

Distribution Agreement

In presenting this thesis or dissertation as a partial fulfillment of the requirements for an advanced degree from Emory University, I hereby grant to Emory University and its agents the non-exclusive license to archive, make accessible, and display my thesis or dissertation in whole or in part in all forms of media, now or hereafter known, including display on the world wide web. I understand that I may select some access restrictions as part of the online submission of this thesis or dissertation. I retain all ownership rights to the copyright of the thesis or dissertation. I also retain the right to use in future works (such as articles or books) all or part of this thesis or dissertation.

Signature:

Olumayowa Dayo

Date

Baseline Analysis of Ground Water Quality Around Open Dumpsites in Lagos, Nigeria:
Focus on Polynuclear Aromatic Hydrocarbons.

By

Olumayowa Dayo
Master of Public Health

Global Environmental Health

P. Barry Ryan, PhD
Committee chair

Paige Tolbert, PhD
Committee Member

Baseline Analysis of Ground Water Quality Around Open Dumpsites in Lagos, Nigeria:
Focus on Polynuclear Aromatic Hydrocarbons.

By

Olumayowa Dayo

BSc.

Cornell University

2011

Thesis Committee Chair: P. Barry Ryan, PhD

An abstract of a thesis submitted to the Faculty of the Rollins School of Public Health of
Emory University in partial fulfillment of the requirements for the degree of Master of
Public Health in Global Environmental Health.

2013

Abstract
Baseline Analysis of Ground Water Quality Around Open Dumpsites in Lagos, Nigeria:
Focus on Polynuclear Aromatic Hydrocarbons

By

Olumayowa Dayo

Background: Providing a sustainable means of waste disposal is one of the major problems in Lagos. For many years, the government had used improper waste disposal methods to dispose of the waste generated in the city. The physical, chemical and biological processes that occur simultaneously at open dumpsites can result in generation of leachate and other waste gases. The leachate and waste gases formed are the source of pollutants that can lead to environmental and health problems (Rushbrook, 2001). Therefore, communities that tap into polluted groundwater may be exposed to various levels of harmful chemical contaminants that can lead to chronic diseases such as cancer.

Objective: To evaluate groundwater contamination around open dumpsites, the presence of polynuclear aromatic hydrocarbon pollution in the study area was ascertained by sampling water from boreholes and wells in houses around open dumpsites.

Method: Water samples were collected from households around two open dumpsites in Lagos Nigeria. Samples were collected over a two-day period in 2012 and analyzed at a Lagos State Environmental Protection Agency Laboratory in Lagos. Coordinate points for each sample site were collected on field and used to evaluate the dispersion of total PAHs. Non-parametric methods were used for statistical data analysis and Monte Carlo Simulation (MCS) based analysis was used to impute non-detected values.

Result: Seven of the sixteen PAH compounds tested for were present in at least four sites of the fourteen sampling sites. Before MCS, four of the seven compounds were significantly higher than the maximum contamination level (MCL). After MCS all sites had PAHs level higher than MCL and maximum contaminant level goal (MCLG). Also, there was no difference in PAHs level between sites.

Discussion: A combination of the laboratory, statistical and geographic information analysis provided evidence of groundwater contamination at both study sites. The Lagos state government needs to improve on the waste management system to avoid contamination of groundwater aquifer that may pose future health risk.

Baseline Analysis of Ground Water Quality Around Open Dumpsites in Lagos, Nigeria:
Focus on Polynuclear Aromatic Hydrocarbons.

By

Olumayowa Dayo

BSc.

Cornell University

2011

Thesis Committee Chair: P. Barry Ryan, PhD

An abstract of a thesis submitted to the Faculty of the Rollins School of Public Health of
Emory University in partial fulfillment of the requirements for the degree of Master of
Public Health in Global Environmental Health.

2013

Acknowledgment

I owe my deepest gratitude to my exceptional thesis advisor, Dr Barry Ryan for his guidance and patience throughout my thesis project. I am also very grateful to Dr Owen Devine for his remarkable guidance during the statistical analysis planning and execution.

I also want to thank the following outstanding Researchers in Nigeria, Dr Victor Adetimirin, Dr Adebola Oketola and Dr Adeoluwa at the University of Ibadan Oyo, Nigeria for their accommodation and guidance during my fieldwork. In addition, I am grateful to Mr Majolagbe and Mr. Adesoji Ademoroti for their guidance during the sampling and laboratory analysis in the field.

Finally, I am indebted to God, my family and friends for their love and support throughout this incredible journey

Table of Contents

Chapter 1: Introduction.....	1
1.1. Background.....	1
1.2. Significance	5
1.3. Objective	5
Chapter 2: Literature Review	6
2.1. Introduction.....	6
2.2. Waste Management in Lagos	6
2.3. Water sources in Lagos	9
2.4. Geology and Hydrogeology of the study area.....	11
2.5. Polynuclear aromatic hydrocarbons.....	12
2.6. Physical properties of PAHs that determine flow in groundwater.....	15
2.7. GIS and Public Health.....	16
2.8. Gaps in literature.....	17
Chapter 3: Methodology.....	19
3.1. Hypotheses.....	19
3.2. Study Design.....	19
3.3. Ethics	20
3.4. Field sampling.....	20
3.5. Laboratory Tools	21
3.6. Reagents.....	21
3.7. Extraction procedure.....	21
3.7. Concentration and Drying.....	22
3.8. Instrument.....	22
3.9. Experiment	23
3.10. Method validation.....	24
3.11. Statistical Analysis.....	24
Chapter 4: Results	26
4.1. Preliminary Analysis	26
Table 1: Total PAHs concentration by sampling site (mg/L)	26
Table 2: PAHs concentration in groundwater samples in (mg/L), prior to MCS	27
4.2. Monte Carlo Simulation Analysis.....	27
Table 3: PAHs concentration in groundwater samples (mg/L), after MCS	28

Table 4: PAHs concentrations in groundwater samples by site (mg/L).....	28
Table 5: PAHs concentration in groundwater samples Control vs. Both Dumpsites (mg/L)	29
Table 6: Total Uncertainty Interval for MCS (mg/L).....	29
Table 7: Non-detected PAHs concentration imputed by MCS (mg/L)	29
Chapter 5: Summary	30
5.1. Discussion.....	30
5.1.1. PAHs Concentration	30
5.1.2. Physical Environment and PAHs.....	34
5.1.3. Limitations.....	35
5.2. Conclusion and Recommendations	36
5.3. Maps & Graphs.....	38
NE areas have higher PAHs concentrations.....	40
References	43
Appendix	47
Table1: Characterization of groundwater samples	47
Table 2: PAH analysis using GC-FID instrument.....	47

Abbreviations

HHW	HouseHold Waste
OD	Open Dumpsites
WHO	World Health Organization
VOCs	Volatile Organic Compounds
PAHs	Polynuclear Aromatic Hydrocarbons
MoELS	Ministry of Environment Lagos State
LAWMA	Lagos Waste Management Authority
LWC	Lagos Water Corporation
ATSDR	Agency for Toxic Substances and Disease Registry
LASEPA	Lagos State Environmental Protection Agency
DNA	DeoxyriboNucleic Acid
LGA	Local Government Area
GPS	Geographic Positioning System
GC-FID	Gas Chromatograph-Flame Ionization Detector
ASTER	Advanced Spaceborne Thermal Emission and Reflection Radiometer
SRTM	Shuttle Radar Topography Mission
MCS	Monte Carlo Simulation
GIS	Geographic Information System
LoD	Limit of Detection
BAA	Benzo (a) anthacene

BAP	Benzo (a) pyrene
BKF	Benzo (k) fluoranthene
BBF	Benzo (b) fluoranthene
PYR	Pyrene
CHR	Chrysene
FLU	Fluoranthene
MCLG	Maximum Contaminant Level Goal

Chapter 1: Introduction

1.1. Background

Safe drinking water is one of the most essential basic needs of humans universally. Most communities tap into the closest water source in their area, whether it is groundwater via a borehole or surface water such as a river (Odukoya & Abimbola, 2010). The safety of drinking water is thus very important and needs to be properly monitored. In most developing countries, surface and ground water are the main sources of water for all basic needs. These water sources are also easily susceptible to contamination by anthropogenic sources such as household waste (HHW), municipal waste dumps, agricultural runoff and industrial waste, among other pollution sources (Han et al., 2013). The degree of pollution from any of these sources is dependent on environmental control, waste management practices and environmental protection laws in each area.

Of the multiple culprits of water pollutants, municipal dumpsites are one of the well-studied and documented sources. In developing countries, most municipal dumpsites are unplanned, open dumpsites (OD) with little to no engineering measures to protect the environment. Open dumpsites are the simplest and initially the cheapest method of waste disposal, and they are the primary means of waste management in many developing countries (Taylor & Allen, 2006). The cost of remediating these sites can exceed the cost of maintaining an open dumpsite and the environmental damage can take decades to be ameliorated (Kurian, 2002). Also, the disadvantages of open dumpsite go beyond the environmental impact and can lead to negative health outcomes such as cancer (ATSDR, 2009). Sanitary landfills are an

improvement to the OD waste management system because they have an engineered, protective flooring layer that can prevent the contamination of groundwater. They also have predesigned leachate collection systems, waste gas collection or flaring practices, registered collection and compaction of waste and effective placement and control of land use (Kurian, 2002).

Since, groundwater contamination around open dumpsites is mainly due to the insufficient mechanical construct of a waste management system, rainwater and other nearby water sources can infiltrate and permeate through the dumpsite and through, producing leachate. The leachate may contain undesirable and toxic chemicals, and can seep through the soil and into the groundwater. In addition, open dumpsites may produce a pool of wastewater that can also seep into the ground water if it is not properly collected. The risk of groundwater contamination by leachate that is not caught by a collection system is determined by multiple factors such as the concentration of contaminants in leachate, the permeability of leachate contents through the soil and aquifer layers, the general geologic makeup, the toxicity of the contaminants, and the groundwater flow. Therefore, communities near open dumpsites are at a high risk of having contaminated water and substantial negative health outcomes (Taylor & Allen, 2006).

Common chemical pollutants found in the groundwater around open waste dumpsites are dependent on components of disposed waste, and the byproducts of the natural degradation of waste products. Waste with harmful byproduct includes paints, inks, plastics, electronics, pesticides, gasoline, kerosene, and heating oil. Byproducts and pollutants may include

inorganic metals, volatile organic compounds (VOCs), furans, dioxins, polynuclear aromatic hydrocarbons (PAHs), chlorinated solvents and more (Iwegbue et al., 2010). People can therefore be exposed to these pollutants through dermal absorption, ingestion of contaminated water, inhalation of toxic fumes and through the food chain (ATSDR, 2009).

Furthermore, industrialization and the rapid urbanization of cities in both developed and developing countries pose an increased problem for environmental health and safety. In rapidly urbanized cities, the amount of waste produced can exceed the capacity of a State or a County waste management system, leading to uncontrolled or inefficient waste management (Taylor & Allen, 2006). In many developing countries, the placement of dumpsites within an area is arbitrary and the possibility of environmental pollution is often not considered. Studies from India, Mexico and Nigeria have shown environmental degradation in unplanned settlements due to inappropriate waste management from industries, households and more (Owens & Niemeyer, 2006). Although majority of the research on water contamination in developing countries has focused on contamination due to microorganism pollution and inorganic contaminants, organic chemical contamination is unmistakably an important issue that needs greater attention.

Lagos State, the focus of this study, holds approximately 60% of Nigeria's industrial and commercial centers as well as majority of the foreign trade and import centers in the country. It is situated on the southwestern coast of Nigeria and is surrounded by lagoons, lakes and rivers. It has an estimated population of 9-17 million people, but the smallest political unit in the Country (MoELS, 2010). The Lagos environment is somewhat unplanned with

pharmaceutical, battery, and textile industrial plants in close proximity to residential areas (Yusuf, 2007). Studies in the Southern oil producing States of Nigeria, such as the Niger Delta region, have shown that years of oil rigging, spills and improper waste disposal have affected the ground and surface water quality (Adeleke et al. 2004). In Lagos, many environmental studies have evaluated inorganic, metal pollutants but few have focused on contamination of groundwater by PAHs at open dumpsites.

With its growing population, the Lagos State government has sited the pollution of surface and ground water due to domestic, commercial and industrial activities as one of nine key environmental challenges facing the state. It is clear that the State is experiencing difficulties in maintaining and providing effective waste management services as the managing of HHW, industrial, and healthcare waste has become a tremendous burden (MoELS, 2010). The current system of municipal waste disposal in Lagos is mainly open dumpsite, situated in both residential and commercial areas of the state (MoELS, 2010). Unlike sanitary landfills, in which hazardous and non-hazardous material are separated, the majority of waste dumps in Lagos have a mixture of municipal, health services and industrial waste. In addition, these open dumpsites lack the protective engineered layering that modern sanitary landfills have and as such, byproducts from the dumpsite may easily pass through the soil. The research literature in Nigeria has shown that these dumpsites are prone to the release of harmful pollutants into the environment and the surrounding area groundwater (Odukoya and Abimbola 2010). Also, many studies in Lagos have established the presence of harmful inorganic compounds in groundwater such as the release of heavy metals from open dumpsites and other natural causes (Iwegbue et al., 2010). Therefore, this study assessed the

presence of organic pollutants (PAHs) in the groundwater aquifers around selected open dumpsites in Lagos.

1.2. Significance

The long-term practice of open dumpsites may have caused pollution of groundwater around major open dumpsites in Lagos, Nigeria. People consuming groundwater in close proximity to a dumpsite may be exposed to harmful pollutants. Also, limited clean water supply by the State government in Lagos has leading to an increase in the use of ground water through wells and boreholes homes. Therefore, the Lagos government needs to be aware of the possible contamination of major groundwater aquifers, especially those closest to open dumpsites. Most importantly, Organic pollutants such as PAHs are of prime concern due to their toxicity and persistence in the environment, but very few studies in Lagos State have focused on PAHs contamination in groundwater and the health risk associated with the consumption of such polluted water.

1.3. Objective

To evaluate groundwater contamination around open dumpsites, the presence of polynuclear aromatic hydrocarbon pollution in the study area is ascertained by sampling water from boreholes and wells in houses around open dumpsites.

Chapter 2: Literature Review

2.1. Introduction

The purpose of this literature review is to evaluate the knowledge and links between open dumpsites, contamination of ground water and adverse health outcomes. The scope of this review is rapidly developing setting in urban areas, as a representation of the area of study. The Ministry of Environment, Lagos State released the 2010 update on the State of Environment (MoELS, 2010). This published report provides an in-depth evaluation of the water and solid waste management in Lagos State. This report will serve as a primary resource in evaluating the environmental issues in Lagos, since it is a trusted knowledge on the most recent conditions of the Lagos environment. In addition, an in-depth evaluation of the literature on waste management and groundwater pollution will inform this chapter. Therefore, this review presents established literature knowledge on the effects of open dumpsites: on the surrounding environment, on groundwater; on populations in close proximity to open dumpsites; water usage in Lagos; waste management in Lagos; characterization of PAHs; the mechanism of PAH carcinogenesis; and the physical properties of PAHs that determine groundwater flow. Finally, this review will emphasize knowledge gaps in the literature and areas for knowledge enhancement within this field.

2.2. Waste Management in Lagos

Management of solid waste is under the authority of the Lagos Waste Management Authority (LAWMA), which was first established in 1977. The city is estimated to generate an average of nine thousand metric tons of waste per day (MoELS, 2010). Lagos State

government practices the method of open dumpsites and controlled dumpsites for management of solid waste. Open dumpsites are unplanned, un-engineered and haphazardly placed waste sites used as a form of waste management in most developing countries (Kurian, 2002). In addition, open dumpsites are prone to inadequate or non-existent leachate collection system, and thus can be surrounded by pools of polluted wastewater. Controlled dumps have the same characteristics as open dumps except that they are usually government-regulated and enclosed spaces. These sites are usually open to environmental elements such as rain and are controlled primarily by burning and sorting by scavenger workers.

In Lagos, solid waste is deposited in three major sites namely, Olushosun, Solous and Abule Egba, all three sites are between 17-40 years of age. Olushosun ($6^{\circ}35'33.83''\text{N } 3^{\circ}22'35.58''\text{E}$) is located on an area of 42 hectares and was opened around 1976. It is the largest of the three sites with an estimated 6000 metric tons of waste deposited daily and it is located in the center of Lagos (MoELS, 2010). The Solous I dumpsite ($6^{\circ}34'14.52''\text{N } 3^{\circ}15'12.12''\text{E}$) was the first of five dumpsites in the area and is no longer an active dumpsite. Although burning and scavenging continues on site, LAWMA no longer dumps refuse on Solous I. It is located on an area of 3-hectares and it was opened in 1996. The average waste load per day was about 1000 metric tons of waste per day (Longe et al., 2007). Abule Egba dumpsite ($6^{\circ}87'13.32''\text{N } 3^{\circ}38'11.39''\text{E}$) is the second oldest site and was opened in 1982. It is located on 21-hectares of land and is still an active LAWMA site (Olowofela et al., 2012). These three dumpsites are surrounded by neighborhoods, commercial and business centers. It is estimated that majority of the waste deposited at these sites are vegetables, plastic, paper

products, and medical waste amongst others. Private sector operators collect the waste from homes, commercial, agricultural and industrial sources (MoELS, 2010 & Taiwo, 2009).

The major issue in waste management in Lagos State is due to the inability of LAWMA to effectively gather and dispose of the growing amount of waste generated by the large population (Kofoworola, 2007). LAWMA uses burning to reduce the waste mass (Olowofela, 2012), and this pollutes the air around these dumpsites and also releases harmful by-products of the contents of the disposed waste such as dioxins, furans, methane and PAHs (Kurian, 2002). Another limitation to waste management is the lack of knowledge and poor practice of illegal dumping by some inhabitants of the State. Many people are not well informed on the negative environmental effects of disposing refuse in unassigned waste sites, as is widely practiced. In addition, the use of waste scavengers as a means of sorting and recycling at these sites, although effective in reducing the waste is hazardous (Kofoworola, 2007). These workers are not provided with protective gear. They are exposed to airborne pollution via inhalation of harmful fumes during the scavenging process. This is exacerbated when the waste is controlled with intentional burning and during unintentional fires due to natural combustion when methane gas is in excess (Kurian, 2002). Waste management workers and scavengers (predominantly young men and boys) are also at risk of injury and infection from medical waste, fecal matter, toxic waste and many other harmful exposures.

Therefore, the inappropriate method of open dumpsite system that has been practiced in Lagos State for over forty years is of environmental and public health importance. The

environmental implications of the Lagos State waste management system are numerous and well documented, with fewer studies on the health effects (Taiwo, 2009 & Kofoworola, 2007). The placements of these dumpsites are believed to be for convenience rather than *a priori* knowledge on favorable geology, hydrogeology or environmental protection (Karian, 2002). Although all three major dumpsites are managed by LAWMA, their placement within the State is mostly unplanned and may endanger many Lagos communities in close proximity to these sites. The Lagos State Government is moving towards controlled and sanitary landfill systems, but this change may take years to accomplish due to financial burdens and commitment (MoELS, 2010)

2.3. Water sources in Lagos

The most prominent topographical feature of Lagos is surface water bodies and wetlands; these make up forty percent of the State's allocated land area. The entire area of Lagos is also situated at a low elevation of approximately thirty meters above the sea level on average. Major rivers such as rivers Ogun, Solodu, Yewa and Osun, Owo, Aye, and Oworu, which drain into the Lagos Lagoon, also characterize the State. During the rainy season from May - August, there is flooding in most parts of the State, with lower lying areas with the worst outcomes (MoELS, 2010). Since most of the surface waters drain into brackish lagoons, Lagos inhabitants rely on two main sources of water. The Ogun River is a primary water source for pipe-borne water supply in the State, while other inhabitants rely on hand dug wells, shallow boreholes, and private water supply from uncharacterized sources (MoELS, 2010).

Lagos State is still using the first waterworks system created during the early years of the State's development, with few additions made when the mini-water works were created. Therefore, population expansion has not been met by the expansion of the water works system. The Lagos Water Corporation (LWC) is the State government's agency for water provision [Figure A] and they have not been able to reach the needs of all the State inhabitants and thus people resort to various means to collect fresh water. For example, according to the LWC, the water demand in Lagos in 2007 was approximately 1.4 million liters per day, but only about seven hundred thousand liters per day was supplied. Even with the addition of mini-water works around the State, the supply of clean water still does not meet the need. Therefore, it is estimated that only about 4 million of the State's 9-17 million inhabitants have access to piped water (MOELS, 2010).

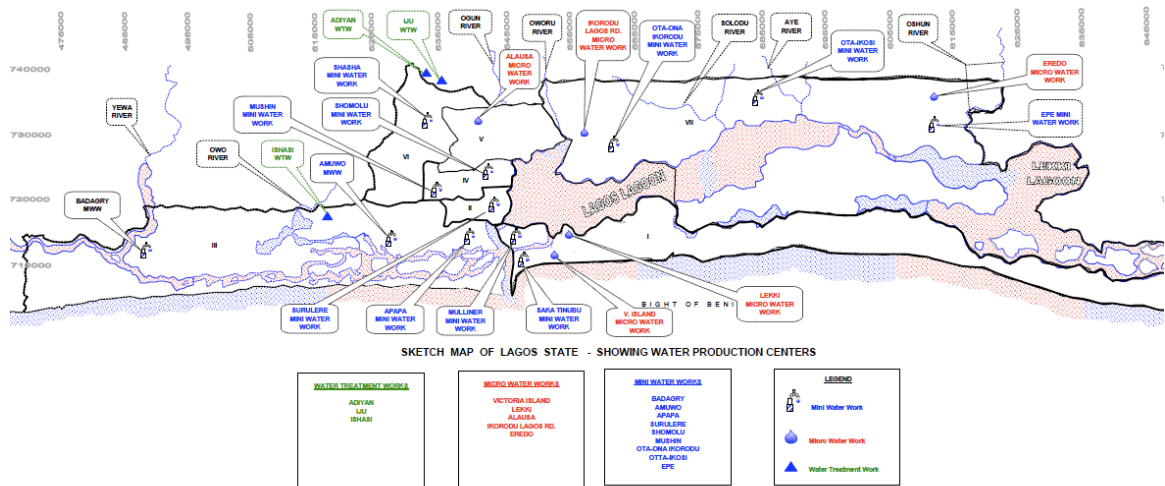


Figure A: Showing the designated water production centers in Lagos; accessed from Lagos State Base Map Management (http://www.lagoswater.org/lwc_pdf/management.PDF)

Majority of Lagos Inhabitants rely on the primary aquifer for fresh water, since less than thirty percent of State inhabitants receive pipe-borne water. This practice is legal only with a permit from the Town Planning Committee, but it is generally unregulated and boreholes and wells are usually not dug to the pre-specified 100-meter depth. This poses a strain on the ground water aquifers as well as on the structural capacity of the lithosphere in this area. In addition, improperly dug wells and boreholes may be tapping into parts of the primary aquifers that are prone to contamination from multiple industries and uncontrolled environmental hazards. Although the state has made attempts to curb illegal water tapping, the main challenge to water distribution in the State is the lack of adequate power supply to facilitate the distribution of water to all homes (Egwari & Aboaba, 2002). Regardless, the availability and pursuit of clean water is one that continues to plague this mega-city and continued efforts by the State Government to curb illegal tapping of water have been ineffective and inconsistent (MoELS, 2010).

2.4. Geology and Hydrogeology of the study area

To evaluate the permeability of leachate and other chemicals through the surface to groundwater around Lagos, an understanding of the geology of the study area is essential (Longe & Enekwechi, 2007). Lagos State has a complex lithology with alternating sequence of sand and clay deposits. There are three main aquifer horizons in the sub-surface geology of Lagos. The primary aquifer is found at a depth of 38 meters above the sea level. It has an average thickness of 8m and is the main layer tapped for water through shallow wells. These wells are prone to contamination due to the nearness of the aquifer to the surface. It consists of relatively loose sand that changes in depth to a fairly consistent layer of sandy clay soil as

it approached the secondary layers. The secondary aquifer has an average thickness of 10-25 meters and is tapped by boreholes and mini water works in Lagos. The secondary aquifer is found at 42-108 meters below the sea level by the coast and between 10-20 meters above the sea level further inland. It has a thickness of 6-19 meters of medium-coarse grainy sand, underlain by relatively impermeable clay. The third aquifer is tapped by wells exceeding 80 meters in depth. It occurs between 30-100 meters below the seas level in areas close to the coast, with a thickness of 10-35 meters and has an alternating sequence of clay and sandy soils. It is the main water source for mini-water works and legally constructed wells within the State (Longe et al., 1983).

2.5. Polynuclear aromatic hydrocarbons

PAHs are organic compounds that are produced when complex organic substances undergo incomplete combustion or are exposed to high-pressure processes. They are made up of 3 or more conjugated aromatic rings with only carbon or hydrogen atoms; differences in the property of each PAHs is due to ring arrangement. They are solid and have a low volatility at room temperature, are relatively insoluble in water and have a high molecular weight (200 – 500 amu). They tend to be light sensitive and can easily degrade to simpler substances (ATSDR, 2009). Although some PAHs occur naturally in the environment, most are produced through anthropogenic processes such as incomplete combustion of refuse, tires, petroleum, coal, from motor exhaust and smoking. PAHs are ubiquitous and persistent in the environment and can be found in soil, water, air and some foods (ATSDR, 1995).

Issues of water & air quality in the United States led to the creation of the Environmental Protection Agency. Likewise, in Lagos State a similar body called the Lagos State Environmental Protection Agency (LASEPA) was created in 1996. With a similar vision as the US EPA, it has the goal to protect the Lagos environment while regulating effluents from industries and other sources of possible environmental hazards (LASEPA, accessed 2013). Unlike the US EPA, LASEPA is yet to create water quality standards for Lagos State, and there are presently no known national standards. Therefore, majority of water quality studies have focused on biological and metal contaminants and have been performed by researchers in academia. There is limited knowledge on the presence of organic compounds such as PAHs in groundwater in Lagos, and the possible health effects are also untested. PAHs are known carcinogens (ATSDR, 1995) and the US EPA in 1980 developed ambient water quality criteria to protect humans from environmental abuses that may lead to drinking water contamination. The EPA thus set a maximum contaminant level (MCL) for benzo(a)pyrene, the most carcinogenic PAHs, at 0.2 ppb (0.0002 mg/L). Other PAHs with set MCLs include benz(a)anthracene (0.1ppb), benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, and chrysene at 0.2ppb, dibenz(a,h)anthracene at 0.3 ppb and indeno(1,2,3-c,d)pyrene at 0.4ppb (US EPA, 2009). It should be noted that generally, the EPA's MCL for PAHs in drinking water is 0.2ppb (ATSDR, 2009).

The exposure pathways and biological fate of PAHs is complicated, but well studied. Once emitted into the environment, specific compound factors such as the molecular weight and solubility determine the fate of PAHs. Ingestion, inhalation, dermal absorption, breast milk, and placental transfer are common methods for PAHs exposure. Also, it is difficult to

attribute a health effect to specific PAHs as people are exposed to multiple compounds at a time. People working in industrial and waste management settings have a greater likelihood of exposure to PAHs. Smokers are also susceptible to direct exposure to PAHs as well as second hand smokers (ATSDR, 1995). Since PAHs are known to be present in breast milk and can be passed through placental transfer, a growing fetus can also be exposed. Environmental studies have also evaluated the linkage between industries, dumpsites and pollution of soil, water and air. Therefore if PAHs are found in large concentrations in such areas, surrounding populations may also be affected (ATSDR, 2009). PAHs distribution is guided by the lipophilic characteristics of each compound. Once these compounds are absorbed, they enter the lymph, and circulate in the blood. Metabolism of PAHs takes place in numerous organs such as liver and kidneys, adrenal glands, testes, thyroid, lungs, skin, sebaceous glands, and small intestines. The main site of metabolism is in the liver via CYP enzymes of the P-450 mixed function oxidase system. PAHs are broken down into smaller metabolites within the body such as epoxides, then to dihydrodiol derivatives and phenols. They are then excreted in bile, breast milk and urine and sometimes stored in adipose tissue. Pyrene is often used as a marker of general PAHs exposure and a commonly measured biomarker found in urine is 1-hydroxypyrene (ATSDR, 1995).

The effects on human health depend on the concentration, the type of PAHs and the exposure an individual is subjected to (DHGSA, 2009). The toxic nature of PAHs is ascribed to the transformation during metabolism that creates reactive metabolites. Therefore not all PAHs are of the same toxicity due to differences in structure that affect metabolism. The biologic effective dose – amount that reaches target cell – is another factor that determines

the pathogenicity of PAHs exposure. The main pathway of carcinogenesis is therefore through PAHs metabolite interaction with DNA. When PAHs reactive metabolites join with DNA to form adducts, they can affect the normal cell replication cycle especially during differentiation or growth. Therefore cells that are most susceptible to PAHs exposures are those with rapid replicative turnover such as cells of the lungs, skin and bone marrow, as seen in carcinogenesis. In addition, there is evidence of genetic susceptibility to carcinogenesis when exposed to PAHs, primarily in relation to the main metabolism enzymes like the P-450 system. The most significant health outcome as a result of chronic PAHs toxicity is cancer. In animal studies, an increase of skin, lung, bladder, liver and stomach cancer have been well documented (ATSDR, 2009).

2.6. Physical properties of PAHs that determine flow in groundwater

It is important to understand the movement of PAHs in groundwater to be able to determine the potential for adverse health and environmental outcomes. Since PAHs are persistent, semi-volatile, organic compounds that have distinct physical properties, each PAH compound may have a different fate within the environment. The principles behind the dispersion of organic chemicals in groundwater are not well defined beyond the specific physical properties of compounds such as solubility, size, boiling point, and melting point amongst others. Of those tested in drinking water, the most water soluble PAHs (1.93 mg/L - 0.0012 mg/L at 25° C) are pyrene, phenanthrene, fluoranthene, fluorene, benzo(a)anthracene, benzo(b)fluoranthene, acenaphthene, acenaphthylene and anthracene (ATSDR, 2009). Also PAHs are generally grouped into smaller molecular weight compounds such as naphthalene, phenanthrene, fluoranthene, fluorene, while the larger

molecular weight compounds are chrysene, benz(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, dibenz(a,h)anthracene and indeno(1,2,3-c,d)pyrene. Solubility in water can affect how much and how far PAHs will be transported in groundwater. In laboratory studies simulating the movement of PAHs through sediments and into groundwater, compounds with the smaller molecular weight were observed to move more rapidly than larger compounds (Gidley et al., 2012). In addition, each PAH compound has a unique rate of biodegradation and photodegradation that accounts for how long it will remain in the environment. One way to measure PAH degradation in groundwater is through dissolved oxygen level and biological activity, since oxygen is needed to activate the aromatic ring. Generally, the biodegradability of PAHs decreases with an increase in molecular size. If the rate of groundwater transport is faster than the rate of PAH biodegradation, the possibility of human populations coming in contact with polluted water is high. Therefore, an assessment of the groundwater flow, the adsorption properties of the aquifer soils, rates of PAH degradation and demographic and environmental constraints provide a complete account of point of contact within a population (Landmeyer et al., 1998).

2.7. GIS and Public Health

Geographic representation of the study area can be used to analyze environmental data for spatial factors; therefore an understanding of this method in public health is useful. Geographic information system (GIS) in support of public health research has become a means of improving study design, implementation and decision making efforts within the field. The utility of GIS transects environmental studies, health policy, infectious disease, disaster relief and more. GIS technologies are primarily used to produce or enhance policy

reports and research. Therefore, GIS technologies have the capability to show complex results quickly and in a clear manner (Richards et al., 1999). In addition, the use of remotely sensed data is very effective for data that is far away. Satellites such as the Shuttle Radar Topography Mission and the Advanced Spaceborne Thermal Emission and Reflection Radiometer (ASTER) have been used to collect data remotely. This includes world data on land coverage, soil type, elevation, temperature and rain amongst others. These datasets enable researchers to enhance research through descriptive and analytical maps from regions that may be difficult to reach. Likewise, GIS technology is used in this study to improve the knowledge of PAHs in groundwater. It is also used to present the study results in a clear and useful manner for other researchers working on groundwater contamination in this area.

2.8. Gaps in literature

Although there is vast knowledge on the state of environment, on the solid waste collection systems and on water allocation in Lagos State, this knowledge has not informed conclusive health outcomes. Many studies have looked at the health effects of PAHs exposure at many sites worldwide, but no known studies were found for the study site or within Lagos, Nigeria. The lack of an up-to-date health registry is another factor that is unaccounted for in the literature and at the State or Local government level. In addition, physical characteristics such as soil type, rainfall and other region specific variables that could inform the dispersion of PAHs are not well defined or publicly available for Lagos State. The hydrology in Lagos is not well documented as the most recent hydrology data are from the 1980s. Therefore, it is unclear if communities very close to dumpsites are at risk if they utilize groundwater within those areas. There is also limited knowledge on the depth of wells and borehole within the

State. The depth information would be useful in determining what layer of the aquifer the wells are tapping into and therefore the possibility for contamination.

Although these lapses, affect the depth of this study, they also guided the study scope and application of results. For example, prior hydrology knowledge of the study area would have improved the sampling plan for this study. Therefore this data was developed post-study based on the field data collected and additional readily available spatial data. Regardless, there is a depth of information to support the evaluation of open dumpsite contamination of ground water in Lagos Nigeria. Therefore, this evaluation will not only add to the growing body of environmental knowledge in Lagos, but it will also direct future studies that can fill the remaining gaps.

Chapter 3: Methodology

3.1. Hypotheses

Hypothesis 1: PAHs are not present in water samples from wells in homes around Solous I and Olushosun dumpsites.

Ho: Mean levels of PAHs in Samples at S & O = 0

Ha: Mean levels of PAHs in Samples at S & O \neq 0

Where: S = Solous I and O = Olushosun

Hypothesis 2: If present, PAHs level in water samples from homes around Solous I and Olushosun are not different.

Ho: Mean levels of PAHs in Samples at S = O

Ha: Mean levels of PAHs in Samples at S \neq O

Hypothesis 3: If present, PAHs level in water samples from wells in homes around Solous I and Olushosun are less than MCL (US EPA MCL = 0.0002 (mg/L))

Ho: Mean levels of PAHs in Samples at S & O < MCL

Ha: Mean levels of PAHs in Samples at S & O > MCL

Hypothesis 4: If present, PAHs level in water samples from control site is less than PAHs levels in water samples in homes around Solous I and Olushosun.

Ho: Mean levels of PAHs at control site < Samples around S & O

Ha: Mean levels of PAHs at control site > Samples around S & O

3.2. Study Design

The sampling study design was replaced due to unforeseen changes while on the field. The steep cost of analyzing water samples for PAHs in Lagos allowed for a cap of eight samples per site. The dumpsites were selected because they are two of the three State regulated waste management sites that are geographically separated. In addition, Olushosun is the second oldest site while Solous I is the youngest State managed site. Lagos State has two major climate seasons, a dry and rainy season. The sampling period selected corresponded with the

rainy season and a time when PAH levels were expected to be higher than at baseline (Manoli & Samara, 1999). The neighborhoods where sampling took place were selected based on their proximity to the dumpsites. All home samples were within 1000 meters of the dumpsite. Household selection was based on a case-by-case response, giving permission to retrieve water from wells and boreholes. This led to an arbitrary sampling of homes with unknown bias within each study site.

The spatial study design was based on providing a descriptive representation of the study site. Population density, rivers and streams, and the local government area (LGA) division data were collated from the Lagos Bureau of Statistics, as well as freely available data sources online. These data were used to show population density around the selected dumpsites, industrial areas in Lagos and to create other descriptive maps that informed the discussion section. The main focus was on the LGAs where the dumpsites were located, namely Alimosho and Kosofe LGAs for Solous I and Olushosun respectively.

3.3. Ethics

This project did not entail human research and was therefore exempted from review by the Emory University International Review Board. In addition, all sample sites have been spatially adjusted to ensure exact locations of sampled homes are protected.

3.4. Field sampling

The study was conducted during the first rainy season peak in July 2012. Water samples were collected over a two-day period, July 9th and July 10th. Using Amber borosilicate glass

containers with PTFE-lined tops, a total of 8 samples were collected from the Solous I site and 6 samples from the Olushosun site. Samples were collected from wells and boreholes in labeled vials and the temperature of the water samples was recorded on site using a thermometer. Solous I samples were labeled S1- S8 and Olushosun samples were labeled O1-O6. In addition, the GPS coordinate of each sampling point was recorded as well as the distance from the dumpsite. Samples were then stored in a refrigerator at 4°C for a maximum of 10 days until analysis.

3.5. Laboratory Tools

All glassware were washed with detergent and rinsed with tap water. Deionized water was then used to rinse the glassware, followed by an acetone and hexane bath for the removal of polar and non-polar compounds. All glassware was stored in a drying oven until use.

3.6. Reagents

Primary solvent, dichloromethane (Sigma Aldrich, Jos, Nigeria) and the acetone (J.T Baker, Lagos, Nigeria) used in standard solution preparation of PAHs in concentrations of 10, 20, and 30 (mg/L) were prepared prior to analysis.

3.7. Extraction procedure

Extraction was performed with the liquid-liquid extraction methodology and 100mL of the sample was measured with a graduated cylinder and extracted with 20mL of dichloromethane (DCM) in a separatory funnel. The mixture was shaken for 2 minutes and allowed to separate for 5 minutes. The bottom layer was decanted into a pre-cleaned and

labeled flask and wrapped in foil. This step was repeated twice per sample (60 mL DCM total) and all samples were stored in the refrigerator until GC-FID analysis. The separatory funnels were cleaned between sample extractions with a detergent and tap water rinse followed by deionized water rinse. The funnel was then rinsed with acetone and again with dichloromethane. A clean-up step was deemed unnecessary since the samples were well and borehole water that were not notably contaminated with other particulate matter.

3.7. Concentration and Drying

An evaporation step using a stream of gaseous nitrogen was passed over the solution to help volatilize the solvent thereby concentrating the PAHs. Each sample was reduced to a volume below 3mL and was recorded for each sample. Anhydrous sodium sulfate was then used to remove the excess water and the extract was stored in small amber vials.

3.8. Instrument

A Thermo- Finnigan Traceultra GC equipped with flame ionization detector and a DB-5 column was used in the PAHs analysis. Helium was used as the carrier gas with a set column flow of 16.5 mL/min. The oven was set to 40°C for 0.50 minutes and then it increased from 40°C to 320°C at 20°C /min at hold for 15 minutes. The injection port temperature was at 300°C and samples were run in a split mode with a mean split pressure at 15.9psi. The detector was FID set at 300°C, with nitrogen makeup gas at 25mL/minute and hydrogen gas at 35mL/min (4).

3.9. Experiment

A calibration mixture containing naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, benzo[e]pyrene, dibenzo[a,h]anthracene, indeno[1,2,3-cd]pyrene, and benzo[ghi]perylene at 2.0 µg/mL per component was prepared in dichloromethane. This mixed stock solutions containing equal concentrations of analytes was used in preparing standard solutions of increasing concentration 10, 20, and 30 mg/L, following an external standard method (USEPA, 1984). Blank solutions and spiked solutions were analyzed in order to ensure adherence to quality control procedures. Chromatograms were obtained and identified and the quantification was performed using the Chromcard software compatible only with Traceultra GC. A micro syringe was used to inject 2µl of sample extract into the GC inlet and allowed to run according to the settings described. All samples were analyzed using the above settings. PAHs concentration detected by the GC-FID in mg/L was used to determine the final concentration of PAHs in each sample after dilution and re-concentration.

The formula below was used for the calculation:

$V_w/V_t = \text{Concentration factor}$

$C_{gc}/\text{Concentration factor} = \text{Final PAHs concentration in sample (mg/L)}$

Where:

$V_w = \text{Total Volume of water extracted (100mL)}$

$V_t = \text{Total Volume of total extract (mL per sample)}$

V_s = Total Volume of solvent used (60mL DCM)

C_{gc} = Concentration read by GC-FID per PAH molecule ((mg/L))

3.10. Method validation

A procedure blank was analyzed periodically and it was prepared using the same reagent and procedures for the samples. In addition, to assess efficiency of recovery procedure, two of the 14 samples were spiked with 20(mg/L) PAHs standard. Since the LoD calculation performed in the lab was insufficient, the LoD was determined based on an interpolated method using the calibration curves provided by the laboratory. Percent recovery calculations = $\{(Spike\ result/expected\ result) * (spike\ volume/original\ volume)\} * 100$

3.11. Statistical Analysis

Of the 16 PAHs compounds tested, only sites with at least four compounds present were used in this analysis (7 compounds). SAS 9.3 was used for all statistical analysis for this data set. Since the data set contained an average of 10-50% non-detect values per compound, Monte Carlo-based simulation (MCS) of a thousand repetitions, with a triangular distribution below the LOD was used to impute values for the non-detected PAHs levels. The US EPA and many other environmental agencies use the MCS method to better predict the contamination levels of sampled sites (Helsel, 2005). Standard analyte concentrations used to determine calibration curve were beyond the sample ranges. An in-depth literature review of PAHs analysis with GC-FID helped determine a plausible LOD range (Table 2, Appendix). In the simulation method, all data below the LOD were randomly selected from their corresponding uncertainty distribution. The distribution range was based on a priori

knowledge of the sample distribution, literature estimates of LOD ranges from GC-FID analysis of PAHs and the lowest detected sample concentrations per compound.

Since the concentrations in the calibration curve from the laboratory analysis had a larger range than the concentrations found in the samples, two methods (laboratory derived LoD and literature review) were evaluated to account for the non-detects. The in-depth review for LoD directed the Monte Carlo based simulation. To determine the variance in the MCS imputation method, an uncertainty interval for each distribution was created with a one-sample t-test procedure. The mean was evaluated for each dataset that was generated, creating another dataset with 1000 confidence intervals. The confidence interval for the mean of each distribution at the 2.5 and 97.5 percentiles was used to determine the total uncertainty interval.

Once the non-detected values were statistically imputed, the four study hypotheses were tested. The difference between PAHs concentrations around Solous I and Olushosun were evaluated with a non-parametric Wilcoxon rank sum test. The non-parametric test was used due to small sample size ($n=14$). Average sample concentrations were compared to the MCL of PAHs in drinking water (0.0002 (mg/L)) and to zero, using a non-parametric Wilcoxon signed rank test. Finally average sample concentrations were compared to that found at the control site.

Chapter 4: Results

4.1. Preliminary Analysis

Of the 16 PAHs measured in the water samples, only 7 appeared consistently in at least 4 sites. The PAHs, BAA, BAP, BKF, BBF, PYR, CHR & FLU were chosen as the compounds of focus for the statistical analysis. The percent recovery for PYR from site O6 was 88%, 84% from site O5, and 93.95% for BBF. Total PAHs concentration ranged from 0.0026 – 0.2043 (mg/L), while human carcinogenic PAHs (BAP, BBF, BKF, BAA, and CHR) ranged from 0.001 – 0.133 (mg/L). The sampling site S6 had the highest total PAHs concentration, while S3 had the lowest concentration [Table 1]. Since the average concentrations of BAP, BKF, BBF, & PYR were statistically significant at the 95% confidence level, we reject the null of hypothesis 3 for these compounds. Therefore average concentrations of the 4 PAHs are significantly higher than the USEPA MCL [Table 2].

Table 1: Total PAHs concentration by sampling site (mg/L)

<i>Site</i>	<i>Human Carcinogenic PAHs*</i>	<i>All PAHs**</i>
S1	0.0047	0.0117
S2	0.0028***	0.0103
S3	0.0010	0.0026
S4	0.0189	0.0252
S5	0.0287	0.0455
S6	0.1327	0.2043
S7	0.0229	0.0350
S8	0.0294	0.0595
O1	0.0020***	0.0092
O2	0.0390	0.0522
O3	0.0077	0.0281
O4	0.0058	0.0154
O5	0.0070	0.0184

O6	0.0041***	0.0070
----	-----------	--------

*Prior to MCS Total Human Carcinogenic PAHs (US EPA classification), includes all 16 priority PAHs

** Prior to MCS Total PAHs concentrations, includes all 16 priority PAHs.

***Based on MCS values

Table 2: PAHs concentration in groundwater samples in (mg/L), prior to MCS

<i>Compound</i>	<i>N</i>	<i>Mean</i>	<i>STD</i>	<i>Minimum</i>	<i>Maximum</i>	<i>P-value*</i>
BAA	4	0.0095	0.0032	0.0051	0.0120	0.13
BAP	6	0.0076	0.0055	0.0010	0.0172	0.031
BKF	6	0.0113	0.0092	0.0020	0.0229	0.031
BBF	8	0.0075	0.0034	0.0025	0.0139	0.008
PYR	13	0.0102	0.0061	0.0039	0.0288	<0.0001
CHR	4	0.0217	0.0328	0.0035	0.0701	0.13
FLU	4	0.0057	0.0009	0.0047	0.0068	0.13

*Hypothesis 3 where H_0 : Mean levels of PAHs in Samples at S \leq O < MCL.

4.2. Monte Carlo Simulation Analysis

After MCS, the average concentration of PAHs ranged from 0.0027 – 0.0095 (mg/L), FLU had the lowest levels and PYR had the highest levels. All PAHs concentrations were statistically significantly at a 95% confidence level, we reject the null of hypothesis 1 and conclude that mean PAHs level are greater than zero at all sampled sites [Table 3]. Also, comparing mean PAHs concentrations to the MCL showed that concentrations were significantly different from the MCL at a 95% confidence level. Therefore we reject the null of hypothesis 3 and conclude that PAHs concentrations (post-MCS) still exceed the USEPA MCL. Comparing PAHs levels between Solous I and Olushosun, showed that concentrations were *not* significantly different at the 95% confidence level. Therefore we fail to reject the null of Hypothesis 2, and conclude that PAHs level at both sites are *not* statistically different [Table 4]. Also, comparing PAHs levels between the control site and all sites revealed that PAHs concentration at the control site is significantly different from the levels found at the two dumpsites at the 95% confidence level. Therefore we fail to reject

the null of hypothesis 4 and conclude that PAHs level at the control site are less than levels found at all sites [Table 5]. The final part of this analysis was the MCS total uncertainty interval, validating the imputed non-detects. Results showed that the null value (zero) is *not* within the confidence intervals for all compounds *except* CHR [Table 6]. The distribution of the PAHs range imputed for the non-detects is presented below, and provides a practical comparison of the MCS total uncertainty interval to the data used for this analysis [Table 7].

Table 3: PAHs concentration in groundwater samples (mg/L), after MCS

<i>Compound</i>	<i>N</i>	<i>Mean</i>	<i>STD</i>	<i>Minimum</i>	<i>Maximum</i>	<i>P-value *</i>	<i>P-value **</i>
BAA	14	0.0037	0.0043	0.00001	0.01197	< 0.0001	0.001
BAP	14	0.0034	0.0050	0.00002	0.01719	< 0.0001	< 0.0001
BKF	14	0.0053	0.0078	0.00010	0.02292	< 0.0001	< 0.0001
BBF	14	0.0045	0.0044	0.00022	0.01387	< 0.0001	< 0.0001
PYR	14	0.0095	0.0063	0.00134	0.02878	< 0.0001	< 0.0001
CHR	14	0.0070	0.0185	0.00001	0.07095	< 0.0001	< 0.0001
FLU	14	0.0027	0.0021	0.00061	0.00682	< 0.0001	< 0.0001

* Hypothesis 1 where H_0 : Mean levels of PAHs in Samples at $S \neq O = 0$

** Hypothesis 3 where H_0 : Mean levels of PAHs in Samples at $S \neq O < MCL$.

Table 4: PAHs concentrations in groundwater samples by site (mg/L)

<i>Compound</i>	<i>Mean Score – O*</i>	<i>Mean Score – S**</i>	<i>P- value***</i>
BAA	0.0035	0.0039	0.87
BAP	0.0022	0.0044	0.41
BKF	0.0021	0.0077	0.19
BBF	0.0037	0.0051	0.57
PYR	0.0084	0.0104	0.55
CHR	0.0019	0.0108	0.37
FLU	0.0023	0.0030	0.51

* O = Olusbosun, with N = 6

** S = Solous I, with N = 8

*** Hypothesis 2 where H_0 : Mean levels of PAHs in Samples at $S = O$

Table 5: PAHs concentration in groundwater samples Control vs. Both Dumpsites (mg/L)

<i>Compound</i>	<i>Mean – D*</i>	<i>Mean – C**</i>	<i>P- value***</i>
BAA	0.0037	0.0003	0.22
BAP	0.0034	0.0007	0.30
BKF	0.0053	0.0011	0.30
BBF	0.0045	0.0006	0.19
PYR	0.0095	0.0053	0.26
CHR	0.0070	0.0014	0.27
FLU	0.0027	0.0003	0.14

* D signifies samples from Solous I & Olushusun dumpsites, N= 14

** C signifies sample from Control site, N= 1

*** Hypothesis 4 where H_0 : Mean levels of PAHs at control site < Samples around S & O

Table 6: Total Uncertainty Interval for MCS (mg/L)

<i>Compound</i>	<i>N</i>	<i>Mean</i>	<i>Mean LCL</i>	<i>Mean UCL</i>
BAA	1000	0.0039	0.0012	0.0058
BAP	1000	0.0034	0.0005	0.0060
BKF	1000	0.0052	0.0008	0.0093
BBF	1000	0.0046	0.0018	0.0066
PRY	1000	0.0095	0.0058	0.0127
CHR	1000	0.0070	-0.0033	0.0165
FLU	1000	0.0026	0.0014	0.0037

Table 7: Non-detected PAHs concentration imputed by MCS (mg/L)

<i>Compound</i>	<i>Minimum</i>	<i>Mean</i>	<i>Maximum</i>
BAA	0.000006	0.0014	0.0043
BAP	0.000024	0.0003	0.0006
BKF	0.0005	0.0008	0.0016
BBF	0.0002	0.0024	0.0139
PRY	0.0013	0.0013	0.0013
CHR	0.000006	0.0011	0.0023
FLU	0.0006	0.0015	0.0028

Chapter 5: Summary

5.1. Discussion

The current waste management system in Lagos may be detrimental to the environment, and in the long term, may affect the health of people living near open dumpsites. Therefore, each step of this study was aimed at providing a concise description of the current environmental situation, as well as understanding some social and historical constructs of waste management in Lagos, that are of public health interest. Although this is not the focus of this study, some of these factors help understand the link between groundwater pollution and health of the populations at risk. Therefore, the overall discussion of this study will utilize distal factors (possible underlying risk factors) and indices in evaluating the analysis of groundwater contamination around open dumpsites.

5.1.1. PAHs Concentration

The quality assurance steps during the laboratory analysis helped to validate the results reported for PAHs level in the sampled water. Since the spike recovery results are above 80% it supports the accuracy of the analysis methods (storage – isolation) and shows that our method was efficient at recovering PAHs in water samples. Also, the purpose of the analytical blank was to check for the presence of contamination or other interference with the instrument that may affect the quantification of real PAHs presence in the samples. The blank results therefore support the conclusion that the instrument was generally efficient and not significantly contaminated.

Furthermore, although most sampling sites had 10 - 50% non-detected concentrations, which made statistical analysis difficult due to the “missing” values, the total PAHs level is still calculated to assess the overall PAHs concentration per sampling site. Four of these compounds are at significant concentrations, and should be further analyzed in other studies. Also, since the total sample size is 14, which violates the normality of distribution of a parametric test, non-parametric test is used to analyze the data. This method is valid for data with any distribution, regardless of normality, and is much less sensitive to outliers than the two-sample t-test.

Since the average concentration of each sample was higher than the MCL, it was assumed that the non-detected concentrations were causing a wrong estimation of the actual PAHs significance levels (Kayhanian, 2002). Non-detected values can cause inappropriate prediction of contamination levels in environmental studies, as these values can be interpreted as zero in statistical analysis. Since the presence of a non-detected compound does not mean that the compound is not present, but simply that the detection instrument is unable to measure concentrations beyond a particular value, statistical methods can be applied. The MCS method helped test this assumption since it created plausible concentration levels for the non-detects and provided a realistic picture of PAHs concentration in the samples.

The MCS method applied depends on the LoD to direct the distribution of imputed values. The LoD used in this simulation was directed by plausible values from literature because of circumstantial evidence that the calibration method performed in the laboratory was

insufficient for this study. The analyte concentration range (20, 30, 40 (mg/L)) of the standard solutions used to create the calibration curves were orders of magnitude higher than the concentration range measured in the samples. This error was due primarily to unavailability of appropriate analyte standards and lack of prior knowledge of the levels of PAHs expected in this unexplored study area. Although the total uncertainty interval had a mean range of 0.0026 – 0.0095 mg/L, the imputed values used in the analysis had a mean range of 0.0003 – 0.001 mg/L, showing that the MCS method provided realistic ranges (when compared to actual sample values) for our analysis. The minimum imputed values had a range of 0.001– 0.000006 mg/L, and a maximum range of 0.001 – 0.0006 mg/L [Table 7]. The imputed ranges are similar to that found in the literature and therefore provided the post MCS dataset with reasonable estimates.

Once the non-detected compounds were imputed, the four hypotheses of this study were tested accordingly. The public health goal for PAHs level in usable water is set as zero since this is the level at which no negative health effects is experienced. This is called the maximum contaminant level goal (MCLG). Hypothesis 1 is used to evaluate this goal and results showed that all sites had samples significantly greater than zero at a 95% confidence level [Table 3]. This signifies that there is cause for public health concern for people living and using the water sources around these open dumpsites. Also, since the age of an open dumpsite can be indicative of the pollution potential the dumpsite has (Kurian, 2002), hypothesis 2 was used to evaluate this factor. Since Solous I is a younger dumpsite than Olushosun, both sites may have different contamination potential. The results show that the PAHs concentrations found around both sites are not statistically different, despite the age

difference. Since these sites are over 5 years apart in age – the duration that dumpsites are estimated to begin impacting their environment – age might not play a significant role in the contamination capability of these dumpsites.

Furthermore, the USEPA set the MCL for drinking water at 0.0002 mg/L, and this is an enforceable and feasible level based on the availability of treatment and analytical technologies, the cost of remediation/removal of the target compounds from the environment and other testing/evaluation factors. Hypothesis 3 was used to test this factor, and the results showed that the average PAHs levels were significantly greater than the MCL. This signifies that the levels found at the sampling sites are at environmentally significant levels and therefore further analysis should be undertaken to ascertain possible health effects. Since the cancer registry in this area is not comprehensive, it is difficult to determine if the high PAHs levels (relative to MCL) have affected cancer rates in this area. This observation simply informs the State government that nearby communities tapping into contaminated aquifers could be at risk of negative health outcomes related to chronic PAHs exposure.

Additionally, PAHs were found at the control site and this infringes on the validity of the control site. Since the site was chosen based on its distance from a dumpsite and industrial activities, it was unexpected to find PAHs at this site. Further evaluation of the control site LGA showed that it is not in an area with industrial estates as we previously noted, but it is bounded by other LGAs with industrial estates [section 5.3, Figure 7]. Since exhaust fumes from motor vehicles are known to have some levels of PAHs (Manoli & Samara, 1999), this

may generally contribute to the low levels found at the control site. In addition, the control site is almost on the border of the LGA, which is next to a LGA with industrial estates. Therefore, the presence of PAHs in the water samples may be from these surrounding industries, but should be confirmed with additional evidence such as the groundwater flow information. Most importantly, the PAHs level found at the control site are significantly lower than the levels found at the sampling sites around the dumpsites. This further supports our assumptions of low-level contamination of this area by other factors.

5.1.2. Physical Environment and PAHs

An evaluation of the geography of the study sites enhances the interpretation of the baseline analysis of PAHs in groundwater. Both dumpsites are situated in relatively populous LGAs within Lagos [Figure 8 and 9]. These dumpsites are also surrounded by LGAs with the highest population of people per area in the entire State. This is important because knowledge on the groundwater flow was unavailable for our purpose and the effects of the dumpsite may extend beyond our study areas. In addition, Olushosun is situated within a LGA (Kosofe) that has industrial estates, while Solous I is not (Alimosho LGA) [Figure 7]. This is also an important observation as groundwater quality in LGAs with industrial estates is at a higher risk of pollution. Regardless, Solous I is also bounded by LGAs with industrial estates and therefore pollution from these areas may have an effect on groundwater quality. Although Solous I is currently an inactive dumpsite, it is one of three established dumpsites within the Alimosho LGA [Figure 4], and thus there are multiple avenues for open dumpsite contamination of groundwater.

The total PAHs concentrations found in water samples around Olushosun is depicted in Figure 2. The highest PAHs concentration is found on the dumpsite, while PAHs level to the South of the dumpsite have similar concentrations. To better understand the relationship between distance and PAHs concentration, a greater number of water samples must be evaluated in other areas around the dumpsite (North, East, and West) [Figure 3]. Solous I has a slightly different pattern for the relationship between PAHs level and distance as samples on the Eastern part of the dumpsite are higher than PAHs level on the Southern end [Figure 5]. This relationship is *not* distinct enough to draw concrete conclusions, but graphical evidence also supports that water sample closer to the dumpsite have lower PAHs concentrations when compared to samples further off [Figure 6]. This is yet another relationship that groundwater hydrology could clarify.

5.1.3. Limitations

A few limitations that are apparent in this study include the sample size, and the concentrations used for the calibration curve. The sample size was limited due to the availability of funds for the laboratory analysis as well as the ease of sampling on site. Prior to field sampling, the sample estimated size was 40, with 20 samples from each site, but this was impossible due to unforeseen laboratory restrictions in price for analyzing PAHs in Lagos. Also, many households around the two dumpsites were not open to the sampling of their water source, as they feared that we were government officials. This mainly affected sampling around Olushosun, as this is a site that has been greatly analyzed. Regardless, we expect that this restriction did not gravely affect the distribution of sampling as households that allowed for sampling were arbitrarily selected across the study site, in which majority of

households with boreholes/wells tap from the same source. Since the initially proposed solid phase micro-extraction technique was not used due to mismatch of the GC instrument to this technology, the alternative isolation method of liquid-liquid extraction has a different sensitivity. The recovery data helps support the accuracy of the laboratory method and is sufficient for this purpose.

Loss of PAHs could have occurred during the isolation step as well as the multiple extraction and purification steps required prior to chromatographic analysis. Also, some PAHs compounds may have been lost through natural process of photo-degradation during the storage period. The choice of analyte concentration for the calibration curve made the quality assurance and MCS evaluation difficult since the laboratory defined LoD for the instrument was not useful. A better calibration curve would have contained values closer to ranges found in usable well water and entailed 5 or more concentrations in this range. Also, the lack of knowledge on the groundwater hydrology is one that hinders the interpretation of PAHs contamination spread beyond the study site. Regardless, this study is still able to utilize geographic information data to enhance the interpretation and usefulness of the laboratory and statistical analysis of PAHs in ground water.

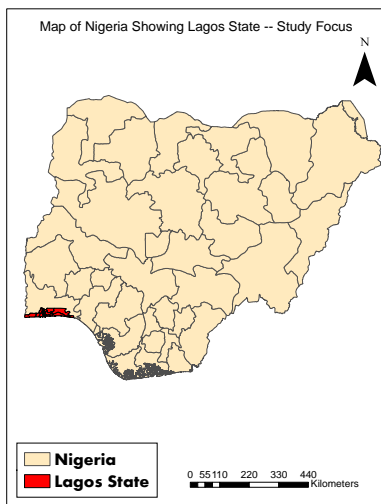
5.2. Conclusion and Recommendations

The dangers of open dumpsites and environmental contamination are widely known and an accepted cause for concern. This study is unique in its focus on usable water and in its approach of evaluating water sources from the homes of community members close to pollutant sites. As a baseline analysis, it was clear that the dumpsite does have an impact on

the water quality, especially water tapped from the first aquifer through shallow boreholes. Since well depths were unrecorded, it will be beneficial for prospective studies to evaluate this information in the classification of access to contaminated water. During the spatial evaluation of this study, there was an attempt to create a groundwater hydrology model for the study area. Unfortunately, numerous data for this model were unavailable to the public as local and State government collects them. It would be beneficial to the State government to make some of this data available for academic research as this could enhance the knowledge of groundwater contamination and help identify populations at risk. Also, the cancer registry data for this area is not comprehensive or up to date. This data could have further improved this study by evaluating trends in cancer rates per LGA and determining if there is a link between the dumpsites and cancer rates in high-risk areas.

Based on this preliminary analysis, the goal of the Lagos State government should be to transition from open dumpsites to sanitary landfills with better protection for the environment and the people. This move will include the training of service workers to manage the landfills and education of the public to emphasize the negative health effects of environmental pollution. In addition, the State government should pay close attention to the location of the landfills that they will transition to. These sites should be strategically located in less densely populated areas such as those shown in Figure 8. These measures will ensure that less people are exposed to possible contamination due to open dumpsites.

5.3. Maps & Graphs



Olushosun Dumpsite

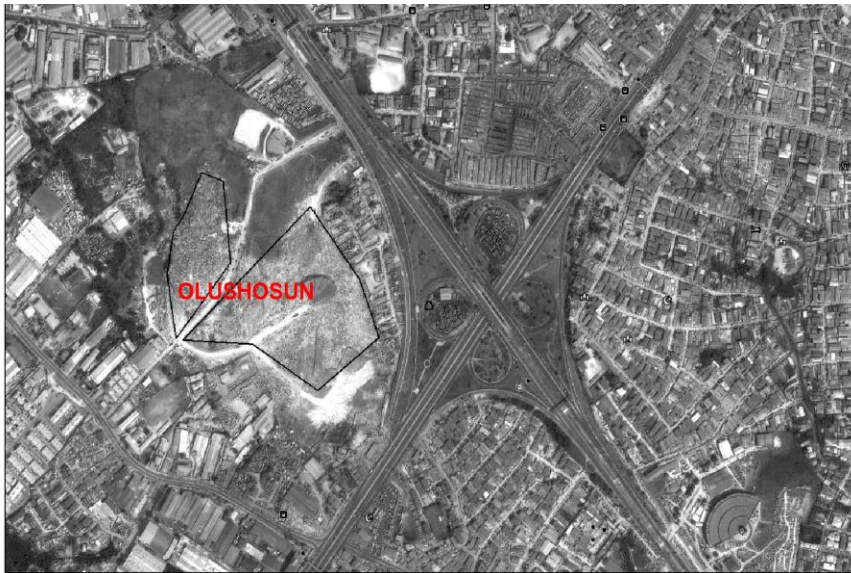


Figure 1: Study Area 1, Olushosun Dumpsite highlighted, a highly dense area with both industrial and residential areas in close proximity to dumpsite.

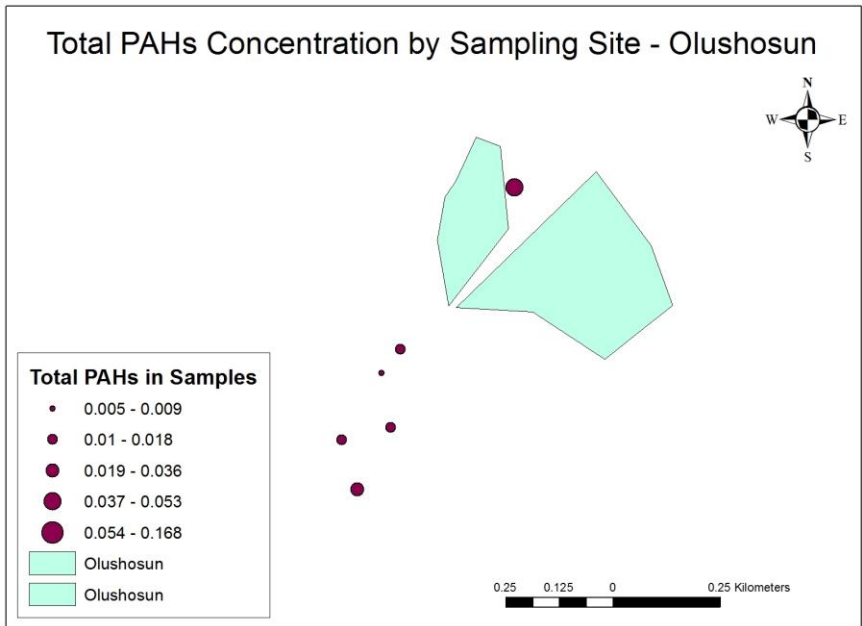


Figure 2: Depicting PAHs concentration at sampling sites relative to dumpsite, water samples south of dumpsite appear to have similar PAHs concentrations

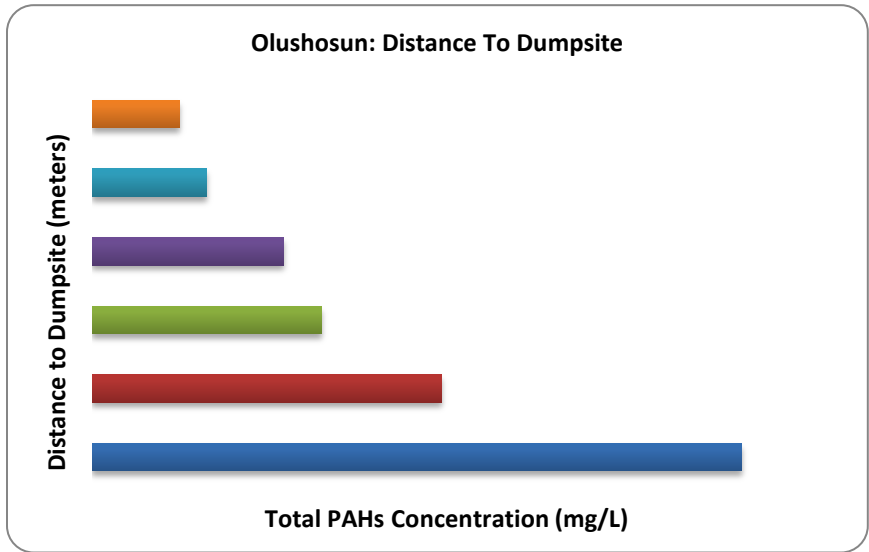


Figure 3: Graphical representation of PAHs by distance to dumpsite, except water source closest to dumpsite has highest PAHs concentration



Figure 4: Study Area 2, Solous I dumpsite highlighted, highly populated area with mostly residential communities surrounding dumpsites.

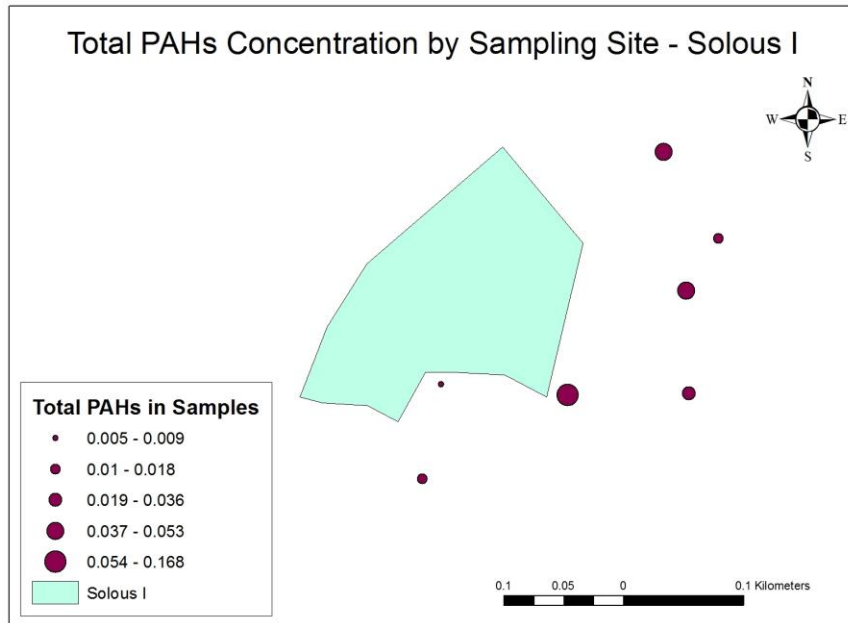


Figure 5: Depicting PAHs concentration at sampling sites relative to dumpsite, water samples from NE areas have higher PAHs concentrations.

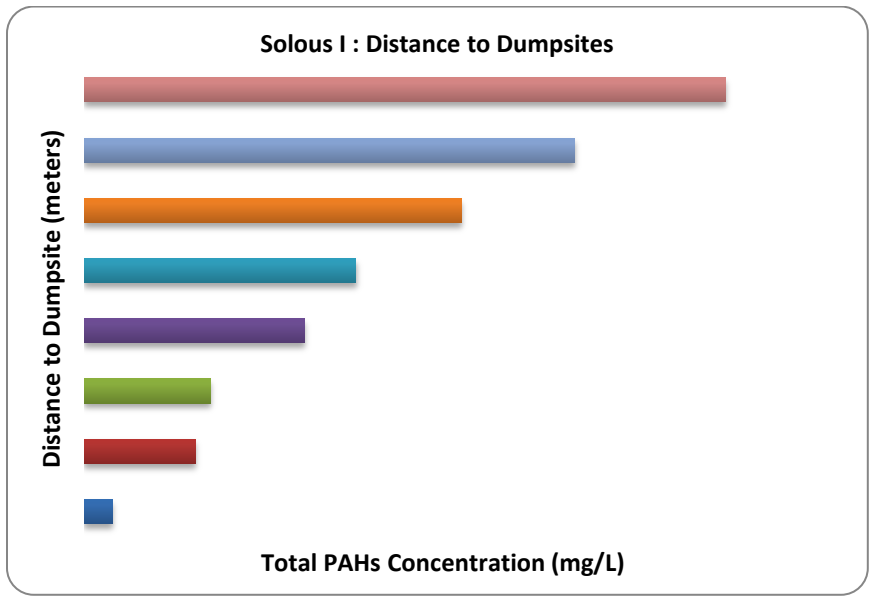


Figure 6: Graphical representation of PAHs by distance to dumpsite, no clear pattern, except water source closer to dumpsite have lesser PAHs concentrations.

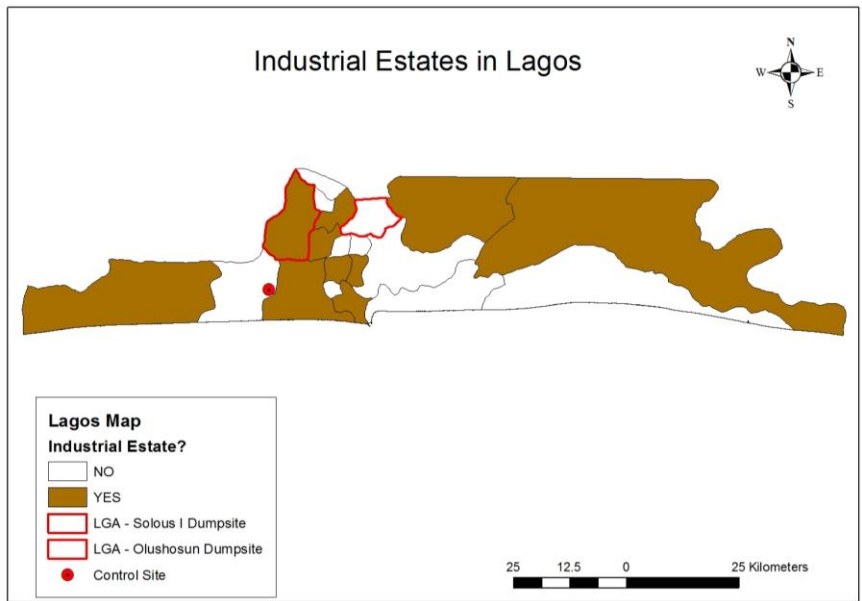


Figure 7: Officially designated industrial areas in Lagos, Olushosun is within an industrial area while Solous I is not.

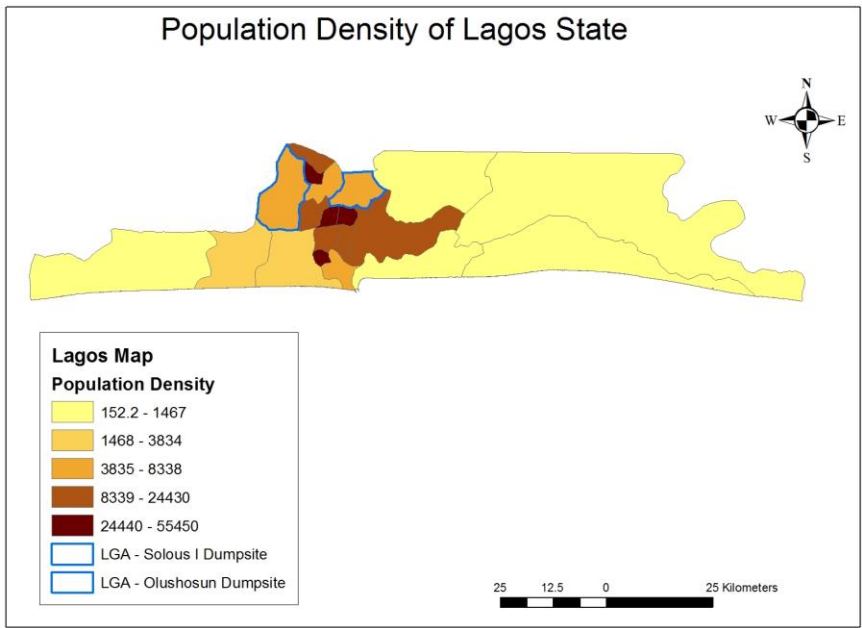


Figure 8: Population Density of Lagos State with both dumpsites in relatively high density LGA's.

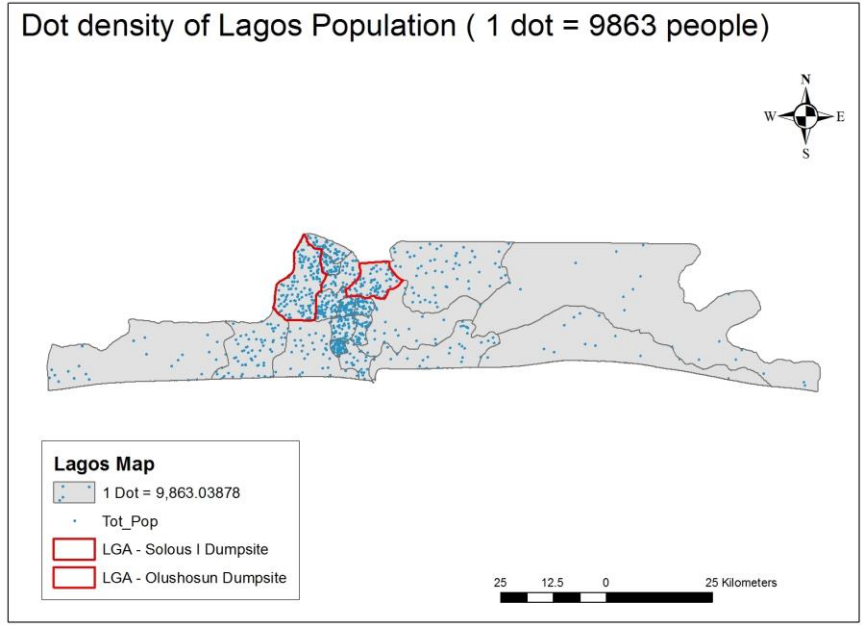


Figure 9: Dot density map with both dumpsites are in areas were majority of Lagos inhabitants reside.

References

- Abdulmunim, A. N., Chanbasha, B., Ashfaq, A. S., & Abdul Rahman, A.-A. (2012). Determination of Polycyclic Aromatic Hydrocarbons in Water Using Nanoporous Material Prepared from Waste Avian Egg Shell. *Journal of Nanomaterials*, 1-7.
- Armbruster, D. A., & Pry, T. (2008). Limit of blank, limit of detection and limit of quantitation. *Clinical Biochemist Review*, 29, S49-S52.
- Department of Health, Government of South Australia (DHGSA). (2009). *Public Health Fact Sheet, Polycyclic Aromatic Hydrocarbons (PAHs): Health Effects*. Adelaide. Retrieved from <http://www.health.sa.gov.au/pehs/PDF-files/ph-factsheet-PAHs-health.pdf>
- Doong, R.-a., Chang, S.-m., & Sun, Y.-c. (2000). Solid-phase microextraction for determining the distribution of sixteen US Environmental Protection Agency Polycyclic Aromatic Hydrocarbons in Water Samples. *Journal of Chromatography*, 879(2), 177-188. Drog, M. (2007). Dealing with Uncertainties: A Guide to Error Analysis. *Springer*, XIV(190), 24.
- Egwari, L., & Aboaba, O. O. (2002). Environmental impact on the bacteriological quality of domestic water supplies in Lagos, Nigeria. *Rev Saúde Pública*, 36(4), 513-520.
- Gidley, P. T., Kwon, S., Yakirevich, A., Magar, V. S., & Ghosh, U. (2012). Advection dominated transport of polycyclic aromatic hydrocarbons in amended sediment caps. *Environmental Science & Technology*, 46(9), 5032-5039.
- Han, D. M., Tong, X. X., Jin, M. G., Emily, H., Tong, C. S., & Song, X. F. (2013). Evaluation of organic contamination in urban groundwater surrounding a municipal landfill, Zhoukou, China. *Environmental Monitoring & Assessment*, 185(4), 3413-3444.
- Helsel, D. R. (2005). More Than Obvious: Better Methods for Interpreting Nondetect Data. *Environmental Science and Technology*, 39(20), 419A-423A.
- Hosseini, M. H., Rezaee, M., Akbarian, S., Mizani, F., Pourjavid, M. R., & Arabieh, M. (2013). Homogeneous liquid-liquid microextraction via flotation assistance for rapid and efficient determination of polycyclic aromatic hydrocarbons in water samples. *Analytica Chimica Acta*, 762, 54-60.
- Iwegbue, C. M., Nwajei, G. E., Ogala, J. E., & Overah, C. L. (2010). Determination of trace metal concentrations in soil profiles of municipal waste dumps in Nigeria. *Environmental Geochemistry and Health*, 32(5), 415-30.
- Kayhanian, M., Singh, A., & Meyer, S. (2002). Impact of non-detects in water quality data on estimation of constituent mass loading. *Water Science & Technology*, 45(9), 219-225.

- Kofoworola, O. (2007). Recovery and recycling practices in municipal solid waste management in Lagos, Nigeria. *Waste Management*, 27(9), 1139-43.
- Kurian, J. (2002). Solid waste dump sites to sustainable landfills. *EnviroVision*, B1(3), 1-14.
- Lagos State Environmental Protection Agency (LASEPA). About Us: Our Goal. *Lagos State Environmental Protection Agency*. Accessed April 17, 2013 from, <http://www.lasepa.org/goal.php>
- Landmeyer, J. E., Chapelle, F. H., Petkewich, M. D., & Bradely, P. M. (1998). Assessment of natural attenuation of aromatic hydrocarbons in ground water near a former manufactured-gas plant, South Carolina, USA. *Environmental Geology*, 34(4), 279-292.
- Langenfeld, J. J., Hawthorne, S. B., & Miller, D. M. (1996). Quantitative Analysis of Fuel-Related Hydrocarbons in Surface Water and Wastewater Samples by Solid-Phase Microextraction. *Analytical Chemistry*, 68, 144-155.
- Longe, E. O., & Balogun, M. R. (2010). Groundwater Quality Assessment near a Municipal Landfill, Lagos, Nigeria. *Research Journal of Applied Sciences, Engineering and Technology*, 2(1), 39-44.
- Longe, E. O., & Enekwechi, L. O. (2007). Investigation on potential groundwater impacts and influence of local hydrogeology on natural attenuation of leachate at a municipal landfill. *International Journal of Environmental Science and Technology*, 4(1), 133-140.
- Longe, E. O., Malomo, S., & Olorunniwo, M. A. (1983). Hydrogeology of Lagos Metropolis. *Journal of African Earth Sciences*, 6(2), 163-174.
- Maidment, D. R. (1996). GIS and Hydrologic Modeling - An Assessment of Progress. *The Third International Conference on GIS and Environmental Modeling*. Sante Fe. Retrieved from <http://www.ce.utexas.edu/prof/maidment/gishydro/meetings/santafe/santafe.htm#Part1>
- Manoli, E., & Samara, C. (1999). Polycyclic aromatic hydrocarbons in natural waters: sources, occurrence and analysis. *Trends in Analytical Chemistry*, 18(6), 417-428.
- Ministry of the Environment, Lagos State (MoELS) . (2010). *State of the Environment Report*. Lagos: Beachland Resources Limited.
- Odukoya, A. M., & Abimbola, A. F. (2010). Contamination assessment of surface and groundwater within and around two dumpsites. *International Journal of Environmental Science and Technology*, 7(2), 367-376.
- Olowofela, J. A., Akinyemi, O. D., & Ogungbe, A. S. (2012). Imaging and detecting underground contaminants in landfill sites using electrical impedance tomography (EIT): A case study of Lagos, Southwestern, Nigeria. *Research Journal of Environmental and Earth Sciences*, 4(3), 270-280.

- Oke, A. S. (2004). Alternative designs for petroleum product storage tanks for groundwater protection. *Journal of Toxicology and Environmental Health*, 67(20-22), 1717-26.
- Owens, J. E., & Niemeyer, E. D. (2006). Analysis of Chemical Contamination in a Canal within a Mexican Border Colonia. *Environmental Pollution*, 140, 506-515.
- Richards, T. B., Croner, C. M., Rushton, G., Brown, C. K., & Fowler, L. (1999). Geographic information systems and public health: mapping the future. *Public Health Reports*, 114, 359-373.
- Rushbrook, P. (2001). Waste Management. In W. H. Organization, *Guidance on Minimum Approaches for Improvements to Existing Municipal Waste Dumpsites* (pp. 1-23). Copenhagen.
- Taiwo, A. (2009). Waste management towards sustainable development Nigeria: A case study of Lagos state. *International NGO Journal*, 4(4), 173-179.
- Tavakoli, L., Yamini, Y., Ebrahimzadeh, H., & Shariati, S. (2008). Homogeneous liquid-liquid extraction for preconcentration of polycyclic aromatic hydrocarbons using a water/methanol/chloroform ternary component system. *Journal of Chromatography*, 1196, 133-138.
- Taylor, R. G., & Allen, A. (2006). Waste Disposal and Landfill: Information Needs. In W. H. Organization, *Protecting Groundwater for Health: Managing the Quality of Drinking-water Sources* (pp. 339-362). London: IWA.
- United States Department of Health and Human Services, Agency for Toxic Substances and Disease Registry (ATSDR). (1995). *Toxicological Profile for Polycyclic Aromatic Hydrocarbons*. Atlanta. Retrieved from <http://www.atsdr.cdc.gov/toxprofiles/tp69.pdf>
- United States Department of Health and Human Services: Agency for Toxic Substances and Disease Registry (ATSDR). (2009). *Case Studies in Environmental Medicine (CSEM): Toxicity of Polycyclic Aromatic Hydrocarbons (PAHs)*. Atlanta. Retrieved from <http://www.atsdr.cdc.gov/csem/pah/docs/pah.pdf>
- United States Environmental Protection Agency (USEPA). (1984). *Guidelines Establishing Test Procedures of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule*. Washington, DC. Retrieved from <http://nepis.epa.gov/Exe/ZyNET.exe/9100G1TL.PDF?ZyActionP=PDF&Client=EPA&Index=1981%20Thru%201985&File=D%3A%5CZYFILES%5CINDEX%20DATA%5C81THRU85%5CTXT%5C00000017%5C9100G1TL.txt&Query=&SearchMethod=1&FuzzyDegree=0&User=ANONYMOUS&Password=anonymous&QField=&UseQField=&IntQFieldOp=0&ExtQFieldOp=0&Docs=>

- United States Environmental Protection Agency (USEPA). (1996). *Method 3630C: Silica Gel Cleanup*. Washington, DC. Retrieved from <http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/3630c.pdf>
- United States Environmental Protection Agency (USEPA). (2009). *National Primary Drinking Water Regulations*. Washington, DC. Retrieved from <http://www.epa.gov/ogwdw/consumer/pdf/mcl.pdf>
- United States Environmental Protection Agency, Office of Water (USEPA). (2009). *Drinking Water Standards and Health Advisories*. Washington, DC. Retrieved from <http://water.epa.gov/action/advisories/drinking/upload/dwstandards2009.pdf>
- Yusuf, K. A. (2007). Evaluation of groundwater quality characteristics in Lagos-City. *Applied Sciences*, 7(13), 1780-1784.

Appendix

Definitions

- The limit-of-detection (LOD) is defined as the concentration of analyte required to give a signal equal to the background (blank) plus three times the standard deviation of the blank
- External standard calibration involves the comparison of instrument responses from the sample to the responses from target analyte of known concentration in the calibration standards.

Table1: Characterization of groundwater samples

<i>Sample Site</i>	<i>Distance to Dumpsite</i>	<i>Temperature</i>	<i>pH</i>	<i>Water Source</i>	<i>Time of Sampling</i>	<i>Date of Sampling</i>
O1	146	28°C	5	Borehole	12:15pm	July 10, 2012
O2	96	34°C	6.9	Borehole	1:00pm	July 10, 2012
O3	367	31°C	5.2	Borehole	1:50pm	July 10, 2012
O4	287	29°C	5.8	Borehole	2:05pm	July 10, 2012
O5	434	28°C	5.6	Well	2:25pm	July 10, 2012
O6	208	30°C	7.3	Borehole	3:02pm	July 10, 2012
S1	46	28°C	7.5	Well	11:39pm	July 9, 2012
S2	101	30°C	6.6	Well	3:05pm	July 9, 2012
S3	9	28°C	NA	Well	12:00pm	July 9, 2012
S4	103	29°C	6.9	Borehole	1:30pm	July 9, 2012
S5	83	28°C	6	Borehole	1:45pm	July 9, 2012
S6	15	31°C	NA	Well	1:00pm	July 9, 2012
S7	354	31°C	6.3	Well	2:40pm	July 9, 2012
S8	90	30°C	6.9	Well	2:50pm	July 9, 2012

Table 2: PAH analysis using GC-FID instrument

<i>LOD_Range</i>	<i>Paper</i>	<i>Author</i>
$(8.0 * 10^{-6}) - (5.9 * 10^{-7})$	Solid-phase microextraction for determining the distribution of sixteen US Environmental Protection Agency polycyclic aromatic hydrocarbons in water samples.	Doong et al
$(3.0 * 10^{-5}) - (7.0 * 10^{-7})$	Quantitative Analysis of Fuel-Related Hydrocarbons in Surface Water and Wastewater Samples by Solid-Phase Microextraction.	Langenfeld et al

$(1.4 \cdot 10^{-5}) - 4.1$	Homogeneous liquid–liquid microextraction via flotation assistance for rapid and efficient determination of polycyclic aromatic hydrocarbons in water samples.	Hosseini et al
$(8.0 \cdot 10^{-8}) - (1.0 \cdot 10^7)$	Homogeneous liquid–liquid extraction for preconcentration of polycyclic aromatic hydrocarbons using a water/methanol/chloroform ternary component system	Tavakoli et al