volumes I-IV. FHWA/RD-81-042-046. Federal Highway Authority, Envirex, Inc., Environmental Sciences Division, Milwaukee, WI.
- Gupta, M. K., Agnew, R. W. and Meinholz, T. L. (1981b). Constituents of highway runoff, volume II - Procedural manual for monitoring highway runoff. Federal Highway Administration Report, Federal Highway Administration, Northborough, Massachusetts, US.
- Hall, H. J. and Anderson, B. C. (1988). The toxicity and chemical composition of urban stormwater runoff. *Canadian Journal of Civil Engineering*, 15, 98 106.
- Haney, R. L., Haney, E. B., Hossner, L. R. and Arnold, J. G. (2006). Development of a new soil extractant for simultaneous phosphorus, ammonium, and nitrate analysis. *Communications in Soil Science and Plant Analysis*, 37, 1511 - 1523.
- Hansen, E. H. and Miro, M. (2007). How flow-injection analysis (FIA) over the past years has changed our way of performing chemical analysis. *Trends in Analytical Chemistry*, 26(1), 18 - 26.
- Harned, D. A. (1988). Effects of highway runoff on streamflow and water quality in the Sevenmile Creek Basin, a rural area in the Piedmont Province of North Carolina, July 1981 to July 1982. Water-Supply Paper 2329, US Geological Survay.
- Hart, M. R., Quinn, B. F. and Nguyen, M. L. (2004). Phosphorus runoff from agricultural land and direct fertilizer effects: a review. *Journal of Environmental Quality*, 33, 1954 1972.
- Helmers, E. (1996). Elements accompanying platinum emmited from automobile catalysts. *Chemosphere*, 33(3), 405 - 419.
- Helmreich, B., Hilliges, R., Schriewer, A. and Horn, H. (2010). Runoff pollutants of a highly trafficked urban road - Correlation analysis and seasonal influences. *Chemosphere*, 80, 991 - 997.

- Hettiarachchi, G. M., Pierzynski, G. M. and Ransom, M. D. (2000). *In situ* stabilization of soil lead using phosphorus and manganese oxide. *Environmental Science Technology*, 34(21), 4614 - 4619.
- Hewitt, C. H. and Rashed, M. B. (1990). An integrated budget for selected pollutants for major rural highway. *The Science of the Total Environment*, 93, 375 384.
- Hooda, P. S., Rendell, A. R., Edwards, A. C., Withers, P. J. A., Aitkens, M. N. and Truesdale, V.
 W. (2000). Relating soil phosphorus indices to potential phosphorus release to water. *Journal of Environmental Quality*, 29, 1166 - 1171.
- Hope, B. K. (1996). An assessment of global impact of anthropogenic vanadium. *Biogeochemistry*, 37, 1 - 13.
- Horowitz, A. J. (1995). The use of suspended sediment and associated trace elements in water quality studies Special Public. No. 4, International Association of Hydrological Sciences, IAHS: 58.
- Howarth, R. W., Anderson, D. A., Church, T. M., Greening, H., Hopkinson, C. S. and Huber, W. (2000). Clean coastal waters: Understanding and reducing the effects of nutrient pollution, National Academy Press, Washington, D. C.
- Howarth, R. W. and Marino, R. (2006). Nitrogen as the limiting nutrient for eutrophication in coastal marine ecosystems: Evolving views over three decades. *Limnology and Oceanography*, 5(1, part 2), 364 - 376.
- Huang, X.-L. and Zhang, J.-Z. (2008). Rate of phosphoantimonylmolybdenum blue complex formation in acidic persulfate digested matrix for total dissolved phosphorus determination: Importance of post-digestion pH adjustment. *Talanta*, 77, 340 345.
- Impelliteri, C. A., Lu, Y., Saxe, J. K., Allen, H. E. and Peijnenburg, W. J. G. M. (2002). Correlation of the partitioning of dissolvedorganic matter fractions with the desorption of

Cd, Cu, Ni, Pb and Zn from 18 Dutch soils *Environment International*, 28, 401 - 410.

- Jacoby, F. J. (2005). Extractable soil phosphorus, correlation with P forms in soil runoff, and relationships with the Texas P Index as a nutrient management tool for CAFOs. College Station, Texas, Texas A&M University, US. Ph.D.
- Jakmunee J. and Junsomboon J. (2009). Determination of available phosphorus in soils by using a new extraction procedure and a flow injection amperometric system. *Talanta*, 79, 1076 - 1080.
- Jartun, M., Ottesen, R. T. and Steinnes, E. (2003). Urban soil pollution and the playfields of small children. *Journal de Physique IV*, 107, 671 674.
- Jartun, M., Ottesen, R. T., Steinnes, E. and Volden, T. (2008). Runoff of particle bound pollutants from urban impervious surfaces studied by analysis of sediments from stormwater traps. *Science of the Total Environment*, 396, 147 163.
- Jiang, G., Hu, H., Liu, Y., Cai, Z. and Yang, H. (2010). Immobilizing soil exogenous lead using rock phosphate. *Journal of Food, Agriculture & Environment*, 8(1), 275 280.
- Jordan, R. N., Yonge, D. R. and Hathhorn, W. E. (1997). Enhanced mobility of Pb in the presence of dissolved natural organic matter. *Journal of Contaminant Hydrolology*, 29, 59-80.
- Joshi, U. M. and Balasubramanian, R. (2010). Characteristics and environmental mobility of trace elements in urban runoff. *Chemosphere*, 80, 310 318.
- Kalbitz, K. and Wennrich, R. (1998). Mobilisation of heavy metals and arsenic in polluted wetland soils and its dependence on dissolved organic matter. *Science of the Total Environment*, 209(1), 27 39.
- Kang, J.-H., Kayhanian, M. and Stenstrom, M. K. (2008). Predicting the existence of stormwater first flush from the time of concentration. *Water Research*, 42, 220 228.

- Karlberg, B. and Pacey, G. E. (1989). Flow Injection Analysis A Practical Guide, Elsevier, Amsterdam.
- Karouna-Renier, N. K. and Sparling, D. W. (2001). Relationship between ambient geochemistry, watershed land-use and trace metal concentrations in aquatic invertebrates living in stormwater treatment ponds. *Environmental Pollution*, 112, 183 - 192.
- Kayhanian, M., Stransky, C., Bay, S., Lau, S.-L. and Stenstrom, M. K. (2008). Toxicity of urban highway runoff with respect to storm duration. *Science of the Total Environment*, 389, 386 - 406.
- Kayhanian, M., Suverkropp, C., Ruby, A. and Tsay, K. (2007). Characterization and prediction of highway runoff constituent event mean concentration. *Journal of Environmental Mnagement*, 85, 279 - 295.
- Khan, M. N., Wasim, A. A., Sanwar, A. and Rashedd, M. F. (2011). Assessment of heavy metal toxicants in the roadside soil along the N-5, National Highway, Pakistan. *Environmental Monitoring Assessment*, 182(1-4), 443 - 454.
- Kobringer, N. P. (1984). Volume I. Sources and migration of highway runoff pollutants-Executive Summary, FHWA/RD-84/057. Federal Highway Administration, Rexnord, EnviroEnergy Technology Center, Milwaukee, WI.
- Kolev, S. D. and McKelvie, I. D. (2008). Advances in flow injection analysis and related techniques.Comprehensive Analytical Chemistry, Elsevier B. V.
- LAMATA (2013). Traffic Management. Lagos Metropolitan Area Transport Authority. www.lamata-ng.com/traffic-mgt.php. Accessed on 21st February, 2014.
- Lapa, R. A. S., Lima, J. L. F. C., Reis, B. F., Santos, J. L. M. and Zagatto, E. A. G. (2002). Multi-pumping in flow analysis: concepts, instrumentation, potentialities. *Analytical Chimical Acta*, 466, 125 - 132.

- Lee, F. L., Maruya, K. A. and Bulski, K. (2004). Exposure of grass shrimp to sediments receiving highway runoff: Effects on reproduction and DNA. *Marine Environmental Research*, 58, 713 - 717.
- Lee, J. H. and Bang, K. W. (2000). Characterization of Urban Stormwater Runoff. *Water Research*, 34(6), 1773 - 1780.
- Lee, J. Y., Kim, H., Kim, Y. and Han, M. Y. (2011). Characteristics of the event mean concentration (EMC) from rainfall runoff on an urban highway. *Environmental Pollution*, 159, 884 - 888.
- Lee, P.-K., Yu, Y.-H., Yun, S.-T. and Mayer, B. (2005). Metal contamination and solid phase partitioning of metals in urban roadside sediments. *Chemosphere*, 60, 672 689.
- Leenheer, J. A., Brown, G. K., MacCarthy, P. and S.E. Cabaniss (1998). Models of metal binding structures in fulvic acid from the Suwannee River, Georgia. *Environmental Science and Tecgnology*, 32(16), 2410.
- Legret, M. and Pagotto, C. (1999). Evaluation of pollutant loadings in the runoff waters from a major rural highway. *Science of the Total Environment*, 235, 143 150.
- Li-qing, L., Cheng-qing, Y., Qing-ci, H. and Ling-li, K. (2007). First flush of storm runoff pollution from an urban catchment in China. *Journal of Environmental Sciences*, 19(3), 295 - 299.
- Li, L. Y. (2006). Retention capacity and environmental mobility of Pb in soils along highway corridor. *Water, Air, and Soil Pollution,* 170, 211 227.
- Li, Y., Lau, S. L., Kayhanian, M. and Stenstrom, M. K. (2005). Particle size distribution in highway runoff. *Journal of Environmental Engineering*, 131, 1267 1276.

Li, Y. and Ma, H. (1995). Two trends of sample dispersion variation with carrier flow rate in a single flow-injection manifold. *Talanta*, 42(11), 2033 - 2038.

- Linge, L. K. and Oldham, C. E. (2001). Interference from arsenate when determining phosphate by the malachite green spectrophotometric method. *Analytica Chimica Acta*, 450, 247 252.
- Linsinger, T. (2005). Comparison of a measurement result with the certified value. Application Note 1. Geel, Belgium, European Commission - Joint Research Centre Institute for Reference Materials and Measurement (IRMM)
- Lopes, T. J. and Dionne, S. G. (1998). A review of semivolatile and volatile organic compounds in highway runoff and urban stormwater. Open-File Report 98-409, US Geological Survey.
- Lu, D. and Weng, Q. (2006). Use of impervious surface in urban land-use classification. *Remote Sensing. Environment*, 102, 146 160.
- Lyddy-Meany, A. J., Ellis, P. S., Worsfold, P. J., Butler, E. C. V., McKelvie I. D. (2002); A compact flow injection analysis system for surface mapping of phosphate in marine waters. *Talanta*, 58, 1043 1053.
- Malin, M. A., Johnson, V. L., Ensign, S. H. and MacPherson, T. A. (2006). Factors contributing to hypoxia in rivers, lakes, and streams. *Limnology and Oceanography*, 51(1, part 2), 690 701.
- Mallarino, A. P. (2003). Field Calibration of corn of the Mehlich-3 soil phosphorus test with colorimetric and inductively coupled plasma emission spectroscopy determination methods. *Science Society of American Journal*, 68, 1928 - 1934.
- Maltby, L., Forrow, D. M., Boxall, A. B. A., Calow, P. and Betton, C. I. (1995). The effects of motorway runoff on fresh-water ecosystems: 1 Fiels study. *Environmental Toxicology* and Chemistry, 14, 1079 - 1092.

- Mangani, G., Berloni, A., Bellucci, F., Tatano, F. and Maione, M. (2005). Evaluation of the pollutant content in road runoff first flush waters. *Water, Air, and Soil Pollution*, 160, 213 228.
- Marsalek, J., Rochfort, Q., Brownlee, B., Mayer, T. and Servos, M. (1999). An exploratory study of urban runoff toxicity. *Water Science Technology*, 39(12), 33 39.
- McKelvie, I. D. (2008). Principles of Flow Injection Analysis. Comprehesive Analytical Chemistry. Amsterdam, Elsevier.
- McKelvie, I. D., Peat, D. M. W., Mattews, G. P. and Worsfold, P. J. (1997). Elimination of the Schlieren effect in the determination of reactive phosphorus in estuarine waters by flow-injection analysis. *Analytica Chimica Acta*, 351, 265 271.
- McKelvie, I. D., Peat, D. M. W. and Worsfold, P. J. (1995). Techniques for the quantification and speciation of phosphorus in surface waters. *Analytica Proceedings including Analytical Communications*, 32, 437 - 445.
- McKenzie, M. R., Money, J. E., Green, P. G. and Young, T. M. (2009). Metals associated with stormwater-relevant brake and tire samples. *Science of the Total Environment*, 407, 5855 - 5860.
- McLean, E. O. (1982). In methods of soil analysis, part 2. Chemical and microbiological properties. Agronomy Monograph. Wisconsin, USA, American Society of Agronomy: 11 - 59.
- Mehlich, A. (1984). Mehlich 3 soil test extractant: A modification of the Mehlich 2 extractant. *Communications in Soil Science Plant Analysis*, 15, 1409 -1616.
- Mendham, J., Denney, R. C., Barnes, J. D. and Thomas, M. (2002). Vogel's Textbook of Quantitative Chemical Analysis, 6th Edition, Perason Education Ltd, Delhi.

- Miranda, K., Espey, M. M. and Wink, D. A. (2001). A rapid, simple spectrophotometric method for simultaneous detection of nitrate and nitrite. *Nitric Oxide-Biology and Chemistry*, 5(1), 62 - 71.
- Miro, M., Estela, M. and Cerda, V. (2004a). Application of flowing-stream techniques to water analysis Part II. General quality parameters and anionic compounds: halogenated, sulphur and metalloid species. *Talanta*, 62, 1 - 15.
- Miro, M., Estela, M. and Cerda, V. (2004b). Application of flowing-stream techniques to water analysis Part III. Alkaline-earth metals, elemental and harmful transition metals, and multielemental analysis. *Talanta*, 63, 201 - 223.
- Miro, M., V. Cerda and J. M. Estela (2002). Multisyringe flow injection analysis: characterisation and applications. *Trends in Analytical Chemistry*, 21(3), 199 210
- Monbet, P., McKelvie, I. D. and Worsfold, P. J. (2009). Sedimentary pools of phosphorus in the eutrophic Tamar estuary (SW England). *Journal of Environmental Monitoring*, 12, 296 -304.
- Monks, P. S., Monksa, P. S., Granierb, C., Fuzzie, S., Stohlf, A., Williamsg, M. L., Akimotoh, H., Amanni, M., Baklanovj, A., Baltenspergerk, U., Beyl, I. and al, e. (2009).
 Atmospheric composition change global and regional air quality. *Atmospheric Pollution*, 43, 5268 5350.
- Monrais, I. P. A., Toth, I. V. and Angel, A. O. S. S. (2005). An overview on flow methods for the chemiluminescence determination of phosphorus. *Talanta*, 66, 341 347.
- Moorcroft, M. J., Davis, J. and Compton, R. G. (2001). Detection and determination of nitrate and nitrite: a review. *Talanta*, 54, 785-803.
- Mota, A. M. and Goncalves, M. L. S. (1996). Element speciation in bioinorganic chemistry; Edited by S. Carolli. Analytical Chemistry and Its Applications, John Wiley & Sons, New York.

- Murphy, J. and Riley, J. P. (1962). A modified single solution method for the determination of phosphate in natural waters. *Analytica Chimica Acta*, 27, 31 36.
- Nathan, M. V., Mallarino, A., Elliason, R. and Miller, R. (2002). ICP vs. colorometric determination of Mehlich III extractable phosphorus. *Commununications in Soil Science and Plant Analysis*, 33, 2432 - 2447.
- Neal, C., Neal, M. and Wickham, H. (2000). Water quality of a tributary of the Thames, the Pang, southern England. *Science of the Total Environment*, 251/252, 511 522.
- Neves M. A. C., Souto M. R. S., Toth I. V., Victal S. M. A., Drumond M. C., and Rangel O. S. S. (2008). Spectrophotometric flow system using vanadomolybdophosphate detection chemistry and a liquid waveguide capillary cell for the determination of phosphate with improved sensitivity in surface and ground water samples, *Talanta* 77, 527 532.
- Ng-Kee-Kwong, K. F., Bolah, A., Volcy, L. and Pynee, K. (2001). Nitrogen and phosphorus transport by surface runoff from a silty clay loam under sugarcane in humid tropical environment of Mauritius. *Agriculture Ecosystem and Environment*, 91, 147 157.
- Nixon, S. W. (1995). Coastal marine eutrophication: A definition, social causes, and future concerns. *Ophelia* 41: 199 219.
- Nixon, S. W., Buckley, B. A., Granger, S. L., Entsua-Mensah, M., Ansa-Asare, O., White, M. J., McKinney, R. A. and Mensah, E. (2007). Anthropogenic enrichment and nutrients in some tropical lagoons of Ghana, West Africa. *Ecological Applications*, 17(5), S144 -S164.
- Nriagu, J. O., Jinabhai, C., Naidoo, R. and Coutsoudis, A. (1996). Childhood lead poisoning in Africa: a growing public health problem. *Science of the Total Environment*, 191, 69 76.
- Ogunleye M. and Awomosu T. (2010). Lagos as a region. State of the Environment Report, 2010, Edited by Ogunleye, M. and Alo, B. Published by Ministry of the Environment,

Lagos State / Beachland Resources Limited. Page 2.

- Okoye, B. C. (1991). Heavy metals and organisms in the Lagos Lagoon, Nigeria. *International Journal of Environmental Studies*, 37(4), 285 292.
- Olayinka, K. O. and Alo, B. I. (2001). The effects of extraction techniques on the determination of lead in street dust samples from some cities in Nigeria. *International Journal of Chemistry*, 11(4), 219 226.
- Olayinka, K. O. and Alo, B. I. (2004). Studies on industrial pollution in Nigeria: the effects of textile effluents on the quality of groundwater in some parts of Lagos. *Nigeria Journal of Biomedical Sciences*, 3(1), 44 50.
- Oluseyi, T. O., Olayinka K. O., Alo, B. I. and Smith, R. M. (2012). Distribution and source identification of polycyclic aromatic hydrocarbons in surface sediments from the Lagos Lagoon, *Nigeria. Journal of Chemical Society of Nigeria*, 37 (1), 92 98.
- Olsen, S. R., Cole, C. V., Watanabe, F. S. and Dean, L. A. (1954). Estimation of available phosphorus in soils by extraction with sodium bicarbonate. USDA circular no. 939. Washinton D.C., U.S., Government Printing Office.
- Omaka, O. N., Keith-Roach, M. J. and Worsfold, P. J. (2007). Flow injection spectrophotometric method for the determination of filterable phosphorus (FRP) in natural waters in the presence of high concentrations of arsenate and silicate. *Journal of the Chemical Society Nigeria*, 32(1), 143 149.
- Opher, T., Ostfeld, A. and Friedler, E. (2009). Modeling highway runoff pollutant levels using a data driven model. *Water Science Technology*, 60, 19 27.
- Osmond, D.L., Line D.E., Gale J.A., Gannon R.W., Knott C.B., Bartenhagen K.A., Turner M.H., Coffey S.W., Spooner J., Wells J., Walker J.C., Hargrove L.L., Foster M.A., Robillard P.D., and Lehning D.W.(1995). WATERSHEDSS: Water, Soil and Hydro-environmental Decision Support System, http://h2osparc.wq.ncsu.edu. Accessed on 14th July, 2013.

- Osuntogun, B. A. and Koku, C. A. (2007). Environmental-impacts of Urban Road Transportation in South-western States of Nigeria. *Journal of Applied Sciences*, 7, 2356 -2359.
- Oyeyiola, A. O., Olayinka, K. O. and Alo, B. I. (2011). Comparison of three sequential extraction protocols for the fractionation of potentially toxic metals in coastal sediments. *Environmental Monitoring Assessment*, 172, 319 327.
- Paerl, H. W., Valdes, L. M. and Peierls, B. L. (2006). Anthropogenic and Climatic Influences on the Eutrophication of Large Estuarine Ecosystems. *Limnology and Oceanography*, 51(1, part 2), 448 - 462.
- Park, S., Cheng, Z., Yang, H., Morris, E., Sutherland, M., McSpadder, G. and Grewal, P. (2010). Differences in soil chemical properties with distance to roads and age of development in urban areas. *Urban Ecosystems*, 13(14), 483 - 497.
- Patel, J. (2004). The impact of highway runoff on water quality downstream of a highway outfall, School of Engineering, University of Birmingham, UK and Atkins Consultants Ltd.
- Patey, M. D., Rijkenberg M. J. A., Statham, P. J., Stinch-combe M. C., Achterberg E. P., and Mowlem M. (2008). Determination of nitrate and phosphate in seawater at nanomolar concentrations. *Trends in Analytical Chemistry*, 27, 169 - 182.
- Patton, C. J. and Kryskalla, J. R. (2011). Colorimetric determination of nitrate plus nitrite in water by enzymatic reduction, automated discrete analyzer methods, U.S. Geological Survey Techniques and Methods, Book 5, Chap. B8, 34.
- Paul, M. J. and Meyer, J. L. (2001). Streams in the urban landscape. Annual Review of Ecological Systems, 32, 333 - 365.
- Peat, D. M. W., McKelvie, I. D., Matthews, G. P., Haygarth, P. M. and Worsfold, P. J. (1997).

Rapid determination of dissolved organic phosphorus in soil leachates and runoff waters by flow injection analysis with on-line photo-oxidation. *Talanta*, 45, 47 - 55.

- Perdikaki, K. and Mason, C. F. (1999). Impact of road runoff on receiving streams in eastern England. *Water Research*, 33(7), 1627 1633.
- Pereira, E., Baptista-Neto, J. A., Smith, B. J. and McAllister, J. J. (2007). The contribution of heavy metal pollution from highway runoff to Guanabara Bay sediments-Rio de Janeiro, Brazil. Annals of the Brazilian Academy of Sciences, 79, 739 - 750.
- Perkins, R. G. and Underwood, G. J. C. (2000). The potential fro phosphorus release across the sediment-water interface in an eutrophic reservoir dosed with ferric sulphate. *Water Research*, 35(6), 1399 - 1406.
- Petterson, C., Hakansson, K., Kalsson, S. and Allard, B. (1998). Metal speciation in a humic surface water system polluted by acidic leachates from a mine deposit in Sweden. *Water Research*, 27, 863 - 871.
- Pierzynski, G., Zhang H., Wolf A., Kleinman P., Mallarino A., and Sullivan D. Phosphorus (2005). Determination in waters and extracts of soils and by-Products: Inductively Coupled Plasma spectrometry versus colorimetric procedures; SERA-17. www.sera-17.ext.vt.edu/SERA_17_Publications.htm; Accessed on 20th March, 2013.
- Pitt, R., Field, R., Lalor, M. and Brown, M. (1995). Urban stormwater toxic pollutants: assessment, sources, and treatability. *Environmental Research*, 67(3), 260 275.
- Pittman, J. J., H. Zhang, J. L. Schroder, and M. E. Payton (2005). Differences of phosporus in Mehlich 3 extracts determined by colorimetric and spectroscopic methods. *Communications in Soil Science and Plant Analysis*, 36, 1641 - 1659.
- Preininger, C., Klimant, I. and Wolfbeis, O. S. (1994). Optical fiber sensor for biological oxygen demand. *Analytical Chemistry*, 66, 1841 1846.

- Quinton, J. N., Catt, J. A. and Hess, T. M. (2001). The selective removal of phosphorus from soil: is event size important? *Journal of Environmental Quality*, 30, 538 545.
- Redfield, A. C. (1958). The biological Control of chemical factors in the environment. *American Scientist*, 46, 1 221.
- Redshaw, C. J., Mason, C. F., Hayes, C. R. and Roberts, R. D. (1990). Factors influencing phosphate exchange across the sediment-water interface of eutrophic reservoirs. *Hydrobiologia*, 192, 233 - 245.
- Robards, K., McKelvie, I. D., Benson, R. I., Worsfold, P. J., Blundell, N. J. and Casey, H. (1994). Determination of carbon, phosphorus, nitrogen and silicon species in water. *Analytica Chimica Acta*, 287, 147 - 190.
- Robertson, D. J. and Taylor, K. G. (2007). Temporal variability of metal contamination in urban road deposited sediment in Manchester, UK: implication for urban pollution monitoring. *Water, Air, and Soil Pollution,* 186, 209 - 220.
- Robertson, D. J., Taylor, K. G. and Hoon, S. R. (2003). Geochemical and mineral magnetic characterisation of urban sediments particulates, Manchester, UK. *Applied Geochemistry*, 18, 269 - 282.
- Rocha, F. R. P., Reis, B. F., Zagatto, E. A. G., Lima, J. L. F. C., Lapa, R. A. S. and Santos, J. L.
 M. (2002). Multicommutation in flow analysis: concepts, applications and trends. *Anaytica Chimica Acta*, 468, 119 - 131.
- Rossini, P., Guerzoni, S., Molinaroli, E., Rampazzo, G., De-Lazzari, A. and Zancanaro, A. (2005). Atmospheric bulk deposition to the lagoon of Venice Part I. Fluxes of metals, nutrients and organic contaminants. *Environment International*, 31, 959 - 974.
- Ruzicka, J. (1991). The second coming of flow injection analysis. *Analytica Chimica Acta*, 261, 3 10.

- Ruzicka, J. (2008). From beaker to programmable micrufludics. Advances in Flow Injection Analysis and Related Techniques -Ed. S. D. Kolev and I. D. McKelvie. Comprhensive Analytical Chemistry; Elsevier, Netherland.
- Ruzicka, J. (2009). Flow injection analysis: From beaker to micrfluidics- 4th Edition. FIAlab Instruments Inc. (www.flowinjection.com)
- Ruzicka, J. and Hansen, E. H. (1975). Flow injection analysis. Part II. Ultra fast determination of phosphorus in plant material by continuous flow spectrophotometry. *Anal. Chim. Acta* 79: 79 - 91.
- Sakai, T., Takio, H., Teshima, N. and Hishikawa, H. (2001). Extraction-flow injection spectrofluorimetric measurement of dissolved oxygen in environmental waters using 2thionaphthol. *Analytica Chimica Acta*, 438, 117 - 121.
- Sansalone, J. J. and Buchberger, S. G. (1997). Partitioning and first flush of metals in urban roadway storm water. *Journal of environmental Engineering, ASCE,* 123, 134 143.
- Sansalone, J. J. and Cristina, C. M. (2004). First flush concepts fro suspended and dissolved solids in small impervious watersheds. *Journal of Environmental Engineering*, 130, 1301 - 1314.
- Scott, T., Craig, S. and Zhu, W. (2011). The effects of simulated nitrate and salt deposition on nitrogen mineralization and soil chemistry in a roadside ecosystem. *Bulletin of the New Jersey Academy of Science*, 56(2), 101 - 106.
- SEOES (2009). Determination of nutrients in natural waters using an air segmented continuous flow analyser (autoanalyzer). COSHH Assessment, School of Earth, Ocean and Environmental Sciences, University of Plymouth, UK.
- Shaheen, D. G. (1975). Contributions of urban roadway usage to water pollution. US Government Printing Office Washinton D.C., Environmental Protection Agency, US.

- Sharpley, A. N. (1985). Depth of surface soil-runoff interaction as affected by rainfall, soil slope and management. *Soil Science Society of America Journal*, 49, 1010 1015.
- Sharpley, A. N., Kleinma, P. J. A., McDowell, R. W., Gitau, M. and Bryant, R. B. (2002). Modelling phosphorus transport in agricultural watersheds: processes and possibilities. *Journal of Soil Water Conservation*, 57, 425 - 439.
- Sheet, R. W., Kyger, J. R., Biagioni, R. N., Probst, S., Boyer, R. and Barke, K. (2001). Relationship between soil lead and airborne lead concentrations at Springfield, Missouri, USA. Science of the Total Environment, 271, 79 - 85.
- Shigaki, F., Sharpley, A. and Prochnow, L. I. (2007). Rainfall intensity and phosphorus source effects on phosphorus transport in surface runoff from soil trays. *Science of the Total Environment*, 373, 334 343.
- Singer, M. J. and Munns, D. N. (1999). Soil: an Introduction. 4th Edition. Prentice-Hall, Inc, Upper Saddle River, USA.
- Sjosten, A. and Blomqvist, S. (1996). Influence of phosphate concentration and reaction temperature when using the molybdenum blue method for determination of phosphate in water. *Water Research*, 31(7), 1818 1823.
- Skeegs, L. T. (1957). An automatic method for colorimetric analysis. American Journal of Clinical Pathology, 28, 311 - 322.
- Skoog, D. A., West, D. M., Holler, F. J. and Crouch, S. R. (2004). Fundamentals of analytical chemistry, Brooks/Cole of Thompson Learning, Inc., Singapore.
- Solbu, K., Thorud, S., Hersson, M., Ovrebø, S., Ellingsen, G., Lundanes, E. and Molander, P. (2007). Determination of airborne trialkyl and triaryl organophosphates originating from hydraulic fluids by gas chromatography-mass spectrometry. Development of methodology for combined aerosol and vapor sampling. *Journal of Chromatography A*,

- Sorme, L. and Lagerkvist, R. (2002). Sources of heavy metals in urban wastewater in Stockholm. *Science of the Total Environment*, 298, 131 145.
- Stelzer, R. S. and Lamberti, G. A. (2001). Effects of N:P ratio and total nutrient concentration on stream periphyton community structure, biomass, and elemental composition. *Limnology* and Oceanography, 46(2), 356 - 367.
- Sutherland, R. A. (2000). Bed sediment-associated trace metals in an urban stream, Oahu, Hawaii. *Environmental Geology*, 39(6), 611 627.
- Sutherland, R. A. and Tolosa, C. A. (2000). Multi-element analysis of road-deposited sediment in an urban drainage basin, Honolulu, Hawaii. *Environmental Pollution*, 110. 483 495.
- Taylor, G. D., Fletcher, T. D., Wong, T. H. F. and Research, P. F. B. W. (2005). Nitrogen composition in urban runoff - implications for stormwater management. *Water Research*, 39(10), 1982 - 1989.
- Terzakis, S., Fountoulakis, M. S., Georgaki, I., Albantaki, D., Sabathianakis, I., Karathanasis, A. D., Kalogerakis, N. and Manios, T. (2008). Contructed wetlands treating highway runoff in the central Meditterranean region. *Chemosphere*, 72, 141 149.
- The-Center-for-Watershed-Protection (1994). Watershed Protection Techniques Vol.1 No. 2. Center for Watershed Protection, Silver Spring, MD, USA.
- Tissue, B. M. (2000). "Inductively coupled plasma (ICP) excitation source. http://www.files.chem.vt.edu/chem-ed/spec/atomic/emission/icp.html. Accessed on 20th March, 2013.
- Tiyapongpattana W., Pongsakul P., Shiowatana J. and Nacapricha D. (2004). Sequential extraction of phosphorus in soil and sediment using a continuous-flow system. *Talanta*, 62, 765 - 771.

- Toda, K. and Dasgupta, P. K. (2008). Advances in flow injection analysis and related techniques: Atmospheric gas analysis, Elsevier, Netherland.
- Traina, S. J. and Laperche, V. (1999). Contaminant bioavailability in soils, sediments, and aquatic environments. *Proceedings of the National Academy of Science*, USA, 96, 3365 -3371.
- Trojanovic, M. (2000). Flow Injection Analysis: Instrumentations and Applications. World Scientific, London.
- Tsukuda, S., Sugiyama, M., Harita, Y. and Nishimura, K. (2005). Atmospheric bulk deposition of soluble phosphorus in Aishu experimental forest, central Japan: source apportionment and sample contamination problem. *Atmospheric, Environment*, 39, 823 836.
- Tuccillo, M. E. (2006). Size fractionation of metals in runoff from residential and highway storm sewers. *Science of the Total Environment*, 355, 288 300.
- Tue-Ngeun O., Ellis P., McKelvie I. D., Worsfold P., Jakmunee J., and Grudpan K (2005).
 Determination of dissolved reactive phosphorus (DRP) and dissolved organic phosphorus (DOP) in natural waters by the use of rapid sequenced reagent injection flow analysis. *Talanta*, 66, 453 460.
- Turer, D. (2005). Effect of non-vehicular sources on heavy metal concentrations of roadside soil. Water, Air, and Soil Pollution, 166, 251 - 264.
- Turer, D., Maynard, J. B. and Sansalone, J. J. (2001). Heavy metals contamination in soils of urban highways. Comparison between runoff and soil concentrations at Cincinnati, Ohio. *Water, Air, and Soil Pollution*, 132, 293 - 314.
- Turer, D. G. and Maynard, J. B. (2003). Heavy metal contamination in highway soils. Comparison of Corpus Christi, Texas and Cincinnati, Ohio shows organic matter is key to mobility. *Clean Technologies and Environmental Policy*, 4, 235 - 245.

- Turner, B. L., McKelvie, I. D. and Haygarth, P. M. (2002). Characterisation of water-extractable soil organic phosphorus by phosphatase hydrolysis. *Soil Biology and Biochemistry*, 34, 27 - 35.
- U.S. Department of Energy (2013). Laser Ablation Inductively-Coupled-Plasma Mass-Spectroscopy (LA-ICP-MS). Energy Storage and Distributed Resources Department, National Laboratory Operated by the University of California. http://teamd.lbl.gov/chemanalysis.html. Accessed on 5th August, 2013.
- U.S.-EPA (1995). National primary drinking water regulations-Nitrates and nitrites; 811-F-95-002f-T. U.S. Environmental Protection Agency EPA.
- Ubogu, A. E. and Essoka, P. A. (2006). Highway contribution to the build-up of heavy-metals in adjacent soils: The case of Kaduna-Zaria expressway, Nigeria. *Pollution Research*, 25(3), 455 - 458.
- UK-IHT (2001). Guidelines for the environmental management of highways, The Institution of Highways and Transportation, London, UK.
- US-ASTM (1997). Standard guides for monitoring sediments in watersheds. D 6145-97, American Society for Testing and Materials.
- US-EPA (1998). Water quality conditions in the United States: a profile from the 1996 National Water Quality Inventory Report to Congress, Office of Water, Washington, DC.
- US-EPA (2000). Quality of Our Nation's Water. EPA841-S-00-001, United States Environmental Protection Agency.
- US-FHWA (1996). Evaluation and management of highway runoff water quality. Washinton, DC, US Federal Highway Administration.

USGS (1998). A review of semivolatile and volatile organic compounds in highway runoff and

urban stormwater. National Highway Runoff data and Methodology Synthesis. Lopes, J. L. and Dionne, S. G., US Geologcal Survey.

- USGS (2013). Water hardness and alkalinity. http://water.usgs.gov/owq/hardness-alkalinity.html Accessed on 21st February, 2014.
- Valcarel, M. and Casro, M. D. (1987). Flow-injection analysis: principles and applications, Ellis Horwood, Chichester, UK.
- van-Bohemen, H. D. and Janssen-Van-De-Laak, W. H. (2003). Influence of road infrastructure and traffic on soil, water, and air quality. *Environmental Management*, 31, 50 68.
- van-der-Linden, W. E. (1982). Flow injection analysis; the manipulation of dispersion. *Trends in Analytical Chemistry*, 1(8), 188 - 191.
- Vase, J. S. and Chew, F. W. S. (2004). Nutrients loads associated with different sediment sizes in urban stormwater and surface pollutants *Journal of Environmental Engineering*, 130, 391 - 396.
- Vesper, D. J. and White, W. B. (2003). Metal transport to Karst springs during storm flow: an example from Fort Cambell, Kentuckey/Tennesse, USA. *Journal of Hydrology*, 276, 20 -36.
- Vijverberg, T., Reneerkens, M. J. J., Winterwerp, J. C., Scholl, O. and Haruna, Y. (2012)"Sediment dynamics in Lagos harbour reconnaissance on effects of dredging." Coastal Engineering 2012, 1-12 DOI:
- von Uexkull, O., Skerfving, S., Doyle, R. and Braungart, M. (2005). Antimony in brake pads a carcinogenic component? *Journal Cleaner Production*, 13, 19 31.
- Vorreiter, L. and Hickey, C. (1994). Incidence of the first flush phenomenon in catchments of the Sidney region. *National Conference Publication Institute of Engineers*, 3, 359 364.

- Walkley, A. and Black, I. A. (1934). An examination of Degjareff method for determining soil organic matter and a proposed modification of the chromic acid titration method. *Soil Science*, 37, 29 - 37.
- Watson, M. E. and Brown, J. R. (1998). pH and lime requirement. Recommended chemical soil test procedures for the North Central Region, Missouri Agricultural Experiment Station SB 1001.
- Wei, Q., Zhu, G., Wu, P., Cui, L., Zhang, K., Zhou, J. and Zhang, W. (2010). Distribution of typical contaminants species in urban short-term storm runoff and their fates during rain events: A case of Xiamen city. *Journal of Environmental Sciences*, 22(4), 533 - 539.
- Wess, J., Olsen, L. D. and Sweeney, M. H. (2004). Consise International Chemical Assessment Document 59.Asphalt (Bitumen), World Health Organisation, Geneva.
- Westerlund, C. and Viklander, M. (2006). Particles and associated metals in road runoff during snowmelt and rainfall. *Science of the Total Environment*, 362, 142 156.
- Whaley, T. P. and Ferrara, L. W., Eds. (1973). Environmental phosphorus handbook, Wiley, New York.
- WHO (2013). Global Alliance to Eliminate Lead in Paints. Available at http://www.who.int/ipcs/features /pb alliance/en/ Accessed on 15th March, 2013.
- Withers, P. J. A. and Jarvie, H. P. (2008). Delivery and Cycling of Phosphorus in Rivers: A Review. *Science of the Total Environment*, 400, 379 395.
- Wolf, A. M., Kleinman, P. J., Sharpley, A. N. and Beegle, D. B. (2005). Development of a water extractable phosphorus test for manure: An interlaboratory study. *Soil Science Society of America Journal*, 69, 695 - 700.
- Wolfgang, F. and McKelvie, I. D. (2008). Photometry.Comprehensive Analytical Chemistry. Amsterdam, The Netherland, Elsevier.

- Wong, C. S. C., Li, X. and Thornton, I. (2006). Urban environmental geochemistry of trace metals. *Environmental Pollution*, 142, 1 16.
- Worfold, P. J., Mckelvie I. D., and G. Hanrahan (2008). Advances in flow injection analysis and related techniques-Environmental Applications: Waters, sediments and soils. Comprehensive Analytical Chemistry Volume 54. Elsevier Netherlands.
- Worsfold, P. J., Gimbert, L. J., Mankasingh, U., Omaka, O. N., Hanrahan, G., Gardolinski, P. C. F. C., Haygarth, P. M., Turner, B. L. and Keith-Roach, M. J. (2005). Sampling, sample treatment and quality assurance issues for the determination of phosphorus species in natural waters and soils. *Talanta*, 66, 273 293.
- Wu, J. S., Allan, C. J. and Saunders, W. L. (1998). Characterization and pollutant loading estimate fro highway runoff. *Journal of environmental Engineering*, ASCE, 124(7), 584 -592.
- Xu X. and Spikes H. (2007). Study of zinc dialkyldithiophosphate in di-ethylhexyl sebacate using electrochemical techniques. *Tribology Letters*, 25, 141 148.
- Yang, G., Zhu, B., Wang, T., Tang, J.-L., Zhou, P. and M., C.-Y. (2010). Bioavailable phosphorus transport from a hillslope cropland of purple soil under natural and simulated rainfall. *Environmental Monitoring Assessment*, 171, 539 550.
- Yaqoob, M., Nabi, A. and Worsfold, P. J. (2004). Determination of nanomolar concentrations of phosphate in freshwater using flow injection with liminol chemiluminescence. *Analytica Chimica Acta*, 510, 213 - 224.
- Yin, Y., Impelliteri, C. A., You, S.-J. and Allen, H. E. (2002). The importance of organic matter distribution and extract soil:solution ratio on the desorption of heavy metals from soils. *Science of the Total Environment*, 287, 107 - 119.

- Yisa, J. (2010). Heavy metals contamination of road-deposited sediments. *American Journal of Applied Sciences*, 7(9), 1231 - 1236.
- Yousef, Y. (1985). Consequential species of heavy metals. BMR-85-286, Florida Department of Transport, Tallahassee, Fla. US.
- Yu, S., He, Z. L., Stoffella, P. J., Calvert, D. V., Yang, X. E. and Banks, D. J. (2006). Surface runoff phosphorus loss in relation to phosphatase activity and soil P fractions in Florida sandy soils under citrus production. *Soil Biology and Biochemistry*, 38, 619 - 628.
- Yuanrong, Z., Runyu, Z., Fengchang, W., Xiaoxia, Q., Fazhi, X. and Zhiyou, F. (2012). Phosphorus fractions and bioavailability in relation to particle size characteristics in sediments from Lake Hongfeng, Southwest China. *Environmental Earth Sciences* DOI: 10.1007/s12665-012-1806-9.
- Zhang, J.-Z., Fischer, C. J. and Ortner, P. B. (1999). Optimization of performence and minimization of silicate interference in continuous flow phosphate analysis. *Talanta*, 49, 293 - 304.
- Zhang, M. and Zhang, H. (2010). Co-transport of dissolved organic matter and heavy metals in soils induced by excessive phosphorus applications. *Journal of Environmental Sciences*, 22(4), 598 - 606.
- Zhu, W.-X. and Carreiro, M. M. (2004). Temporal and spatial variations in nitrogen cycling in deciduous forest ecosystems along an urban-rural gradient. *Soil Biology and Biochemistry*, 36, 267 - 278.
- Zsolnay, A. (2003). Dissolved organic matter: artifacts, definitions, and functions. *Geoderma*, 113, 187 209.

APPENDIX

Appendix 1: Effect of Injection Volume on Customised FIA System



Figure 1(a): Absorbance Profile of PO_4^{-3} -P Standard Solution of Customised FIA at Injection Volume of 25 μ L.



Figure 1(b): Absorbance Profile of PO_4^{-3} -P Standard Solution of Customised FIA at Injection Volume of 62.5 µL.



Figure 1(c): Absorbance Profile of PO_4^{-3} -P Standard Solution of Customised FIA at Injection Volume of 110 μ L.



Figure 1(d): Absorbance Profile of PO_4^{-3} -P Standard Solution of Customised FIA at Injection Volume of 250 µL.



Appendix 2: Effect of Temperature on Customised FIA System



 μ g L⁻¹) at 30°C.



Figure 2b: Effect of Temperature on the Absorbance of Standard Phosphate Solution (250 μ g L⁻¹) at 40°C.



Figure 2c: Effect of Temperature on the Absorbance of Standard Phosphate Solution (250 $\mu g \ L^{\cdot 1})$ at 50°C.



Appendix 3: Effect of Molybdate Concentration on Customised FIA System

Figure 3a: Absorbance of 250µg L⁻¹ PO₄⁻³- P solution at 0.010 M Molybdate Concentration.



Figure 3b: Absorbance of 250 µg L⁻¹ PO₄⁻³- P solution at 0.012 M Molybdate Concentration.



Figure 3c: Absorbance of 250 µg L⁻¹ PO₄⁻³- P solution at 0.014 M Molybdate Concentration.



Figure 3d: Absorbance of 250 µg L⁻¹ PO₄⁻³- P solution at 0.015 M Molybdate Concentration.



Appendix 4: Effect of Reaction Coil Length on Customised FIA System

Figure 4a: Absorbance of 250 µg L⁻¹ PO₄⁻³- P Solution at Reaction Coil Length of 30 cm.



Figure 4b: Absorbance of 250µg L⁻¹ PO₄-³- P Solution at Reaction Coil Length of 90 cm.



Figure 4c: Absorbance of 250 μ g L⁻¹ PO₄⁻³- P Solution at Reaction Coil Length of 120 cm.

Appendix 5: Effect of Ascorbic Acid on Customised FIA System



Figure 5a: Absorbance of 250 μ g L⁻¹ PO₄⁻³- P Standard Solution at 0.26 M Ascorbic Acid Concentration.



Figure 5b: Absorbance of 250 µg L⁻¹ PO₄⁻³- P Standard Solution at 0.28 M Ascorbic Acid Concentration.


Figure 5c: Absorbance of 250 μ g L⁻¹ PO₄⁻³- P Standard Solution at 0.31 M Ascorbic Acid Concentration.



Figure 5d: Absorbance of 250 µg L⁻¹ PO₄⁻³- P Standard Solution at 0.34 M Ascorbic Acid Concentration.



Appendix 6: Effect of Flow Rate on Customised FIA System

Figure 6a: Absorbance of 250 µg L⁻¹ PO₄⁻³- P Standard Solution at 0.12 mL min.⁻¹ Manifold Flow Rate.



Figure 6b: Absorbance of 250 µg L⁻¹ PO₄⁻³- P Standard Solution at 0.18 mL min.⁻¹

Manifold Flow Rate.



Figure 6c: Absorbance of 250 µg L⁻¹ PO₄⁻³- P Standard Solution at 0.31 mL min.⁻¹ Manifold Flow Rate.



Figure 6d: Absorbance of 250 μ g L⁻¹ PO₄⁻³- P Standard Solution at 0.34 mL min.⁻¹ Manifold Flow Rate.

Appendix 7: List of Conference/Seminar Presentations

* September 23rd – 28th, 2012: 12th International Conference on Flow Analysis Thessaloniki, Greece.

Paper Presented: Determination of the Eutrophic Potential of the Lagos Lagoon, Nigeria using Flow Injection Analysis (**Abayomi A. A.,** Azeez T. A. and Olayinka K. O.)

* December, 2009: 5th Beach/Biogeochemical Research Conference, University of Plymouth, UK.

Paper Presented:

Potential Contribution of Roadside Soil to the Nutrient Pool of the Lagos Lagoon.

(**Abayomi A. A.**, Olayinka K. O., Osuntogun B., Alo B. I., Nimmo M. and Worsfold P.)

* December, 2007: 3rd Annual University of Lagos Research Fair and Conference

Paper Presented:

Contribution of Atmospheric Depositions to the Levels of Some Heavy Metals in Highway Runoff and Roadside Soil.

(Abayomi A. A., Olayinka K. O., Osuntogun B. and Alo B. I.).

* September, 2006: 29th Annual International Conference of the Chemical Society of

Nigeria.

Paper Presented:

Urban Highway Runoff and Pollution of Roadside Soil in Lagos Metropolis. (**Abayomi A. A.**, Olayinka K. O., Osuntogun B. and Alo B. I.).

* August, 2006: 2nd Annual University of Lagos Research Fair and Conference.

Paper Presented:

Urban Highway Runoff and Pollution of Roadside Soil in Lagos Metropolis. (**Abayomi A. A.**, Olayinka K. O., Osuntogun B. and Alo B. I.).