

**STUDIES ON POTENTIALLY TOXIC METALS (PTMs) AND ANIONIC
NUTRIENTS IN HIGHWAY RUNOFF AND ROADSIDE SOILS AND
THEIR EFFECTS ON THE LAGOS LAGOON, NIGERIA**

STUDIES ON POTENTIALLY TOXIC METALS (PTMs) AND ANIONIC NUTRIENTS IN HIGHWAY RUNOFF AND ROADSIDE SOILS AND THEIR EFFECTS ON THE LAGOS LAGOON, NIGERIA

A Thesis submitted to the Department of Chemistry, School of Postgraduate Studies, University of Lagos, Nigeria, in Partial Fulfilment of the Requirements for the Award of Doctor of Philosophy (Ph.D.) in Chemistry

By

ABAYOMI, AKINDELE AKEEM

A. A. ABAYOMI

PROF. B. I. ALO, *FAS*
(SUPERVISOR)

PROF. (MRS) K. O. OLAYINKA
(SUPERVISOR)

DATE

**SCHOOL OF POSTGRADUATE STUDIES
UNIVERSITY OF LAGOS**

CERTIFICATION

This is to certify that the Thesis:

**“STUDIES ON POTENTIALLY TOXIC METALS (PTMs) AND ANIONIC
NUTRIENTS IN HIGHWAY RUNOFF AND ROADSIDE SOILS AND THEIR
EFFECTS ON THE LAGOS LAGOON, NIGERIA.”**

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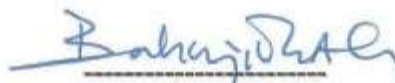
ABAYOMI, AKINDELE AKEEM
In the Department of Chemistry

ABAYOMI A. A.
AUTHOR'S NAME


SIGNATURE

31/01/14
DATE

Prof. B. I. ALO
1ST SUPERVISOR'S NAME


SIGNATURE

31/1/14
DATE

Prof. K. O. Olayinka
2ND SUPERVISOR'S NAME


SIGNATURE

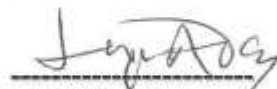
31/1/14
DATE

Dr. O. O. AYEJUYO
1ST INTERNAL EXAMINER


SIGNATURE

31/01/14
DATE

DR L-A ADAMS
2ND INTERNAL EXAMINER


SIGNATURE

31-1-14
DATE

Prof. P. C. Onianwa
EXTERNAL EXAMINER


SIGNATURE

31/01/14
DATE

DR. O. S. ODESANMI
SPGS REPRESENTATIVE


SIGNATURE

31/01/14
DATE

DEDICATION

To the memories of

Afis Oriyomi (2008)

Salamot Aduke (2009)

Lateef Oluwatoyin (2011)

..and all the recently departed in the family

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LIST OF ABBREVIATIONS

AAS	-Atomic Absorption Spectroscopy
ADT	-Average Daily Traffic
AIA	-All Injection Analysis
ASCFA	-Air Segmented Continuous Flow Analysis (Analyzer)
ASV	-Anodic Stripping Voltammetry
BDL	-Below Detection Limit
BI	-Bead Injection
BOD	-Biochemical Oxygen Demand
COD	-Chemical Oxygen Demand
DO	-Dissolved Oxygen
DOM	-Dissolved Organic Matter
FES	-Flame Emission Spectroscopy
FIA	-Flow Injection Analysis
GC-MS	-Gas Chromatography-Mass Spectrometer
HPLC	-High Performance Liquid Chromatography
ICP-AES	- Inductively Coupled Plasma-Atomic Emission Spectrophotometer
ICP-MS	-Inductively Coupled Plasma-Mass Spectrometer
ICP-OES	-Inductively Coupled Plasma-Optical Emission Spectrophotometer
MCFIA	-Multi Cummutated Flow Injection Analysis
MSFIA	-Multi Syringe Flow Injection Analysis
N:P	-Nitrogen to Phosphorus ratio
PTM	-Potentially Toxic Metal
RF	-Radio Frequency
SIA	-Sequential Injection Analysis
SIC	-Sequential Injection Analysis
SVOC	-Semi Volatile Organic Compounds
SWV	-Square Wave Voltammetry
TDS	-Total Dissolved Solids
TP	-Total Phosphorus
TS	-Total Solids
TSS	-Total Suspended Solids
VDS	-Vehicle During Storm
VOCs	-Volatile Organic Compounds

ABSTRACT

Roadside soils serve as a significant mechanism for pollutants entrapment on the highways. These pollutants are eventually mobilized to catchments, particularly during runoff events in the rainy season. Highway runoff has been recognised as a major source of potentially toxic metals (PTMs) and anionic nutrients' transport to receiving waters with attendant environmental impacts. This study examined the influence of runoff from highways and roadside soils in the PTMs and anionic nutrient pollution of the Lagos Lagoon. Dry atmospheric fallout, highway runoff and roadside soils were sampled from three major highways in the Lagos metropolis during rainy and dry seasons between 2005 and 2009. Sediment samples from some highway watersheds along the Lagoon were also obtained within this period.

The physico-chemical parameters of the runoff and roadside soil samples were determined thus; pH, temperature and conductivity by electrometric methods; the total solids and total dissolved solids by gravimetric methods; the dissolved oxygen (DO) by the Winkler's azide modification method; chemical oxygen demand (COD) by the open reflux method; chloride by the mercuric nitrate method; the acidity, alkalinity and hardness by titrimetric methods; phosphate by the molybdenum blue colorimetric method. The total organic carbon in the roadside soils was determined by the Walkley-Black method. The PTM levels in the atmospheric fallout and highway runoff samples were determined by flame Atomic Absorption Spectrophotometry (AAS) after each sample was digested with concentrated nitric acid. The roadside soil and sediment samples were digested with *aqua-regia* at 50°C for 60 min. and then at 100°C for 5 hours after which their PTMs and total phosphorus concentrations were determined. Concentrations of Cu, Cr, Ni, Pb and Zn in the digests were determined by Inductively Coupled Plasma Optical Emission Spectrophotometer, ICP-OES and concentrations of Cd, Pd, Pt and V determined by Inductively Coupled Plasma Mass Spectrophotometer, ICP-MS. An Air Segmented Continuous Flow Analyser, ASCFA was used for the colorimetric anionic nutrients determination of total and bioavailable (Olsen-P) phosphorus and bioavailable nitrate in the roadside soil and Lagoon sediment samples. A customised and fully optimized four channel flow injection analysis (FIA) system and ICP-OES were also used to determine the total phosphorus in the samples.

The results of the physico-chemical parameters showed that the pH levels of the runoff samples ranged from 6.20 – 7.25 in the runoff samples and 6.42 – 7.42 in the roadside soils. The mean concentrations of the total dissolved solids were 126 ± 34 , 145 ± 57 and 375 ± 335

mg L⁻¹ for the respective study locations. 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. On the average, the selected studied highways; A, B and C contributed 0.11 ± 0.04 , 0.34 ± 0.26 and 0.67 ± 0.75 mg L⁻¹ dissolved phosphorus respectively to the Lagoon system through the sampled highway runoff. Mean concentration of dissolved oxygen in the runoff samples were 3.20 ± 1.37 , 3.60 ± 1.32 and 4.50 ± 1.33 mg L⁻¹ at the respective study locations. Chemical oxygen demand (COD) levels in the runoff samples at these locations were 248 ± 122 , 135 ± 71 and 198 ± 106 mg L⁻¹. The concentrations of PTMs in the atmospheric deposits, highway runoff, roadside soil and sediment samples were in the order of Zn>Pb> Cu. In the roadside soils, concentrations of these PTMs were higher in the wet season than in the dry season at most of the sampling locations except for Zn which had higher concentration values in the dry season than in the wet season at more of the sampling sites. Mean dry season concentration values were 202 ± 110 mg kg⁻¹ Zn; 125 ± 96 mg kg⁻¹ Pb and 39 ± 19 mg kg⁻¹ Cu. The mean wet season concentration values were 151 ± 63 mg kg⁻¹ Zn; 130 ± 93 Pb and 65 ± 68 Cu mg kg⁻¹. Mean concentration range observed in the highway runoff samples were 0.057 – 2.029 mg L⁻¹ Zn; 0.096 – 1.153 mg kg⁻¹ Pb and 0.002– 0.442 mg L⁻¹ Cu. These concentrations were mostly higher than the 0.030 mg L⁻¹ Zn, 0.001 mg L⁻¹ Pb and 0.002– 0.004 mg L⁻¹ threshold prescribed for water with aquatic life by the Federal Ministry of Environment (FMEnv), in Nigeria. The concentrations of the PTMs including Pt (a catalytic engine fingerprint) were comparatively higher at sampled Lagoon watersheds which directly receive highway runoff, roadside soils' leachate and road derived sediment. A concentration range of 1.18 – 4.50 µg kg⁻¹ was obtained at these watersheds. These concentrations are higher than the 0.41 mg kg⁻¹ obtained at the sampling site which is was not directly receiving these highway inputs. This strongly indicates possible highway influence in the Lagos lagoon PTMs concentration. The mean total phosphorus concentrations in roadside soils was 285 ± 279 mg kg⁻¹ in the wet season and 424 ± 629 mg kg⁻¹ in the dry season, indicating that rainwater leaching of roadside soils accumulated on the highways during the dry season is probably a major mechanism for phosphorus transport from the roadside soils into the Lagos lagoon. The bioavailable fractions were 3.47 - 5.17 mg kg⁻¹ in the wet season and 8.7 - 13.0 mg kg⁻¹ in the dry season. The bioavailable nitrates in the samples had a mean concentration of 3.19 ± 3.07 and 4.31 ± 5.62 mg kg⁻¹ for the wet and dry season respectively. The total P concentrations from the customised FIA system had significant correlation of up to 0.996 with the ASCFA and ICP-OES techniques used in the study indicating the suitability of the

developed FIA method for subsequent phosphorus studies in highway runoff and roadside soils.

The study showed that highway runoff and roadside soils are major contributors of PTMs and anionic nutrients to the Lagos lagoon and therefore impact negatively on the water quality of the Lagoon.