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# A geospatial assessment of human exposure pathways to chemical contaminants in the environment: A cause for action in Owerri, Imo State, Nigeria

by

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# Abstract

The indiscriminate dumping of refuse and its potential threat to groundwater in Owerri, Nigeria remain a public health concern. This thesis applied multi-disciplinary techniques (environmental chemistry, health studies, geospatial statistics, social sciences, soil science and horticulture) to assess various pathways through which humans can be exposed to contaminants. A bi-seasonal random geospatial sampling of environmental matrices (groundwater, river water, dumpsites leachates, soil, and plant samples) impacted by urbanisation and anthropogenic activities was carried out between 2015 and 2017. Laboratory analysis reveals that concentration of nitrate in groundwater is above the maximum concentration limit (MCL) of 50µg/mL stipulated by the Nigerian Standard for Drinking Water Quality (NSDWQ) in approximately 12% of sampled wells. This presents nitrate as a critical contaminant in groundwater. Concentrations of Pb and Cd exceeded the MCL by about 1.6% and 0.25% respectively. All measured parameters in the river samples were within the acceptable threshold limits, whereas Pb concentration in soil measured above the 85 µg/g target value stipulated by the Nigeria Department of Petroleum Resources in about 0.9% of sampled soils. Pb measured above the thresholds of 0.3 µg/g and 0.1µg/g specified by the Food and Agricultural Organisation (FAO) in 99.8% of pumpkin leaf (*Telfaiara occidentalis*) and 51.6% of cassava tuber (*Manihot occidentalis*) samples respectively. Findings suggest review of groundwater risk evaluation techniques such as DRASTIC to incorporate more relevant soil and climatic attributes. In Owerri, urbanisation appears to have influenced groundwater nitrification as reflected in wells close to various contaminant sources, such as landfills and septic tanks. The wider implication of this study lies on the application of redox chemistry in the mini catchment assessment of contaminants behaviour that could help in the formulation of large-scale groundwater exploitation programmes and water management policies. Health risk assessment shows that children are significantly more vulnerable to contaminant exposure.

**Keywords: Geospatial assessment, urbanisation, vulnerable, exposure, groundwater**

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## Presentations arising from investigations carried out in this Study

Although investigations and findings generated from this study have not been published yet, some of its contents has been communicated to the public at the following conferences and academic gatherings:

1. Environmental chemistry of water, sediment and soil: Early Career Researchers Meeting organised by the Royal Society of Chemistry on 14th November 2016

Title: Nitrate contamination of groundwater in Owerri, South East Nigeria: A public health risk (Poster Presentation)

2. Goldschmidt, 2017 (Paris, France) on the 16th August 2017

Title: Impact of Urbanisation on Groundwater Geochemistry and Public Health (Poster Presentation)

3. Geochemistry and mineralogy of contaminated environments organised by the Royal Society of Chemistry on 6th June 2018

Title: Urban Development and human exposure to chemical contaminants: Owerri, Southeast Nigeria (Oral Presentation)

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## ACRONYMS AND ABREVIATIONS

**ANOVA**………….Analyses Of Variance

**ASTDR**…………..Agency for Toxic Substances and Disease Registry

**CRM**……………..Certified Reference Material

**ERM**……………..European Reference Material

**DEFRA**…………..Department of Environment, Food, and Rural Affairs

**DNRA**……………Dissimilatory Nitrate Reduction to Ammonium

**DOC**……………..Dissolved Organic Carbon

**DO**…..…………....Dissolved Oxygen

**DPR**……………...Department of Petroleum Resources

**DRASTIC…..**…..Depth to water table, Recharge, Aquifer, Soil, Topography, Influence of vadose zone, Conductivity

**EC**……………….Electrical Conductivity

**EDTA**……………Ethylenediaminetetraacetic acid

**EIA**………………Environmental Impact Assessment

**ESAI**…………….Environmental Sensitive Area Index

**EUSDW**………...European Standards for Drinking-Water

**FAO**……………..Food and Agricultural Organisation

**FUTO**…………...Federal University of Technology, Owerri

**GCS**…………….Geographical Coordinate System

**GHG**……………Green House Gases

**GIS**……………..Geographic Information Systems

**GOD**…………....Groundwater, Overlying lithology, Depth to water table

**GPS**…………….Global Positioning System

**THQ**………………Target Hazard Quotient

**IC**……………….Ion Chromatography

**ICP-OES**…….....Inductively Coupled Plasma - Optical Emission Spectrophotometry

**ICP-MS**…………Inductively Coupled Plasma – Mass Spectrophotometry

**IDW**…………….Inverse Distance Weighting

**IQR**……………..Interquartile Range

**IPCC**................Intergovernmental Panel on Climate Change

**IVZM**…………...Integrated Vulnerable Zone Management

**LGC**……………Laboratory of the Government Chemist

**LLD**……………Lower Limit of Detection

**LOD**……………Limits of detection

**LOQ**……………Limits of Quantification

**MCL**……………Maximum Concentration Limit

**MSW**…………..Municipal Solid Waste

**NAFDAC**……...National Agency for Food and Drug Administration and Control

**NDIR**…………..Non-Dispersive Infrared

**NOC**…………...N-Nitroso Compounds

**NPC**……………National Population Commission

**NSDWQ**……….Nigeria Standard for Drinking Water Quality

**OECD**…………Organisation for Economic Co-operation and Development

**PQRA**………....Preliminary Quantitative Risk Assessment

**QA/QC**………..Quality Assurance/ Quality Control

**RfDo**…………. Oral reference dose

**SD**……………. Standard Deviation

**SIGA**………… Soil, Intermediate zone material, Ground surface slope, Aquifer material

**SOC**………… Soil Organic Carbon

**SOM**…………Soil Organic Matter

**SSA**…………..Sub-Saharan Africa

**THM**…………..Trihalomethane

**TEAP**…………Terminal Electron-Accepting Process

**TIC**……………Total Inorganic Carbon

**UNDP**………...United Nations Development Programme

**UNICEF**………United Nations International Children’s Emergency Fund

**USEPA**……….United States Environmental Protection Agency

**UTM**…………..Universal Transverse Mercator

**VFAs**…………Volatile Fatty Acids

**WQI…………..**Water Quality Index

**WHO**…………World Health Organisation

**WGS**…………World Geodetic System

**XRD**…………X-ray Diffraction

# CHAPTER 1

# INTRODUCTION

This introductory chapter presents the background and motivation of the research, including an overview of Nigeria in Africa and the challenges of environmental contamination in Owerri (the study area). It outlines the main aims and objectives that guided the research and concludes with a highlight of the thesis structure a statement of the research problems, aims and objectives, research design and significance.

## 1.1 Study background

The Earth's natural systems are facing diverse forms of modification largely because of the exploratory and migratory activities of humans. World population is increasing – a global projection indicates that by 2030 urban population and urban land cover will reach approximately 1.35 billion and 1.2 million km$^2$ respectively, based on the current global urban population increase of 1.3 million per week (Seto et al., 2014). Currently, population growth is driving urban expansion and altering natural interactions between different biotic and abiotic features in the human-environment systems (Scanes, 2018). In particular, waste management and sanitation problems have intensified in several hugely populated urban areas, especially in the sub-Saharan Africa (SSA), where about 250 million people are estimated to live in urban centres (Lapworth et al., 2017). This has spurred up rapid release of toxic elements at concentrations beyond and above the attenuation capacity of the environment (Lapworth et al., 2017; Kowarik, 2011). A 2014 joint WHO/UNICEF report indicates that about 2.5 billion people lack access to modern sanitation facilities (Organization and UniCeF, (2014)), creating increased hazards/risks from human waste and leading to release of chemical elements and pathogenic organisms into the food chain (Graham and Polizzotto, 2013; Pujari et al., 2012)

Humans are exposed to toxic chemical elements/contaminants through various pathways created largely by urbanisation and anthropogenic activities. Different forms of land use (e.g. for residential, industrial and agricultural purposes and landfills) influence soil attenuation capacity through alteration of soil bulk density, organic matter contents and microbial functions (Xie et al., 2018). This can trigger waste generation that could be hazardous to both human and plants (Greenberg, 2017). Soil is particularly central to assessments of human exposure pathways to contaminants. Several geophysical, chemical and biological interactions taking place in the soil can have direct or indirect influence on human health. In particular, investigating the role of the soil in determining the chemical and biological characteristics of groundwater and surface water, and the broader human food chain, can provide insights on human exposure pathways to contaminants (Abrahams, 2002).

Most urban residential estates, especially in developing nations, have been sited without prior risk assessment in terms of proximity to contaminant pathways/routes (Hiscock, 2009). Humans are the ultimate receptors of potential health hazards emanating from contaminants, and as such a two-directional pathway risk assessment (approach) along contaminant pathways is essential to ensure humans are protected and the environment secured for humans to thrive (Hiscock, 2009). This implies assessments of pollution sources to proximate wells, to reveal site-specific concentration of contaminants in receptor wells and the use and effects of contaminated wells. This approach works well using GIS (Geographical Information System) to unravel contaminant hot spots and to identify people at high risk of health challenges resulting from exposure to contaminants (Minolfi *et al*., 2018; Rahman *et al*., 2018; Zhang *et al*., 2013).

Several other related approaches (tools and techniques), have been used by previous researchers to identify sources, pathways and receptors of contaminants in the environment. For example, the GIS and DRASTIC (Depth to water table, Recharge, Aquifer media, Soil type, Topography, Impact of vadose zone, and hydraulic Conductivity) vulnerability model can provide spatial support for urban planning and groundwater resource management (Kihumba *et al.*, 2017; Muhammad *et al*., 2015; Ibe *et al*., 2001). Among the hydrogeological parameters applied in the DRASTIC model, depth to water table was the most significant factor indicating imminent groundwater pollution (Liu et al., 2005; Lake et al., 2003; Rupert, 2001). DRASTIC identifies areas of similar hydrological characteristics, as well as potential contaminant sources; it is reportedly useful in the delineation of groundwater contamination zones (Zhang *et al*., 2013). To substantiate the appropriateness of DRASTIC (i.e. the DRASTIC vulnerability model) in delineating polluted zones, previous studies suggest carrying out assessments focusing on nitrate ($NO_3^-$) as a target contaminant (Asadi et al., 2017; Kihumba et al., 2017; Kazakis and Voudouris, 2015; Gogu et al., 2003). Although $NO_3^-$ (which is naturally low or absent in groundwater) is seen as a non-conservative tracer, its correlation with faecal contaminants in groundwater can provide useful information on the spatiotemporal patterns of contaminants (Lapworth et al., 2017). This can inform groundwater resource management (Nestler et al., 2011; Widory et al., 2004). Similarly, a linear relationship between $NO_3^-$ concentration and the DRASTIC model could reveal groundwater vulnerability to pollution (Javadi et al., 2011; Thirumalaivasan et al., 2003). Other past studies have also revealed a correlation between residential population density and high groundwater $NO_3^-$ concentration; in the same way that soils, geology and land-use patterns have been highlighted as critical underlying factors influencing groundwater $NO_3^-$ concentration (Lapworth et al., 2017; Di and Cameron, 2002). Previous studies have also assessed toxicity of metals contamination on staple plants as a way of documenting various pathways through which humans can be exposed to contaminants (Oladele and Fadare, 2015; Bo et al., 2009). Whereas past studies have focused on either agronomy or hydro-geochemistry issues, there exists a gap in terms of in-depth assessments of human exposure to contaminants using multi-disciplinary approaches - especially in highly fragile urban areas. There is a need for a multidisciplinary study to better unravel the complex environmental factors influencing the spatiotemporal characteristics of chemical contaminants in cities.

This thesis analyses a variety of environmental media (such as soils, water, groundwater and plants species) to unravel the spatial variability of contaminants emanating from diverse sources using statistical and geospatial models. The approaches employed span various disciplines such as environmental chemistry, social sciences, geospatial analyses, health studies, GIS and agronomy. The thesis identifies human exposure pathways to chemical contaminants, including some of the critical health risk issues urban populations face. The research is focused on Owerri in southeast Nigeria, but with broader implications for human waste and health management in hugely populated urban centres.

## 1.2 An overview of Nigeria and the challenges of environmental contamination in Owerri

Nigeria has a population of over 180 million people, and is generally regarded as the most populous nation in Africa (Statistics, 2011). The country is located between latitudes 4°16'N and 13°53'N, and longitudes $2^0$40'E and $14^0$41'E, in the west coast of Africa (Figure 1.1). It occupies a landmass of 923,768 km$^2$ and 13,000 km$^2$ of water, ranking as the 14th largest country in the world. It has a tropical climate characterised by a bimodal seasonality, i.e. rainy and dry seasons. The rainy season occurs between April and September, with average annual rainfall ranging from 2,650 mm in the southeast to less than 600 mm in some parts of the northern region, especially on the fringes of the Sahara Desert. The dry season occurs between October and March, with air temperatures varying between 25°C and 40°C. Nigeria faces huge human-induced environmental problems, ranging from oil pollution spills, massive industrial and human waste generation, and erosion and flooding challenges (Adeyinka *et al*., 2005).

These problems are compounded by poor implementation and sometimes non-existent sanitation policies (Prüss-Üstün and Corvalán, 2006). Owerri is located in southeast Nigeria and faces poor implementation of land-use policies that align with the city's development master plan. Spontaneous city expansion, irrepressible urban congestion, poor solid waste management, land cover removal, and sand mining burden the area. Siting of groundwater boreholes in Owerri is unregulated, and most boreholes are located in close proximity to potential contaminant sources. Also, commercialisation of untreated polluted groundwater (for public consumption) is prevalent (Adogu et al., 2015; Pat-Mbano and Ezirim, 2015).

Figure 1.1: Geographical map of Nigeria (adapted from the National Geographic, Map, Esri). Study area is Owerri in southeast Nigeria and is circled in red.

Empirical groundwater vulnerability assessment based on a DRASTIC model (Ibe et al., 2001) delineated the southeastern and western parts of Owerri as highly vulnerable to surface contaminants, due to the aquifer being overlain by a coarse sand to gravel sediment. Coincidentally, urban development and congestion had become dominant in these regions, generating waste that threaten the groundwater quality thereby exposing inhabitants to contaminated groundwater (Okoro et al., 2016). With the increase in rural to urban migration in Owerri and the associated waste generation, local waste management authorities remain inefficient in managing the massive solid waste that are indiscriminately dumped at both approved and unapproved (designated) areas, including drains and river banks (Figure 1.2). Contamination of water resources increasingly poses public health risks as contaminants from dump sites pollute groundwater resources either by surface runoff or infiltration (Morales and Albassam, 2017). The Environmental Sanitation Authority in Owerri collects waste from homes regularly, yet the sanitary condition of Owerri (see Table 1.1) has remained a subject of concern to environmental practitioners.

Figure 1.2: A scene depicting indiscriminate dumping of solid waste along major streets in the city of Owerri (this obstructs traffic and water flow in drainages). Average rate of waste generation in Owerri is put at 1474 $m^3$ per day (Nwoke, 2013)

Table 1.1: Percentage refuse disposal by weight in Owerri (2007-2009) (Adapted from Nigeria Annual Abstract of Statistics, 2012)

| Year | Government Agency | Private Agency | Government Bin | Onsite | Unauthorised dumpsites | Others |
|---|---|---|---|---|---|---|
| 2007 | 4.4 | 0.6 | 0.7 | 54.3 | 31.3 | 8.7 |
| 2008 | 1.2 | 0.7 | 2.0 | 56.0 | 20.2 | 19.9 |
| 2009 | 1.3 | 0.6 | 0.8 | 59.4 | 11.7 | 26.2 |

## 1.3 Research aim and objectives

This thesis is motivated by the impacts of increasing urbanisation and poor waste management practices on the health of the inhabitants of Owerri and focuses on the following overarching aims and objectives:

Aims:

I) Determine the spatial distribution and implications of potentially toxic elements in different environmental samples that result from urbanisation and anthropogenic activities.

II) Provide reliable environmental baseline data for health risk assessment and management.

To contextualise the study, the first aim addresses the following research objectives:

a. Collect different environmental samples that could potentially be impacted through improper waste management systems in the study area.
b. Characterise systematically, via in-situ fieldwork measurements and subsequent laboratory work, the physicochemical attributes of waste dumpsite leachate, groundwater, river water, soil and plant samples that may be associated with potential contaminants from both natural and anthropogenic sources.
c. Assess physicochemical datasets in a spatial context, using GIS and multivariate statistical analysis of relationships between parameters, in order to map the extent and significance of contaminants.

While the second aim targets the objective below:

d. Identify the most vulnerable population groups to chemical contaminants and quantify the public health risks associated with critical pollutants such as $NO_3^-$ and Pb in both groundwater and plants in the exposed regions.

The thesis uses datasets generated from fieldwork as well as secondary datasets and techniques from: (i) guidance on Human Health Preliminary Quantitative Risk Assessment (PQRA); and (ii) the public health assessment guidance manual of the Agency for Toxic Substance and Disease Registry (ASTDR) (Canada, 2004; Calabrese, 1992).

## 1.4 Thesis structure

This thesis is organised in six chapters. Following this chapter, the next chapter (Chapter 2) presents a detailed literature review on the various thematic issues that cross-cut this research, covering critical toxic elements, the chemistry of environmental waste and theories on human exposure pathways to chemical contaminants. Chapter 3 outlines the research approach and methods, encompassing the environmental samples collected and the field and laboratory techniques applied. Chapter 4 highlights the groundwater, river water, open waste dumpsite leachate, soil, and staple plant chemical datasets generated during the study. Chapter 5 discusses the research findings based on the datasets generated. Finally, Chapter 6 presents the conclusions and recommendations resulting from a synthesis of the research findings.

# Chapter 2

# Literature Review

## 2.0 Urban-induced ecosystem disruptions as a global challenge

The concept of urbanisation has been viewed from different perspectives based on its diverse impact on the ecosystem (Seto et al., 2014). Weber and Puissant, (2003) view urbanisation as the mass migration or concentration of people to a specified location in such a manner as to induce a general transformation of land cover and land use types.

Approximately 0.28 to 3.5 million km$^2$ landmass has been classified as urban land cover less than 0.5% of the Earth's land surface. This is a major impact on the natural environment and is directly linked to climate change (Seto et al., 2014; Klein Goldewijk et al., 2010). Population growth, being the major driving force of urban sprawl has assumed an increasing trend with a resultant urban expansion and exploitation of natural resources (Sudhira et al., 2004). In a review of the United Nations Development Programme (UNDP) report on global population growth trend (Weber and Puissant, 2003), stated that 14% of the global population growth of 1920 tripled between 1950 – 1985 and that older industrial cities seemed to have reached their threshold and therefore not affected by population increase. The UNDP report noted that 17% to 34% urban population growth between 1950 and 1990 took place in the developing countries (DeSA, 2013), but out of the nearly 1,000 urban agglomerations with a population of 500,000, three quarters are within developing countries.

In a separate review Seto et al.(2014) estimated weekly global population increase of 1.3 million based on urban population prediction of between 2.5 to 3 billion by 2050, with a greater rural-urban shift in the developing countries. In an appraisal of biotic responses to urbanization, Kowarik, (2011), remarked that human activities have directly altered urban biodiversity through habitat loss, fragmentation and indirect modification of urban climate, soils, hydrology, and biogeochemical cycles. While assessing ecological flexibility in an urban ecosystem (Alberti and Marzluff, 2004) argued that ecosystem dynamics and resilience to human disturbance is a function of variability in urban development pattern and demand. Irrespective of economic developments associated with urbanisation Alam et al. (2007) reported a linear relationship between increased population-urbanisation rate and environmental degradation. Population explosion and related economic activities within urban cities in most developing nations have often enhanced solid waste generation beyond the control of municipal authorities and funding (Guerrero et al., 2013; Minghua et al., 2009; Sujauddin et al., 2008; Burnley, 2007)

## 2.1 Anthropogenic modification of atmospheric chemistry and water balance.

The Earth's water reservoir is predominantly defined by the ocean that occupies about 97.25% of its surfaces with other hydrologic components accounting for remaining 2.75%. The remaining components (besides ice caps and glaciers) are explained by the different water phases in the following proportions deep groundwater (0.38%), shallow groundwater (0.30%), whereas, soil moisture (0.005%) and others, describe the remaining phases (Hiscock, 2009). However, despite the minor percentage of 0.001% occupied by atmospheric moisture (Hiscock, 2009), it significantly influences the chemical qualities of the other water phases through chemical adsorptions and precipitations.

The emission of greenhouse gases (GHG) through human activities has modified both the atmospheric and biogeochemical structure (Clarke et al., 2007). The natural atmospheric composition includes 78% nitrogen, 21% oxygen, 0.93% argon and trace amounts of neon, helium, methane, krypton, hydrogen and water vapour (Sharp, 2012). Hiscock, (2009) reported that whereas an estimated $6.5 \times 10^9$ tonnes per annum of carbon emitted into the atmosphere mainly resulted from the burning of fossil fuel, other anthropogenic activities like deforestation and land use changes further account for further $1 – 2 \times 10^9$ tonnes per annum.

The Intergovernmental Panel on Climate Change (IPCC) synthesis report of 2007, opined that among other primary GHG (water vapour ($H_2O$), Nitrous oxide ($N_2O$), methane ($CH_4$), and Ozone ($O_3$)), $CO_2$ remains the prime GHG (IPCC, 2007). $CO_2$ contributes more than one-half of the greenhouse effect due to the increasing use of fossil fuel and urbanisation driven land-use change (Judkins et al., 1993).
Climate change has, therefore, been considered as posing a significant threat to the quality of both the surface and groundwater resources (Marcinkowski et al., 2017),

through the increasing impact of global warming and rainfall, runoff and groundwater recharge patterns (Hiscock, 2009).

## 2.2 Global conventions on eco- resilience and environmental sustainability

The increasing rate of environmental degradation and its debilitating effect on the capacity of ecosystem engineers and service providers to sustain the natural environmental qualities (Rapport et al., 1998), has been the focus of successive global conferences of the United Nations. Following resolution number 44/228 of December 1989, the United Nations General Assembly summoned the first conference on Human Environment to scrutinize ways of preserving and enhancing the human environment which later came up with the "Green and Brown Agenda" that focused on urbanisation, environment, and development (Hoelting, 1994; Sand, 1991).

An international conference on Environment and Development which convened in Rio de Janerio, Brazil, by the United Nations in June 1992, called for cooperation of key social actors on vital issues of environment and development, hence, the concept of sustainable development as reflected in Agenda 21 (Lafferty and Eckerberg, 2013; Allen and You, 2002; Keating, 1994). UN-Habitat II was held in Istanbul in 1996 with focus on urbanisation and allied issues of land, housing and urban management. It specifically called for the sustainable provision of human settlements (Allen and You, 2002).

The global summit on sustainable development held in Johannesburg, South Africa, in September 2002, stressed the need for regional and global cooperation in the area of Water, Energy, Health, Agriculture and Biodiversity with special emphases on Water and Sanitation (UN, 2002). The United Nations Conference on Sustainable Development in 2002 (Rio de Janiero), in recognition of the essential role of access to safe drinking water and sanitation for global sustainable development reaffirmed its commitment towards the Millennium Declaration of increasing access to good drinking water by the year 2015 (UN, 2012).

More recently, in Goal number 6.0 of its resolution entitled “Transforming our world: the 2030 Agenda for Sustainable Development” the UN General Assembly in

September 2015 reiterated its target of ensuring safety of water from all forms of pollution, improvement of water recycling and reuse as well as sustainable use of the water resources by the year 2030. The document also re-emphasised the UN General Assembly's resolve to the restoration of water-related ecosystems by the year 2020 (Assembly, 2015).

### 2.3 Challenges of open dump system of waste management in the developing countries

Open dump system of waste management implies the unsystematic waste collection, sorting, processing (modification and treatment), containment and disposal (Ogwueleka, 2009). This disposal technique is commonly practiced as a general and cheapest means of waste management in most developing countries (Ogwueleka, 2009, Taylor and Allen, 2006 ). Industrial and municipal solid waste has a heterogeneous composition with hazardous substances capable of causing long-term problems, such as pollution of soil and groundwater systems years after deposition, due to continuing chemical reactions (Bozkurt et al., 1999). However, the concentration of contaminants in the leachate decreases as they disperse from the waste deposit in the direction of groundwater flow (Taylor and Allen, 2006). Leachate is the liquid by-product of interaction between decomposing wastes and rainwater, mainly composed of organic compounds and metals (Sánchez-Chardi and Nadal, 2007).

Many factors (topography, geology, and hydrology as well as the protective capacity of the local soil), that are necessary for consideration before siting a landfill, have been compromised, reducing contaminant attenuation potentials of the natural environment and making the ecosystem more vulnerable to pollution (Yong and Mulligan, 2003). Apart from the attenuation capacity of an organic component of waste against metal toxins, there is further degradation of leachate contaminants migrating to the groundwater by bacteria within the vadose zone (Kirkeby et al., 2007). Bozkurt et al., (1999) reported that water at the base of landfill released as a product of various stages of organic decomposition carries with it metals in a concentration determined by the sorbing materials such as humic acid, which controls metal mobility to the groundwater. The characteristics of contaminants formed (released into the environment in the form of liquid or gaseous pollutants) from these chemical reactions largely depend on the composition of waste. Waste prevention, recycling, composting and reuse as commonly practiced in most developed nations have reduced waste volume for landfill. The opposite of the situation is the open dump landfill system that dominates disposal practices in the developing nations (Kjeldsen et al., 2002). These waste containment practices minimise chances of environmental pollution by landfill sites. Besides, hazardous industrial wastes, solid incinerator residues, bottom and fly ash are sorted, and systematically disposed of, into designated landfill (Taylor and Allen, 2006).

The environmental and public health risks of open dump system of waste disposal are not limited to leachate release into soil and groundwater or biogas emission (Christensen et al., 2001), but includes possible uptake of toxins by food crops from the soil. However, the direct and very significant problem associated with an unsanitary waste management system is leaching of hazardous substances into shallow groundwater table with the attendant health implications (Calvo et al., 2005). Water contamination by leachate and eventual usage for drinking purposes does not often have an immediate health impact, but a bio-accumulative and destructive effect on human tissues. Hence, landfill proximity to residential areas could be the course of some carcinogenic and cardiovascular ailments due to leachate contamination of the groundwater system (Kloppenborg et al., 2005).

### 2.3.1 Solid waste decomposition stages in a landfill

Solid waste in a typical landfill system assumes different decomposition stages to produce leachate that often characterises its components. The first phase involves quick consumption of available oxygen in the aerobic decomposition of organic matter to produce carbon dioxide (approximately equivalent volume to the utilized oxygen) and bacterial cells to initiate the anaerobic phase (El-Fadel et al., 1995; Barlaz and Ham, 1993). Besides moisture, the rate of oxygen depletion is dependent on the level of refuse compaction (Figure 2.1); as initial pores in the waste materials that serve as a pathway for oxidation decreases as the anaerobic phase progresses (Bozkurt et al., 1999). The anaerobic phase, which is the central phase in the decomposition process, involves the conversion of cellulose and hemicellulose (glucose polymers), which forms about 90% of the organic mass in municipal solid waste (MSW) (Meraz et al., 2004). A drop in the pH usually ensues at this phase, which expedites the fermentation and solubility of numerous compounds (Barlaz et al., 1989). The acidic medium results from the formation of volatile fatty acids (VFAs) and the increased partial pressure of $CO_2$, while the concentration of inorganic ions, e.g. $Cl^-$, $SO_4^{2-}$, $Ca^{2+}$, $Mg^{2+}$, $Na^+$, leached from dissolved organics in the wastes, increases (Taylor and Allen, 2006). The third phase, otherwise known as the inception of early methanogenic phase involves the gradual build-up of methane ($CH_4$) concentration with a resultant increase in pH and a decrease in $H_2$, $CO_2$, and VFAs. The accumulated VFAs are converted by the methanogenic bacteria to yield an increased concentration of methane and carbon dioxide (Taylor and Allen, 2006; Christensen and Kjeldsen, 1989; Barlaz et al., 1989); with an ensuing reduction in solubility of calcium, iron, manganese and heavy metals possibly precipitated as sulphide, releasing ammonia in anoxic environment. This immobilisation can be attributed to the adsorption and attenuation capacity of the soil and organic contents of the waste especially at a neutral to alkaline pH level (Bozkurt et al., 1999). The last stage of decomposition results to the stabilisation of methane whose rate of formation is dependent on the rate of hydrolysis of cellulose and hemicellulose (Kjeldsen et al., 2002). There is a steady increase in pH almost to neutrality as carboxylic acid is rapidly consumed, signifying the near completion of the solubilisation of organic matter in the waste, releasing a biogas of over 50% methane and ammonia by the action of acetogens. The product of the entire process is characterised by very low biochemical oxygen demand and chemical oxygen demand ratio (Taylor and Allen, 2006; Meraz et al., 2004).

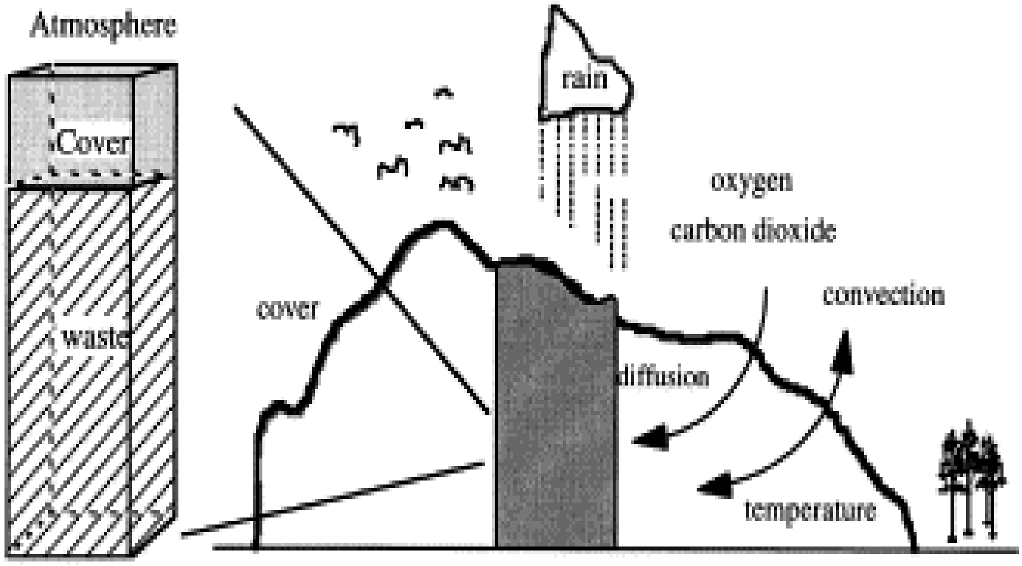


Figure 2.1: Schematic diagram of an ideal landfill indicating heterogeneous factors that could influence rate of waste decomposition and leachate production; as presented in Bozkurt et al. (1999).

## 2.4 Geospatial assessment and groundwater vulnerability studies

Several applications of groundwater vulnerability assessment and mapping techniques have been reviewed with a view to investigating different deterioration stages of the groundwater quality (Hua et al., 2010). This report cites numerous other innovative techniques for valuation of seawater intrusions, correlation among thickness of aquifer overlaying burden, groundwater recharge and transit time and prominently evaluation of potential risk of nitrate pollution in the aquifer. According to the National Research Council, groundwater, vulnerability implies "*the tendency or likelihood for contaminants to reach a specified position in the groundwater system, after introduction at some location above the uppermost Aquifer*" (Council, 1993); associating sandy soils and shallow groundwater with high vulnerability.

Site identification and quantification of chemical hazards and pathways to the exposed population remain a viable tool for a sustainable environment. This practice of risk assessment is crucial in the prevention and mitigation of potentially harmful sources and areas threatened by contaminations. It provides a significant resource for different forms of environmental planning and decision making, e.g. land planning, groundwater monitoring, agricultural development, etc.(Wang et al., 2012).

Studies have revealed that factors that influence the state of vulnerability or high risk to contamination include internal aquifer characteristics, external pressures and geological settings (Gemitzi et al., 2006; Mendoza and Barmen, 2006). According to Gogu and Dassargues, (2000), attributes of significance in vulnerability assessment also include recharge value, soil properties, topography, groundwater /surface water relation and the nature of the underlying unit of the aquifer. Shallow water tables at very permeable and alluvial soils have the least favourable attributes for activities such as landfill siting due to its effective porosity that provides pathways for contaminant migration to the groundwater (Simsek et al., 2006). Groundwater vulnerability and catchment pollution might be indicated by nitrate pollution (Bruggeman et al., 1995). Although solute transport in groundwater under natural gradient can be complexed by natural factors like the aquifer structure, irregular flow pattern and the solute-matrix interactions (Dagan, 1987), nitrate movement into the groundwater is mainly influenced by the soil water content in an increased clayey sediment (Addiscott and Bland, 1988).

Before the recent advancements in the spatial assessment in groundwater and general environmental resource management, vulnerability assessments of aquifers to surficial contaminants was carried out using overlay and index models such as DRASTIC, SIGA, GOD etc. (Kihumba et al., 2017; Ibe et al., 2001;Gogu and Dassargues, 2000). These techniques simply evaluate groundwater sensitivity to contamination with respect to major hydrogeological processes (Şimşek et al., 2008). DRASTIC scales: **(D)** depth of water table, **(R)** net recharge, **(A)** aquifer media **(S)** soil **(T)** topography **(I)** influences of vadose zone **(C)** hydraulic conductivity in assessing groundwater vulnerability. SIGA applies the rating of **(S)** soil media, **(I)** intermediate zone material, **(G)** ground surface slope and **(A)** aquifer material, whereas GOD considers parameters like **(G)** groundwater mode of occurrence, **(O)** overlying lithology and **(D)** depth to water table. Besides characteristic uncertainties associated with the techniques, generation of vulnerability maps based on the assessment can be difficult (Dixon, 2005).

### 2.4.1 Application of GIS in vulnerability assessments

Various studies have therefore underscored the need to employ the application of spatial analysis using different Geographical Information System (GIS) techniques in both land use management and groundwater quality monitoring. A combination of remote sensing and GIS tools were applied in the parameterisation and mapping of the Environmentally Sensitive Area Index (ESAI) in the island of Lesvos, Greece (Symeonakis et al., 2016). The study used relevant soil, groundwater, and demographic parameters to delineate areas that are critically sensitive to human activities.

In an assessment of groundwater quality in the alluvial Nasuno basin, Tochigi, Japan, Babiker et al., (2007) used the spatial autocorrelation tool in ArcGIS in the spatial assessment of borehole data to investigate the spatial variability of groundwater quality. Groundwater quality index was then generated from a combination of spatial measurements and groundwater quality data transformed into a matching index rating value, and ultimately produced an interpolation map. Many interpolation techniques exist such as the inverse distance weighting (IDW), Spline, etc. but the geostatistical technique (e.g. Kriging) have been widely employed in most studies (Gorai and Kumar, 2013). Similar techniques have been employed in many other studies (Babiker et al., 2007; Hiscock et al., 1995).

### 2.4.2 Geostatistical and spatial mapping by Kriging technique

Geostatistics has been described as a spatial statistical study that assumes that all values within an area result from a dependent random process (Network, 2011).In order to uncover the degree of dependence and make predictions different interpolation methods exist, prominent among which is the Kriging method. This technique can be used to explain and model spatial distribution patterns and above all, predict values at unmeasured locations, while evaluating the level of uncertainty of such prediction (Network, 2011). Kriging interpolation technique is based on the assumption of Gaussian distribution of random field; a premise that hardly exists in practical terms and often results in an underestimation of prediction error (Pilz and Spöck, 2008). However, this underestimation is minimised by use of the Bayesian

Kriging technique, which automatically accounts for the underlying error through a process of subsetting and simulations prediction approach (Network, 2011). This implies that true semivariogram which introduces prediction error is chosen from a subset of semivariograms with probabilistic conditions based on their potential values (Vélez et al., 2018; Gribov and Krivoruchko, 2012).

## 2.5 Concept of redox and influence on the groundwater chemical properties

### 2.5.1 Redox processes in a typical soil-groundwater system

Hiscock (2009) described redox or oxidation-reduction as reactions that result to loss or gain of an electron with an eventual change of oxidation state, hence, oxidation and reduction are coupled in a hydrochemical process. Oxidation involves donation of electron ($e^-$) by chemical elements whereas reduction involves acceptance of electrons by chemical elements, while having microbial activities as the principal driving force, by the use of species as either electron donor (mostly dissolved organic carbon (DOC)) or acceptor (oxygen) in an oxidised environment (Fendorf, 2000).

The solubility and transport of both minor elements (Fe and Mn) and redox-sensitive components ($O_2$, $NO_3^-$/$N_2$/ $NH_4^+$, $SO_4^{2-}$/$HS^-$,Mn (II)/Mn(IV) and Fe(II)/Fe (III)), as well as organic chemicals in pristine and contaminated groundwater, are dependent on prevalent redox condition (Hiscock, 2009; Drever, 2005). The dissolution and change in state of these elements and compounds can influence the soil-groundwater pH, as reducing condition increases pH, whilst oxidising condition reduces pH (Evangelou and Evangelou, 1998).

Besides, redox conditions in the soil and groundwater system could also be influenced by microbial activities. Drever, (2005) argued that supposition of a balanced redox condition in a sterile environment (devoid of microbial activities) in the 1960s and 1970s was rational, but that such insinuation was invalidated in the 1980s via scientific discoveries of dominant microbial influences on redox processes in the groundwater system. This study, however, stated that the degree of microbial activities is determined by the availability of substrates such as particulate or dissolved organic carbon (DOC), which serve as electron donors, and oxidants such as oxygen, nitrate and other electron acceptors. Hence, redox processes could be described by the characteristic responses of electron donors and acceptors to a changing condition in a typical groundwater system (Drever, 2005; Christensen et al., 2000).

Furthermore, (McMahon and Chapelle, (2008) assessed redox processes and groundwater quality in an aquifer system based on an ecological succession of such electron acceptors mentioned above and the corresponding threshold of substrates required to sustain microbial metabolism. However, even as (Christensen et al., 2000) argue that such insinuations can inaccurately describe redox process if solid phases are disregarded, especially for redox-sensitive species such as reduced iron, McMahon and Chapelle (2008) state that the production of $Mn^{2+}$ and $Fe^{2+}$ could be an indication of microbial utilisation of solid-phase electron acceptors such as Mn (IV) and Fe (III). Experimental assessment of the isotopic composition of dissolved Fe(II) revealed its fractionation from dissolved minerals which implies that Fe(II) dissolution can be ligand controlled (Drever, 2005; Wiederhold et al., 2006).

## 2.6 Redox sequence in groundwater flow path

Redox processes are most prevalent along the groundwater flow path and in landfill leachate plumes (Rivett et al., 2008; Christensen et al., 2000; Edmunds et al., 1982). Redox occurrence has been described using a two type hydrochemical systems namely closed and open oxidant systems (Hiscock, 2009; Champ et al., 1979). In a typical groundwater system, which could be described as a closed system due to its isolation from the atmosphere, oxygen inclines to be consumed from recharge along groundwater flow path to discharge and followed in sequence of other electron acceptors (Hiscock, 2009; McMahon and Chapelle, 2008; Champ et al., 1979). Fendorf, (2000) described such sequence of electron acceptors as in sequence 1 and reduced species in the reverse order:

$$O_2 > NO_3- > Mn\ (VI) > Fe\ (III) > AsO_4^{3-} > SO_4^{2-}\ \text{(Sequence 1)}$$

Such sequence of an oxidation-reduction process occurring in the flow system which influences mobility and concentration of most ions have been considered in three redox zones namely oxygen-nitrate,iron-manganese and sulfide zones (Hiscock, 2009; Champ et al., 1979). Similarly, Fendorf, (2000) recommended soil redox state classification by electron activity(pe) and redox potential (Eh) with a relation Eh (mV) = 59.2pe. The study then simply described zones characterised by the reduction of Fe and Mn-oxides as suboxic (pe 2-7, 100 <400 mV) and anoxic for zones where sulphate becomes the key electron acceptor. Illustrating with redox response to contaminant plumes introduced into a groundwater environment (Christensen et al., 2000) observed a strongly reducing condition towards the contaminant source with a redox gradient along the groundwater flow direction. This process which mirrors an electron cycle from a reduced electron donor to acceptance by oxidised species could be a demonstrative description of a redox process as a terminal electron-accepting process (TEAP) This study described the implication of a downgradient elevation of redox-sensitive chemical species and large plume reduction in an aerated environment as redox functions.

## 2.7 Water flow system and solute distribution pattern in groundwater

### 2.7.1 Water flow pattern

Surface water transport in the soil can adapt two defined patterns which are either by horizontal or vertical flow; with the former describing solute movement through the soil to the discharge point (river or lake) whereas the latter involves similar movement through the soil profile to the groundwater (Evangelou and Evangelou, 1998). Under constant temperature and pressure, water flow through a homogeneous medium was first described with Darcy’s Law of proportionality of flow from high pressure to low pressure region in a porous medium (Hiscock, 2009; Evangelou and Evangelou, 1998).

$$q = -K\,(\Delta Ø / \Delta X) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

While q stands for hydraulic flux in volume per unit cross-sectional area and K representing hydraulic conductivity, Ø is the sum of the change in pressure (Ᵽ) and elevation (z), whereas, X, represents distance travelled by water (Evangelou and Evangelou, 1998). This principle was described as the theoretical foundation of groundwater flow (Hiscock, 2009) and applies in both saturated (soil pores filled with water) and unsaturated (large pores drained soil) conditions (Evangelou and Evangelou, 1998). Water movement is controlled by the hydraulic gradient in a saturated medium which gradually shifts to matrix gradient control, as soil pores drain (Evangelou and Evangelou, 1998).

### 2.7.2 Solute transport mechanism in groundwater

Studies have remarked that the dominant transport mechanism for dissolved contaminants in groundwater in sand and gravel aquifer system is by advection; which implies solute transport alongside groundwater flow (Anderson et al., 2015; Mackay et al., 1985). In a review of organic contaminants transport in groundwater (Mackay et al., (1985) stated that topography usually influences groundwater flow pattern in a uniform sand and gravel aquifer in gentle topography and that groundwater flow rate is projected to within a factor of 10, given a general description of the geologic medium. The study added an estimated groundwater velocity range of between 1 m/year and 1000 m/year in such aquifers, implying that it takes decades for contaminants to travel downgradient; except in high capacity wells where artificially induced local gradient can reduce average travel time.

## 2.8 Water-rock interaction influence on the groundwater quality

The water chemistry is largely influenced by the interaction between the recharging water and mineral components of both solid and gaseous phases of the soil. The effect of water-rock interaction, aquifer heterogeneity on groundwater mineralisation and general hydrogeochemical background have been recognised in several studies (Santoni et al., 2016; Ledesma-Ruiz et al., 2015; Hiscock, 2009; Lasaga, 1984). Concentrations and distribution of elements mobilized by geogenic processes have further been altered by anthropogenic activities beyond their natural background value and soils' attenuation capacity (Macdonald et al., 2000; Nriagu, 1990). The chemical characteristics of the hydrosphere is a product of geochemical interactions and eventual dissolution of ions and other dissolved solutes formed through species exchanges between water and aquifer sediments (Manahan, 2002). Studies have therefore asserted that concentrations of major ions in groundwater, which may vary spatially, and temporary can indicate the degree of the water-rock interaction (Elango and Kannan, 2007; Frape et al., 1984). Besides, the fluctuation of water pH could also be a geochemical signature of minerals dissolution resulting from water-rock interactions (Worrall and Pearson, 2001).

This, therefore, underlines the need for a better understanding of the water/rock interactions in the study of the spatiotemporal characterisation of groundwater geochemistry.

## 2.9 Nitrate prevalence in global aquifer and denitrification potentials

Studies have adjudged nitrate as the most prevalent contaminant in most surface water and groundwater aquifers in the world due to its high solubility, mobility and weak adsorption by soil hence its leaching and accumulation in the groundwater (Shukla and Saxena, 2018; Ward et al., 2005; Clawges and Vowinkel, 1996). A projected 36% increase in the mean nitrate concentration in global waterways since 1990 above 50 µg/mL health-based threshold as stipulated by the World Health Organisation have been reported, with geometrically increasing values recorded in the Eastern Mediterranean and Africa. However, a study on the impact of agriculture on water pollution in the Organisation for Economic Co-operation and Development (OECD) countries shows agriculture as a major source of nitrate in groundwater in OECD countries with approximate 28% for Finland to 80% for Ireland (Parris, 2011).

As a vital component of the nitrogen cycle (Figure 2.2), which can be introduced into the groundwater by both natural and anthropogenic means, nitrate influx into the groundwater and eventual ingestion can result to severe health conditions especially the infantile Methemoglobinemia among others (See section 2.7) (Shukla and Saxena, 2018). The increasing rate of nitrate contamination of the groundwater resources has also been associated with rapid global population especially with regards to land use change and land cover removal which increases N mineralisation and reduces possible plants uptake and reduction of the leaching nitrate flux (Goodale and Aber, 2001; Vitousek et al., 1982). Studies have recognised four major sources of nitrate in drinking water as natural sources, waste materials, raw crop, and irrigated crop agriculture has been recognised (Canter, 1996).

In a study on the natural and artificial denitrification of groundwater Hiscock et al., (1991) cited examples of natural denitrification in an aquatic environment and further reviewed two stimulated nitrate treatment (above-ground and under-ground) techniques considering several limitations of the natural denitrification process.

Among such limitations of natural denitrification identified in this study is the inadequate availability of oxidizable organic matter that is vital for microbial denitrification. Furthermore, the study discussed other natural factors such as availability of oxygen, which competes with nitrate as an electron donor for cells break down, essential nutrients required to sustain biological growth, sulphur compounds etc. as important factors that control natural denitrification. It concludes that the conventional denitrification technique was more efficient while recommending rather a site-specific assessment of the biological denitrification.

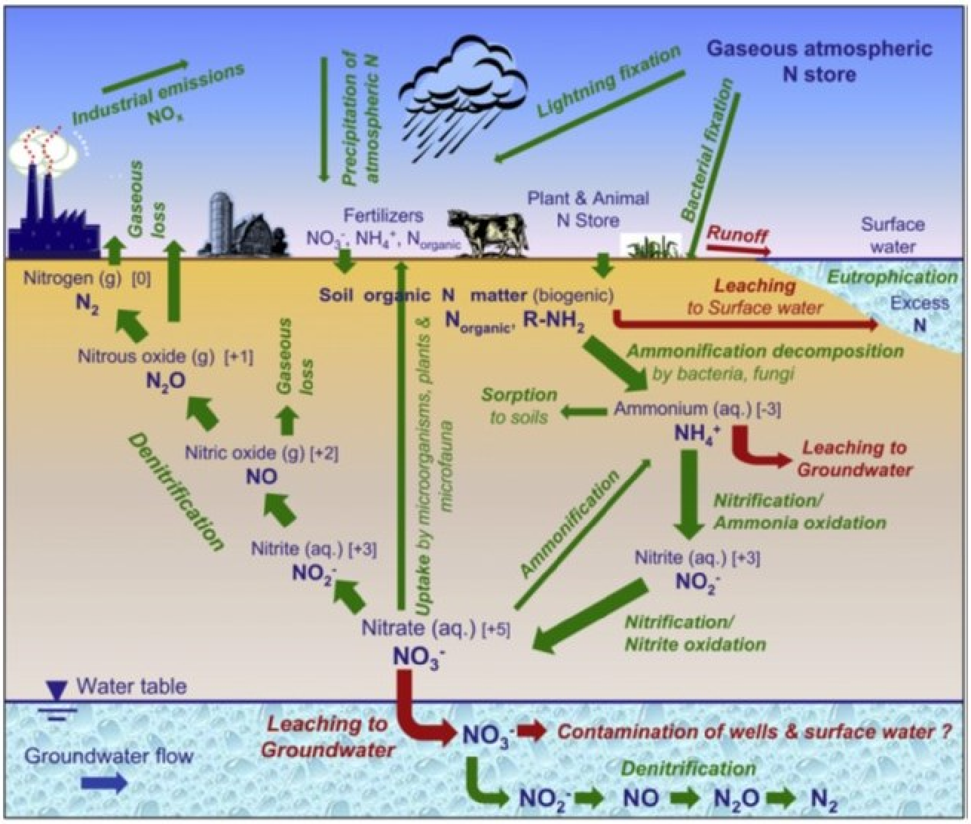


Figure 2.2: Nitrogen cycle and hydrogeochemical processes that threaten quality of the aquatic environment (Source: Rivett, 2008)

Consequently, several pieces of research have been focused on ways of minimising nitrate concentration in groundwater and by implication reduce human exposure to contaminated water.

In a study on the natural and artificial denitrification of groundwater Hiscock et al., (1991) cited examples of natural denitrification in an aquatic environment and further reviewed two artificial stimulation nitrate treatment (above-ground and under-ground) techniques considering several limitations of the natural denitrification process. Among such limitations of natural denitrification identified in this study is the inadequate availability of oxidizable organic matter that is vital for microbial denitrification. Furthermore, the study discussed other natural factors such as availability of oxygen, which competes with nitrate as an electron donor for cells break down, essential nutrients required to sustain biological growth, sulphur compounds etc. as important factors that control natural denitrification. It concludes that the conventional denitrification technique was more efficient while recommending rather a site-specific assessment of the biological denitrification (Rivett et al., 2008) stated that nitrate removal mechanisms in groundwater besides denitrification include:

(a) Dissimilatory nitrate reduction to ammonium (DNRA):

Represented by the equation (2), this process is known to occur under similar condition as the denitrification but differs by the limited niche occupied by the anaerobic fermentative bacteria that carry out the DNRA unlike the normal denitrifies that occupy wider niche especially within the vadose zone)

$$2H^+ + NO_3^- + 2CH_2O \rightarrow NH_4^+ + 2CO_2 + H_2O \ldots\ldots\ldots \; (2)$$

This mechanism involves the spontaneous oxidation of ammonium or nitrite generated by DNRA to nitrate or adsorbed by vegetation on exposure to the aerobic environment. The study, however, remarked that since sufficient sorption and ion exchange of ammonium are necessary for this process in many aquifers, this natural mechanism could only be short-lived.

(b) Nitrate absorption into microbial biomass

This implies the conversion of nitrate to biomass growth in the presence of organic substrates since the availability of ammonium often hinders the natural assimilation of nitrate for growth by heterotrophic microorganisms. Besides, the report anticipates the impossibility of natural absorption of the significant amount of nitrate by microbial organisms.

## 2.10 Common contaminants in drinking water and associated public health risks

### 2.10.1 Health implications of elevated nitrate in drinking water

With the increasing global dependence on surface and groundwater resources for drinking purposes (Eckstein and Eckstein, 2003), there is a high tendency of human exposure to nitrate above health-based regulatory standard (Shukla and Saxena, 2018). End-users of groundwater abstracted from wells overlain by shallow and coarse-textured soils with potential nitrogen sources are most susceptible to nitrate ingestion-related diseases (Ward et al., 2005; Nolan et al., 2002). Some of such adverse health conditions include the widely researched Methemoglobinemia, endogenous formation of N-Nitroso Compounds (NOC), thyroid infection, etc.

Methemoglobinemia or blue baby syndrome has become the most debated infant-related ill health that is believed to be associated with ingestion of high nitrate in drinking water and mostly interferes with the oxygen-carrying capacity of the human hemoglobin (Ward et al., 2005). Studies have narrated that this mainly infantile health condition was first reported in 1945; and that the maximum concentration limit was established following survey report of no case observation of such ailment in children at nitrate concentration in drinking water <50 µg/mL (Ward et al., 2005; Walton, 1951; Comly, 1945). Researchers have commonly reported that this ailment is formed by the endogenous conversion of nitrate in drinking water to nitrite, which subsequently oxidizes the oxygen-carrying ferrous iron in the hemoglobin (Hb) to the oxygen-inhibiting ferric state (Fewtrell, 2004; Kross et al., 1992). Symptoms of this ailment were reported to appear from 10% Methemoglobinemia with chocolate-coloured blood (cyanosis) and blue-coloured nails (clubbing) (Figure 2.3) and may ultimately lead to high morbidity risk depending on its concentration (%) in the blood (Shukla and Saxena, 2018; Fewtrell, 2004; Kross et al., 1992).

However, infants less than 4 months are referred to as the most susceptible to the Methemoglobinemia sickness, which according to (Ayebo et al., (1997) are centred on the following four factors

1. The alkaline pH of infants' gastric system is conducive for enhanced bacterial conversion of ingested nitrate to nitrite, though still disputed (Fewtrell, 2004).
2. The high rate of fluid intake by infants due to body weight increases the chances of infection through contaminated water.
3. A higher percentage of fetal hemoglobin which could be easily oxidised to methemoglobinemia
4. Limited presence of bacteria that can convert any produced methemoglobinemia to normal hemoglobin as found in adults.

Besides, older children between the ages of 1 – 7 years can also be susceptible to methemoglobinemia (Sadeq et al., 2008).

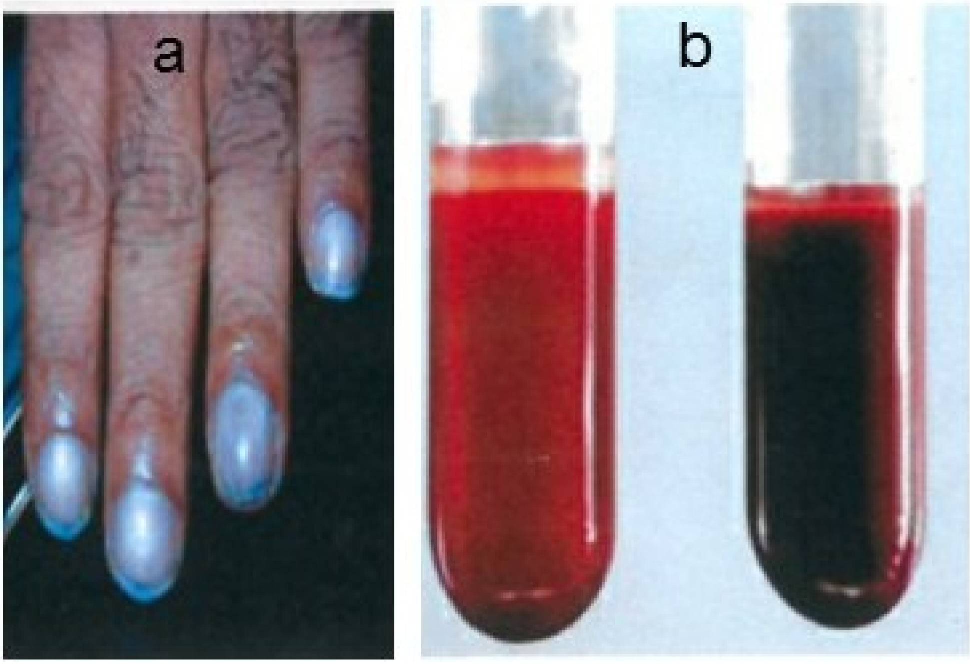


Figure 2.3: Methemoglobinemia influence on human body system illustrated by (a) clubbing (blue-nailed colouration) and (b) cyanosis (from normal to chocolate-coloured blood) following ingestion of high concentrations of nitrate in drinking water as adapted from (Shukla and Saxena, 2018).

Epidemiological studies have linked Methemoglobinemia with spontaneous abortion (Ward et al., 2005). In a review of prenatal nitrate intake from drinking water and selected birth defects Brender et al., (2013) reported an association between prenatal intake of nitrate-contaminated water and neural tube defects (NTD), oral cleft defects, and limb deficiency in offspring. The report referred to similar findings by (Croen et al., 2001; Dorsch et al., 1984) which recorded a significant relationship between drinking water nitrate and birth defect. Brender et al., (2013) however rejected a hypothesis of the contributory role of ingested nitrate in the endogenous formation of N-nitroso compounds; as there was no observed relationship between nitrosable drugs and birth defects among frequent consumers of nitrate-contaminated water.

Studies have also suggested that elevated $NO_3^-$ inhibits uptake of thyroidal iodide, thereby altering the function of thyroid hormones which might lead to development of goitre (Mervish et al., 2015; Gatseva and Argirova, 2008) Besides, reports of animal studies suggested that a small percentage of dietary nitrate could alter thyroid gland metabolism (Bloomfield et al., 1961). Thyroid function disruption has been associated with exposure to potential sodium iodide symporter (NIS) inhibitors such as perchlorate, thiocyanate, and nitrate that hinders iodine uptake (Mervish et al., 2015). There remain several uncertainties surrounding adverse health conditions associated with a daily intake of elevated nitrate in drinking water.

Besides causing methemoglobinemia studies have shown that while nitrate could remain stable in human body its bacterial-aided reduction to nitrite and other bioactive nitrogen compounds could potentially affect the physiological processes and human health. The protonation of nitrite to nitrous acid ($HNO_2$) under acidic condition in human stomach that lead to the spontaneous production of dinitrogen trioxide ($N_2O_3$) , nitric oxide (NO), and nitrogen dioxide ($NO_2$), presents nitrite as the major factor that modulate endogenous nitrosation capacity of human body and associated health risks (Ward et al., (2005).

## 2.11 Prevalence of groundwater contamination in most urban cities in Africa

Groundwater degradation following contaminations arising from surface water pollution, overexploitation and land activities have been postulated as the most serious water resource problems on the African continent (Usher, 2006). Although many African cities lack accurate information on both the quality and quantity of groundwater resources (Re et al., 2011; Usher, 2006), studies have identified improper waste management as a major source of groundwater pollution, with nitrate as the predominant pollutant (Ouedraogo and Vanclooster, 2016; Wang et al., 2012; Usher, 2006).

Increasing urban population across the sub-Saharan African (SSA) nations, with just about 40% of sanitation facilities, is described as grossly inadequate for proper waste containment (Lapworth et al., 2017; Information et al., 2012). According to Foster et al. (1999), urbanisation has posed a major threat to groundwater quality in Africa by increasing peak runoff, caused by urban fringe impermeability, as well as changes in groundwater recharge patterns. An assessment of urban development threat on the groundwater quality of some major west African coastal cities located around the Gulf of Guinea (Cotonou, Abidjan, Douala and Lagos) known for rapid urbanisation trends, presents major constraints to quality water supply (Nlend et al., 2018). These cities, accounting for approximately 2% of the entire African population, are faced with challenges of potable water and adequate sanitation facilities mainly as a result of insufficient funding and poor maintenance of water supply amenities to meet the demands of the growing population (Nlend et al., 2018; UN, 2014). For instance, the absence of suitable drainage infrastructures needed to discharge sewage in Dakar Senegal (as is also prevalent in most cities in Africa) is considered a major threat to groundwater quality (Re et al., 2011).

Review of groundwater quality across these cities suggests that the influence of urbanisation requires urgent contingency plans for water development, to match with prevailing demographic changes (Nlend et al., 2018). Furthermore, in a review of studies on groundwater degradation at an African scale (Ouedraogo and Vanclooster, 2016; Sorichetta et al., 2013) identified population density and depth to groundwater as two variables that have predominantly influenced groundwater nitrate concentrations. Ouedraogo and Vanclooster,(2016) attributed the inefficiency of waste management mechanisms in most African urban areas to high population density. This assertion was in agreement with a UNEP/UNESCO project report on pollution status and vulnerability of aquifers in African cities, which also related water pollution to poor on-site sanitation and solid waste disposal systems (Usher, 2006).

Besides population density, high groundwater nitrate concentrations have often been associated with geological attributes such as depth to water table (Buvaneshwari et al., 2017; Kazakis and Voudouris, 2015), hence a major health concern, since about 85% of Africa’s population reside in regions underlain by shallow aquifers (Ouedraogo and Vanclooster, 2016). Moreover, land use change and vegetation removal resulting from urban development can alter biogeochemical processes and degrade soil quality by reducing organic matter input to soil making it susceptible to erosion and contaminants leaching (Jacobs et al., 2018; Stamati et al., 2011).

Taylor et al.(2009) ascribed widespread faecal-oral transmission of pathogenic microorganisms in most urban areas in SSA to the wide range of contaminant pathways between faecal sources and consumption of untreated groundwater abstracted from domestic wells. That study specifically established a correlation between heavy rainfall events (of more than 10 mm/day) with increased incidence of gross contamination of groundwater by faecal bacteria in the city of Kampala, Uganda, and emphasised the need for improved hygiene to avert imminent disease outbreak. Lapworth et al.(2017) suggested that although diarrhoeal disease burden is often associated with bacteria contamination, there exists a link between high nitrate and faecal indicator bacteria counts, with faecal contamination of groundwater in most African cities. However, with the dominant reliance on groundwater for drinking water purposes in many African cities and the existence of significant groundwater storage and conducive hydrogeological conditions for borehole drilling across Africa, (Lapworth et al., 2013) emphasised the need for groundwater development that will increase access to portable drinking water. Besides, due to the pervasiveness of urban-induced contamination of the groundwater resources in urban centres of Africa, a multidisciplinary approach could be employed to delineate vulnerable areas during urban planning to minimise human exposure to contaminated water and avert imminent water-related diseases.

## 2.12 Soil and plant contamination from anthropogenic activities

There has been increased metals contaminant burden on soils and plants in most global urban centres following environmental modifications arising from intense human activities posing severe threat to soil quality and food security (He et al., 2015). Human activities involving industrial emissions, agriculture and transportation give rise to the release of metals, such as Cd, Ni, Pb, Cr, Cu, Zn, Fe, into the various components of the Earth system, i.e. surface water, groundwater, atmosphere and biosphere (Nazir et al., 2015). Studies have associated such environmental conditions with various public health risks, especially on susceptible young children, often exposed to contaminated soil via hand-to-mouth routes (Wang et al., 2018; von Lindern et al., 2016), besides ingestion of contaminated locally grown vegetables by both adults and children (Ma et al., 2016; Ferri et al., 2015).

Poor urban planning and unregulated agricultural activities remain major causes of metal distributions in soils and plants across many urban centres in sub-Saharan Africa (Perrin et al., 2015). Three factors responsible for metals migration to the food chain include: a need to feed increasing populations, curb urban poverty and ensure food security amidst land scarcity; resulting to improper fertilizer application and release of toxic chemicals (Perrin et al., 2015; Abdulkadir et al., 2012). Although wastewater used for irrigation of vegetables within urban gardens can introduce contaminants into the food chain, most toxic elements that pose imminent health risk to consumers are caused by emissions from combustion of fossil fuel, subsequent deposition on soil (Nazir et al., 2015; Sherene, 2010). Soils with high sorption capacity serve as sink and could mobilise the emitted metals into the soil solution and taken up by plants or transported to the surface or groundwater.(Nazir et al., 2015; Sherene, 2010; Pandey and Pandey, 2009). However, where low metal concentrations are measured in soils due to poor adsorption capacity of well-drained sandy soils, as commonly found in most tropical soils (Lal, 1995), elevated metal values in plants could imply direct adsorption from atmospheric deposition (Pandey and Pandey, 2009). This observation therefore informs the need for proper assessment of atmospheric deposition of metals as a way of understanding different pathways through which metals can migrate into the food chain. Such an approach could include measurement of carbon (C) and Nitrogen (N) ratios of soil and food plants, such as fluted pumpkin leaves (*Telfaiara occidentalis*) and Cassava tuber (*Manihot occidentalis*) within densely populated areas, to assess adsorption tendencies of such food crops. Fluted pumpkin, a creeping vegetative shrub commonly grown in Africa, has nutritious leaves that are known for high adsorption capacity of toxic metals (Jnr and Spiff, 2005), whereas cassava peel has also been used for removal of metals from aqueous solution (Jorgetto et al., 2014; Nwabanne and Igbokwe, 2008).

Besides, measurement of carbon and nitrogen ratios of both soil and plants in environmental monitoring could help in the assessment of biogeochemical processes, dynamics of net N immobilization, accumulation and mineralisation (Manzoni et al., 2008). Such information could reveal the relationship between carbon input in the soil and decomposition rate of existing carbon, especially in comparing the influence of vegetation on evaporation which regulates soil microbial activities (Lange et al., 2015).

# CHAPTER 3

# MATERIALS AND METHODS

## 3.1 Study area

### 3.1.1 Location and demography

Owerri, the capital of Imo State in the southeast of Nigeria, comprises three local government areas, i.e. Owerri Municipal, Owerri North and Owerri West, with a combined land area ca. 740 $km^2$ (Ibe et al., 2001).

The city is bounded by latitudes 05° 21' N and 05° 30' N and longitudes 006° 57' E and 007° 03 E', with a population of 403,425 in 2006 (NPC, 2006), an approximately 39% increase from the 1991 census data. Nwachukwu et al. (2010) reported a population density of 1400 persons/$km^2$ within the Owerri Metropolitan area of 100 $km^2$. This high population density is most likely attributed to the high rate of rural to urban migration, resulting from the establishment of various Owerri government and privately-owned institutions, including five tertiary educational institutions. Although Owerri is predominantly an administrative city, migrants and inhabitants, who originate from various socio-cultural and political backgrounds, engage in a variety of social and economic activities including trading, craftwork, and farming.

### 3.1.2 Hydrogeology of the study area

The study area basin, the Anambra-Imo River Basin, is one of the three lithostratigraphic subdivisions of the Niger Delta basin that make up the Benin Formation. Others are the Agbada Formation (characterised by irregular units of sandstone and shale) and the shaly Akata Formation, all being located in southern Nigeria (Short and Stauble, 1967).

The Benin Formation is one of the very significant aquifers within the Niger Delta Basin as it is characterised by good groundwater transmitivity value, unconsolidated, coarse to fine-grained sands, with clay intercalations (Adelana and MacDonald, 2008; Offodile, 1992). The features of the formation are detailed elsewhere (Amadi et al., 2010; Ibe et al., 2001; Onyeagocha, 1980; Short and Stauble, 1967).

### 3.1.3 Drainage pattern

The Otamiri and Nworie Rivers, which transverse the area with a northeast to southwest direction flow pattern, drain the study area that has an average elevation of 72 m above sea level. The Nworie River covers about 9.2 km from its source, or headwater, to its confluence with the Otamiri River (Nwagbara et al., (2013) while the Otamiri River flows southwards before emptying into the River Niger near the Imo-Rivers States border (Onyekuru et al., 2014) (see Figure 3.1a). The Otamiri River, with a length of 105 km, is the major drainage unit within the study area, with the average maximum flow rate of 10.7 $m^3s^{-1}$ in the rainy season and minimum average flow rate of 3.4 $m^3s^{-1}$ in the dry season (Ibe and Njemanze, 1999). Egboka and Uma (1985) also put the total annual discharge of the Otamiri River at $1.7x\ 10^8$ $m^3$. The Owerri study area has a nearly flat terrain that experiences frequent flooding especially after heavy rain, due to blocked and inadequate drainage systems (Ibe and Uzoukwu, 2001). It has an average annual groundwater recharge of about 2.5 billion $m^3$ per year (Ijeh and Onu, 2012) with annual precipitation rate of between 1990 and 2200 mm, with a fluctuating regional temperature of 24° C to 33°C (Figure 3.1b). This high recharge rate could enhance advective flow and contaminant transport into the groundwater (Musa et al., 2013).

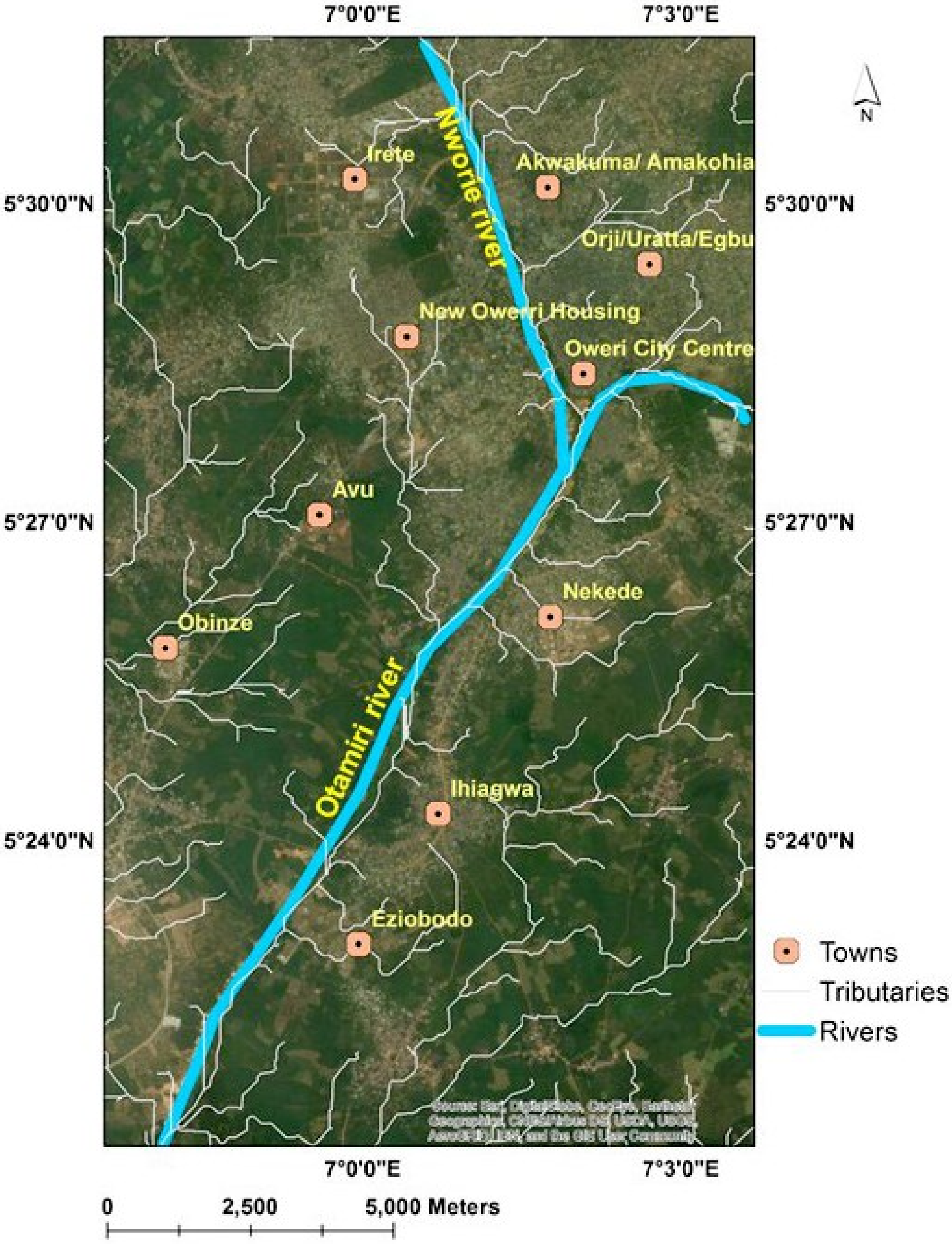


Figure 3.1a: Drainage map of the study area displaying the North-South flow direction of the two draining rivers (Nworie and Otamiri rivers). Green patches represent land cover (vegetation) which with high capacity to adsorb surficial nitrate and reduce groundwater pollution (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)

### 3.1.4 Land-use pattern and change

The increasing rate of urbanization means that the built-up area is the fastest growing land-use type in the Owerri study area (Chukwuocha, 2015; Nnaji et al.,2014) This trend has led to various forms of environmental modifications and hazards including biodiversity loss through unregulated intrusion of the riparian regions by sand miners (Chukwuocha, 2015). Table 3.1 summarises the land use changes in the area with an overall increase in built-up area and farmland, as well as decreasing vegetation, suggesting more development of impervious land surfaces due to urbanisation pressure (Okeke,2014).

Table 3.1: Decadal assessment of land use in Owerri indicating how the increasing built-up area has modified the urban environment of the study area, as adapted from (Okeke,2014).

| Decade | Residential area (%) | Urban gardens (%) | Recreational parks (%) | Conservation regions (%) | Fallowed agricultural land (%) | Rivers (Otamiri and Nworie) (%) |
|---|---|---|---|---|---|---|
| 1994 | 27.3 | n.a | n.a | n.a | 33.2 | n.a |
| 2004 | 33.7 | 16.2 | 10.9 | 5.5 | 31.1 | 2.6 |
| 2014 | 65.0 | 21.6 | 6.9 | 3.4 | 2.8 | 0.3 |

n.a. = Not available

## 3.2 Fieldwork in Owerri

A comprehensive sampling of Owerri groundwater, open waste dumpsite leachates, river water, and soils and plants was completed (Table 3.2). Fieldwork and sample collection were undertaken during two field trips to Owerri, Nigeria, between 3rd July 2015 and 25th September 2015 for the initial field season, and between 5th December 2016 and 26th January 2017, for the second season. The PhD project fieldwork timing thus broadly allowed sampling under two contrasting meteorological conditions, i.e. the rainy (2015) and dry (2016 to 2017) seasons, respectively (Figure 3.1b) and sampling points distributed as shown in (Figures 3.2, 3.3, and 3.4).

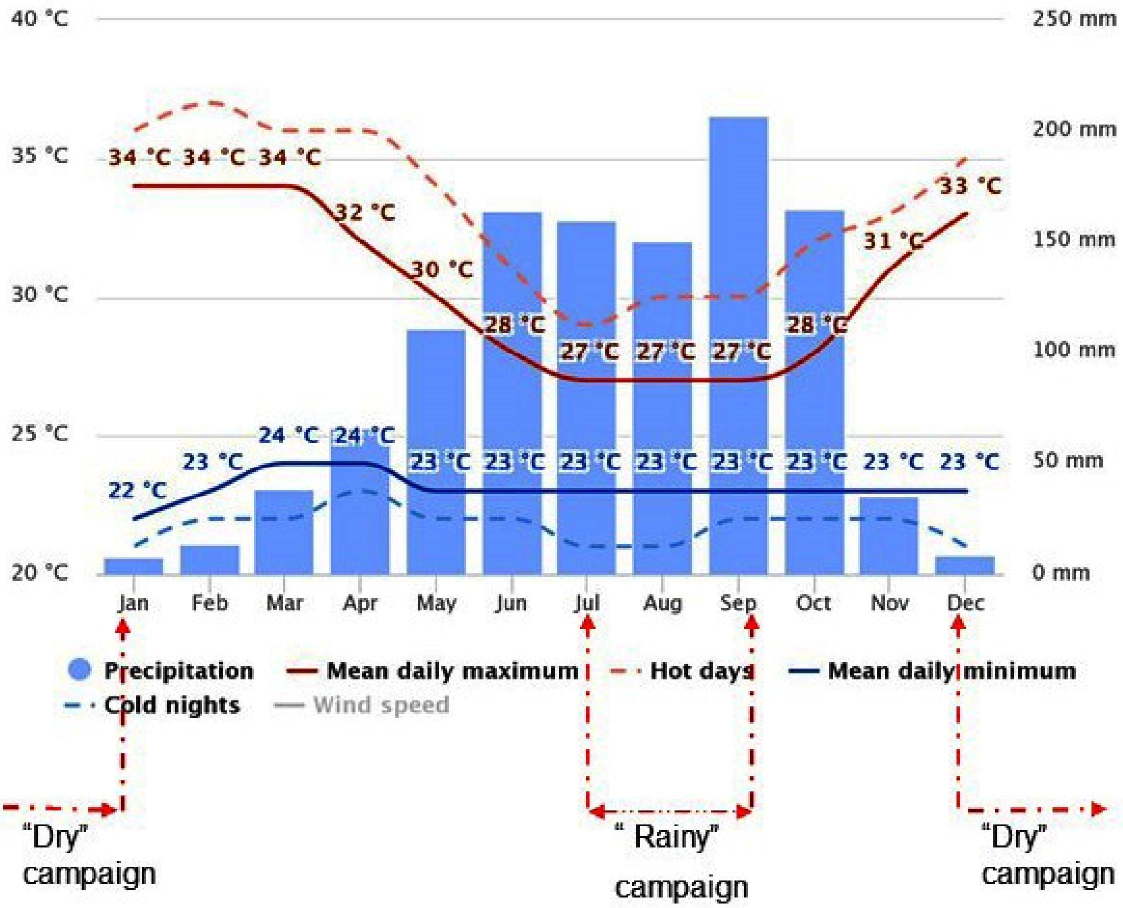
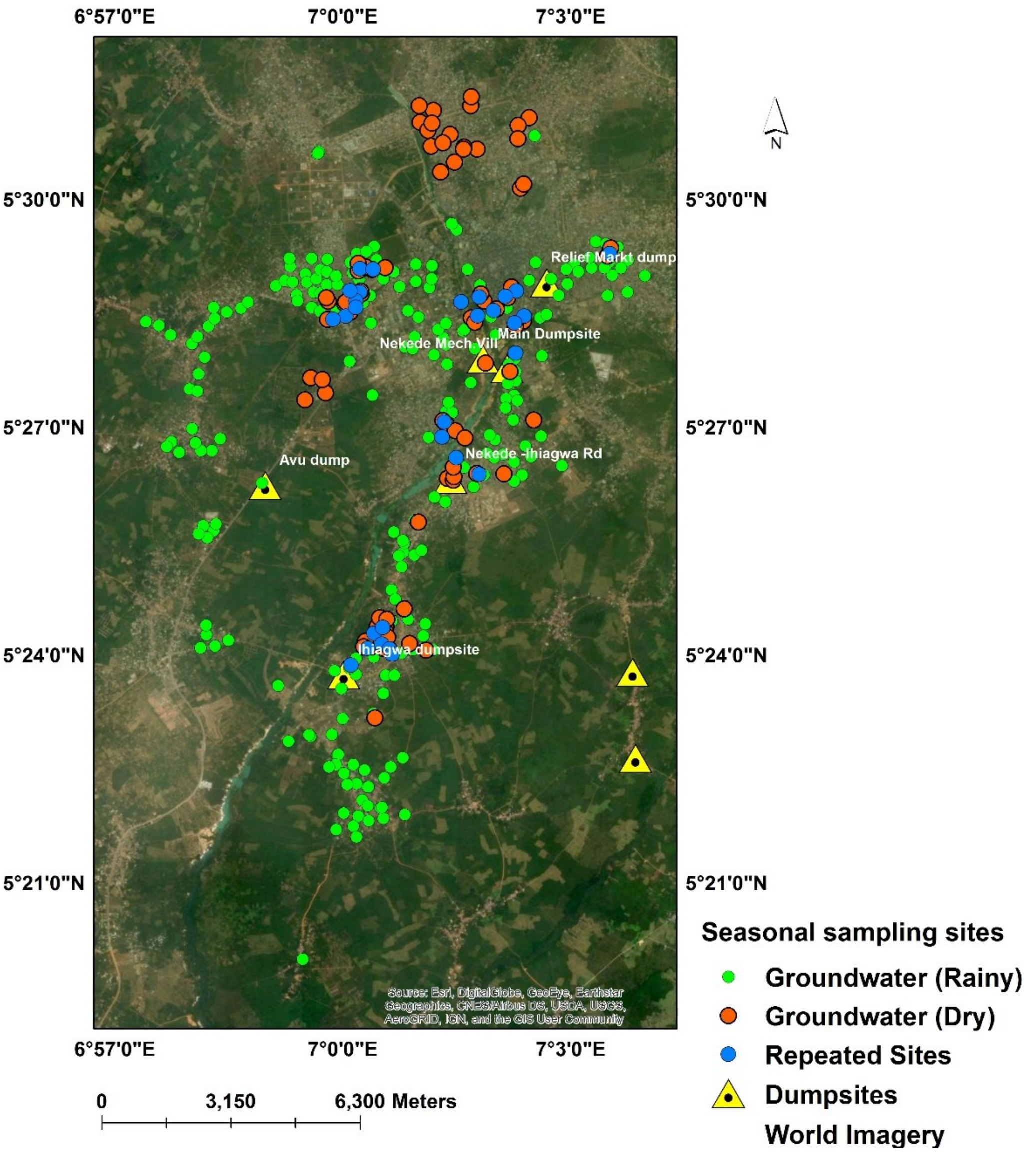


Figure 3.1b: Average temperature ($^{0}$C) and precipitation (mm) of the study area (adapted from meteoblue, 2018) displaying climatic conditions during the rainy and dry sampling seasons (campaigns). Solid red and blue lines represent the mean daily maximum and minimum temperature in a month respectively. Conversely, dashed red and lines denote temperature variabilities (hot days and cold nights) implying colder days during the rainy than dry sampling periods. Monthly precipitation values below 30mm depicts dry season, whereas values above 150mm describe frequent rainfall; hence increased groundwater recharge rate.

One overall concept was to capture the spatial variability of, and seasonal impact on, groundwater chemistry, in order to inform the development of appropriate management and remediation strategies by relevant Nigerian authorities. The first fieldwork activities, completed during the rainy season, were carried out at a sampling interval of approximately 250 m, in order to have an initial overview of potential contaminants across the Owerri study area. Subsequent laboratory activities generated datasets that informed the design of the follow-up second phase fieldwork, which focused on the investigation of the spatial extent of contaminant hotspots in groundwater.

Table 3.2: Number of environmental samples collected in Owerri, Nigeria, during the 2015 (rainy) and 2016 to 2017 (dry) fieldwork seasons. (NS = not sampled)

| **Sampling phase** | **Groundwater** | **Soil** | **River water** | **Leachate** | **Plant leaf** | **Plant tuber** |
|---|---|---|---|---|---|---|
| 1 (2015) | 270 | 190 | 16 | 75 | 106 | 88 |
| 2 (2017) | 117 | 26 | 4 | 3 | NS | NS |



Source: Esri, DigitalGlobe, GeoEye, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community

Figure 3.2: Collection points for all groundwater borehole and river samples across the Owerri study area, for the 2015 (rainy; green symbols) and 2016 to 2017 (dry; orange symbols) sampling seasons. Boreholes that were sampled during both field seasons are shown in blue. Six open waste dumpsites from which leachates were collected also are shown. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)

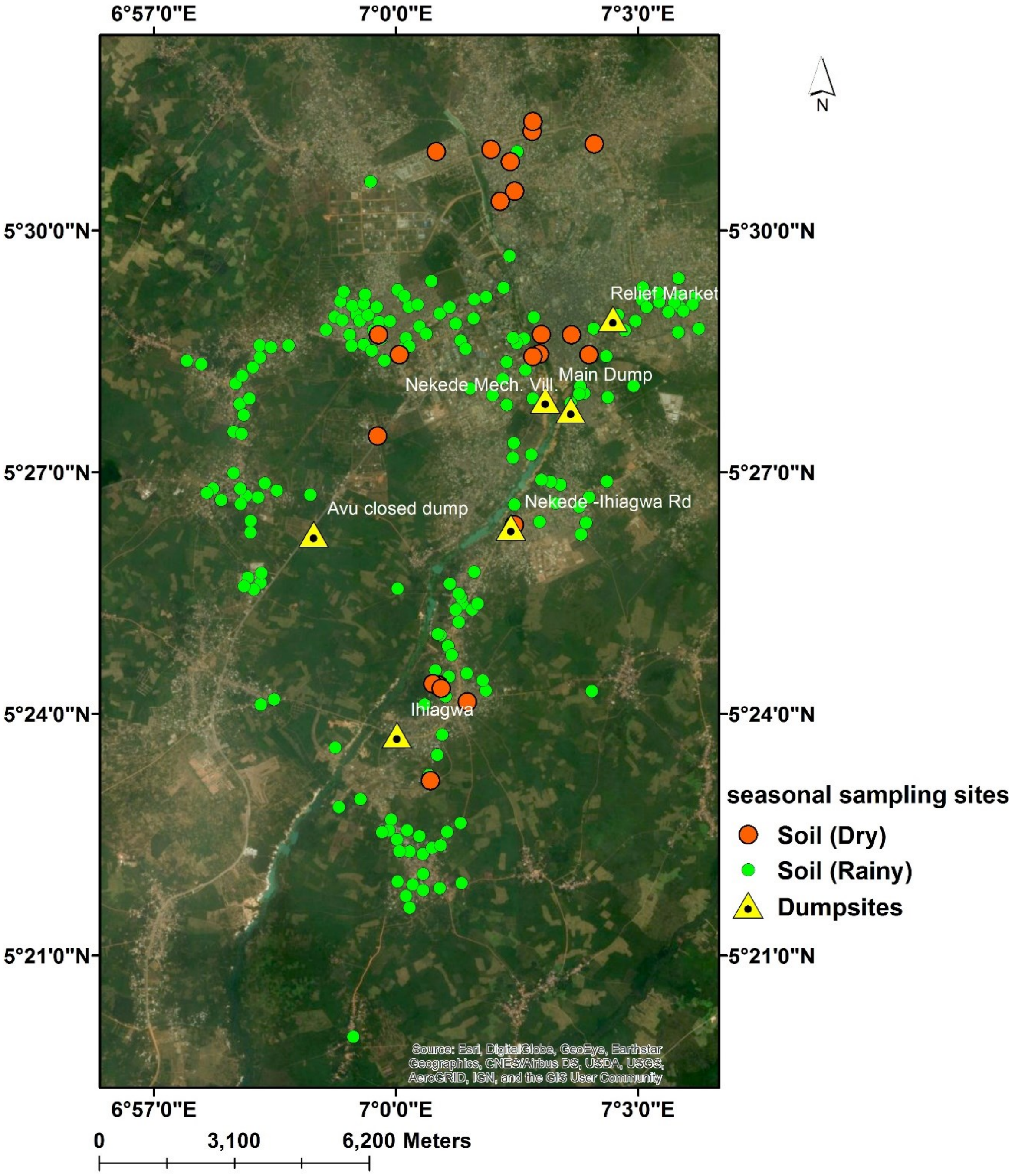


Figure 3.3: Soil sample collection points across the Owerri study area, for the 2015 (rainy; green symbols) and 2016 to 2017 (dry; orange symbols) sampling seasons. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)

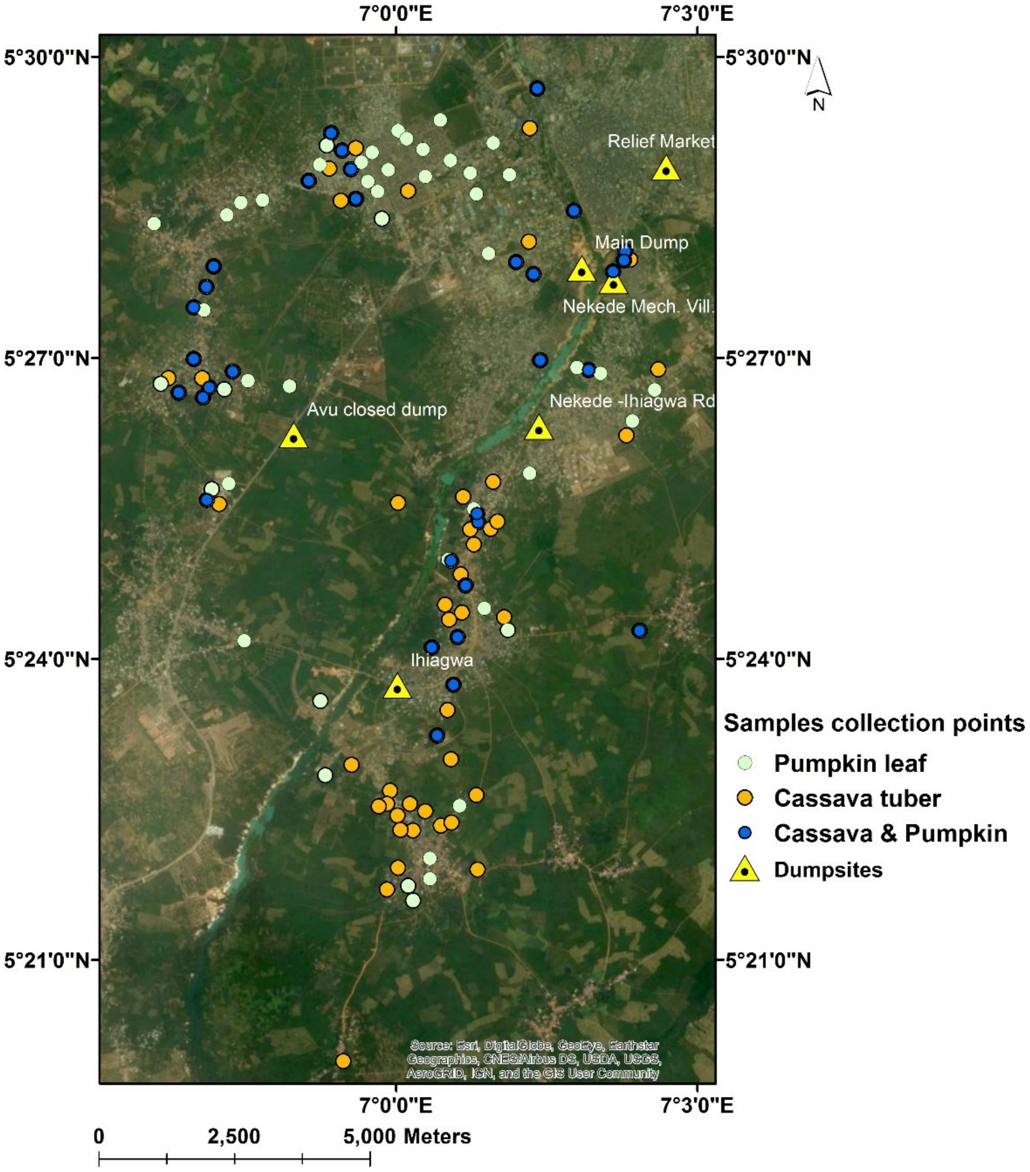


Figure 3.4: Sample collection points for the food plants *Telfaira occidentalis* (Fluted pumpkin leaf; light green symbols) and *Manihot esculanta* (Cassava tuber; orange symbols), for the 2015 rainy season. Blue symbols also indicate sampling sites where both plant species (*Telfaira occidentalis* (Fluted pumpkin leaf and *Manihot esculanta*) were collected. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)

## 3.3 Groundwater sampling and chemical analyses

Groundwater samples were collected from private boreholes drilled into the coastal plain sand (Benin Formation) aquifer, during phase one (rainy season) initially according to a sampling framework designed prior to undertaking fieldwork, which reflected spatial variability in elevation, depth to water table and population density within the Owerri study area. Dry season sampling (phase two) then targeted more detailed investigation of the spatial extent of nitrate ($NO_3^-$ ) contamination, by focusing on the ca. 13% of wells sampled during phase one that had groundwater $NO_3^-$ concentrations greater than 50 µg/mL, i.e. above the human health-based regulatory standards of the WHO and Nigeria Standard for Drinking Water Quality (NSDWQ). Considering the fact that elevated groundwater $NO_3^-$ is an indisputable indicator of anthropogenic inputs and pollution (Wendland et al., 2007; Christensen et al., 2000), 30 boreholes sampled during phase one were identified for a more detailed sampling in the dry season. This approach was designed to investigate any seasonal variability of groundwater chemistry in the study area, using this subset of sampled boreholes. Additional borehole sampling during the dry season also helped to unravel further the spatial extent of groundwater nitrate contamination, because other proximate wells also were sampled.

### Well conditions

Observations made and interviews carried out during field campaigns showed that most wells were shabbily constructed (manually drilled) with some terminated at very shallow depths of less than 15m. Borehole linings were predominantly made of poly vinyl chloride (PVC) (5 inches diameter) and protected with steel wellhead (Appendix 3B). Casing pipe diameters were determined by size of well and while choice of PVC over steel lining were mainly health and safety based, as steels are usually rusted with the potential to contaminate groundwater. PVC pipes of average length of 12ft were commonly used for both casing and screen except that the later were perforated intermittently to allow water permeability while maintaining its quality (rigidity).

### 3.3.1 Groundwater sample collection procedure and challenges

Groundwater was pumped to the surface using either electrical power or a hand-pumping technique. Initial well purging was undertaken at each sampled borehole, with three consecutive measurements of pH used as a purge adequacy parameter, i.e. once measurements stabilized within 0.1 pH unit. A one-litre plastic bottle, pre-washed with deionised water and then rinsed with the individual borehole sample water four times, was used for sample collection at each borehole. Collected groundwater samples then were rendered sterile by syringe filtration, through separate 0.2 µm Minisart® NML Plus (cellulose acetate/ glass-fibre) syringe filters (Sartorius Stadim Biotech, Germany). 10 ml of each groundwater sample was first flushed to waste through the filter before syringe filtering collected 50 ml (5 x 10 ml) in metal-free centrifuge tubes.

However, sampling in the study area often bedevilled by security challenges, encountered much hesitation from property owners. For example, out of over 1000 households approached during the initial campaign (rainy), only 270 granted access to their wells. Besides, most reluctance were caused by insistence of the research team to collect fresh samples directly from wellhead after purging in order to have a representative sample that could reflect true aquifer condition; contrary to expectations of well owners for samples collection from stored water in the overhead tank.

### 3.3.2 Measurement of *in-situ* groundwater parameters during fieldwork

During fieldwork, *in-situ* measurements of pumped groundwater sample temperature (°C), pH, electrical conductivity (EC; µs/cm) and dissolved oxygen (DO; mg/l) were undertaken using a Hanna Instrument (HI) 9828 Multiparameter with HI 769828 probe. All readings were taken after 2 minutes equilibration time. Instrument calibration followed the HI guidelines and was performed every six samples, using the HI 9828-25 quick calibration standard solution for a single-point calibration of the pH, EC and DO saturation datasets; the equipment was factory calibrated for temperature. Groundwater sample extraction and *in-situ* measurements for field parameters were taken consecutively three times at each station and average values recorded. However, flow cell was not used; precautionary measures were taken to avoid changes in characteristics of in-situ parameters such as pH, temperature, EC and DO. Pumping during samples collection were set to flow in a low and steady manner to minimize aeration while collecting samples directly from the discharge point (See Appendix 3A).for in-situ measurements carried out immediately. Collected samples were put in an insulated cooler with water ice, preserved at temperature of 4ºC in refrigerator at the collaborating laboratory (see Appendix 3C), then later transported to the UK within 3 days. All samples analysed for ion measurements were carried out within the two days while samples for metals measurements were first acidified.

### 3.3.3 Laboratory determinations of groundwater ions and metal concentrations

Within the MMU laboratory, I ml of each syringe-filtered groundwater sample was pipetted into an ion chromatography (IC) vial and introduced directly into a Thermo Scientific Dionex ICS-5000 ion chromatography system, to determine groundwater anions and cations concentrations. Three randomly selected samples were distributed repeatedly within each batch of 90 samples, these replicate measurements enabling determination of analytical precision. Seven anions (Thermo Fisher product no. 056933) and six cations (Thermo Fisher product no. 046070) calibration standard solutions were prepared at four different concentrations. The concentrations ranged between 0.025 µg/mL and 2.50 µg/mL for cations, and from 0.02 µg/mL to 2.00 µg/mL for anions, these made up in 18.2 MΩ ultra-pure deionised water, with 1 ml of the deionised water syringe-filtered into an IC vial and analysed as a blank. All groundwater samples were analysed alongside the Certified Reference Material (LGC 6020) from the UK’s Laboratory of the Government Chemist, to enable a robust assessment of the accuracy of measured groundwater anion and cation concentrations.

MMU's Thermo Scientific – iCAP6300 DUO Inductively Coupled Plasma - Optical Emission Spectrophotometry (ICP-OES) and Agilent 7900 Inductively Coupled Plasma – Mass Spectrophotometry (ICP-MS) instrumentation were used to determine groundwater metals concentrations using appropriate calibration standards. ICP - MS was used for detection of low concentration metals, such as As, Cd, Co, Cr, Cu, Ni, Pb, and V, due to its higher sensitivity. All syringe-filtered groundwater samples and Certified Reference Materials (CRMs) for metal analyses were prepared with 3% Aristar grade nitric acid ($HNO_3$), i.e. 0.3 ml $HNO_3$ and 9.7 ml of sample, for the ICP-OES. Solutions comprising 4.85 ml of sample and 0.15 ml of Aristar grade $HNO_3$ were prepared for ICP-MS analyses. An equivalent proportion of Aristar grade $HNO_3$ was scaled-up in a litre of 18.2 MΩ deionised water (Millipore water purification system), and used as acid wash during each sample sequence. Equivalent proportions of the European Reference Material (ERM® CA615) solution and Aristar grade $HNO_3$ also were prepared to validate the analytical measurement procedure. Appropriate procedural syringe-filtered blanks (for samples) and unfiltered blanks (for CRMs) were prepared using the 18.2 MΩ deionised water with the same proportion of Aristar grade $HNO_3$ as included within the samples.

All ICP-OES and ICP-MS calibration standards were prepared by dilution of stock standards in the 18.2 MΩ deionised water on a volume-by-volume dilution basis. Calibration standards for ICP-OES metals determinations were prepared by systematic dilution of a 1000 ppm multi-element stock solution (SCP Science plasma Cal) made in Switzerland and acidified to matrix-match 3% Aristar grade $HNO_3$. An ICP-OES drift monitor solution made up of 1.25ml of the standard solution and acidified deionised water was prepared. Drift monitor solutions were distributed between every 10 samples throughout each ICP-OES analytical sequence in order to identify and correct any instrumental signal drift. Similarly, calibration standards for ICP-MS were prepared by dilution of the Agilent multi-element calibration standard 2A to produce calibration solutions in a concentration range of 10 to 250 ppb (ng/ml), again using 18.2 MΩ deionised water acidified with Aristar grade $HNO_3$; calibration standards were measured from the start of the ICP-MS autosampler sequence. A 10 ppb (ng/ml) drift monitor solution also was measured repeatedly after every unknown sample or CRM to monitor and enable correction of ICP-MS instrument signal drift (which generally is significantly greater in magnitude than that observed for ICP-OES).

Thirteen elements were measured by the Agilent 7900 ICP-MS for the groundwater (and dumpsite leachate) samples (Table 3.3). The minimisation of ICP-MS polyatomic interferences was achieved by using the helium (He) collision cell technology for all measured elements (May and Wiedmeyer, 1998; Takahashi, 2014).

Table 3.3: Target metals and their possible ICP-MS polyatomic interferences (Neubauer, 2010), as measured by MMU's Agilent 7900 ICP-MS

| Isotope measured | Isotope abundance | Possible polyatomic interferences |
|---|---|---|
| **$^{51}$V** | 99.76 | $^{34}S^{16}O^{1}H+$,$^{35}Cl^{16}O+$,$^{38}Ar^{13}C+$,$^{36}Ar^{15}N+$,$^{36}Ar^{14}N^{1}H+$, $^{37}Cl^{14}N+$, $^{36}S^{15}N+$, $^{33}S^{18}O+$, $^{34}S^{17}O+$ |
| **$^{52}$Cr** | 83.76 | $^{35}Cl^{16}O^{1}H+$,$^{40}Ar^{12}C+$,$^{36}Ar^{16}O+$,$^{37}Cl^{15}N+$,$^{34}S^{18}O+$, $^{36}S^{16}O+$, $^{38}Ar^{14}N+$, $^{36}Ar^{15}N^{1}H+$,$^{35}Cl^{17}O+$ |
| **$^{55}$Mn** | 100 | $^{40}Ar^{14}N^{1}H+$,$^{39}K^{16}O+$,$^{37}Cl^{18}O+$,$^{40}Ar^{15}N+$, $^{38}Ar^{17}O+$,$^{36}Ar^{18}O^{1}H+$,$^{38}Ar^{16}O^{1}H+$,$^{37}Cl^{17}O^{1}H+$,$^{23}Na^{32}S+$, $^{36}Ar^{19}F+$ |
| **$^{57}$Fe** | 2.19 | $^{40}Ar^{16}O^{1}H+$,$^{40}Ca^{16}O^{1}H+$,$^{40}Ar^{17}O+$,$^{38}Ar^{18}O^{1}H+$,$^{38}Ar^{19}F+$ |
| **$^{59}$Co** | 100 | $^{43}Ca^{16}O+$,$^{42}Ca^{16}O^{1}H+$,$^{24}Mg^{35}Cl+$,$^{36}Ar^{23}Na+$, $^{40}Ar^{18}O^{1}H+$, $^{40}Ar^{19}F+$ |
| **$^{60}$Ni** | 26.16 | $^{44}Ca^{16}O+$,$^{23}Na^{37}Cl+$,$^{43}Ca^{16}O^{1}H+$ |
| **$^{63}$Cu** | 69.1 | $^{31}P^{16}O2+$,$^{40}Ar^{23}Na+$, $^{47}Ti^{16}O+$, $^{23}Na^{40}Ca+$, $^{46}Ca^{16}O^{1}H+$, $^{36}Ar^{12}C^{14}N^{1}H+$, $^{14}N^{12}C^{37}Cl+$, $^{16}O^{12}C^{35}Cl+$ |
| **$^{66}$Zn** | 27.81 | $^{50}Ti^{16}O+$, $^{34}S^{16}O_{2+}$, $^{33}S^{16}O^{21}H+$, $^{32}S^{16}O^{18}O+$, $^{32}S^{17}O_{2+}$, $^{33}S^{16}O^{17}O+$, $^{32}S^{34}S+$, $^{33}S_{2+}$ |
| **$^{75}$As** | 100 | $^{40}Ar^{35}Cl+$, $^{59}Co^{16}O+$, $^{36}Ar^{38}Ar^{1}H+$,$^{38}Ar^{37}Cl+$,$^{36}Ar^{39}K$, $^{43}Ca^{16}O_{2}$, $^{23}Na^{12}C^{40}Ar$,$^{12}C^{31}P^{16}O_{2+}$ |
| **$^{77}$Se** | 7.58 | $^{40}Ar^{37}Cl+$, $^{36}Ar^{40}Ar^{1}H+$, $^{38}Ar^{21}H+$, $^{12}C^{19}F^{14}N^{16}O_{2}+$ |
| **$^{111}$Cd** | 12.8 | $^{95}Mo^{16}O+$,$^{94}Zr^{16}O1H+$,$^{39}K_{2}{}^{16}O^{21}H+$ |
| **$^{136}$Ba** | 7.854 | $^{104}Ru^{16}O_{2}+$ |
| **$^{208}$Pb** | 52.4 | $^{192}Pt^{16}O+$ |

Table 3.4a and 3.4b detail the selected wavelengths for ICP-OES metals determinations and measured isotopes in ICP-MS with their respective Limits of detection (LOD) and Limits of Quantification (LOQ), which refer to the minimum concentrations of metals that can be reliably detected and quantified.

Table 3.4a: Target analytes for the groundwater metals determinations by ICP-OES, including calculated Limit of Determination (LOD) and Limit of Quantification (LOQ) defined as 3 x SD and 10 x SD, respectively, where SD is the standard deviation of 5 measured blanks. Different Ca and Mg wavelengths were measured due to suspected interferences in the first batch.

| Analyte | Wave-length (nm) | LOD µg/ml | LOQ µg/ml | LOD µg/ml | LOQ µg/ml | LOD µg/ml | LOQ µg/ml |
|---|---|---|---|---|---|---|---|
| Al | 167.0 | N.D. | N.D. | N.D. | N.D. | 0.002 | 0.005 |
| As | 193.7 | 0.001 | 0.004 | 0.002 | 0.007 | 0.004 | 0.014 |
| Ca | 317.9 | 0.003 | 0.009 | 0.009 | 0.032 | - | - |
| Ca | 422.6 | - | - | - | - | 0.085 | 0.284 |
| Cd | 214.4 | 0.00005 | 0.0002 | 0.0001 | 0.0003 | 0.0001 | 0.0004 |
| Co | 228.6 | N.D. | N.D. | N.D. | N.D. | 0.001 | 0.003 |
| Cr | 267.7 | 0.0003 | 0.001 | 0.001 | 0.002 | 0.008 | 0.026 |
| Cu | 324.7 | 0.001 | 0.004 | 0.002 | 0.008 | 0.002 | 0.005 |
| Fe | 259.9 | 0.001 | 0.004 | 0.003 | 0.011 | 0.001 | 0.003 |
| Hg | 194.2 | 0.0002 | 0.001 | 0.001 | 0.002 | N.D. | N.D. |
| K | 769.8 | 0.010 | 0.034 | 0.021 | 0.070 | 0.030 | 0.101 |
| Mg | 285.2 | 0.0003 | 0.001 | 0.001 | 0.002 | - | - |
| Mg | 280.2 | - | - | - | - | 0.036 | 0.118 |
| Mn | 257.6 | 0.0001 | 0.0002 | 0.0001 | 0.0004 | 0.0003 | 0.001 |
| Na | 589.5 | N.D. | N.D. | N.D. | N.D. | 0.408 | 1.360 |
| Ni | 231.6 | 0.0004 | 0.001 | 0.001 | 0.003 | 0.001 | 0.003 |
| P | 178.2 | N.D. | N.D. | N.D. | N.D. | 0.002 | 0.007 |
| Pb | 220.3 | 0.001 | 0.004 | 0.002 | 0.007 | 0.003 | 0.009 |
| S | 182.0 | N.D. | N.D. | N.D. | N.D. | 0.278 | 0.928 |
| Zn | 213.8 | 0.00005 | 0.0002 | 0.0002 | 0.001 | 0.007 | 0.022 |

(N.D. = Not Determined)

Table 3.4b: Target analytes for the groundwater metals determinations by ICP-MS, including Limit of Determination (LOD) and Limit of Quantification (LOQ) defined as 3 x SD and 10 x SD, respectively, where SD is the standard deviation of 5 measured blanks. LOD and LOQ values presented in this table are the overall average of 10 different batches of measurements in ICP-MS.

| Isotope measured | LOD | LOQ |
|---|---|---|
| $^{51}V$ | 0.007 | 0.022 |
| $^{52}Cr$ | 0.03 | 0.097 |
| $^{55}Mn$ | 0.07 | 0.212 |
| $^{57}Fe$ | 2.22 | 6.77 |
| $^{59}Co$ | 0.005 | 0.016 |
| $^{60}Ni$ | 5.12 | 15.4 |
| $^{63}Cu$ | 1.64 | 4.9 |
| $^{66}Zn$ | 5.81 | 19.6 |
| $^{75}As$ | 0.021 | 0.067 |
| $^{77}Se$ | 0.19 | 0.615 |
| $^{111}Cd$ | 0.019 | 0.059 |
| $^{136}Ba$ | 11.1 | 33.9 |
| $^{208}Pb$ | 0.046 | 0.217 |

### 3.3.4 Fieldwork serial nitrate ($NO_3^-$) and ammonium ($NH_4^+$) measurements

During the second fieldwork season, a programme of serial groundwater sampling and field-based measurement of nitrate and ammonium concentrations was initiated at 30 groundwater boreholes previously identified as having high nitrate. The choice of borehole sites was based on the groundwater nitrate concentration data generated for the phase one samples by the ion chromatographic technique (see Section 3.3.3). This serial sampling and measurement exercise lasted for five months, December 2016 to April 2017, being continued by my colleagues Christian Opara and Kingsley Anaele of Imo State University and the Federal University of Technology, Owerri Imo State, Nigeria, upon my return to MMU. The field-based measurements were undertaken using a portable Palintest (model 7500) instrument.44 (See Appendix 3A (iv)).

The Palintest nitrate (expressed as mg/l) technique works by adding a level spoonful of the nitrate powder and Nitratest tablet into sample solution in a 20 ml test tube. The mixture test tube was covered, shaken and gently inverted four times to aid flocculation. The solution was then allowed to stand for three minutes to ensure settlement before decanting into a 10 ml vial (Appendix 3D (i)). A Nitricol tablet was crushed and added into the solution then stirred for complete dissolution. This formed a reddish dye colour (Appendix 3D (ii)) which was further allowed to stand for 10 minutes for full-colour development. The coloured solution was then inserted into the Palintest photometer, which measures nitrate concentration proportional to the solution colour intensity. Samples containing nitrate concentrations above 20 mg/l had to be diluted with deionised water in a 50 ml test-tube, and the Palintest instrument nitrate concentration readings corrected using the dilution factor.

The Palintest ammonia (expressed as mg/l) test is a quick way of measuring ammonia (ammonical nitrogen) over the concentration range of 0 to 1.0 mg/l. It works on the principle of the reaction of alkaline salicylates with ammonia, in the presence of chlorine, to form a green-blue indophenol ($OC_6H_6NC_6H_4OH$) complex (Appendix 3D (iii)). This test incorporates catalysing reagents prepared in the form of two tablets, which are crushed and added to 10 ml of groundwater sample, then stirred for swift reaction and complete dissolution. 10 minutes were allowed for solution colour development before inserting into the Palintest photometer, which measured ammonium concentration proportional to the solution colour intensity.

### 3.3.5 Groundwater dissolved organic carbon (DOC) determinations

Groundwater dissolved organic carbon (DOC) concentrations were determined using a Shimadzu TOC-V CPN series analyser (School of Earth and Environmental Sciences, University of Manchester) directly on the syringe-filtered groundwater samples. This technique oxidises dissolved organic carbon into carbon dioxide ($CO_2$), by combustion at 680°C. A dehumidified carrier gas transports the generated $CO_2$, via a halogen scrubber, into a Non-Dispersive Infrared (NDIR) cell detector. The NDIR generates a signal peak, which is directly proportional to the concentration of the $CO_2$ and thus the DOC. This technique involves a two-phase analytical procedure that first determines the total dissolved carbon (TC) and second the total dissolved inorganic carbon (TIC); the total dissolved organic carbon then is calculated as the difference between these two values. The TC port directly connects to the combustion furnace, converting sample carbon contents to $CO_2$ in the presence of a platinum catalyst, while $CO_2$ generated in the TIC port results from an interaction of the sample inorganic carbon with a highly acidic quartz medium (Moore, 1998).

### 3.4 Open waste dumpsite leachates

Open waste dumpsite leachates were collected from 34 different points distributed across six selected open waste dumpsites (Figure 3.1), that are found within the Owerri study area (Table 3.5). Samples were collected from 8 different points at the main dumpsite in Nekede and six points at the other five dumpsites. Samples from the main dumpsite and that of Nekede-FUTO road were collected after every intense rainfall event during the fieldwork season, directly from the different plastic drain carefully inserted at the base of the solid waste heaps by this study field group. Leachates from the Nekede mechanic village, Avu, Relief market, and Ihiagwa dumpsites were sampled from trenches (dimensions 0.4 m x 0.4 m and 0.5 m depth) dug around each dumpsite, collection again also after heavy rainfall events.

All collected waste dumpsite leachate samples were first taken to the Owerri laboratory, where 30 ml of each sample was also made sterile by 0.2 μm syringe filtration (3 x 10 ml aliquots, each 10 ml passed through a new filter due to increased potential for blockages) into 50 ml metal-free centrifuge tubes. Unfiltered aliquots of each leachate sample were used to measure electrical conductivity and pH, using the Hanna Instruments multiparameter probe (see Section 3.3.2), which was washed with deionized water between samples.

Table 3.5: Summary of leachate samples collected from six open waste dumpsites in Owerri, including the number of points sampled at each dumpsite.

| **S/N** | **Dumpsite** | **Northing** | **Easting** | **Location** | **Samples collected** | **No of Points** |
|---|---|---|---|---|---|---|
| 1 | Central | 05$^{0}$27.065′ | 007$^{o}$ 01.339′ | Old Nekede Road | 31 | 8 |
| 2 | Nekede | 05° 26.315′ | 007$^{o}$ 01.419′ | Nekede/ FUTO Road | 8 | 6 |
| 3 | Mechanic Village | 05° 27.767′ | 007$^{o}$ 02.167′ | Nekede village | 7 | 6 |
| 4 | Ihiagwa | 05° 23.735′ | 007$^{o}$ 00.014 | Ihiagwa/ Obinze Road | 12 | 6 |
| 5 | Avu | 05° 26.231′ | 006$^{o}$ 58.979 | Avu/ Obinze Road | 10 | 6 |
| 6. | Relief | 05° 28.900′ | 007$^{o}$ 02.687 | Relief Market | 10 | 6 |

### 3.4.1 Leachate ions and metals determinations

Ion chromatography determination of leachate sample anions and cations concentrations followed the same technique as used for groundwater samples (see Section 3.3.3), although all leachates were diluted by a factor of 50 (0.2 ml of leachate and 9.8 ml of 18.2 MΩ deionised water) prior to analyses.

ICP-OES and ICP-MS determination of leachate metals concentrations followed the same techniques as used for groundwater samples (see Section 3.3.3). However, leachate samples were diluted with 18.2 MΩ deionised water in the ratios 1:100 and 1:10, for the rainy season and dry seasons, respectively. Such dilution could reduce the concentration of organic compounds and matrix effect that could obstruct detection and quantification of target analytes. Moderate dilution of 1:10 was then used to enable the detection and measurement of both samples with very high analytes concentration and those with lower values. 9.7 ml of each of the diluted samples were then pipetted into different 13 ml ICP tubes, acidified with 0.3 ml Aristar grade $HNO_3$ and analysed by ICP-OES. All leachate samples measured by ICP-MS were prepared with a 1:10 dilution, i.e. 1.0 ml syringe-filtered leachate sample, 8.7 ml 18.2 MΩ deionised water and 0.3 ml of Aristar grade $HNO_3$. The acid blanks used for both ICP techniques comprised 9.7 ml 18.2 MΩ deionised water and 0.3 ml $HNO_3$.

## 3.5 Soils and plants

### 3.5.1 Soil sampling, electrical conductivity and pH determinations

Where possible, soil samples were collected from the garden nearest to the sampled groundwater boreholes, using a soil auger within a specified depth of 15 cm. A 5 m × 5 m quadrat was marked in each garden, from within which five topsoil samples were randomly collected. A composite sample was obtained by homogenising those five samples within a plastic bag.

Within the Owerri laboratory, ca. 5 grams of each wet soil sample was weighed into a beaker with 12.5 ml of deionized water. The solution was vigorously stirred for about 5 seconds, then allowed to equilibrate for one hour before measurement of electrical conductivity and pH using the same equipment as described in section 3.3.2.

The remaining soil samples were air-dried in an air-conditioned room for three days, ground in a ceramic pestle and mortar and passed through a 2 mm plastic sieve. 50 g of each processed soil sample was packed in a 4 x 6mm plastic Ziploc bag, in strict adherence to the UK Department of Environment, Food, and Rural Affairs (DEFRA) guidelines on the importation of foreign soils/sediment into the UK, for the return to MMU for laboratory analyses.

### 3.5.2 Soil organic matter (SOM) determinations

The loss-on-ignition technique was used to determine the weight percentage of organic matter in all sampled soils, a technique that is based on the principle of thermal destruction of organic matter (Bengtsson and Enell, 1986; Dean Jr, 1974). Soil samples were crushed and passed through a 2 mm sieve. 2.5 g of each soil sample was weighed into pre-cleaned and oven-dried ceramic crucibles of known weight. The combined soil sample and crucible were reweighed and then oven-dried at $105^0$C (Gallenkamp hotbox oven size 2) for 24 hours to constant weight, allowed to cool and reweighed to determine the dry weight of the soil samples. These dried soils (and crucibles) were then heated in a muffle furnace at 550°C for another 5 hours, left in the furnace to cool, and finally reweighed to calculate the soil organic matter content as a percentage (Heiri et al., 2001)), where:

%SOM = (Weight at 105°C – Weight after 5 hours at 550°C)/Weight at 105°C… (3)

### 3.5.3 Soil Carbon/Nitrogen ratio (C: N) measurements

Soil samples were analysed for their carbon and nitrogen content (expressed as wt% values) using MMU's Truspec CN elemental analyser (Leco Corporation, USA), based on the Dumas method. This technique involves the direct combustion of samples in an optimized temperature zone of about 900°C, in the presence of oxygen. Carbon-containing compounds are oxidized to carbon dioxide ($CO_2$). The combustion produces nitrogen gas ($N_2$) and nitrogen monoxide (NO) species with the latter reduced back to $N_2$ by copper and dried, while the $CO_2$ is trapped. $N_2$ is then quantified in the thermal detector equipped compartment, while the carbon is quantified using an infrared gas analyser.

About 0.15 g of well-pulverized and dried ($105^0$C) soil samples were compressed into a 502-186 tin foil cup, sealed and introduced into the Truspec CN elemental analyser autosampler. Approximately 0.15 g of EDTA, having concentrations of 41.1±0.23 %C and 9.56±0.04 %N, was used as a single calibration standard, measured before each sample sequence, for drifts correction.

The automated instrumental procedural blank was run to stabilise the machine for sample analyses. 23 replicate measurements of the soil calibration samples for CHNS (Lot No. 1014) containing 2.01±0.03 %C and 0.192±0.008 %N was used as reference material to validate the analytical procedure and for quality assurance.

### 3.5.4 Soil metals determinations

Soil preparations for metals determinations followed a USEPA 3051A standard method of sample decomposition for metal analytes extraction, through conventional microwave heating with nitric acid (Link et al., 1998). 0.5 g of each soil sample was weighed into a pre-cleaned microwave digestion Teflon tube, to which 1 ml of de-ionised water was added, this solution then acidified with 10 ml of Aristar grade nitric acid.

Certified reference materials (containing the target metal analytes) was prepared in triplicate, following the same experimental procedure. The reference material used was the River Clay Sediment (LGC 6139). Teflon microwave digestion tubes were arranged within the carousel of the Mars 5 version 194A02 microwave oven (CEM (Marsxpress technology) corporation, USA), optimised at 1200W power rating and 40 mins hold time (Element, 2007). Following completion of the microwave program, nitric acid digest solutions were allowed to cool and then filtered using Whatman$^{Tm}$ (a trademark of GE Healthcare companies, China) 150 mm Qualitative filter papers into 100 ml volumetric flasks and made up to volume with 18.2 MΩ deionised water. Soil metal concentrations were only measured by ICP-OES (Table 3.6); ICP-MS was not used since all target analytes were quantified.

Table 3.6: Target analytes for the soil metals determinations by ICP-OES, including calculated Limit of Determination (LOD) and Limit of Quantification (LOQ) defined as 3 x SD and 10 x SD, respectively, where SD is the standard deviation of 25 measured blanks. These values have been corrected for the dilution factors (applied during soil digest); hence, detection limits are within the solid soil samples.

| **Analytes** | **Wavelength (nm)** | **Phase 1** | **Phase 1** | | **Phase 2** | **Phase 2** |
|---|---|---|---|---|---|---|
| | | LOD µg/g | LOQ µg/g | | LOD µg/g | LOQ µg/g |
| **Al** | 396.1 | 3.44 | 5.73 | | 0.746 | 2.49 |
| **As** | 189.0 | 1.24 | 2.07 | | 0.130 | 0.434 |
| **Ca** | 422.6 | 83.3 | 138.8 | | 52.5 | 175.1 |
| **Cd** | 214.4 | 0.365 | 0.609 | | 0.005 | 0.017 |
| **Cd** | 228.8 | 0.361 | 0.601 | | 0.016 | 0.054 |
| **Co** | 228.6 | 0.350 | 0.583 | | 0.060 | 0.199 |
| **Cr** | 267.7 | 0.409 | 0.681 | | 0.043 | 0.142 |
| **Cr** | 284.3 | 0.388 | 0.646 | | 0.196 | 0.653 |
| **Cu** | 324.7 | 0.600 | 1.00 | | 4.13 | 13.8 |
| **Fe** | 240.4 | 4.43 | 7.39 | | 1.37 | 4.56 |
| **K** | 766.4 | 3.86 | 6.43 | | 4.09 | 13.6 |
| **K** | 769.8 | 10.4 | 17.4 | | 3.55 | 11.8 |
| **Mg** | 280.2 | 13.1 | 21.8 | | 27.5 | 91.8 |
| **Mn** | 257.6 | 0.455 | 0.759 | | 0.025 | 2.42 |
| **Na** | 589.5 | 208.5 | 347.5 | | 12.7 | 42.2 |
| **Ni** | 231.6 | 0.493 | 0.822 | | 0.075 | 0.251 |
| **P** | 177.4 | 1.87 | 3.12 | | 0.199 | 0.662 |
| **P** | 178.2 | 1.93 | 3.21 | | 0.285 | 0.949 |
| **Pb** | 220.3 | 0.342 | 0.570 | | 0.112 | 0.372 |
| **Zn** | 206.2 | 4.25 | 7.09 | | 6.39 | 21.3 |

## 3.6. Plant sampling

The cassava tuber (*Manihot esculanta*) and fluted pumpkin leaf (*Telfaira occidentalis*) are the most frequently grown and most affordable food crops within gardens and farmlands in the Owerri study area. These were sampled only during fieldwork season one (i.e. the rainy season) because the subsequent dry season was too dry to sample plants.

Edible parts of the fluted pumpkin leaf were plucked, washed with 18.2 MΩ deionised water and subsequently placed on foil in an oven to dry at 60ºC for 18 hours. Cassava tubers were uprooted, periderm and cortex removed by peeling, and 10 $cm^3$ sub-samples cut out using a knife. These sub-samples then were oven dried at 80ºC for 24 hours. Each of the dried plant samples was pulverised, using a plastic pestle and mortar, and sieved through a 2 mm plastic sieve. 50 g of each of the processed plant samples was packed in a plastic Ziploc bag and shipped to the MMU laboratory.

### 3.6.1 Plant metals determinations

Approximately 0.4 g of the cassava tuber (*Manihot esculanta*) and 0.25 g of the fluted pumpkin leaf (*Telfaira occidentalis*) were weighed into microwave digestion Teflon tubes, to which 5 ml of Aristar grade nitric acid and 1 ml of 18.2 MΩ deionised water were added prior to microwave digestion. 0.4 g of the Certified Reference Material LGC 7162 *Strawberry Leaves* (Batch: 001, sample: 0682; Laboratory of the Government Chemist, Middlesex, UK) was also prepared (seven replicates). Digestion followed the same experimental procedure as used for soils, but the filtered solutions were made up within a 50 ml volumetric flask. Table 3.7 details the metals measured in the plants using ICP-OES (ICP-MS was not used for plant samples as all target analytes were quantified), as well as the limits of detection (LODs and LOQs) for the two measurement batches.

Table 3.7: Target analytes for metals determinations in Fluted pumpkin leaf (*Telfaira occidentalis*) and Cassava tuber (*Manihot esculanta*) by ICP-OES, including calculated Limit of Determination (LOD) and Limit of Quantification (LOQ) defined as 3 x SD and 10 x SD, respectively, where SD is the 25 standard deviation of measured blanks. These values have been corrected for the dilution factors (applied during soil digest); hence, detection limits are within the solid plant samples.

| | | **Fluted Pumpkin (*Telfaira occidentalis*)** | | **Cassava tuber (*Manihot esculanta*)** | |
|---|---|---|---|---|---|
| **Analyte** | Wavelength (nm) | LOD µg/g | LOQ µg/g | LOD µg/g | LOQ µg/g |
| **Al** | 396.1 | 1.31 | 4.39 | 1.27 | 4.23 |
| **As** | 189.0 | 0.016 | 0.053 | 0.015 | 0.051 |
| **Ca** | 422.6 | 254.2 | 847.2 | 61.2 | 204.1 |
| **Cd** | 214.4 | 0.001 | 0.002 | 0.001 | 0.002 |
| **Cd** | 228.8 | 0.001 | 0.004 | 0.001 | 0.003 |
| **Co** | 228.6 | 0.002 | 0.007 | 0.002 | 0.007 |
| **Cr** | 267.7 | 0.005 | 0.015 | 0.005 | 0.016 |
| **Cr** | 384.3 | 0.059 | 0.198 | 0.063 | 0.210 |
| **Cu** | 324.7 | 0.291 | 0.970 | 0.255 | 0.850 |
| **Fe** | 240.4 | 3.48 | 11.6 | 3.23 | 10.8 |
| **K** | 769.8 | 18.7 | 62.3 | 11.6 | 38.7 |
| **Mg** | 280.2 | 28.7 | 95.7 | 6.92 | 23.1 |
| **Mn** | 257.6 | 0.111 | 0.371 | 0.010 | 0.033 |
| **Na** | 589.5 | 180.6 | 602.0 | 222.0 | 740.1 |
| **Ni** | 231.6 | 0.069 | 0.230 | 0.004 | 0.014 |
| **P** | 178.2 | 0.844 | 2.814 | 0.840 | 2.80 |
| **Pb** | 220.3 | 0.009 | 0.029 | 0.009 | 0.030 |
| **Zn** | 206.2 | 2.56 | 8.53 | 1.26 | 4.20 |

## 3.7 River water samples and *in-situ* measurements

River water samples were collected from 16 different points along the Otamiri and Nworie Rivers direct from the flowing water (Figure 3.1). These sampling points were selected to identify potential contaminant entry points into the river water bodies as presented in Table 3.7.

Samples were collected by grab-sampling technique, upstream of swimming or sand mining areas, while standing on the edge of the riverbank. The choice of edge of the river for samples collection was because it could represent prevalent aquatic condition based on the identified potential contaminant entry points.

Pre-washed plastic containers were rinsed three times with river water at each point of collection and then filled with samples. Subsequently, the collected river water samples were sterilised by 0.2 µm syringe filtration (5 x 10 ml aliquots, using a single different filter for each sample) into new 50 ml metal-free centrifuge tubes and labelled. *In-situ* measurements of temperature ($^{0}$C), pH, electrical conductivity (µs/cm) and dissolved oxygen (mg/l) were measured using the same equipment as for the groundwater samples (see Section 3.3.2).

Table 3.8: Sampling points and potential pollution sources and activities along the two rivers (Otamiri and Nworie) draining the study area.

| River sampling points | Coordinates (Northings; Eastings) | Potential pollution sources or activities |
|---|---|---|
| Otamiri river head | $05^{0}$ 28.105'; $07^{o}$03.484' | Farming and swimming |
| Otamiri river 2 | $05^{0}$ 28.314'; $07^{o}$02.502' | Sand excavation |
| Otamiri Nworie confluence | $05^{0}$ 27.979'; $07^{o}$02.078' | Mechanic village dumpsite |
| Otamiri river 4 | $05^{0}$ 26.506'; $07^{o}$01.232' | Domestic/Poultry waste |
| Otamiri river 5 | $05^{0}$ 26.306'; $07^{o}$01.213' | Sand excavation |
| Otamiri river 6 | $05^{0}$ 26.700'; $07^{o}$00.774' | Domestic/Poultry waste |
| Otamiri river 7 | $05^{0}$ 25.503'; $07^{o}$00.430' | Domestic/Poultry waste |
| Otamiri river 8 | $05^{0}$ 25.017'; $07^{o}$00.413' | Sand excavation |
| Otamiri river 9 | $05^{0}$ 24.900'; $07^{o}$00.354' | Sand excavation |
| Otamiri river 10 | $05^{0}$ 23.429'; $06^{o}$59.461' | Sand excavation/farming |
| Nworie river head | $05^{0}$ 31.501'; $07^{o}$00.630' | Sand dredging |
| Nworie river 2 | $05^{0}$ 31.270'; $07^{o}$00.751' | Sand dredging |
| Nworie river 3 | $05^{0}$ 29.741'; $07^{o}$01.306' | Sand excavation |
| Nworie river 4 | $05^{0}$ 26.408'; $07^{o}$01.456' | Hospital waste |
| Nworie river 5 | $05^{0}$ 28.470'; $07^{o}$01.776' | Akachi closed dumpsite |
| Nworie river 6 | $05^{0}$ 28.032'; $07^{o}$01.968' | Main dumpsite |

## 3.8 Spatial measurements and analyses

### 3.8.1 Sample coordinates

During fieldwork, the latitude and longitude of each sampling station were recorded with a hand-held GPS map 62 unit (Garmin International, Inc., USA). These coordinates, measured in degrees, minutes and seconds, subsequently were converted to decimal degrees for the plotting and analysis of data within ArcMap version 10.2. Distances between a well and potential pollution sources were extracted from the coordinates of the target points (well to dumpsite and well to septic tanks), using the near (analysis) tool in ArcMap. Prior to extraction of a distance the coordinates originally recorded in decimal degree (Geographical Coordinate System (GCS) 1984) were projected to the x-y Projection Coordinate System (PCS) WGS,1984_UTM, ZONE 32N in metre using the data management's projection and transformation feature tool in ArcMap. Nigeria Map was downloaded from the National Geographic World Map, while river shapefile of the study area was downloaded from the Opens database Geofabrik, extracted in ArcMap.

### 3.8.2 Contaminant distribution patterns and spatial interpolations

The concentrations and spatial distribution pattern of measured groundwater, soil and plant (*Manihot esculanta* and *Telfaira occidentalis*) parameters have been displayed at each of the sampling points in ArcMap. Concentrations of each of the reported parameters are represented using symbols with graduated sizes. Spatial interpolation of datasets was done using the Empirical Bayesian Kriging technique in the geostatistical analyst of ArcMap. This method is preferred to other kriging techniques due to its ability to accurately account for errors introduced by estimating the underlying semivariogram (Network, 2011) (See Chapter 2, Section 2.4.2).Both interpolation and standard error maps of relevant datasets in this study are produced by this technique (See Chapter 5, Section 5.7).

## 3.9 Multivariate statistical analysis of groundwater datasets

Multivariate statistical methods have been widely applied in the evaluation of various environmental processes (Belkhiri and Narany, 2015). Analyses of variance (ANOVA) was applied on the groundwater to identify hydrogeochemical variability in relation to nitrate concentration at different regions of depths to the water table and urbanisation in the study area (See Chapter 5, Section 5.3). All datasets were tested for skewness, which assessed the probability distribution of each variable about its mean and a $\text{Log}_{10}$ transformation was applied to all skewed datasets to ensure a normal distribution of the datasets prior to analysis.

# CHAPTER 4

# RESULTS

This results chapter presents the descriptive statistics of all analysed samples in the order: groundwater, dumpsite leachate, soil, plants and river water. All datasets are summarised using mean and standard deviation to describe normally distributed data while skewed values are presented with median and quartiles. Datasets generated from samples collected during rainy (2015) and dry seasons (2016 -2017) are presented in this chapter, while the analyses of variances, correlations and clustering as well as the principal components analysis are presented in Chapter 5.

Whereas some analytes showed measurable values during analysis, others such as $PO_4$, $NO_2$, $Fl^-$, $NH_4^+$, P as well as metals (except Pb, Mn, Cd), displayed concentrations below lower limits of detection (see Section 4.2) – as such they are not reported. The chapter also reports the general chemical datasets of soil samples collected from the study area, including attributes such as percentage soil organic matter (SOM) as well as the carbon: nitrogen (C:N) ratio for both soil and plant samples.

## 4.1 Field-based measurements of groundwater characteristics

Results of *in-situ* measurements of field parameters (temperature, pH, electrical conductivity and dissolved oxygen) are summarised in Table 4.1, while a brief description of their concentrations in the rainy and dry seasons is outlined below. Concentrations and distribution patterns of the parameters measured are shown in Figures 4.1 (a-d), 4.2 & 4.3 respectively.

Table 4.1: Descriptive summary of *in-situ* measured groundwater parameters in Owerri, Nigeria.

| | **Variable** | | | | |
|---|---|---|---|---|---|
| | **Temp.** | **pH** | **EC** | **DO** | **TDS** |
| **Unit** | ($^0$C) | | μScm$^{-1}$ | (μg/mL) | |
| **Median** | 27.6 | 4.90 | 36.0 | 2.93 | 23.0 |
| **Standard Deviation** | 0.80 | 1.40 | 81.4 | 1.74 | 52.1 |
| **Minimum** | 26.7 | 3.20 | 10.0 | 7.60 | 6.40 |
| **Maximum** | 32.0 | 8.90 | 489 | 15.9 | 313 |

**Temperature:** Median temperature values for the rainy and dry seasons were 27.8$^0$C (IQR = 27.5$^0$C - 28.1$^0$C) and 28.4$^0$C (IQR = 28.0$^0$C - 28.9$^0$C) respectively.

**pH:** Median pH value of 3.80 (IQR = 3.50 – 4.10) was recorded in the rainy season, while the recorded dry season value is 6.90 (IQR = 6.60 – 8.90).

**Electrical Conductivity (μS/cm)** Median value in the rainy season was 31.0 μS/cm (IQR = 15.8 – 78.3 μS/cm), whereas 53.5 μS/cm (IQR = 32.3 – 167.5 μS/cm) was recorded in the dry season.

**Dissolved Oxygen (DO):** Median concentrations in the rainy and dry seasons were 9.70 μg/mL (IQR = 7.0 – 11.5 μg/mL) and 6.4 (IQR = 5.9 – 6.9) respectively.

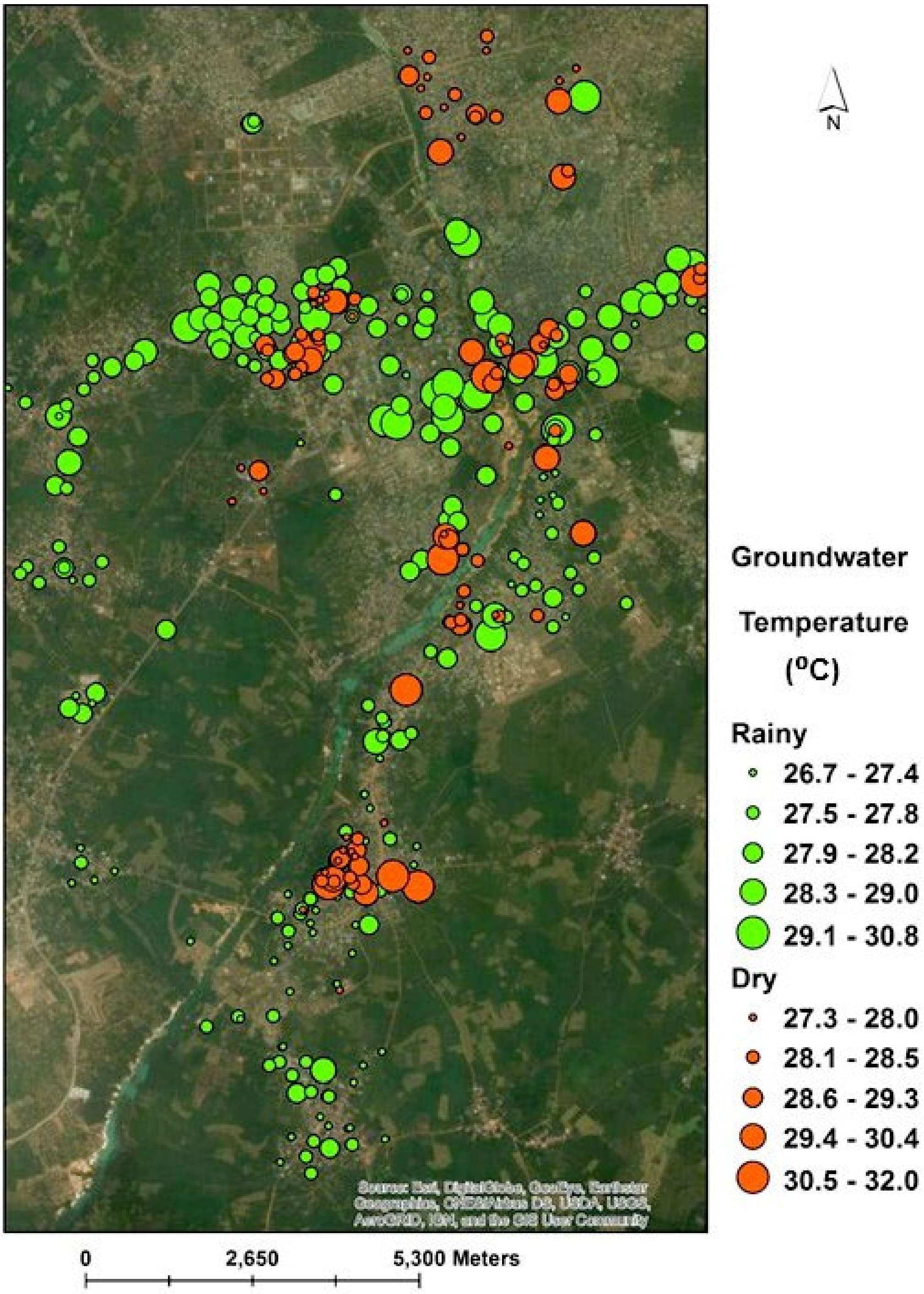
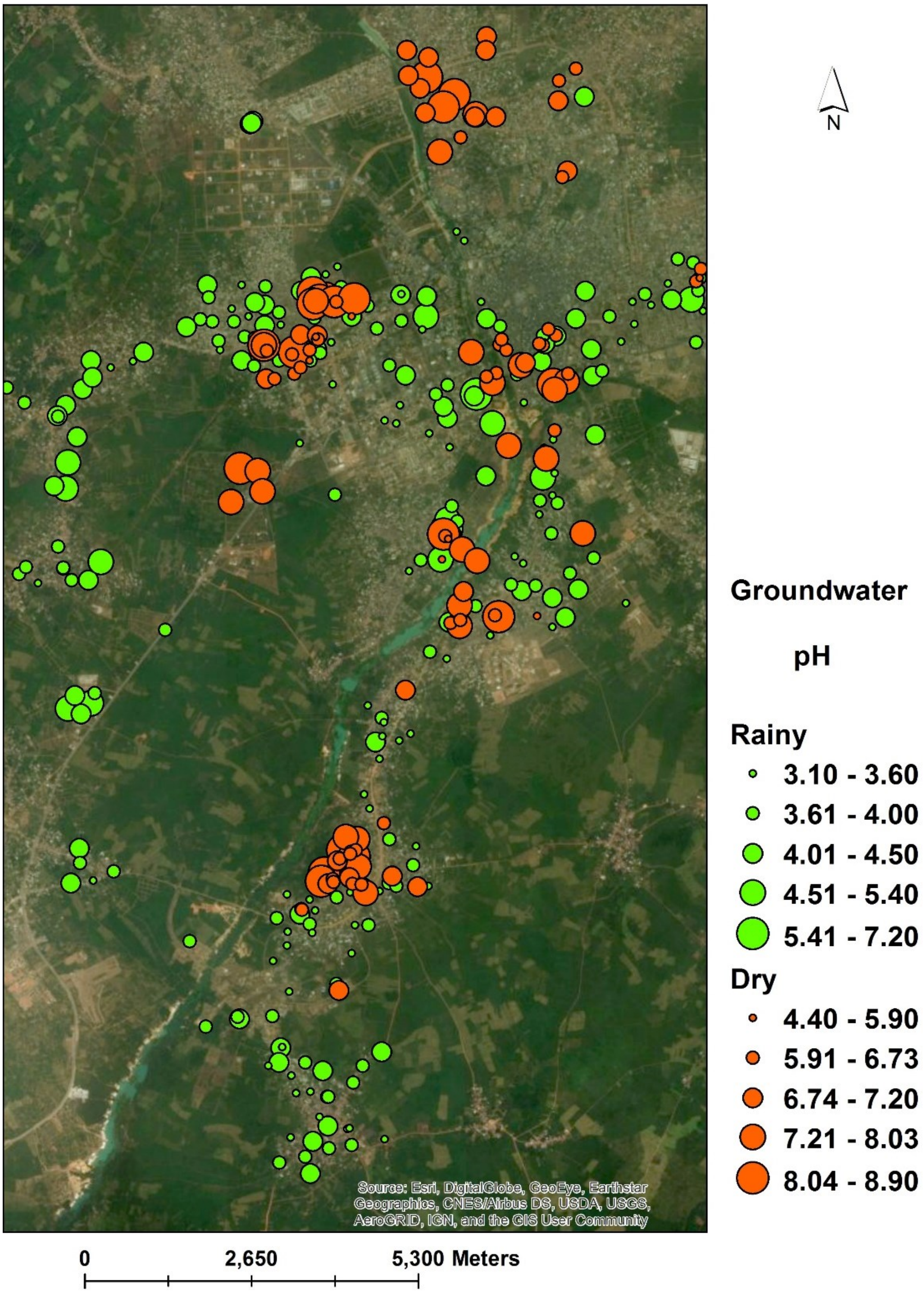


Figure 4.1a: Groundwater temperature measured during two sampling seasons in Owerri, Nigeria. Green symbols represent the rainy season, while orange signifies the dry season. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)



Source: Esri, DigitalGlobe, GeoEye, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community

Figure 4.1b: Groundwater pH measured during two sampling seasons in Owerri, Nigeria. Green symbols represent rainy season, while orange signifies dry season. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)

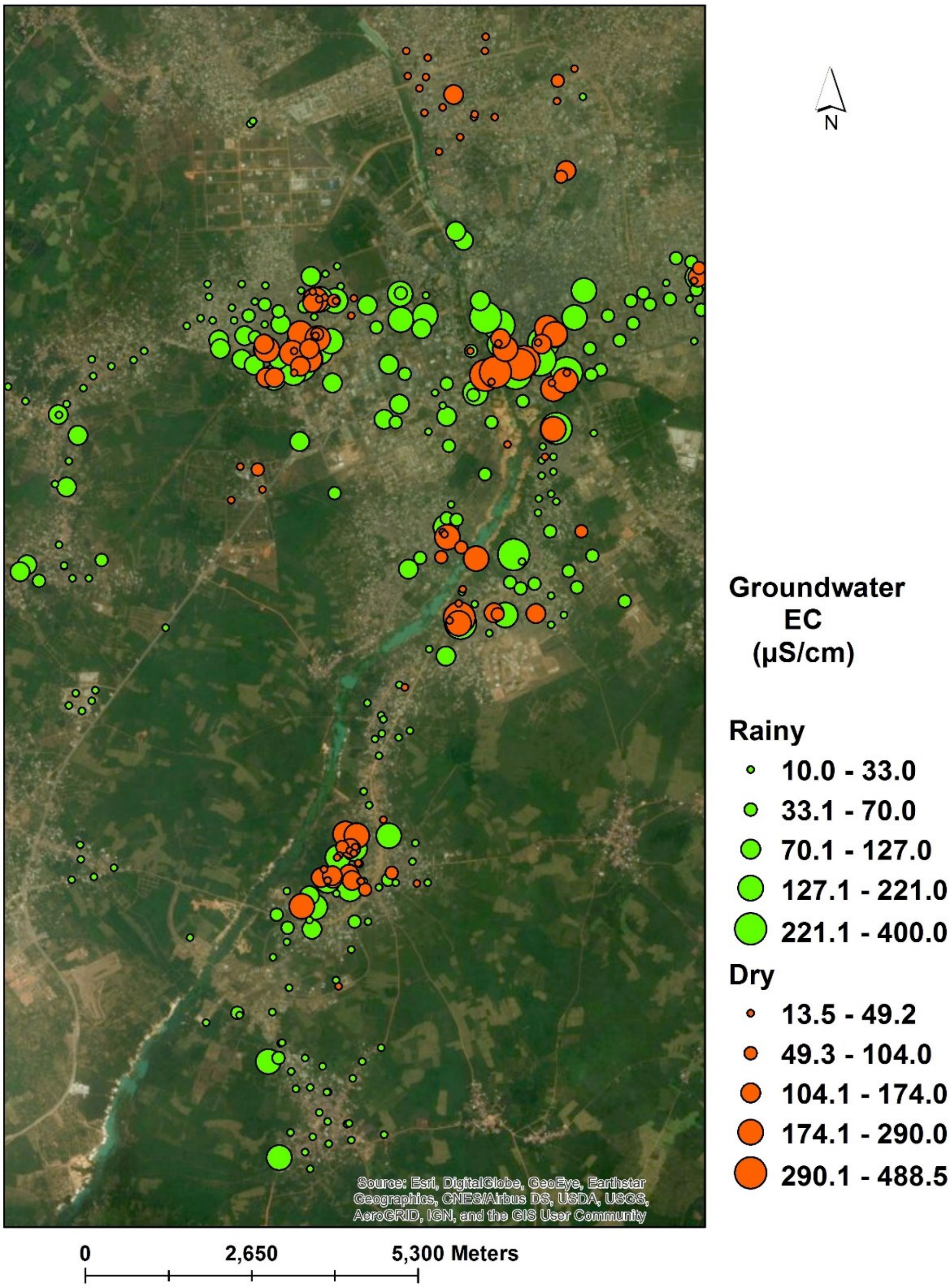


Figure 4.1c: Groundwater Electrical Conductivity (EC) measured during two sampling seasons in Owerri, Nigeria. Green symbols represent rainy season, while orange signifies dry season. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)

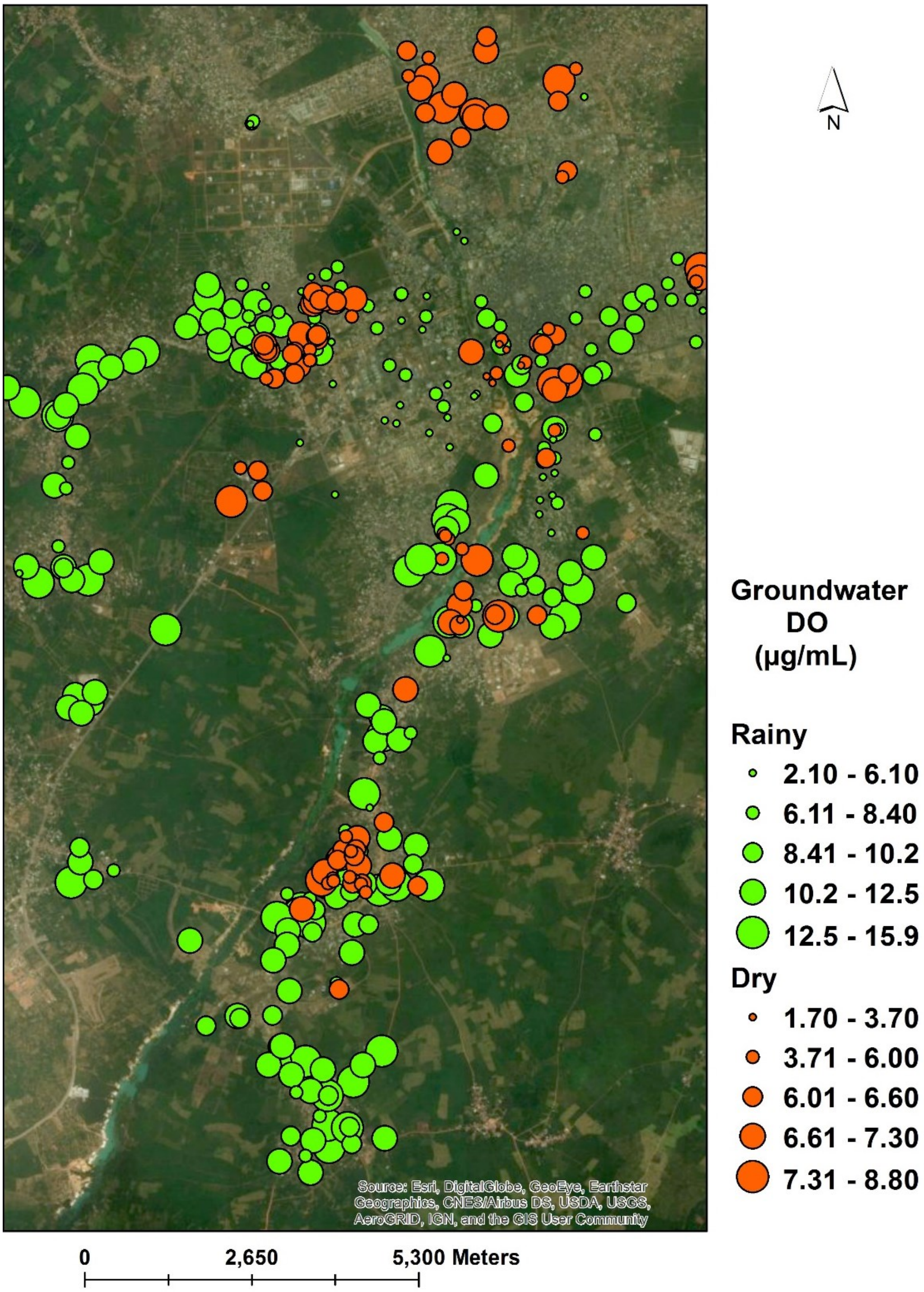


Figure 4.1d: Groundwater dissolved oxygen (DO) measured during two sampling seasons in Owerri, Nigeria. Green symbols represent rainy season, while orange signifies dry season. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)

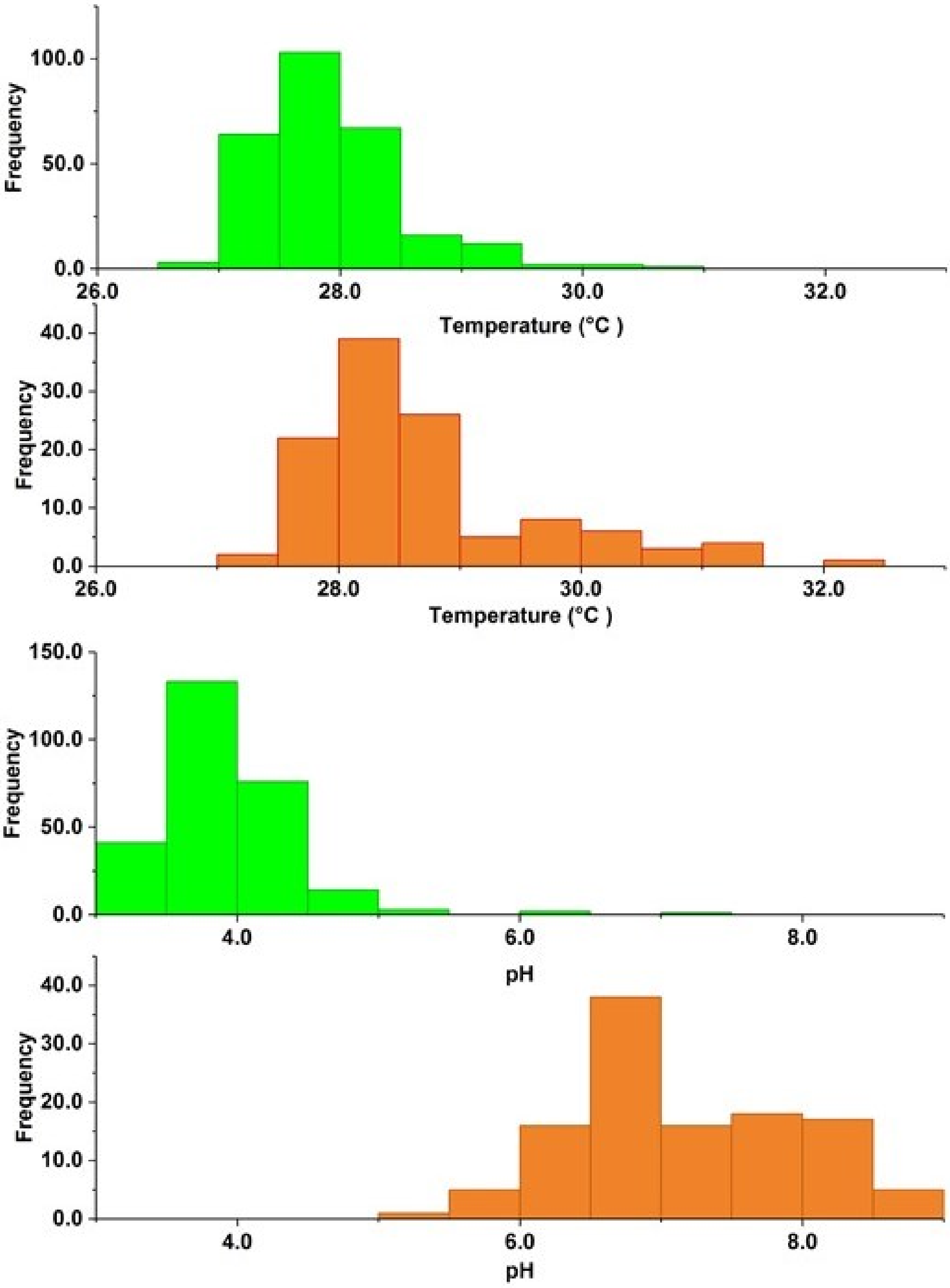


Figure 4.2: Groundwater temperature and pH in the two sampling seasons in Owerri Nigeria, displaying a non-parametric distribution pattern (except for pH in the rainy seasons). Green symbols/bars represent rainy season samples and orange represent dry season samples.

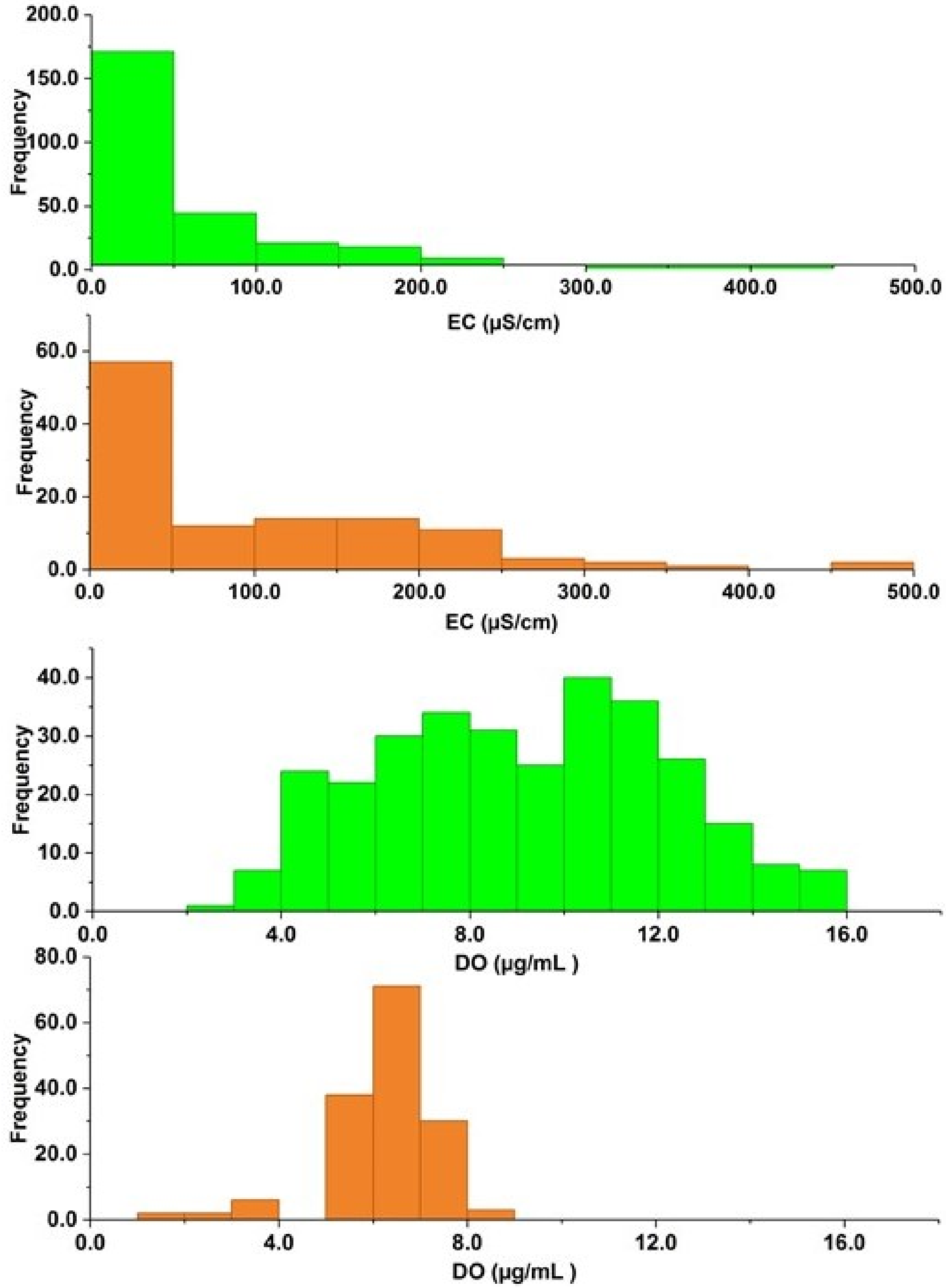


Figure 4.3: Groundwater EC and DO in the two sampling seasons displaying their non-parametric distribution pattern. Green symbols represent rainy season variables; orange bars represent dry season values.

## 4.2 Chemical characterisation of samples

**Two terms - Limit of detection (LOD) and quantification (LOQ) – are used here.** LOD used in all sample analyses refers to the lowest concentration of analytes that can be reasonably detected during an analytical process. LOQ implies the lowest concentration of an analyte that can be quantified with accuracy and precision. Both LOD and LOQ were calculated based on the respective signal-to-noise ratio of 3:1(3*SD) and 10:1(10*SD); where SD refers to the standard deviation of measured blanks (Armbruster and Pry, 2008; Lawson, 1994).

### 4.2.1 Evaluation of analytical accuracy and precision using results of replicate samples of groundwater and the certified reference materials (CRM) for ion chromatography

As a quality assurance/control (QA/QC) technique, randomly selected samples were replicated during the analyses and results showed good precision with less than 5 % relative standard deviation values (Table 4.2). In addition, samples were analysed by ion chromatography together with CRM- 6020 produced by the Laboratory of Government Chemist (LGC), Teddington, UK. Percentage recovery for target anions ($NO_3^-$, $SO_4^-$ and $Cl^-$) were all within the range of 90.0% - 110.0% and consistent with the acceptable standard for groundwater ion analyses stipulated in the USEPA methods 300.0(9.3); except for $Fl^-$ with 78.0% (Pfaff, 1993). However, other analytes like Ammonium ($NH_{4+}$) and Lithium (Li) were detected at very low concentrations – these are not reported.

Table 4.2: Replicate analyses of randomly selected groundwater samples used as additional quality assurance technique of assessing analytical precision in ion chromatography

| **Label** | **$\text{Fl}^{-}$ (µg/ml)** | **$\text{Cl}^{-}$ (µg/ml)** | **$\text{SO}_4^{-}$ (µg/ml)** | **$\text{NO}_3^{-}$ (µg/ml)** | **$\text{Na}^{+}$ (µg/ml)** | **$\text{K}^{+}$ (µg/ml)** |
|---|---|---|---|---|---|---|
| **GWA 01** | 0.161 | 26.8 | 0.751 | 116.4 | 24.6 | 10.4 |
| | 0.171 | 26.9 | 0.853 | 117.2 | 25.3 | 10.8 |
| | 0.167 | 26.3 | 0.765 | 114.4 | 25.2 | 10.7 |
| MEAN | 0.166 | 26.7 | 0.789 | 116.0 | 25.0 | 10.6 |
| STDEV. | 0.005 | 0.301 | 0.055 | 1.43 | 0.358 | 0.223 |
| % RSD | 3.10 | 1.13 | 7.02 | 1.23 | 1.43 | 2.10 |
| **GWA02** | 0.111 | 7.21 | 1.85 | 31.8 | 6.90 | 2.08 |
| | 0.115 | 7.03 | 1.78 | 30.9 | 6.84 | 2.01 |
| | 0.114 | 7.14 | 1.79 | 31.1 | 6.83 | 2.01 |
| MEAN | 0.113 | 7.13 | 1.81 | 31.3 | 6.86 | 2.03 |
| STDEV. | 0.002 | 0.089 | 0.040 | 0.452 | 0.033 | 0.040 |
| % RSD | 1.72 | 1.25 | 2.20 | 1.44 | 0.475 | 1.97 |
| **GWA03** | 0.034 | 2.55 | 0.651 | 9.66 | 3.70 | 0.705 |
| | 0.029 | 2.55 | 0.651 | 9.54 | 3.68 | 0.883 |
| | 0.029 | 2.58 | 0.668 | 9.74 | 3.60 | 0.665 |
| MEAN | 0.031 | 2.56 | 0.657 | 9.65 | 3.66 | 0.751 |
| STDEV. | 0.003 | 0.018 | 0.010 | 0.100 | 0.057 | 0.116 |
| % RSD | 9.49 | 0.695 | 1.500 | 1.04 | 1.56 | 15.5 |
| **GWY07** | 0.020 | 2.77 | 0.455 | 17.7 | 5.51 | 0.481 |
| | 0.020 | 2.78 | 0.452 | 17.8 | 5.56 | 0.516 |
| | 0.022 | 2.88 | 0.492 | 18.4 | 5.69 | 0.645 |
| MEAN | 0.021 | 2.81 | 0.466 | 17.9 | 5.58 | 0.548 |
| STDEV. | 0.001 | 0.064 | 0.022 | 0.376 | 0.092 | 0.086 |
| % RSD | 3.53 | 2.26 | 4.762 | 2.10 | 1.65 | 15.8 |
| **GWZ01** | 0.037 | 5.66 | 0.225 | 37.9 | 8.57 | 1.16 |
| | 0.037 | 5.62 | 0.225 | 37.6 | 8.57 | 1.19 |
| | 0.037 | 5.70 | 0.233 | 38.0 | 8.56 | 1.21 |
| MEAN | 0.037 | 0.060 | 0.227 | 37.9 | 8.57 | 1.18 |
| STDEV. | 0.000 | 0.025 | 0.005 | 0.19 | 0.003 | 0.027 |
| % RSD | 0.000 | 41.4 | 2.17 | 0.49 | 0.037 | 2.31 |
| **GWZ02** | 0.045 | 5.87 | 0.409 | 34.6 | 8.40 | 1.99 |
| | 0.043 | 6.03 | 0.426 | 35.5 | 8.53 | 2.08 |
| | 0.042 | 5.78 | 0.404 | 34.1 | 8.52 | 2.03 |
| MEAN | 0.043 | 5.89 | 0.413 | 34.7 | 8.48 | 2.03 |
| STDEV. | 0.001 | 0.129 | 0.012 | 0.750 | 0.075 | 0.050 |
| % RSD | 2.94 | 2.19 | 2.86 | 2.16 | 0.884 | 2.44 |

### 4.2.2 Normality check and box plot presentation of CRM values

Descriptive statistics of target analytes are presented with recovery range of between 78.0% to 96.6% (Table 4.3). Values were log-transformed prior to representation in box-whiskers plot (Figure 4.4) because they are not normally distributed.

Table 4.3: Evaluation of analytical precision and accuracy using the percentage recovery of analytes in the 36 replicates of Certified Reference Material (*SPS-SWI batch 234*) used during groundwater analyses by ion chromatography

| **Analyte** | **Values (µg/mL)** | | **%** | |
|---|---|---|---|---|
| | **Certified** | **Measured** | **RSD** | **Accuracy** |
| **$Cl^-$** | 33.1±1.20 | 31.3 ± 1.94 | 6.12 | 96.0 |
| **$Fl^-$** | 0.273± 0.023 | 0.228 ± 0.029 | 12.7 | 78.0 |
| **$NO_3^-$** | 28.2 ±1.20 | 27.2± 0.999 | 3.67 | 96.6 |
| **$SO_4^-$** | 82.8 ±2.40 | 77.8± 2.51 | 3.22 | 96.6 |

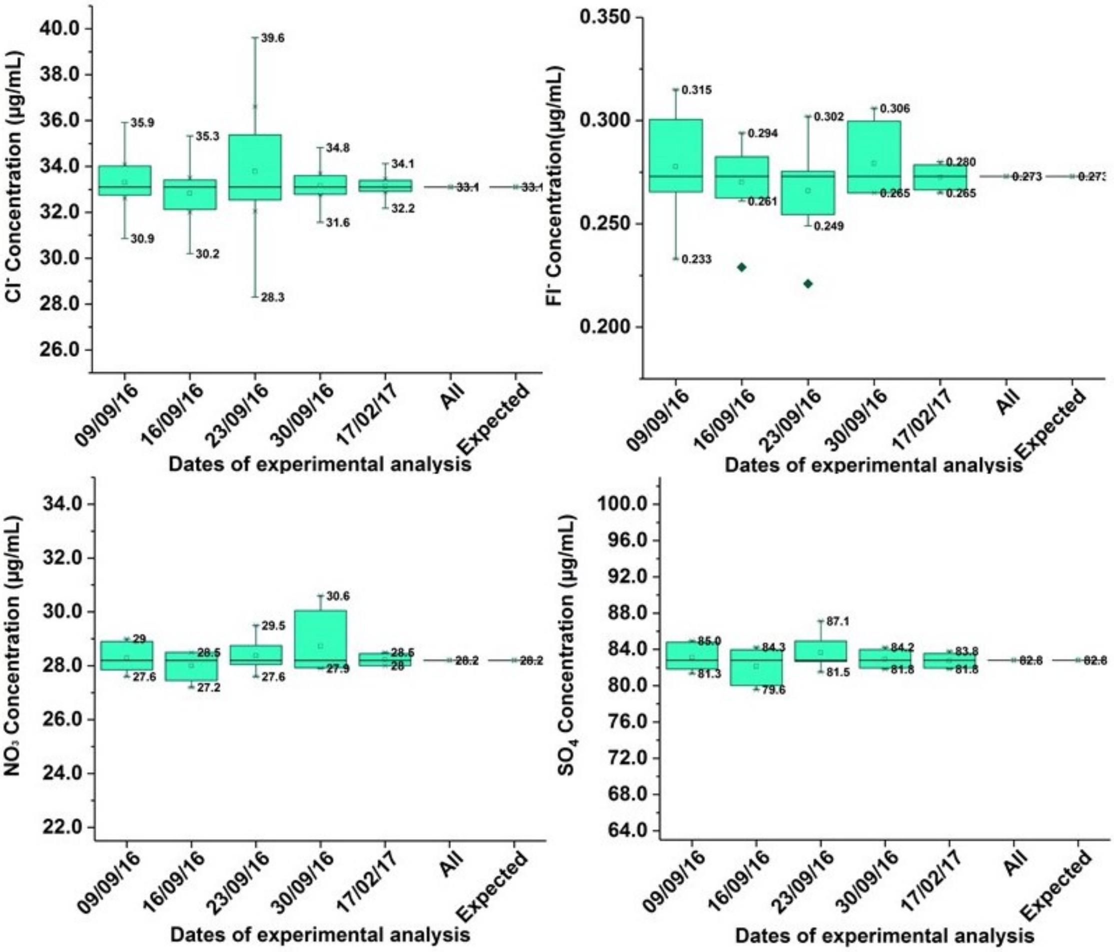


Figure 4.4: Distribution pattern of target anions in the certified reference materials (*SPS-SWI batch 234*) as measures in Ion Chromatography during the respective batch analyses of groundwater samples.

## 4.3 Cations and anions in sampled groundwater

### 4.3.1 Introduction

The following groundwater priority elements, which include nitrate ($NO_3^-$), fluoride ($Fl^-$), chloride ($Cl^-$), nitrite ($NO_2^-$), sulphate ($SO_4^-$), phosphate ($PO_{4-}$) and bromide (Br) for anions; as well as cations like lithium (Li), ammonium ($NH_4^+$), potassium ($K^+$), calcium ($Ca^{2+}$), sodium ($Na^+$), and magnesium ($Mg^{2+}$) were measured.

While $NO_3^-$, $Cl^-$ , $Na^+$, $Ca^{2+}$, $K^+$, and $Mg^{2+}$ recorded values above the lower limit of detection (LLD), which is the lowest concentration that can be reliably detected during analysis, other cations and anions measured low concentrations in small proportion of wells hence just introduced and displayed in Figure 4.5 (a-i). The ions and the percentage proportion of wells where they were measured include $NO_2^-$ (5.16 %), $Fl^-$ (3.63 %), $SO_4^-$ (2.07 %) and $NH_4^+$ (23.0%). Lithium (Li), Bromide (Br), and Phosphate ($PO_4$) had all their values measured below the LLD (Table 4.4) and were not reported.

Table 4.4: LOD and LOQ for cations and anions as derived from 20 replicate measurements of deionised water used as blanks during groundwater analysis by ion chromatography

| **Analyte** | **LOD (µg/mL)** | **LOQ (µg/mL)** |
|---|---|---|
| **Fluoride** | 0.129 | 0.447 |
| **Chloride** | 0.138 | 0.481 |
| **Nitrite** | 0.019 | 0.062 |
| **Sulphate** | 2.20 | 7.66 |
| **Nitrate** | 0.537 | 1.82 |
| **Sodium** | 1.30 | 4.34 |
| **Ammonium** | 0.009 | 0.031 |
| **Calcium** | 0.032 | 0.097 |
| **Potassium** | 0.020 | 0.070 |
| **Magnesium** | 0.008 | 0.026 |

Distribution pattern of the respective ions in groundwater across the study area are presented in maps (Figures 4.5 a-h) with graduated green and orange symbols representing their concentrations in the rainy and dry seasons respectively. However, these seasonal variabilities are discussed fully in Chapter 5.

**Nitrate ($NO_3^-$)**

Median concentrations of $NO_3^-$ was 9.92 µg/mL (IQR = 3.31 µg/mL - 34.7 µg/mL). Approximately, 18.4% had values less than the limit of detection.

**Ammonium ($NH_4^+$)**

Only 23.0% of sampled wells had detectable ammonium ($NH_4^+$) concentrations, which ranged between 0.011 µg/mL and 4.34 µg/mL, with a median concentration of 0.038 µg/mL.

**Chloride ($Cl^-$):** Median chloride concentration was 2.04 µg/mL (IQR = 0.689 µg/mL – 5.80 µg/mL).

**Sodium ($Na^+$):** Median concentration was 8.00 µg/ml (IQR = 3.91µg/mL - 16.2µg/mL). About 198 samples generated values above the lower limit of detection, representing 51.2% of the sampled wells.

**Calcium ($Ca^{2+}$):** Median $Ca^{2+}$ concentration across the study area was 0.852 µg/mL (IQR = 0.411 µg/mL – 3.49 µg/mL)

**Potassium ($K^+$):** Median potassium concentrations across the study area was 0.687 µg/mL (IQR = 0.252 µg/mL - 2.27 µg/mL)**.** 60.7% of the dataset showed concentrations below 1.00 µg/mL, while a single sample had value that was below the LLD.

**Magnesium ($Mg^{2+}$):** Median magnesium concentration of 0.163 µg/mL (IQR = 0.073 µg/mL – 0.52 µg/mL) was recorded. $Mg^{2+}$ had no value below LLD, but only 9.27% was measured above 1.00 µg/mL.

**Sulphate ($SO_4^-$)** Median sodium concentration was 4.45 µg/mL (2.27 – 10.1 µg/mL). with only 2.07% that measured values above the lower limit of detection.

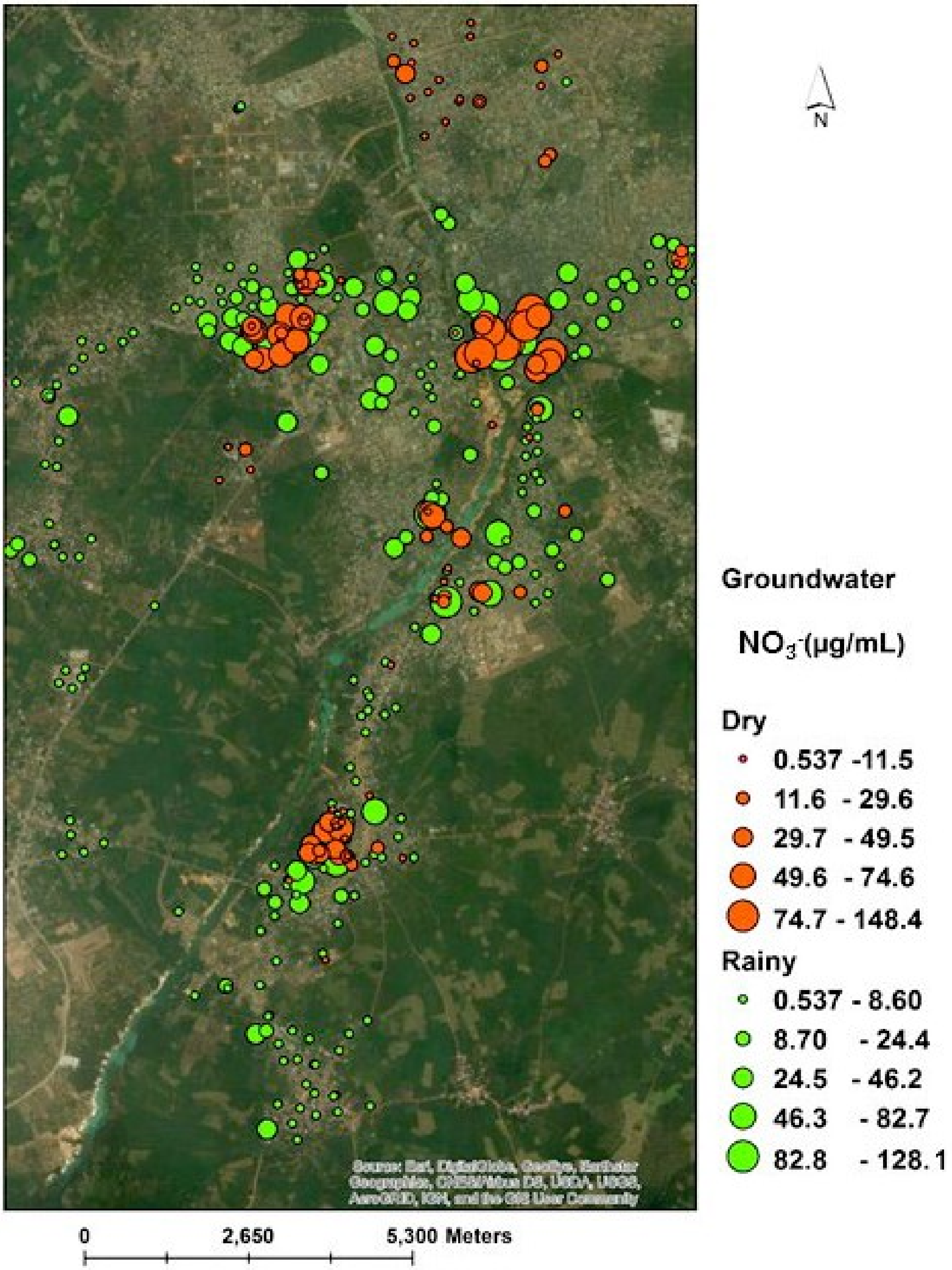


Figure 4.5a: Rainy and dry season nitrate ($NO_3^-$) concentration and distribution patterns in groundwater in Owerri, Nigeria as determined by ion chromatography. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)

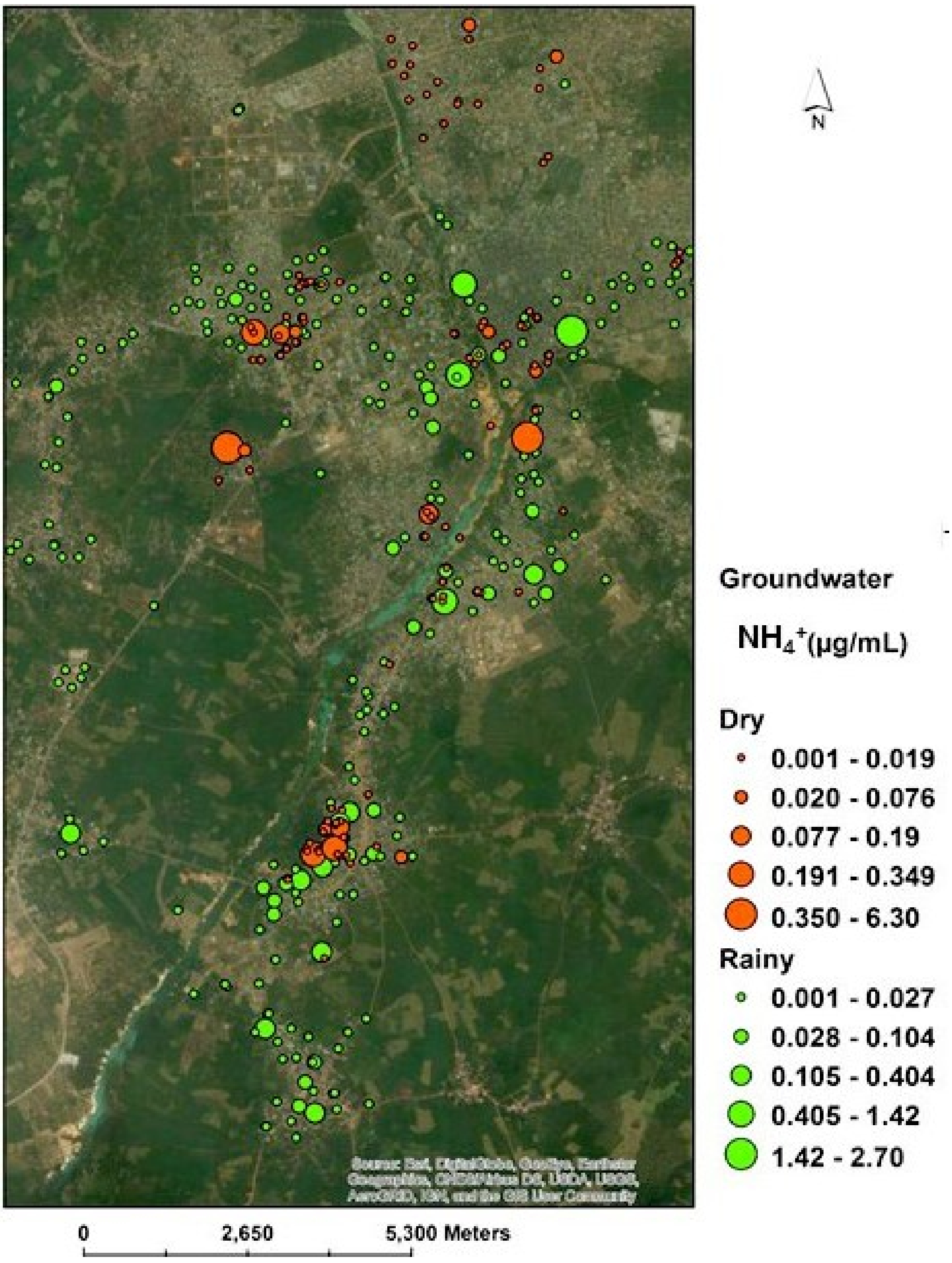


Figure 4.5b: Rainy and dry season ammonium ($NH_4^+$) concentration and distribution pattern in groundwater in Owerri, Nigeria, as determined by ion chromatography. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)

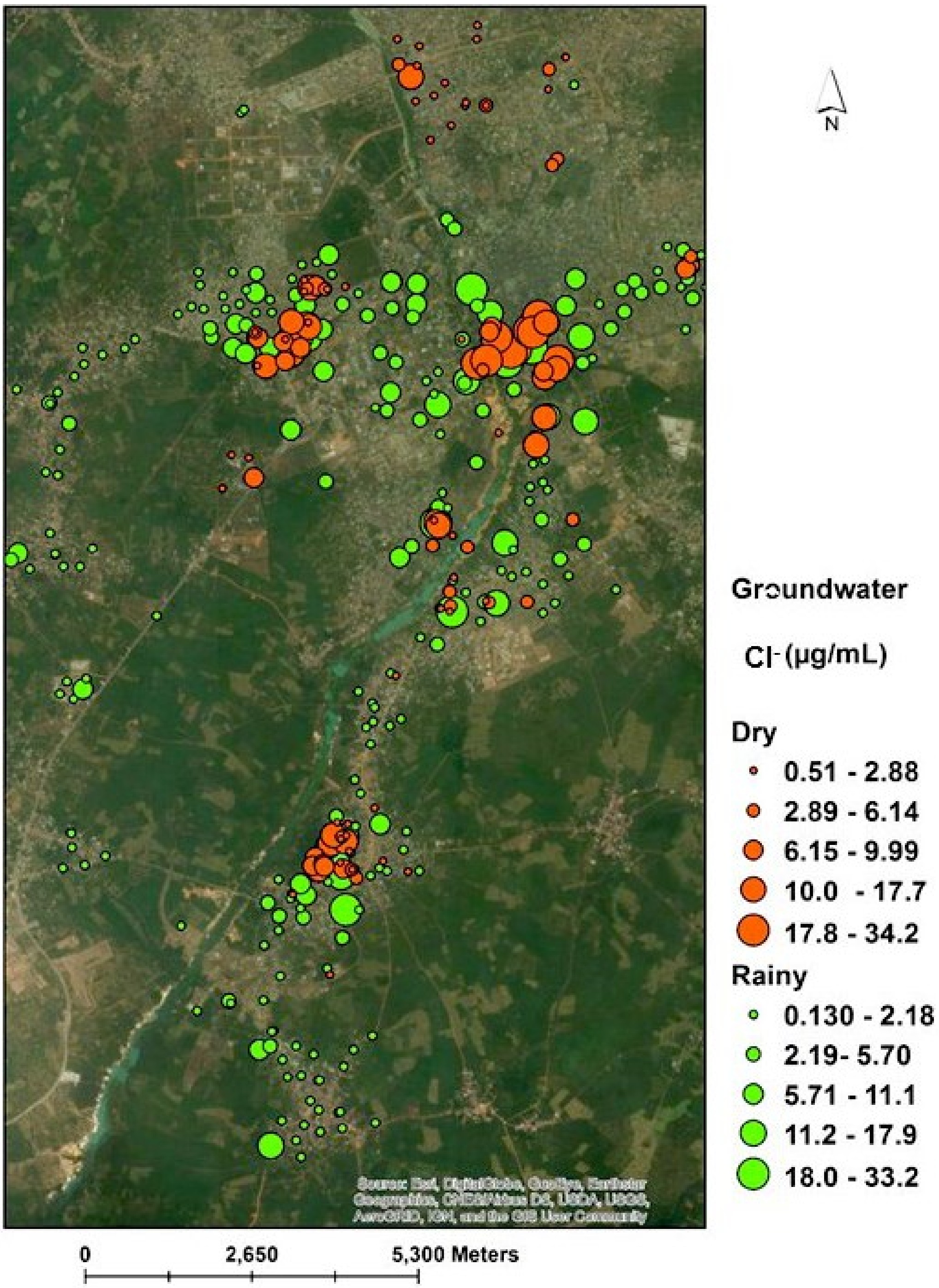


Figure 4.5c: Rainy and dry season chloride ($Cl^-$) concentration and distribution pattern in groundwater in Owerri, Nigeria, as determined by ion chromatography. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)

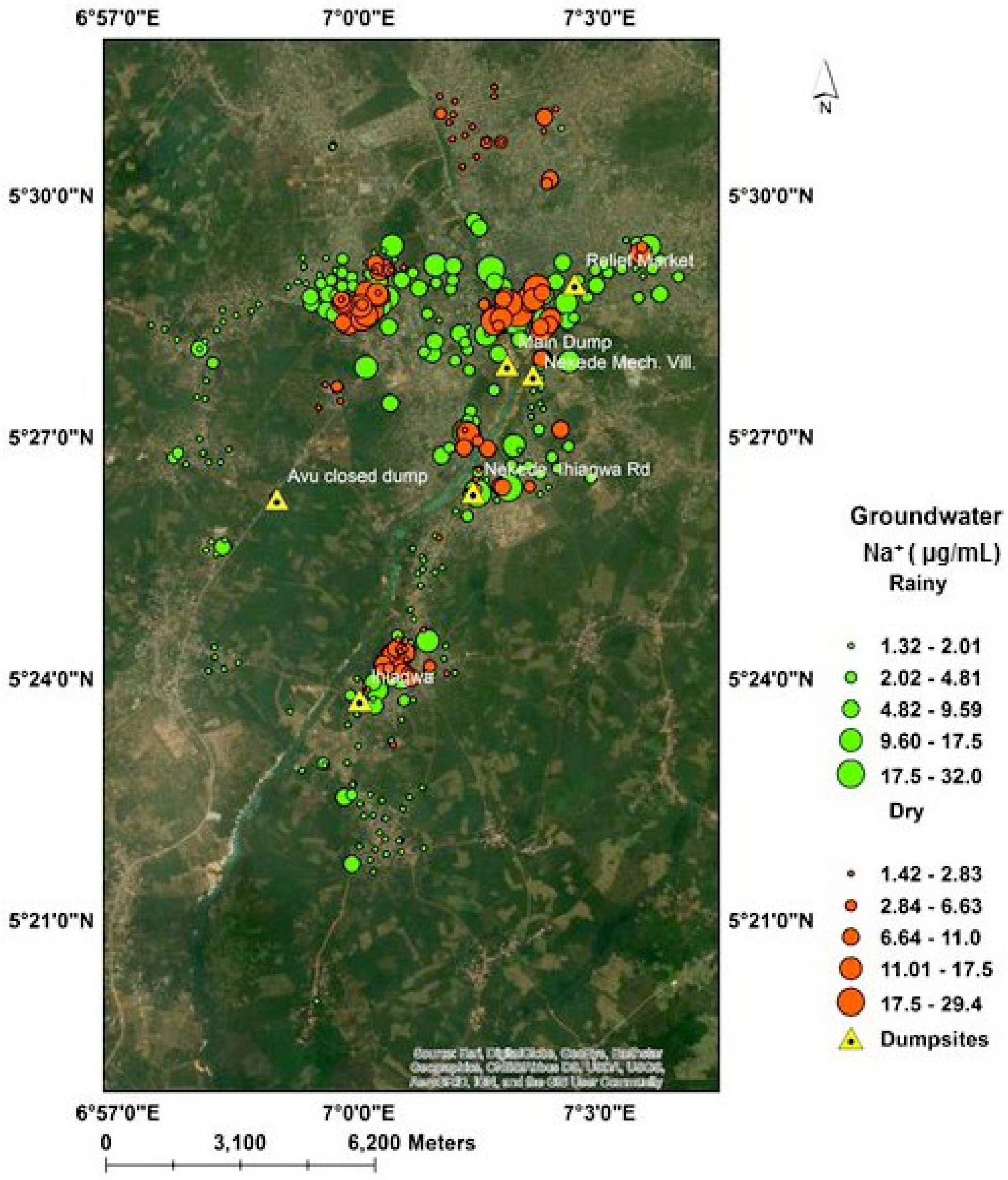


Figure 4.5d: Rainy and dry season sodium ($Na^+$) concentration and distribution pattern in groundwater in Owerri, Nigeria, as determined by ion chromatography. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)

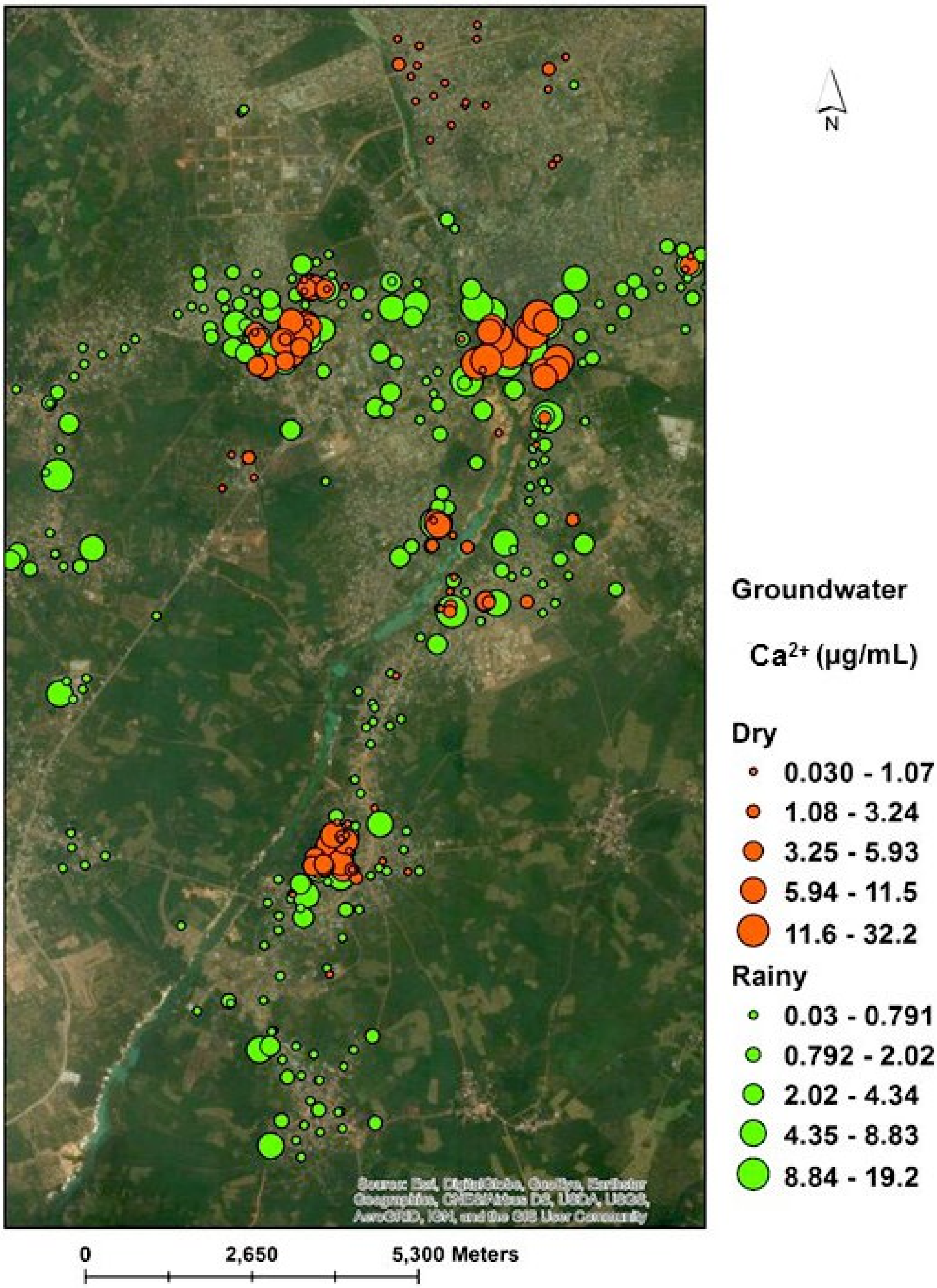


Figure 4.5e: Rainy and dry season calcium ($Ca^{2+}$) concentration and distribution pattern in groundwater in Owerri, Nigeria, as determined by ion chromatography. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)

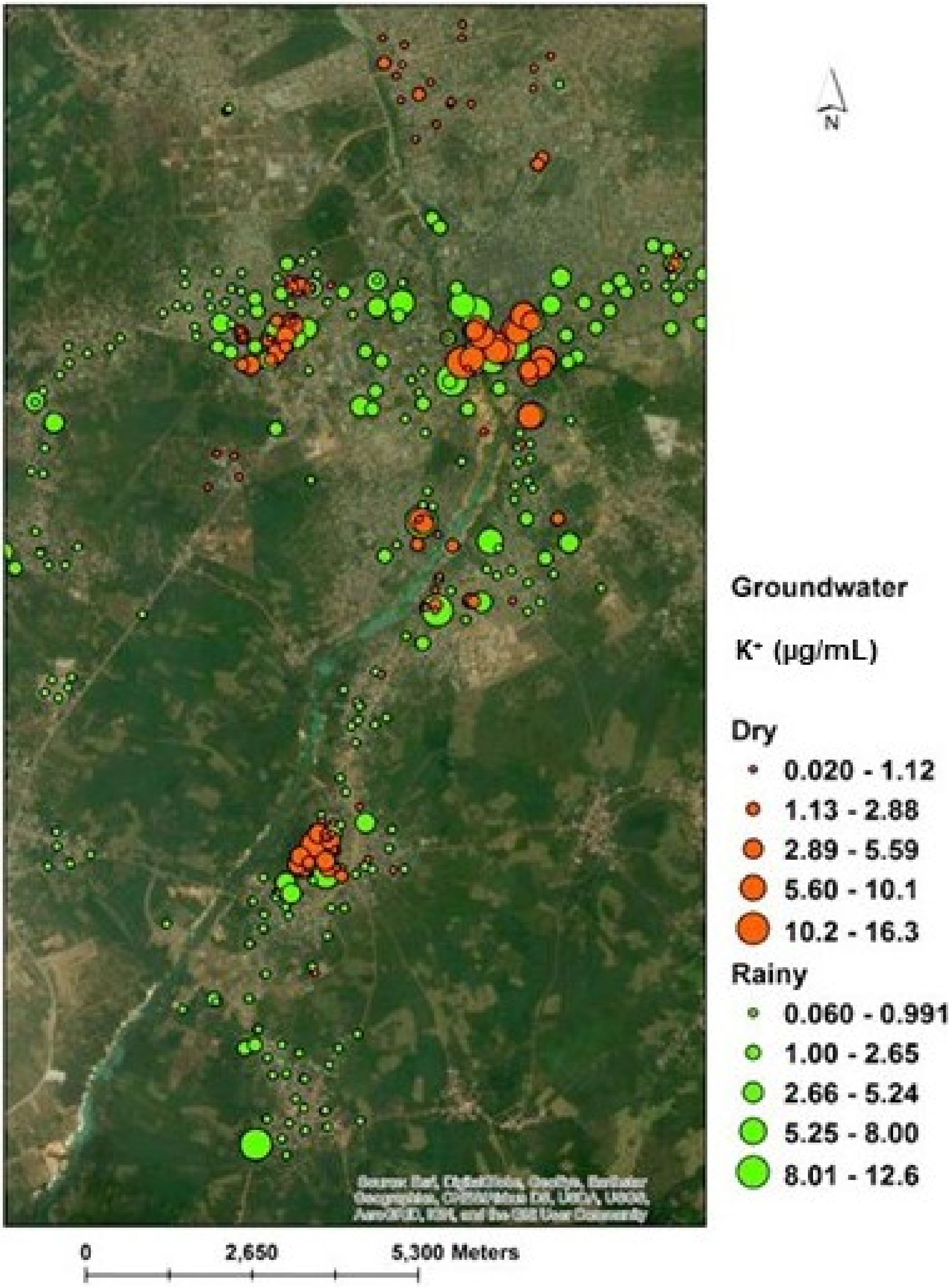


Figure 4.5f: Rainy and dry season potassium ($K^+$) concentration and distribution pattern in groundwater in Owerri, Nigeria, as determined by ion chromatography. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)

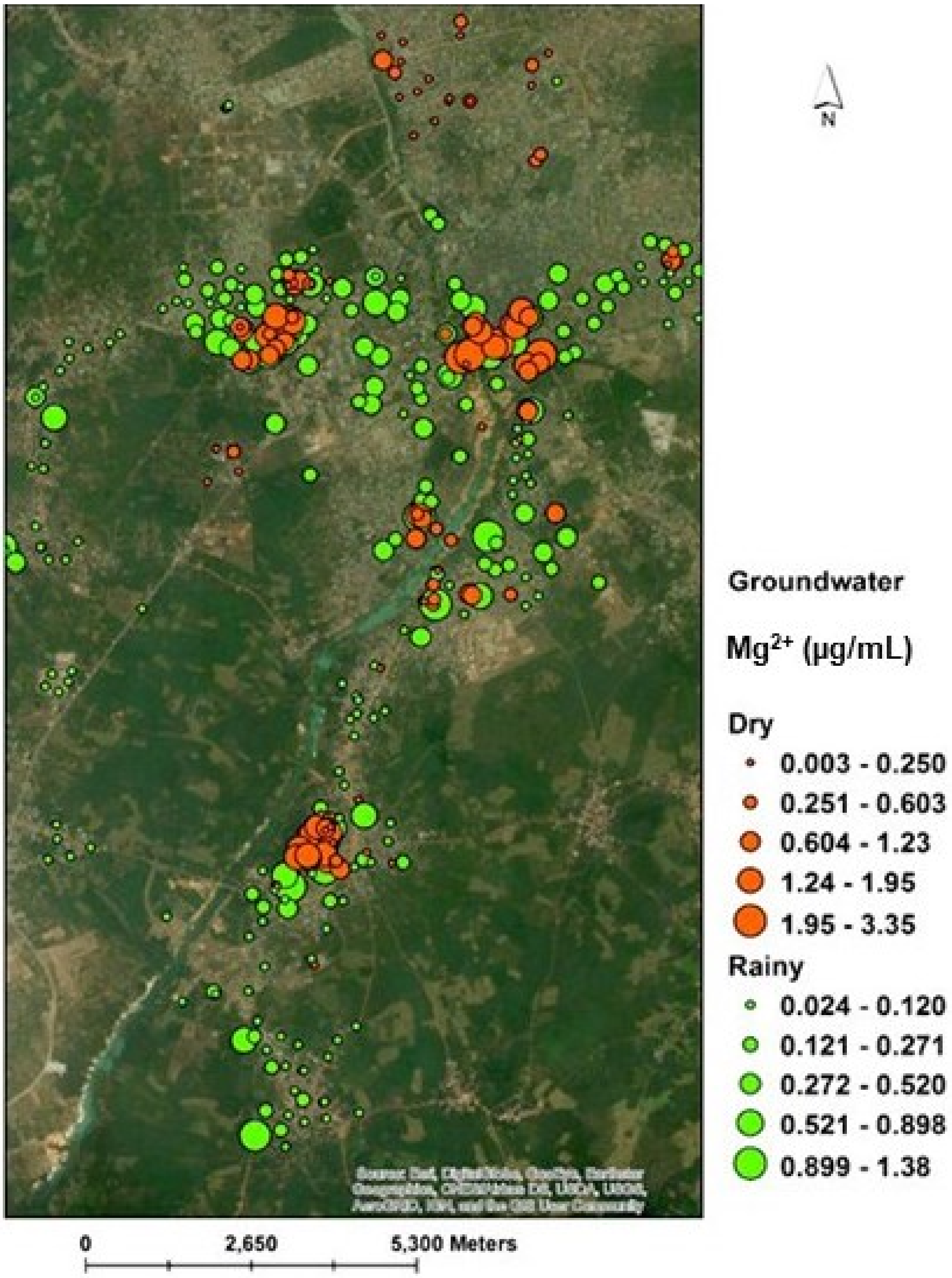


Figure 4.5g: Rainy and dry season magnesium ($Mg^{2+}$) concentration and distribution pattern in groundwater in Owerri, Nigeria, as determined by ion chromatography. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)

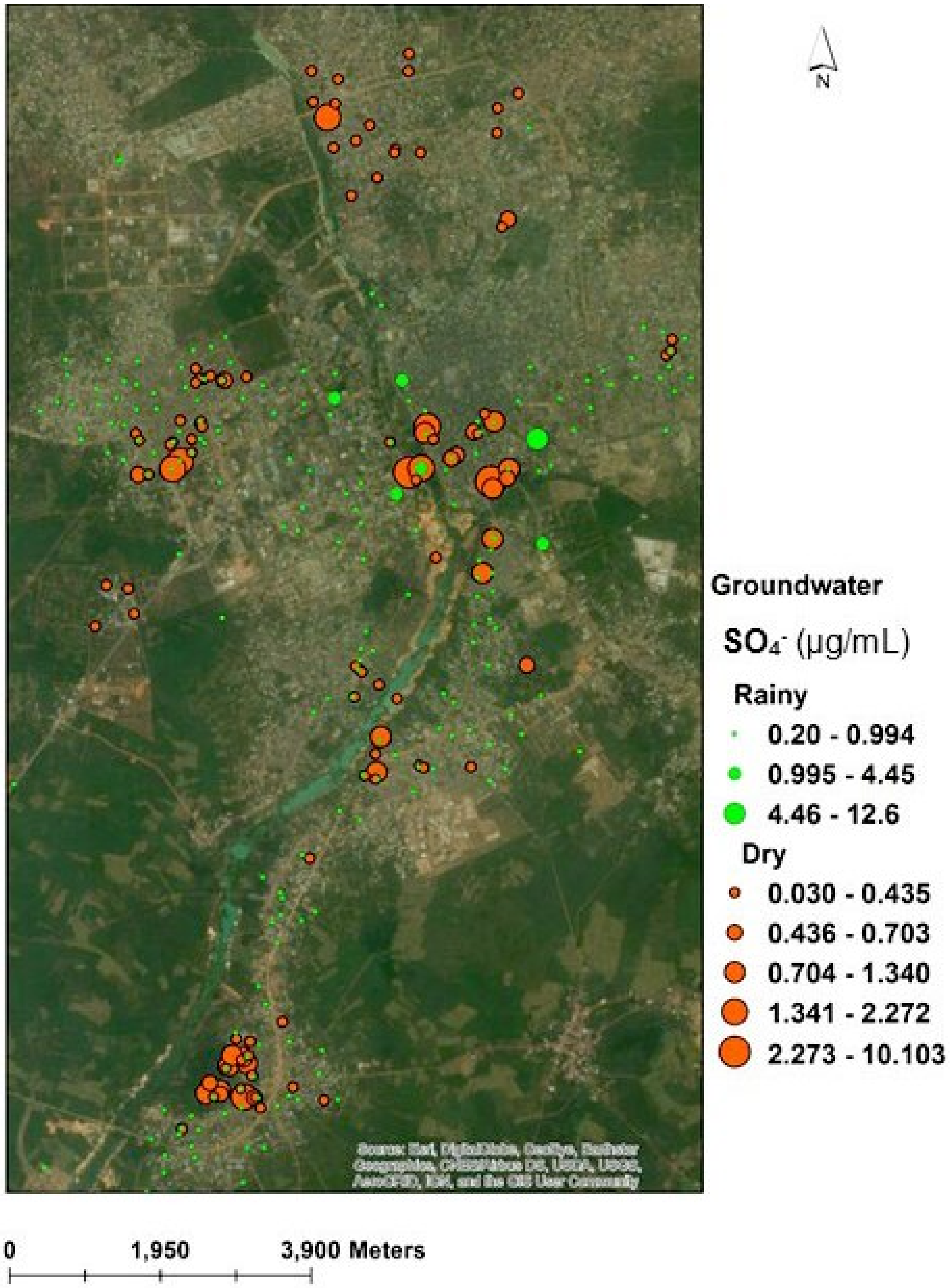


Figure 4.5h: Seasonal (Rainy and dry) sulphate ($SO_4^-$) concentration and distribution pattern in groundwater in Owerri, Nigeria, as determined by ion chromatography. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)

### 4.3.2 Serial sampling for nitrate ($NO_3^-$) and ammonium ($NH_4^+$) concentrations in randomly selected wells to monitor their temporal variability

Results of the time series sampling for $NO_3^-$ and $NH_4^+$carried out for five months using the Palin test (PT) technique are shown in Appendix 4D. Monthly mean concentrations are presented in Figures 4.6.

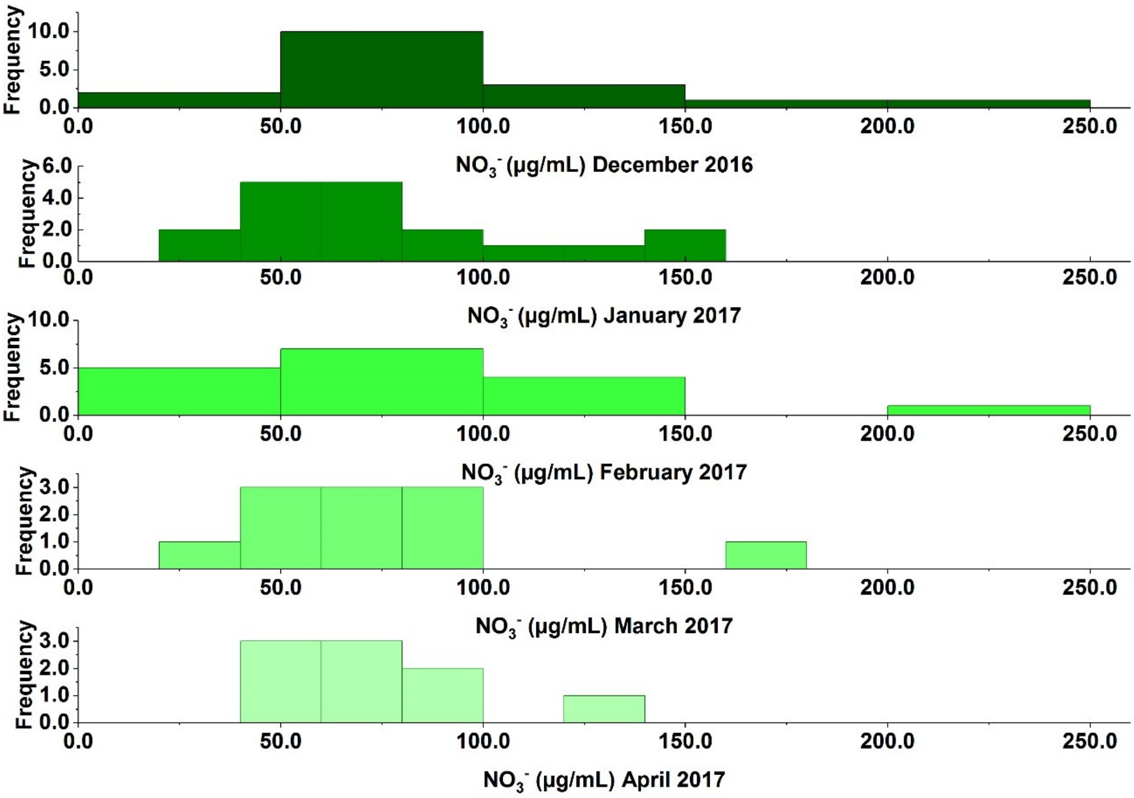


Figure 4.6: Histograms of monthly concentrations of $NO_3^-$ in selected wells across the study area (Owerri, Nigeria) following the 5-month *in-situ* measurements by Palin test.

### 4.4 Metal analyses in groundwater

All elements analysed by ICP-MS were obtained in He mode with the aim to eliminate possible polyatomic interferences. Whilst sixteen priority metals were analysed (Appendix 4B) for drinking water quality, measured concentration of only three were of aesthetic and public health concern *viz*. manganese (Mn), lead (Pb) and cadmium (Cd), while their respective LOD and LOQ are presented as Table 4.5.

Table 4.5: Limits of detection and quantification for three metals with elevated concentrations in groundwater of Owerri, Nigeria.

| **Analyte** | **LOD (ng/mL)** | **LOQ (ng/mL)** |
|---|---|---|
| **Manganese** | 0.067 | 0.208 |
| **Lead** | 0.046 | 0.217 |
| **Cadmium** | 0.019 | 0.059 |

### 4.4.1 Accuracy and precision of metals measurement in the groundwater samples

Results of groundwater samples analysed by ICP-OES/MS were assessed for precision and accuracy through the CRM recovery (*ERM –CA 615*), with recoveries ranging from 93.7% to 103.2%.CRM values of all other metals have been presented in Table 4.6 to display general analytical accuracy during the groundwater metals analyses. However, only analytical precision of the three aforementioned metals are presented as percentage relative standard deviation (% RSD).

Table 4.6: Evaluation of analytical precision and accuracy using the percentage recovery of selected analytes in the 32 replicates of Certified Reference Material (*ERM –CA 615*) used during the analyses by ICP-MS/OES

| **Analyte** | **Expected (ng/mL)** | **Uncertainty (ng/mL)** | **Analytical techniques** | | **RSD** | **Accuracy** |
|---|---|---|---|---|---|---|
| | | | ICP-MS | ICP-OES | % | % |
| **As** | 10.0 | 0.1 | 10.3 | - | | 102.5 |
| **Cd** | 0.50 | 0.01 | 0. 546 | - | 13.4 | 109.1 |
| **Co** | 2.00 | 0.02 | 2.03 | - | | 101.5 |
| **Cr** | 2.00 | 0.02 | 2.05 | - | | 102.4 |
| **Mn** | 10.0 | 0.1 | 10.4 | - | 7.63 | 101.8 |
| **Ni** | 10.0 | 0.1 | 10.3 | - | | 103.2 |
| **Pb** | 5.00 | 0.1 | 4.68 | - | 6.39 | 93.7 |
| **Cu** | 0.020 | 1.0 | - | 0.021 | | 102.9 |
| **Fe** | 20.0 | 1.0 | 22.1 | - | | 110.7 |
| **V** | 10.0 | 0.1 | 10.3 | - | | 102.9 |

### 4.4.2 Detailed concentration pattern of the selected metals in groundwater across the study area.

**Lead (Pb):** Concentrations of Pb (Figure 4.7a) ranged between 0.047ng/mL and 39.6 ng/mL with a median concentration of 0.379 ng/mL (IQR = 0.200ng/mL - 1.48 ng/mL). However, concentrations in 173 boreholes were less than the LOD.

**Manganese (Mn)** Median concentration of Mn (Figure 4.7b) in groundwater was 16.8 ng/mL (IQR = 6.79 ng/mL - 57.4 ng/mL).

**Cadmium (Cd)** Median concentration of Cd (Figure 4.7c) 0.019 ng/mL ± 0.405 (IQR = 0.007 ng/mL - 0.032 ng/mL).

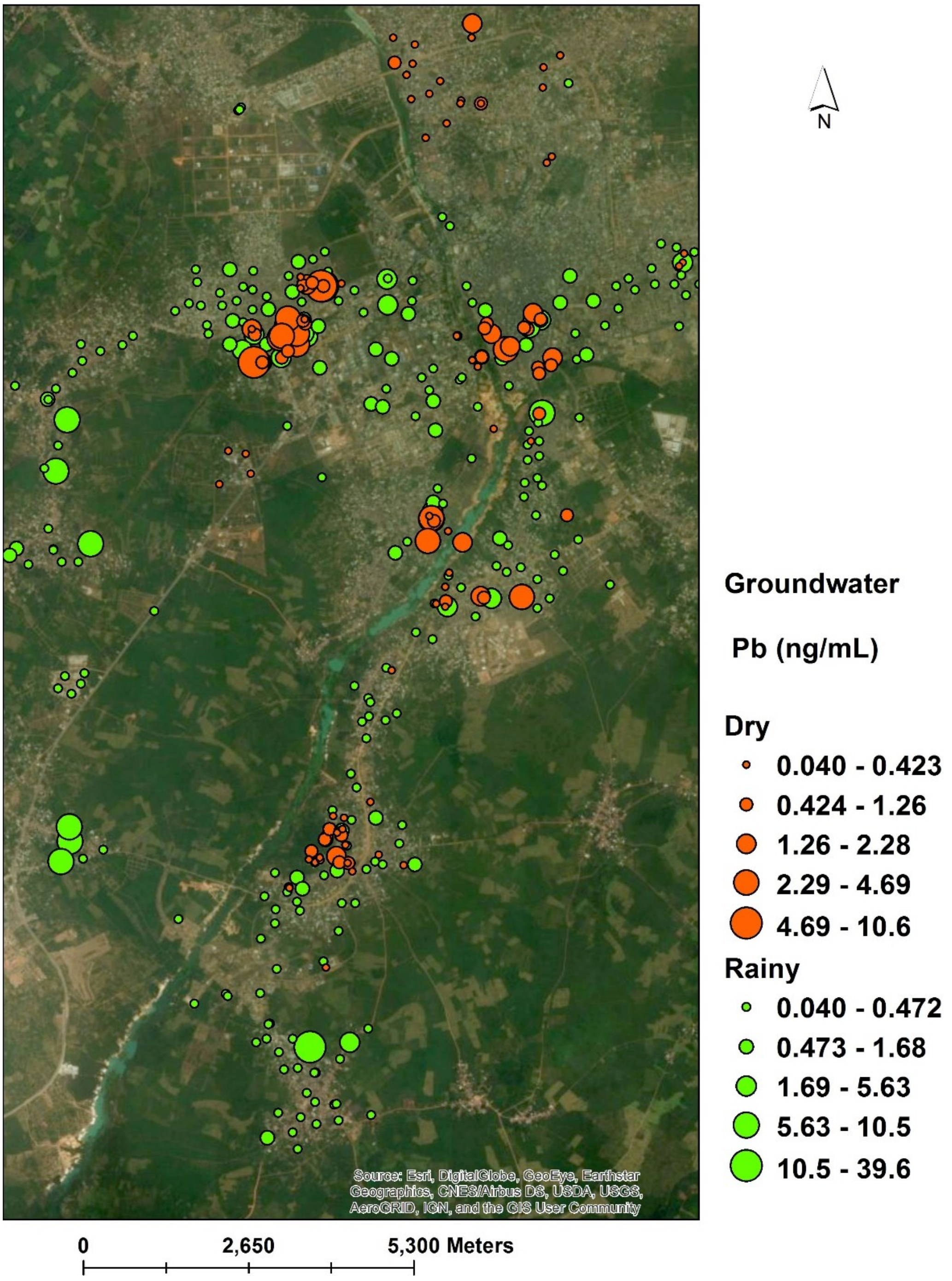


Figure 4.7a: Lead (Pb) concentrations in groundwater across the study area (Owerri, Nigeria) with green and orange symbols representing rainy and dry seasons respectively. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)

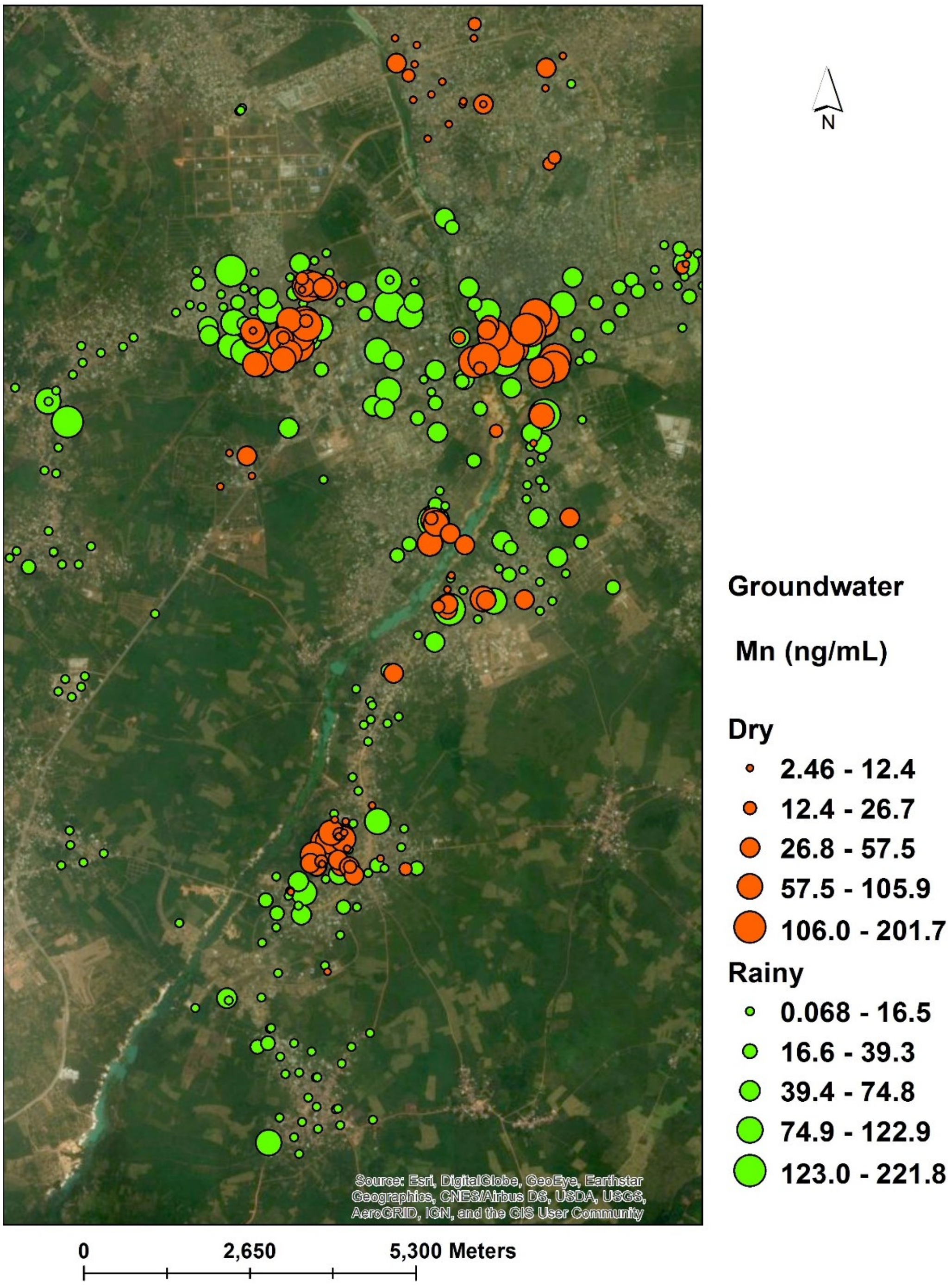


Figure 4.7b: Manganese (Mn) concentrations in groundwater across the study area (Owerri, Nigeria) with green and orange symbols representing rainy and dry seasons respectively. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)

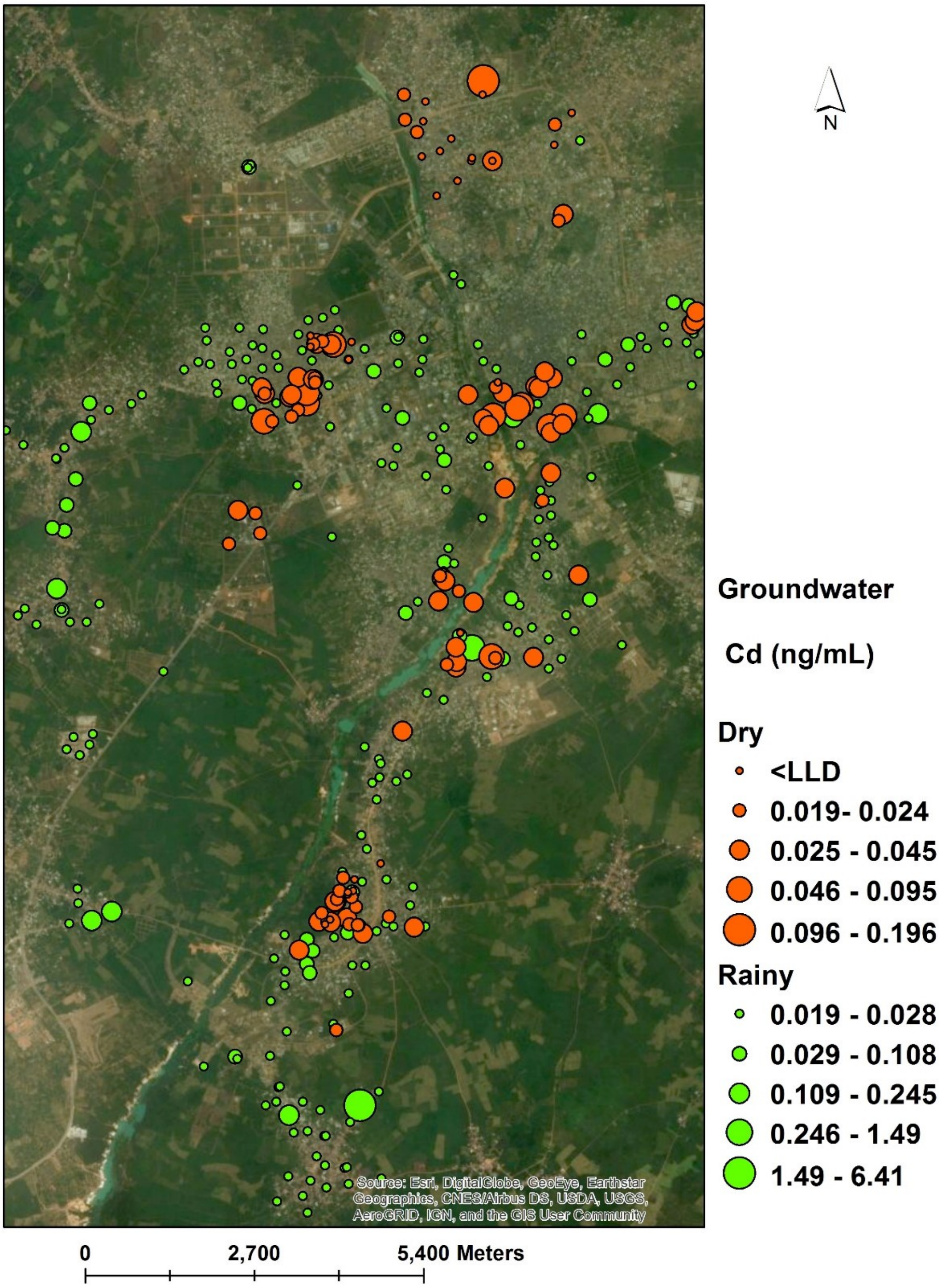


Figure 4.7c: Cadmium (Cd) concentrations in groundwater across the study area (Owerri, Nigeria) with green and orange symbols representing rainy and dry seasons respectively. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)

## 4.5 Dissolved Organic Carbon (DOC) in the groundwater

Mean and standard deviation DOC concentration in the rainy season was 7.28 ± 1.12 while that in the dry season was 3.78 ± 0.860 (Figure 4.8)

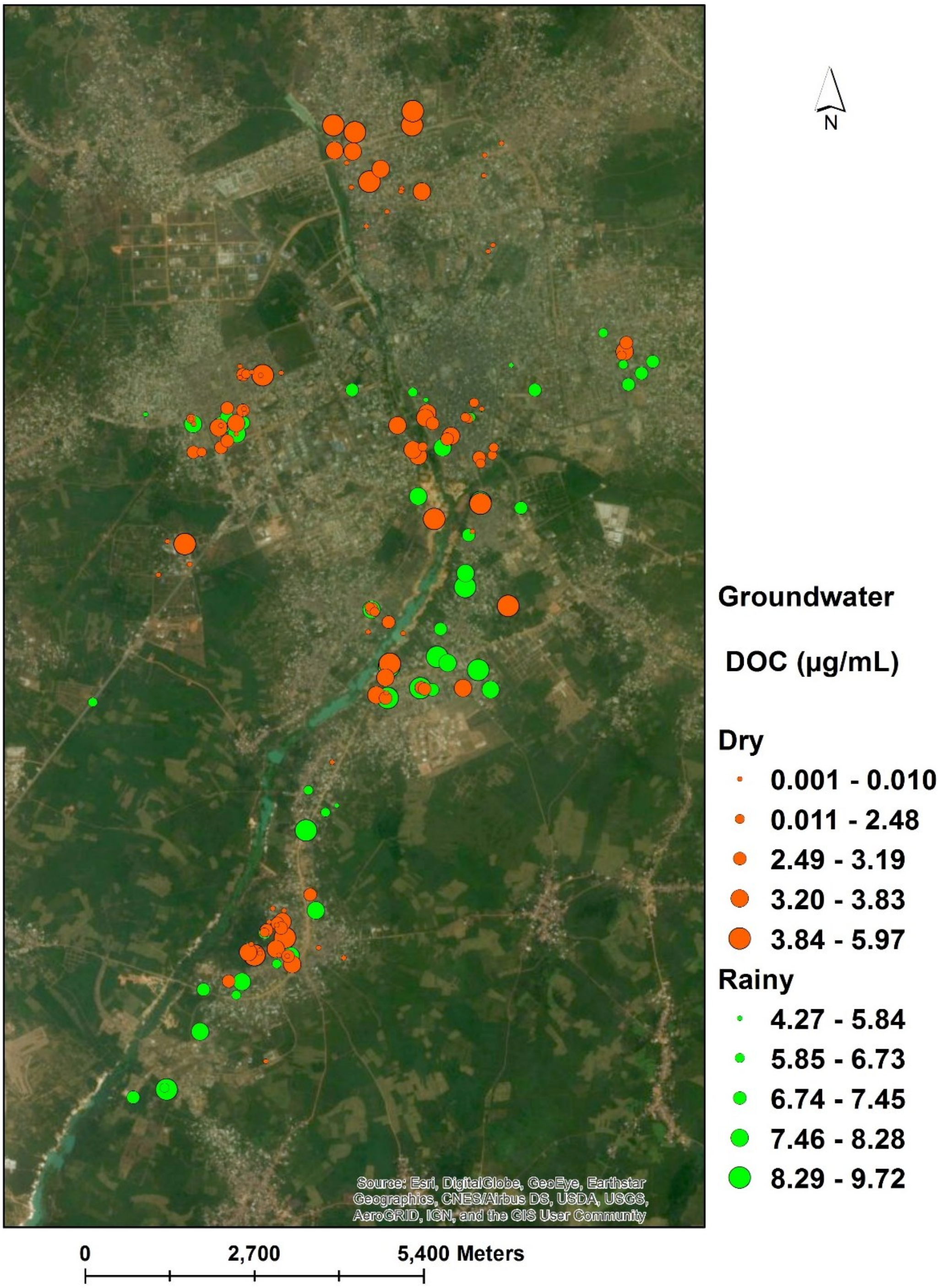


Figure 4.8: Dissolved organic carbon (DOC) concentrations in groundwater across the study area (Owerri, Nigeria) with green and orange symbolising rainy and dry seasons respectively. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)

## 4.6 Analyses of metals and ions in the dumpsites leachate samples

Samples of leachate were analysed for both metals and ions alongside same the CRM and analytical techniques as applied for groundwater. LODs and LOQs of the target analytes are presented in Table 4.7 while the CRM report is presented in Table 4.8. All variables analysed in the groundwater samples were replicated in the leachate analysis.

Table 4.7: LOD and LOQ for cations and anions as derived from 20 replicate measurements of deionised water (blanks) in the respective techniques.

| Analyte | LOD | LOQ | Technique |
|---|---|---|---|
| **$Cl^-$ (µg/mL)** | 0.22 | 2.24 | IC |
| **$NO_3$ (µg/mL)** | 0.066 | 0.219 | IC |
| **$SO_4{}^-$(µg/mL)** | 0.306 | 1.02 | IC |
| **$NH_{4+}$ (µg/mL)** | 0.000 | 0.000 | IC |
| **$Ca^{2+}$ (µg/mL)** | 0.122 | 0.408 | IC |
| **K (µg/mL)** | 0.101 | 0.338 | IC |
| **Mg (µg/mL)** | 0.045 | 0.165 | IC |
| **Na (µg/mL)** | 0.251 | 0.836 | IC |
| **Mn (ng/mL)** | 0.092 | 0.025 | ICP-MS |
| **Fe (ng/mL)** | 5.34 | 17.8 | ICP-MS |
| **Pb (ng/mL)** | 0.015 | 0.050 | ICP-MS |
| **Cd (ng/mL)** | 0.012 | 0.039 | ICP-MS |
| **Ni (ng/mL)** | 0.742 | 2.45 | ICP-MS |

Table 4.8: Evaluation of analytical accuracy using percentage recovery of target analytes in the 9 replicates (3 for each technique) of the Certified Reference Material (*ERM – CA 615*) used during leachate analyses by both IC and ICP-MS

| Analyte | Certified | Measured | % RSD | Technique | % Accuracy |
|---|---|---|---|---|---|
| **$Cl^-$ (µg/mL)** | 33.1±1.20 | 32.0 ± 0.81 | 2.56 | IC | 96.6 |
| **$NO_3$ (µg/mL)** | 28.2 ±1.20 | 27.0 ± 0.69 | 2.56 | IC | 95.7 |
| **$SO_4$ (µg/mL)** | 82.8 ± 2.40 | 79.4 ± 2.25 | 2.84 | IC | 95.9 |
| **$Fe^{+2}$ (ng/mL)** | 20.0 | 20.9 ± 1.70 | 8.17 | ICP-MS | 104.4 |
| **Mn (ng/mL)** | 10.0 ± 0.10 | 9.90 ± 0.56 | 5.71 | ICP-MS | 98.8 |
| **Pb (ng/mL)** | 5.00 ± 0.10 | 4.60 ± 0.22 | 4.86 | ICP-MS | 91.0 |
| **Cd (ng/mL)** | 0.500 ± 0.02 | 0.500 ± 0.03 | 5.36 | ICP-MS | 95.7 |

### 4.6.1 Physical and chemical characteristics of sampled Open Solid Waste Dumpsites

In-situ measurements of pH, EC and DO from leachate of all the six open solid waste dumpsites across the study area are presented in Tables 4.10 to 4.15. Whereas analytes with trace concentrations are reported, those below the respective LODs are not presented in the tables. Generally, samples across different dumpsites showed a broad pH range of 3.50 to 8.50 units. Most analytes like Fe, $Cl^-$, and $NH_4^+$ recorded high concentration in this order: Main dumpsite > Relief Market dumpsite> Nekede-Ihiagwa Road dumpsite > Ihiagwa dumpsite > Avu dumpsite > Nekede Mechanic Village (Tables 4.9 – 4.14).

Table 4.9: Chemical characteristics of 31 leachate samples collected from the **main dumpsite**.

| **Parameters > LLD** | **Mean or Median/IQR** | **Minimum – Maximum** |
|---|---|---|
| **pH** | 7.11 ± 0.62 | 6.00 - 8.50 |
| **EC (µs/cm)** | 281.1±108.9 | 46.0- 550.0 |
| **DO (µg/mL)** | 2.62 ± 0.41 | 1.83 - 3.50 |
| **$Cl^-$ ( µg/mL)** | 773.2 ± 258.0 | 455.6 -1416.8 |
| **$SO_4$ (µg/mL)** | 17.2 (7.68 – 105.6) | 19.5 - 75.6 |
| **$Ca^{2+}$ (µg/mL)** | 64.5 ± 67.6 | 4.30 -225.7 |
| **K (µg/mL)** | 498.8 ± 156.3 | 222.8 -904.0 |
| **$NH_4^+$ (µg/mL)** | 526.0 ± 201.7 | 150.7 -941.7 |
| **$Br^-$ (µg/mL)** | 9.28 (0.476 – 30.7) | 0.476 -124.2 |
| **Na (µg/mL)** | 518.2 ± 138.5 | 21.3 -188.7 |
| **Mn (ng/mL)** | 9.80 (3.20 – 31.9) | 0.300 - 512.9 |
| **Fe (ng/mL)** | 1380 (846 - 2518). | 116.0 -13214.0 |
| **Pb (ng/mL)** | 0.383 ± 0.436 | 0.016 -1.414 |
| **Zn (ng/mL)** | 35.2 (25.6 – 105.6). | 6.20 - 542.5 |
| **Ni (ng/mL)** | 30.2 ± 15.1 | 4.76 - 60.1 |

Table 4.10: Chemical characteristics of 12 leachate samples collected from the **Ihiagwa dumpsite**.

| **Parameters > LLD** | **Mean or Median/IQR** | **Minimum –Maximum** |
|---|---|---|
| **pH** | 6.90 ± 0.69 | 5.50 -7.50 |
| **EC (µs/cm)** | 215.0 ± 106.6 | 150 -550.0 |
| **DO (µg/mL)** | 2.53 ± 0.55 | 1.82 -3.42 |
| **$Cl^-$ ( µg/mL)** | 57.2 ± 22.4 | 4.61 -70.9 |
| **$SO_4$ (µg/mL)** | 13.1 ± 13.7 | 15.4 -43.0 |
| **$NO_3^-$ (µg/mL)** | 6.65 ± 2.75 | 0.087-1.22 |
| **$Ca^{2+}$ (µg/mL)** | 13.0 ± 8.70 | 3.19 - 30.2 |
| **K (µg/mL)** | 82.9 ± 44.8 | 1.30 -94.0 |
| **$NH_4^+$ ( µg/mL)** | 0.211 ( 0.137 – 0.374 ) | 0.100 - 0.415 |
| **Na (µg/mL)** | 33.8 ± 12.2 | 15.4 - 66.8 |
| **Fe (ng/mL)** | 1758.2 (190 – 1436). | 130 -2416 |
| **Pb (ng/mL)** | 1.038 (0.394 – 2.688). | 0.020- 3.56 |

Table 4.11: Chemical characteristics of 10 leachate samples collected from the **Avu dumpsite**.

| **Parameters>LLD** | **Mean or Median/IQR** | **Minimum – Maximum** |
|---|---|---|
| **pH** | 4.31 ± 0.76 | 3.50 - 5.50 |
| **EC (µs/cm)** | 27.7 ± 11.3 | 10.0 - 55.0 |
| **DO (µg/mL)** | 4.59 ± 0.69 | 3.60 -5.76 |
| **$SO_4$ (µg/mL)** | 6.28 ± 1.00 | 2.80 -7.00 |
| **$NO_3^-$ (µg/mL)** | 0.667 ± 0.797 | 0.250 - 6.35 |
| **$Ca^{2+}$ (µg/mL)** | 2.81 ± 2.06 | 0.406 - 6.56 |
| **K (µg/mL)** | 3.13 ± 2.27 | 0.224 - 0.620 |
| **Na (µg/mL)** | 5.61 ± 2.06 | 3.51 - 9.24 |
| **Mn (ng/mL)** | 8.44 (1.69 – 11.6). | 0.41 - 29.4 |
| **Fe (ng/mL)** | 512.7 (176.0 - 714.0 ) | 16.0 -1219 |
| **Pb (ng/mL)** | 1.87 (0.037 – 5.87). | 0.037 - 5.87 |

Table 4.12: Chemical characteristics of 10 leachate samples collected from the **Relief Market dumpsite.**

| **Parameters> LLD** | **Mean** | **Minimum – Maximum** |
|---|---|---|
| **pH** | 5.31 ± 0.929 | 3.80 - 7.00 |
| **EC (µs/cm)** | 231.0 ± 176.3 | 34.0 - 450. |
| **DO (µg/mL)** | 1.98 ± 0.41 | 1.04 - 2.66 |
| **$Cl^-$(µg/mL)** | 64.8 ± 38.7 | 10.7- 123.7 |
| **$SO_4$ (µg/mL)** | 6.26 ± 2.87 | 1.67 - 8.22 |
| **$NO_3^-$ (µg/mL)** | 4.53 ± 1.73 | 0.100 - 167.3 |
| **$NH_4^+$ (µg/mL)** | 26.6 ± 291.1 | 34.9 - 70.7 |
| **K (µg/mL)** | 22.8 ± 72.2 | 6.60 – 181 |
| **Mg (µg/mL)** | 0.201 ± 0.553 | 2.55 - 35.3 |
| **Na (µg/mL)** | 100.8 ± 107.9 | 22.2 - 278.2 |
| **Mn (ng/mL)** | 258.5 ± 488.5 | 3.00 -1606 |
| **Fe (ng/mL)** | 2415.5 ± 3676.4 | 170 -12569 |
| **Pb (ng/mL)** | 0.302 ± 0.244 | 0.077- 0.589 |

Table 4.13: Chemical characteristics of 8 leachate samples collected from the **Nekede-Ihiagwa dumpsite.**

| Parameters > LLD | Mean | Minimum - Maximum |
|---|---|---|
| **pH** | 6.40 ± 0.62 | 5.50 - 7.20 |
| **EC (µs/cm)** | 62.4 ± 30.5 | 38.0 -120.0 |
| **DO (µg/mL)** | 2.20 ± 0.320 | 1.82 - 2.86 |
| **$Cl^-$ ( µg/mL)** | 26.0 ± 18.7 | 6.21 - 54.7 |
| **$SO_4$ (µg/mL)** | 10.0 ± 7.27 | 3.32 - 9.90 |
| **$Ca^{2+}$ (µg/mL)** | 25.5 ± 14.2 | 13.6 - 58.7 |
| **K (µg/mL)** | 70.8 ± 65.0 | 6.70 -160.0 |
| **$NO_3^-$ (µg/mL)** | 2.69 ± 2.48 | 0.023 – 2.51 |
| **$NH_4^+$ (µg/mL)** | 4.92 ± 7.63 | 1.80 – 21.2 |
| **Mg (µg/mL)** | 10.8 ± 9.47 | 1.39 - 24.2 |
| **Na(µg/mL)** | 28.1 ± 19.7 | 4.39 - 56.2 |
| **Mn (ng/mL)** | 28.3 ± 27.9 | 9.98 - 85.3 |
| **Pb (ng/mL)** | 1.70 ± 3.91 | 0.020 - 9.69 |
| **Ni (ng/mL)** | 772.7 ± 754.9 | 1.11 - 10.4 |
| **Zn(ng/mL)** | 22.5 ± 31.2 | 0.820 - 97.0 |

Table 4.14: Chemical characteristics of 7 leachate samples collected from the **Nekede Mechanic Village dumpsite.**

| Parameters >LLD | Mean | Minimum – Maximum |
|---|---|---|
| **pH** | 6.17 ± 1.47 | 5.50 - 7.20 |
| **EC (µs/cm)** | 202.6 ± 169.2 | 45.0 - 380.0 |
| **DO (µg/mL)** | 2.42 ± 0.390 | 1.82 - 2.86 |
| **$NO_3^-$ (µg/mL)** | 3.83 ± 2.04 | 0.741 -5.56 |
| **$NO_2$ (µg/mL)** | 16.1 ± 17.1 | 0.304 - 40.5 |
| **$NH_4^+$ ( µg/mL)** | 73.1 ± 60.9 | 0.400 -130.4 |
| **$Cl^-$ ( µg/mL)** | 257.2 ± 184.5 | 40.8 - 485.0 |
| **$Ca^{2+}$ (µg/mL)** | 18.5 ± 10.9 | 7.31 -38.4 |
| **K (µg/mL)** | 207 ± 163.6 | 14.4 - 403.9 |
| **Mg (µg/mL)** | 7.87 ± 6.50 | 2.06 -19.2 |
| **Na (µg/mL)** | 25.5 ± 13.4 | 8.73 - 45.4 |
| **Fe (ng/mL)** | 639.8 ± 721.9 | 30.0 -1900 |
| **Ni (ng/mL)** | 7.70 ± 6.99 | 1.13 - 15.9 |
| **Zn(ng/mL)** | 15.5 ± 18.4 | 0.281 - 50.9 |
| **Pb (ng/mL)** | 0.195 ± 0.120 | 0.038 - 0.315 |

## 4.7 River water

Results of the physicochemical analysis of river water samples are presented in Table 4.15. Samples were analysed alongside groundwater hence measurement accuracy and precision remain as shown in Table 4.3.

Table 4.15: Descriptive statistical summary of the physicochemical characteristics of the river water samples in River Otamiri in Owerri, Nigeria.

| Parameters | Mean or median/IQR | Minimum-Maximum |
|---|---|---|
| **pH** | 4.56± 0.56 | 4.02 - 6.00 |
| **DO (µg/mL)** | 10.1 ± 3.00 | 3.18 -16.2 |
| **EC (µS/cm)** | 44.8 ± 3.00 | 22.0 – 121.0 |
| **Temp ($^0$C)** | 28.2 ± 1.2 | 27.0 – 31.7 |
| **Fl- (µg/mL)** | 0.049 ± 0.012 | 0.037 – 0.077 |
| **$Cl^-$ (µg/mL)** | 3.47 ± 1.27 | 1.87 – 6.41 |
| **$SO_4^-$ (µg/mL)** | 2.56 (2.30 – 3.02) | 1.92 – 19.9 |
| **$NO_3^-$ (µg/mL)** | 6.75 ± 3.22 | 4.51 – 12.7 |
| **Na (µg/mL)** | 5.25 ± 2.08 | 2.94 – 10.1 |
| **$NH_4^+$ (µg/mL)** | 0.046 ± 0.047 | 0.004 -0.172 |
| **Mg (µg/mL)** | 0.461 ± 0.204 | 0.239 – 1.07 |
| **K (µg/mL)** | 0.990 ± 0.394 | 0.521 – 2.02 |
| **$Ca^{2+}$ (µg/mL)** | 2.68 ± 1.10 | 1.44 – 5.44 |
| **Pb (ng/mL)** | 0.033 ± 0.004 | 0.030 -0.036 |
| **Zn (ng/mL)** | 71.5 ± 23.0 | 44.6 - 110.3 |
| **Mn (ng/mL)** | 34.0 ± 21.3 | 0.536 – 93.6 |
| **Cd (ng/mL)** | 0.020 ± 0.009 | 0.008 – 0.031 |
| **As (ng/mL)** | 0.097 ± 0.043 | 0.041 – 0.197 |
| **Fe (ng/mL)** | 24.1 ± 28.3 | 2.45 – 112.2 |

## 4.8 Soil physico-chemical characteristics

Both the macro elements (Al, Mg, Mn, Ca, Fe, Na, K and P) and trace elements (As, Ni, Cr, Cu, Pb, Zn, Cd and Co) were selected as target analytes during the simultaneous analyses of both soil samples and Certified Reference Materials (CRMs). However, only results of As, Cd, Cr, Cu, Ni, Pb and Zn present in the CRM were randomly chosen to validate analytical technique. Table 4.16 presents the respective elements, wavelengths as well as limits of detection (LOD) and quantification (LOQ).

Table 4.16: Wavelengths used and LOD and LOQ of metals analysed in soil samples as derived from the 25 replicate measurements of deionised water (blanks) in ICP-OES.

| **Analyte** | **Wavelength (nm)** | **LOD µg/g** | **LOQ µg/g** |
|---|---|---|---|
| **Al** | 396.1 | 3.44 | 5.73 |
| **As** | 189.0 | 1.24 | 2.07 |
| **Ca** | 422.6 | .0.83 | 138.8 |
| **Cd** | 228.8 | 0.361 | 0.601 |
| **Co** | 228.6 | 0.350 | 0.583 |
| **Cr** | 267.7 | 0.409 | 0.681 |
| **Cu** | 324.7 | 0.600 | 1.00 |
| **Fe** | 240.4 | 4.43 | 7.39 |
| **K** | 769.8 | 10.4 | 17.4 |
| **Mg** | 280.2 | 13.1 | 21.8 |
| **Mn** | 257.6 | 0.455 | 0.759 |
| **Na** | 589.5 | 2.08 | 347.5 |
| **Ni** | 231.6 | 0.493 | 0.822 |
| **P** | 177.4 | 1.87 | 3.12 |
| **Pb** | 220.3 | 0.342 | 0.570 |
| **Zn** | 206.2 | 4.25 | 7.09 |

### 4.8.1 Assessment of analytical accuracy and precision using the Certified Reference Material (Metranal QCM 32 light sandy soil) used in ICP-OES

Recovery rates between 81% and 96% were recorded for elements present in the CRM used in the analyses (Table 4.17) with the general CRM characteristics presented in Appendix 4E.

Table 4.17: Percentage recovery for the six replicates of Certified Reference Material (Metranal QCM 32 light sandy) used during soil analyses.

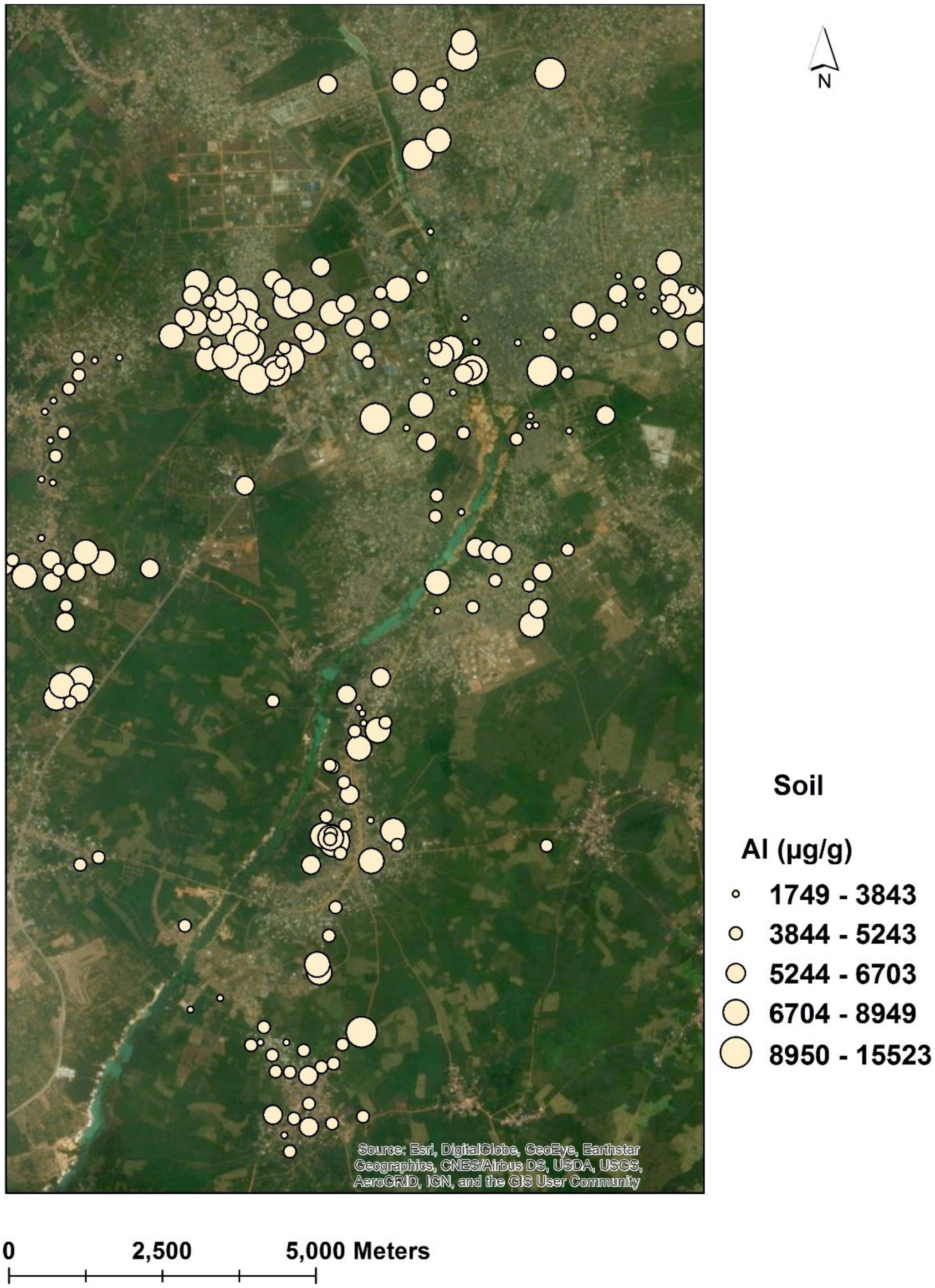
| **Analyte** | **Wavelength (nm)** | **Values (µg/g)** | | **%** | |
|---|---|---|---|---|---|
| | | **Certified** | **Measured** | **RSD** | **Accuracy** |
| **As** | 189.0 | 27.0 | 22.7± 1.69 | 7.44 | 84.1 |
| **Cd** | 228.8 | 2.30 | 2.22± 0.24 | 10.9 | 96.4 |
| **Cr** | 267.7 | 80.0 | 64.4 ± 6.07 | 9.43 | 80.5 |
| **Cu** | 324.7 | 92.0 | 79.7± 6.46 | 8.10 | 86.6 |
| **Ni** | 231.6 | 38.0 | 31.8± 5.09 | 16.0 | 83.6 |
| **Pb** | 220.3 | 160.0 | 137.8 ± 7.40 | 5.37 | 90.6 |
| **Zn** | 206.2 | 513.0 | 464.9 ± 22.1 | 4.74 | 90.6 |

### 4.8.2 Field and experimental result of soil in the study area

Summary description and concentrations range of different parameters analysed in the soil samples are shown in Table 4.18, while their spatial distributions are displayed in Figures 4.9a - k.

Table 4.18: Physical and chemical composition of soil across the study area (Owerri, Nigeria)

| Parameter | Mean or median/IQR | Minimum-Maximum |
|---|---|---|
| **pH** | 5.61± 0.80 | 3.73 - 8.92 |
| **Al (µg/g)** | 5304 (4263 - 6990) | 1749 -15523 |
| **As (µg/g)** | 0.499 (0.203 – 0.794) | 0.013 - 5.78 |
| **Ca (µg/g)** | 956.9 (586 – 1742.8) | 22.3 - 8855.7 |
| **Cu (µg/g)** | 3.70 (2.57 – 6.72) | 1.13 - 203.3 |
| **K (µg/g)** | 86.1 (59.1 – 111.6) | 20.5 - 951.4 |
| **Mg (µg/g)** | 141.9 (99.6 – 202.3) | 24.2 - 978.5 |
| **Mn (µg/g)** | 51.2 (59.5– 388.8) | 7.66 - 224.1 |
| **Fe (µg/g)** | 9577 ± 2925 | 2335 - 24464 |
| **P (µg/g)** | 234.3 (176.0 – 415.7) | 64.7 -1463.7 |
| **Pb (µg/g)** | 5.71 (4.29 – 8.93) | 2.70 -1463.7 |
| **Zn (µg/g)** | (12.7 – 84.0) | 0.060 - 436.2 |
| **Na (µg/g)** | 142.9 (61.6 – 388.3) | 8.66 – 471.5 |
| **Cd (µg/g)** | 0.16 (0.12 – 0.24) | 0.02 – 0.94 |



Source: Esri, DigitalGlobe, GeoEye, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community

Figure 4.9a: Aluminium (Al) concentrations in soil represented with graduated symbols to show variability across the study area of Owerri, Nigeria. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)

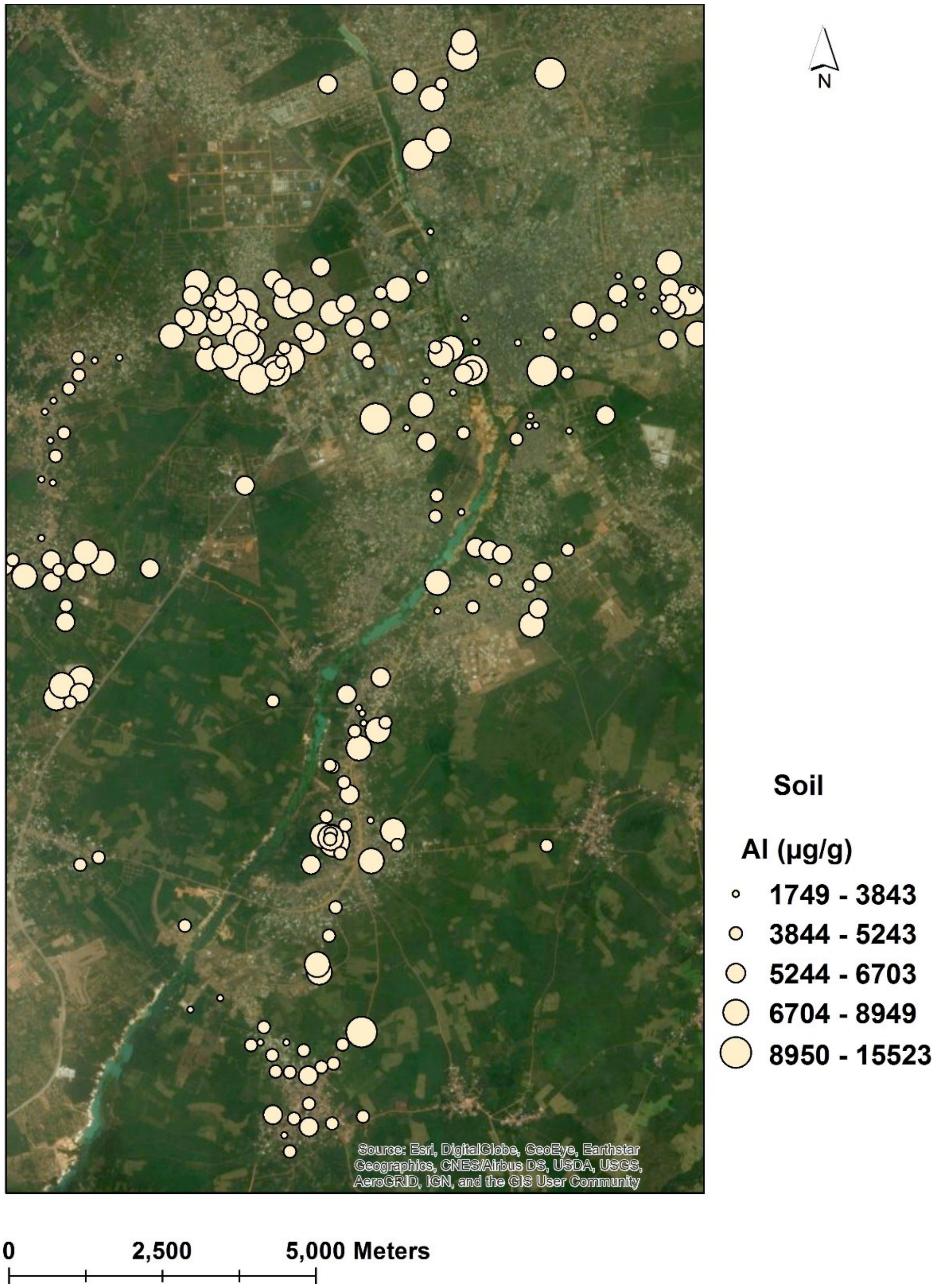


Figure 4.9b: Arsenic (As) concentrations in soil represented with graduated symbols to show variability across the study area of Owerri, Nigeria. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)

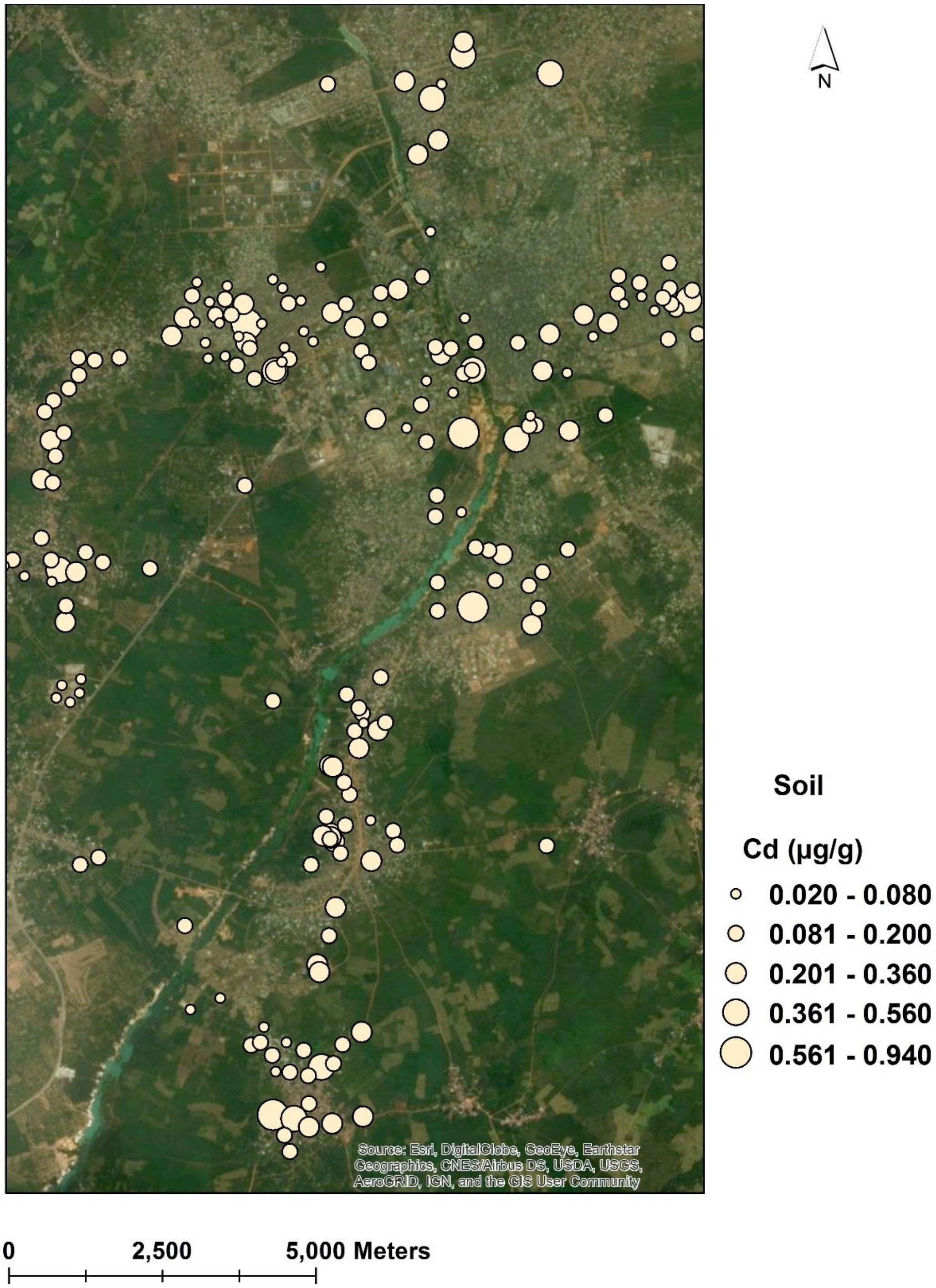


Figure 4.9c: Cadmium (Cd) concentrations in soil represented with graduated symbols to show variability across the study area of Owerri, Nigeria. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)

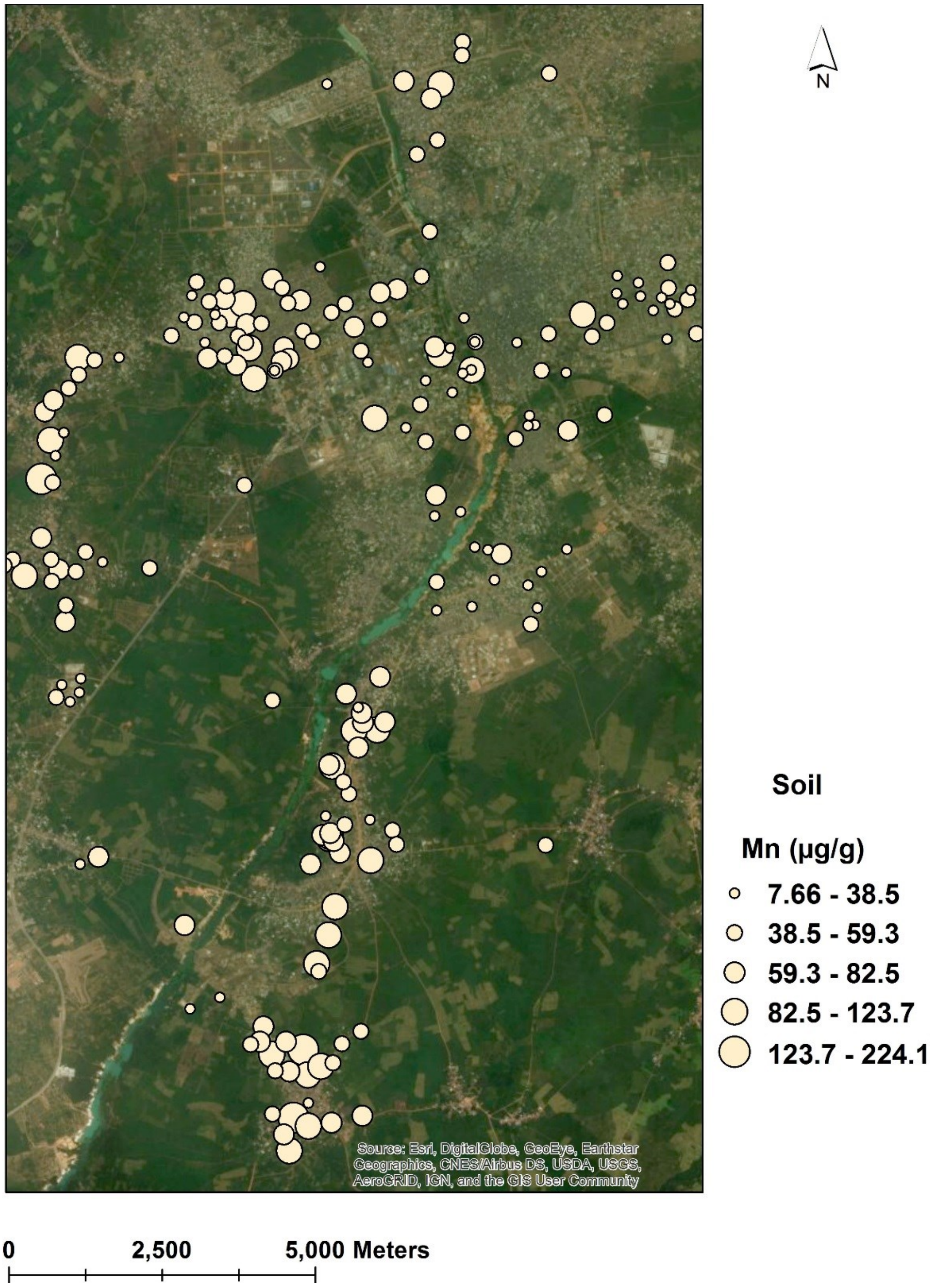
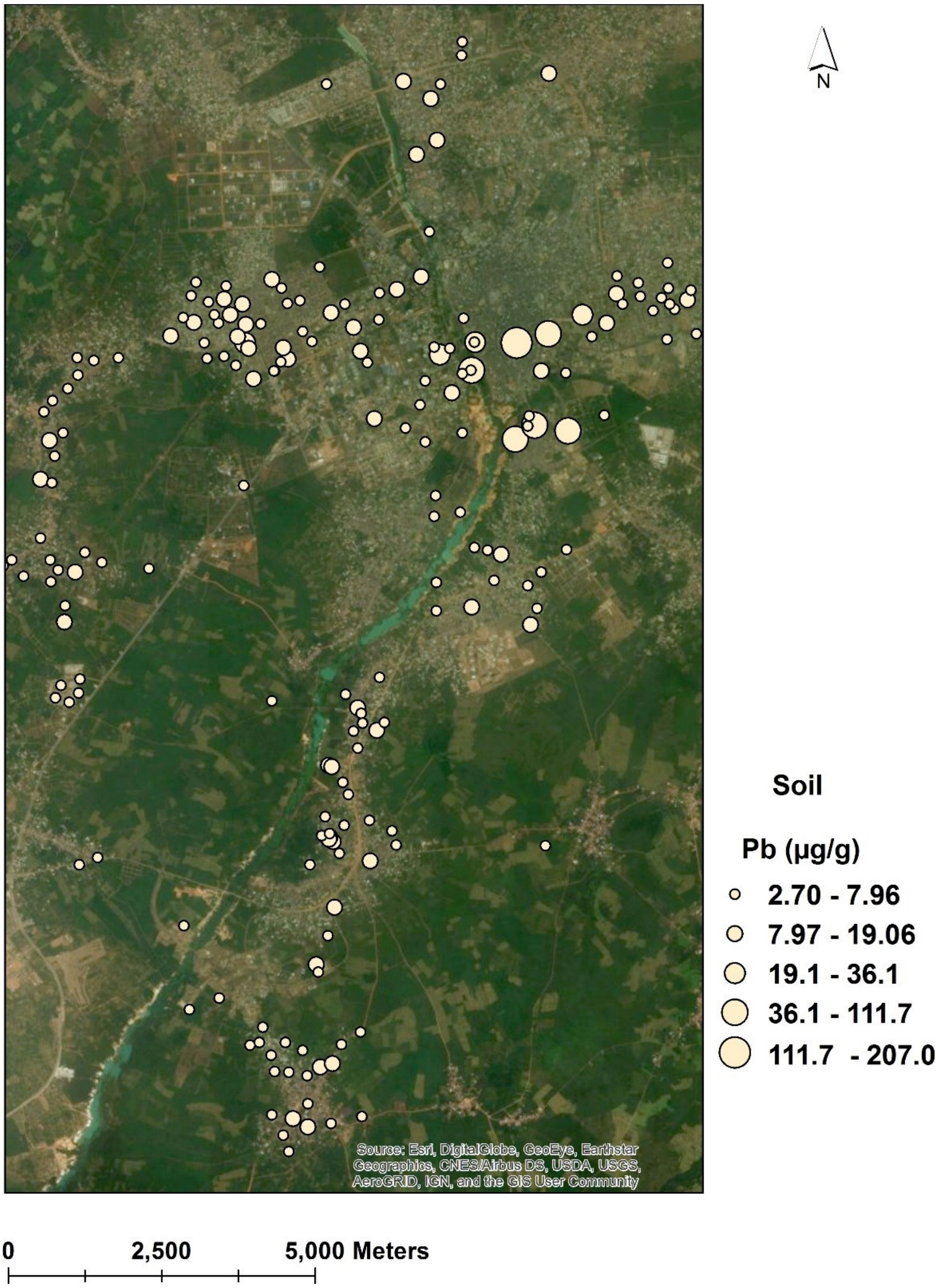
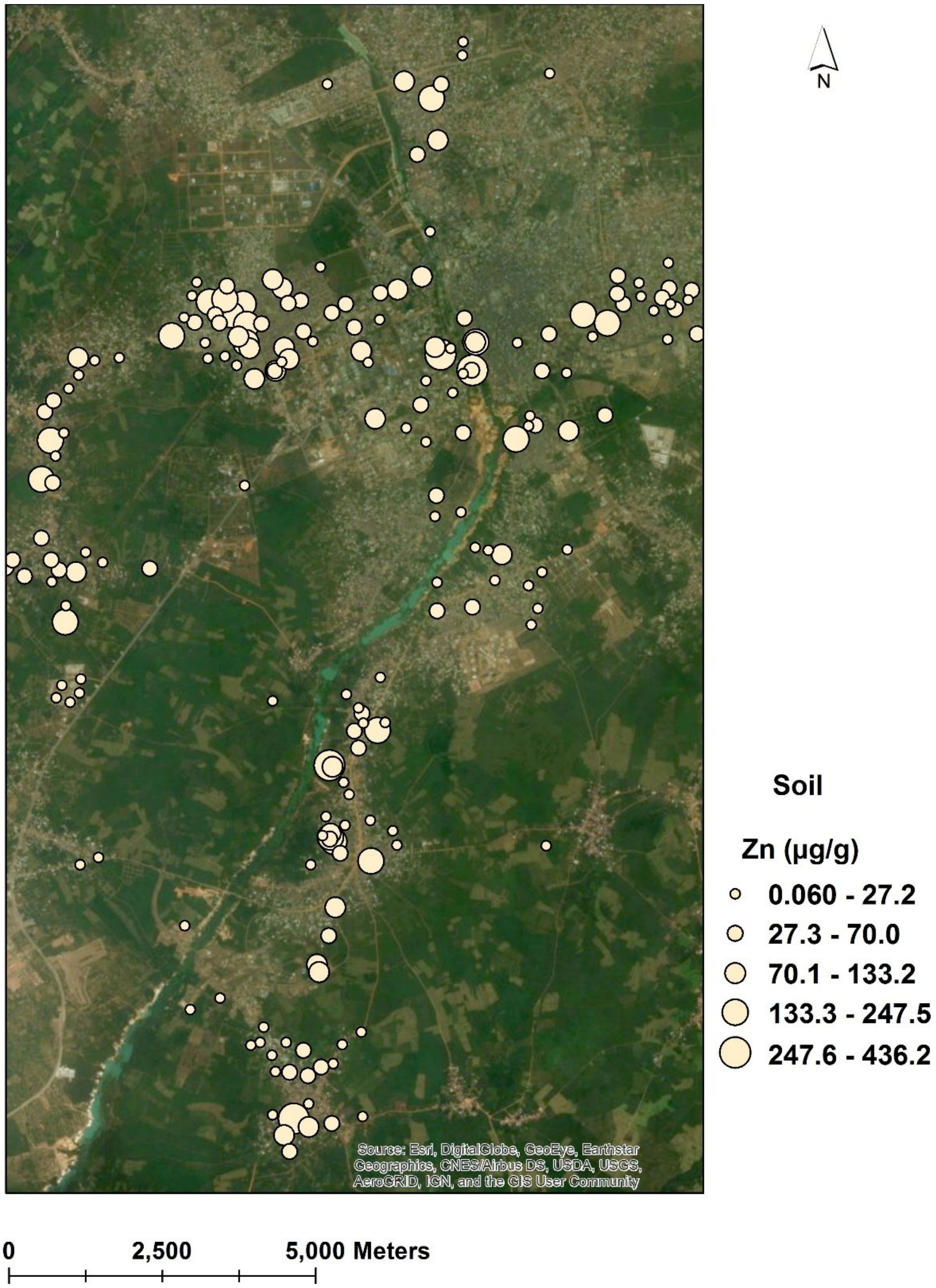


Figure 4.9d: Manganese (Mn) concentrations in soil represented with graduated symbols to show variability across the study area of Owerri, Nigeria. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)



Source: Esri, DigitalGlobe, GeoEye, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community

Figure 4.9e: Lead (Pb) concentrations in soil represented with graduated symbols to show variability across the study area of Owerri, Nigeria. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)



Source: Esri, DigitalGlobe, GeoEye, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community

Figure 4.9f: Zinc (Zn) concentrations in soil represented with graduated symbols to show variability across the study area of Owerri, Nigeria. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)

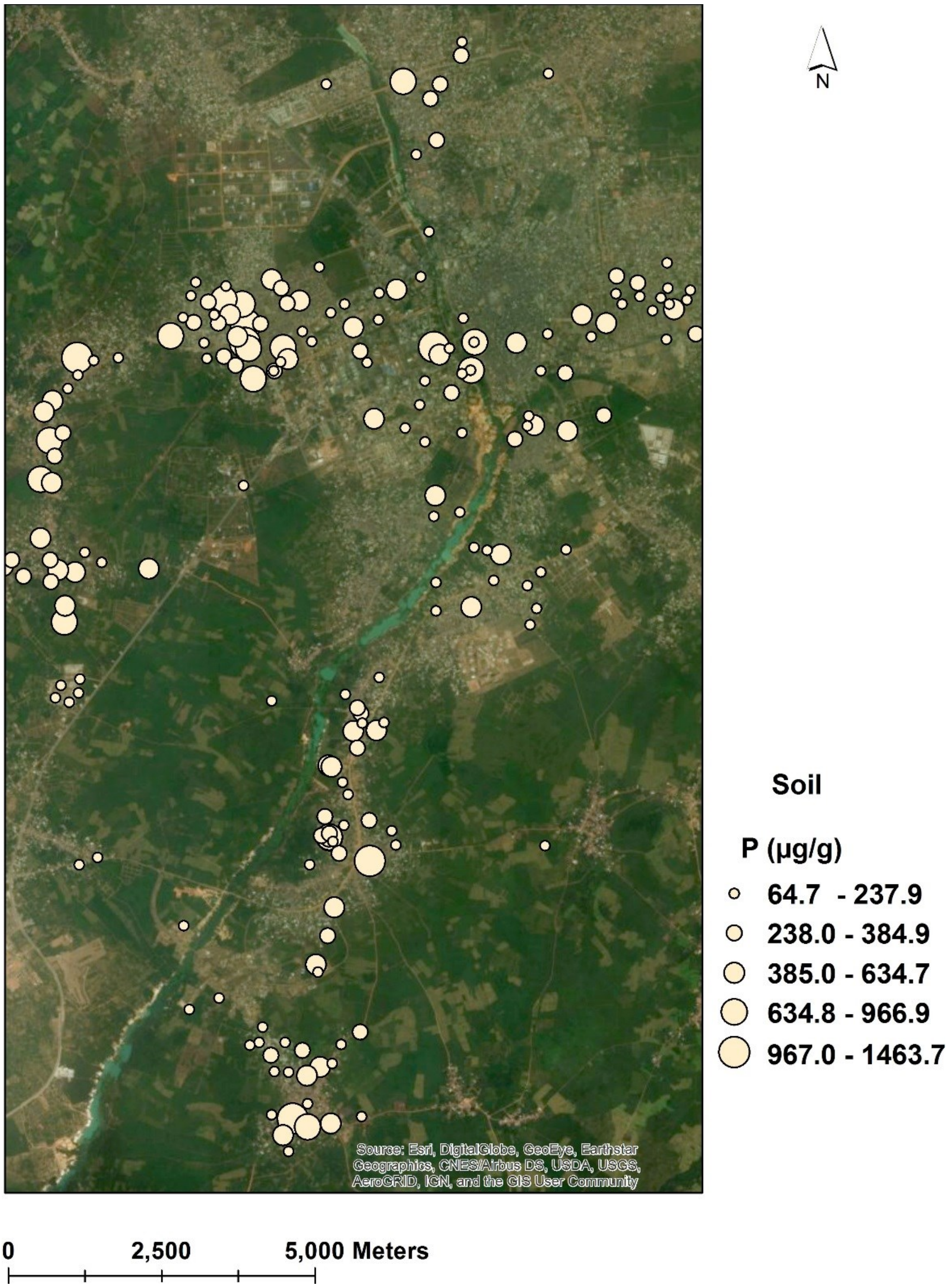


Figure 4.9g: Phosphorus (P) concentrations in soil represented with graduated symbols to show variability across the study area of Owerri, Nigeria. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)

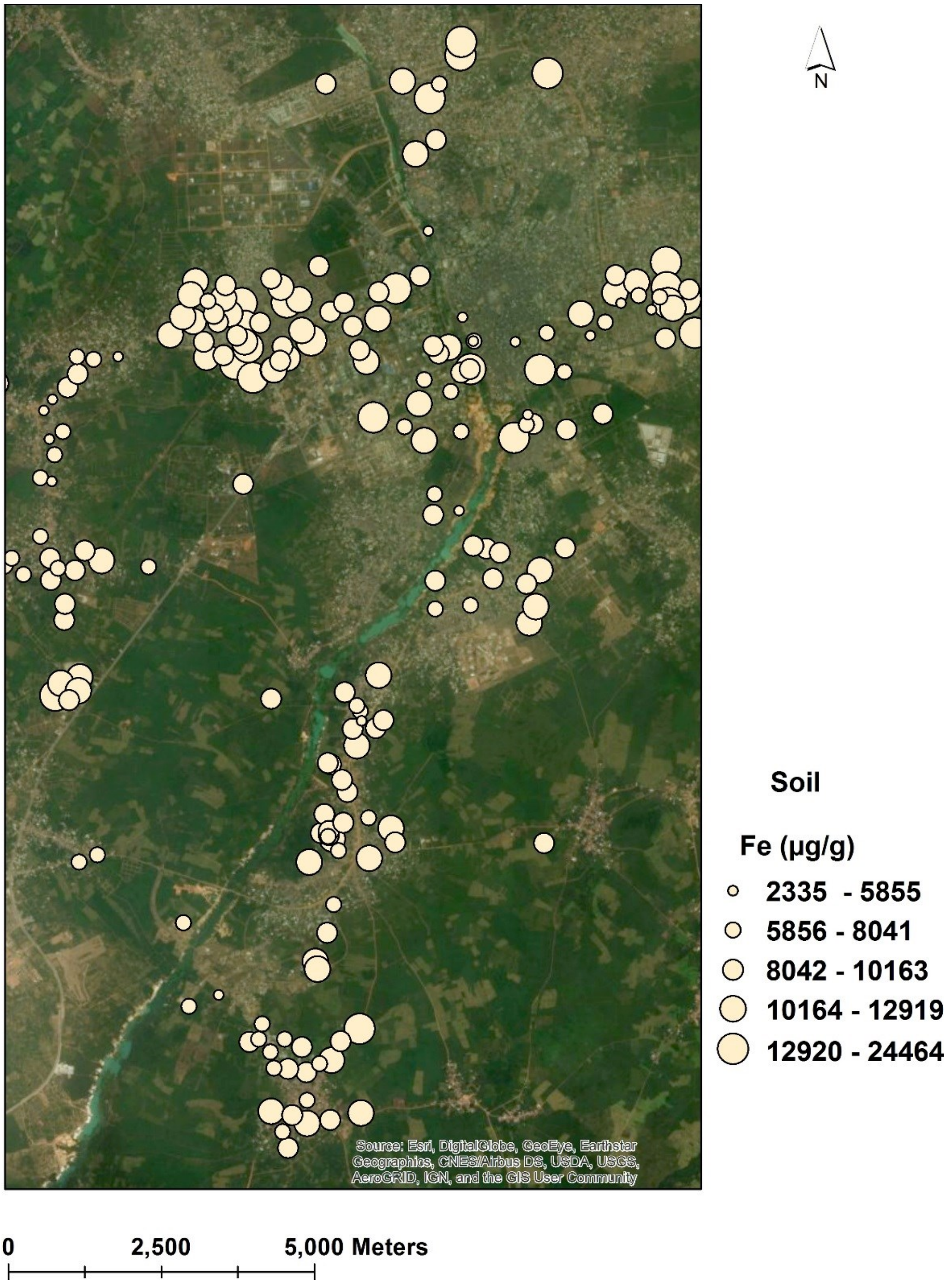


Figure 4.9h: Iron (Fe) concentrations in soil represented with graduated symbols to show variability across the study area of Owerri, Nigeria. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)

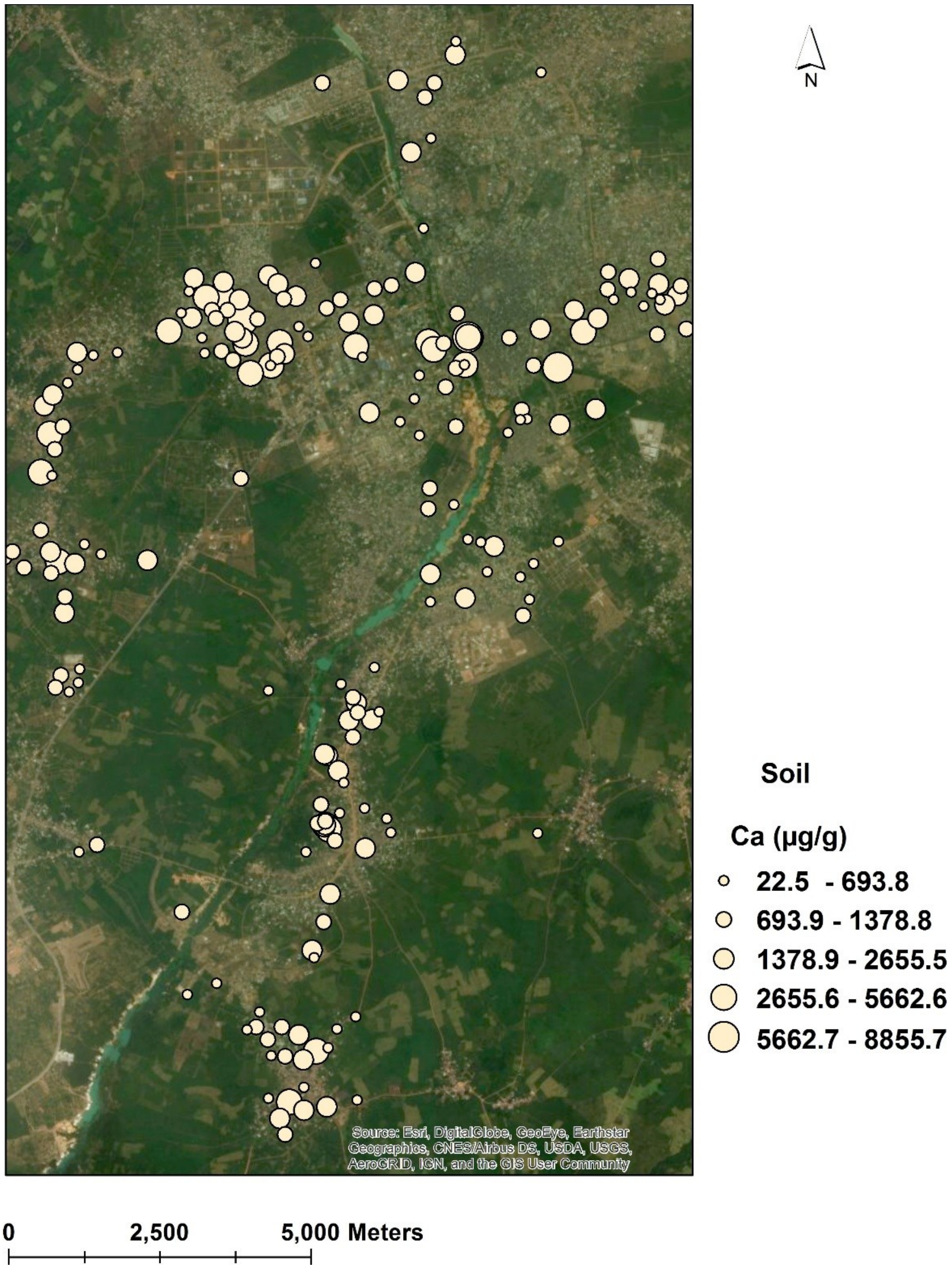
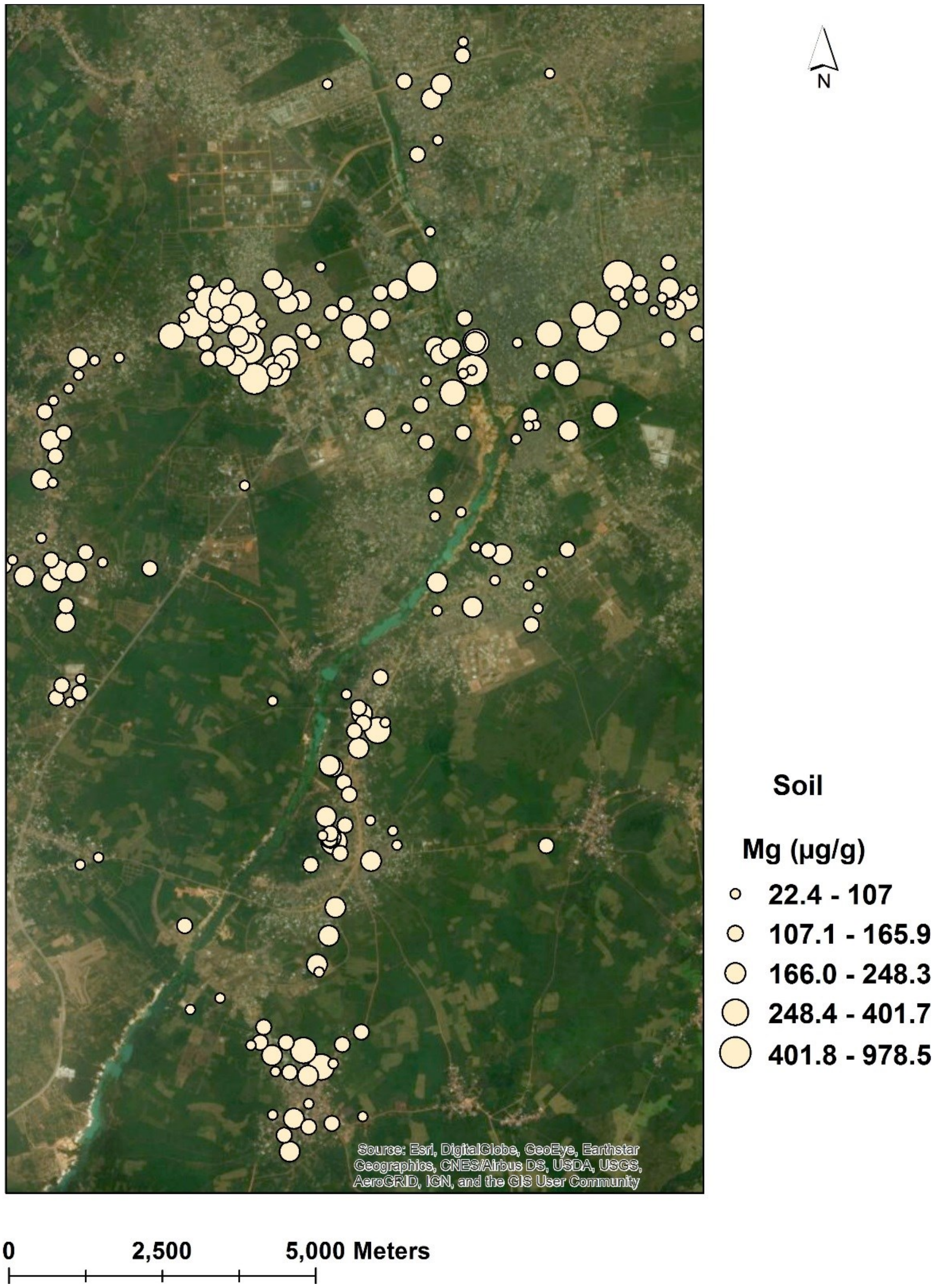


Figure 4.9i: Calcium (Ca) concentrations in soil represented with graduated symbols to show variability across the study area of Owerri, Nigeria. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)



Source: Esri, DigitalGlobe, GeoEye, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community

Figure 4.9j: Magnesium (Mg) concentration in soil represented with graduated symbols to show variability across the study area of Owerri, Nigeria. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)

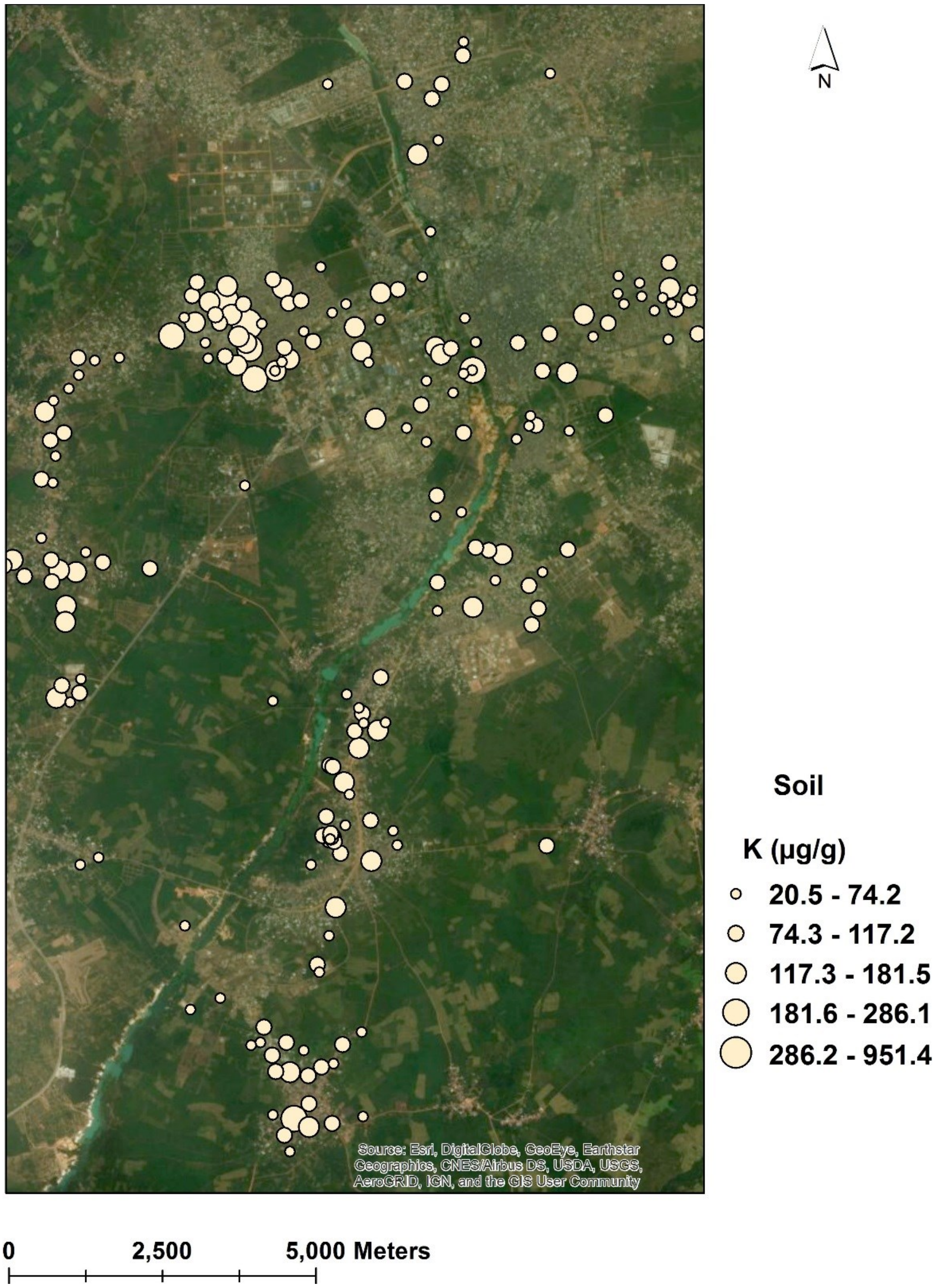


Figure 4.9k: Potassium (K) concentration in soil represented with graduated symbols to show variability across the study area of Owerri, Nigeria. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)

## 4.9 Basic soil attributes of potential influence on groundwater contamination

Soil attributes that are relevant to this study include: Soil Organic Matter (SOM), Soil Organic Carbon (SOC), and C: N ratio. These are presented in Table 4.19. Twenty-three replicate samples of reference materials used for the C:N ratio in the soil samples showed a recovery rate of 103.0% and 97.4% for carbon and nitrogen respectively (Appendix 4H). Mean N was 0.189 ± 0.041%; while median carbon value was 2.12% (IQR of 2.10% - 2.14%). Soil organic matter had a median concentration of 3.32 % (IQR = 2.51% - 3.87%) across the study area.

Table 4.19: Basic soil attributes as analysed by loss-on-ignition and elemental analyser.

| Range | SOM (%) | SOC (%) | % Carbon | % Nitrogen | C:N ratio |
|---|---|---|---|---|---|
| **Median** | 3.34 | 1.94 | 1.10 | 0.088 | 13.7 |
| **IQR** | 2.51 – 3.89 | 1.46 – 2.26 | 0.768 – 1.42 | 0.066 - 0.131 | 11.9 – 16.6 |
| **Minimum** | 0.727 | 0.423 | 0.011 | 0.028 | 0.10 |
| **Maximum** | 36.1 | 21.0 | 2.90 | 2.26 | 30.4 |

## 4.10 Plant (*Manihot esculanta* & *Telfaira occidentalis*) elemental characteristics

### 4.10.1 Calibration and estimation of LOD and LOQ for the analysed elements in plants

Similar calibration procedures as conducted for all previous ICP-OES analyses were followed. Using the already established protocol, the LOD and LOQ of target analytes were calculated and presented in Table 4.20 for the respective plant species.

Table 4.20: LOD and LOQ for metals as derived from 20 replicate measurements of 5 ml of nitric acid and 1 ml of deionised water (blanks), during the analyses of plants (*Telfaria occidentalis* and *Manihot esculanta)* samples in ICP-OES.

| **Analyte** | **λ (nm)** | **LOD** (µg/g) *Telfaria occidentalis* | **LOQ** *(µg/g) Telfaria occidentalis* | **LOD** (µg/g) *Manihot esculanta* | **LOQ** (µg/g) *Manihot esculanta* |
|---|---|---|---|---|---|
| **Al** | 396.1 | 1.05 | 3.45 | 0.730 | 2.44 |
| **As** | 189.0 | 0.083 | 0.278 | 0.079 | 0.262 |
| **Cd** | 214.4 | 0.002 | 0.007 | 0.001 | 0.004 |
| **Co** | 228.6 | 0.000 | 0.000 | 0.012 | 0.040 |
| **Ca** | 422.6 | 379.3 | 1264.2 | 97.2 | 324.1 |
| **Cr** | 267.7 | 0.018 | 0.058 | 0.018 | 0.061 |
| **Cu** | 240.4 | 0.742 | 2.47 | 0.464 | 1.55 |
| **Pb** | 220.3 | 0.045 | 0.151 | 0.048 | 0.159 |
| **Mn** | 257.6 | 0.885 | 2.95 | 0.044 | 0.145 |
| **Na** | 589.5 | 155.5 | 518.3 | 217.7 | 725.7 |
| **Fe** | 240.4 | 1.14 | 3.82 | 1.39 | 4.62 |
| **K** | 766.4 | 25.8 | 86.0 | 14.4 | 48.1 |
| **Mg** | 280.2 | 93.6 | 312.0 | 13.5 | 45.0 |
| **Ni** | 231.6 | 0.440 | 1.47 | 0.156 | 0.519 |
| **P** | 178.2 | 0.003 | 0.005 | 1.75 | 5.83 |
| **Zn** | 206.2 | 3.61 | 12.0 | 6.83 | 0.159 |

### 4.10.2 Analytical accuracy and precision using the recovery rate of selected analytes in LGC 7162 Strawberry leaves via ICP-OES

All plants samples were analysed alongside CRM LGC 7162 (strawberry leaves). The percentage recovery of measured macronutrients (P, K, Ca, and Mg), ranged between 79.7% to 92.0%, and 77.6% to 100.0%.Table 4.21 presents the CRM report.

Table 4.21: Evaluation of analytical precision and accuracy using percentage recovery rate of target analytes in the 25 replicates of CRM LGC 7162 (strawberry leaves) via ICP-OES.

(*= indicative value (µg/g), NS = Not Specified)

| **Analyte** | **Values(µg/g)** | | | **% RSD** | **% Recovery** |
|---|---|---|---|---|---|
| | **Certified** | **Measured** | **Error** | | |
| **Zn** | 24.0 ± 5.00 | 27.2 | 3.20 | 39.7 | 113.4 |
| **Ca** | 15300.0 ±700.0 | 15298.9 | 1.10 | 3.70 | 100.0 |
| **Cd** | 0.170 ± 0.040 | 0.170 | 0.000 | 2.50 | 100.0 |
| **P** | 2600.0 ± 230.0 | 2549.7 | 50.3 | 1.90 | 98.1 |
| **Pb** | 1.80 ± 0.400 | 1.61 | 0.190 | 15.3 | 89.2 |
| **K** | 19600.0 ±1000.0 | 16900.6 | 2699.4 | 2.70 | 86.2 |
| **Mn** | 171.0 ±10.0 | 140.1 | 30.9 | 5.60 | 81.9 |
| **Cu** | 10.0* | 7.97 | NS | 11.3 | 79.7 |
| **Ni** | 2.60 ± 0.700 | 2.05 | 0.550 | 5.20 | 78.8 |
| **Mg** | 3770.0 ±170.0 | 2927.1 | 842.9 | 5.10 | 77.6 |
| **Co** | 0.470 ± 0.110 | 0.300 | 0.170 | 3.80 | 63.3 |
| **Cr** | 2.15 ± 0.340 | 1.31 | 0.840 | 3.10 | 60.9 |
| **Fe** | 818.0 ± 48.0 | 478.2 | 339.8 | 5.40 | 58.5 |

### 4.10.3 Chemical characteristics of elements in pumpkin (*Telfaira occidentalis*) leaves and cassava (*Manihot esculanta)* tubers.

Descriptive summary of analysed macronutrients (Ca, K, P, Mg), and trace elements with more than 80 % CRM recovery (Mn, Cu, Pb, Cd) have been presented as Tables 4.22 and Figures 4.10 a - p. All micronutrients and trace element were normally distributed in leaf except Pb, Cd, and percentage carbon (%) which did not show normal distribution pattern while none of the analytes was normally distributed in tuber plant.

Table 4.22: Chemical composition of sampled plant (*Telfaira occidentalis* and *Manihot esculanta*) species

| **Parameter** | ***Telfaira occidentalis*** | | ***Manihot esculanta*** | |
|---|---|---|---|---|
| | **Mean or Median** | **Minimum Maximum** | **Median(IQR)** | **Minimum - Maximum** |
| **Ca (µg/g)** | 15591 ±7634 | 2673 - 41213 | 872 (575- 1245), | 308 - 15777 |
| **K (µg/g)** | 28125 ± 7467 | 9028 - 54458 | 6551 (4495 - 9469) | 2360 - 52913 |
| **Mg (µg/g)** | 4091.0 ±1266.0 | 1254 - 7742 | 555.3 (424.6 - 724) | 200.7 - 3657.8 |
| **P (µg/g)** | 4961.0 ±1783.0 | 1676 - 10603 | 1099 (927- 1529) | 605 - 11648 |
| **Mn (µg/g)** | 96.3 ±53.9 | 19.1 - 275.1 | 2.92 (1.81-4.60) | 0.690 - 20.1 |
| **Cu (µg/g)** | 12.1 ±3.64 | 4.18 - 21.8 | 2.10 (1.36 - 2.60) | 0.490 - 13.2 |
| **Pb (µg/g)** | 0.851 (0.639 - 1.22) | 0.249 -5.26 | 0.130 (0.077 - 0.223) | 0.048 - 0.881 |
| **Cd (µg/g)** | 0.025 (0.018-0.038) | 0.006 -1.29 | 0.010 (0.005 - 0.017) | 0.001 - 0.752 |
| **N (%)** | 5.55 ± 1.12 | 3.33 - 9.78 | 0.38 (0.28 - 0.5) | 0.15 - 2.62 |
| **C (%)** | 42.5 (41.3 - 43.8) | 30.5 - 62.6 | 40.0 (39.5 - 40.9) | 35.9 - 43.5 |

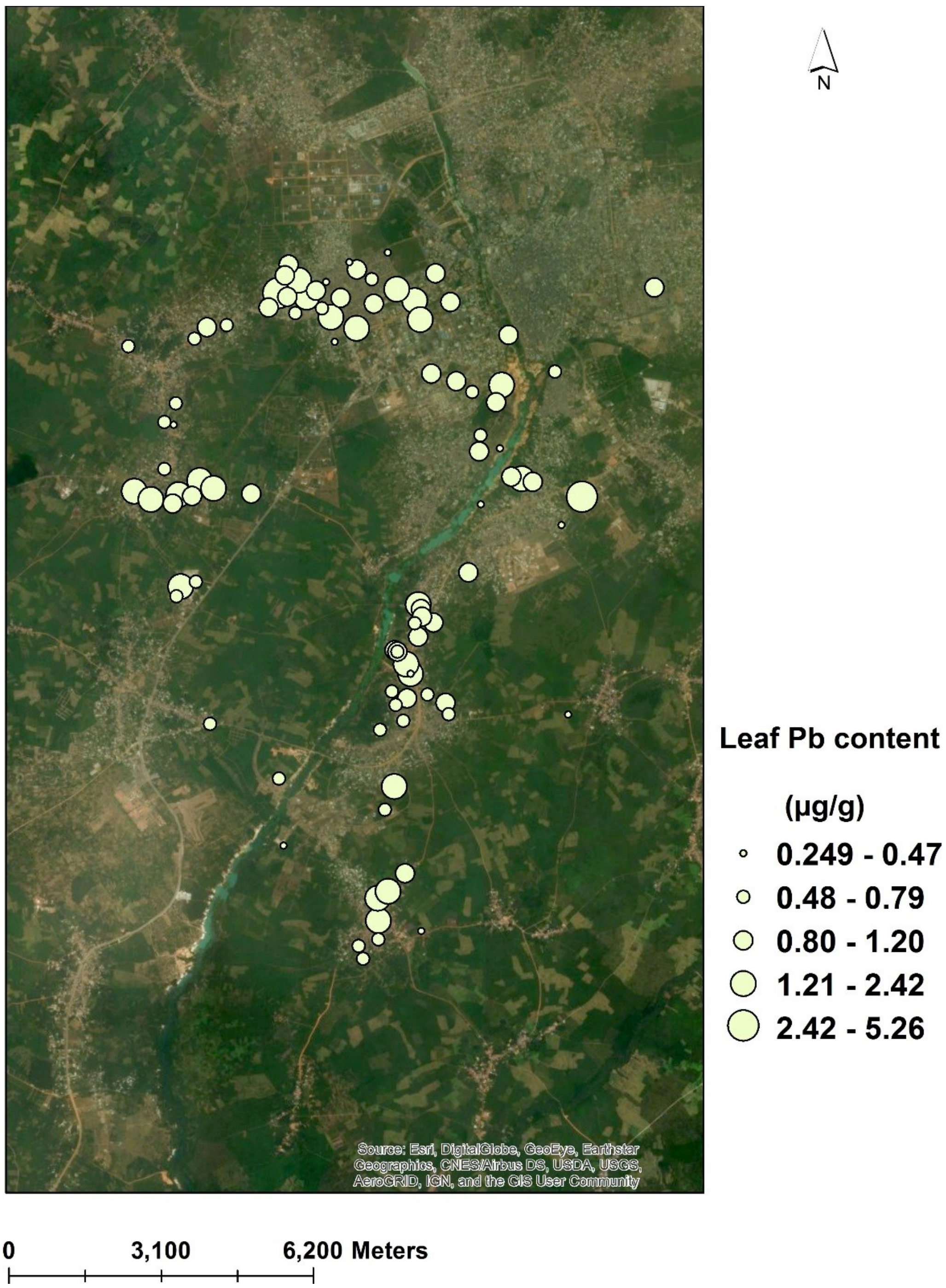


Figure 4.10a: Lead (Pb) concentration pattern in pumpkin leaf (*Telfaira occidentalis*) represented with graduated symbols to show variability across the study area of Owerri, Nigeria. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)

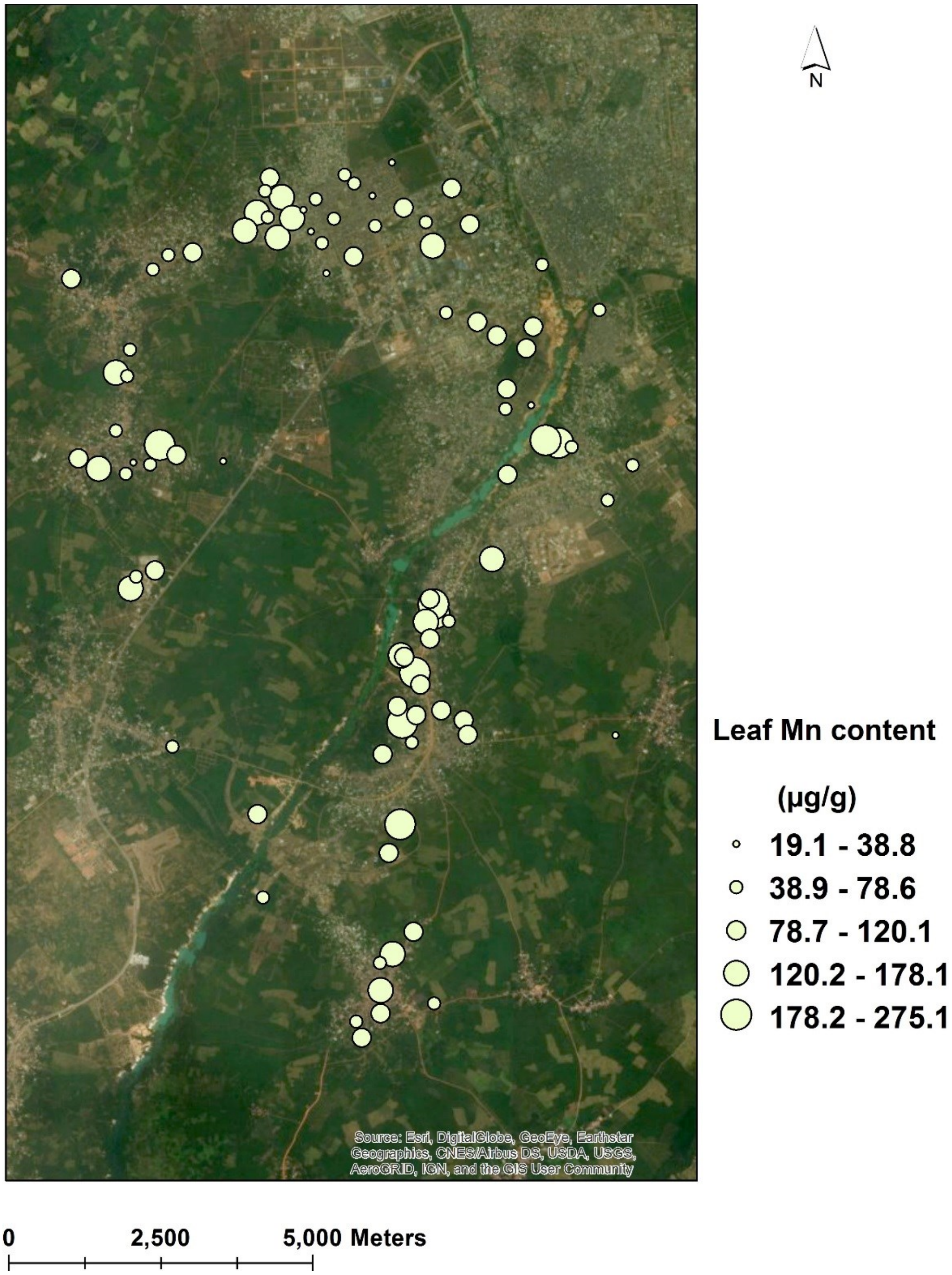


Figure 4.10b: Manganese (Mn) concentration pattern in pumpkin leaf (*Telfaira occidentalis*) represented with graduated symbols to show variability across the study area of Owerri, Nigeria. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)

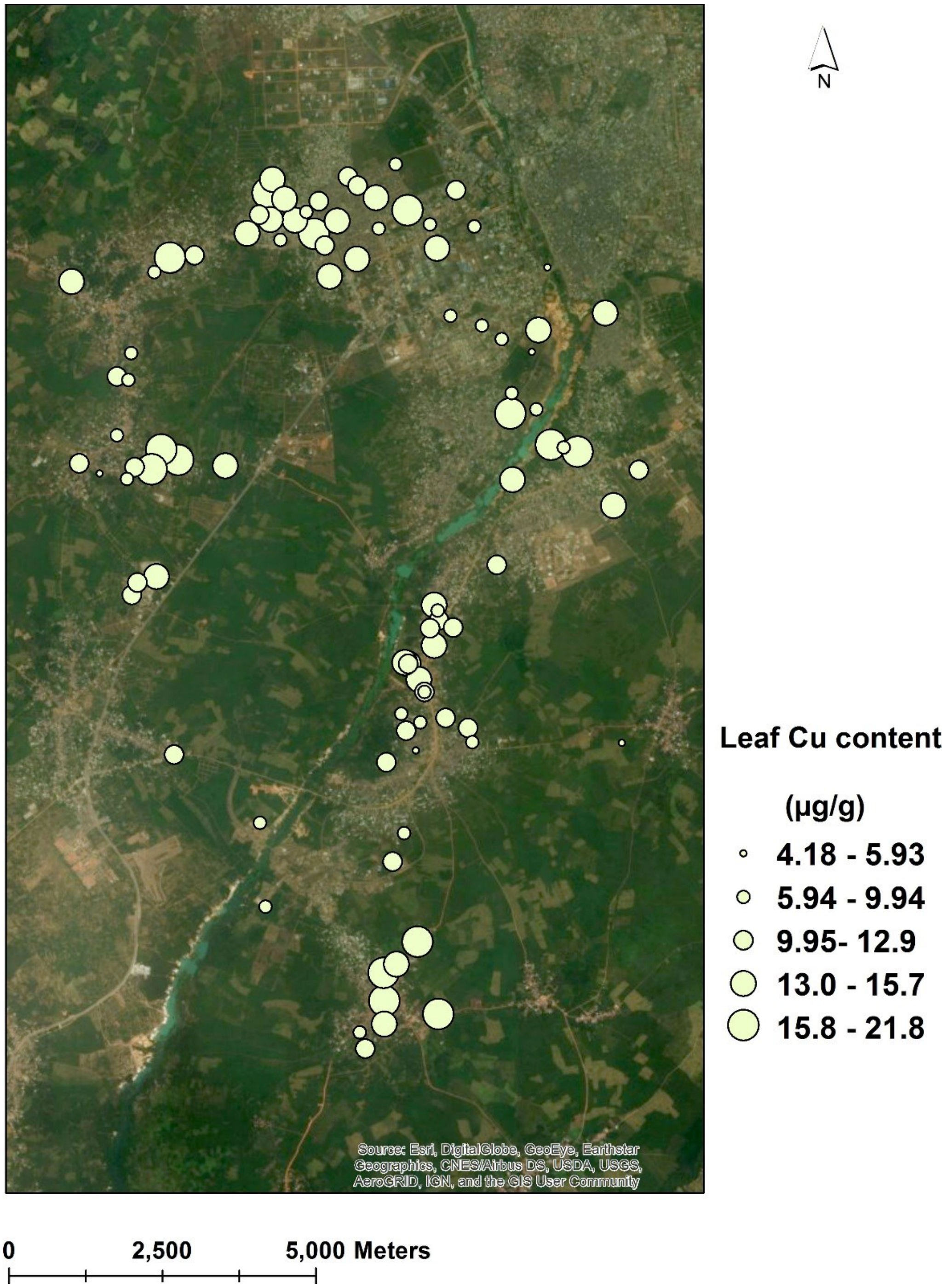


Figure 4.10c: Copper (Cu) concentration pattern in pumpkin leaf (*Telfaira occidentalis*) represented with graduated symbols to show variability across the study area of Owerri, Nigeria. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)

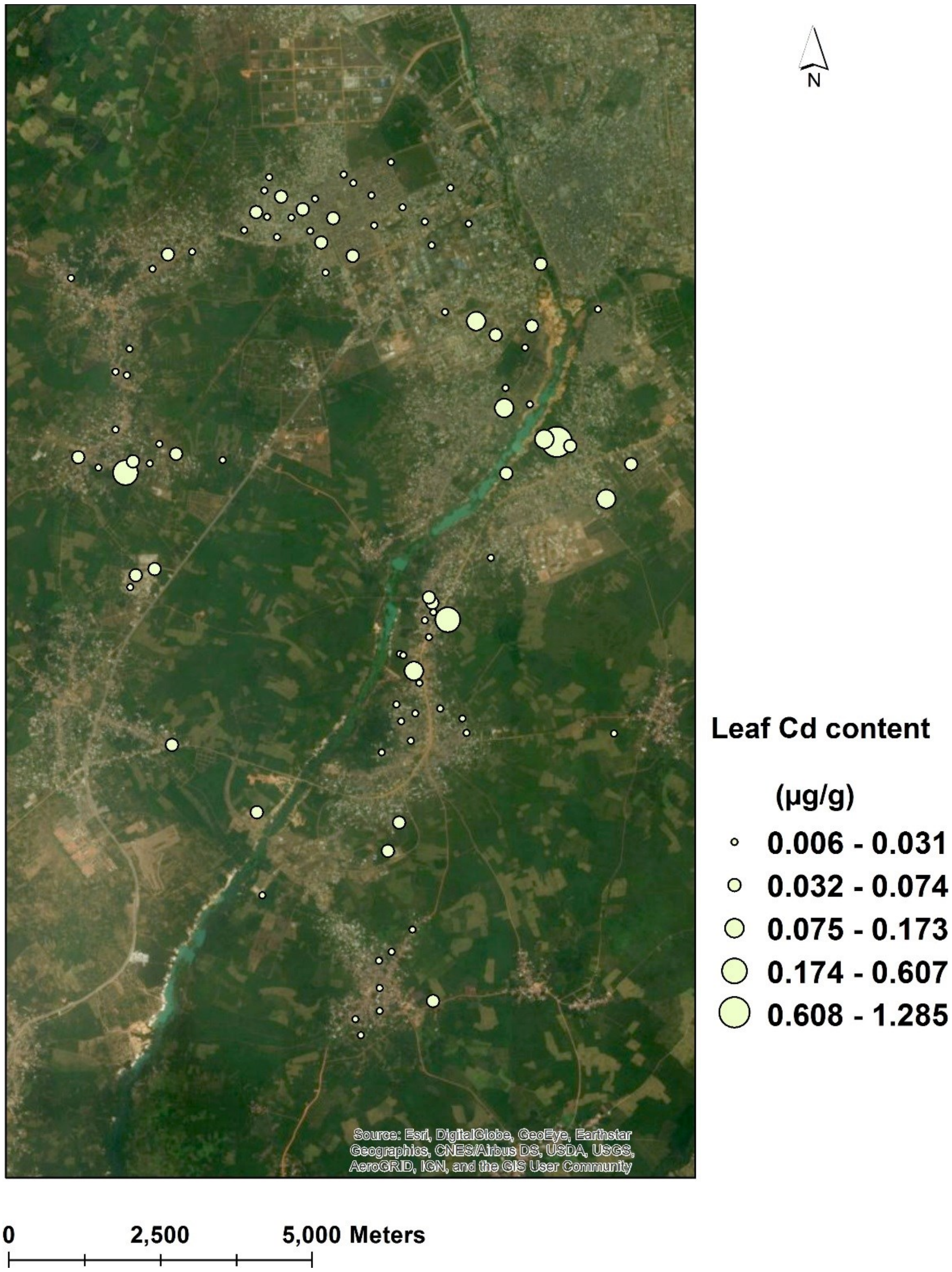


Figure 4.10d**:** Cadmium (Cd) concentration pattern in pumpkin leaf (*Telfaira occidentalis*) represented with graduated symbols to show variability across the study area of Owerri, Nigeria. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)

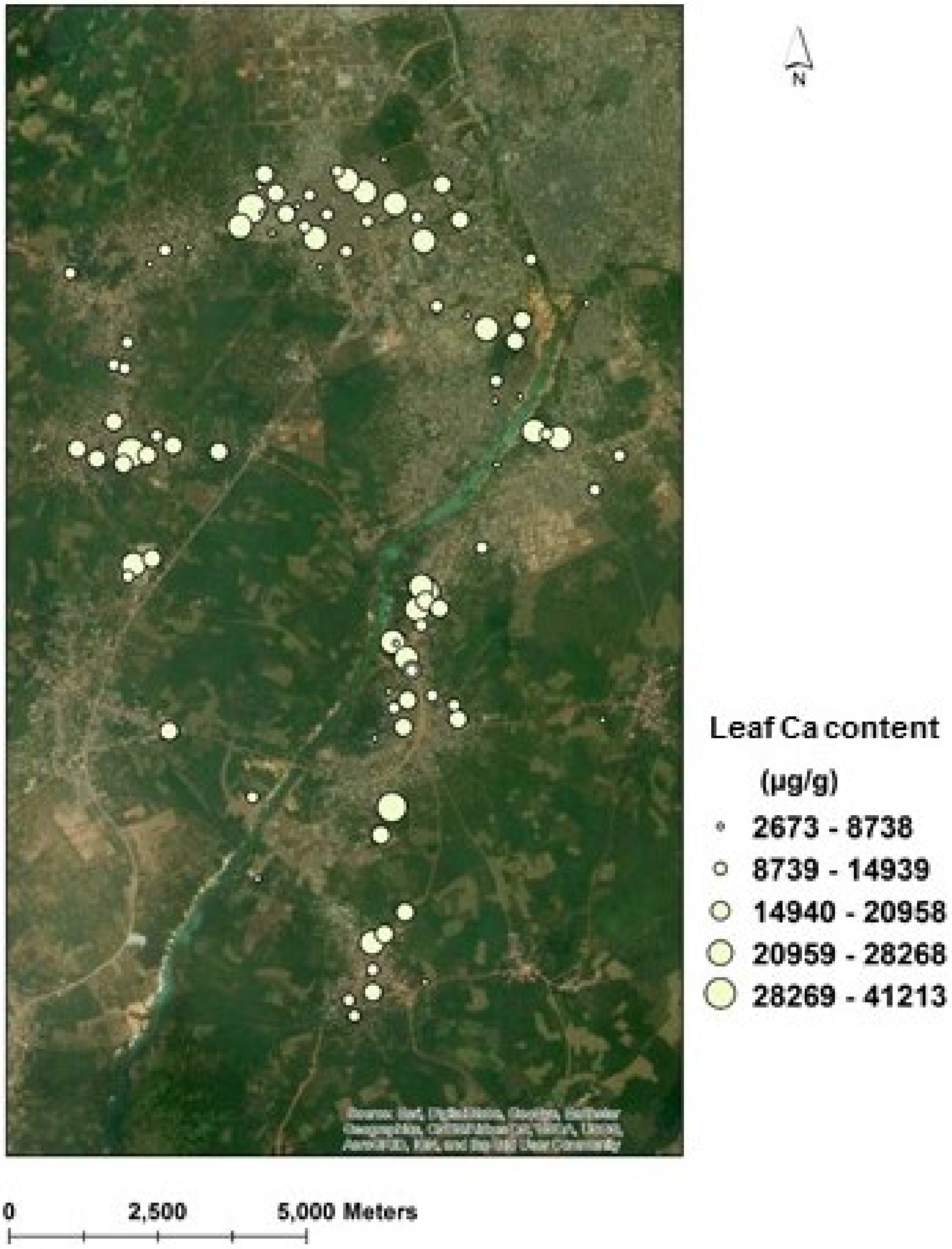


Figure 4.10e: Calcium (Ca) concentration pattern in Pumpkin Leaf (*Telfaira occidentalis*) represented with graduated symbols to show variability across the study area of Owerri, Nigeria. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)

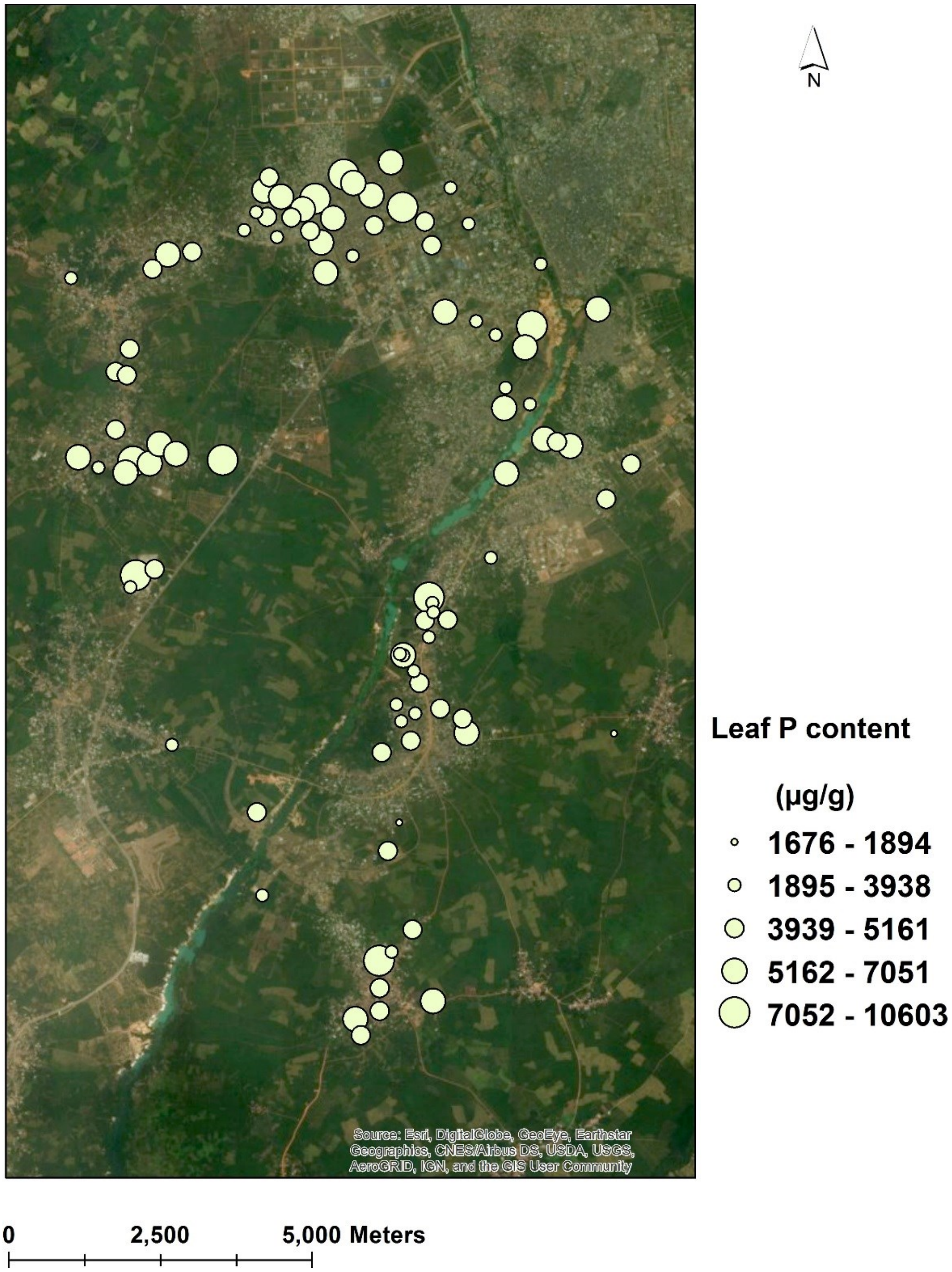


Figure 4.10f: Phosphorus (P) concentration pattern in pumpkin leaf (*Telfaira occidentalis*) represented with graduated symbols to show variability across the study area of Owerri, Nigeria. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)

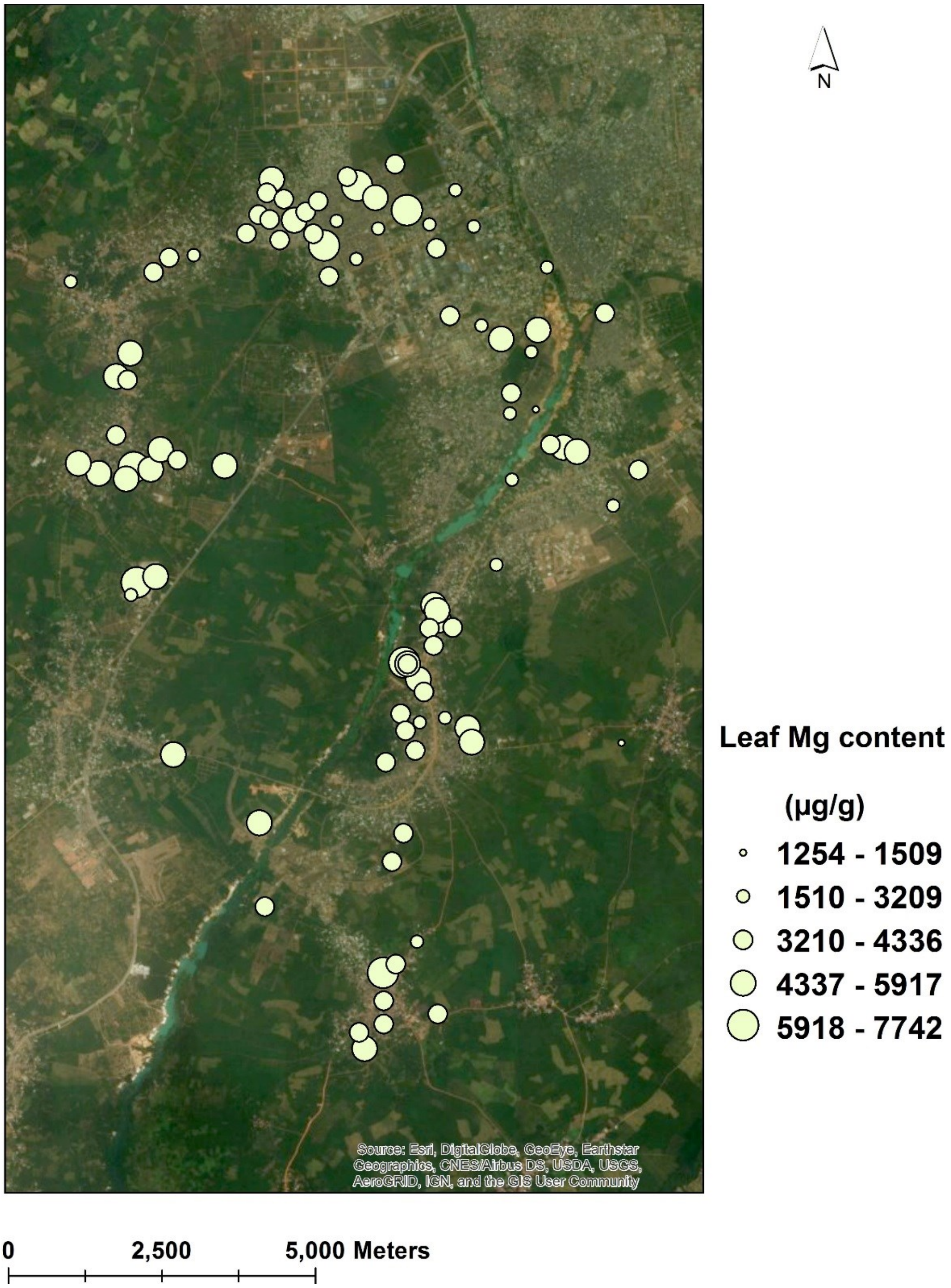


Figure 4.10g: Magnesium (Mg) concentration pattern in pumpkin leaf (*Telfaira occidentalis*) represented with graduated symbols to show variability across the study area of Owerri, Nigeria. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)

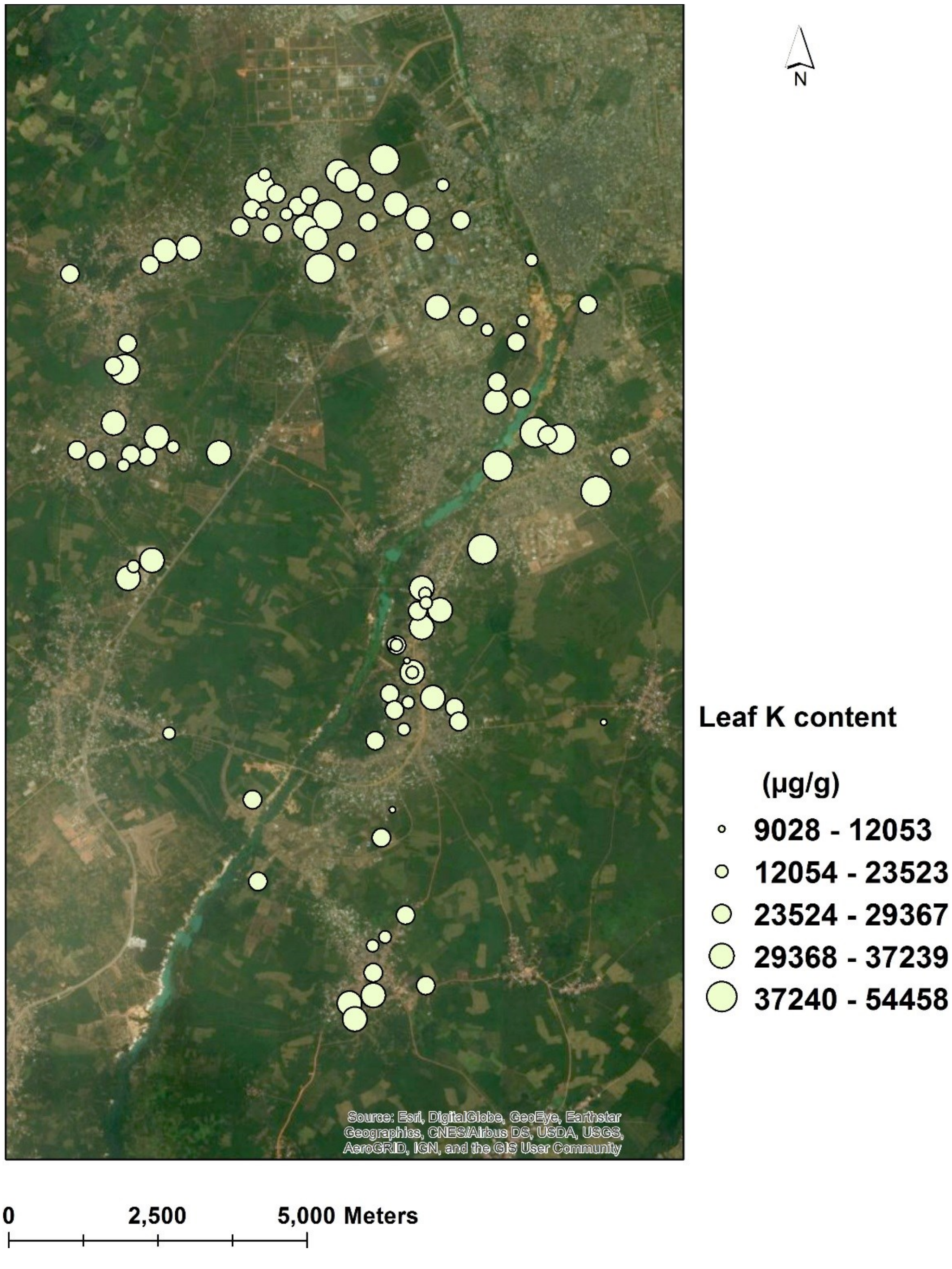


Figure 4.10h**:** Potassium (K) concentration pattern in pumpkin leaf (*Telfaira occidentalis*) represented with graduated symbols to show variability across the study area of Owerri, Nigeria. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)

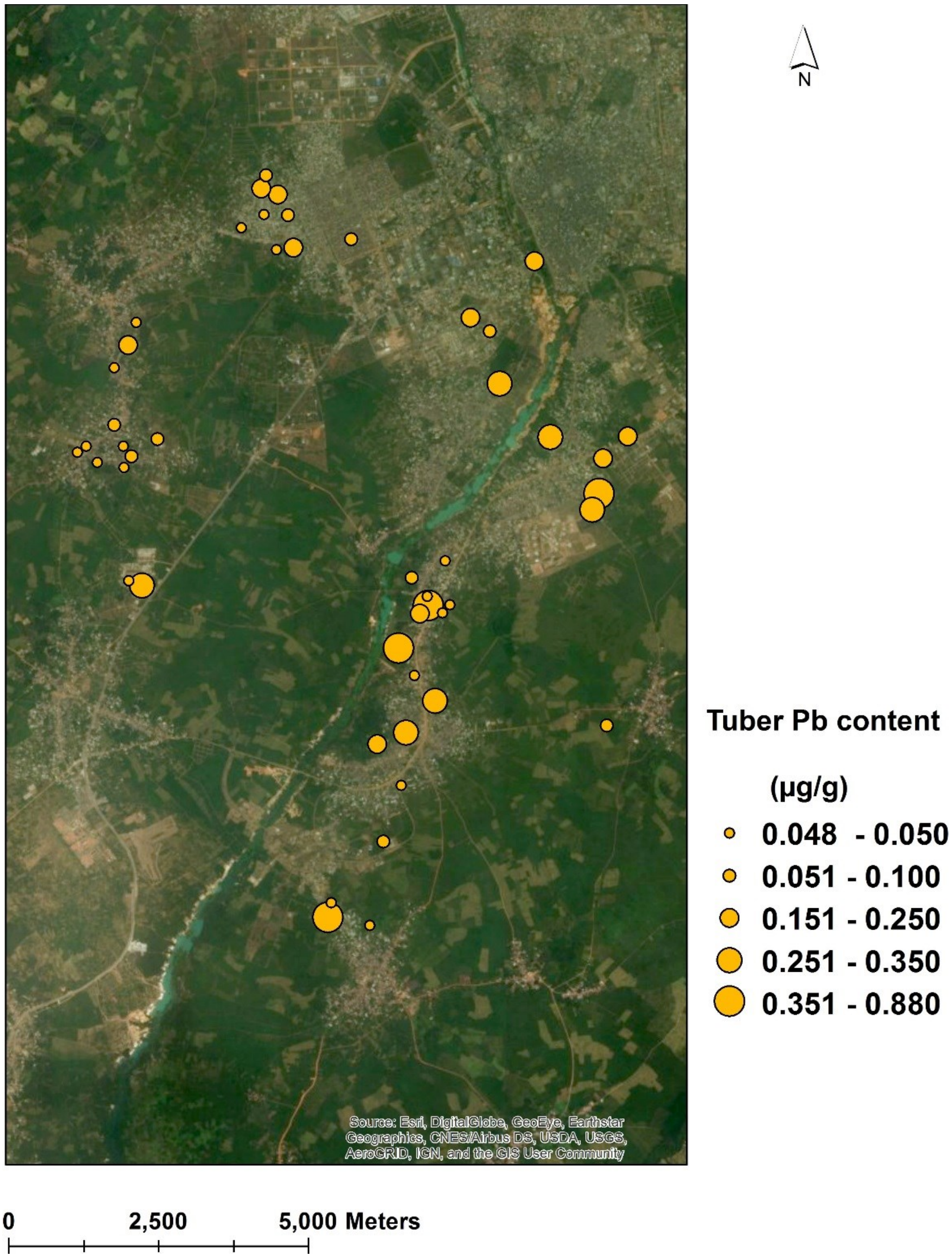


Figure 4.10i**:** Lead (Pb) concentration pattern in cassava tuber (*Manihot esculanta*) represented with graduated symbols to show variability across the study area of Owerri, Nigeria. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)

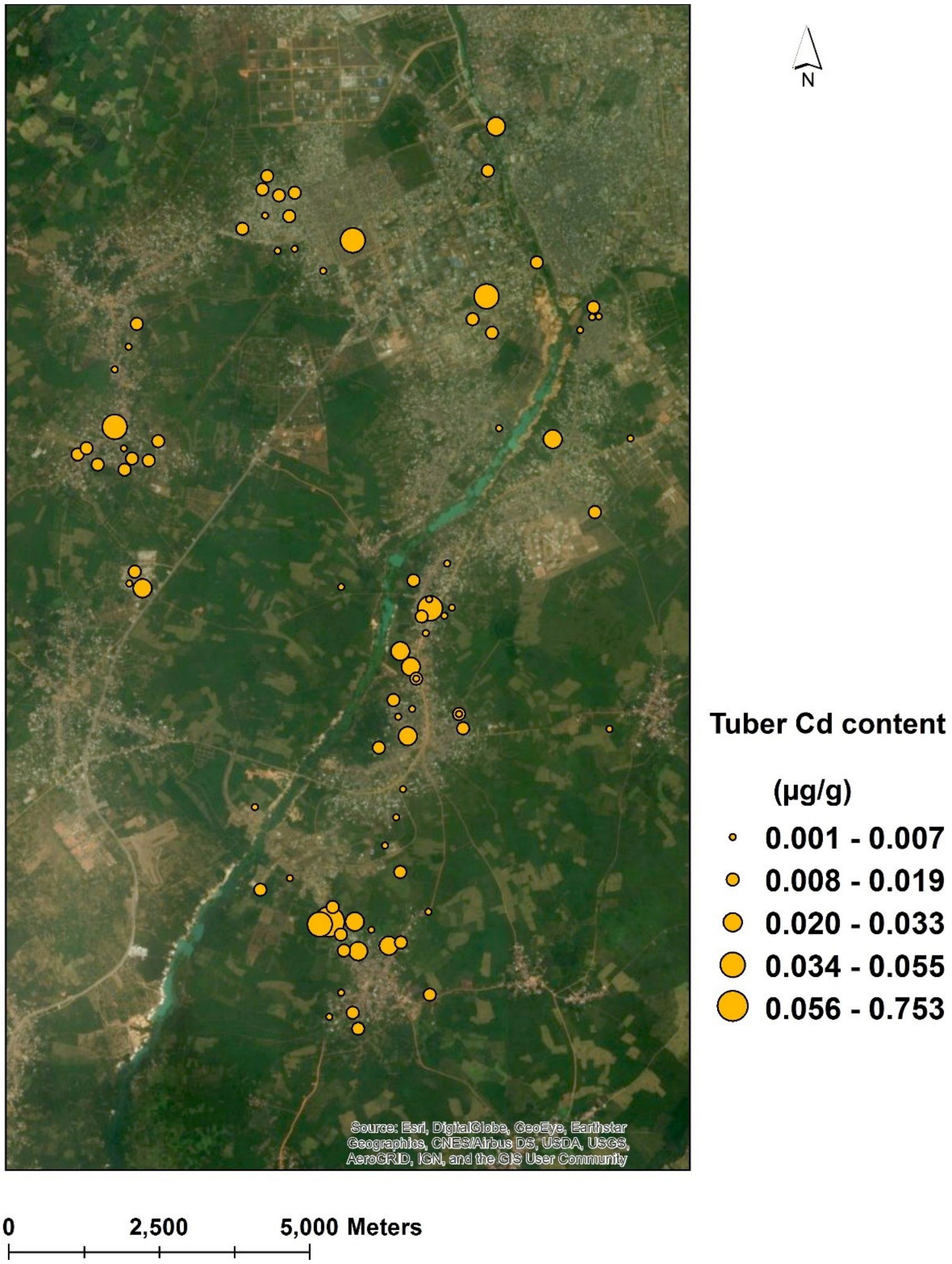


Figure 4.10j**:** Cadmium (Cd) concentration pattern in cassava tuber (*Manihot esculanta*) represented with graduated symbols to show variability across the study area of Owerri, Nigeria. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)

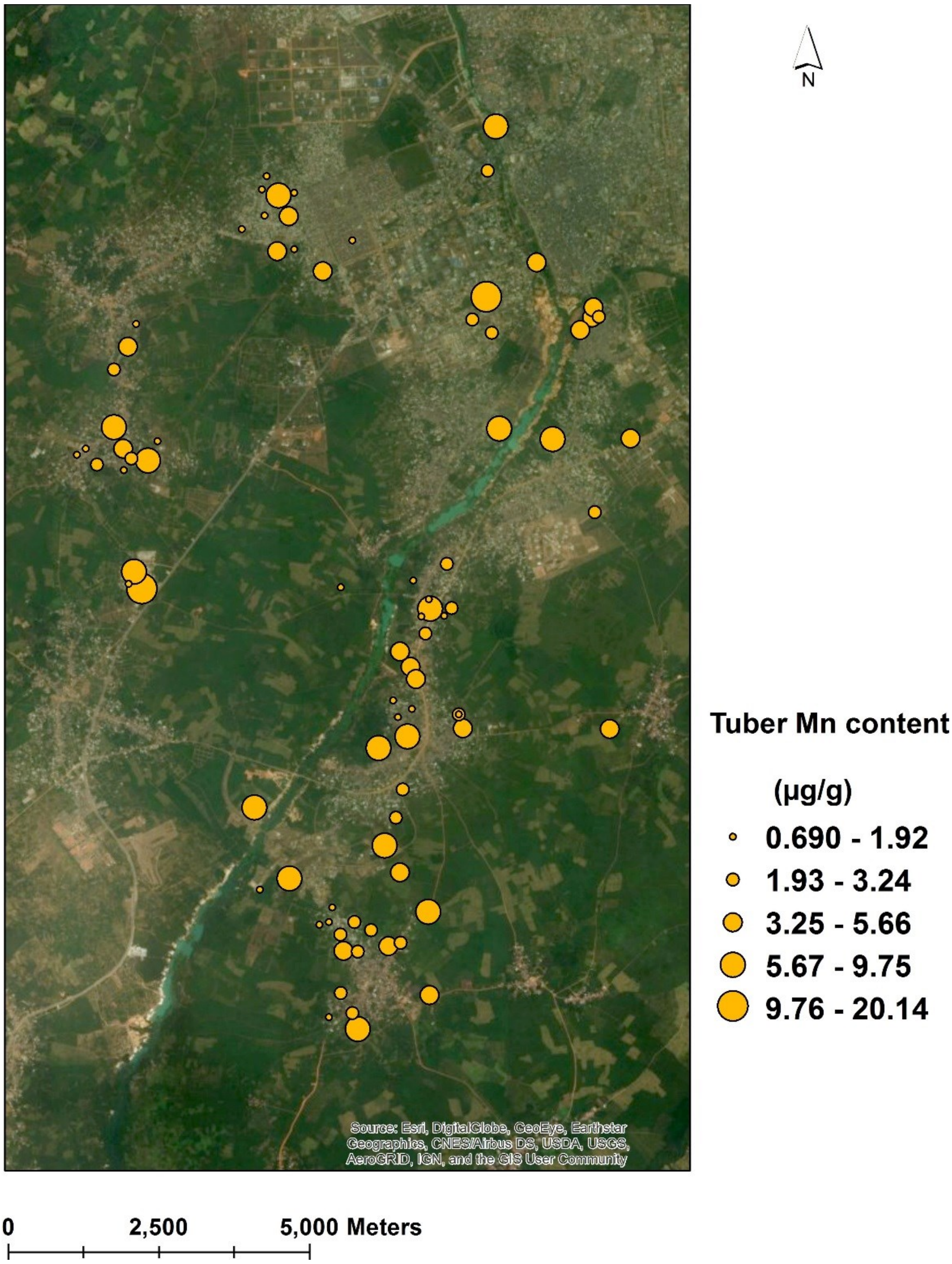


Figure 4.10k**:** Manganese (Mn) concentration pattern in cassava tuber (*Manihot esculanta*) represented with graduated symbols to show variability across the study area of Owerri, Nigeria. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)

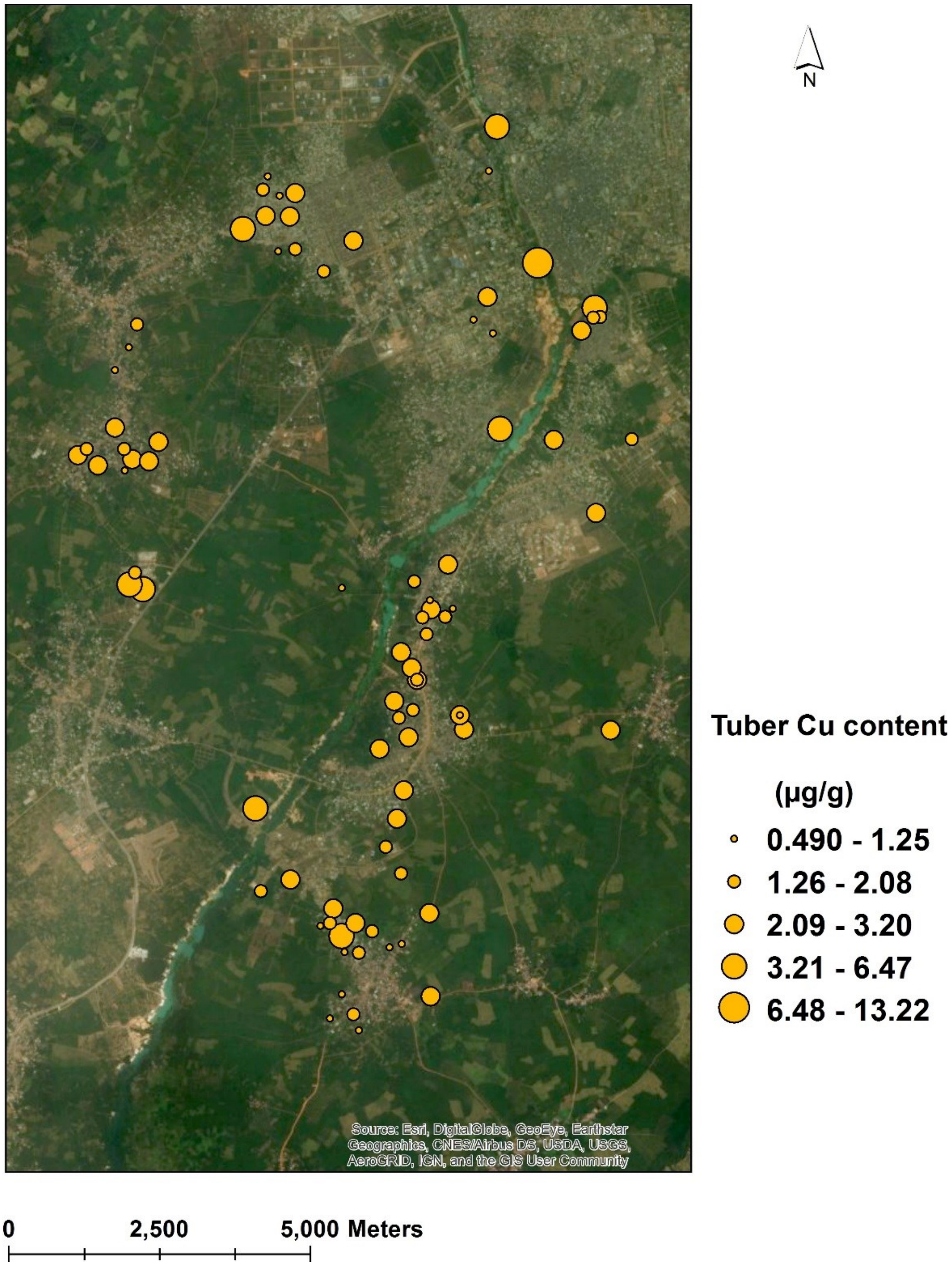
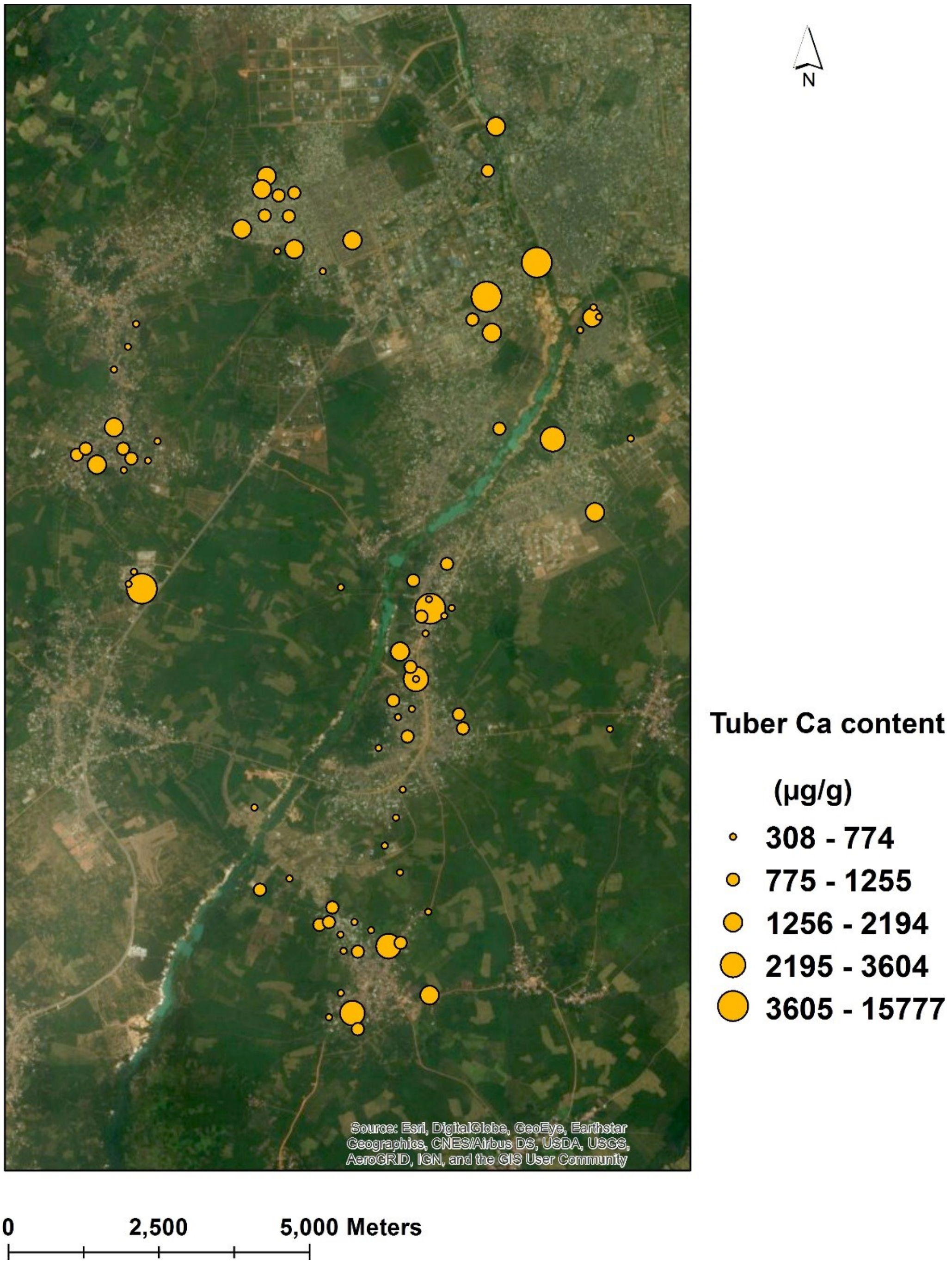


Figure 4.10l: Copper (Cu) concentration pattern in cassava tuber (*Manihot esculanta*) represented with graduated symbols to show variability across the study area of Owerri, Nigeria. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)



Source: Esri, DigitalGlobe, GeoEye, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community

Figure 4.10m**:** Calcium (Ca) concentration pattern in cassava tuber (*Manihot esculanta*) represented with graduated symbols to show variabilities across the study area. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)

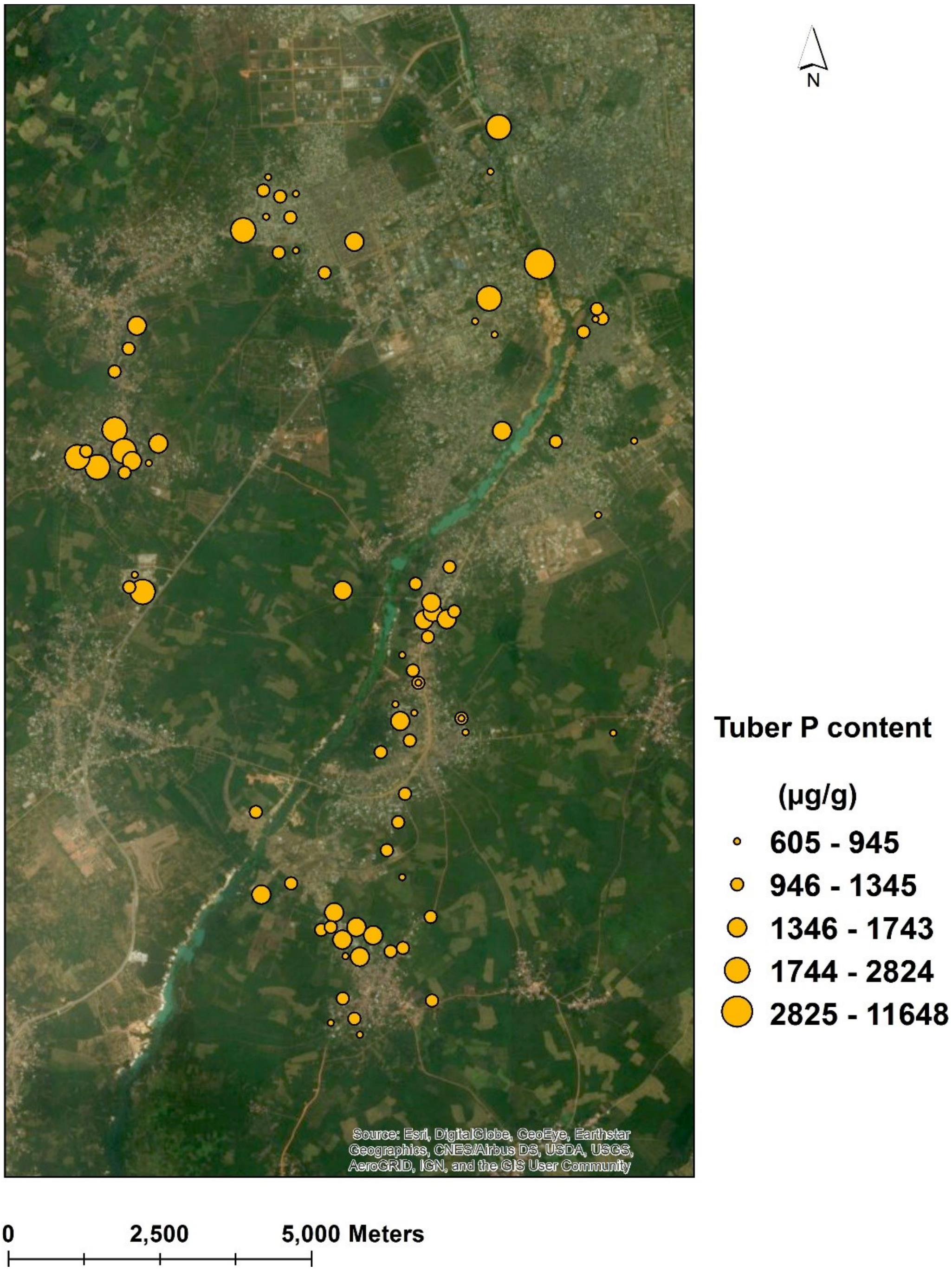


Figure 4.10n: Phosphorus (P) concentration pattern in cassava tuber (*Manihot esculanta*) represented with graduated symbols to show variability across the study area of Owerri, Nigeria. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)

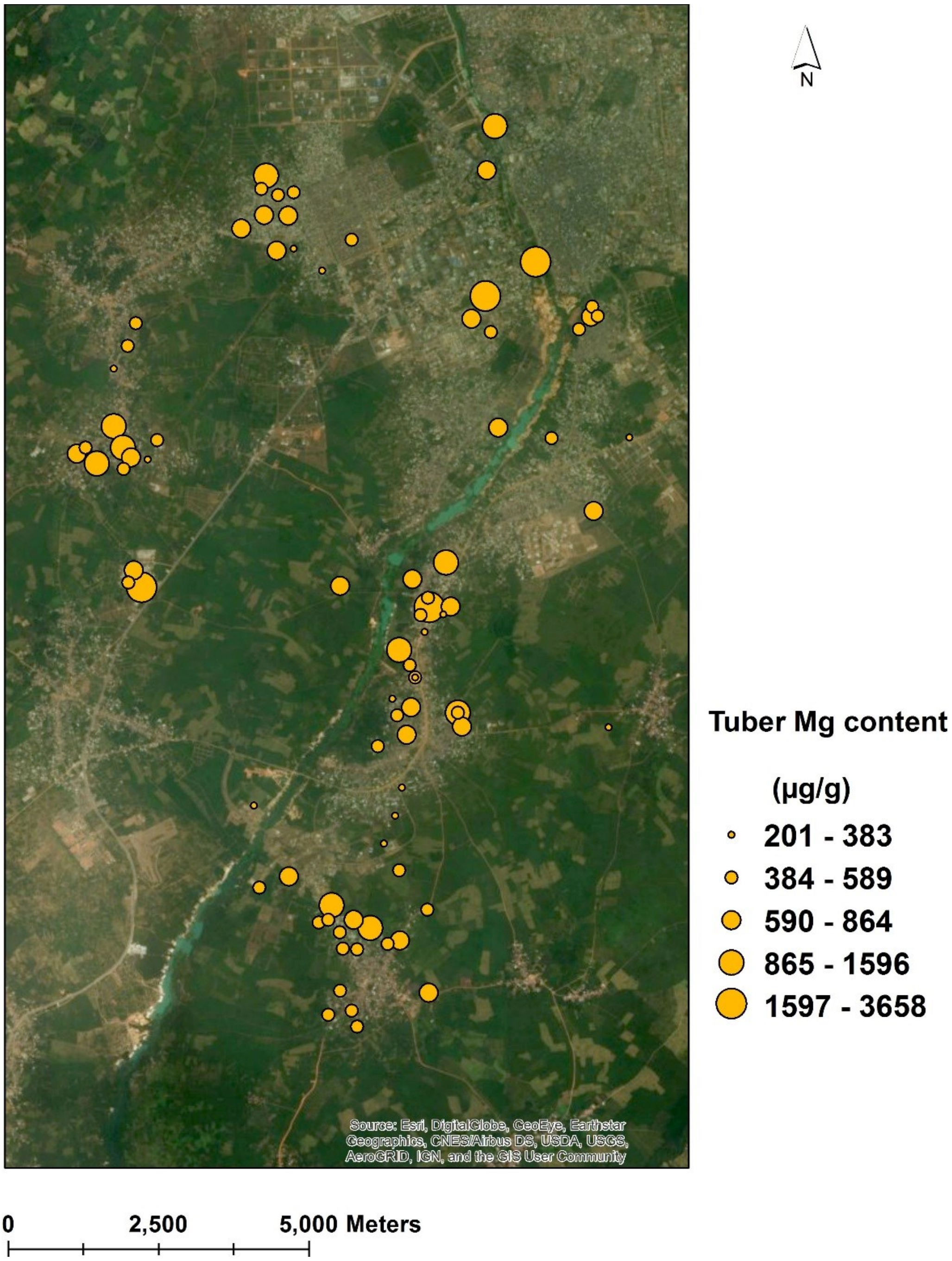


Figure 4.10o**:** Magnesium (Mg) concentration pattern in cassava tuber (*Manihot esculanta*) represented with graduated symbols to show variability across the study area of Owerri, Nigeria. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)

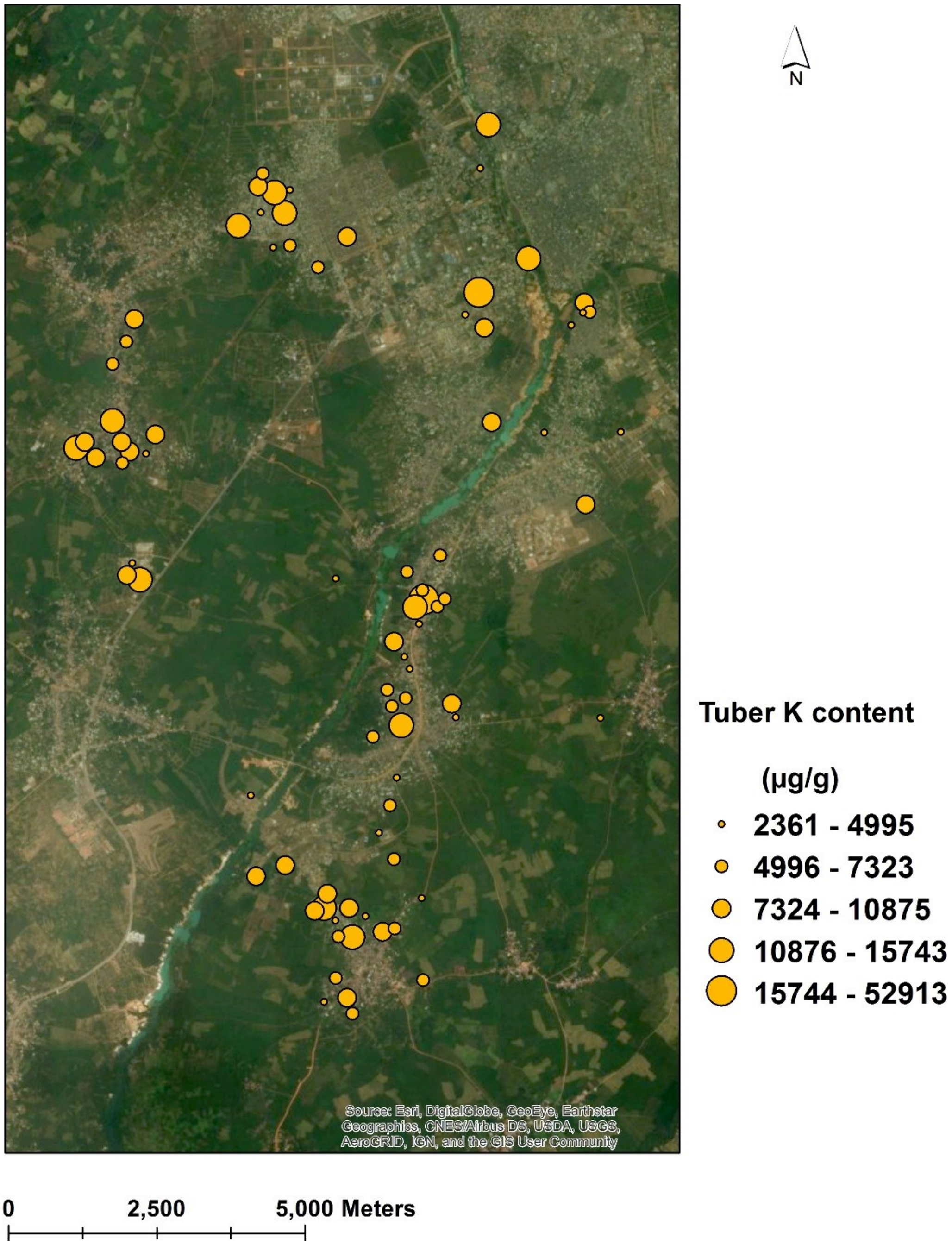


Figure 4.10p**:** Potassium (K) concentration pattern in cassava tuber (*Manihot esculanta*) represented with graduated symbols to show variability across the study area of Owerri, Nigeria. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)

## 4 .11 Evaluation of the Carbon-Nitrogen(C: N) ratio in sampled plants species

### 4.11.1 Equipment calibration using the percentage recovery rate of carbon and nitrogen in the rice flour Leco CHNS (Lot no.1009) during the analyses of C: N ratio in plants

Result of the five replicate samples of the rice flour used during the C: N ratio analyses in the leaf samples (*Telfaiara occidentalis*) for measurement accuracy showed recovery rate of 97.8% and 95.4%, for carbon and nitrogen respectively (Appendix 4H). Mean value for nitrogen was 1.04% ± 0.082%, whereas carbon was 43.2% ± 3.47%.

Similarly, six replicate samples of rice flour used for the C: N ratio analyses in the tuber samples showed recovery rate of 96.4% and 88.2% for carbon and nitrogen respectively. Mean nitrogen was 0.962% ± 0.019%; while C had 42.6% ± 0.777%**.**

### 4.11.2 Carbon-Nitrogen ratio in *Telfaira occidentalis* and *Manihot esculanta*

This significance of this assessment is to assess potential adsorption capacity of contaminants by these plants species with respect to contamination of food chain (see Chapter 2, Section 2.12). Results of the analyses of Carbon-Nitrogen ratio in *Telfaira occidentalis* and *Manihot esculanta* are included in Table 4.23 above.

## 4.12 Exposure and health risk assessment.

Descriptive dataset of assessment on human exposure to contaminated water and the vulnerable age group are presented and discussed in Chapter 5 (see Section 5.8.1, Table 5.10) and Appendix 5B. Similarly, total hazard quotient associated with human exposure to contaminated food plants are presented and discussed in Chapter 5 (see Section 5.8.1 and appendix 5C)

# CHAPTER 5

# DISCUSSION

## 5.1 Summary of chemical characteristics of Owerri hydrogeochemistry

### 5.1.1 Critical contaminants across the various media

The result of this study presented in Chapter 4 provide the descriptive statistics of distribution and characterisation of potentially toxic elements i.e. fairly rudimentary and likely non-toxic parameters, analysed in all the environmental matrices collected during the sampling seasons. $NO_3^-$ was found as the most critical contaminant in groundwater hence shall form the major focus of discussion in groundwater. Metals were not found as a major threat to public health in groundwater of most wells across the study area, except for some sites that recorded concentrations above health-based threshold values. For example, Pb concentrations surpassed the Nigeria Standard for Drinking Water Quality Maximum Concentration Limit (MCL) of 10.0 ng/mL in 1.6 % of sampled wells, whereas, Cd concentration exceeded the WHO MCL of 0.5ng/mL at only a single sampling point with a measured concentration of 6.41 ng/mL. Though Mn measured the maximum concentration of 221.8 ng/mL below the WHO guideline value of 400 ng/mL, it could be considered as an emerging contaminant with imminent public health risk (See Chapter 2, Section 2.10.1).

Furthermore, results of soil and plants also showed Pb and Cd as contaminants of health concern. While Pb concentration exceeded the Nigeria Department of Petroleum Resources (DPR, (1991) target value of 85 µg/g in about 0.9 % of sampled soils, Cd was above the DPR target value of 0.8 µg/g in about 1.42 % of sampled soils.

Similarly, Pb and Cd were found as human health-threatening contaminants in the two plant species (i.e. *Telfaira occidentalis* and *Manihot esculanta*), as summarised in Table 5.1 with respect to the Food and Agricultural Organisation (FAO)/WHO Codex Stan 193 – 1995.

Table 5.1: Summary of Pb and Cd contaminant concentrations (μg/g) in the two sampled pumpkin leaf (*Telfaiara occidentalis*) and cassava tuber (*Manihot esculanta*) compared with health regulatory agencies standards. Median values are presented because each dataset was not normally distributed (Kolmogorov_smirnov test).

| Metal (μg/g) | *Telfaira occidentalis* | | | *Manihot esculanta* | | | % above standard |
|---|---|---|---|---|---|---|---|
| | Median | Minimum - Maximum | FAO MCL | Median | Minimum - Maximum | FAO MCL | |
| Pb | 0.9 | 0.2-5.3 | 0.3 | 0.130 | 0.05-0.9 | 0.1 | 99.8 (Leaf)<br>51.6 (Tuber) |
| Cd | 0.03 | 0.006-1.3 | 0.2 | 0.010 | 0.001- 0.8 | 0.1 | 3.1 (Leaf)<br>1.1 (Tuber) |

Although results presented in Chapter 4 broadly characterise the contaminant load of the various environmental media, the current chapter seeks to interpret how those contaminants affect environmental qualities using different statistical and geospatial techniques. A risk assessment is also computed using groundwater and plants datasets generated in this study, to predict pathways through which inhabitants in the study area are exposed to these contaminants. This provides prediction models of high-risk regions as a management technique.

## 5.2 General characterisation of groundwater quality across the study area

The chemical characteristics of groundwater can be a reflection of the prevalent hydrogeochemical pattern and anthropogenic influences on the groundwater chemistry of an area. Spatial distribution of measured major cations and anions of groundwater in the study area have been displayed in this study (See Chapter 4, Figures 4.5 (a – i)). Observed changes in the concentration and distribution pattern ions across the study area could be attributed to seasonal variability (See Figure 3.1), depth to water table and urbanisation based on which the general characterisation of the groundwater quality shall be focused.

### 5.2.1 Seasonal variation of major chemical components in groundwater

Seasonal assessment of groundwater chemistry is important since contaminant fate and distribution that determine its quality can largely be influenced by precipitation, recharge and discharge rates (Green et al., 2011). Table 5.2 presents the overall concentration of the different parameters analysed in groundwater samples across the study area in the respective seasons. Parameter values indicate increased concentration trend among variables in the dry season attributed to likely natural or anthropogenic occurrences, hence the need for analyses of the variances.

Based on the fact that not all sites sampled in the first (rainy) season were repeated in the second season (dry), a subset of 30 wells sampled in both seasons were selected to investigate probable underlying factors driving such observed seasonal changes in the overall groundwater chemistry of the study area. Selection of these sites was based on the analytical result of samples collected in the initial (rainy season) field trip which revealed potentially contaminated wells based on their relatively higher $NO_3^-$ concentrations. Elevated $NO_3^-$ concentrations is often regarded an indicator of groundwater pollution (Jiménez-Martínez et al., 2011; Johnson et al., 2006).

While Table 5.2 reflects the chemical characteristics of all sampled wells in the study area, statistical analyses such as the two-sample t-test (Table 5.3) and correlation analyses ( Appendix 5A and B) have been applied on the groundwater parameters of the selected 30 referenced wells. This is aimed at assessing the significance of any observed seasonal variability, evaluate the pattern of relationship among parameters in the two seasons and possibly draw inferences that could best describe the groundwater chemistry from relevant studies. Datasets of groundwater parameters in the respective seasons are also displayed as box-whiskers plot (Figure 5.1a – c) for visual assessment of seasonal variabilities.

Table 5.2: Summary comparison of measured Owerri groundwater parameters between rainy (270 samples) and dry (116 samples) seasons. Median values are presented because each dataset was not normally distributed (Kolmogorov_smirnov test).

| Parameter | Rainy Season | | | Dry Season | | |
|---|---|---|---|---|---|---|
| | Min. | Median | Max. | Min. | Median | Max. |
| Temp ($^0$C) | 26.7 | 27.8 | 30.8 | 27.3 | 28.4 | 32.0 |
| pH | 3.1 | 3.80 | 7.2 | 5.1 | 6.9 | 8.9 |
| EC (µS/cm) | 10.0 | 31.0 | 400.0 | 13.5 | 54.5 | 488.5 |
| DO (µg/mL) | 2.1 | 9.7 | 15.9 | 1.7 | 6.4 | 8.8 |
| $Ca^{2+}$ (µg/mL) | 0.165 | 0.715 | 19.3 | 0.085 | 1.93 | 32.2 |
| $Mg^{2+}$ (µg/mL) | 0.024 | 0.129 | 1.38 | 0.059 | 0.516 | 3.35 |
| $Na^+$ (µg/mL) | 3.1 | 4.0 | 8.9 | 0.42 | 5.87 | 29.4 |
| $K^+$ (µg/mL) | 1.7 | 7.6 | 15.9 | 0.081 | 1.36 | 16.3 |
| DOC (µg/mL) | 4.27 | 7.3 | 9.72 | 1.37 | 3.19 | 5.97 |
| $NO_3^-$ (µg/mL) | 0.533 | 12.5 | 128.1 | 0.651 | 24.5 | 148.4 |
| $NH_4^+$(µg/mL) | 0.002 | 0.03 | 2.7 | 0.009 | 0.067 | 6.3 |
| $Cl^-$ (µg/mL) | 0.383 | 1.47 | 33.2 | 0.514 | 4.79 | 34.2 |
| $Fl^-$ (µg/mL) | 0.019 | 0.112 | 0.633 | 0.116 | 0.154 | 0.221 |
| $SO_4^{2-}$ (µg/mL) | 3.09 | 4.45 | 12.6 | 2.21 | 5.89 | 10.1 |
| Pb (ng/mL) | 0.048 | 0.315 | 39.6 | 0.054 | 0.423 | 10.6 |
| Mn (ng/mL) | 1.02 | 14.2 | 221.8 | 2.46 | 39.6 | 201.7 |
| Fe (ng/mL) | 0.032 | 4.26 | 75.7 | 0.662 | 5.47 | 47.5 |
| Cd (ng/mL) | 0.019 | 0.039 | 6.41 | 0.019 | 0.029 | 0.196 |

Table 5.3: Two-sample *t*-test assessment of difference in Owerri groundwater parameters between rainy and dry seasons, for samples only from the 30 boreholes that were sampled during both fieldwork seasons. Column inscriptions show: analytes, which outlines groundwater parameters; t-statistics representing values that produced the level of significance; Mean difference that displays differences between sample means in the two seasons, and p-values (probability level) that quantifies the significance of any variation.

| Analytes | t-statistic | Mean difference | p- values |
|---|---|---|---|
| Temperature ($^0$C) | -4.76 | -0.893 | 0.0001* |
| pH | -12.3 | -2.33 | 0.0001* |
| EC (µS/cm) | 1.82 | 44.3 | 0.07 |
| DO (µg/mL) | 5.45 | 2.87 | 0.0001* |
| $Ca^{2+}$ (µg/mL) | 0.078 | 0.098 | 0.94 |
| $Mg^{2+}$ (µg/mL) | -3.33 | -0.442 | 0.002* |
| $Na^+$ (µg/mL) | -0.254 | -0.465 | 0.8 |
| $K^+$ (µg/mL) | 1.34 | 1.06 | 0.19 |
| $NH_4^+$ (µg/mL) | -0.101 | -0.01 | 0.92 |
| $NO_3^-$ (µg/mL) | 1.04 | 8.63 | 0.3 |
| $Cl^-$ (µg/mL) | 0.336 | 0.678 | 0.73 |
| DOC (µg/mL) | 14.2 | 4.01 | 0.0001* |
| $Fl^-$ (µg/mL) | -1.62 | -0.02 | 0.11 |
| $SO_4^{2-}$ (µg/mL) | -5.08 | -1.72 | 0.0001* |
| Pb (ng/mL) | 1.55 | 1.40 | 0.126 |
| Mn (ng/mL) | 0.728 | 0.01 | 0.5 |
| Fe (ng/mL) | 0.748 | 3.09 | 0.458 |
| Cd (ng/mL) | 0.984 | 263 | 0.325 |
| * statistically significant at the 0.05 confidence level | | | |

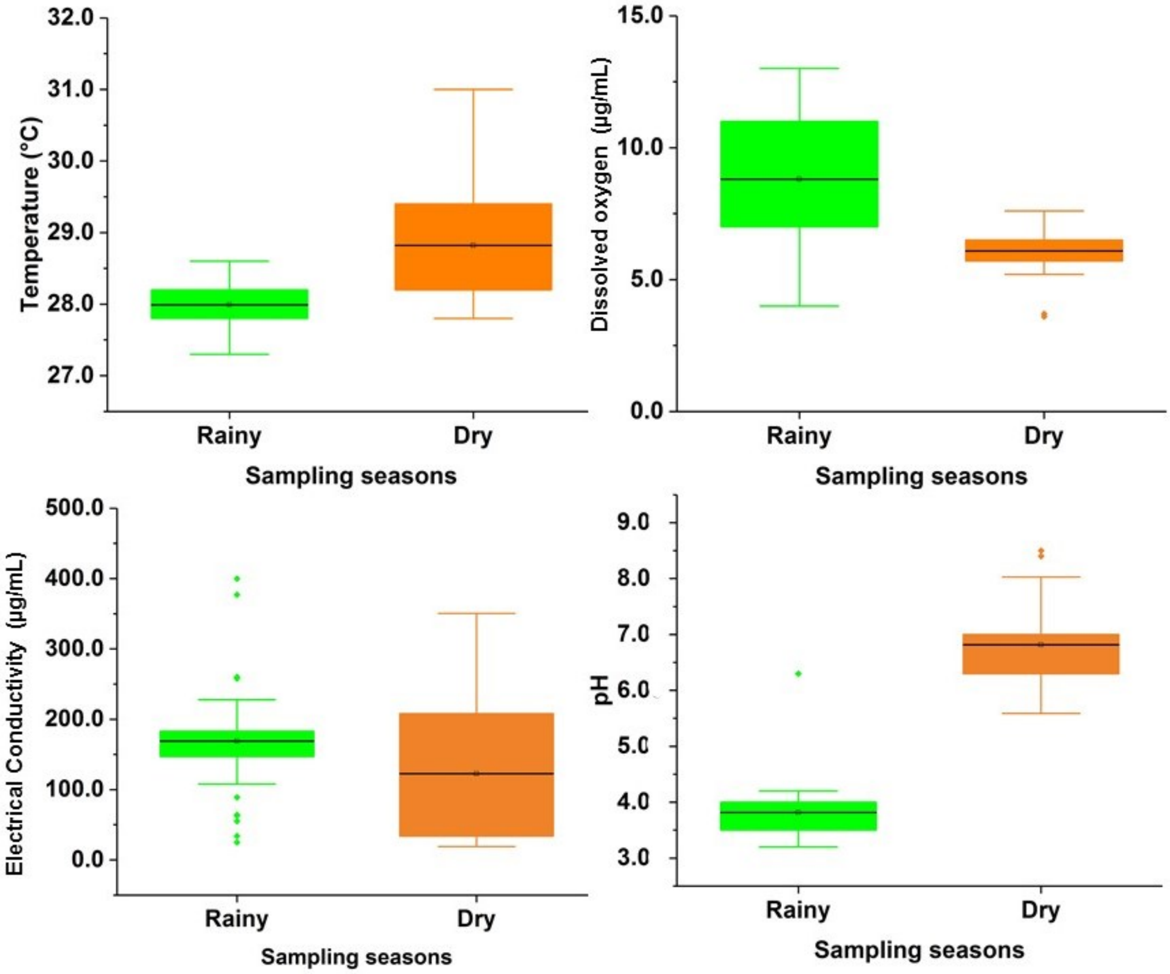


Figure 5.1a: Box-whisker plots of the variability of field-measured Owerri groundwater parameters between rainy and dry seasons, for the 30 boreholes that were sampled during both fieldwork seasons (see Table 5.3 for *t*-test results). Green and orange colours plots represent the rainy and dry seasons, respectively.

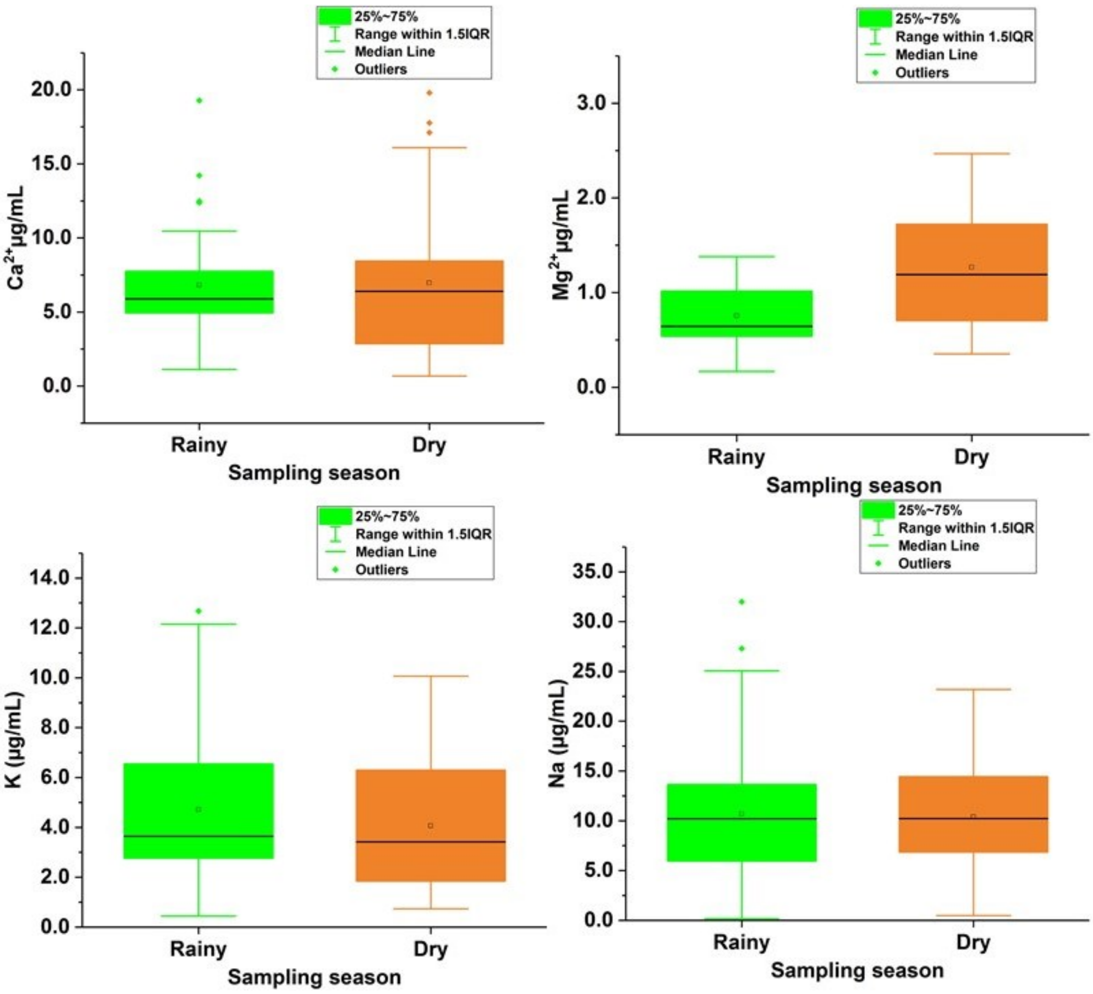


Figure 5.1b**:** Box-whisker plots of the variability of Owerri groundwater cations between rainy and dry seasons, for the 30 boreholes that were sampled during both fieldwork seasons (see Table 5.3 for *t*-test results). Green and orange colours plots represent the rainy and dry seasons, respectively.

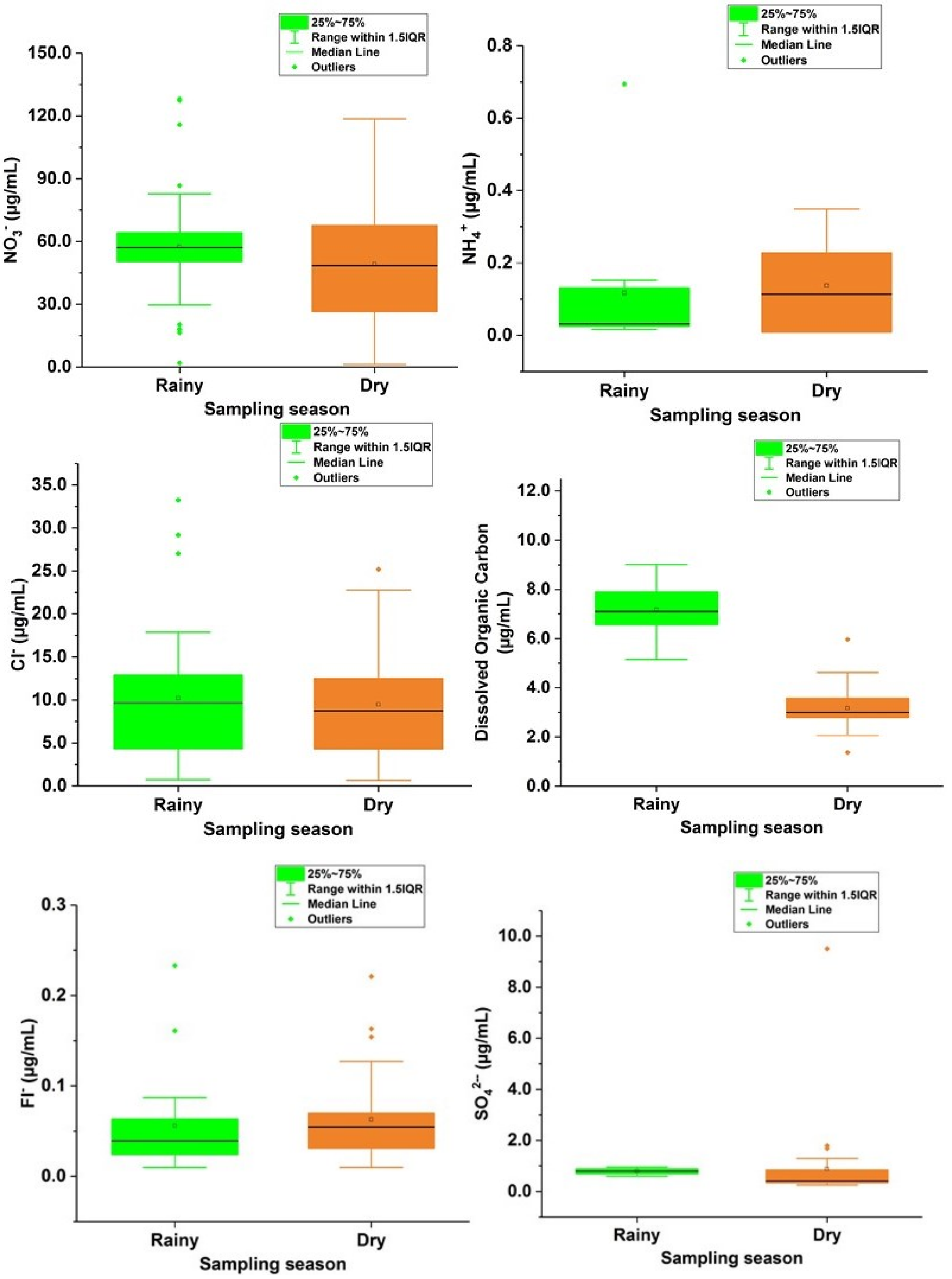


Figure 5.1c: Box-whisker plots of the variability of Owerri groundwater anions between rainy and dry seasons for the 30 boreholes that were sampled during both fieldwork seasons (see Table 5.3 for t-test results). Green and orange colours plots represent the rainy and dry seasons, respectively.

The results of the two-sample t-test presented in Table 5.3 and displayed in box-whiskers plot (Figure 5.1a – c) shows changes in the mean concentration of all parameters across the seasons, However, statistically significant differences in groundwater parameters are evident for temperature, pH, dissolved oxygen (DO), dissolved organic carbon (DOC), and sulphate ($SO_4^{2-}$) based on the $p\text{-value} < 0.05$. This could be related to the inherent hydrogeochemical interactions in the respective seasons.

### 5.2.2 Hydrogeochemical interactions and influence on contaminants distributions in groundwater of the study area.

The recorded -2.34 mean difference of pH between the rainy and dry seasons respectively could imply prevalent geochemical interactions between the natural acidic rain ( though not measured in this study) percolating through soil profiles and the microbial – induced $CO_2$ produced from organic decompositions (Knutsson, 1994). Elevated dissolved organic carbon (DOC) in groundwater during the rainy season with a median value of 7.3 µg/mL as against 3.19 µg/mL recorded in the dry season, suggests infiltration of surface runoff through the permeable soil in the area. This assertion could be supported by the low median soil organic matter of ca.3.48% as measured in this study to imply further the possibility of soil organic matter being washed off by percolating catchment runoff. Studies have shown that DOC which explains more than 90% of total dissolved carbon, characterises the carbon fraction of dissolved organic matter in groundwater (Regan et al., 2017; Batiot et al., 2003). Reduction of surface runoff and eventual infiltration rate was also reflected in the dry season by the drop in DOC concentration hence, the significant difference at $p<0.01$ (Table 5.3). Studies have affirmed that the source of high DOC in groundwater can be either through the surface organic matter or by bacterial decomposition of organic matter in the geologic materials (Hiscock et al., 1991). Strong positive correlation between DOC and Na (0.711; $p < 0.01$) in the rainy season (Appendix 5A) could infer possible interaction between percolating water and soil materials.

Water infiltrates through the soil horizons until it reaches the aquifer during the rainy season. This hydrological process could involve geochemical interactions and eventual dissolution of ions and other dissolved solutes through species exchanges between water and aquifer sediments (Manahan, 2002). Dissolution of major ions ($Ca^{2+}$, $Mg^{2+}$, $Na^{+}$) during infiltration of rainwater through the soil profile normally increases pH of groundwater, and could show the magnitude of interaction between the percolating water and soil materials (Ellis and Mahon, 1967). However, the median concentration of measured cations in the rainy season suggest possible dilution by percolating rainwater, besides creating an oxidising condition that favoured depression of the pH value. This conclusion is drawn from the corresponding dry season's values that showed higher concentration with increased pH. Such increased concentration of cations and variables such as electrical conductivity, temperature, and pH (Tables 5.2 and 5.3) could suggest a longer interaction between groundwater and geologic materials in the dry season due to reduced flow rate and reducing condition. Besides, seasonal comparison of median values of dissolved cations (Table 5.2) indicates higher Na values 4.0 µg/mL and 5.87 µg/mL in the rainy and dry seasons. This implies prevalent cation exchange where $Ca^{2+}$ and $Mg^{2+}$ are exchanged for the monovalent $Na^{+}$ probably attached in aquifer grains by a process explained in Hiscock (2009), suggesting cation exchange as part of mechanisms that control groundwater chemistry in the area. Evangelou and Evangelou (1998) remarked that dissolution and change in state of dissolved elements and compounds could influence the soil-groundwater pH as reducing condition increases pH whilst oxidising condition reduces pH. However, hydrogeochemical processes such as oxidation-reduction (redox) could also influence the characterisation of the groundwater chemistry.

### 5.2.3 Hydrogeochemical characterisation and redox process in groundwater of the study area

Studies have shown that redox potential of groundwater can be evaluated by changes in the concentration of redox-sensitive species such as DO, Fe (II) and Mn (II) and $NO_3^-$ (Fendorf, 2000; White et al., 1990). Previous studies postulated groundwater flow in the northeast and southwest direction of the Otamiri and Nworie rivers that drain the study area (Nwachukwu et al., 2010; Ibe and Uzoukwu, 2001; Onyeagocha, 1980). Consequently, the prevalent redox condition of the study area is assessed in this study by the spatial concentrations pattern of these outlined redox species$^{-}$ along with the river flow path. Dry season samples were used for this evaluation to eliminate likely effects of recharge and dilution on the groundwater quality during the rainy season. Sampled wells were grouped to assess changes in the concentration of redox-sensitive species in the groundwater shown in Figure 5.2a and median concentration trends displayed in Figure 5.2b.This assessment becomes important considering its important role in determining the mobility and availability of contaminants in groundwater (Ioka et al., 2017).

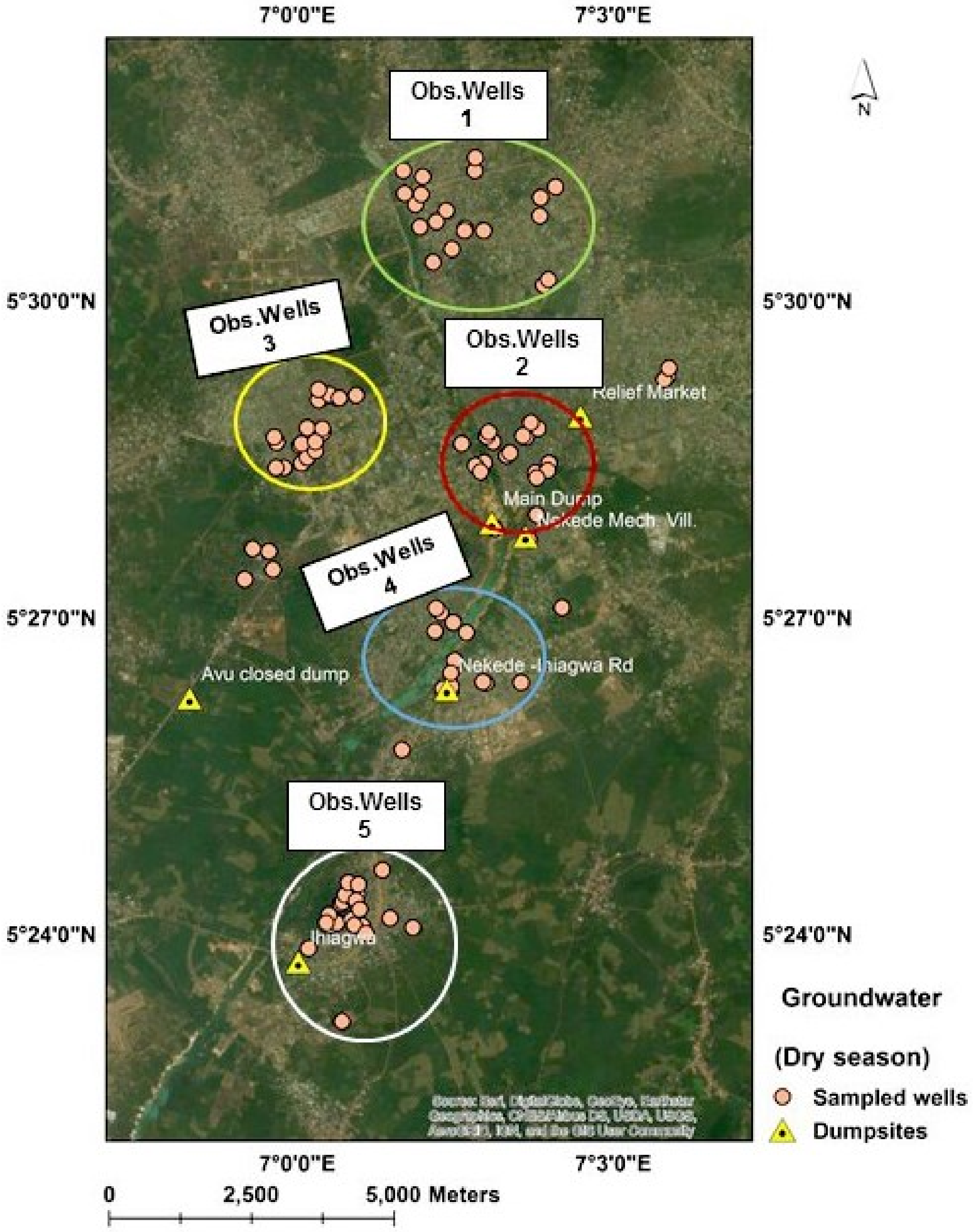


Figure 5.2a: Dry season sampled wells (109) grouped as Observation wells (1 - 5) based on proximity to one another along river flow direction and coloured – circled according to redox potential of each group in the order red > yellow > light blue > light green > white. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)

Table 5.4: Median and interquartile range (IQR) of redox species, which are groundwater parameters that are sensitive to environmental conditions that lead to electron transfer among chemical parameters, as assessed in 109 sampled wells spread along the river flow direction (Figure 5.2a). The table shows wells grouped into 5 observation wells (Obs.wells 1-5) reflecting concentration trend during normal groundwater flow in the dry season. Observation wells comprise of 22 for groups 1 and 2, 26 for group 3, 16 and 23 for groups 4 and 5 respectively.DOC was included in the table for easier comparison with redox trend.

| Redox species/ DOC | Obs.wells 1 | Obs.wells 2 | Obs.wells 3 | Obs.wells 4 | Obs.wells 5 |
|---|---|---|---|---|---|
| DO (µg/mL) | 6.7<br>(6.3 – 7.0) | 5.9<br>(4.5 – 6.5) | 6.55<br>(6.4 – 6.8) | 6.1<br>(5.8 – 7) | 6.4<br>(6.0 – 6.8) |
| $NO_3^-$ (µg/mL) | 3.42<br>(2.2 – 18) | 61.6<br>(33 – 102) | 43.2<br>(12.7 – 75) | 21.4<br>(11.5 – 33) | 20.6<br>(2.6 – 69) |
| $Mn^{2+}$ (ng/mL) | 7.9<br>(6.3 – 22) | 113.9<br>(53 – 137) | 81.5<br>(35 – 105) | 42.9<br>(23 – 73.5) | 16.2<br>(9.2 – 56) |
| $Fe^{2+}$ (ng/mL) | 1.56<br>(0.8 – 4.2) | 16.5<br>(7.2 – 23) | 10.4<br>(6.1 – 10) | 5.89<br>(2.7 – 9.7) | 3.38<br>(1.2. – 9.5) |
| DOC (µg/mL) | 3.58<br>(2.3 – 4.5) | 3.02<br>(2.3 – 3.6) | 2.82<br>(2.5 – 3.2) | 3.03<br>(2.7 – 3.6) | 3.00<br>(2.7 – 3.7) |

The observed trend of median values of redox species in each observation group as displayed in Table 5.4 suggests the prevalence of redox process along the groundwater flow path.

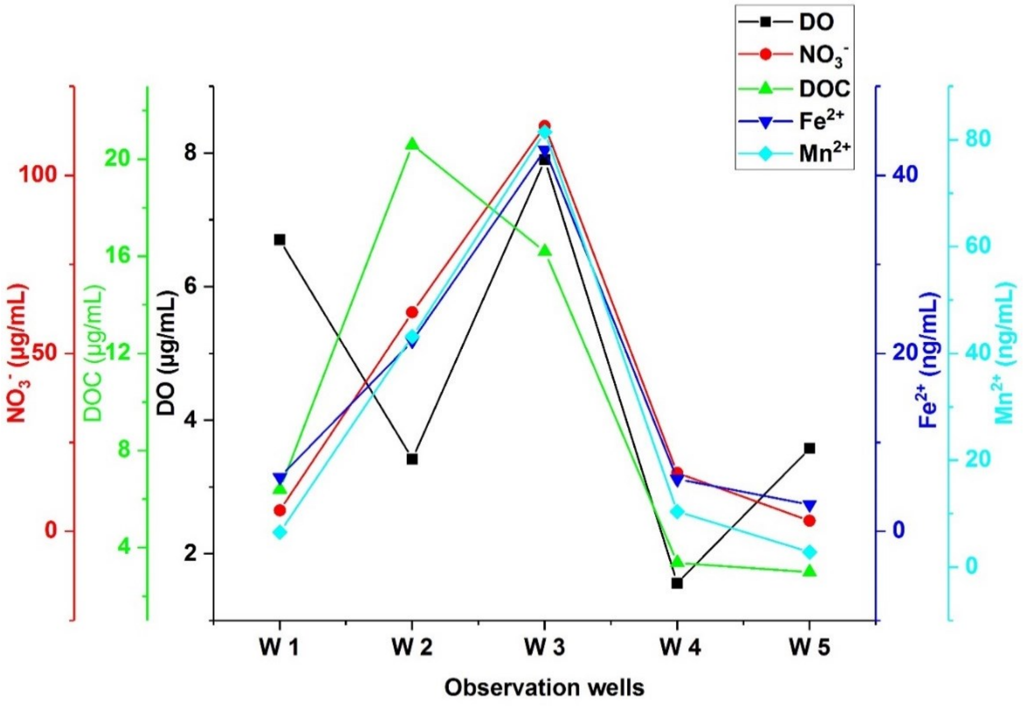
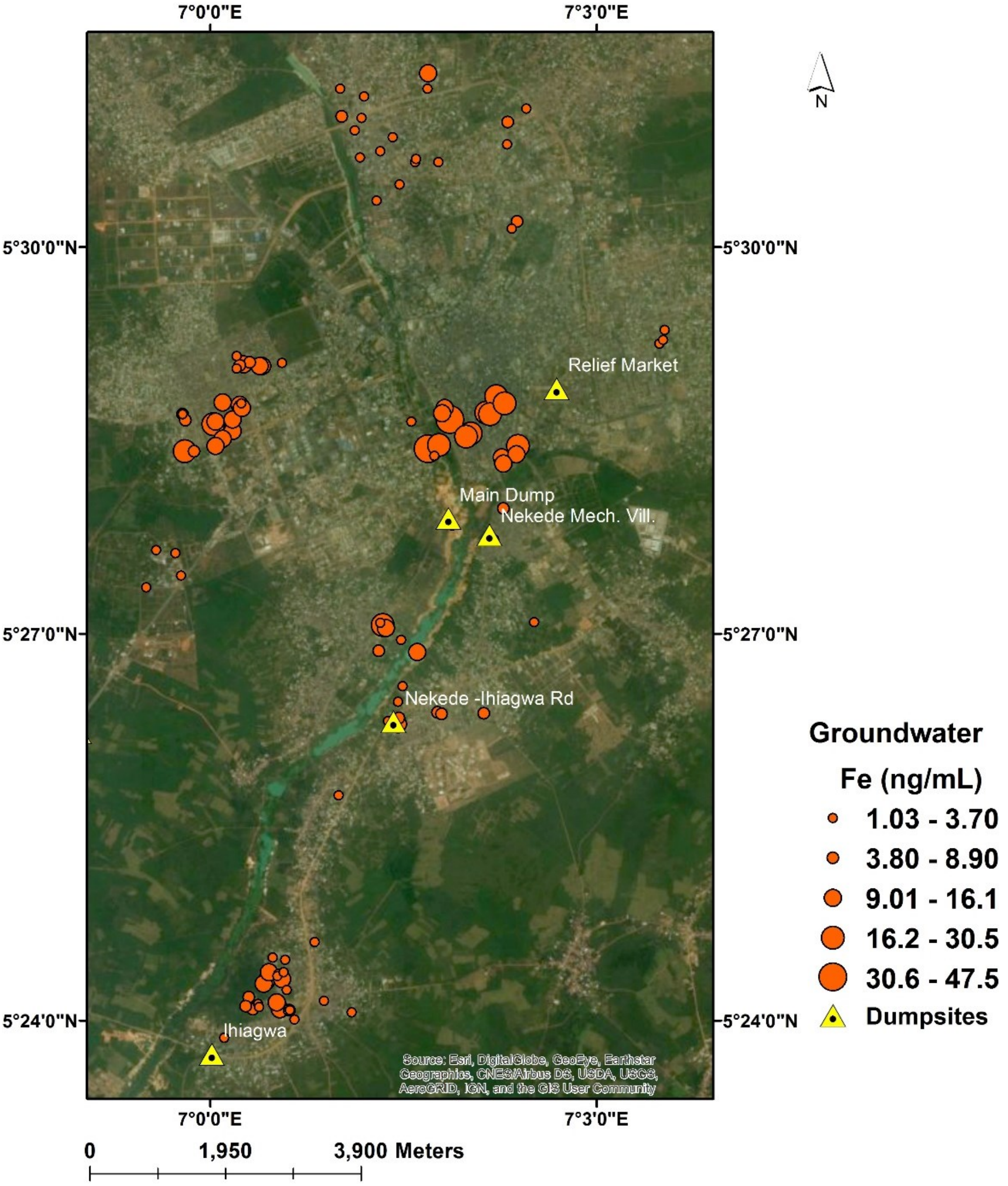


Figure 5.2b: Graphical presentation of median values of redox species reported in Table 5.4.The figure showing observation wells numbered 1-5 suggests microbial - induced oxygen depletion inferred from the inverse relationship between DO and DOC whereas other redox sensitive species assume similar reducing trend.

Dissolved oxygen, which is first in the redox order (See chapter 2, section 2.5.2), dropped from 6.7 µg/mL in Observation wells 1 to 5.9 µg/mL in observation wells 2 at an approximate distance of 2km. This is a geochemical footprint of the reduction process, which favoured the release of Fe (II) and Mn (II) from the respective oxides of Fe (III) and Mn (IV), which are more stable in the oxidised environment. Both the median and interquartile range values of Fe (II) and Mn (II) imply higher solubility in reducing form (Figures 5.3 and 5.4) than within the regions of observation wells 1 and 2, while reduced concentrations from observation wells 3 to 5 could suggest oxidation to their insoluble oxyhydroxide forms. Furthermore, the DOC values (Table 5.4) show a similar trend to suggest possible microbial activities and eventual DOC (substrate) reduction within the regions of observation wells 1 and 2.The observed drop in oxygen could be associated with bacteria degradation of DOC using oxygen as terminal electron acceptor. With the reduction of DOC (electron donor), there could be limited attenuation of contaminants such as nitrate (Hiscock, 2009).

Analysis of redox processes in groundwater in this study is however limited to hydrogeological conditions that could help in explaining fate and spatial distribution of nitrate in groundwater as a contaminant of public health concern in the study area. However, a range of other hydrogeochemical factors could enhance or impede the subsurface transport of contaminants to the water table (Jardine et al., 1989). In the study area, which is characterised by coastal plain-sand aquifer (Amadi et al., 2010) water passes through varying soil thickness to the groundwater during which dissolved cations, nitrate, and organic carbon are conveyed to the groundwater. Such variability of aquifer-overlaying burden could influence the concentration and spatial distribution of nitrate which could be attenuated within the vadose zone (Wiedemeier et al., 1999).



Source: Esri, DigitalGlobe, GeoEye, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community

Figure 5.3: Spatial changes in the concentration trend of dissolved iron (Fe) in groundwater across the study area suggestive of high reducing trend near the river. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)

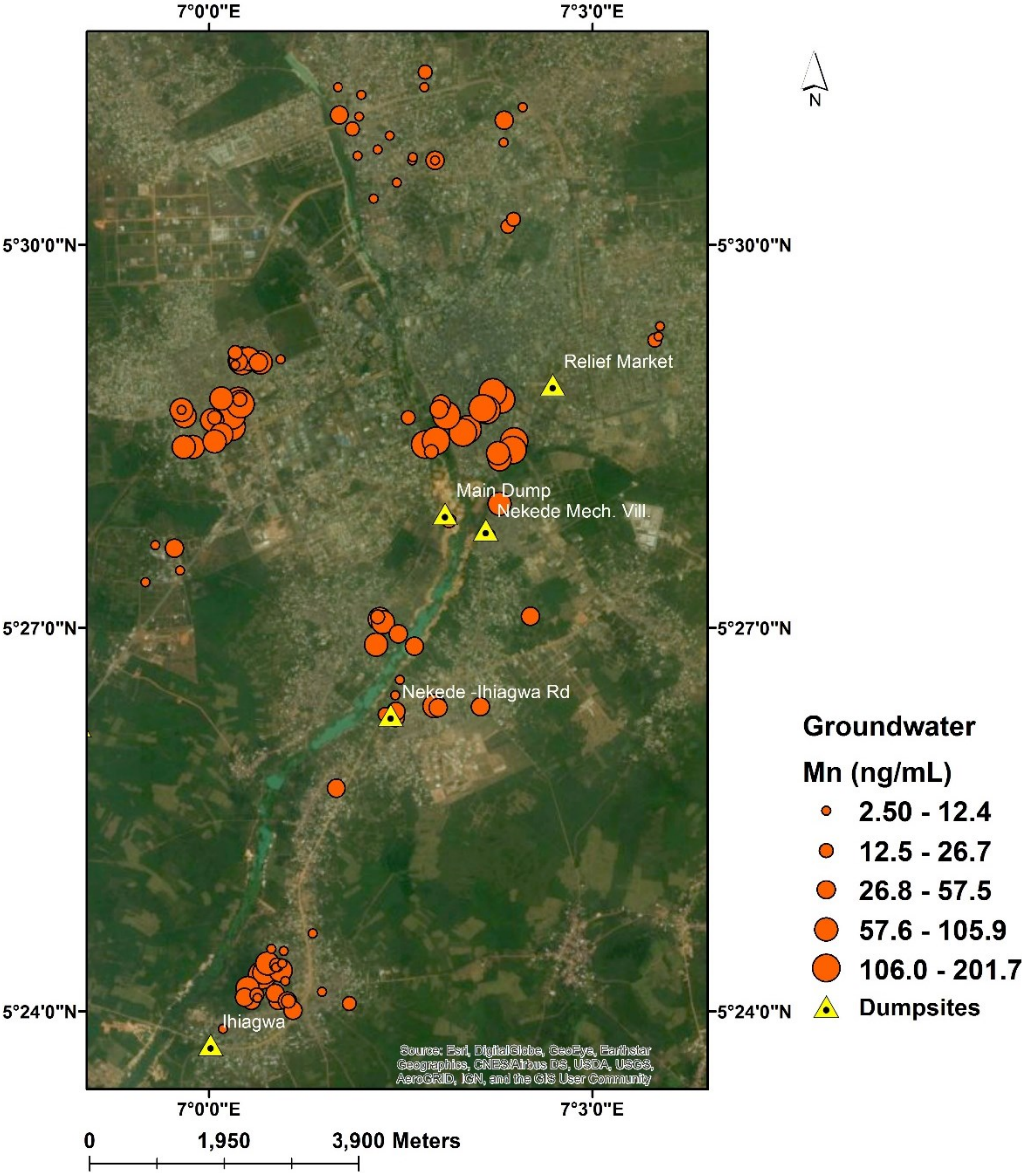


Figure 5.4: Spatial changes in the concentration trend of dissolved manganese (Mn) in groundwater across the study area suggestive of high reducing trend near the river. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)

## 5.3 Regionalisation of the groundwater quality analyses

For clarity and coherency, the discussion in this chapter has been designed according to regions of varying depth to water table and urbanisation spread.

The uncooperative disposition of well owners and eventual breakdown of the measuring equipment limited measurement of depth to water table in sampled wells beyond the approximate 12.7% recorded in this study (Figure 5.5). The measurements that randomly covered the different regions in the study area are in agreement with the average regional measurements reported in previous vulnerability studies in this study area (Nwachukwu et al., 2010; Ibe et al., 2003; Ibe et al., 2001). These studies, which focused on contaminant tracking and intrinsic assessment of groundwater vulnerability in the area, assigned higher vulnerability index value to the southern part, i.e. in the direction of the river flow. Consequently, delineation according to depth variability was based on the average regional measurements noted in the previous studies, while the distribution map generated with measured points in the few wells in this study (though limited) can represent the average depth variability pattern.

Categorisation according to urbanisation spread was based on congestion pattern and its associated environmental problems. These include city centre, suburban and peri-urban regions respectively. City centre includes settlements within the Owerri ancient kingdom (deep and majorly the shallow regions). It is the most congested and highly clustered region in the study area as it is the administrative headquarters of most government establishments; hence there exists relatively more basic amenities and job opportunities. It is characterised by impervious surfaces such as asphalted roads and concrete drainages. Consequent upon its location at a lower region and along drainage flow path, some dissolved contaminants found in wells within the region could originate from the upgradient zones. The area's ease of groundwater abstraction due to high yielding aquifer has given rise to an explosion of private boreholes constructed by artisans who often terminate drilling at a very shallow depth of about 15m (based on water table measurements during sampling), thereby exposing users to various water-borne diseases. Sub-urban refers to satellite towns; that is developed to ease pressure within the city centre.

It is characterised by excessive land fragmentation as most housing units and on-site sanitation facilities were indiscriminately sited at unapproved locations and along drainage pathways. Peri-urban represents areas in the outskirts of Owerri (which denote outer parts of the deep well and moderately shallow), with pristine environment compared with other regions. This region has fairly distributed residential patterns, except for areas predominantly inhabited by students of the Federal University of Technology, Owerri; which is generally semi-urban structure and apparent elevated $NO_3^-$ concentrations.

These delineations could suggest possible patterns of contaminant distribution in the area and probably calibrate previous vulnerability assessments done in the study area.

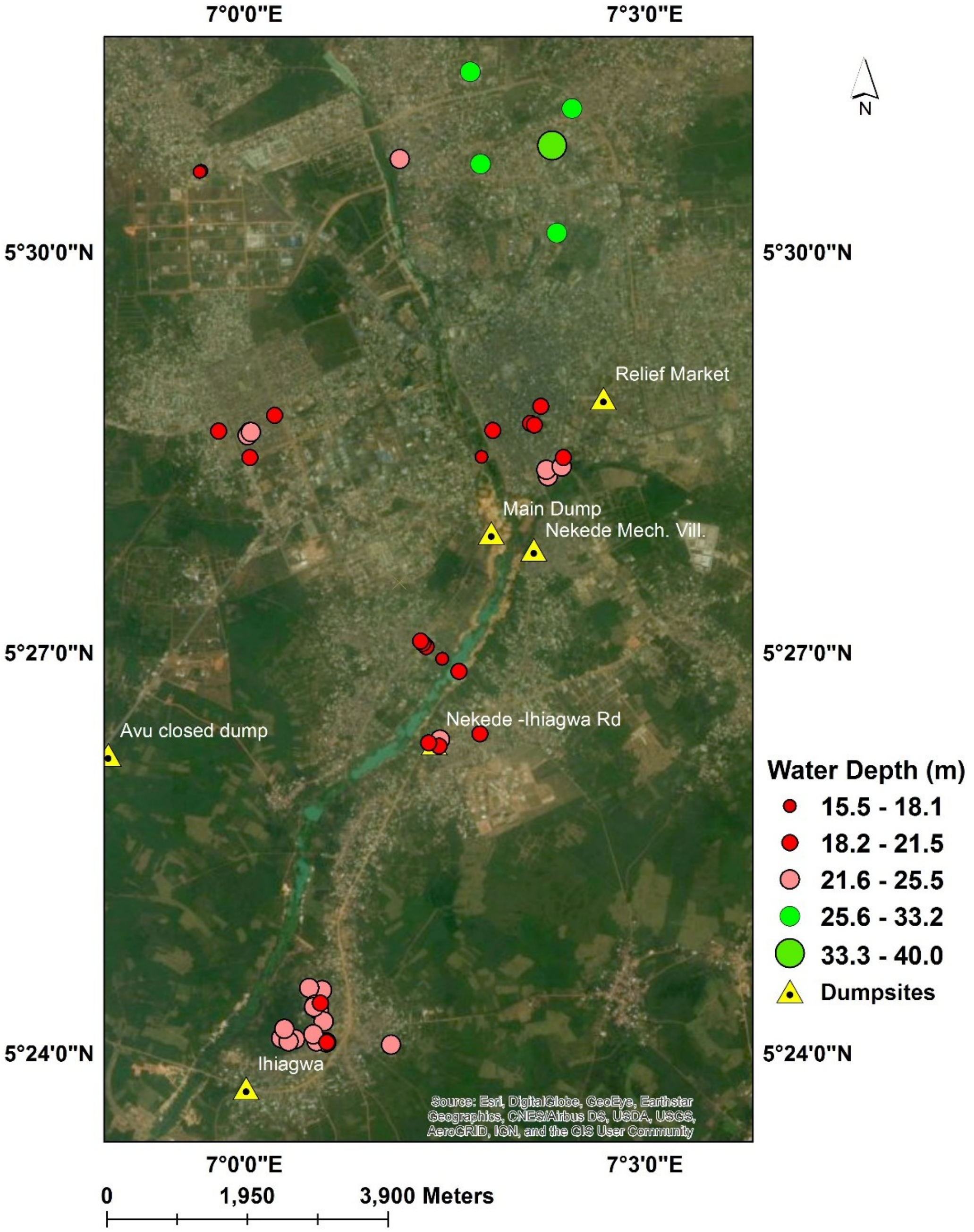


Figure 5.5: Measured depth to water table in some wells across the study area. Green-coloured symbols represent the deep are wells, whereas the medium coral light and red coloured symbols show a combination of shallow and moderately shallow wells. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)

The discussion also considers the level at which identified contaminants exceed health-based regulatory standards of World Health Organisation (WHO), Nigerian Standard for Drinking Water Quality (NSDWQ), European Commission, and the Codex General Standard for Contaminants and Toxins in Food and Feed, as well as possible human health implications.

### 5.3.1 Regional assessment of nitrate concentration in groundwater by the depth to water table

Several factors have been associated with unconfined aquifer pollution prominent among which is depth to water table that determines the susceptibility of groundwater to surficial pollutants (Pociene and Pocius, 2005). This study has classified the study area into three hydrogeological regions using average values of previous studies which include: deep wells with depth 25 - 34m and covering about 29.0 km$^2$, moderately shallow wells (20-24m) with an area of about 173 km$^2$ and shallow wells (12 -19m) of about 49.8 km$^2$. Table 5.5 presents $NO_3^-$ concentration trend of shallow > deep > moderately shallow in the rainy season and shallow >moderately shallow > deep wells in the rainy and dry seasons respectively based on recorded median values. Generally, lower $NO_3^-$ concentration was measured in all regions during the rainy season. Gold et al., (2001) remarked that wet soils overlaying an aquifer have greater potential for denitrification, unlike the dry soil. This assertion can be supported by the lowest $NO_3^-$ value of 4.68 µg/mL recorded in the downgradient moderately shallow region, where flood from the deep and shallow regions tends to discharge to form swamp. However, to evaluate the statistical significance of changes across regions further statistical analysis was conducted using $NO_3^-$ datasets generated in this study. Datasets were transformed by log base 10 to assume normality and a two-way analysis of variance (ANOVA) applied to assess the difference of $NO_3^-$ concentration in groundwater by depth and seasonal variabilities in the study area. Difference among $NO_3^-$ concentration in groundwater in wells across seasons in the respective regions were considered statistically significant, for depth ($F = 82.8$, $p < 0.001$) and seasons ($F = 4.39$, $p < 0.03$) respectively. However, tukey post hoc multiple – comparison test result used to compare differences among regions showed a statistically significant difference between the shallow and deep wells ($p < 0.001$), shallow and moderately shallow wells ($p < 0.001$) but no significant difference between moderately shallow wells and deep well regions ($p < 0.07$) at 95 % significant level. A similar technique was applied in the analyses of locational and seasonal influences on groundwater variables in the floodplain of a headwater catchment of Rio Calaveras, New Mexico, USA (Baker et al., 2000). Besides, ANOVA and Tukey test have been commonly used in the analysis of both seasonal and spatial variability of groundwater quality (Tokalıoğlu et al., 2018; Belkhiri and Narany, 2015).

The ANOVA, therefore, suggests that variability in depth to water table is a significant factor that controls the fate and distribution of nitrate in groundwater across the study area. Hence, the trend in the rainy season showed a relatively oxidised deep (recharge) region, which also recorded elevated $NO_3^-$ concentration of 57.9 μg/mL at a sampling site and interquartile range (IQR) of 5.43 – 13.2 μg/mL. This however dropped in the dry season with all sites recording values below the 50.0 μg/mL and IQR of 2.73 – 9.92 μg/mL. This suggests that thick-layered soil structures overlaying aquifers in the deep region could have significantly attenuated the contaminants. However, the recorded elevated value at a well in the rainy season could be attributed to interception by a well along the drainage pathway during catchment runoff in the rainy season.

Based on the health-based focus of this research, $NO_3^-$ distributions in groundwater across the three regions are presented as box plots in comparison with health-based regulatory threshold required by the Nigeria Standard for Drinking Water Quality (NSDWQ), as presented in Figure 5.6. Elevated value of $NO_3^-$ above regulatory limit has been associated with severe health conditions as discussed in subsequent sections.

Table 5.5: Owerri groundwater nitrate ($NO_3^-$) concentrations across the study area according to depth to water table and sampled seasons. The table shows percentage of groundwater boreholes that recorded values above the lowest limit of detection (LLD) and the $NO_3^-$ Maximum Concentration Limit (MCL) of 50 µg/mL World Health Organisation (WHO), Nigeria Standard for Drinking Water Quality (NSDWQ), European Standards for Drinking-Water (EUSDW), but 45 µg/mL by the United States Environmental Protection Agency (USEPA) standard.

| **Number of sampled wells with $NO_3^-$ > LLD = 294** | **Deep wells** | | **Moderately Shallow wells** | | **Shallow wells** | |
|---|---|---|---|---|---|---|
| Sampling Season | Rainy | Dry | Rainy | Dry | Rainy | Dry |
| Number per Season | 14 | 16 | 73 | 26 | 110 | 55 |
| Minimum (µg/mL) | 0.71 | 1.58 | 0.55 | 0.65 | 1.08 | 0.65 |
| Median (µg/mL) | 8.40 | 6.01 | 4.68 | 18.6 | 18.1 | 43.0 |
| Maximum (µg/mL) | 57.9 | 26.2 | 128.1 | 69.3 | 127.3 | 148.4 |
| % >WHO MCL | 0.07 | Nil | 11.0 | 11.5 | 19.1 | 43.6 |
| % >NSDWQ MCL | 0.07 | Nil | 11.0 | 11.5 | 19.1 | 43.6 |
| % >EUSDW MCL | 0.07 | Nil | 11.0 | 11.5 | 19.1 | 43.6 |
| % >USEPA MCL | 0.07 | Nil | 12.3 | 19.2 | 21.8 | 49.1 |

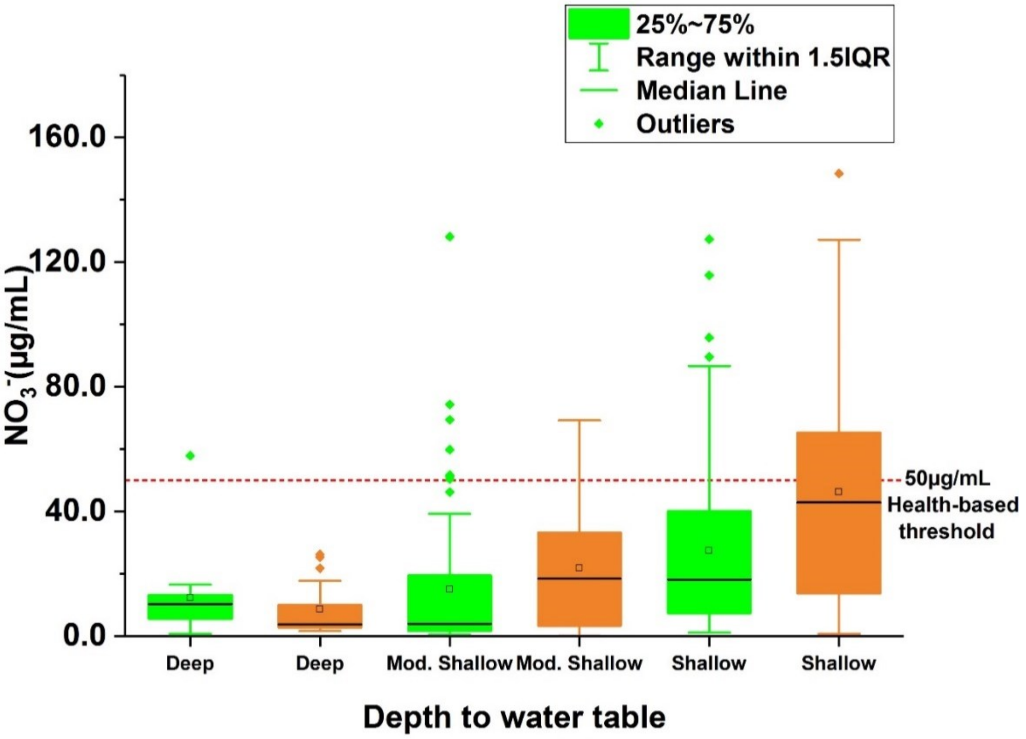


Figure 5.6: Variability of Owerri groundwater nitrate (NO$_3^-$) concentrations by depth to water table and sampled season in comparison with a health-based threshold of 50 µg/mL stipulated by the Nigeria Standard for Drinking Water Quality (NSDWQ). Seasonal differences are symbolised by green and orange colouration for the rainy and dry seasons, while depth differences are defined by deep, moderately shallow (Mod. Shallow) and shallow well regions respectively.

Lowest NO$_3^-$ concentration recorded in the moderately shallow regions could in addition to denitrification (as explained earlier) or be associated with dilution due to the possible interaction between wells in the riparian zone of the region and river overflow during high storm flow, though low NO$_3^-$ concentration was recorded in the river. This implies that there could be a high potential for denitrification due to the artificial anoxic condition often created by such interaction. However, dilution effect may be more prevalent based on the low median ammonium (NH$_4^+$) concentration of 0.029 µg/mL (IQR= 0.011 – 0.077) and 0.029 µg/mL (IQR= 0.043 – 0.289) recorded in the rainy and dry seasons respectively.

Shallow wells showed highest NO$_3^-$ concentration in the two seasons with an interquartile range of 6.55 – 37.7 µg/mL in the rainy season and 28.1 – 74.6 µg/mL in the dry season. Flooding from the elevated regions during the rainy season can induce anoxic conditions and denitrification in the downgradient wells. This could be likened to a closed system whereby oxygen is consumed from the recharge end (deep region) of the groundwater flow system (See Chapter 2, Section 2.5.2). Under this condition, organic carbon is oxidised by facultative anaerobes and nitrate used as electron acceptor under such anoxic condition, hence the reduced nitrate (Rivett et al., 2008). Besides, there could be easy infiltration of the necessary dissolved organic carbon through runoff into the groundwater in this region, based on its near-surface lithology, median DOC value of 7.3 µg/mL measured in the rainy season, as well as the general soil characteristics of the study area. Analyses of the area's soil mineralogy as measured in XRD in this study indicate predominant sandy soil (>90% $SiO_2$ and <10%. kaolinite).With median dissolved oxygen (DO) values of 7.9 µg/mL (IQR= 5.8 – 10.5) and 6.6 µg/mL (IQR= 5.7 – 8.2) recorded in the rainy and dry seasons respectively, denitrification could be inhibited (Hiscock et al., (1991). However, both field and laboratory studies have shown that denitrification can occur at DO greater than 1 µg/mL (Tesoriero et al., (2015); Hiscock et al., (1991). Nitrate can be stable in groundwater under an oxic environment and denitrified to nitrogen gas ($N_2$) or ammonium ($NH_4^+$) in an anoxic condition (Slomp and Van Cappellen, 2004).

Nevertheless, Hiscock et al., (1991) also remarked that natural denitrification processes by denitrifying bacteria can occur in both shallow and deep aquifers and the rate of occurrence can be dependent on the availability of dissolved organic carbon (DOC) for biosynthesis.

The possibility of $NO_3^-$ conversion to ammonium ($NH_4^+$) during denitrification as opined in Slomp and Van Cappellen (2004) is however contrasted in this context by the low median ammonium ($NH_4^+$) concentration of 0.032 µg/mL (IQR= 0.009 – 0.055) in the rainy season, against 0.029 µg/mL (IQR= 0.01 – 0.09) recorded in the dry season. Hence, serial measurements in selected wells were conducted to further evaluate temporal characteristics of $NO_3^-$ and $NH_4^+$ in groundwater in the study area.

### 5.3.2 Temporal variability of contaminants ($NO_3^-$and $NH_4^+$) concentration at in groundwater using the Palin test technique

As part of the assessment of temporal characteristics of $NO_3^-$ concentration trend across seasons a serial sampling and in-situ measurement of $NO_3^-$ and $NH_4^+$ concentrations was carried out for five consecutive months in selected wells across the study area (Figure 5.7). The result of the measurements could suggest that $NO_3^-$ and $NH_4^+$, responded to soil moisture fluctuations, as concentrations declined with increasing soil dryness, during the dry season. Average $NO_3^-$ concentrations of 86.3 µg/mL, 76.8 µg/mL, 77.7 µg/mL, 75.6 µg/mL, and 72.6 µg/mL were recorded in the months of December 2016 through April 2017 respectively.

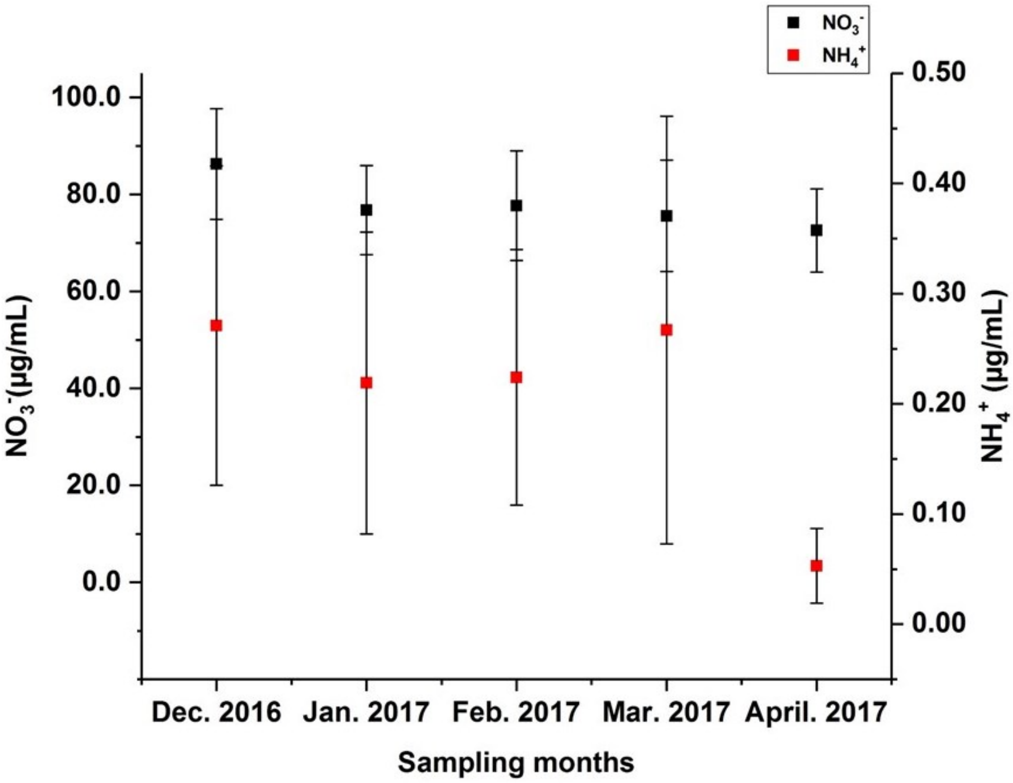


Figure 5.7: Mean monthly concentrations of $NO_3^-$and $NH_4^+$ in the 18 selected wells across the study area (Owerri, Nigeria) during the 5-month *in-situ* measurements by Palin test. Displayed error bars represents the level of uncertainty of measurements taken with overlapped bars suggesting insignificant variabilities.

The slight variation on the declining $NO_3^-$ concentration followed a short rainfall in the month of February 2017 suggesting rapid mineralisation of organic matter by microbes after rewetting. Studies have explained that under anoxic conditions, $NH_4^+$ could be produced from soil organic matter breakdown by heterotrophic bacteria and oxidised to $NO_3^-$ under aerobic conditions by *Nitrobacter* bacteria (Lingle, 2013). However, this sampling period for temporal variability was within the dry season such that oxidation of $NH_4^+$ may have been enhanced by the frequent abstraction of groundwater, which incidentally was also at its peak due to high water demand. Therefore, relative overall increase in the concentration of these nitrogen species ($NO_3^-$ and $NH_4^+$) measured in the dry season across the different regions as discussed in Section 5.3.1 could be attributed to decomposed organic matter from septic and solid waste hence could be the major sources of groundwater pollution in the study area. Nevertheless, analyses of variance of $NO_3^-$ concentration across the sampled months showed no significant difference ($F = 4.14$, $p < 0.076$) unlike the $NH_4^+$ concentration which showed significant difference ($F = 17.4$, $p < 0.003$), suggesting prevalent redox and soil moisture influences. This is consistent with postulations that decomposition rate in the subsurface decreases as soils get drier reducing energising substrates (e.g. organic carbon) needed for microbial activities (Smith *et al.*, 2015; Stark and Firestone, 1995).

## 5.4 Urbanisation influences on groundwater nitrification and human exposure

### 5.4.1 Criteria for urban delineation for groundwater quality assessment

Following the urban congestion structure as observed during the sampling seasons, this study delineates the study area into three broad categories namely city centre, sub-urban and peri-urban regions respectively as already introduced in Section 5.3 and symbolised in Figure 5.8. Most residential plots within the city centre and sub-urban were far below 15 x 30m in size within which all the necessary facilities including building structure, borehole, on-site sanitation system, and urban garden are installed.

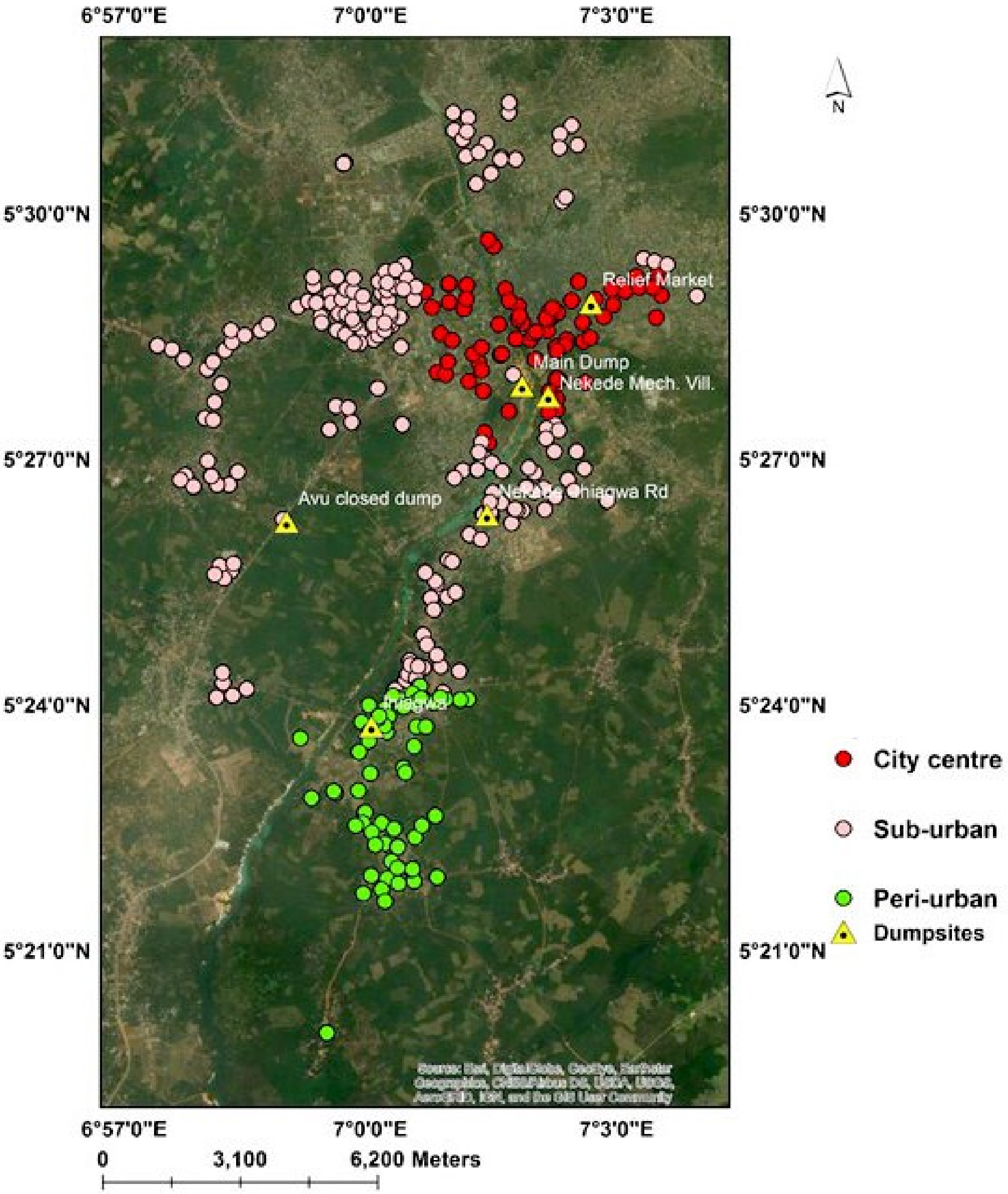


Figure 5.8: Urbanisation structure of the study area delineated on the ground of residential congestion pattern as observed during the sampling periods. Symbol colours (shown in the legend) reflect vulnerability trend of wells in each region to $NO_3^-$ concentration. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)

### 5.4.2 Assessment of $NO_3^-$ concentration pattern according to urban spread

Table 5.6 presents the spatial and seasonal variabilities of $NO_3^-$ concentration pattern, indicating elevated concentration order of city centre > sub-urban > peri-urban. The percentage of wells that exceed the health-based regulatory standard of the various agencies as presented in the box-whiskers plot in Figure 5.9 could also infer anthropogenic input on the groundwater quality. A spatial distribution map of $NO_3^-$ in groundwater across the study area is also displayed as Figure 5.10, and concentration pattern classified with graduated symbols.

Table 5.5: Owerri groundwater nitrate ($NO_3^-$) concentrations across the study area according to urbanisation and sampled seasons. The table shows percentage of groundwater boreholes that recorded values above the lowest limit of detection (LLD) and the $NO_3^-$ Maximum Concentration Limit (MCL) of 50 µg/mL World Health Organisation (WHO), Nigeria Standard for Drinking Water Quality (NSDWQ), European Standards for Drinking-Water (EUSDW), but 45 µg/mL by the United States Environmental Protection Agency (USEPA) standard.

| Number of sampled wells with $NO_3$ > LLD = 298 | City centre | | Sub urban | | Peri urban | |
|---|---|---|---|---|---|---|
| Sampling Season | Rainy | Dry | Rainy | Dry | Rainy | Dry |
| Number per Season | 66 | 15 | 105 | 76 | 31 | 5 |
| Minimum (µg/mL) | 0.710 | 0.700 | 0.55 | 1.01 | 0.550 | 1.47 |
| Median (µg/mL) | 17.9 | 63.9 | 9.94 | 18.7 | 5.25 | 6.90 |
| Maximum (µg/mL) | 127.3 | 148.4 | 128.1 | 74.6 | 69.4 | 31.7 |
| % > WHO MCL | 16.7 | 66.7 | 17.1 | 19.7 | 9.68 | Nil |
| % > NSDWQ MCL | 16.7 | 66.7 | 17.1 | 19.7 | 9.68 | Nil |
| % > EUSDW MCL | 16.7 | 66.7 | 17.1 | 19.7 | 9.68 | Nil |
| % >USEPA MCL | 19.7 | 73.3 | 18.1 | 26.3 | 12.9 | Nil |

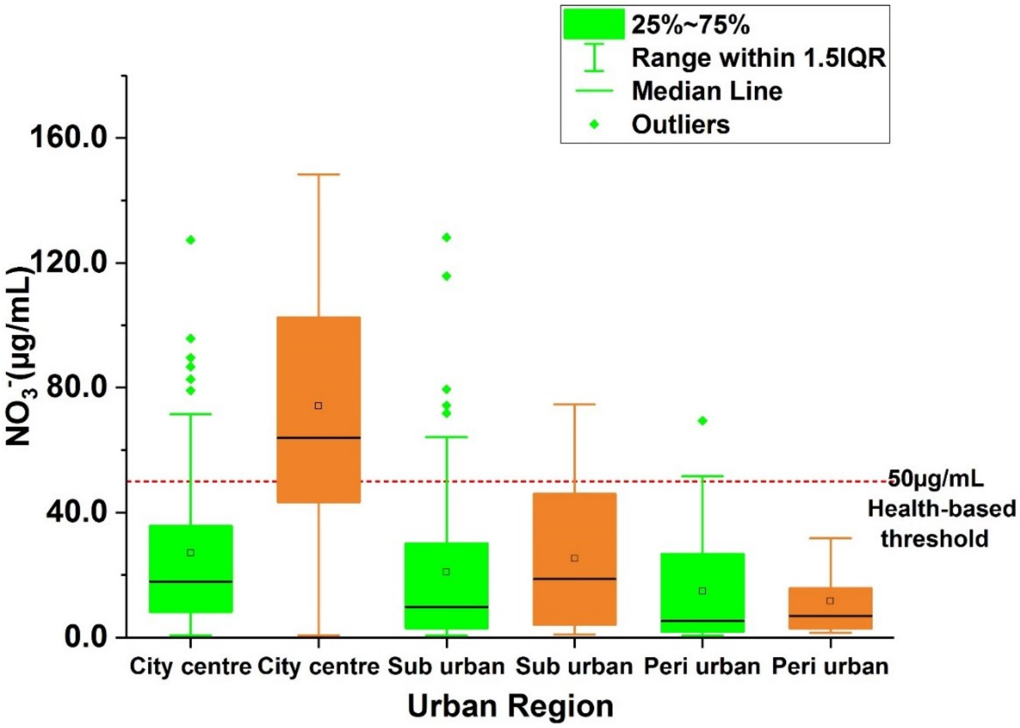


Figure 5.9: Regional variability of Owerri groundwater nitrate ($NO_3^-$) concentrations in comparison with a health-based threshold of 50 µg/mL as stipulated by the Nigeria Standard for Drinking Water Quality (NSDWQ).The seasonal difference is symbolised with green and orange colouration for the rainy and dry seasons respectively.

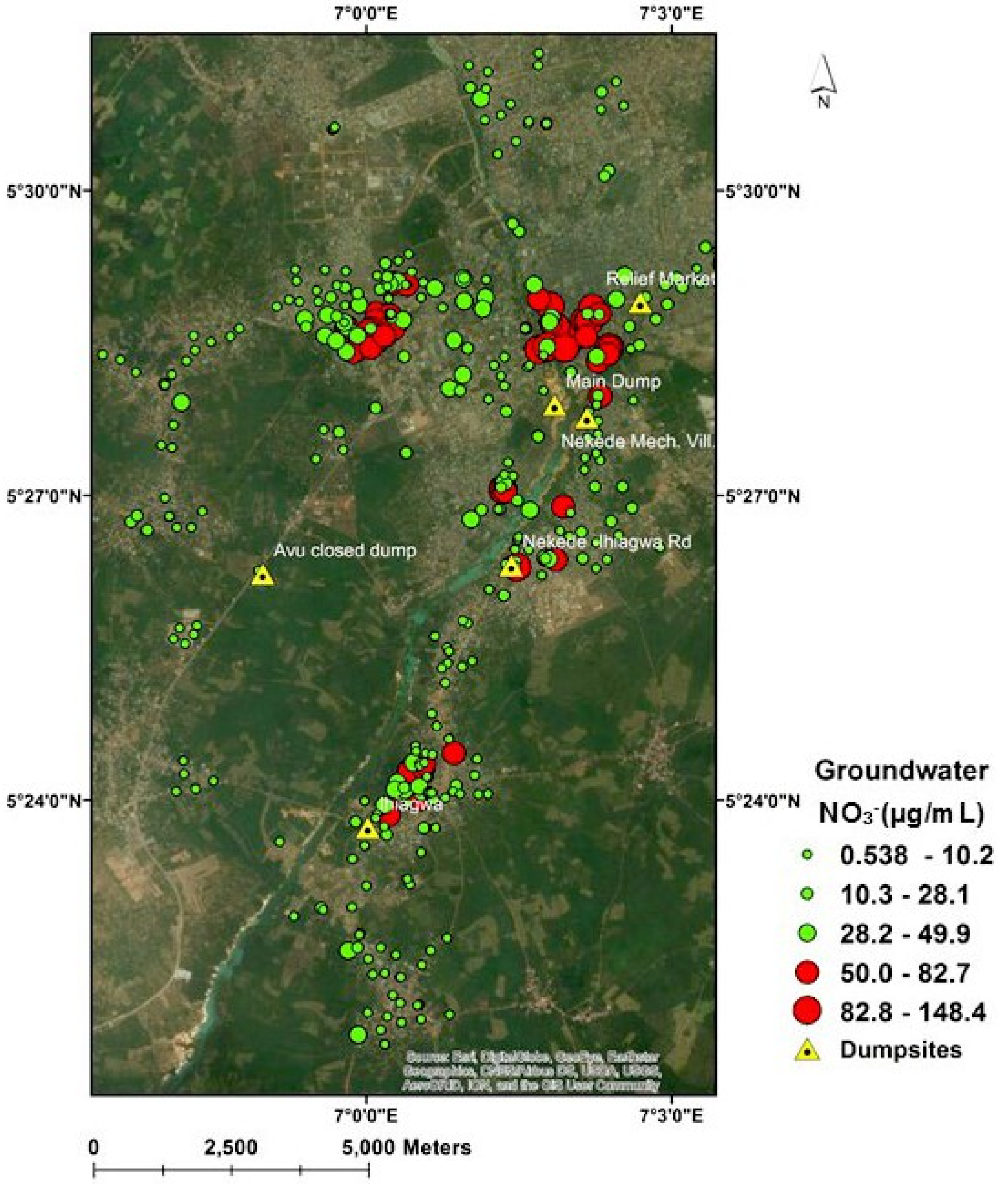


Figure 5.10: Spatial distribution of Owerri groundwater nitrate ($NO_3^-$) concentrations in comparison with a health-based threshold of 50 µg/mL as stipulated by the Nigeria Standard for Drinking Water Quality (NSDWQ).Green coloured symbols represent wells where $NO_3^-$ measured below the threshold, whereas red symbols indicate wells with elevated $NO_3^-$concentration above stipulated health-based threshold. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)

Both the values presented in Table 5.5 and distribution map displayed as Figures 5.6 & 5.7 indicate that $NO_3^-$ in Owerri groundwater is population - density driven, as $NO_3^-$concentration trend is consistent with urban density pattern. Besides, the two most contaminated regions fall within the vulnerable shallow and redox zones (Table 5.4, Section 5.2.3). This implies that anthropogenic activities especially inefficient disposal of human and animal waste (septic tank), as well as indiscriminate dumping of solid waste, could have introduced contaminants into the groundwater.

### 5.4.3 Anthropogenic impact on groundwater quality

Anthropogenic influence on the $NO_3^-$ concentration in groundwater in Owerri is most evident in the highly congested regions within the city centre. A comparison of $Cl^-$ concentration in groundwater, which is a non-conservative tracer of domestic waste pollution with $NO_3^-$ concentration assumed a similar trend. $Cl^-$ median and IQR values are 1.26 µg/mL (IQR = 0.943 – 2.94 µg/mL), 0.85 µg/mL (IQR = 0.585 – 3.35 µg/mL), 4.34 µg/mL (IQR = 1.67 – 10.4 µg/mL) for the deep, moderately shallow and shallow wells respectively. Common sources of anthropogenic pollution of groundwater in the area are through leachates from on-site sanitation systems and indiscriminately sited open solid waste dumpsites.

#### Proximity to Septic tank

Septic effluent is adjudged as a major source of groundwater contamination in most developing countries due to the unsewered method of human waste management. An average nitrogen loading of between 25 – 75 µg/mL (Seiler, 1996; Otis et al., (1980)) or up to 5kg/year/capita could be introduced to the environment through human excreta (Elisante and Muzuka, 2017; Lewis et al., 1980). Following observed proximity of wells to septic tank during sampling, this study has compared measured $NO_3$ concentrations in groundwater of wells located between less than 20 m and more than 20m from septic tanks. Recommended approximate distance of water well to septic tanks has been placed at 15m to 30.5 m with regards to public health (Dismas et al., 2018; Comar, 2011).

This evaluation becomes necessary in view of the potential threat, which septic tanks could pose to groundwater quality, especially within vulnerable regions. Groundwater samples from wells situated at the different redox observation zones introduced in Section 5.2.3 and their respective distances to nearest septic tanks were used for this assessment. Visual display of a result of the evaluation (Figure 5.11) suggests variability across the respective zones.

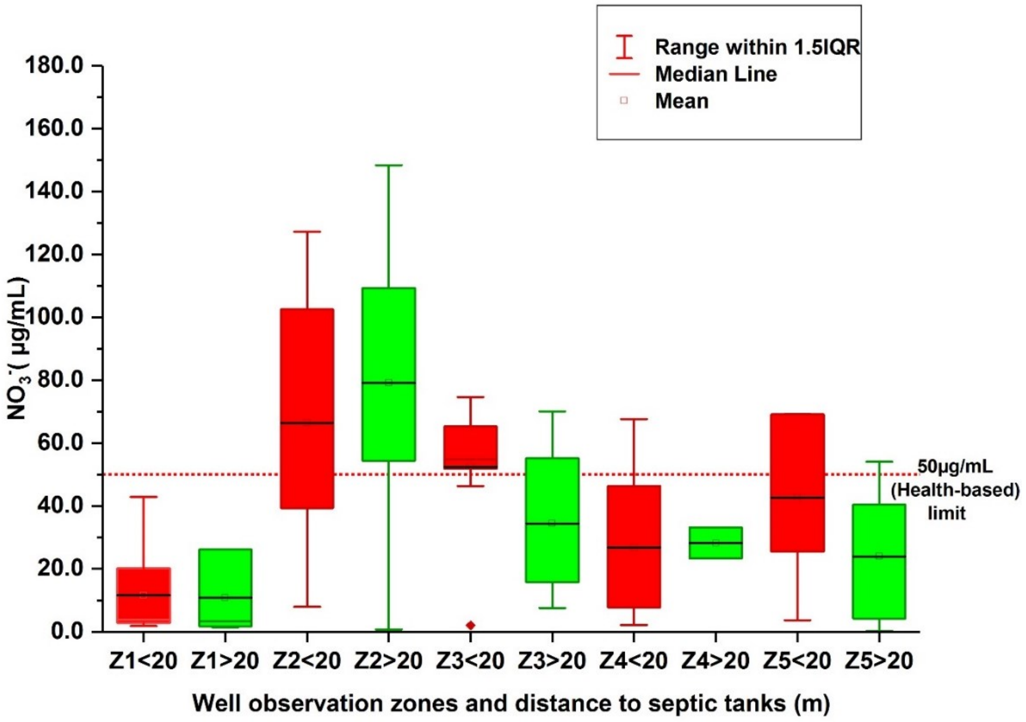


Figure 5.11: Owerri groundwater nitrate ($NO_3^-$) concentrations for wells located within 20 m of septic tanks, compared to the NSDWQ health-based threshold limit of 50 µg/mL. Wells located within the different observation zones (Obs.1-5) introduced in Section 5.2.3 and their respective distance to nearest septic tanks were used for this assessment. Red and green boxes symbolise the respective samples from wells located less than 20m (Z<20m) and greater than 20m (Z >20m) at each of the zones numbered 1 - 5. All datasets were normally distributed except for wells in Z1 and Z3 <20m hence, median value applied for comparison.

Groundwater datasets from each of the selected wells were log-transformed to assume normality in order to evaluate mean difference within and between each group. A one-way ANOVA was then carried out and an overall report shows F-value 3.81, $p < 0.001$ at $p< 0.05$ significant level suggesting a statistically significant mean difference in the datasets. Consequently, Tukey post-hoc analyses were conducted to determine the specific means that were different, which only indicates a statistically significant difference between means at $p < 0.05$. The identified difference (acronyms as defined in Figure 5.8) were between Z2 < 20 and Z1 < 20 ($p < 0.04$), Z2 < 20 and Z1 > 20 ($p < 0.008$), Z2 > 20 and Z1 > 20 ($p < 0.014$), Z3 <20 and Z1 > 20 ($p < 0.02$). This suggests that whereas septic to well distance at less or greater than 20m in Zone 1 may not affect groundwater nitrate ($NO_3^-$) concentrations, similar distance in Zone 2 could influence groundwater $NO_3^-$ concentrations. This interpretation also extends to the significant difference between the mean value of Z3 < 20m and Z1 > 20 m. These significant differences could be associated with the higher tendency of soil attenuation of $NO_3^-$ leaching contaminants from septic to groundwater in zone 1 located in the deep region than in zones 2 and 3 in the shallow region

Studies have opined that proximity of wells to on-site facilities in areas characterised by high-density septic systems can contaminate groundwater as there are high chances of pumping leachate from the septic tank into domestic wells (Bremer and Harter, 2012). Notwithstanding, siting a septic tank close to drinking water wells can be a conduit for biological contamination of the groundwater. Contamination from such pathogens like bacteria and viruses may result in severe gastrointestinal disorder especially among infants with a fragile immune system (EPA, 2015).

### 5.4.4 Open solid waste dumpsite leachate contamination of groundwater

Apart from Cd concentration value of 4.71 µg/g measured in soil sampled at the main dumpsite, only the Nekede - Ihiagwa road dumpsite seems to have a direct impact on the groundwater chemistry in the nearest well located approximately 105m downgradient (Figure 5.12a). Ideally, the minimum distance of landfill location to a well is 365m (Bagchi, 2004).

Concentration of $NO_3^-$ in the dumpsite leachate as measured during the rainy season was below the detection limit and could be attributed to anoxic conditions created by high decomposition rate of moisturised organic materials by bacteria (see Chapter 2, Section 2.3.2). This is evidenced in the measured mean and standard deviation value of $NH_4^+$ concentration in the dumpsite leachate of 7.87 ± 8.54 µg/mL and 0.609 µg/mL in the well. Such $NH_4^+$ concentration in the dumpsite leachate may have been oxidised to $NO_3^-$ while being leached through the soil profile to the groundwater (See Figure 5.12b). Researchers have opined that lack of proper containment and management of waste can be a major threat to water resources and public health; as pollutants from a waste dump can travel up to a distance of 120m if its leachates are directly connected to water in saturated soil (Nwachukwu et al., 2010; Liu et al., 2007). Although some other dumpsites such as main dumpsite relief market and Nekede mechanic village dumpsites seem to have no adverse impact on nearby wells, the probability of influencing elevated $NO_3^-$ recorded in groundwater of wells beyond 1000m away may not be ignored. This suggestion is informed by the high median $NH_4^+$ concentration range of 26.6 to 526 µg/mL measured in leachate samples of these dumpsites (see Chapter 4, Section 4.6.1), variability in depth to water table and redox potentials across the study area. This could contrast with the conventional practice of assessing contaminant impacts on groundwater based on proximity to potential pollution sources. Furthermore, a Spearman's correlation analysis of some common ions analysed in both the leachate from these dumpsites and groundwater from wells within 1km proximal distance showed a significant relationship between $NH_4^+$ concentration in leachate and $NO_3$ concentration in groundwater ( $R^2 = 0.672$, $p < 0.001$) (see Appendix 5F). Redox conditions in groundwater and hydrogeological features (vulnerability) have been identified as two important factors that influence the stability of $NO_3^-$ in groundwater (Lapworth et al., 2017). Besides, studies have remarked prevalence of fast horizontal pathways in tropical soils (transmissivities greater than 300 $m^2$/day) which could enhance migration of contaminants in the subsurface (Lapworth et al., 2017; Bonsor et al., 2014)

Figure 5.12a: Proximity of the Nekede – Ihiagwa road dumpsite to residential buildings with wells potentially contaminated by the dumpsite leachate.

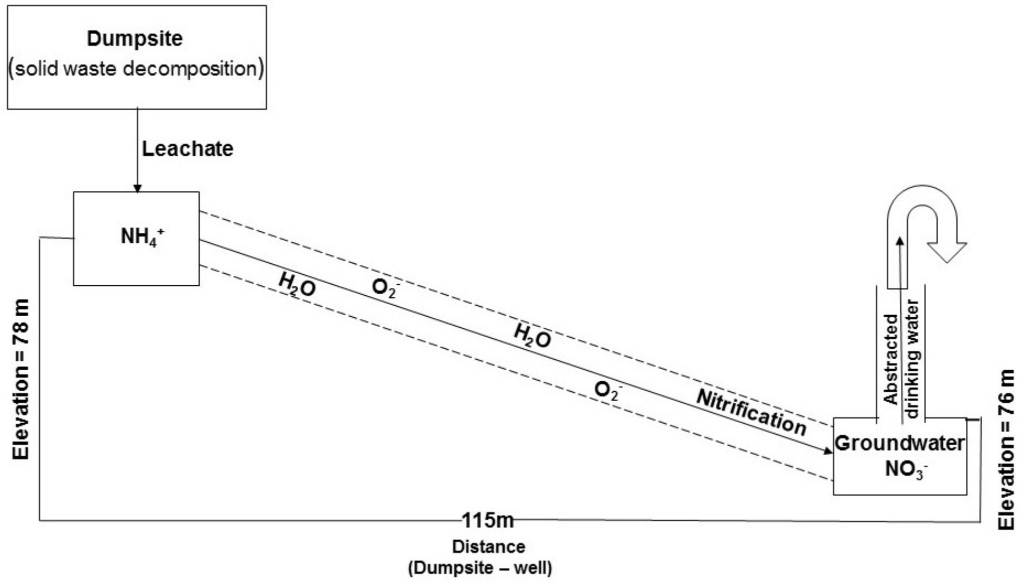


Figure 5.12b: Conceptual model describing processes responsible for nitrate contamination of groundwater in wells in close proximity to the Nekede - Ihiagwa road dumpsite. Arrows indicate fluxes just as dashed lines represent soil profile and conditions, which enhanced oxidation of ammonium while reactants and products are presented in rectangle.

## 5.5 Overview of measured soil parameters with potential influence on groundwater nitrification

### 5.5.1 Soil Organic Matter (SOM)

Measured percentage mean and standard deviation of soil organic matter in the respective seasons were 3.70 ± 2.86 and 1.94 ± 0.809 for rainy and dry seasons. The variation can be attributed to possible decomposition of organic residues in the topsoil horizon during flooding in the rainy season. Percentage mean and standard deviation of SOM recorded across the different urban areas in the order city centre (3.81 ± 4.41), sub-urban (3.79 ± 0.94) and peri-urban (3.72± 0.80) during the rainy season showed no significant variation. This could suggest that though elevated SOM might be associated with $NO_3^-$ concentration in groundwater through microbial processes and leaching, it may not account for its regional variability. Haynes and

Naidu, (1998) also opines that though overland flow depositions and accumulation of high SOM could improve soil characteristics with respect to hydraulic conductivity, porosity, and infiltration capacity and decreasing bulk density, it increases the susceptibility of groundwater to $NO_3^-$ contamination.

### 5.5.2 Soil Carbon-Nitrogen (C: N) ratio

Measured percentage mean and standard deviation values of carbon in soil were 1.23 ± 0.473 and 0.86 ± 0.416 for the rainy and dry seasons respectively. Decline in the percentage of soil carbon from 1.23 in the rainy to 0.862 in the dry could suggest high deposition and decomposition of organic matter by microbial activity due to the relatively higher moisture content of the soil. This could enhance production of $CO_2$ and probably be responsible for the depressed pH and elevation of increased DOC in groundwater via soil wash by runoff. Similarly, percentage median soil organic carbon (SOC) for the rainy and dry seasons were 2.01 (IQR = 1.72 – 2.30) and 1.0 (IQR = 0.85 –1.33) respectively, and implies soil organic carbon loss by leaching during the rainy season due to the characteristics of poor soil aggregation of the study area. Besides, DOC in groundwater and percentage of soil organic carbon showed moderate correlation (0.505, $p < 0.05$) in the dry season and none in the rainy season.

Studies have reported significant increase of DOC in streams and lakes across Northern Europe and north-eastern North America due to loss of soil carbon (Oulehle et al., 2011; Monteith et al., 2007; Evans et al., 2007; Worrall et al., 2004; Freeman et al., 2001). On the other hand, percentage mean and standard deviation values of soil nitrogen were 0.088 ± 0.036 and 0.052 ± 0.033 for the rainy and dry seasons respectively. This could infer high leaching rate of soil nitrogen through the porous soil profile to the groundwater that could also enhance groundwater nitrification. These attributes, however, differ across the respective regions of depth variability trend.

## 5.6 Interpolation and error maps of contaminant distribution across the study area

Empirical Bayesian Kriging interpolated technique has been applied in mapping both measured datasets and calculated exposure index of contaminants in both groundwater and plants in this section while reintroducing Figure 5.13 showing sampled points of groundwater $NO_3^-$concentrations for better appreciation of the interpolation output. This geostatistical interpolation technique requires no manual adjustment of parameters for result accuracy unlike other kriging techniques but automatically calculates parameters by simulating subsets of the dataset. Predictions are made using scaled sums of prediction from respective intersecting subsets while accounting for prediction errors by estimating the underlying semivariogram (Krivoruchko and Gribov, 2014).

Parameters considered include $NO_3^-$ in groundwater and Pb in plant and groundwater. Green graduated symbols are used to show sites with fewer health risks, while red colour signifies contaminated wells.

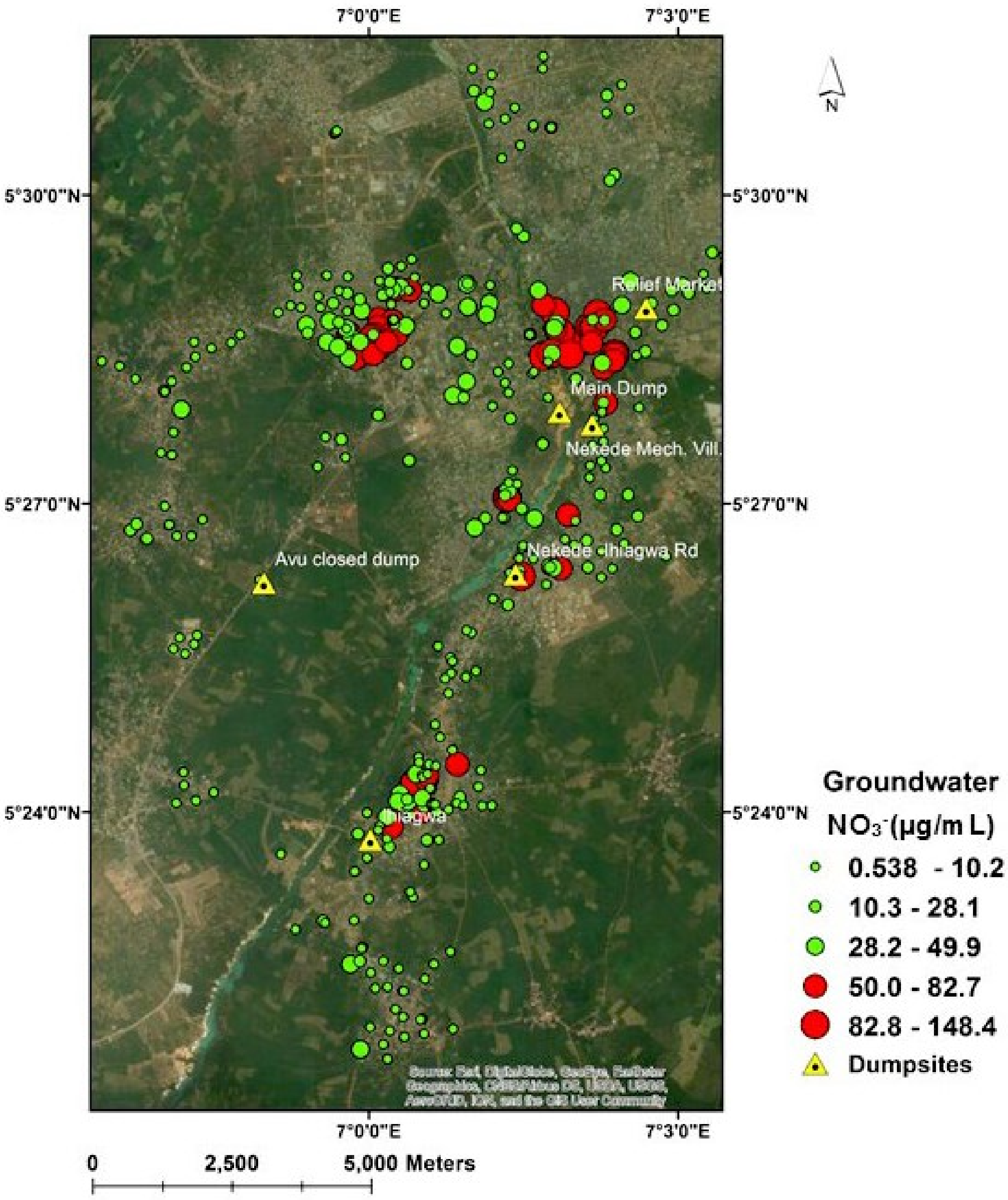


Figure 5.13: Owerri groundwater nitrate ($NO_3^-$) concentrations, highlighting the most vulnerable groundwater exposure sites with values above the health-based threshold of 50 µg/mL indicated with red symbols (especially for the most vulnerable toddlers). (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community).

### 5.6.1 Nitrate ($NO_3^-$) interpolation in groundwater

Although the increased concentration of $NO_3^-$ in groundwater was recorded higher within the city centre, interpolated values (Figure 5.14a) suggest greater concentration in groundwater within the clustered wells in the southwest sub-urban and southeast peri-urban regions as deduced from the relatively low (<10%) error values. This implies a higher exposure risk of water contamination and eventual health risk challenge in the areas**.**

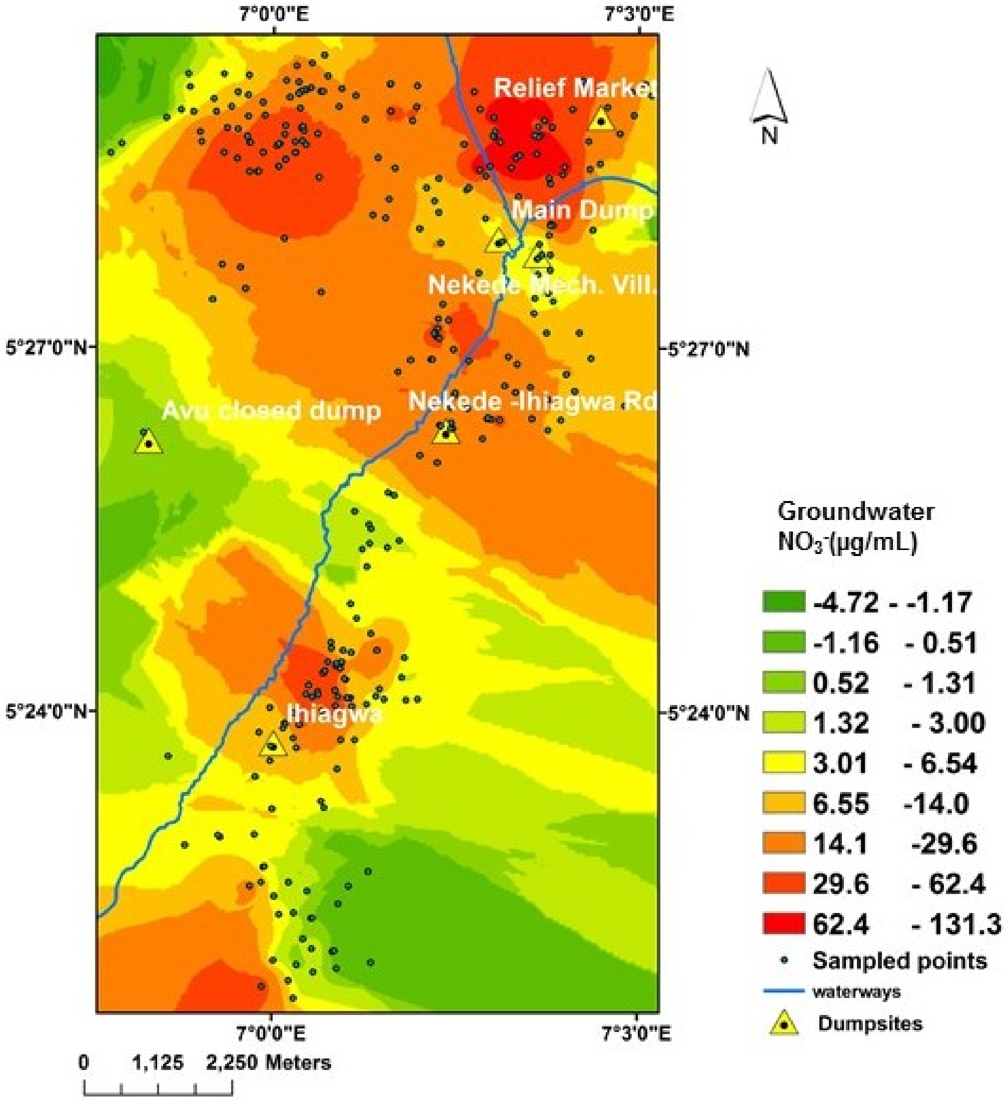


Figure 5.14a: Interpolation map of nitrate concentration in the groundwater of the Owerri study area suggests better prediction of $NO_3^-$ contaminant plume within the southwest sub-urban and the downgradient southeast peri-urban regions based on the standard prediction error displayed in Figure 5.14b.

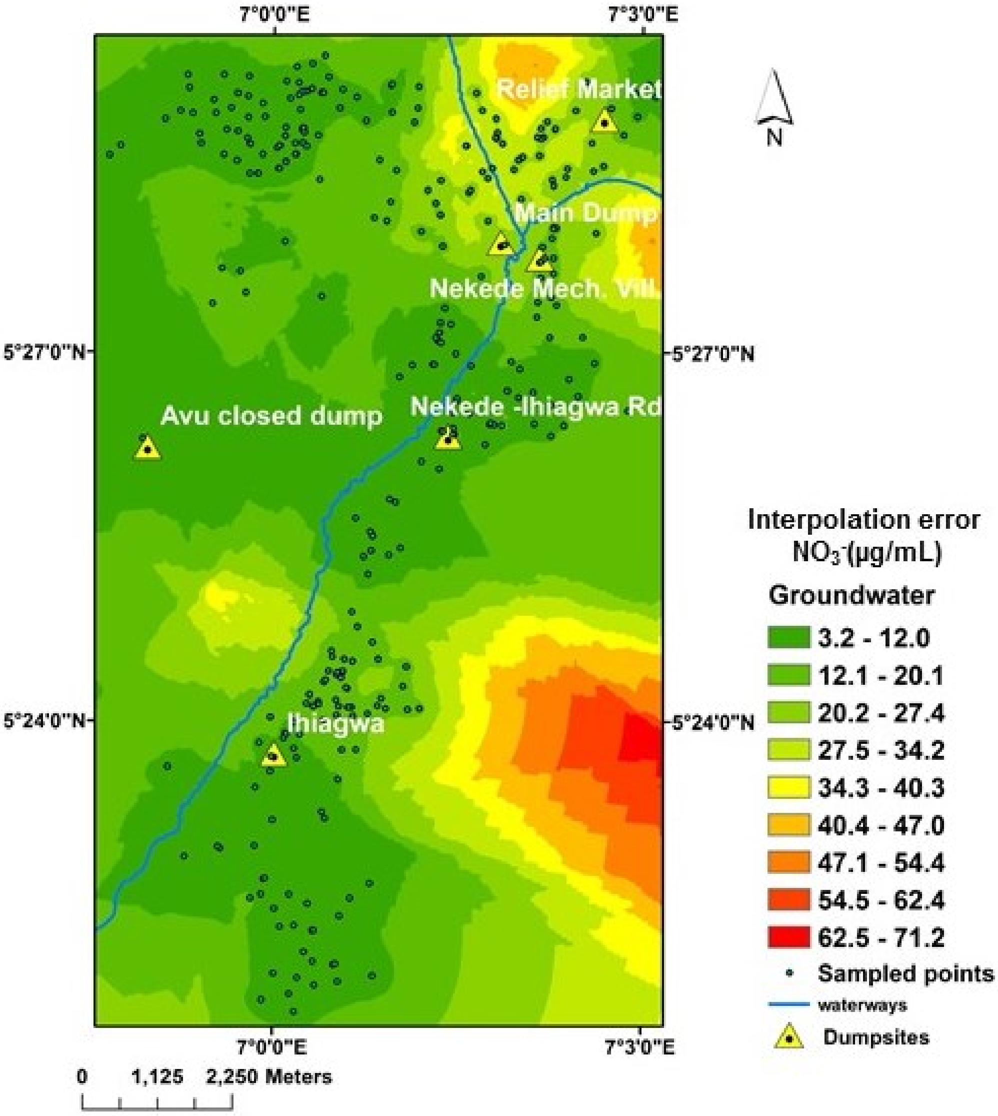


Figure 5.14b: Error map of $NO_3^-$ contaminant in the groundwater of the Owerri study area in an ascending order of standard prediction error. Predictions assessment are compared with real values in Figure 5.14a with conclusion best drawn from lower error values.

### 5.6.2 Lead (Pb) interpolation in staple plants

Similar interpolation and error maps were produced for Pb distribution in cassava tuber (*Manihot esculanta*) (Figures 5.15a & b) and pumpkin leaf (*Telfaira occidentalis*) (Figure 5.16a &b).

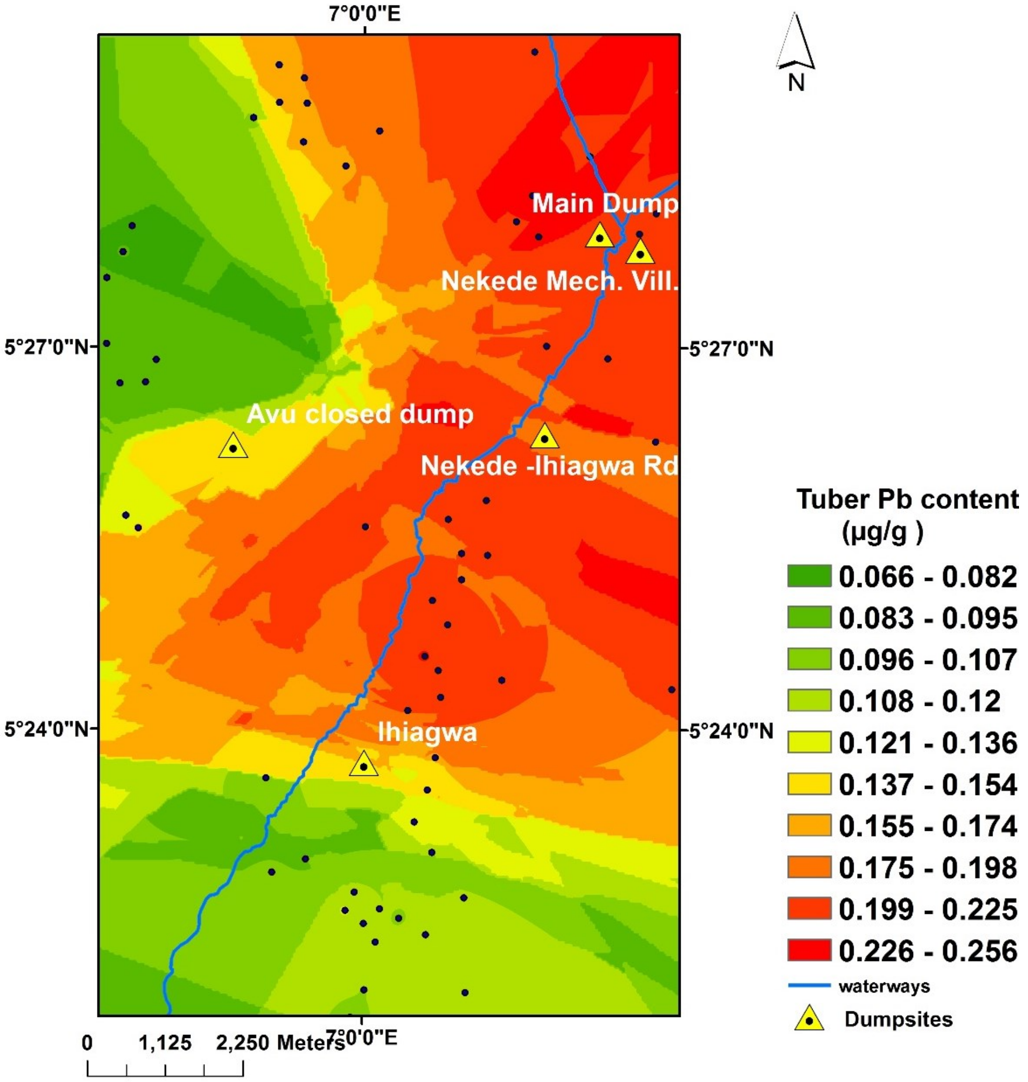


Figure 5.15a: Interpolated data of Pb concentration in sampled cassava tuber (*Manihot esculanta*) collected from urban gardens across the study area. 56.7% of samples exceed the FAO/WHO Codex Alimentarius MCL of 0.10 µg/g for tuber vegetables.

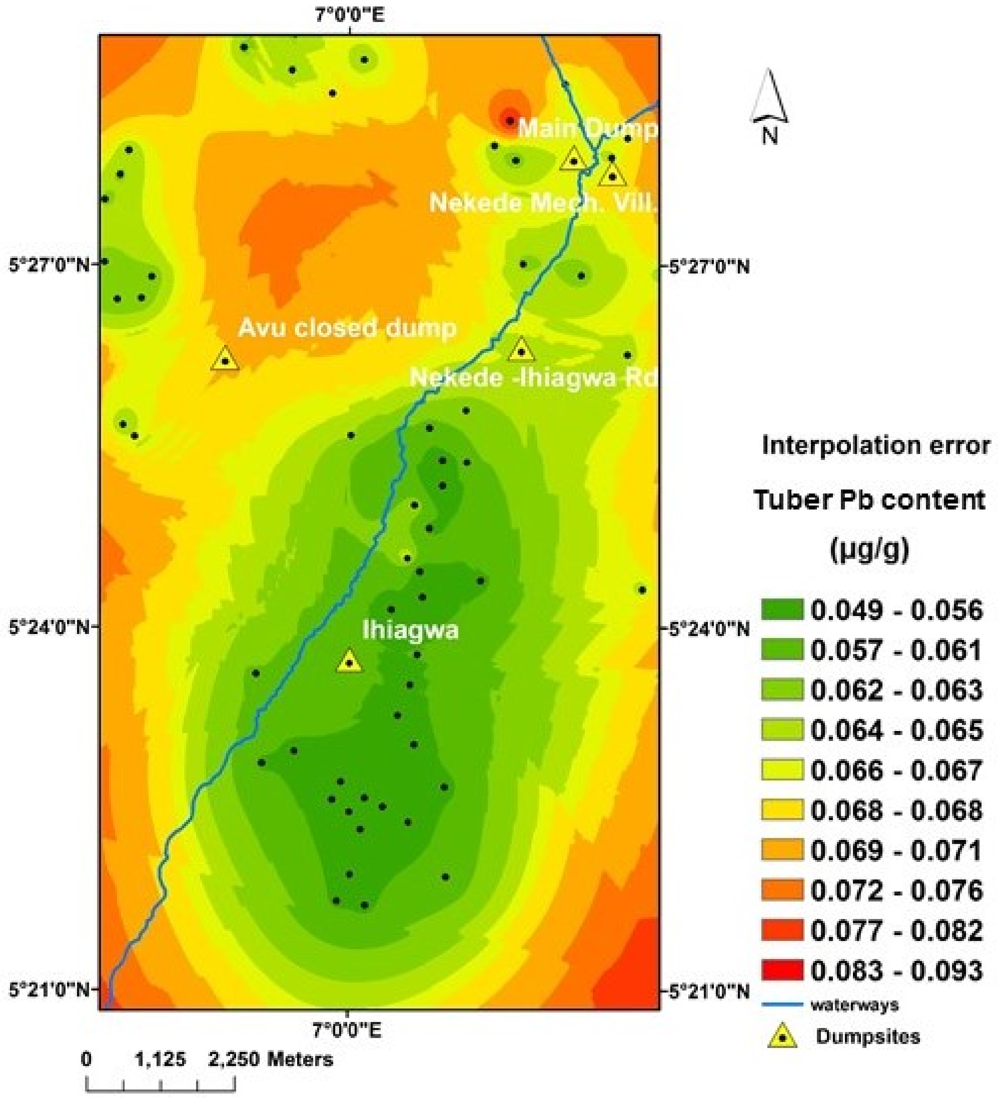


Figure 5.15b: Interpolation error map for the Pb content in sampled cassava tuber (*Manihot esculanta*) collected from urban gardens across the study area implying relative prediction accuracy within the discharge region of the study area.

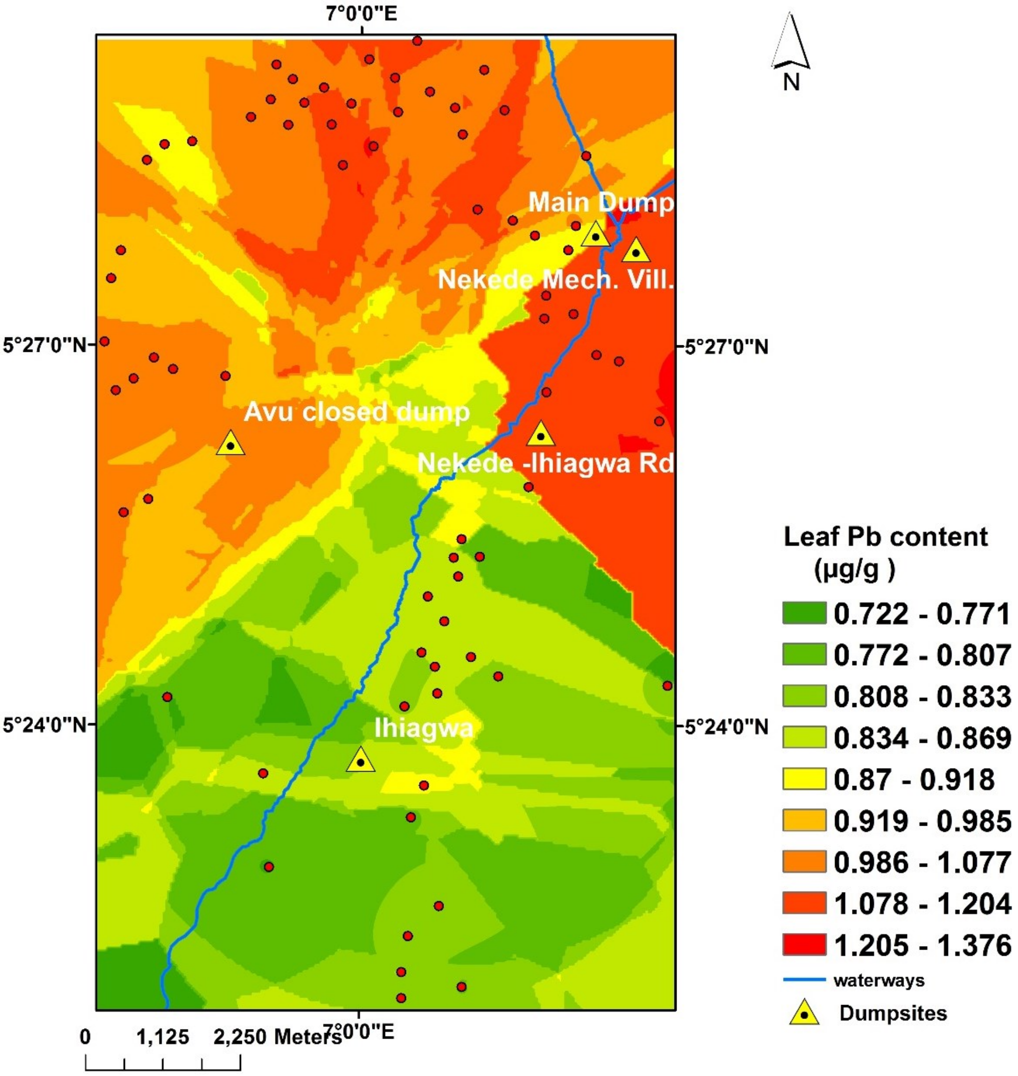


Figure 5.16a: Interpolated data of Pb concentration in sampled pumpkin leaf (*Telfaira occidentalis*) collected from urban gardens across the study area. 99.0% of samples have Pb concentrations exceed in the joint Food and Agricultural Organisation/World Health Organisation Codex Alimentarius health based maximum concentration limit of 0.30 µg/g for leafy vegetables (Commission, 2016)

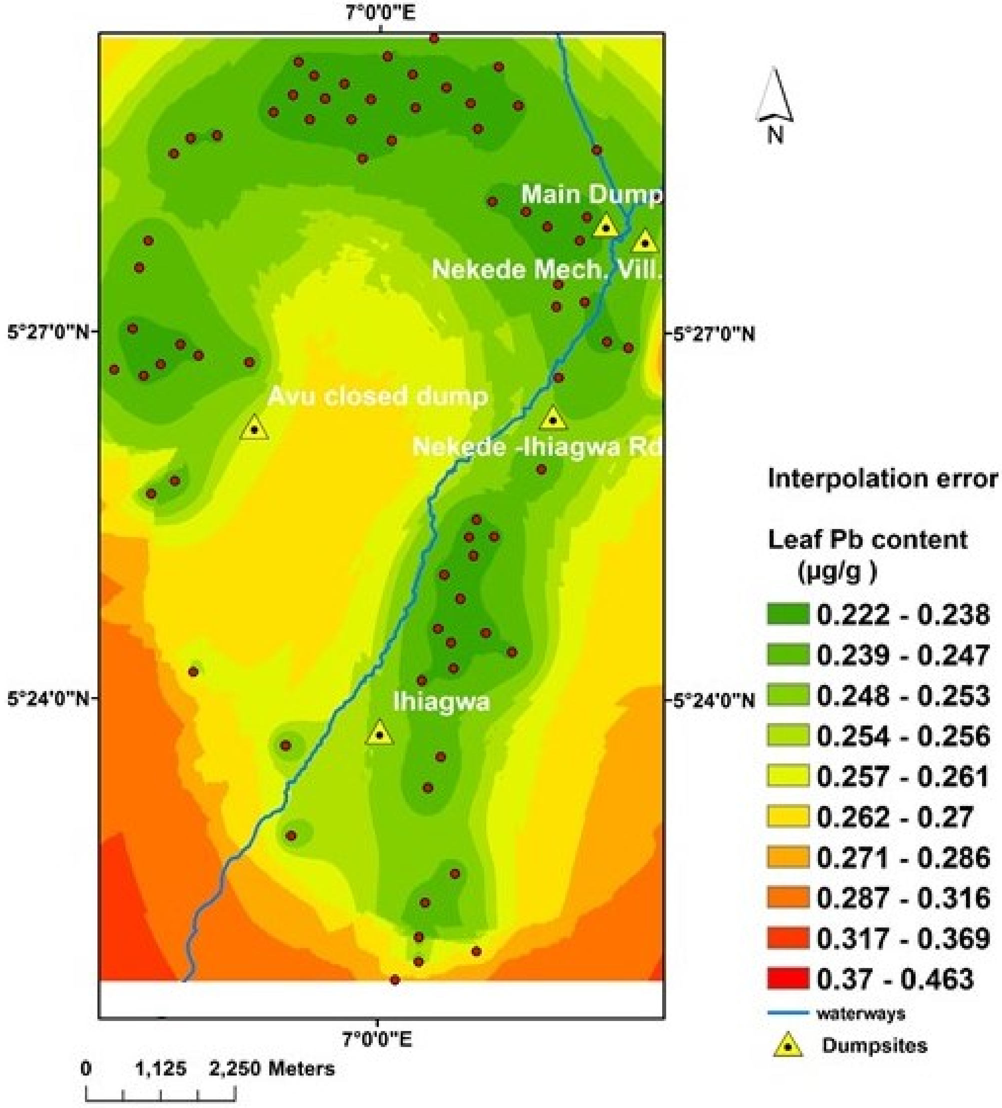


Figure 5.16b: Interpolation error map for the Pb content in pumpkin leaf (*Telfaira occidentalis*) collected from urban gardens across the study area, implying relative prediction accuracy within the discharge region of the study area.

Although virtually all the sampled pumpkin leaf (*Telfaira occidentalis*) showed leaf Pb concentration above the FAO/WHO stipulated threshold of 0.30 µg/g for leafy vegetables, an interpolated map of the contaminant's distribution pattern seems to reflect urban congestion pattern. In a study of trace metal contaminants and dispersion in some parts of Owerri (Orji and Nekede communities), Nwachukwu et al. (2011) reported that an average dispersion rate of Pb and Mn in the topsoil across the study area during the rainy season are 9.2 µg/g/m and 6.7 µg/g/m respectively. Nwachukwu et al. (2011) further opined that there is a high tendency of adsorption of these metals by both tuberous and leafy vegetables and subsequent transfer to the food chain. However, this study could not establish a correlation between Pb concentrations in the soil and plants probably due to the poor metal adsorption capacity of the quartz dominated soil of the area. This, could therefore, suggest that while elevated Pb in cassava tuber (*Manihot esculanta*) could be attributed to direct adsorption from solute flow, such measured Pb concentration in pumpkin leaf (*Telfaira occidentalis*) may have resulted from combustion engines and subsequently adsorbed by plant leaf.

### 5.7 Groundwater Quality index and mapping

Following the prevalence of identified contaminants in the groundwater and the increasing demand by residents for drinking purposes, this study finds it important to assess and map suitability of the groundwater for human consumption at the various urban regions. This assessment will unravel and communicate the spatial variability of water quality in the study area to the average consumers and policymakers through a map display.

Groundwater quality assessment follows different stages as in Vasanthavigar et al. (2010) and outlined thus

> 11 Parameters whose concentrations in this study portend health challenges are selected and assigned weight ranging from 1– 5 in the order of significance in drinking water quality assessment. Maximum weight of 5 was assigned to nitrate due to its critical concentration in groundwater across the study area. Mn, Pb, DOC were assigned 4 based on their potential health impact at high concentration (See Table 5.6) and elevated values measured

in this study. In addition, pH was assigned 4 on the basis of its central role in regulating the groundwater quality. Number 3 was assigned to EC and $Cl^-$ as indicator variables of domestic pollution and ionic dissolution in groundwater, but no obvious public health threat, while 2 was used as least value in this assessment for Na, Mg, and Fe that do pose any direct public health threat.

A. Relative weight ($W_i$) of parameters is also calculated and presented in Table 5.6 alongside the respective health-based standard according to the Nigerian Standard for Drinking Water Quality (NSDWQ). Values for Wi were derived from the relation:

$$Wi = wi / \sum^{n}_{i=1} wi \text{ ……………………….. } (4)$$

where Wi = relative weight of parameter (parameter weight/total weight)

n = total number of parameters

B. Each of the parameters is then assigned a quality rating scale (qi) obtained by the ratio of its concentration in groundwater as measured and the respective health-based standard as stipulated by the (NSDWQ) multiplied by 100.

$$qi = (C_m / C_s) * 100 \text{ …………………………}(5)$$

Where qi is quality rating, Cm represents concentration as measured in this study and $C_s$ stands for concentration of each parameter specified by NSDWQ, all in µg/mL.

C. A sub-index value (SI) is generated as a product of the relative weight (Wi) and quality rating scale (qi), which is then summed up to obtain the water quality index (WQI).

$$SI = Wi * qi \text{ ……………………… } (6)$$

$$WQI = \sum SI \text{ ……………………… } (7)$$

Water quality index (WQI) in the respective urban regions are then presented in Table 5.7.

Table 5.6: Owerri groundwater quality assessment based on the comparison of the parameter with respect to health-based standards as provided by the Nigeria Standard for Drinking Water Quality (NSDWQ)(Council, 2007).

| Chemical Parameters | NSDWQ | Parameter Weight ($w_i$) | Relative weight ($W_i$) | Potential Health Impact |
|---|---|---|---|---|
| pH | 6.5 – 8.5 | 4 | 0.108 | None |
| EC (µS/cm) | 1000 | 3 | 0.081 | None |
| $NO_3^-$ (µg/Ml) | 50 | 5 | 0.135 | Cyanosis |
| DOC (µg/mL) | 5 | 4 | 0.108 | Cancer |
| $Cl^-$ (µg/mL) | 250 | 3 | 0.081 | None |
| Fl- (µg/mL) | 1.5 | 4 | 0.108 | Fluorosis |
| Mg (µg/mL) | 0.20 | 2 | 0.054 | None |
| Na (µg/mL) | 200 | 2 | 0.054 | None |
| Fe (µg/mL) | 0.3 | 2 | 0.054 | None |
| Mn (µg/mL) | 0.2 | 4 | 0.108 | Neurological disorder |
| Pb (µg/mL) | 0.01 | 4 | 0.108 | Cardiovascular diseases |
|  |  | $\sum w_i$ =37 | $\sum W_i$ =0.999 |  |

Table 5.7: Result of groundwater quality rating (qi) calculated as a ratio of parameter concentrations in groundwater as measured and the respective health-based standard as stipulated by the (NSDWQ) multiplied by 100. Parameter median values in the different urban regions and sampled season are presented due to the non-normal distribution pattern of datasets.

| Parameter quality rating qi | Urban regions and sampling seasons | | | | | |
|---|---|---|---|---|---|---|
| | City centre | | Sub-urban | | Peri-urban | |
| | Rainy | Dry | Rainy | Dry | Rainy | Dry |
| pH | 44.7 | 77.6 | 44.7 | 83.5 | 43.5 | 79.4 |
| EC (µS/cm) | 6.20 | 19.5 | 2.80 | 6.55 | 1.60 | 3.76 |
| $NO_3^-$(µg/mL) | 35.4 | 127.9 | 19.5 | 53.5 | 7.11 | 9.73 |
| DOC (µg/mL) | 132.7 | 56.0 | 153.9 | 60.5 | 153.8 | 60.0 |
| $Cl^-$ (µg/mL) | 1.38 | 5.48 | 0.387 | 1.94 | 0.287 | 0.770 |
| $Fl^-$ (µg/mL) | 0.267 | 6.47 | -1.20 | 1.23 | -3.60 | 0.267 |
| Mg (µg/mL) | 119.5 | 719 | 58.8 | 301.5 | 33.0 | 132.8 |
| Na (µg/mL) | 1.95 | 6.20 | 0.411 | 3.41 | -0.308 | 0.519 |
| Fe (µg/mL) | 0.928 | 6.15 | 1.75 | 2.25 | 7.52 | 7.04 |
| Mn (µg/mL) | 20.2 | 57.2 | 6.64 | 22.9 | 3.10 | 7.56 |
| Pb (µg/mL) | 6.37 | 10.5 | 7.08 | 3.19 | 0.485 | 1.24 |
| $\sum qi$ | 369.6 | 1,092.0 | 280.6 | 537.1 | 246.5 | 303.1 |

A median value of groundwater quality rating (qi) shown in Table 5.7 suggests a general seasonal impact on the groundwater quality across regions with a relatively good quality observed in the rainy season. This could be attributed to dilution of contaminants while the excessive abstraction of water, increased rate of fluctuation of the water table and eventual oxidation of contaminants complexed in aquifer grains in the dry season could be responsible for the poor quality.

Table 5.8 displays water quality classification as adapted from (Vasanthavigar et al., 2010) as applicable while calculated index values are interpolated and shown as Figures 5.17a with error ( Figure 5.17b). Groundwater quality at regional basis is presented to further understand its spatial variabilities.

Table 5.8: Water quality grading based on Water Quality Index (WQI) value

| WQI Value | Water quality |
|---|---|
| <50 | Excellent |
| 50 - 100 | Good water |
| 100 - 200 | Poor water |
| 200 - 300 | Very poor water |
| >300 | Unsuitable water for drinking |

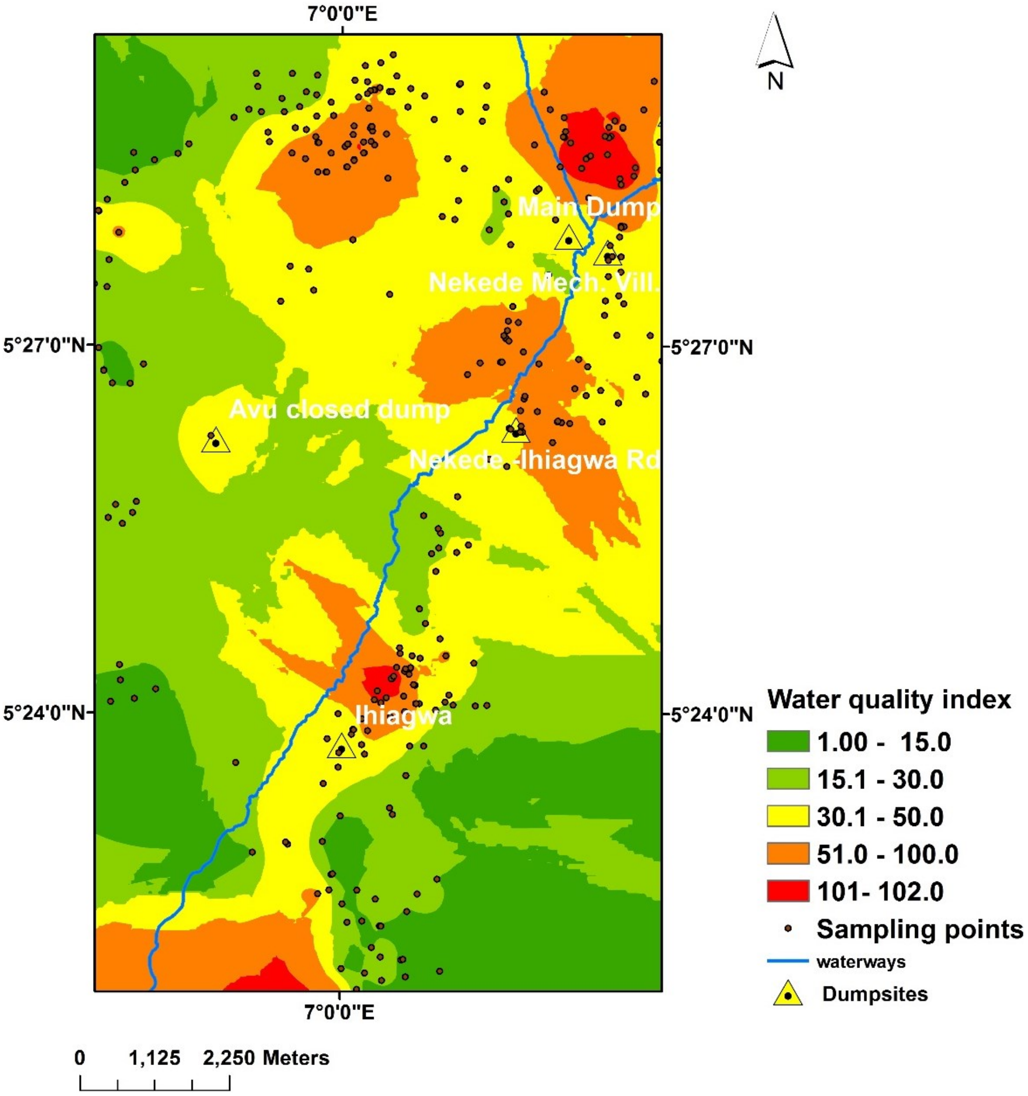


Figure 5.17a: Predicted Owerri groundwater water quality index (WQI), suggestive of poor water quality at some sites near the confluence of the rivers (Nworie and Otamiri) in the city centre and some points along the river flow path in the peri-urban area.

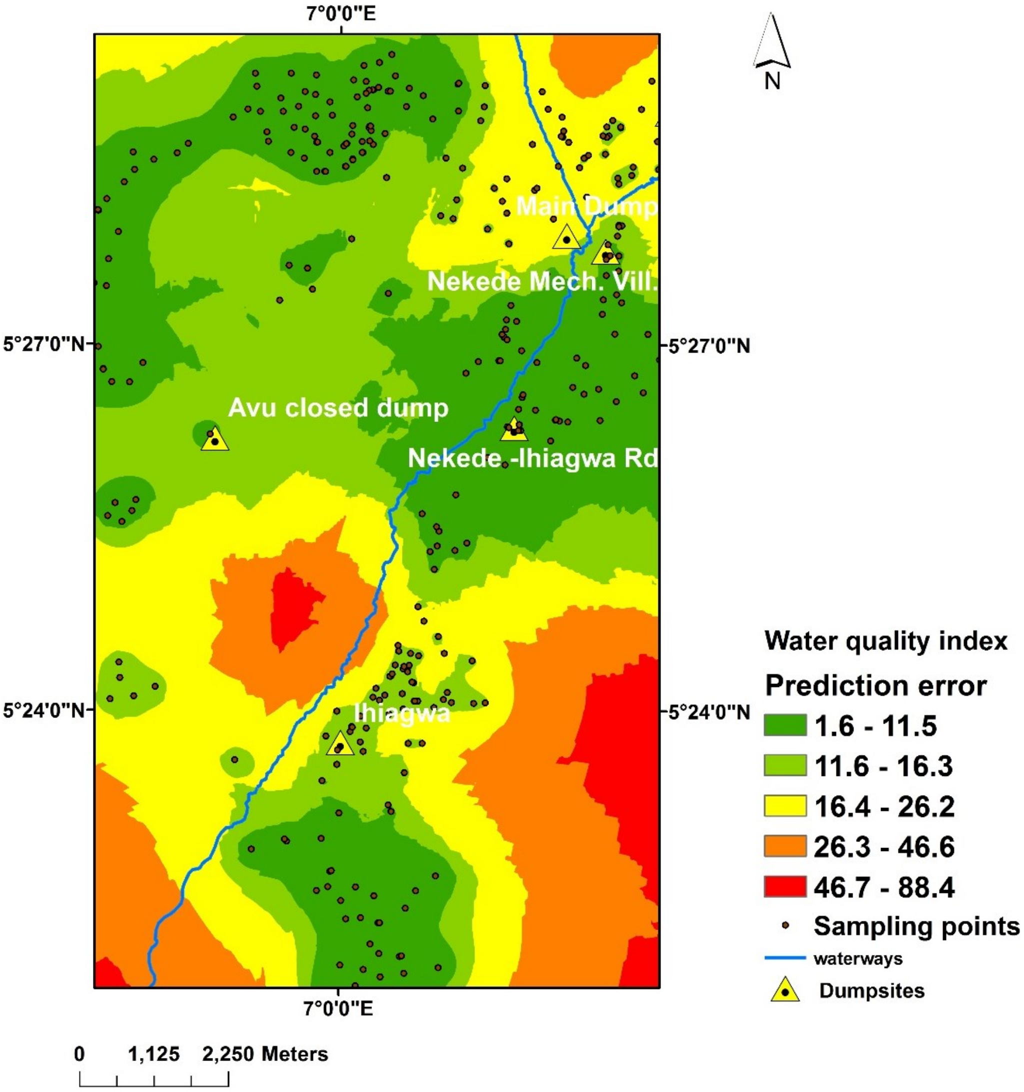


Figure 5.17b: Prediction error of Owerri groundwater water quality index (WQI), inferring good prediction of an index for regions with minimum error.

Following the water quality index generated from the groundwater dataset in the respective regions across sampling seasons (Table 5.8), suitability of the groundwater resource for human consumption varied in the different regions. Whereas excellent to good quality water are found away from congested areas, poor quality water unsuitable for human consumption is found within the high-density area (city centre) near the confluence of the draining rivers.

Water quality in the outskirt regions (Figure 5.17a) are rated good based on the classification (Table 5.8) except for a location along the downgradient of the southeast of peri-urban region. This could be attributed to relatively lesser urban activities and waste generation potentially reduced contaminants' source.

This WQI assessment, therefore, submits that urbanisation and human activities could have a significant adverse effect on the groundwater especially resulting from high population-induced waste generation rate and improper management. Leakages from such dilapidated tanks within unsewered cities harbour pathogenic organisms and leach them into the shallow aquifer (Morris et al., 1994). Here, this report has not only validated previous groundwater vulnerability reports of the study area (Ibe et al.(2003)) but communicates the need for groundwater quality assessment in the context of public exposure and health.

## 5.8 Health risk assessment of human exposure to identified contaminants

This section is informed by the potential health risks posed by the identified contaminants whose concentrations exceeded health-based guidelines at the different locations of the study area. Although, experimental analyses for parameters in this study revealed elevated concentration of contaminants like Pb, Cd, DOC and $NO_3$ in almost all the analysed environmental matrices, this assessment risk assessment shall focus on $NO_3$ and Pb in groundwater and the staple crops, being the principal pathways through which contaminants in the environment can easily enter the study area. Several similar non-cancer risk evaluation methods have been applied in some studies (Storelli, 2008; Chien et al.2002) to assess the exposure pattern of humans to contaminants. While the measured concentration of the target contaminants ($NO_3$ and Pb) were used in this assessment some receptors' characteristics such as body weight, water, and food ingestion rate were assumed from the references and techniques contained in the Guidance on Human Health Preliminary Quantitative Risk Assessment (PQRA) (Canada, 2004).

Nevertheless, such assumptions and characterisation that are applicable to the study area include target receptors or age categories:

A (Adult = Life Expectancy), T (Teen = 12-19 yrs.), C (Child = 5 -11 yrs.), Tod (Toddler = 7months – 4 yrs.), average exposure frequency and time, while Nigeria life expectancy of 47.6 yrs. and body weight for Adult was adopted from (Eke, 2017).

### 5.8.1 Exposure assessment to $NO_3$ in drinking water across the study area

The average daily dosage was calculated to predict the exposure risk of residents to $NO_3$ in groundwater with toxicity reference dosage of 1.6 μg/g/day (Macler, 2007; Calabrese 1992); above which potential health risk occurs using the relation

$$\text{Exposure dose (D)} = (C \times IR \times EF) / BW \qquad (8)$$

Where

D = Exposure dose (μg/g/day)
C = Nitrate concentration (μg/mL)
IR = Ingestion rate of water (L/day)
EF= Exposure factor (EFr x ED) / AT).
BW = Body weight (kg)
EFr = Exposure frequency
ED = Exposure duration (days /year or assumed age)
AT = Averaging time (ED x 365 days/year)

Table 5.9 summaries the exposure dose to nitrate in groundwater across the study area. While the detailed exposure dosage assessment is presented in Appendix 5D. Figure 5.14 presents the average dosage pattern with regards to the recommended acceptable daily intake value of 1.6 μg/g/day (Macler, 2007).

Table 5.9: Descriptive presentation of estimated human exposure dose to nitrate ($NO_3^-$) concentration in groundwater among the different age categories, in comparison with the recommended acceptable daily intake value of 1.6 µg/g/day.

| Age Category | Toxicity reference dose =1.6 µg/g/day | | | |
|---|---|---|---|---|
| | % exceedance | Median | Minimum | Maximum |
| Adult | 4.40 | 2.13 | 1.68 | 3.15 |
| Teen | 2.59 | 1.97 | 1.65 | 2.49 |
| Child | 7.51 | 2.11 | 1.62 | 3.61 |
| Toddler | 18.9 | 2.19 | 1.63 | 5.4 |

Exposure dosage values presented in both table 5.10 and figure 5.18 show Toddlers as most susceptible to the contaminants risks, as interpolated in Figure 5.19a & b

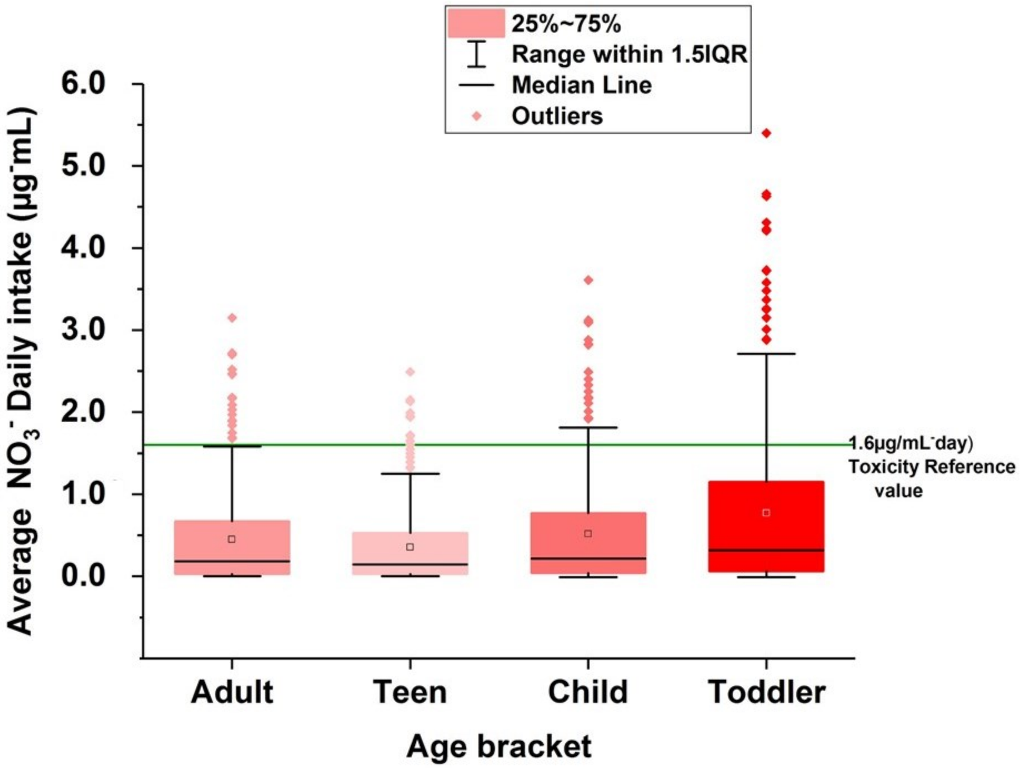


Figure 5.18: Estimated average daily intake of groundwater $NO_3^-$ in drinking water by different age categories, calculated using nitrate concentrations measured in this study, compared to the acceptable daily dosage from the USEPA drinking water standards and health advisories. Boxes are coloured in the order of vulnerability.

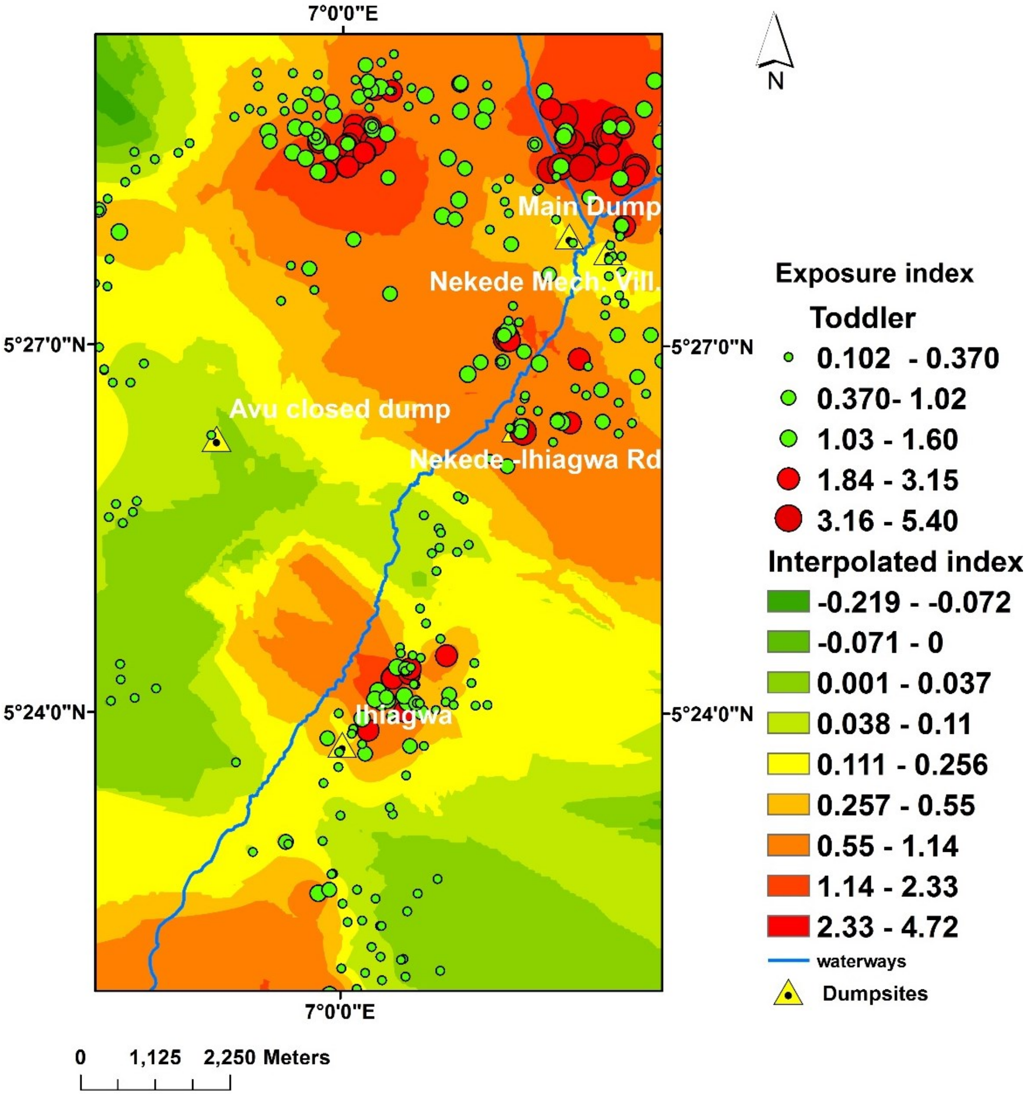


Figure 5.19a: Interpolation map of toddler's exposure dose (ED) to groundwater nitrate across the Owerri study area, indicating higher risk around the city centre where most wells exceed the acceptable daily intake. Graduated symbols are used to indicate the site exposure variability trend with red showing values above the 1.6 µg/g/day, while green indicates safer wells.

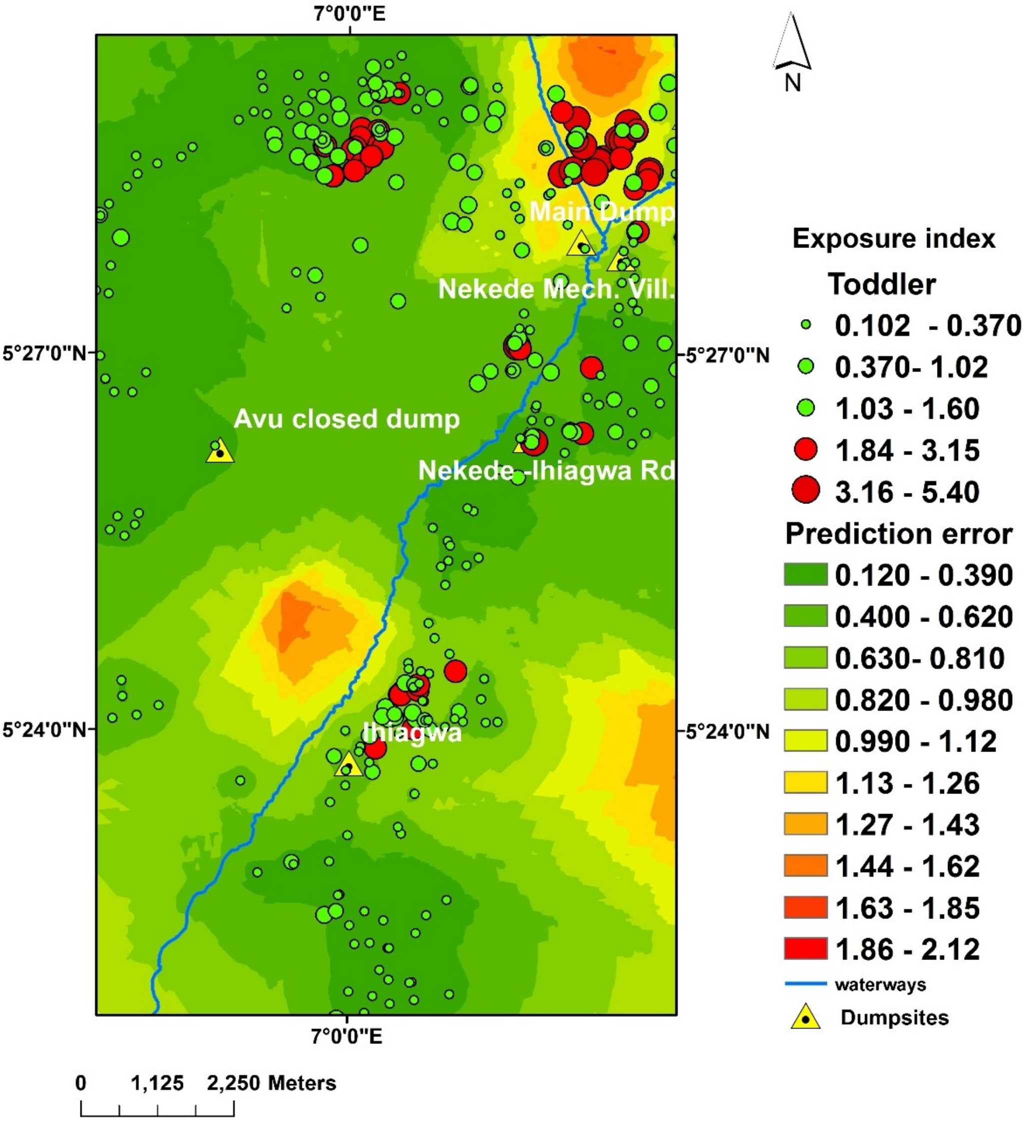


Figure 5.19b: Interpolation error map of toddlers' exposure dose (ED) to groundwater nitrate across the Owerri study area, inferring lesser prediction accuracy for wells in the city centre region.

On the other hand, target hazard quotient (THQ) was used to estimate exposure risks associated with consumption of Pb in each of the plants species pumpkin leaf (*Telfaiara occidentalis*) and cassava tuber (*Manihot esculanta*) based on the ratio of the average daily dosage of an individual to safe reference dose (Yang et al., 2017). Average target hazard quotient (THQ) greater than 1.0 is taken to be a public health threat (Chien et al. 2002) and calculated using the relation

$$THQ = (EFr \times ED \times IR \times C) / (RfDo \times BW \times AT) \times 10^{-3} \qquad (9)$$

Where,

RfDo = Oral reference dose for Pb in food (mg/kg/d) ($3.50 \times 10^{-3}$); which is the maximum dose without substantial risk of harmful health effects.

IR (g/day) while other attributes remain as introduced in equation 8 above.

A summary result of the assessment is presented as Appendix 5E while graphs are presented as Figures 5.20a & b. Although both mean values of the assessments displayed in the graphs suggest higher exposure risk for toddlers, all the age groups are susceptible to health effects from Pb at different levels of exposure.

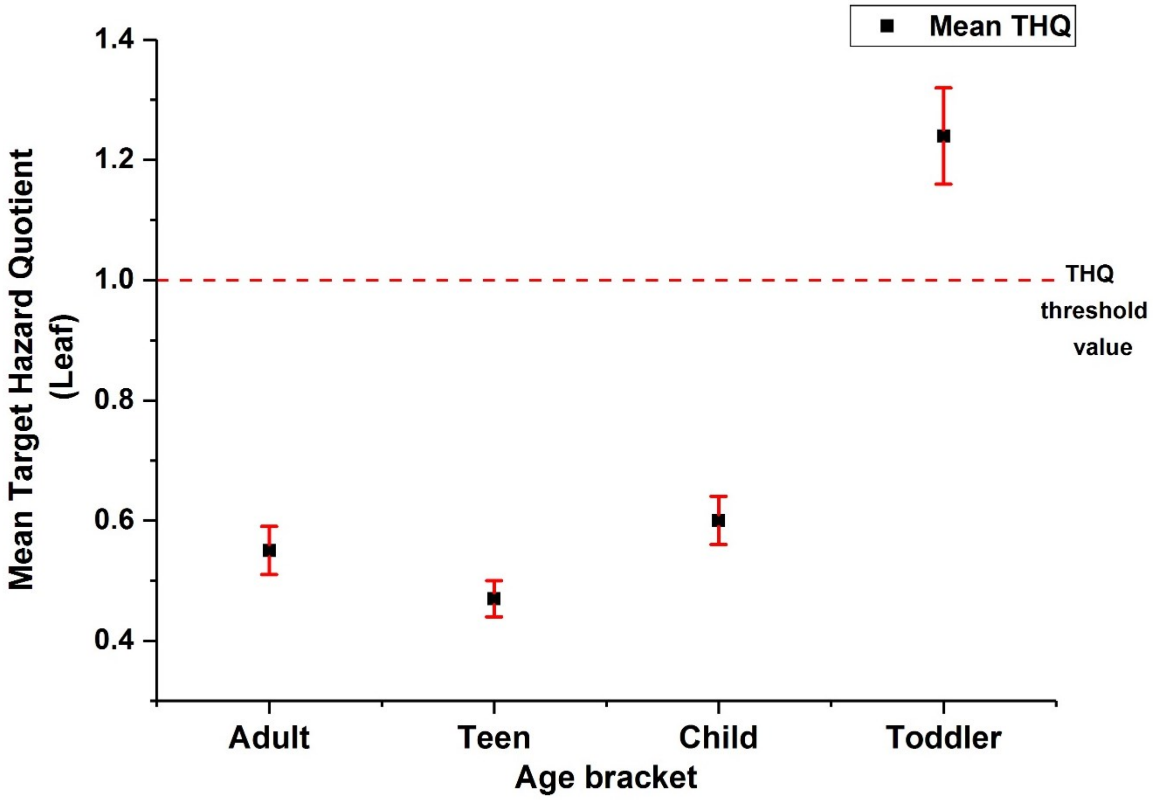


Figure 5.20a: Estimated Target hazard quotient (THQ) of different age groups to Pb contamination in the fluted pumpkin leaf *Telfaira occidentalis* collected from the Owerri study area. Toddler age bracket exceed the target hazard quotient of 1.0, suggesting potential health risk to those groups due to exposure to Pb. The mean THQ is represented with the black box and while red bar symbolises standard error.

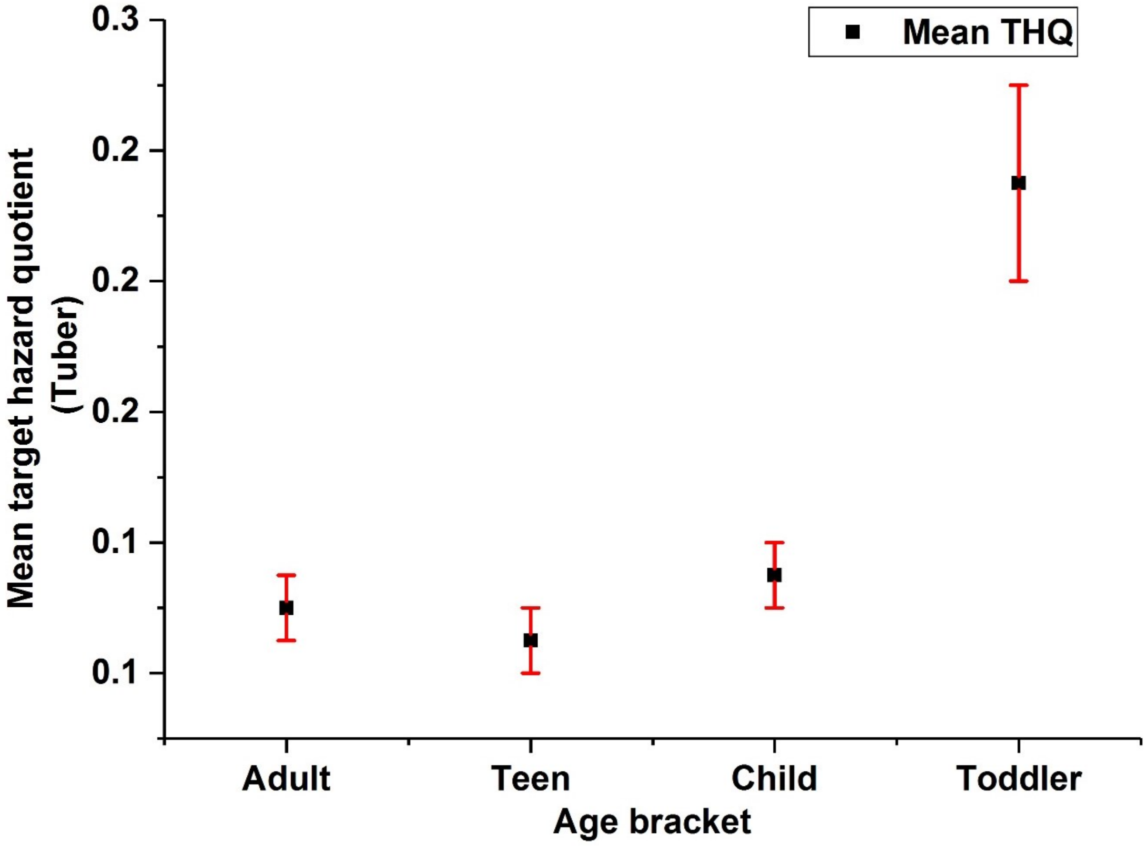


Figure 5.20b: Estimated mean target hazard quotient (THQ) of different age groups to Pb contamination in the cassava tuber *Manihot esculanta* collected from the Owerri study area. Although, mean THQ of all age brackets fall below threshold value of 1.0 (above the axis scale), 51.6% of Pb concentrations in cassava tuber (*Manihot occidentalis*) exceed the 0.1 µg/g FAO health-based maximum concnetration value, suggesting potential health risk to those groups due to exposure to Pb. The mean THQ is represented with the black box while red bar symbolises standard error.

## 5.9 Public health Implications of exposure to identified contaminants

### 5.9.1 Exposure to high nitrate concentration above the Maximum Concentration Limit (MCL) of 50 µg/mL

In view of the potential health challenges associated with high nitrate values in drinking water, the Nigeria Standard for Drinking Water Quality, alongside various global health regulatory agencies like WHO,EU Commission and USEPA placed 50 µg/mL as the maximum concentration limit of nitrate in drinking water (Ward, 2005;and therein). These standards and guidelines have been established to protect humans from potential health challenges that have been associated with elevated nitrate in drinking water, especially the infantile blue baby syndrome otherwise known as the Methemoglobinemia.

Methemoglobinemia is formed from through the conversion of nitrate in drinking water to nitrite by endogenous bacteria which then oxidises the oxygen-transporting ferrous ($Fe^{2+}$) iron to the oxygen – inhibiting ferric ($Fe^{3+}$) iron in the haemoglobin and can result in adverse health conditions such as cyanosis and death (Guay, 2009; Kross et al., 1992) (See Chapter 2 Section 2.7.1). Clinical findings reported by Kross et al.(1992) reveals the symptomatic stages of this health condition as shown in Table 5.10.

Table 5.10: Clinical signs and complications of the Methemoglobinemia compound at various percentage levels in human body adapted from (Fewtrell, 2004; Kross et al., 1992)

| Methemoglobinemia concentration (%) | Clinical Signs |
|---|---|
| 0 - 10 | Normal |
| 10 - 20 | Central cyanosis of limbs/trunk |
| 20 - 45 | Central nervous system depression (a headache, dizziness, fatigue, lethargy), dyspnea |
| 45 - 55 | Coma, arrhythmias, shock, convulsions. |
| >60 | High risk of mortality |

Results of groundwater analyses which have shown nitrate burden of wells in the order City Centre > Urban agglomeration with respect to % exceedance to the MCL of regulatory agencies, could, therefore, infer imminent cases of Methemoglobinemia; within the City Centre and Sub- urban , while peri-urban with just a sampling point above MCL seems relatively safer. Such sampling points are thus displayed on street map of Owerri (figure 5.21a &b).

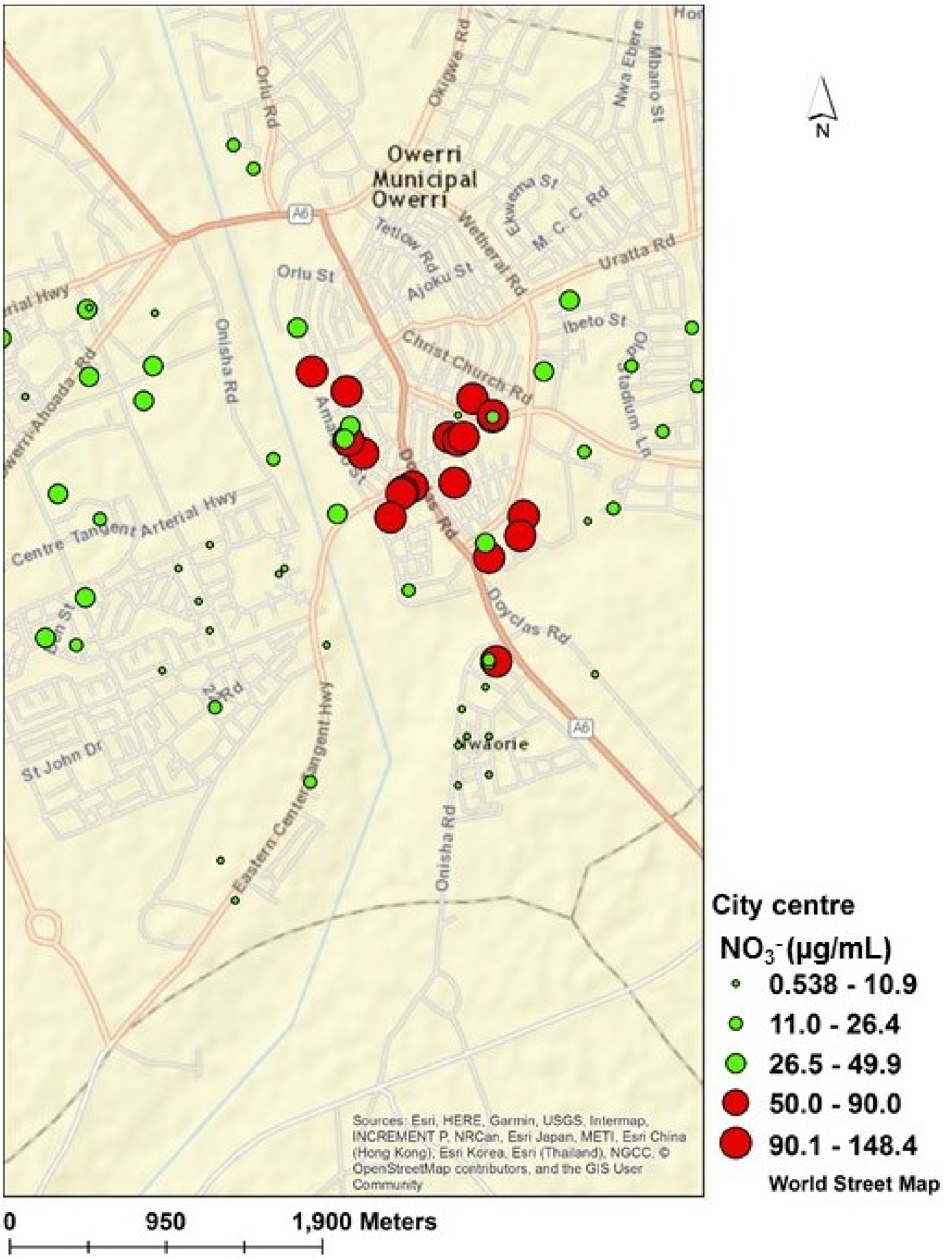
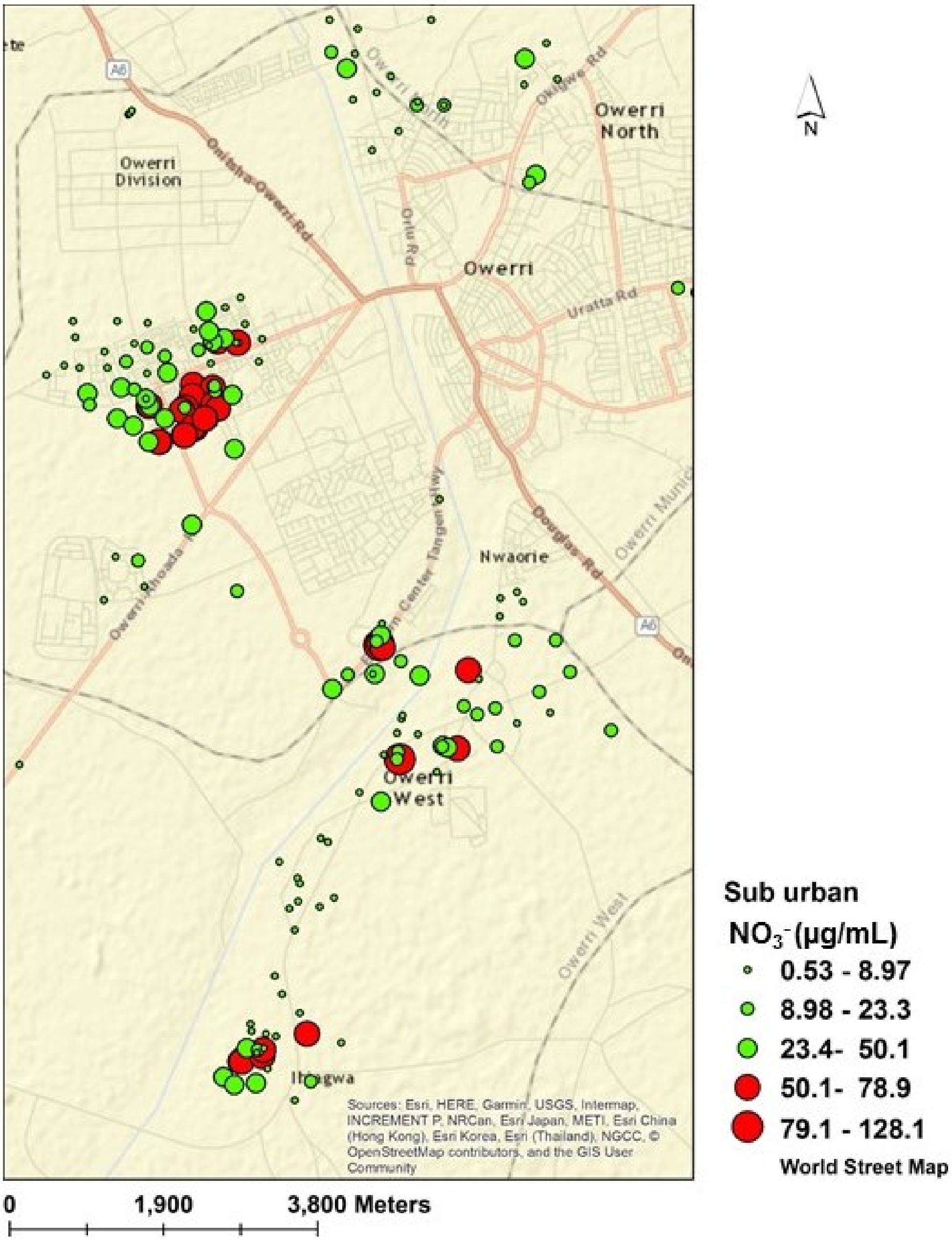


Figure 5.21a: Spatial distribution of groundwater nitrate within Owerri city centre, with red symbols representing concentrations above the Maximum Concentration Limit (MCL) stipulated by the Nigeria Standard for Drinking water Quality of 50 µg/mL. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)



Sources: Esri, HERE, Garmin, USGS, Intermap, INCREMENT P, NRCan, Esri Japan, METI, Esri China (Hong Kong), Esri Korea, Esri (Thailand), NGCC, © OpenStreetMap contributors, and the GIS User Community

Figure 5.21b: Spatial distribution of groundwater nitrate within the Sub-urban region, with red symbols representing concentrations above the Maximum Concentration Limit (MCL) stipulated by the Nigeria Standard for Drinking water Quality of 50 µg/mL. (Source of base map: Esri, Digital Globe, GeoEye, Earthstar, Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)

Infants less than six months are described as most susceptible to this health problem because their bodies have not developed sufficient enzyme-reduction mechanism that could allow a spontaneous conversion of the methemoglobinemia to hemoglobin for excretion as it is in adults (Burt et al., 1993).

Although no survey of infants for Methemoglobinemia within these vulnerable zones was carried out as it is outside the scope of this study, the elevated nitrate measured in wells in this study could imply that most infants within the regions are fed with water containing nitrate above the 50 µg/mL threshold limit. Besides, no drinking water monitoring and treatment mechanism was put in place by government health agencies hence; it is possible that most residents consume water taken directly from the well without any form of treatment. This inference was drawn from informal interviews conducted during the sampling periods, where approximately 45% of well owners admitted occasional disinfection by chlorination as the only treatment technique with no expertise advice hence, often not proportionately applied.

High DOC in groundwater can harbour pathogenic organisms, especially during rain (Berk et al., 2006). The reaction of chlorine with humic substances characterised with high aromatic carbon contents and specific ultraviolet absorbance could lead to the formation of disinfection by-products (Singer (1999)) among which is the carcinogenic trihalomethane (THM) (Koivusalo et al., 1997). Although, assessment of the occurrence of cancer-related cases at the DOC hotspot areas is outside the scope of this study, epidemiologic studies have established chlorinated drinking water and cancer of the gastrointestinal and urinary tract (Koivusalo et al.,1997 and therein).

### 5.9.2 Exposure to metals in food plants and groundwater and the associated health risks

Elevated Pb in the human system may cause a series of adverse health conditions which include neurological disorder, especially among children (Lei et al., 2016). The result of Pb analyses carried out on the various environmental matrices, especially in the two staple food crops with which an intense high-dose exposure has been predicted could result in Pb poisoning with severe symptoms like nervous disorder, coma, and death (Piomelli, 2002). These symptoms may often be misdiagnosed unless in-depth studies like this are carried out to predict such possibilities for further epidemiological studies.

Target human organs most affected by Pb poisoning include the cardiovascular, gastrointestinal and immune system; among others (Piomelli, 2002). The assessments have shown that children, especially toddlers are more exposed to drinking water contaminants like Pb because they relatively consume more water than an adult, due to their body weight, hence, exposed more to Pb contamination.

# CHAPTER 6

# CONCLUSIONS AND RECOMMENDATIONS

## 6.0 Introduction

This chapter summarises the findings of this PhD project and offers recommendations to Nigerian government and regulatory agencies, as well as other stakeholders, on ways to minimise human exposure to contaminants identified within Owerri groundwater and soils. Some recommendations will require a critical review of environmental policies and standards and attitudinal/behavioural changes within the local population. Follow-on epidemiological studies also will be necessary to forestall possible public health issues. Such studies, e.g. targeting vulnerable children and pregnant women, should reveal exposure risks associated with unsustainable management of both human waste and groundwater resources. Future collaborative efforts by government authorities and stakeholders can foster the realisation of a sustainable Owerri environment, where public health is guaranteed for human wellbeing.

## 6.1 Overview of the key findings

This study applied both field and laboratory techniques in the geospatial assessment of contaminant distributions in different environmental samples that result from urbanisation and anthropogenic activities, as well as has identified potential toxicity to exposed individuals. Research outcomes reveal that both natural processes ( variability of depth to water table and season) and anthropogenic activities contributed to the generation and distribution of different contaminants across different regions in Owerri. Among the environmental parameters analysed in this study (see Chapter 3), only four parameters (nitrate - $NO_3^-$, dissolved organic carbon - DOC, Pb and Cd) are identified as posing public health risks, due to high concentrations above the maximum concentration limit (MCL) specified by relevant Nigerian regulatory agencies. Following findings in this study that depict widespread distributions of elevated $NO_3^-$ in groundwaters, and Pb in two staple food crops (i.e. *Manihot esculanta and Telfaira occidentalis*), in addition to inferences drawn from inter-relationships among parameters, this thesis concludes with the following key outcomes:

- Owerri groundwater nitrate concentrations showed consistency with depth to water table, decreasing with increased depth to water table. This pattern indicates higher vulnerability of groundwater in shallow boreholes to surface contaminants and potential health risks to end users within such regions.

- Quartz - dominated soil minerology in Owerri likely enhances infiltration of contaminants into groundwater due to its weak adsorption capacity. This behaviour is demonstrated by elevated groundwater dissolved organic carbon (DOC) in the rainy season, which is suggestive of high rate of organic-rich runoff infiltrating through the porous soil profile to the groundwater. A moderate correlation found between the percentage soil organic carbon and DOC in groundwater supports this assertion (see Chapter 5, Section 5.5.2).

- Indiscriminate disposal of solid waste at open dumpsites located within shallow depth to water table regions in Owerri could be responsible for elevated $NH_4^+$ and subsequent oxidation to $NO_3^-$ in groundwater of wells located within 1000m from dumpsites (see Chapter 5, Section 5.4.4).

- Proliferation of groundwater boreholes (due to increasing population) and excessive abstraction of the groundwater during the dry season may have lowered the water table, and increased nitrification of the groundwater resources This simply implies that the increasing rate of pumping following high demand for groundwater draws in oxygen that led to the sequential oxidation of ammonium ($NH_4^+$) to nitrite ($NO_2^-$) and then to nitrate ($NO_3^-$) in groundwater.

- Higher population density is the larger source of nitrate ($NO_3^-$) in the Owerri groundwater as evidenced by higher $NO_3^-$ concentration in the much urbanised regions.

- Septic tank pollution of groundwater was more evident in the shallow water table regions than in the regions with a deeper water table.This could be attributed to variabilities in the different oxidising and reducing regions within the Owerri groundwater aquifer.(see Chapter 5,Section 5.4.3).

- Water quality index (WQI) asssessment carried out by this study showed consistency with previous vulnerability studies (i.e. designated vulnerable regions align with lowest water quality determined from chemical measurements).

- Groundwater lead (Pb) concentrations exceeded Nigeria Standard for Drinking Water Quality limit of 10ng/mL in 1.6% of sampled wells. This could be attributed to point sources such as lead-containing pipes or plumbing materials at various homes, building wall paints especially within the sub-urban regions, unhygienic handling and disposal of used batteries, as well as the incessant use of fossil fuels at various homes for electric power generation.

- Only one borehole, situated in the commercial area of Owerri city centre, recorded a cadmium (Cd) concentration (6.0 ng/mL) above the maximum concentration limit of 5.0 ng/mL stipulated by the Nigeria Standard for Drinking Water Quality (NSDWQ) and the World Health Organisation (WHO). The elevated cadmium concentration could be attributed to its proximity to a septic tank separated by a distance of 11.1m.

- Unabated migration of people to Owerri city centre and the ultimate high population density of the area is reflected in the water quality index assessment undertaken by this study. Overall water quality index rating shows improvement (i.e. better water quality) from city centre to sub-urban to peri-urban regions, reflecting population density patterns (as observed during the field trips) implying anthropogenic influence on groundwater quality.

- Assessment of human exposure to elevated $NO_3^-$ in groundwater-derived drinking water indicates the following trend of susceptibility to adverse health conditions such as the Methemoglobinemia (mainly Toddlers), diabetes and thyroid infections: Toddler (7 months to 4 years) > Child (5 to 11 years) > Adult (20 years and above) > Teen (12 to 19 years). This human exposure assessment was determined on the degree to which each of the age categories exceeded acceptable $NO_3^-$ daily intake of 1.67 µg/g/day.

- The groundwater nitrate human exposure assessment portends imminent cases of various hazardous health conditions that are associated with consumption of high $NO_3^-$ concentration drinking water, especially Methemoglobinemia (which is often refered to as blue baby syndrome).
- Pb also is identified as a critical contaminant in both soil and the staple food plants (*Telfaira occidentalis* and *Manihot esculanta*), albeit with no correlation with soil Pb concentrations. The absence of such a relationship suggests direct adsorption of the Pb contaminant onto plants from vehicular and private power-generating plants emission.
- Only 0.9% of soil Pb concentrations exceed the Nigeria Department of Petroleum Resources (DPR) target soil value of 85 µg/g. Whereas 99.8% of Pb concentrations in pumpkin leaf (*Telfaiara occidentalis*) measured above threshold limits of 0.3 µg/g, 51.6% of Pb concentrations in cassava tuber (*Manihot occidentalis*) exceed threshold of 0.1µg/g all stipulated by the Food and Agricultural Organisation (FAO).
- Elevated Pb concentrations in the two staple food plants could be attributed to the prevalent combustion of leaded fuel within Owerri and adsorption of Pb emissions directly by the plants. This conclusion is based on the fact that both plants species were sampled from urban residential gardens exposed to combustion emission from vehicles and the frequently used petrol and diesel engine power generating plants observed in almost every home visited.
- Following estimation of a Pb contamination hazard quotient for different age groups, teen, child and toddler classifications all exceed the target hazard quotient of 1.0 for Pb in cassava tuber (*Manihot esculanta*), suggesting highest exposure risk and imminent health hazard among those individuals within those age brackets from across the Owerri study area as a result of ingestion of this food product.
- Similar Pb contamination hazard assessment carried out for pumpkin leaf (*Telfaira occidentalis*) reveals that only toddler and child age classifications exceed the target hazard quotient of 1.0, implying potential health risk among these two groups across the Owerri study area resulting from consumption of this plant food.

- Exposure of individuals within the toddlers and child age classifications to Pb contaminated food plants could lead to reduction of their intelligence quotient efficiency and increased attention-related behavioural problems, according to the report issued by the United States Environmental Protection Agency (2015).

## 6.2 Recommendations

Based on the identified environmental pollution problems and human exposure risks outlined above, this study makes the following recommendations to relevant government agencies such as the Nigeria Federal Ministry of Water Resources, Federal Ministry of Environment and the Imo State Ministry of Public Utilities, as a way of ensuring proper and sustainable utilisation of uncontaminated groundwater resources and protection of human exposure to hazardous chemicals through ingestion of contaminated food and water. These recommendations would go a long way to preventing continous and long-term exposure to contaminants by the public and forestall development of determinental health conditions within the Owerri population.

### 6.2.1 Review of ImoState environmental policies and framework, particularly addressing groundwater quality and management

There is need for adequate review, and strict implementation, of a policy framework that would regulate the siting and ownership of groundwater boreholes across the study area, in order to ensure access to clean and safe water supply by all Owerri residents. The proper and safest way to achieve this improvement would be for Imo State government to take full responsibility for managing groundwater abstraction and distribution across the different regions of the area, via the Imo State Water Board,which is under the supervision of the Ministry of Public Utilities, Imo State. Due to the dilapidated water distribution facilities in Imo State, increasing demand for water and subsequent pressure on the groundwater resources, it is proposed that the Imo State government introduce what is widely known as abstraction licences through implementation of appropriate legislation. This form of regulation has been used in many advanced societies such as the United Kingdom (Fox and Walker, 2002), to ensure an appropriate regulatory framework that will guarantee siting of groundwater wells at locations that are not exposed to potential contaminant sources and help in ensuring control of groundwater volume extracted on a daily basis (Fox and Walker, 2002; Bough, 2000). Such regulations shall require proper sensitisation of the public on the proposed well locations in the form media advertisements prior to approval by the relevant government agency.

Putting such regulatory mechanisms in place in Owerri would not only help in controlling the indiscriminate drilling of groundwater boreholes within vulnerable regions, but would also ensure more efficient and safer utilisation of the critically important groundwater resource. Furthermore, the regulations would effectively control the proximity of wells to septic tanks and dumpsites, since there would be mandatory site assessment prior to any well installation. Above all, the regulations would control all land-surface activities where the underlying groundwater would be susceptible to contamination. This approach would not only avert the imminent health risk associated with ingestion of contaminated water (see Chapter 5, section 5.9) but will also place Imo Sate and Owerri on the path to achieving the United Nations sustainable development goal of ensuring sustainable use of water resources in 2030 (See Chapter 2,Section 2 2).

### 6.2.2 Development and implementation of an Owerri sustainable urban management strategy

Given the various environmental menaces that are generated by uncontrollable migration and development of new residential areas in Owerri, with utmost disregard for the provisions of the Environmental Impact Assessment (EIA) decree No 86 (1992) which mandates proponents to consider environmental impact assessment prior to construction (Echefu and Akpofure, 2002), there is an urgent need to develop a better urban management strategy for the Owerri area.

This study recommends implementation of an Integrated Vulnerable Zone Management (IVZM) framework under the supervision of Imo Sate Ministry of Environment in line with the 1996 United Nations Habitat II call for sustainable provision of human settlements (See Chapter 2 section 2.2). Such a strategy can be achieved through the following means:

- Adequate sensitisation of residents through the use of electronic media,workshops, religious and town hall gatherings on the need for cooperation in preventing human exposure to hazardous chemicals through consumption of contaminanted food and drinking water.
- Proper review and utilisation of data generated by vulnerability studies and modelling, with a view to identifying and allocating residential estates only for areas considered safe for habitation with regards to exposure to contaminants.Furthermore, urban structures such as petrol stations and gas plants (with underground storage tanks), solid waste dumpsites, agricultural activities (poultry) and abatoirs within areas underlain by very permeable sandy soils should be relocated to forestall further leaching of contaminants to groundwater.
- Installation of groundwater monitoring boreholes at strategic locations across the $NO_3^-$ sensitve zones, for quarterly measurement and assessment of contaminants within groundwater.
- Specifying zones for urban farming through legislations as a pre-emptive measure to discourage urban farming within residential housing units, while promoting sustainable agriculture within pristine environments, as a way of reducing metal contamination of food plants through urban emissions.

Similar initiatives, that are aimed at protecting groundwater drinking water supplies from $NO_3^-$ contamination, including regulating farming activities that threaten groundwater quality, have been in place in England and Wales through the EC Drinking Water Directive (80/778/EEC) (Lake et al., 2003).

### 6.2.3 Establishment of a food and drinking water inspectorate in Nigeria

Considering the fact that human ill-health can result from ingestion of toxic chemicals through food and drinking water, there is an urgent need for the establishment of an inspectorate with responsibilitiy to sampling and measuring food products periodically in order to update residents on practices that could endanger their health status via contaminated food and water. Although related agencies currently exist, such as the National Agency for Food and Drug Administration and Control (NAFDAC; established by amended Decree No.19, 1999) under the Federal

Ministry of Health to regulate and control manufacture and import of regulated products including packaged food and water, average Nigerians remain poorly informed on how to prevent food- and water-related diseases (Idowu et al., 2006).

This recommended inspectorate would particularly focus on aggressive sensitisation of citizens on several water-treatment options, local food production and preservation techniques.

### 6.2.4 In-depth epidemiological assessment of Owerri resident responses to elevated $NO_3^-$ and Pb ingestion, via contaminated groundwater-sourced drinking water and staple plant foods

Following this study's undertaking of exposure and hazard quotient assessments which suggest high exposure risk of residents to $NO_3^-$ and Pb contaminants in drinking water and food plants, respectively there is an urgent need for completion of epidemiological studies across Owerri. This study therefore makes the following recommendations:

- All government hospitals and clinics in Owerri should review medical reports of residents, especially infants, within the identified high vulnerability regions, with a view to assessing any correlation between consumption of drinking water and possible cases of Methemoglobinemia and other diseases such as diabetes and Thyroid infections associated with elevated $NO_3^-$ in groundwater.
- An assessment of Pb concentrations in human blood samples is required for all age groups across the study area, due to the elevated Pb concentrations found in both pumpkin leaf (*Telfaira occidentalis*) and cassava tuber (*Manihot esculanta*) crops. This assessment becomes expedient considering the fact that an average resident in the Owerri study.area ingests these food plants at least once every day, thereby increasing the risk of Pb accumulation and toxicity in sensitive human organs such as the kidney. Other health assessments can involve a less invasive technique of sampling of scalp hair and/ or finger nail cuttings as way of evaluating human exposure to high environmental lead concentrations.

- Application of Pb-isotope ratios for all environmental samples to undertake source apportionment of the Pb that is contaminating the environment.

- Microbiological assessment of pathogenic organisms associated with faecal contamination of groundwater, as a way of substantiating the finding on septic tank contamination of groundwater, since limited time and fund constrained such analyses in this study.

  - The wider implications of the Owerri case study can be summarised by the following points:

    (a) The application of redox chemistry in the study of contaminant behaviour and variability, especially in African urban groundwater settings where major sources of groundwater contamination are in close proximity to wells and boreholes, provides useful insight for groundwater governance. This technique becomes particularly important in the overall appraisal of contaminant heterogeneity along the groundwater flow path, especially concerning risks to down-gradient groundwater resources and in weighing the probability of natural attenuation processes as remediation options in a contaminated aquifer. The novel approach of this study mainly lies on the use of domestic wells for high density monitoring network of redox trend, which revealed factors that could influence contaminants distribution and human exposure pattern.

    (b) Besides calibrating the widely used DRASTIC vulnerability index technique, applied in previous studies using nitrate as a proxy for vulnerability, this Owerri study further suggests that its application could be improved by considering more specific information on those soil characteristics that affect rainwater infiltration in urban areas, as well as the influence of climatic seasonality on contaminant transport. Such soil attributes and functions such as organic matter content (contaminant sorption and desorption), carbon and nitrogen contents (decompositions, carbon and nutrient cycles) are often neglected in vulnerability studies while focusing on soil type.

## 6.3 Overall remarks and further studies

Although this study has not exhaustively assessed the different pathways through which humans residing in the Owerri study area could be exposed to identified environmental contaminants in the environment, findings and recommendations made from this study could enhance environmental quality and public health, if adopted by both the governments of Imo State and Nigeria. This report should provoke policy reviews and focus Imo State Government's attention on the need for a healthy society, which is key to environmental and economic development. A study on the relationship between economic growth and human health states that the latter plays a statistically significant role in the gross domestic output of any nation (Bloom et al., 2004). Significant expenditure on health care, by governments at different levels in Nigeria and international donor agencies, without first undertaking pre-emptive measures in addressing causative human and natural factors that are jeopardising public health, could lead to socioeconmic and environmental setback within a society.

The lack of provision of potable drinking water for human consumption by the Imo State Government, at the expense of industrialisation, education and politics in Nigeria, calls for redress. An inclusive forum of all stakeholders in water resource management across the respective region becomes necessary to review the health and socio-economic impacts of poor drinking water quality, with a view to identifying appropriate remedies since both the Imo State and Nigerian Governments have failed to intervene. A primary challenge of such a forum might include cost benefit analysis of the drilling and maintenance of private wells on one hand and contributing to instal and maintain standard wells at regional or state level within areas that are less vulnerable to contamination. Furthermore, the need for attidudinal change in terms of both solid and liquid waste management across the Owerri study is advocated in this study to prevent further degradation of the groundwater quality by the indiscriminate disposal of solid waste.

Prompt and efficient consideration of this study’s findings, as well as implementation of those recommendations made, is therefore apt, for a sustainable environment and public health.

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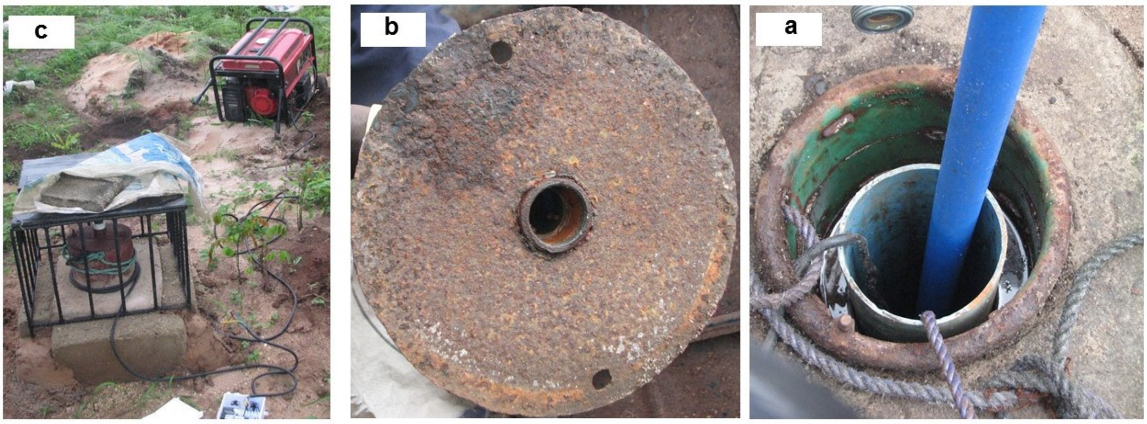
## APPENDICES

Appendix 3A Typical samples collection point for in-situ measurements carried out quickly to minimised samples exposure to air and possible alteration of chemical composition.



Appendix 3B: Casing materials and environmental conditions of most sampled wells in the study area. (a) Steel wellhead protecting inner PVC casing pipes of about 5 inches in diameter from external mechanical damages and floodwater that could flow into the borehole during rainfalls in areas prone to flood (b) Wellhead corroded by floodwater due to poor construction and placement hence serve as conduit for influx of contaminated floodwater into the groundwater. (c) Elevated wellhead systematically filled with cement grouts to prevent flood-induced damage and subsequent contamination.

GOVERNMENT OF IMO STATE OF NIGERIA

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OFFICE OF THE HONOURABLE COMMISSIONER
MINISTRY OF PETROLEUM & ENVIRONMENT
P.M.B. 1299
OWERRI, IMO STATE
Date: 4th May, 2015

**Dr. Leon Clarke**
Manchester Metropolitan University

**LETTER OF ACCEPTANCE FOR COLLABORATION**
**RE: JOSEPH IKECHUKWU NWACHUKWU (STUDENT NO: 13161504)**

I wish to certify that the Laboratory Services and Environmental Research Department of the Ministry of Petroleum and Environment, Imo State, Nigeria is willing and ready to offer Laboratory assistance in the area of BOD and COD determination, pH and Conductivity measurement, and any other analytical procedure required, in respect of **Mr. Joseph Ikechukwu Nwachukwu's** Research Project.

Do accept the assurances of my highest regards.

**T. C. AKUJOBI**
**DIRECTOR/HEAD OF DEPARTMENT.**

Appendix 3C: Letter of collaboration from the Imo State-owned environmental laboratory which supported the research project during the two-season's sampling campaign.

Appendix 3D Palin test experiment during the dry season campaign displaying initial (nitrate powder + nitrates tablet + sample) solution (i) to reddish dye and green-blue colourations for nitrate (ii) and ammonium (iii) solution colour on settlement prior to insertion into the portable Palintest (model 7500) instrument 44(iv) and measurement on solution colour intensity.

Appendix 4A: CRM summary for ions in groundwater analysed by ion chromatography. Expected values refer to known concentrations of each parameter in the CRM used to assess the accuracy of measured values.

| Sampling Phase | Date of analyses | ID | $Fl^-$ | $Cl^-$ | $SO_4$ | $NO_3^-$ |
|---|---|---|---|---|---|---|
| | | Expected values (µg/mL) | 0.27 | 33.1 | 82.8 | 28.2 |
| | | Mean value | 0.220 | 31.3 | 77.9 | 27.1 |
| | | SD | 0.030 | 1.94 | 2.51 | 0.999 |
| | | %RSD | 13.8 | 6.20 | 3.23 | 3.68 |
| | | | | | | |
| | | Accuracy | 80.6 | 94.7 | 96.2 | 96.2 |
| | | | | | | |
| First | 09/09/16 | Mean | 0.225 | 32.3 | 79.9 | 27.7 |
| | | SD | 0.020 | 0.580 | 1.38 | 0.537 |
| | | %RSD | 8.76 | 1.80 | 1.72 | 1.94 |
| First | 16/09/16 | Mean | 0.194 | 30.2 | 75.2 | 25.8 |
| | | SD | 0.013 | 0.573 | 1.74 | 0.499 |
| | | %RSD | 6.89 | 1.90 | 2.32 | 1.931 |
| First | 23/09/16 | Mean | 0.201 | 33.0 | 76.8 | 27.6 |
| | | SD | 0.017 | 1.66 | 1.59 | 0.542 |
| | | %RSD | 8.33 | 5.03 | 2.07 | 1.964 |
| First | 30/09/16 | Mean | 0.253 | 32.2 | 78.0 | 28.0 |
| | | SD | 0.017 | 0.416 | 1.00 | 1.25 |
| | | %RSD | 6.90 | 1.294 | 1.29 | 4.46 |
| Second | 17/02/17 | Mean | 0.266 | 28.0 | 80.9 | 26.8 |
| | | SD | 0.006 | 0.211 | 0.804 | 0.211 |
| | | %RSD | 2.33 | 0.753 | 0.995 | 0.786 |

Appendix 4B: Limits of detection (LOD) and quantification (LOQ) for groundwater metals, using the specified techniques.

| **Analyte** | **Technique** | **LOD (ng/ml)** | **LOQ (ng/ml)** |
|---|---|---|---|
| **$^{51}$V** | ICP-MS | 0.007 | 0.022 |
| **$^{52}$Cr** | ICP-MS | 0.030 | 0.097 |
| **$^{55}$Mn** | ICP-MS | 0.068 | 0.212 |
| **$^{57}$Fe** | ICP-MS | 2.22 | 6.77 |
| **$^{59}$Co** | ICP-MS | 0.005 | 0.016 |
| **$^{60}$Ni** | ICP-MS | 5.12 | 15.4 |
| **$^{63}$Cu** | ICP-MS | 1.64 | 4.92 |
| **$^{66}$Zn** | ICP-MS | 5.81 | 19.6 |
| **$^{75}$As** | ICP-MS | 0.021 | 0.067 |
| **$^{77}$Se** | ICP-MS | 0.190 | 0.615 |
| **$^{111}$Cd** | ICP-MS | 0.019 | 0.059 |
| **$^{137}$Ba** | ICP-MS | 11.1 | 33.9 |
| **$^{208}$Pb** | ICP-MS | 0.046 | 0.217 |
| | | | |
| **Analyte** | Technique | LOD (µg/ml) | LOQ (µg/ml) |
| **K (769.8nm)** | ICP-OES | 0.020 | 0.067 |
| **Mg (285.2nm)** | ICP-OES | 0.014 | 0.048 |
| **Al (167.0nm)** | ICP-OES | 0.002 | 0.005 |

Appendix 4C: Result of the Certified Reference Materials used during analyses of soil analyses using the ICP-MS.

| DATE | ID | 51V | 52Cr | 55Mn | 57Fe | 57Co | 60Ni | 63Cu | 75As | 111 Cd | 137 Ba | 208 Pb |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | | |
| | **EXPECTED** | **10.0** | **2.00** | **10.0** | **20.0** | **2.00** | **10.0** | **20.0** | **10.0** | **0.500** | **50.0** | **5.00** |
| | | | | | | | | | | | | |
| **ALL** | **MEAN** | 10.3 | 2.05 | 10.2 | 22.1 | 2.03 | 10.3 | 19.8 | 10.3 | 0.548 | 49.8 | 4.68 |
| | **SD** | 0.705 | 0.148 | 0.776 | 3.28 | 0.140 | 0.860 | 1.62 | 0.945 | 0.074 | 4.88 | 0.299 |
| | **%RSD** | 6.85 | 7.24 | 7.63 | 14.8 | 6.91 | 8.33 | 8.16 | 9.21 | 13.4 | 9.79 | 6.39 |
| | | | | | | | | | | | | |
| | **Accuracy** | **102.9** | **102.4** | **101.8** | **110.7** | **101.5** | **103.2** | **99.2** | **102.5** | **109.7** | **99.6** | **93.7** |
| | | | | | | | | | | | | |
| 22/03/2017 | MEAN | 10.5 | 2.13 | 10.3 | 31 | 2.04 | 10.3 | 20.5 | 9.99 | 0.518 | 52.0 | 4.75 |
| | SD | 0.050 | 0.012 | 0.079 | 18.5 | 0.029 | 0.036 | 0.163 | 0.091 | 0.023 | 0.370 | 0.044 |
| | %RSD | 0.479 | 0.541 | 0.762 | 60.3 | 1.44 | 0.353 | 0.797 | 0.913 | 4.39 | 0.712 | 0.922 |
| | | | | | | | | | | | | |
| 29/03/2017 | MEAN | 10.6 | 2.08 | 10.6 | 21.4 | 2.11 | 10.6 | 21.0 | 10.4 | 0.543 | <LLD | 4.90 |
| | SD | 0.038 | 0.027 | 0.143 | 0.456 | 0.020 | 0.065 | 0.091 | 0.033 | 0.010 | <LLD | 0.072 |
| | %RSD | 0.355 | 1.31 | 1.35 | 2.13 | 0.958 | 0.616 | 0.431 | 0.314 | 1.82 | <LLD | 1.47 |
| | | | | | | | | | | | | |
| 04/04/2017 | MEAN | 9.76 | 1.915 | 9.62 | 18.7 | 1.86 | 11.0 | 19.1 | 10.9 | 0.525 | 48.0 | 4.55 |
| | SD | 0.284 | 0.073 | 0.266 | 1.19 | 0.075 | 3.27 | 0.794 | 0.359 | 0.041 | 2.39 | 0.241 |
| | %RSD | 2.91 | 3.82 | 2.76 | 6.35 | 4.02 | 29.7 | 4.15 | 3.29 | 7.82 | 4.99 | 5.30 |
| | | | | | | | | | | | | |
| 25/04/2017 | MEAN | 10.9 | 2.20 | 11.0 | 23.4 | 2.19 | 11.4 | 22.2 | 10.9 | 0.658 | 53.9 | 5.23 |
| | SD | 0.988 | 0.201 | 0.899 | 1.651 | 0.161 | 1.97 | 1.90 | 0.740 | 0.107 | 8.665 | 0.584 |
| | %RSD | 9.04 | 9.13 | 8.16 | 7.05 | 7.38 | 17.2 | 8.54 | 6.76 | 16.3 | 16.1 | 11.2 |
| | | | | | | | | | | | | |
| 26/04/2017 | MEAN | 11.4 | 2.28 | 11.4 | 22.3 | 2.22 | 11.3 | 17.5 | 11.7 | 0.650 | 55.2 | 4.73 |
| | SD | 1.55 | 0.271 | 1.54 | 3.10 | 0.274 | 2.49 | 1.99 | 1.60 | 0.104 | 6.02 | 0.572 |
| | %RSD | 13.5 | 11.9 | 13.6 | 13.9 | 12.4 | 22.0 | 11.4 | 13.7 | 16.1 | 10.9 | 12.1 |
| | | | | | | | | | | | | |
| 27/04/2017 | MEAN | 11.0 | 2.19 | 10.9 | 22.2 | 2.19 | 10.8 | 22.2 | 10.9 | 0.645 | 57.3 | 4.99 |
| | SD | 0.499 | 0.081 | 0.385 | 1.20 | 0.074 | 0.286 | 0.815 | 0.218 | 0.098 | 2.09 | 0.156 |
| | %RSD | 4.532 | 3.71 | 3.52 | 5.40 | 3.39 | 2.64 | 3.68 | 2.00 | 15.2 | 3.64 | 3.12 |
| | | | | | | | | | | | | |
| 08/06/2017 | MEAN | 9.82 | 1.87 | 9.52 | 21.8 | 1.96 | 9.62 | 19.5 | 10.4 | 0.494 | 46.4 | 4.50 |
| | SD | 0.566 | 0.115 | 0.557 | 2.442 | 0.116 | 0.578 | 1.23 | 0.481 | 0.051 | 2.78 | 0.274 |
| | %RSD | 5.76 | 6.16 | 5.85 | 11.2 | 5.93 | 6.01 | 6.31 | 4.62 | 10.3 | 6.00 | 6.10 |
| | | | | | | | | | | | | |
| 14/06/2017 | MEAN | 9.23 | 1.88 | 9.14 | 20.1 | 1.85 | 9.05 | 18.2 | 8.71 | 0.476 | 43.4 | 4.26 |
| | SD | 0.080 | 0.009 | 0.116 | 1.22 | 0.009 | 0.063 | 0.243 | 0.045 | 0.030 | 0.428 | 0.034 |
| | %RSD | 0.863 | 0.499 | 1.27 | 6.06 | 0.498 | 0.693 | 1.34 | 0.514 | 6.30 | 0.986 | 0.797 |
| | | | | | | | | | | | | |
| 15/06/2017 | MEAN | 9.68 | 1.92 | 9.41 | 20.0 | 1.89 | 9.23 | 18.5 | 9.03 | 0.492 | 45.4 | 4.32 |
| | SD | 0.079 | 0.025 | 0.161 | 0.440 | 0.026 | 0.121 | 0.067 | 0.101 | 0.031 | 0.480 | 0.044 |
| | %RSD | 0.820 | 1.32 | 1.71 | 2.20 | 1.40 | 1.31 | 0.362 | 1.12 | 6.20 | 1.06 | 1.02 |
| | | | | | | | | | | | | |
| 16/06/2017 | MEAN | 9.99 | 2.01 | 9.83 | 20.8 | 2.00 | 9.80 | 19.8 | 9.48 | 0.483 | 46.8 | 4.63 |
| | SD | 0.065 | 0.025 | 0.028 | 0.705 | 0.025 | 0.127 | 0.156 | 0.106 | 0.014 | 0.633 | 0.062 |
| | %RSD | 0.646 | 1.23 | 0.281 | 3.38 | 1.24 | 1.30 | 0.786 | 1.12 | 2.93 | 1.35 | 1.35 |

Appendix 4D: Average monthly results of the serial measurement of $NO_3^-$ $NO_3^-$ concentration in selected wells by Palin test technique

| ID | **Ion Chromatography (µg/mL)** | | **Palin Test (µg/mL)** | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Dec.2016 | | Jan.2017 | | Feb. 2017 | | Mar 2017 | | Apr 2017 | |
| | Phase 1 | Phase 2 | $NO_3^-$ | $NH_4^+$ | $NO_3^-$ | $NH_4^+$ | $NO_3^-$ | $NH_4^+$ | $NO_3^-$ | $NH_4^+$ | $NO_3^-$ | $NH_4^+$ |
| GWR3 | 115.8 | 67.6 | 102.0 | 0.001 | 92.5 | 0.110 | 84.0 | 0.050 | 89.5 | 0.050 | 71.5 | 0.040 |
| GWE1 | 61.2 | 64.0 | 83.0 | 0.015 | 90.0 | 0.010 | 148.0 | 0.220 | 59.2 | 0.240 | 60.0 | 0.060 |
| GWCC4 | NS | 98.5 | 130.0 | 0.110 | 135 | 0.100 | 100.0 | 0.060 | 90.0 | 0.120 | 85.5 | 0.250 |
| GWCC5 | NS | 127.2 | 205.0 | 2.400 | 155.0 | 2.400 | 205.0 | 1.89 | 175.0 | 2.000 | 130.0 | 0.010 |
| GWK5 | 52.2 | 51.9 | 73.0 | 0.080 | 72.0 | 0.090 | 80.0 | 0.180 | 72.0 | 0.010 | 68.0 | 0.010 |
| GWE2 | NS | 54.9 | 76.0 | 0.053 | 58.0 | 0.070 | 65.0 | 0.220 | 60.0 | 0.060 | 56.3 | 0.001 |
| GWB1 | 50.3 | 69.3 | 71.3 | 0.123 | 54.0 | 0.080 | 56.3 | 0.150 | 54.0 | 0.004 | 42.2 | BDL |
| GWB2 | NS | 69.1 | 27.9 | 0.213 | 20.4 | 0.060 | 20.0 | BDL | | | | |
| GWG1 | 65.2 | 65.2 | 58.0 | 0.523 | 58.0 | 0.260 | 55.0 | 0.523 | 50.1 | 0.001 | | |
| GWJ3 | 82.7 | 59.2 | 73.0 | BDL | 66.0 | 0.001 | 45.0 | 0.001 | 28.1 | BDL | | |
| GWX4 | 127.3 | 118.6 | 140.0 | 0.140 | 110.0 | 0.140 | 103 | 0.030 | 66.0 | 0.080 | 55.0 | |
| GWL4 | 57.0 | 59.7 | 75.0 | 0.215 | 47.0 | BDL | 38.1 | 0.010 | | | | |
| GWC2 | NS | 32.3 | NS | NS | 60.0 | 0.030 | 52.0 | 0.060 | | | | |
| GWE3 | NS | 58.6 | 62.0 | 0.230 | 76.0 | 0.040 | 54.0 | 0.040 | | | | |
| GWH2 | NS | 102.6 | 150.0 | 0.060 | 150.0 | 0.060 | 124.0 | 0.060 | 88.0 | 0.100 | 85.0 | 0.001 |
| GWL1 | 51.7 | 54.8 | 70.0 | 0.090 | 68.0 | 0.090 | 48.0 | 0.090 | | | | |
| GWH1 | 51.7 | 46.4 | 60.0 | 0.045 | 48.7 | 0.180 | 43.5 | 0.002 | | | | |
| GWU6 | 68.6 | 0.793 | 10.1 | 0.045 | 22.5 | 0.010 | | | | | | |

Appendix 4E: Results of the Certified Reference Materials used during analyses of soil using the ICP-OES

| DATE | ID | As1890 | Cd2288 | Cr2677 | Cu3247 | Ni2316 | Pb2203 | Zn2062 |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | | |
| | **EXPECTED** | **27.0** | **2.30** | **80.0** | **92.0** | **38.0** | **160.0** | **513.0** |
| | | | | | | | | |
| | **%ACCURACY** | **84.1** | **96.4** | **80.5** | **86.6** | **83.6** | **86.1** | **90.6** |
| | | | | | | | | |
| **ALL** | **MEAN** | **22.7** | **2.22** | **64.4** | **79.7** | **31.8** | **137.8** | **464.9** |
| | SD | 1.69 | 0.243 | 6.07 | 6.46 | 5.09 | 7.40 | 22.1 |
| | %RSD | 7.44 | 10.9 | 9.43 | 8.10 | 16.0 | 5.37 | 4.74 |
| | | | | | | | | |
| **27/04/2016** | **MEAN** | **23.9** | **2.39** | **68.7** | **84.2** | **35.4** | **143.0** | **480.5** |
| | SD | 3.46 | 0.271 | 9.65 | 10.6 | 3.99 | 17.3 | 56.3 |
| | %RSD | 14.5 | 11.4 | 14.1 | 12.6 | 11.3 | 12.1 | 11.7 |
| | | | | | | | | |
| **12/05/2017** | **MEAN** | **21.5** | **2.05** | **60.1** | **75.1** | **28.2** | **132.6** | **449.3** |
| | SD | 0.367 | 0.018 | 1.78 | 1.77 | 0.343 | 3.90 | 8.94 |
| | %RSD | 1.71 | 0.868 | 2.96 | 2.35 | 1.22 | 2.94 | 1.99 |
| 27/04/2016 | CRM 1 | 22.2 | 2.40 | 65.5 | 78.7 | 35.9 | 134.8 | 451.3 |
| 27/04/2016 | CRM 2 | 24.4 | 2.66 | 71.5 | 88.1 | 39.5 | 149.2 | 509.5 |
| 27/04/2016 | CRM 3 | 19.4 | 2.12 | 56.9 | 69.5 | 31.6 | 119.4 | 408.9 |
| 27/04/2016 | CRM 4 | 18.8 | 2.06 | 54.1 | 67.9 | 30.3 | 116.7 | 391.5 |
| 27/04/2016 | CRM 5 | 23.9 | 2.24 | 66.1 | 81.9 | 33.9 | 140.2 | 470.3 |
| 27/04/2016 | CRM 6 | 23.1 | 2.16 | 64.0 | 79.2 | 33.1 | 136.7 | 469.7 |
| 27/04/2016 | CRM 7 | 24.1 | 2.20 | 70.7 | 83.0 | 34.3 | 139.2 | 489.3 |
| 27/04/2016 | CRM 8 | 32.5 | 3.00 | 92.9 | 107.9 | 45.5 | 183.8 | 617.7 |
| 27/04/2016 | CRM 9 | 25.3 | 2.50 | 74.2 | 91.3 | 35.7 | 153.5 | 481.1 |
| 27/04/2016 | CRM 10 | 22.9 | 2.30 | 69.6 | 86.7 | 33.2 | 146.2 | 474.3 |
| 27/04/2016 | CRM 11 | 26.2 | 2.60 | 70.8 | 91.6 | 36.4 | 153.3 | 509.1 |
| 27/04/2016 | CRM 12 | 24.4 | 2.48 | 67.7 | 85.0 | 35.0 | 143.4 | 493.7 |
| 12/05/2017 | CRM 1 | 21.9 | 2.07 | 62.1 | 77.1 | 28.6 | 137.1 | 457.8 |
| 12/05/2017 | CRM 2 | 21.5 | 2.03 | 59.4 | 74.6 | 27.9 | 130.4 | 450.2 |
| 12/05/2017 | CRM 3 | 21.2 | 2.04 | 58.7 | 73.6 | 28.0 | 130.3 | 440.0 |

## Appendix 4F: Result of the Certified Reference Materials used during analyses of soil C: N ratio analyses

| Sampling phase | Date | ID | % C | %N |
|---|---|---|---|---|
| | Expected | | 2.01 | 0.192 |
| | All | Mean | 2.07 | 0.187 |
| | | SD | 0.118 | 0.030 |
| | | %RSD | 5.70 | 16.0 |
| | | Accuracy | 103.0 | 97.4 |
| | | LOD | 0.002 | 0.03 |
| | | LOQ | 0.006 | 0.100 |
| First | 27/10/16 | Mean | 2.12 | 0.21 |
| | | SD | 0.013 | 0.012 |
| | | %RSD | 0.604 | 5.79 |
| First | 14/11/16 | Mean | 2.12 | 0.187 |
| | | SD | 0.027 | 0.018 |
| | | %RSD | 1.29 | 9.58 |
| First | 18/11/16 | Mean | 1.88 | 0.151 |
| | | SD | 0.504 | 0.083 |
| | | %RSD | 55.1 | 26.8 |
| First | 23/11/16 | Mean | 2.15 | 0.217 |
| | | SD | 0.009 | 0.024 |
| | | %RSD | 11.0 | 0.402 |
| Second | 18/05/17 | Mean | 2.09 | 0.172 |
| | | SD | 0.035 | 0.013 |
| | | %RSD | 1.69 | 7.62 |

Appendix 4G: Result of the Certified Reference Materials used during analyses of plants C: N ratio analyses

| Sample Label | Date | % C | % N |
|---|---|---|---|
| | Expected | 44.2 | 1.09 |
| | Mean | 43.2 | 1.04 |
| | SD | 3.47 | 0.082 |
| | %RSD | 8.03 | 7.91 |
| | Accuracy | 95.4 | 97.8 |
| | LOD | 0.001 | 0.023 |
| | LOQ | 0.071 | 0.075 |

Appendix 4H: CRM results for LGC 7162 strawberry leaves by ICP-OES.

| Parameters values (µg/g) | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Al | As | Ca | Cd | Co | Cr | Cu | Fe | k | Mg | Mn | Na | Ni | P | Pb | Zn |
| 317.2 | 0.654 | 14455.6 | 0.180 | 0.314 | 1.39 | 12.9 | 530.8 | 17950.3 | 3339.5 | 158.5 | <LLD | 2.59 | 2523.3 | 1.43 | 403 |
| 293.3 | 0.309 | 13224.3 | 0.139 | 0.239 | 1.26 | 6.44 | 517.1 | 16564.5 | 3002.9 | 141.7 | <LLD | 1.57 | 2176.6 | 1.32 | 33.9 |
| 330.1 | 0.399 | 13715.3 | 0.169 | 0.307 | 1.48 | 8.42 | 529.9 | 17519.8 | 3153.0 | 150.6 | 132.9 | 1.97 | 2558.1 | 1.47 | 404.2 |
| 327.0 | 0.589 | 13200.1 | 0.183 | 0.303 | 1.34 | 8.00 | 492.2 | 16770.9 | 2959.0 | 140.2 | 171.2 | 1.85 | 2547.9 | 1.60 | 401.9 |
| 310.1 | 0.437 | 12489.6 | 0.181 | 0.291 | 1.25 | 7.07 | 473.5 | 16057.4 | 2826.8 | 134.5 | 158.1 | 1.79 | 2465.9 | 1.19 | 400.4 |
| 279.2 | 0.282 | 12725.8 | 0.168 | 0.289 | 1.23 | 8.04 | 472.2 | 15733.0 | 2809.5 | 130.6 | <LLD | 2.34 | 2449.3 | 1.43 | 400.2 |
| 297.8 | 0.535 | 13542.3 | 0.155 | 0.265 | 1.24 | 5.52 | 465.3 | 17077.5 | 3198.6 | 152.7 | <LLD | 1.58 | 2321.9 | 1.39 | 405.0 |
| 259.0 | 0.620 | 11375.5 | 0.156 | 0.248 | 1.22 | 5.37 | 411.4 | 14795.4 | 2733.3 | 135.3 | <LLD | 1.47 | 2086.3 | 1.50 | 18.1 |
| 313.6 | 0.514 | 14020.3 | 0.173 | 0.285 | 1.38 | 9.93 | 488.4 | 17820.6 | 3321.6 | 159.6 | <LLD | 1.74 | 2554.9 | 1.58 | 412.4 |
| 318.3 | 0.523 | 14133.8 | 0.183 | 0.268 | 2.00 | 9.33 | 484.7 | 15957.1 | 3388.0 | 148.8 | 375.9 | 1.60 | 2352.2 | 1.52 | 411.0 |
| 365.5 | 0.612 | 15677.5 | 0.197 | 0.285 | 1.44 | 16.0 | 527.7 | 17861.8 | 3783.4 | 167.1 | 399.6 | 1.79 | 2658.9 | 2.08 | 410.7 |
| 363.8 | 0.608 | 15333.5 | 0.179 | 0.264 | 1.50 | 11.3 | 515.9 | 17183.7 | 3706.6 | 160.5 | 510.4 | 1.91 | 2567.0 | 1.62 | 413.5 |
| 311.5 | 0.623 | 13875.3 | 0.166 | 0.303 | 1.40 | 32.5 | 503.7 | 17602.4 | 3297.9 | 159.2 | 89.4 | 1.98 | 2624.3 | 1.52 | 415.8 |
| 326.8 | 0.659 | 14662.0 | 0.189 | 0.286 | 1.43 | 11.9 | 520.9 | 18634.3 | 3506.3 | 169.9 | 72.0 | 2.04 | 2774.7 | 1.54 | 24.8 |
| 255.5 | 0.720 | 13510.7 | 0.175 | 0.287 | 1.27 | 6.96 | 442.9 | 17219.1 | 3248.8 | 155.2 | 79.2 | 1.59 | 2549.3 | 1.50 | 415.7 |
| 291.9 | 0.587 | 13449.3 | 0.168 | 0.277 | 1.23 | 7.37 | 473.1 | 17083.4 | 3196.9 | 156.0 | <LLD | 1.64 | 2547.9 | 1.31 | 19.5 |

**APPENDIX 5A:** Pearson's Correlation Table of the Rainy season's groundwater dataset of the referenced 30 sampled wells used in the analyses of seasonal variability of groundwater chemistry in the study area.

| Analyte (µgmL$^{-1}$) | $(^{0}C)$ | DO | EC | pH | DOC | $Fl^-$ | Cl- | $SO_4^-$ | $NO_3$ | $NH_{4+}$ | Ca | K | Mg | Na | Mn | Fe | Pb |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Temperature | 1.000 | | | | | | | | | | | | | | | | |
| DO | | 1.000 | | | | | | | | | | | | | | | |
| EC | | | 1.000 | | | | | | | | | | | | | | |
| pH | .794** | -.708** | | 1.000 | | | | | | | | | | | | | |
| DOC | -.719** | .856** | | -.935** | 1.000 | | | | | | | | | | | | |
| $Fl^-$ | | | | | | 1.000 | | | | | | | | | | | |
| $Cl^-$ | | | .852** | | | .908** | 1.000 | | | | | | | | | | |
| $SO_4$ | .702** | -.658** | | .918** | -.919** | | | 1.000 | | | | | | | | | |
| $NO_3$ | | | .918** | | | .882** | .924** | | 1.000 | | | | | | | | |
| $NH_4$ | | .641* | .505** | | | | | | | 1.000 | | | | | | | |
| Ca | .590* | .709** | .833* | | | .671* | .752** | | .868** | | 1.000 | | | | | | |
| K | | .880** | .719** | | | | .899** | | .908** | .713** | .743** | 1.000 | | | | | |
| Mg | | | .646** | | | | | | | | .562* | | 1.000 | | | | |
| Na | | | | | .711** | .562* | .752** | | | .681* | | | .736** | 1.000 | 1.000 | | |
| Mn | | .903** | .633** | | | .934** | 930** | | .901** | .618** | .670** | .888** | .641** | | | 1.000 | |
| Fe | | | | | | | | | .652* | | .703** | | | | | | 1.000 |
| Pb | | | | | | | | | | | .562* | | | | | | |

** All significantly correlated variables at $p< 0.01$ (2-tailed) level.

* All significantly correlated variables at $p< 0.05$ (2-tailed) level

**APPENDIX 5B:** Pearson's Correlation Table of the dry season's groundwater dataset of the referenced 30 sampled wells used in the analyses of seasonal variability of groundwater chemistry in the study area

| Analyte (µgmL$^{-1}$) | ($^0$C) | DO | EC | pH | DOC | Fl- | Cl- | SO$_4^-$ | NO$_3$ | NH$_{4+}$ | Ca | K | Mg | Na | Mn | Fe | Pb |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Temperature | 1.000 | | | | | | | | | | | | | | | | |
| DO | | **1.000** | | | | | | | | | | | | | | | |
| EC | | ***** | **1.000** | | | | | | | | | | | | | | |
| pH | | | | **1.000** | | | | | | | | | | | | | |
| DOC | | | | | **1.000** | | | | | | | | | | | | |
| Fl$^-$ | | | | | | **1.000** | | | | | | | | | | | |
| Cl$^-$ | | | | | | **.729**** | **1.000** | | | | | | | | | | |
| SO$_4$ | | | | | | | | **1.000** | | | | | | | | | |
| NO$_3$ | | | | | **-.576**** | **.736**** | **.913**** | | **1.000** | | | | | | | | |
| NH$_4$ | | **-.657** | | | **.855*** | | | | **-.830**** | **1.000** | | | | | | | |
| Ca | | | | | **-.537**** | **.819**** | **.883**** | | **.935**** | **-.515** | **1.000** | | | | | | |
| K | | | | | | **.647**** | **.904**** | | **.809**** | | **.848**** | **1.000** | | | | | |
| Mg | | | | | | **.640**** | **.766**** | | **.850**** | **.809**** | **.809**** | **.807**** | **1.000** | | | | |
| Na | | | | | **-.512**** | **.557**** | **.874**** | | **.946**** | **-.827*** | **.801**** | **.745**** | **.780**** | **1.000** | **1.000** | | |
| Mn | | | | | **-.518**** | | **.745**** | | **.787**** | **-.932**** | **.755**** | **.623**** | **.689**** | **.697**** | **.837**** | **1.000** | |
| Fe | | | | | | | **.759**** | | **.810**** | | **.855**** | **.695**** | **.685**** | **.668**** | | | **1.000** |
| Pb | | | | | | | | | | | | | **.535**** | **.514**** | | | |

** All significantly correlated variables at $p< 0.01$ (2-tailed) level.

* All significantly correlated variables at $p< 0.05$ (2-tailed) level

**Appendix 5C:** Mn concentration and distribution pattern in the different urban regions, according to seasons showing percentage exceedance to the 0.20 µg/mL MCL stipulated by the Nigerian Standard for Drinking Water Quality (NSDWQ).

| Number of sampled wells with Mn > LLD = 364 | City Centre | | Sub - urban | | Peri-urban | |
|---|---|---|---|---|---|---|
| Sampling Season | Rainy | Dry | Rainy | Dry | Rainy | Dry |
| Number per Season | 68.0 | 15.0 | 138.0 | 80.0 | 55.0 | 8.00 |
| Minimum (ng/mL) | 3.40 | 4.60 | 1.01 | 3.53 | 3.58 | 6.08 |
| Maximum (ng/mL) | 204.0 | 201.7 | 221.8 | 134.0 | 105.8 | 40.3 |
| Median (ng/mL) | 40.4 | 114.4 | 13.3 | 28.5 | 6.15 | 14.4 |
| Stand. Dev. (ng/mL) | 45.0 | 51.0 | 40.4 | 38.5 | 21.6 | 12.8 |
| % > WHO MCL | 41.2 | 86.7 | 23.2 | 35.0 | 9.09 | Nil |
| % > NSDWQ MCL | 1.47 | 6.67 | 0.720 | Nil | Nil | Nil |
| % > EUSDW MCL | 41.2 | 86.7 | 23.2 | 35.0 | 9.09 | Nil |
| % >USEPA MCL | 41.2 | 86.7 | 23.2 | 35.0 | 9.09 | Nil |

**Appendix 5D**: Calculated exposure dosage of Owerri residents' exposure to nitrate in groundwater across the study area. Acronyms in the table represent individual categories are A (Adults), T (Teenagers), C (Child) and Tod. (Toddlers). Others represent indices used in the assessment like BM (Body weight), EF (Exposure factor), EF (Exposure frequency), AT (Average time) and AD (Average dosage).

| **Ingestion rate (IR)** | **Value (Litres/day)** | | | | **Variables** | **Groundwater $NO_3^-$** | | | |
|---|---|---|---|---|---|---|---|---|---|
| | **Adult** | **Teen** 12 -19 yrs. | **Child** 5 –11 yrs | **Toddler** 7 months – 4 yrs | | **Adult** | **Teen** | **Child** | **Toddler** |
| Groundwater | 1.50 | 1.00 | 0.800 | 0.600 | BM (kg) | 70.7 | 59.7 | 32.9 | 16.5 |
| | | | | | ED (days/year) | 47.6 | 19.0 | 11.0 | 4.00 |
| | | | | | Exposure Frequency | 365 | 365 | 365 | 365 |
| | | | | | AT | 17,374 | 6,935 | 4,015 | 1,460 |
| | | | | | EF | 1 | 1 | 1 | 1 |
| | | | | | AD $NO_3^-$ | 0.45 | 0.35 | 0.51 | 0.77 |

**Appendix 5E**: Calculated hazard quotient of Owerri residents’ exposure to elevated Pb found in the Pumpkin leaf (*Telfaiara occidentalis*) and Cassava tuber (*Manihot esculanta*) collected from different domestic gardens across Owerri. Acronyms in the table represent individual categories are A (Adults), T (Teenagers), C (Child) and Tod. (Toddlers). Others represent indices used in the assessment like BM (Body weight), ED (Exposure duration), EF (Exposure frequency), AT (Average time) and HQ (Hazard quotient). Average hazard quotient above 0.2 is assumed to pose imminent health risk.

| Staple Food | Avg. IR (g/day) | | | | Variable | Value (Pumpkin Leaf) | | | | Value (Cassava Tuber) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | A | T | C | Tod. | | A | T | C | Tod. | A | T | C | Tod. |
| Leaf | 137 | 120 | 98 | 67 | BM (kg) | 70.7 | 59.7 | 32.9 | 16.5 | 70.7 | 59.7 | 32.9 | 16.5 |
| | | | | | ED (days/yr.) | 47.6 | 19.0 | 11.0 | 4.00 | 47.6 | 19.0 | 11.0 | 4.00 |
| Tuber | 188 | 227 | 161 | 105 | Exposure Frequency | 365 | 365 | 365 | 365 | 365 | 365 | 365 | 365 |
| | | | | | AT | 17,374 | 6,935 | 4,015 | 1,460 | 17,374 | 6,935 | 4,015 | 1,460 |
| | | | | | (BW x AT) | 1,228,342 | 414,020 | 132,094 | 24,090 | 1,228,342 | 414,020 | 132,094 | 24,090 |
| | | | | | Avg. ADD | 0.03 | 0.08 | 0.39 | 2.95 | 0.50 | 2.18 | 2.68 | 1.16 |
| | | | | | E± | 0.002 | 0.007 | 0.03 | 0.25 | 0.07 | 0.34 | 0.42 | 0.18 |
| | | | | | THQ | 0.55 | 0.47 | 0.57 | 1.24 | 0.10 | 0.09 | 0.11 | 0.23 |
| | | | | | E± | 0.03 | 0.03 | 0.04 | 0.08 | 0.01 | 0.01 | 0.01 | 0.03 |

**APPENDIX 5F:** Spearman's Correlation Table of groundwater dataset of sampled wells located with leachate of dumpsites within 1km distance ( Main, Relief market, Nekede – Ihiagwa road and Nekede mechanic village) across the study area.

| | **Leachate** | | | | | | | **Groundwater** | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Analyte ($\mu gmL^{-1}$) | DO | pH | $Cl^-$ | $NO_3^-$ | Na | $NH_4^+$ | $K^+$ | DO | pH | $Cl^-$ | $NO_3^-$ | Na | $NH_4^+$ | $K^+$ |
| DO (leachate) | 1.000 | | | | | | | | | | | | | |
| pH (leachate) | **.554**** | 1.000 | | | | | | | | | | | | |
| $Cl^-$ (leachate) | | | 1.000 | | | | | | | | | | | |
| $NO_3^-$ (leachate | **.592**** | **.533**** | **.601**** | 1.000 | | | | | | | | | | |
| Na (leachate) | | | **.964**** | **.651**** | 1.000 | | | | | | | | | |
| $NH_4^+$(leachate) | | | **.915**** | **.635** | **.958**** | 1.000 | | | | | | | | |
| $K^+$ (leachate) | | | **.945**** | **.657**** | **.978**** | **.968**** | 1.000 | | | | | | | |
| DO (groundwater) | | | | | | | | 1.000 | | | | | | |
| pH (groundwater) | | | | | | | | | 1.000 | | | | | |
| $Cl^-$ (groundwater) | | | **.510**** | | **.550**** | **.584*** | **.554**** | | | 1.000 | | | | |
| $NO_3^-$ (groundwater) | | | **.568**** | | **.616**** | **.672**** | **.644**** | | | **.764**** | 1.000 | | | |
| Na (groundwater) | | | **.510**** | | **.565**** | **.602*** | **.579**** | | | **.897**** | **.843**** | 1.000 | | |
| $NH_4^+$ (groundwater) | | **.611**** | | | | | | | | **.637**** | | | 1.000 | |
| $K^+$ (groundwater) | | **.513**** | **.640**** | **.526**** | **.681**** | **.716**** | **673**** | | | **.826**** | **.834**** | | **.777**** | 1.000 |

** All significantly correlated variables at $p < 0.01$ (2-tailed) level

* All significantly correlated variables at $p < 0.05$ (2-tailed) level