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LIST OF CONTRIBUTORS

A. F. Musa is a Lecturer in the Department of Accounting, Kaduna State University, Kaduna – Nigeria

A. H. Mahmoud (Mrs) is currently a Lecturer and a Doctoral student in Department of Accounting, Ahmadu Bello University, Zaria. Her areas of interest are: Islamic Accounting and Finance, Business Mathematics and Quantitative techniques.

A. Mustapha is a lecturer at the Department of Accounting and Finance School of Business and Governance, Kwara State University, Malete

A. S. Kasum Ph.D., ACA, is a Senior Lecturer and Ag. Head of Department of Accounting, University of Ilorin. He specialises in Financial Reporting and Disclosure.

B. K. Gugong Ph.D., is of the Department of Accounting, Kaduna State University, Kaduna – Nigeria

C. O. Adewole PhD., is a Fellow of the Chartered Institute of Bankers of Nigeria and Acting Head of Department of Banking and Finance, University of Jos. He specializes in Corporate Governance, Finance and Financial Institutions.

D. A. Badmus (FCA) lectures at the School of Business & Governance, Kwara State University, Malete, Kwara State

D. Abdulsalam Ph.D., is of Department of Business Administration, Usmanu Danfodiyo University, Sokoto, Nigeria.

E. O. Imouokhome is a doctoral student and a Lecturer with the Department of Marketing, University of Ilorin, Ilorin, Nigeria

F. A. Abdul is of the Department of Business Administration University of Ilorin, Ilorin, Nigeria

F. Q. Dauda (ACA, FPFM London) is of the School of Business & Governance, Kwara State University, Malete, Kwara State

H. O. Afolabi is a Lecturer in the Department of Banking and Finance, Al-Hikmah University, Ilorin

I. B. Kadiri Ph.D., is a Senior Lecturer and Coordinator Post Graduate Programmes, Department of Business Administration, Faculty of Management Sciences, University of Ilorin, Ilorin, Nigeria

I. I. Aun Ph.D., is the Coordinator, Post Graduate Diploma in Strategic Management and a lecturer with the Department of Business Administration University of Ilorin, Ilorin, Nigeria

K. A. Iroye Ph.D., is a Lecturer I in the Department of Geography and Environmental Management, University of Ilorin. His areas of interest are Hydrology and Water Resources.

K. A. Olanrewaju Ph.D., is a Senior Lecturer in Department of Geography and Environmental Management, University of Ilorin. Her area of interest is Climatology.

I.O. Raheem, Graduated from the Department of Geography and Environmental Management, University of Ilorin.

L. A. Oke (ACA) is a Lecturer with the School of Business & Governance, Kwara State University, Malete, Kwara State

M. Kamba is a lecturer and former Examination Officer, Department of Business Administration, Usmanu Dan Fodiyo University, Sokoto.

M. H. Kurfi is a Doctoral candidate in Sociology at Boston University, Massachusetts-U.S.A. & Senior Teaching Fellow with the African Studies Center. His research interests include Civil Society, Gender & Religion.

M. N. Tukur, Ph.D. is a Lecturer in the Department of Business Administration and Examination Officer for the Faculty of Management Sciences, Usmanu Dan Fodiyo University, Sokoto.

O. M. Tijani is a Lecturer with the Department of Accounting, Al-Hikmah University, Ilorin

O. V. Mejabi, Ph.D., is a Senior Lecturer in the Department of Information and Communication Science, University of Ilorin. Her areas of interest are: MIS, Service Quality, Open Data and e-Government.

G. S. Ajiboye is a student in the Department of Information and Communication Science, University of Ilorin.

S. Akanet Ph.D., is a Senior Lecturer in the Department of Accounting, Kaduna State University,Kaduna.He specialises in Financial Accounting, Banking and Finance.

S. Mande ***Ph.D, MIMC, MNIPR, MNIM, rpa*** is Senior Lecturer, and Head of unit/adviser (CEMBA/CEMPA), School of Management Sciences, National Open University of Nigeria. He specializes in Marketing Communication and Entrepreneurship. He is also an Adjunct Research Fellow at the School of Media and Communications, Pan-Atlantic University, Lagos State.

SPATIO-TEMPORAL PATTERNS OF NITRATE CONCENTRATION IN RAINWATER IN ILORIN, KWARA STATE NIGERIA.

By
Iroye, K.A, Olanrewaju, R.M and Oyelakin R.I
Department of Geography and Environmental Management
University of Ilorin, Nigeria.
Email: iroyekayode@yahoo.com

Abstract

This study examined the spatio-temporal pattern of nitrate concentration in rainwater in Ilorin, Kwara State, Nigeria. Thirty five rainwater samples were collected from each of the five different land-uses using sterilized 75 centiliters plastic bottles on event basis between the onset and cessation of rainfall (March 4th – October 24th, 2013) in the study area. The collected water samples were subsequently analyzed for nitrate concentration in University of Ilorin Chemistry laboratory using sodium salicylate (colorimetric) method. Result obtained indicates high variability in both spatial and temporal patterns of nitrate concentration in the study area. While the temporal pattern revealed high concentrations in the months of March, April, July and September; Oja-Oba, Asa Dam and Oke-Oyi areas of the city exhibits high degree of concentrations in that order spatially. Likely reasons for the observed pattern of concentrations were discussed while suggestions towards reducing the rate of pollution to biologically safe levels were presented.

Keywords: Nitrate, N-Nitroso, Pollution, Carcinogens, Land-use.

1.0 Introduction

The utilization of rainwater for domestic activities including cooking is a common practice in Africa (Olorunfemi and Arohunsoro, 2000) during the rainy season and has over the years been advocated, especially in less developed countries (NIRCCWSS, 1988; UNESCAP, 1989 ; Morgan, 1990). This activity which is commonly referred to as rain harvesting is being encouraged because of the failure of modern water supply system and increasing pollution of surface water. However, water from this source which is directly collected from the atmosphere is now being increasingly confronted with problem of quality induced by gases and particulate matter released into the earth's atmosphere as consequence of man's activities.

Among such atmospheric pollutant is nitrate, a pollutant which enter rainwater by the reaction of nitrogen oxides (NO_x species) with water to produce HNO_3, which disassociate into H^+ and NO_3 (MARYP, 1999).

Though NO_x species come from some natural sources such as lighting and volcanic gasses, greater amount of nitrates (more than 95%) come from anthropogenic sources such as automobiles and fossil fuel combustion in homes, vehicles and industries (Botkin *et al.* 1995 ;Long, 2003). According to Ubuoh, *et. al.* (2012), such sources could be point, non-point or mixed in nature. Pollutants once introduced into the atmosphere can be removed through mechanisms of dispersion, rainout or scavenging leading to rainwater contamination (Akhionbare, 2009). This is usually through dissolution of such gases or particles in the air or impaction into pre-existing liquid droplet (Carole *et al.,* 2002). And because such processes can either occur in a cloud or below it during rain, the levels of such gases or particles in resultant rainfall is thus greatly increased, hence the production of relatively strong nitric acid (HNO_3) in regions polluted with oxides of nitrogen.

Worldwide, there is a limit to the amount of nitrate that can be found in drinking water. The World Health Organization (2011) and the United State Environmental Protection Agency (2007) have both set a limit of 10mg/l. Nitrate in drinking water at levels above this limit poses a threat to man. When present in high concentrations in bottle-fed infants, they may give rise to a condition known as methemoglobinemia or blue-baby syndrome. The consequence of this is shortness of breath (cyanosis), blueness of skin and at times death (BGS, 2003). Its high concentration also poses potential health risk to pregnant women (Jennings and Sneed, 1996; Kelter, *et al.,* 1997; Kempster, *et al.,* 1997) and can also cause recurrent acute diarrhea (Gupta, *et al.*, 2001). Ingested nitrate from dietary sources and drinking water can be converted to nitrite and ultimately to N-nitroso compounds, many of which are known to be carcinogens (Sandor, *et. al.,* 2001; Weyer, *et al.*, 2006). In freshwater or estuarine systems close to land, nitrate can reach high levels that can potentially inhibit growth, impair the immune system and cause stress in some aquatic species and eventually cause death. In most cases, excess nitrate concentrations in aquatic systems results from primary sources such as rainfall and surface runoff from agricultural or landscaped areas that have received excess nitrate fertilizer. This is called eutrophication and can lead to algae blooms as well as water anoxia and dead zones. These blooms may cause other changes to ecosystem function, favouring some groups of organisms over others.

As a result of its dangerous effects when present in high concentration, nitrate forms a component of total dissolved a solid that is widely used as an indicator of water quality. Because of the aforementioned problems induced by high nitrate concentration in water and the fact that rainwater chemistry is highly variable both spatially and temporarily; there is need for investigation of this nature which is intended to shed more light on what the future hold in stock concerning the impact of rainwater pollution on both human and animal populations. Identification of pollution sources, transport characteristics and predicted concentrations according to Walker *et al.,* (2000) will no doubt lead to physical or chemical controls that can be used for the development of sound environmental management policies to prevent future damage to sensitive aquatic and terrestrial ecosystem.

2.0 The Study Area

Ilorin, the capital city of Kwara State Nigeria is the study area in this research (Fig I). The city which is located between latitudes $8^{0}24^{1}$ and $8^{0}36^{1}$ north of the equator and between longitudes $4^{0}10^{1}$ and $4^{0}36^{1}$ east of the Greenwich meridian covers an area of about $150km^{2}$. The city is located in the transitional zone between the forest and guinea savannah region of Nigeria.

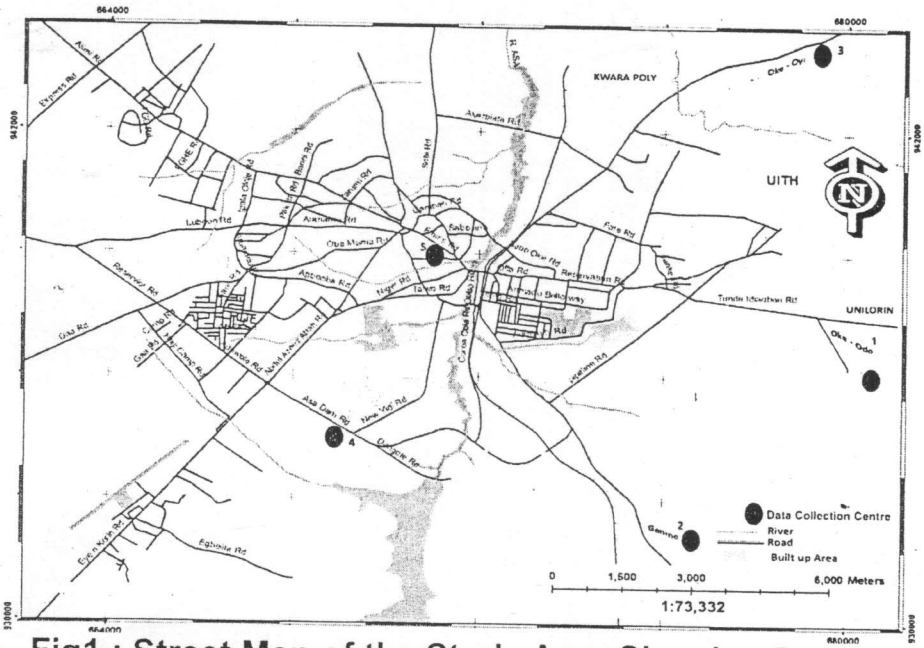

Fig1 : Street Map of the Study Area Showing Data Collection Points

Source: Author's Field Work (2014)

The climate of Ilorin results from the influence of two trade winds prevailing over Nigeria. These are the Tropical Maritime Airmass which originates from the Atlantic Ocean and the Tropical Continental Airmass which originates from Shara desert. The Tropical Maritime Airmass is prevalent in the city between the months of March and October while the Tropical Continental Airmass is prevalent between November and February. These two wind systems produces two climatic seasons of wet and dry seasons. Annual rainfall in Ilorin is around 1,200m with peak periods in July and September (Olaniran,2002). Rainfall type which is conventional in nature exhibits high variability, both temporarily and spatially (Ajadi, 1996). Mean monthly temperature in Ilorin is generally high throughout the year, varying between 25^{0} and $28^{0}C$ (Oyegun, 1983). The average relative humidity in the city in wet season is between 75 and 80% while in dry season, it is about 65% (Tinuoye, 1990). Urbanization and industrialization process are fast taking place within and around the city (Olanrewaju, 2009) with their consequence effects on air pollution and rainwater contamination.

3.0 Methodology

This research work was based on data collected directly from the field. Rainwater samples were collected from five (5) locations within and around Ilorin metropolis based on landuse pattern. Table 1 shows the grid reference and altitude of the sampling points taken with hand-held Global Positioning System (GPS) receiver (Garmin GPS 12 Personal Navigator).

Table 1: Grid Reference and Altitude of Sampling Locations

Sampling Location	Landuse Type	Latitude	Longitude	Altitude (m)
Asa Dam	Industrial	08°27'	004°32'	327
Oja-Oba	Residential	08°30'	004°31'	320
Oke-Oyi	Agricultural	08°36'	004°46'	283
Ganmo	Rural	08°26'	004°36'	330
Oke-Odo	Commercial	08°28'	004°37'	352

Source: Authors' Fieldwork, 2013.

Rainwater samples were collected at each sampling points with a sterilized 75 centiliter plastic polyethylene bottles, filled to the brim and cocked to avoid an air column. In all, thirty-five (35) storm events were sampled in each of the five (5) landuse types between the periods of onset and cessation of rainy season (March 4th – October 24th, 2013) on event basis. The duration of collection however varied from a few minutes to about an hour depending on the intensity of the rainfall.

Rainfall collectors used in this investigation were placed on 2 meter platforms and fitted with sieves to prevent impurities from entering the water samples. The collected samples were subsequently analyzed for nitrate concentrations at University of Ilorin Chemistry laboratory using Sodium (Colorimetric) method. This analytical technique is preferred to the distillation method because it is simple and generates fast results. It can present result in the range of 0.2-20mg/l nitrate in water samples. Table 2 shows the analytical procedure followed in conducting the test.

Table 2: Analytical Procedure used in Testing for Nitrate Concentration

Method	Procedure
Sodium Salicylate (Colorimetric) Technique	**Flocculation** (to remove interfering organic and metallic substances). 20ml of mercury (II) chloride was added into the samples to give a concentration of 1000mg/l, the pH of the samples is adjusted to between 11 and 11.5 with 50% NaOH. The concentration was stirred with magnetic stirrer and allowed to stand for five minutes so that flocculated particles may settle. It was then filtered to discard the first portion of the filtering.
	Evaporation and Drying: 2ml of the filtrate was accurately pipette into a 50ml evaporating dish, 1ml of 1% sodium salicylate was added and evaporate to dryness. The residue was dried for at least thirty minutes in a drying oven at [illegible]
	Colour Development: The samples was removed from oven, allowed to cool and 2ml of concentrated H_2SO_4 was added [illegible], mixed well by swirling. It was allowed to stand for 10 - 15 minutes but swirled occasionally to ensure dissolution of all solids. When cold, 15ml [illegible] free distilled water was added into the sample residue holding the pipette tip against the dish wall to avoid spattering that can lead to loss of part of the residue. 15ml [illegible] solution [illegible] was pipette into the concentration. If nitrate is present, a yellow colour develops immediately. It was swirl again and allows the solution to cool at room temperature for one hour.
	Calibration Standard: From the standard solutions (1ml = [illegible]) 2,4,6,...20ml was pipette into [illegible] beakers. 1ml of 1% sodium salicylate was added to each beaker, the standard was treated as the samples throughout the procedures above. A blank solution containing all reagents and without the samples, and the calibration solutions were treated in the same manner.
	Extrapolating from Calibration Standard: The absorbance of the standard solution was read against the blank on a spectrophotometer at 420nm, making dilution if necessary. Extrapolation were made from standard values:

Dilution Factor	2	[illegible]	6	[illegible]	10	12	14	16	18	20
Values	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Source: Laboratory Manual, Dept. of Chemistry, University of Ilorin (2013)

4.0 Observations and Discussion

Table 3 present the results of the laboratory analysis on nitrate concentration in the sampled rainwater. The data revealed that nitrate concentration in rainwater in Ilorin exhibits high variability, both spatially and temporally in the city.

Table 3: Laboratory Result of Rainwater Samples

Sample Locations / Dates	1 Ganmo	2 Oke-Odo	3 Oke-Oyi	4 Asa-Dam	5 Oja-Oba	Mean Value for Ilorin The Study Area
March 04, 2013	17.25	16.62	16.16	16.96	19.64	17.33
March 16, 2013	17.31	15.35	16.05	16.62	18.40	16.75
March 30, 2013	15.67	14.70	14.91	16.85	17.82	15.99
April 07, 2013	14.16	13.56	14.48	16.28.	15.89	14.87
April 15, 2013	13.78	14.10	14.21	14.81	15.18	14.42
April 19, 2013	14.91	14.27	14.00	14.43	16.05	14.73
April 22, 2013	13.72	13.89	16.21	14.05	15.45	14.66
April 25, 2013	8.06	16.28	15.92	14.21	15.51	14.00
April 28, 2013	13.89	8.13	7.73	14.97	16.00	12.14
April 30, 2013	14.59	8.16	7.96	13.94	17.54	12.44
May 01, 2013	15.50	10.54	15.78	7.73	15.23	14.96
May 04, 2013	16.00	15.36	10.29	13.94	17.02	14.52
May 11, 2013	10.24	10.00	10.39	10.14	16.14	11.38
May 14, 2013	8.16	8.06	7.83	7.90	13.94	12.42
May 20, 2013	14.10	14.00	10.29	10.44	14.54	12.67
May 25, 2013	9.90	9.45	9.16	6.88	10.29	9.94
May 28, 2013	9.55	6.92	6.64	6.16	14.97	8.85
June 11, 2013	7.52	6.00	14.05	4.17	15.18	9.38
June 14, 2013	2.09	4.17	6.32	6.20	6.36	5.03
June 20, 2013	2.41	2.37	6.24	10.19	15.29	7.30
June 23, 2013	2.14	1.72	2.00	4.23	6.08	3.23
June 29, 2013	2.21	2.07	4.08	6.08	2.25	3.34
July 04, 2013	0.23	1.87	2.16	1.11	4.05	1.88
July 14, 2013	1.31	1.40	1.81	1.26	2.19	1.59
July 20, 2013	1.78	1.56	6.64	10.39	16.00	7.27
July 24, 2013	7.12	16.70	10.29	16.49	15.43	13.21
Sept 01, 2013	1.42	1.00	1.04	1.42	1.13	1.20
Sept 05, 2013	6.64	9.50	6.24	9.50	11.92	8.76
Sept 12, 2013	1.87	2.23	1.90	10.05	21.70	9.15
Sept 14, 2013	0.81	2.09	1.13	2.03	1.24	1.46
October 01, 2013	9.50	6.48	6.88	9.65	9.90	8.48
October 09, 2013	6.60	3.91	3.67	7.12	9.55	5.81
October 14, 2013	4.14	3.97	4.05	6.68	9.06	5.68
October 19, 2013	6.36	4.11	3.37	2.05	6.52	4.48
October 24, 2013	3.85	3.62	5.84	4.05	6.96	4.86
TOTAL	294.79	284.96	305.72	328.98	430.37	326.80
RANGE	**17.08**	**15.70**	**15.12**	**15.85**	**20.57**	**15.87**
MEAN	**8.42**	**8.12**	**8.78**	**9.39**	**12.30**	**9.34**
S.D	**5.62**	**5.42**	**5.05**	**5.03**	**5.66**	**5.36**
C.V	**66.74**	**66.75**	**59.76**	**56.33**	**46.01**	**59.12**

Note: Values and in ppm (parts per million)
Source: Authors' Fieldwork, 2013.

Nitrate concentration in rainwater in the study area varied between 0.23ppm observed in Ganmo on July 4th and 21.7 ppm observed in Oja-Oba on 12th of September. All the five (5) sampling points generally recorded high nitrate concentration values in the first 7 rainfall events which span a period of almost 7 weeks from the onset of rainy season in the study area. However, the high concentration values persisted till 11th and 17th weeks respectively in Asa-Dam and Oja-Oba areas of the city from the onset of rainy season. While the general high nitrate concentration in rainwater in the first seven weeks in the rainy season can be attributed to the build-up effect of nitrogen in the atmosphere during the dry season; the persistent high level concentration in Asa-dam and Oja-Oba for additional few weeks may not be unconnected with land use activities in these two areas.

While Asa-Dam is an industrial region, with presence of large sawmill where saw dust is always being burnt, Oja-Oba is urban residential area with high vehicular movement. The high rate of emission of gases from wood burning and combustion of fossil fuels in these two areas may have contributed to the persistent high nitrate concentration of rainwater in the areas. Not only that, the high nitrate concentration in rain water in these two sampling sites may also be linked to the closeness of Asa-Dam to Oja-Oba. Studies such as Morales, *et. al.*, 1998 and Russel, *et. al.* 1998 ; Walker, et. al. 2000; Sarah, 2006; Uboh, *et. al.* 2012 have linked degree of atmospheric pollution in a particular region to the direction and degree of movement of air masses. According to Carole, *et. al.* (2012) atmospheric pollutants may come from any direction, both local and distant areas following different pathways. Thus, Russel *et. al.*, (1998) classified storm trajectories and their associated pollutants into five groups viz: westerly, southerly easterly, northwesterly and southwesterly. According to their observation, the southwesterly trajectory was associated with high concentration of nitrate in their study area. Their findings thus indicate that source region information can be used to determine how much nitrogen is deposited in the atmosphere, what processes produce the nitrogen and where the nitrogen originated.

The relatively high mean nitrate concentration in rainwater at Oke-Oyi may be the result of intensive agricultural production in the area. Oke-Oyi houses plantation agricultural farm where nitrogen rich fertilizer is being used in improving soil fertility. Bocher (1995) observed that there are five fates for such nitrogen once applied to crop; according to him, it may be taken up by plant, stored in the soil, lost to groundwater, lost to runoff or lost to atmosphere where it mixes with rainwater. The generally high nitrate concentrations in rainwater in the study area however reduced in all the sampling points to low level in the months of July and August before picking up in the month of September when it rose to its peak of 21.05 and 21.13ppm in Oja-Oba and Asa-Dam respectively. By late October, the concentration of nitrate in rainwater had also significantly reduced with the cessation of rainfall in all the five sampling points in the study area (Fig. 2).

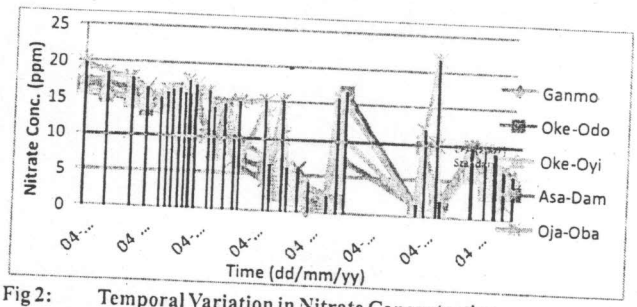

Fig 2: Temporal Variation in Nitrate Concentration Under Different Land-uses

Source: Authors' Fieldwork, 2014.

The sharp increase in level of nitrate concentration in rainwater observed in September may not be unconnected with the August break in rainfall in the study area. Absence of significant amount of rain in August in the study area might have aided the build-up of nitrogen in the atmosphere which thereafter is washed down by September rainfall. Figure 3 depicts rain water nitrate exceedence map for the study area.

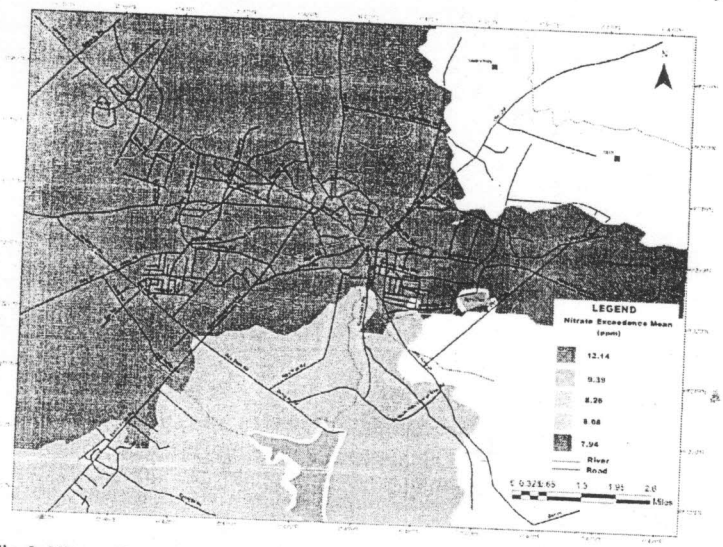

Fig. 3: Nitrate Exceedence Map for the Study Area

Source: Authors' Fieldwork 2014.

Though this particular research did not examine the relationship between rainfall amount and nitrate concentration, studies such as Russel *et al* (1998) ; Walker *et al* (2000) and Dayan and Lamb (2003); have explained that the amount of precipitation is a factor affecting concentration of nitrogen analytes in atmospheric deposition. According to these studies, the term 'washout' is used in explaining the reason why there seems to be smaller concentrations of analytes when precipitation amounts are large.

This according to Sarah *et. al.,* (2006) is because high volume of water dilutes the concentration of the pollutant.

5.0 Conclusion and Recommendations

Nitrate concentration in rainwater in Ilorin exhibits spatio-temporal patterns. While temporal pattern reveals high concentration levels in the months of March, April, July and September; spatially, the concentrations were observed to be high under urban residential, industrial and agricultural land uses. This result presents great danger most especially for residents in high concentrations areas who may use such contaminated water for domestic activities, most especially for cooking. While ingested nitrate from dietary sources and drinking water by man can be converted to nitrite and ultimately to N-nitroso compounds, many of which are known to be carcinogens; high nitrate level in aquatic ecosystem potentially inhibit growth, causes stress and may result in death. Though excess nitrate concentrations in aquatic systems most times results from surface runoff from agricultural land that have received excess nitrate fertilizer, heavily polluted rainfall from atmospheric nitrogen can also impair aquatic systems leading to algae blooms, water anoxia and dead zones. Because nitrate cannot be completely removed from rainwater, efforts should be directed by government agencies responsible towards reducing its rate of pollution to biologically safe levels; this can be through:

i. Legislation aimed at tackling the sources of pollution.
ii. Public enlightment programmes in various mass media on biomass burning, fossil fuel combustion and excessive application of fertilizer containing nitrogen on agricultural farmlands, and,
iii. Development of necessary data base as currently being done in this study to identify and effectively manage the high risk areas.

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