ASSESSMENT OF LEVELS AND DISTRIBUTION OF HEAVY METALS IN LAKE CHILWA CATCHMENT

MSc. (ENVIRONMENTAL SCIENCE) THESIS

By

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DECLARATION

I, the undersigned, hereby declare that this thesis is my own work which has not been submitted to any other institution for similar purposes. Where other people's work has been used acknowledgements have been dully made.

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CERTIFICATE OF APPROVAL

The undersigned certify that this thesis represents the student's own work and effort and has been submitted with our approval.

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To my beloved parents, my brothers (Faith and Tendai Mussa) and my lovely daughter, Chisomo Mussa for being supportive, morally, spiritually and socially.

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ABSTRACT

The aim of this study was to assess the levels and distribution of heavy metals in Lake Chilwa and its catchment. Water and sediment samples were collected from the lake and main inflowing rivers. The samples were analyzed for pH, Conductivity and heavy metals (Cd, Pb, Zn, Cr, Hg, Ni, and As). Six metal elements, in order of decreasing concentration, were detected in the water; Zn > Cu > Pb > Cr > Ni > Cd. Ranges for the mean values were; pH (7.87 – 10.17), Conductivity (97 – 390 µS/cm), Zinc (6.24 - 1168.7 µg/L), Copper (0 – 47.83 µg/L), Lead (0 – 49.94 µg/L), Chromium (0.22 – 33.05 µg/L), Nickel (0.40 – 8.20 µg/L), Cadmium (0 – 0.53 µg/L). Mercury and arsenic were not detected in all sampling locations. Positive correlations were observed between cadmium and Lead (r = 0.70), Copper and Zinc (r = 0.70), Cadmium and Nickel (r = 0.50) and Lead and Nickel (r = 0.41), suggesting similar sources of input. Concentrations in the lake sediments were detected in the following order; Zn > Cr > Ni > Cu > Pb > As. Mercury and cadmium were not detected. Average concentrations in the sediments were; Zn (64.15 and 68.11 mg/Kg), Pb (7.36 and 8.13 mg/Kg), Ni (35.03 and 35.74 mg/Kg), Cu (24.04 and 16 mg/Kg), Cr (53.72 55.89 mg/Kg), and As (1.27 and 0.73 mg/Kg). The heavy metal pollution index ranged from 2.24 to 114.45. All points except Kachulu harbor had values far below the critical pollution index value of 100. Concentrations were low in the upstream locations located in the highlands and high in the lowland areas close to the lake. This indicates the effects of anthropogenic activities that include agriculture and settlements activities.

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LIST OF ABBREVIATIONS AND ACRONYMS

APHA	**American Public Association**
BDL	**Below Detection Limit**
EAD	**Environmental Affairs Department**
GIS	**Geographical Information System**
GPS	**Global Positioning System**
GoM	**Government of Malawi**
HDPE	**High Density PolyEthylene**
HPI	**Heavy metal Pollution Index**
ICP-OES	**Inductively Coupled Plasma Optical Emission Spectrometry**
MBS	**Malawi Bureau of Standards**
UTM	**Universal Transverse Mercator**
UNESCO	**United Nations Educational, Scientific and Cultural Organization**
WHO	**World Health Organization**

CHAPTER ONE

INTRODUCTION

1.1. Background

Lakes and rivers are vital in the provision of ecosystem services as they supply products and possess attributes that are beneficial to almost all forms of life and are a very important part of our natural heritage (Manahan, 2000). They are habitats for a diversity of plants such as reeds, grasses, water lilies, sedges, and trees. These plants in turn provide food, place of attachment and shelter for many species of animals and humans (Njaya et al., 2011).

Water pollution occurs because human activities have altered the structure of rural landscape and increased the quantity of substances that are loaded into the rivers and lake systems. Polluted waters have chemical constituents that are beyond the tolerable levels to support a healthy aquatic ecosystem. It is important to appreciate that all natural waters contain a variety of chemical constituents arising from natural processes such as erosion, leaching and weathering processes, however addition of pollutants from human activities, alters the nature of receiving water and impairs its suitability for various uses. Studies elsewhere have shown elevated levels of chemical pollutants such as heavy metals in streams and rivers passing through urban areas and farm lands. Agrochemicals and waste from industries, institutions and residential areas may contain these metals and their transport to water bodies through erosion and direct disposal contributes to their presence in rivers and lakes (Woitke et al., 2003, Mortvedt, 1996, MacFarlane, Pulkownik & Burchett, 2003). Due to their persistence in nature, heavy metals have the potential to bio accumulate and cause toxic effects in organisms high in the food chain (Paul, 2017). Some heavy metals such as Cu, Mn, Ni and Zn are essential as micronutrients for life in plants and microorganisms, while many other metals such as Cd, Cr and Pb have no known physiological activity. Deadlier diseases such as oedema or eyelids tumours, congestion of nasal mucous membranes and pharynx, stuffiness of the head and gastrointestinal, muscular, reproductive, neurological and genetic malfunctions caused by some of these heavy metals are well documented (Kar, Sur, Mandal, Saha & Kole, 2008). Cases of heavy metal contaminated waters and sediments resulting in death of organisms and microorganisms are also well reported (Egbenni, Okolie, Martins, Teniola, 2011).

Malawi as one of the southern African countries likely to experience absolute water scarcity by 2025 (Singh, Diop, M'mayi, 2006). The country has an extensive network of rivers and lakes, with water bodies covering more than 21% of the territory. However, most water resources have been degraded as a result of the effect of population pressure arising from high population growth and effects of deforestation (Jamu, Chimphamba & Brummet, 2003). At the same time, there is considerable siltation in the rivers greatly affecting water quality due to incorrect land use (Chimwanza, Mumba, Moyo & Kadewa, 2005).

1.2. Problem statement

Heavy metals may be present in an environment through natural and anthropogenic causes and their presence in trace concentrations is important both to animal and plant development. If the concentrations surpass the maximum admissible levels as stipulated by various organizations such as the World Health Organization (WHO), Malawi Bureau of Standards (MBS) and the European Standards on Fisheries and Aquaculture then plant and animal development may be retarded because of malfunctions caused by bio concentration of the heavy metals.

Lake Chilwa and its catchment is an important ecosystem in Malawi providing ecosystem services that include, water purification and storage, fertile lands for agriculture, settlements and maintenance of biodiversity (EAD, 2010). The catchment is also of international importance as a RAMSAR site, seasonally hosting migratory birds that fly from the northern hemisphere escaping the winters cold (Mvula & Haller, 2009). Despite the benefits the catchment provides, it is threatened by pollution from several activities and processes likely to result in the accumulation of heavy metals. Such activities include; indiscriminate disposal of waste, sewage effluent and agrochemicals (Saka, 2006, Kafumbata., 2014, Jamu, Chimphamba & Brummett, 2003, Saka, 2006, Chavula & Mulwafu, 2007, Mulwafu, 2000). Increased deforestation, soil erosion, intensification of agricultural activities and the use of stream banks for agricultural activities accentuates the transport of these metals to the water bodies (Chidya, Sajidu, Mwatseteza, & Masamba, 2011). The UNEP report on Africa's lakes indicates the possibility of heavy metal deposition due to the anthropogenic activities within the catchment (EAD, 2010). Studies elsewhere have shown that agricultural activities constitute the most important sources of heavy metals accumulating in waters and soils (Shazili, Yunus, Ahmad, Abdullah & Rashid, 2006). It is important to note that the possibility of heavy metal pollution in this catchment exists, however the paucity of information on their levels and distribution is regrettable.

This research, therefore, sought to study and understand the levels and distribution of heavy metals in Lake Chilwa and its catchment waters.

The results generated could be used:

1. to formulate holistic management strategies for the sustainable management and conservation of this catchment

2. to provide a baseline for future research.

1.3. Objectives of the study

The general objective of this study was to assess the levels and distribution of heavy metals in the catchment in order to inform the conservation and sustainable utilization of Lake Chilwa catchment. .

Specifically this research sought to:

1. determine the concentrations of heavy metals (As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn) in the lake, rivers and lake sediments.
2. ascertain the spatial variability of the metals in the water
3. identify possible sources of the heavy metals in the Lake Chilwa catchment
4. evaluate the potential risk of heavy metals in the catchment

CHAPTER TWO

LITERATURE REVIEW

2.1. General Background

Heavy metals are naturally occurring elements that have a high atomic weight and a density at least five times greater than that of water. One of the most crucial properties of these metals, which differentiates them from other toxic pollutants, is that they are not easily biodegradable in the environment (Nasrabadi, 2015). Once released to the environment they tend to bio accumulate causing damage to organisms in the food chain. According to World Health Organization, zinc, copper, cadmium, chromium, arsenic, mercury and lead are among 10 heavy metals which are highly toxic (WHO, 2008).

Toxicity of the metals depends on several factors including dose, route of exposure, and chemical species. It is reported that metals such as manganese, nickel and zinc are essential nutrients that are required for various biochemical and physiological functions. They are important constituents of several key enzymes and play important roles in various redox reactions (Strawn, 2002). Inadequate supply of these micro-nutrients results in a variety of deficiency diseases or syndromes. However, an excess of these essential elements produces cellular and tissue damage leading to a variety of adverse effects. Other heavy metals such as arsenic, cadmium, chromium, lead and mercury have no established biological functions and are considered as non-essential metals and also considered as toxic, known to induce multiple organ damage, even at lower levels of exposure (Tchounwou, Yedjou, Patlolla, & Sutton, 2012). Cadmium and lead for example are recorded as extremely poisonous even at low concentrations under certain conditions (Khan, Zaidi, Goel & Musarrat, 2011). Metals such as copper and zinc which are required for metabolic activity in organisms lie in the narrow "window" between their essentiality and toxicity. Whereas, calcium is believed to have antagonistic effect on the potential bioavailability of cadmium and zinc (Adeniyi et al., 2011).

In soils and waters, the metals exist either as separate entities or in combination with other components such as ions, metal compounds, metal complex or organic materials and metals attached to minerals (Marques, Rangel & Castro, 2009). In the water column they can be removed and transferred to the sediment phase through a number of complex processes that include precipitation of insoluble oxy-hydroxide compounds or sorption onto particulate material (Woods, 2009). Adsorption by or co-precipitation with hydrous iron and manganese oxides forming in the water column can scavenge metals from solution, while clay and organic particles already present in the water column can also bind and remove metals (Peltier, Webb & Gaillard, 2003).

Pollution by heavy metals is one of the greatest problems that the world is facing today, increasing with every passing year and causing grave and irreparable damage to the earth. Their multiple industrial, domestic, agricultural, medical and technological applications have led to their wide distribution in the environment; raising concerns over their potential effects on human health and the environment (Tchounwou et al., 2012).

2.2. Heavy metals from industrial and domestic activities

Domestic and industrial activities have drastically changed the biochemical cycles and balance of some heavy metals. The main sources of the heavy metals are various industrial processes, mining, foundries, smelters and waste disposition (Bartram et al., 1996). In many cities all kinds of waste materials are strewn about on the outskirts of towns or are thrown into streams, lakes, and rivers. Aerosol cans, drug containers, hospitals and research laboratories' washings or wastewaters that may contain heavy metals may eventually decay or spread and become transported into water resources. A particularly serious case is recorded in history during the 1950's in Minamata bay, Japan. Waste water from a factory contained mercury and was being discharged into the bay. Due to mercury's bio accumulative properties the fish in the bay were exposed to methyl mercury. The fish passed on the mercury built up in their bodies to the fish consuming residents nearby. Symptoms included uncoordinated movement and numbness of the lips and extremities, followed by constricted vision. The effect upon the infants was even more severe as many were born with a wide range of disabilities. Nearly 1000 people died from the consumption of the polluted fish (Hutton, 1987). In Spain tailings from a mine escaped the dam and reached the Guadiamar River, polluting the river with heavy metals such as cadmium, lead, zinc and copper. The river pollution caused cultivation lands and forests to be affected. Harvests were no longer fit for consumption, causing financial problems of farmers in the area. Major fish mortality occurred and birds died as a result of consumption of polluted fish (Cabrera, Clemente & Barrientos, 1999). In Zambia, southern Africa, effluents from textile factories were reported to have discharged high loads of heavy metals to Kafue River which led to decreased fish catch and fish size (Kaile & Nyirenda, 2016). Similar cases have also occurred in Malawi where a number of water resources within the urban areas have been affected (Kaonga, Chiotha & Monjerezi, 2008). Several studies have found elevated levels of metals in water resources passing through urban areas. Levels were found to exceed limits set by the Malawi Bureau of standards and World Health Organization (Kumwenda, Tsakama, Kalulu & Kambala, 2012). Mudi River situated in the heart of Blantyre has deteriorated, with high levels of heavy metals as a result of input of waste from residential and industrial activities. The following metals were detected, Zn, Cu, Pb, Cr and Cd with average values of 0.12 mg/L, 0.07 mg/L, 0.56 mg/L, 0.22 mg/L and 0.01 mg/L respectively (Phiri, Mumba, Moyo & Kadewa, 2005). Similarly, Lilongwe River, passing through populated areas of Lilongwe has also undergone rapid deterioration from industrial and domestic waste inputs. Indiscriminate disposal of waste from factories, industries and domestic activities has elevated the levels of heavy metals to unacceptable ranges (EAD, 2010). Likangala River, one of the rivers within Zomba city is not spared from pollution from industrial and residential activities. High levels of Lead and Zinc were observed within the river channel that confides with the sewage treatment plant (Chidya et al., 2011).

2.3. Heavy metals from agricultural activities

Agriculture constitutes an important source of metals to water resources. Intensification of agricultural activities with increasing use of fertilizers and pesticides and allied livestock activities has an adverse impact on water quality (Moss, 2008). Agrochemicals used to improve yields contain heavy metals as impurities or as ingredients, and these are transported through erosion and run off to water resources. Since, agricultural pollution occurs over a wide area and its sources are diffuse and difficult to identify, it becomes difficult to control the agricultural water pollution. It also varies unpredictably over time and space and is governed by rainfall patterns, land slope, soil characteristics, land use and crop choices, production techniques and the intensity of fertilizer and pesticide use (Branson & Wentworth, 2014). Metals such as Zn, Cu, Ni, Pb, Cd, Cr, As and Hg are introduced to agricultural soils from sewage sludge, livestock manures, inorganic fertilizers, lime, pesticides, herbicides irrigation water, industrial by-product wastes and compost (Nicholson, Smith, Alloway, Calton-Smith & Chambers, 2003). Manure used in farms usually contains metal impurities such as copper and zinc. These metals are often added to animal feed due to their anti – microbial and growth promoting properties, with significant concentrations of these metals ending up in the manure (Xue, Nhat, Gachter & Hooda, 2003). Long term intensive application of manure can lead to the accumulation of manure borne metals in the soils and could also result in elevated metal concentrations in the drainage. In Switzerland intensive application of manure led to increased concentrations of Zn and Cu to levels above permissible limits for drinking water in the river Kleine, which is a tributary of Lake Sempach (Xue et al., 2003). Similarly, increased use of chemical fertilizers and livestock and poultry manure led to an increase in metals such as Cd, Pb, Cu and Zn in soils of Shandong province, China (Jia, Wang, Li & Yang, 2010). In Nepal, heavy metals in water from agricultural activities were the main cause of neurological problems. These metals were traced to originate from fertilizers, pesticides and industrial waste water which was used for irrigation (Kayastha, 2007). Farming activities along the streams that serve the Owabi reservoir in Nigeria contributed to high levels of heavy metals in the reservoir, rendering the water unfit for consumption (Akoto, Bruce & Darko, 2008).

Phosphate fertilizers in Nigeria was analyzed and found to contain high levels of Cu, Zn, Pb and Cd, and these could act as a source of diffuse metal enrichment of the agricultural soils (Benson, Anake & Etesin, 2014). Transport of the metals within the soils is controlled by many factors that include, pH, soil type and organic matter content (Bird et al., 2005). Zinc for example forms relatively weaker organometallic complexes in soils with high organic matter and hence maintaining greater mobility. The effect of soil organic matter on the transfer of metals from soil to surface water is multi-facet. It 'traps' the metal ions more efficiently and provides dissolved organic ligands to the soil solution that forms dissolved metal complexes and hence increases the metal solubility and mobility (Xue et al., 2003). Some farming practices such as ridge farming encourage soil erosion which results in transporting agrochemical residues including heavy metals from the fields to water bodies (Lopes, Herva, Franco-uria & Roca, 2011). Cultivation along the stream banks is considered favorable especially for vegetable, rice and other crops. This practice exacerbates the transport of pollutants to the water bodies (Chimwanza et al., 2005).

In developing countries, the people and governments place their priorities on food production in enough quantities to stem the tide of hunger and mass deprivation and little or no consideration is given to the pollution implications. The poor farmers, most of whom practice subsistence agriculture, are encouraged to apply fertilizer and use insecticides/herbicides for maximum crop yields. The prices for these chemicals are very low and affordable as the governments have subsidized the costs. Thus, the chemicals may be used indiscriminately.

2.4. Description of common heavy metals and their toxicities

2.5.1 Chromium (Cr)

Chromium is a transition metal with the molar mass of 51.9 g/mol. It is the twenty-first most abundant element in the earth's crust, about 120 g/ton (Mohan & Pittman, 2006). Chromium can occur in several oxidation states such as +2, +3 and +6 although the +2 state is very unstable in the presence of traces of oxygen (Cotton, 2007). In rock minerals the predominant oxidation state is Cr^{3+}. Dissolved chromium, however may be present as trivalent cations or as anions in which the oxidation state is Cr^{6+}. In alkaline oxidizing solutions, chromate ions may be stable, but some cations form chromates having low solubilities. Trivalent chromium hydrolyses easily to soluble $CrOH^{2+}$, $Cr(OH)_2^{+}$, $Cr(OH)_4^{-}$, and poly nuclear complexes as $Cr_2(OH)_2^{4+}$, $Cr_3(OH)_4^{5+}$ and

$Cr_4(OH)_6^{6+}$. Anionic forms present under oxidizing conditions, include dichromate $Cr_2O_7^{2-}$ and chromate CrO_4^{2-}. A metastable hydroxide, Cr $(OH)_3$ has a minimum solubility near 5μg/L at about pH 9.0. This material might precipitate from solutions containing chromate anions if there are reducing agents present. The solubility of chromic oxide is much below 1μg/L between pH 5 and 13, but it is unlikely to be directly precipitated from solution. Chromate anions are the dominant species in solutions that are alkaline and mildly oxidizing.

In organisms, Cr (III) is less absorbed than Cr (VI) and this leads to a difference in their transport methods to cells. Cr (VI) enters into the cell via a non specific anion channel by facilitated diffusion while Cr (III) enters by passive diffusion or phagocytosis (Shekhawat, Chatterjee & Joshi, 2015).

In humans and animals chromium causes allergenicity and carcinogenicity. It is responsible for dermatitis allergy; perforation in nasal septum and some cases of lung cancer (Saha, Nandi & Saha, 2011). In plants chromium is taken up by carriers of essential ions such as sulfate or iron. Toxic effects of Cr on plant growth and development include alterations in the germination process as well as in the growth of roots, stems and leaves, which may affect total dry matter production and yield (Shanker, Cervantes, Loza-Tavera & Avudainayagam, 2005). Cr also causes deleterious effects on plant physiological processes such as photosynthesis, water relations and mineral nutrition. Metabolic alterations by Cr exposure have also been described in plants either by direct effect on enzymes or other metabolites or by its ability to generate reactive oxygen species which may cause oxidative stress (Panda & Choudhury, 2005).

Chromium is mainly used as an alloy metal to increase the hardness, mechanical strength and resistance against corrosion and oxidation. The metal is also used in the production of chemical compounds used for chrome plating, textile dying, wood impregnation and production of color pigment catalysts. The industrial use of chromium may produce waste solutions containing chromate anions. Incidents of water pollution with chromate have occurred in many localities. In such an occurrence on Long island, the chromate moved from an industrial waste disposal pit to contaminate shallow ground water and persisted in concentrations as great as 14 mg/L of Cr^{6+} more than 3,000ft away from the original source some 20 years after the contamination was first noticed in water nearer the source. Concentrations of chromium in natural waters that have not been affected by waste disposal are commonly less than 10µg/L (Hem, 1985).

2.5.2 Zinc (Zn)

Zinc belongs to the post-transitional metals and has the molar mass 65.39 g/mol. It is the twenty-fourth most abundant element in the earth's crust with about 775ppm (C. S. Chung & King, 2004). It occurs in 0, +1, +2 oxidation states and typically in the form of compounds such as zinc oxide, chloride, sulphide, sulphate, phosphate and borate (Strachel, Zaborowska & Wyszkowska, 2016). Zn^{2+} tends to be substantially more soluble in most types of natural water. In weak acidic media Zn^{2+} hydrolyses to form $ZnOH^{+}$ and Zn_2OH^{3+} and in alkaline media to $Zn(OH)_4^{2-}$ and $Zn_2(OH)_6^{2-}$ (Hem, 1985). Zinc is very mobile in well aerated and acidic (pH below 6.5) soils, but it becomes more stable and does not undergo leaching at an increase of pH to neutral (Alvarez, Novillo, Obrador & Lopez-Valdivia, 2001). The activity of zinc decreases hundred fold with a rise of pH by one unit in the range from 5 to 8 (Strachel et al., 2016). In urban areas, huge amounts of zinc are introduced into soils and water as a result of traffic. Increased emission of heavy metals related to traffic arises from their penetration into the environment along with exhaust fumes and as a result of the wearing of surfaces, tyres, brake pads and motor vehicle bodies (Councell, Duckenfield, Landa & Callender, 2004). The second major source is agricultural practice, including fertilization with sewage sludge. In this case, the application of sludge causes an increase in the content of bioavailable zinc. Furthermore, significant pollution of the environment with zinc is a result of waste disposal, especially of post-consumer electronic equipment (Jones, Bankiewicz & Hupa, 2014).

Zinc is an essential element, important for microorganisms, plants and animals and is found in many proteins as an important component in enzymes for metabolism and regulation in the activity of genes (Peltier et al., 2003). Zinc, at doses higher than optimal, inhibits the microbial activity of soil. In a study by Strachel et al. (2008), the pollution of soil with zinc in doses of 500 and 1,000 mg/kg of soil resulted in decreased numbers of soil microorganisms. In animals exposure to zinc, especially at higher doses, may produce toxic effects on various tissues and organs including the hematopoietic system, cytogenetic, biochemistry and endocrine system function (Osman et al., 2000).

Metallic zinc is mainly used for surface finishing and corrosion resistance for iron and steel. Zinc is also used as an ingredient for the production of catalysts, batteries, pigments, impregnation and antiseptic compounds among others (Manahan, 2000). These applications tend to disperse the element widely in the environment, and its availability in water has been greatly enhanced by modern industrial civilization. Waste from farm lands including poultry contains high levels of zinc originating from the feeds (Xue et al., 2003).

2.5.3 Cadmium (Cd)

Cadmium is a low-abundance, charcophile element that most commonly occurs as a substitute for Hg, Cu, Pb, and Zn in sulphode minerals, especially sphalerite (ZnS) such as biotite and amphibole. Cadmium occasionally forms minerals in its own right, most notably greenockite CdS, but also the rarer octavite $CdCO_3$ and monteponite CdO (Reimann & Caritat 1998). There is also evidence of an affinity with organic matter, which may be due to selective adsorption and complexation by humic compounds (Tsiridis et al., 2006). The mobility of Cd released from minerals is likely to be high, especially during conditions of elevated flow, when pH is lower (Hem, 1985). Cadmium is used extensively in industrial processes. Of these, electroplating and battery, paint, ink and plastic manufacture are of greatest importance. Leaching of waste from these processes may have an impact on surface water chemistry. Cadmium tends to volatilize at high temperatures, providing a mechanism for its entry into the hydrological cycle via atmospheric deposition downwind of industrial regions (Manahan, 2000). Phosphate fertilizers contain between 5 and 100 mg kg-1 Cd and up to 300 mgkg-1 Cd may be present in sewage sludge (Vig, 2003). Cadmium has no essential biological function, but it tends to accumulate in plants and aquatic biota, with consequent problems of toxicity. In animals long time exposure to cadmium through air, soil, and food leads to cancer and organ system toxicity such as skeletal, urinary, reproductive, cardiovascular, central and peripheral nervous, and respiratory systems (Rahimzadeh, Rahimzadeh, Kazemi & Moghadamnia, 2017). In plants cadmium causes Chlorosis, leaf rolls and stunted growth. The inhibition of root Fe(II) reductase induced by Cd leads to Fe (II) deficiency, and it seriously affects photosynthesis. In general, cadmium has been shown to interfere with uptake, transport and use of several elements (Ca, Mg, P and K) and water by plants (Benavides, Gallego & Tomaro, 2005). Cadmium produces alterations in the functionality of membranes by inducing lipid peroxidation and disturbances in chloroplast metabolism by inhibiting chlorophyll biosynthesis and reducing the activity of enzymes involved in CO_2 fixation (Shanmugaraj, Malla, & Ramalingam, 2019). In humans inhalation of dust causes lung damage and cancer from long-term exposure (WHO 1996); it is also teratogenic and embryocidal (Smith 1999). The maximum tolerable intake of Cd is regarded as 7 µg kg-1 of body weight (WHO 1996). In Japan, stream pollution by cadmium caused deterioration of bones of farmers and their families who had eaten rice grown in fields irrigated with that stream water (Uraguchi & Fujiwara, 2012).

Zinc and cadmium have some chemical similarities, but cadmium is much less abundant. Generally, cadmium is present in zinc ore minerals such as sphalerite and is recovered from some copper ores during smelting and refining. Cadmium is used for electroplating and for pigments used in paint, printing ink, and plastics. It is also used extensively as a stabilizer in PVC plastic and in electrical batteries and fluorescent and video tubes. The metal tends to be more mobile in soils than other heavy metals, and is therefore more available to plants (Das, Samantaray & Rout, 1997).

2.5.4 Arsenic (As)

Arsenic (As) is the twentieth most common element in the earth's crust (Hering, Wilkie, & Chiu, 1997). Naturally it occurs in the environment in inorganic as well as organic forms. In waters it occurs in inorganic forms as trivalent arsenate (As(III)) or pentavalent arsenate (As(V)), with a minor amount of methyl and dimethyl arsenic compounds (Petrusevski, Sharma, Schippers & Shordt, 2006). The (III) oxidation state is more toxic than the (V) state; whereas, organoarsenic compounds for instance monomethylarsonic acid and dimethylarsonic acid are the least toxic (Tsopelas, Tsakanika & Ochsenkuhn-Petropoulou, 2008).

Arsenic is primarily used as an insecticide and herbicide or preservative for wood due to its germicidal power and resistance to rotting and decay, respectively. Arsenic is also used in medicine, electronics, and industrial manufacturing (Garelick, Jones, Dybowska & Valsami-Jones, 2008). In the environment, arsenic and its compounds are mobile and cannot be destroyed.

However, interaction with oxygen or other molecules present in air, water, or soil, as well as with bacteria that live in soil or sediments can cause arsenic to change form, attach to different particles, or separate from there particles (Cullen, 2013). Many common arsenic compounds can dissolve in water, thus arsenic can contaminate water resources by dissolving in rain or through discarded industrial wastes (Chung, Yu, Do & Hong, 2014).

The effect of arsenic exposure from ingested arsenic-contaminated food and water is found to be associated with detrimental health effects such as burning and dryness of the mount and throat, dyspepsia, colicky abdominal pain, rashes, vomiting, profuse diarrhea and hematuria. Sub-acute arsenic toxicity mainly involves the respiratory, gastrointestinal disorders, cardiovascular, facial cramps, diabetes and hematopoietic systems (Tao & Bolger, 2014). A study by Huyck et al (2007) showed that exposure to arsenic through drinking water has direct effect on the early stages of life when the brain is usually most vulnerable. Exposure to contaminated water during pregnancy is associated with low birth weight and fetal loss and there's concern that the infants' growth may be affected (Harari, Broberg & Vahter, 2014). In plants, As(V) and As(III), are readily taken up by the cells and they disrupt plant metabolism. As (V) is a chemical analog of phosphate that can disrupt some phosphate-dependent aspects of mentalism. As(V) can be translocated across cellular membranes by phosphate transport proteins, leading to imbalances in phosphate supply (Finnegan & Chen, 2012).

2.5.5 Copper (Cu)

Modern industrial civilization uses copper extensively, and many of these uses result in its dispersal in the environment. Copper is an essential element in plant and animal metabolism. It may occur in the earth's crust as the free native metal, Cu^0, or in Cu^+, or Cu^{2+}, minerals (Manahan, 2000).

The abundance of Cu is greater in basaltic rocks than in granitic rocks and is very low in carbonate rocks (Negishi et al., 2009). Elevated levels of Cu are often found near mines, smelters, industrial sites, landfills and waste disposals. Cu has a typical soft metal behavior and binds strongly to organic matter and other components such as Fe/Mn oxides and clays and is therefore mainly concentrated in the top soil rich in organic matter. Copper is not a particularly mobile metal and will stay adsorbed in the vicinity of the point source. Water soluble copper compounds can be transported in surface waters and then preferably associated with suspended particles (Shi, Allen, Grassi, & Ma, 1998). Copper may occur in solution in either Cu^{2+} or Cu^+ oxidation states, but the redox conditions in oxygenated water and the tendency of Cu^+ ions to disproportionate favor the more oxidized form. Cupric ions form complexes with many different ligands. In solution above neutral pH the form $Cu(OH)_3^-$ may predominate. A strong $CuCO_3$(aq) ion pair appears likely to be the major form in aerated natural water containing dissolved CO_2 species (Hem, 1985).

Copper salts are sometimes added in small amounts to water supplies reservoirs to suppress the growth of algae. Organic and inorganic compounds of copper have been used extensively in agricultural pesticide sprays. The element is therefore likely to be more readily available for solution in surface water than its low average abundance in rocks may imply (Shazili et al., 2006).

In animals and humans, copper serves as an essential co-factor for several oxidative stress-related enzymes including catalase, superoxide dismutase, peroxidase, cytochrome c oxidases, ferroxidases, monoamine oxidase, and dopamine monooxygenase (Dawkes & Phillips, 2001).

The ability of copper to cycle between an oxidized state, Cu(II) and reduced state, Cu(I), is used by cuproenzymes involved in redox reactions. However, it is this property that also makes it toxic because the transitions between Cu(II) and Cu(I) can result in the generation of superoxide and hydroxyl radicals causing cellular damage leading to a variety of adverse health effects (Liochev & Fridovich, 2000). In fish, copper is a neurotoxin, which results in the loss of chemosensory function and affects predator-avoidance behavior. Pyle & Mirza, (2007) showed that exposure during embryonic development can lead to permanently impaired chemosensory functions. In contrast, Fish that are exposed to elevated levels later in life can recover their chemosensory ability after the toxicant is removed (Mcintyre, Baldwin, Meador & Scholz, 2008). In plants copper has been reported to affect cellular organelles and components such as cell membrane, mitochondrial, lysosome, endoplasmic reticulum, and some enxymes involved in metabolism, detoxification and damage repair (Tchounwou et al., 2012).

2.5.6 Lead (Pb)

Lead is the most abundant of the transition metal elements and has the most metallic characteristics. The element has two oxidation states, +2 and +4 and forms important minerals including galena, PbS, anglesite, $PbSO_4$, cerussite $PbCO_3$, and minium, Pb_3O_4 (Anyadike, 2002). In aqueous environments, lead is present as Pb^{2+} below pH 6, but it also forms complexes with organic anions, chloride and hydroxide, and insoluble or poorly soluble compounds with sulphide, sulphate, hydroxyl carbonate and phosphate anions. Lead mobility is restricted by sorption on clay, organic matter, secondary iron and manganese oxides, and the formation of secondary minerals with low solubilities such as anglesite, cerussite and pyromorphite (Elbana & Selim, 2013). In natural waters, lead has a tendency to form compounds of low solubility with major anions. The hydroxide, carbonate, sulfide, and the sulfate of lead may act as solubility controls (Martínez & Motto, 2000). The divalent form, Pb^{2+}, is the stable species of lead, while the oxidized solid PbO_2, in which lead has a +4 charge, is stable only in high oxidizing environment; thus Pb^{+4} has very little significance in controlling the behavior of lead in aqueous geochemical systems (Hem, 1985).

Lead has no known physiological importance, it is considered highly toxic. In humans and animals it affects almost every organ of the body. Long time exposure can result in decreased performance in the nervous system, which may contribute to behavior problems, learning deficits and lowered IQ (Gidlow, 2015). In plants, it gets easily absorbed and accumulates in different plant parts causing a number of toxicity symptoms that include; stunted growth, chrolosis and blackening of root system. Lead also inhibits photosynthesis, upsets mineral nutrition and water balance, changes hormonal status and affects membrane structure and permeability (Küpper, 2017).

Some applications of lead by humans have tended to disperse the element in the environment. In the 1920's addition of tetraethyl lead was found promote more efficient combustion of gasoline used in automobile engines. "Leaded gasoline" permitted a higher compression of the fuel air mixture which in turn increased the power output. The lead content in the fuel is emitted as an aerosol in exhaust gases, and the quantities so dispersed increased greatly as the number of auto-mobiles in use grew (Manahan, 2000). Although the introduction of unleaded petrol has reduced this potentially toxic hazard, metalliferous mining, metallic detritus, Pb-bearing glass and pottery glazes, batteries, old lead-based paints, the corrosion of lead pipes in areas of soft water and sewage sludge are all potential sources of Pb (Bryce-Smith & Stephens, 2013).

2.5. Fate of the metals in water

Sediments are considered the ultimate sink of metal elements. In waters with high pH, metal elements tend to bind themselves to the sediments and particulate materials, which later settles to the bottom of the water bed. If the sediments are not disturbed layers can form on top of each other in an orderly manner that can be extrapolated to the history of deposition. Contaminated sediments can threaten creatures in the benthic environment, exposing worms, crustaceans and insects to hazardous concentrations of toxic chemicals (Egbenni et al., 2011). These toxic elements may be lethal to some forms of benthic organisms, reducing food available to larger animals such as fish. As the benthic organisms feed on the contaminated sediments, the metals bioaccumulate in their tissues, when larger animals feed on these contaminated organisms, the toxic area taken into their bodies, moving up the food chain in a process known as biomagnification. As a result, fish and shellfish, waterfowl, and freshwater and marine mammals may accumulate hazardous concentrations of toxic chemicals. Metals in the sediments do not always remain at the bottom of the water body. Anything that stirs up the water can resuspend the sediments. Resuspension may mean that all of the animals in the water, and not just the bottom dwelling organisms, will be directly exposed to the toxic contaminants.

CHAPTER THREE

MATERIALS AND METHODS

3.1. DESCRIPTION OF THE STUDY AREA

Lake Chilwa catchment is an important ecosystem covering an area of 2000 km^2. It is located in the southern part of Malawi encompassing Zomba, Phalombe and Machinga districts (EAD, 2010) as shown in figure 1.

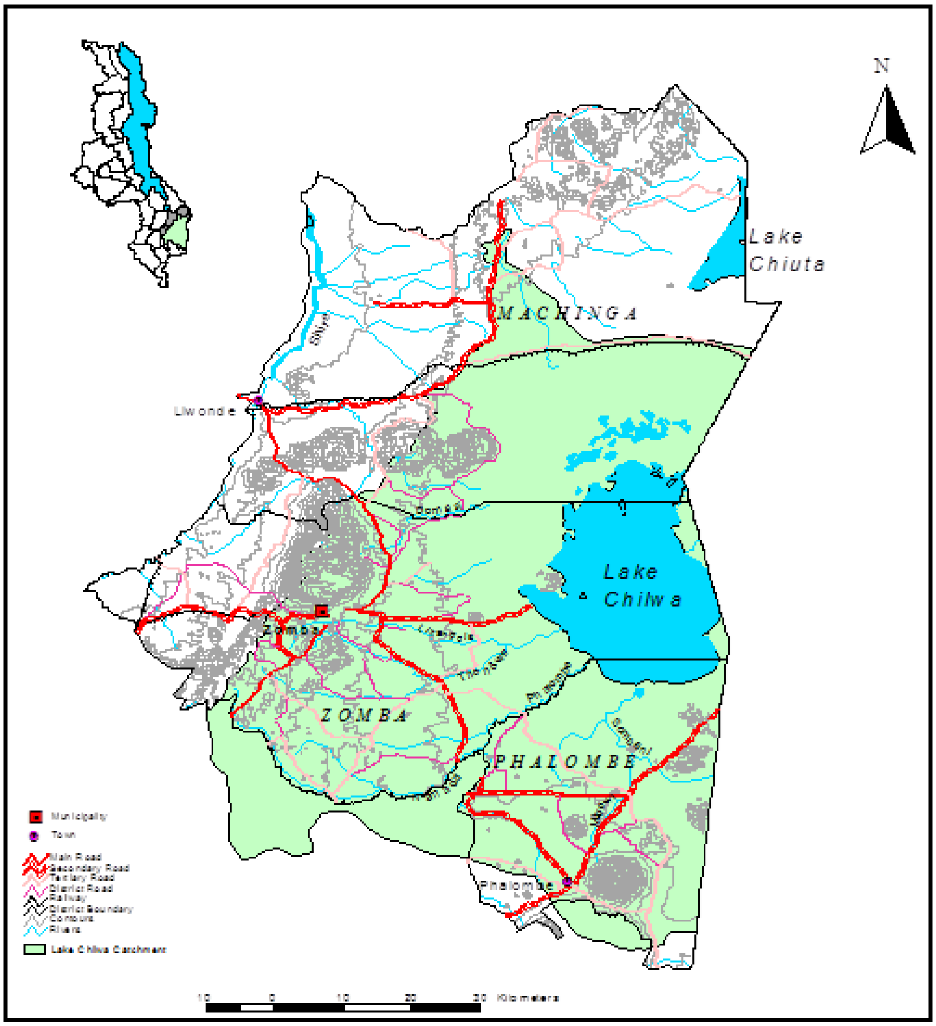

Figure 1: Lake Chilwa catchment (source: Chidya 2011)

The Basin wetland is an important RAMSAR site supporting a waterfowl population of 354,000 which by far exceeds the 20,000 water RAMSAR criteria. The lake seasonally hosts migratory birds that fly from the Northern Hemisphere seeking to breed and escape winter's harsh cold (Parker, Chandra, Barkaszi, & Beal, 1995). The catchment is one of the most populated areas in the country, with population largely in the rural areas and directly dependent on natural resources such as land, water, trees, birds, fish, rodents and others for survival (EAD, 2010).

3.1.1 Geology

Most of the Chilwa basin is underlain by ancient metamorphic and igneous rocks of the Malawi Basement complex (Figure 2). The basement complex is represented in the Shire highlands by a group of high grade metamorphic rocks, mostly chamokitic granulites of quartz and fieldspar, with a NE-SW trend. North of the Chikala Hills in the Makongwa Escarpment, and around Mulanje Mountain these are replaced by biotite gneisses, coarse grained crystalline rocks derived from granite which may weather to give rather sandy soils. Intruded into the gneisses and granite are a series of Pre- Cambrian granitic and perthitic rocks, which frequently form prominent hills, such as Chiradzulu Mountain and the Lungwe Hills north of lake Chiuta. At Tundulu, south of the lake, there is a complex of alkaline silicate rocks, carbonatites and rocks rich in sodium and calcium carbonates (Kalk M, McLachlan A.J, Williams C, 1979).

A large part of the Chilwa basin is underlain by quaternary alluvial and lacustrine deposits, which increase in depth eastwards to a line extending from Nayuchi, on the northern east of the sand bar, to the Phalombe River (Lancaster, 1979).

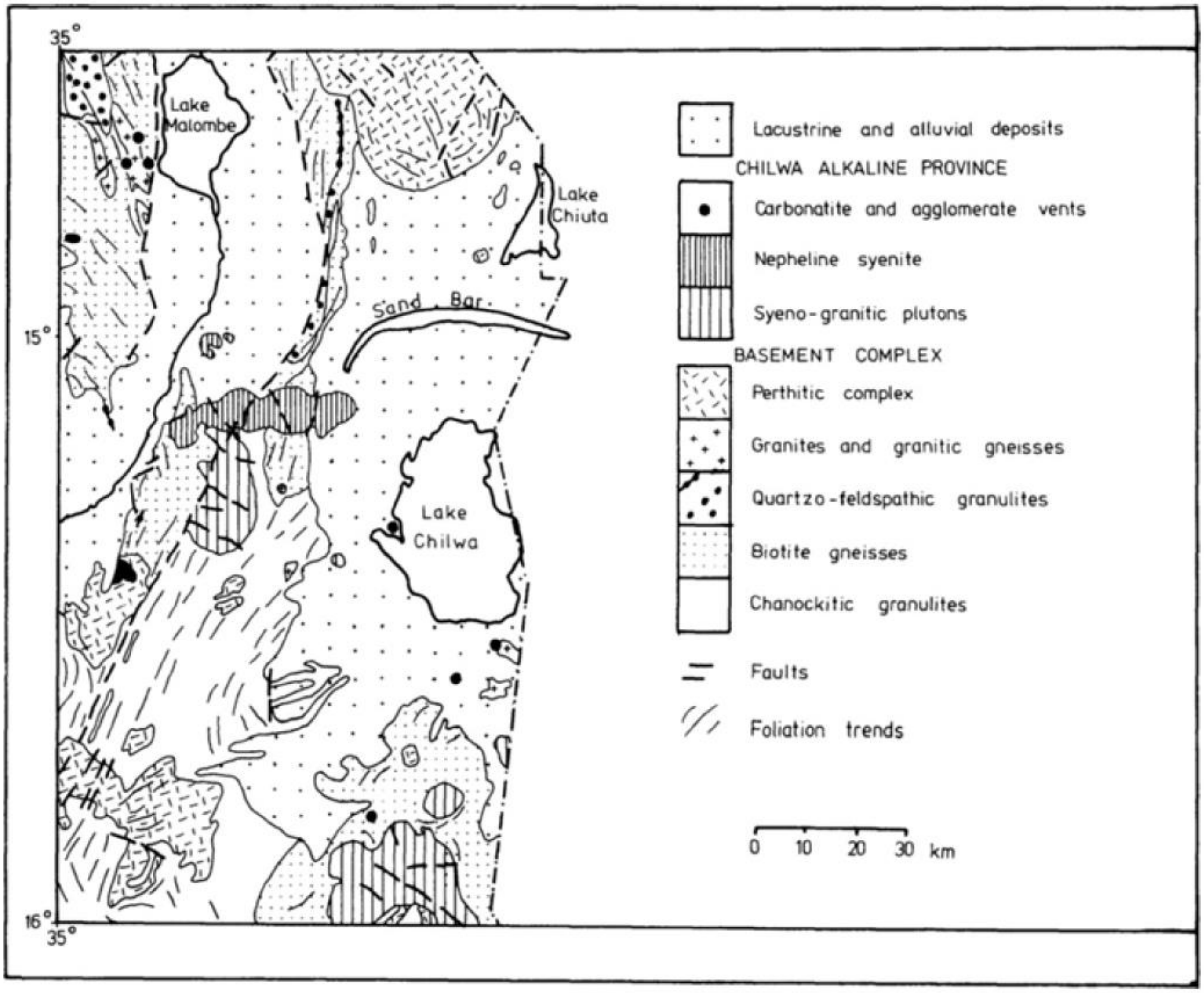

Figure 2: Geology map of Chilwa catchment area (Source: Kalk et al., 1979)

Lancaster (1979) mapped four major soil groups in the Lake Chilwa wetland and catchment area: calcimorphic alluvial soils, hydromorphic soils, latosols and lithosols. Calcimormorphic alluvial soils are widespread in the basin. Their colour ranges from grey to dark brown and they are of medium fertility. Hydromorphic soils occur in the low-lying areas and those on the flood plains are seasonally water logged. They are clay soils with a strongly developed blocky or prismatic structure. They are of variable fertility. Latosols are red to yellow soils of freely drained sites and are widespread in the basin. Lithosols include regosol soils which are sandy soils and of low fertility.

3.1.2 Hydrology

Five major rivers drain into the closed lake from the Shire highlands and Zomba Mountain. These rivers are; Domasi, Likangala, Thondwe, Namadzi and Phalombe. Between them they contribute 70 percent of the total inflow to the lake. As they drain an area of intensive traditional agriculture, these streams, particularly the Likangala, Namadzi and Thondwe, carry a high suspended load during the rainy season. Most of these rivers have a low base or minimum flow and a very high peak flow in the months of February-March. Other important influent rivers include the Sumulu and Lingoni from the Chikala Hills; the Sombani which drains the eastern flanks of Mulanje and Mchese Mountains and enters Chilwa via Mpoto lagoon and its associated extensive marshes in Mozambique; and the Mnembo and Nalaua rivers which drain the hills east of Mecanhelas. These ten streams are perennial, although the inflow of some of them, for example the Phalombe and Sombani, may be very small during October and November, at the end of the dry season. In addition, there are many small seasonal streams draining to the lake, especially on the wetter Malawi side (Beadle, 1979).

3.1.3 Climate

In the period May to September, the climate of the sub-continent is dominated by the Southern African anticyclone, situated over the eastern Transvaal. Out blowing winds from this reach Malawi from the south and southeast and bring dry, stable air, which gives rise to warm days and cool nights. At this time of year, drainage of cold air from the highlands surrounding the Chilwa basin frequently causes early morning mists over the lake and the Phalombe Plain. From time to time, particularly in the early part of this period, movements of the anticyclone towards the Natal coast bring about invasions of cool moist air from the southeast, which result in mists and light rain, *chiperone* conditions over Mulanje and the Shire Highlands, and cool cloudy weather over Lake Chilwa. From September to November, the South African anticyclone moves southeast, and a weak thermal low pressure area develops over the Kalahari. In late October and November convectional storms begin to develop in the late afternoon, particularly over high ground, where orographic effects induced by the interaction of warm wet winds and the mountain slopes, trigger off the latent instability of the air. During the period, late December to March, southern Malawi comes within the Inter-Tropical Convergence Zone (Moss & Moss, 1969). Rainfall occurs as a result of the convergence of deep moist unstable airstreams from the northwest (Congo Air) and from the east and southeast (Maritime or Monsoon Air). In this situation vertical movement of air takes place freely and convectional rainfall is often widespread and heavy. The amount of rainfall and the duration of the rainy season is strongly influenced by the position and movement of the Inter-Tropical Convergence Zone. Strong convergence and the persistence of the Zone over southern Malawi results in heavy rainfall throughout the region. Conversely, periods of weak convergence and the influx of the stable northeasterly air tend to result in dry spells. The relative proportions of these conditions during the period December to March largely determine whether rainfall totals for that year will be above or below the long term average. Periodically, intense tropical depressions, or cyclones, may cross the Chilwa basin. Normally these pass through the Mozambique Channel, but occasionally their tracks may pass over southern Malawi, giving rise to concentrated heavy rainfall, often leading to flooding. During March, the Inter-Tropical Convergence Zone begins to move north, and southeasterly air masses gradually extend over the region. In time these air masses become drier and more stable. Periods of rainfall and cloudy conditions become less frequent and the intervals of warm sunny 'dry season' weather longer. Rainfall over the Chilwa basin declines from a maximum in the highlands surrounding the basin, which receive 1100-1600 mm per year, rising to 2000 mm or more on Mulanje and Zomba Mountains, towards an area of low rainfall over the lake which extends towards the southern Phalombe Plain, in the rain shadow of Mulanje Mountain. Rainfall totals in this zone are 800-900 mm per year (Morgan & Kalk, 1970).

The Chilwa-Phalombe area is one of the hottest areas in Malawi, with a mean annual temperature of 24°C. Once again, a seasonal pattern occurs, with maximum temperatures of 32-34°C in October, November and December, when solar radiation is at a maximum. Temperatures drop slightly with the onset of the rains, but may still reach 30°C. The coolest months are May to August, when maximum temperatures fall to 24-25°C. Clear skies at night, together with cool air draining from surrounding highlands give minimum temperatures at this time of year of 13-15^{o}C. The temperature range is greatest, at 13-14°C, during September and October, and least during the rains when it is 9-10°C (Beadle, 1979).

3.1.4 Land use

Since the country attained independence in 1964, the rate of agricultural activities in the catchment area has increased. Expansion of agricultural enterprises, including rice, tobacco and maize growing, has been due to the increased use of agrochemicals such as fertilizers and pesticides in the catchment, most of which have been washed into the lake due to increased soil erosion (Saka, 2006). Figure 3, shows the increase in cultivation land (shown by the purple color) and depletion of forest cover from 1990, through 2000 to 2010. This increase has been driven by the increase in population which has resulted in an increase in demand for food (Pullanikkatil, Palamuleni & Ruhiiga, 2017).

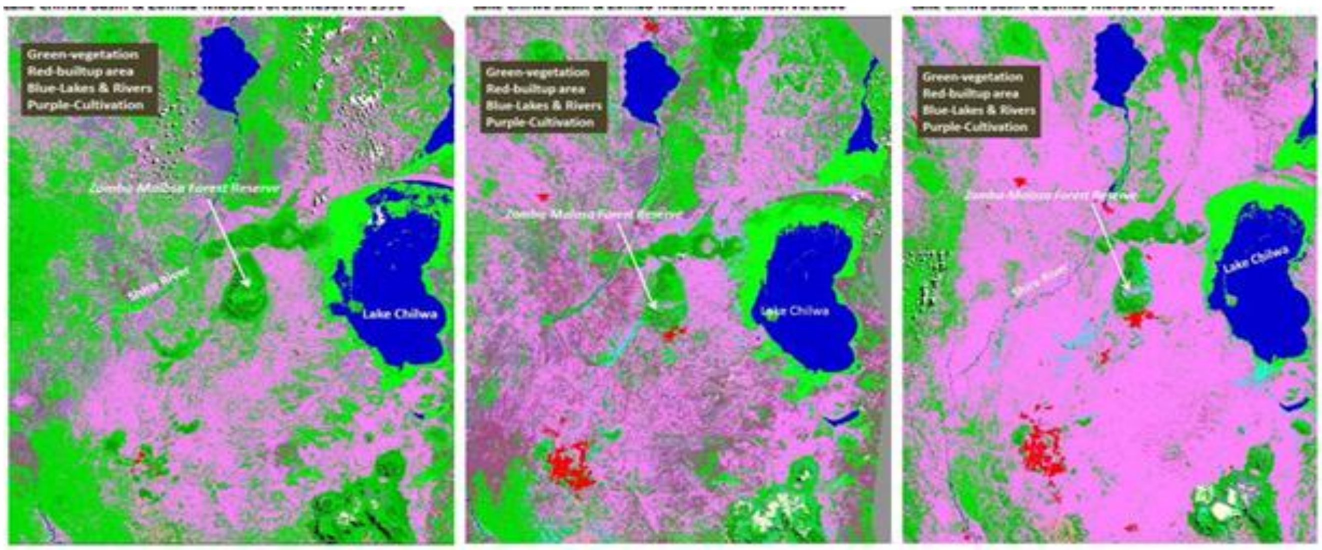

Figure 3: Land use change in the Chilwa catchment from 1990 to 2010 (Source: LEAD 2015)

3.2 CHEMICALS, REAGENTS AND ANALYTICAL INSTRUMENTS

3.2.1 Chemicals and reagents

The following analytical grade (AR) chemicals and reagents were used during analysis of various parameters: Nitric acid, Sulfuric acid, Hydrogen peroxide, 32% Hydrochloric acid, pH 4 ± 0.02 and pH 7 ± 0.02 buffer solutions. ICP mixed standard solution (1000 ppm): Pb, Cd, Zn, Cr, Cu, Hg and As.

3.2.2 Instruments

The following analytical instruments were used during analyses either in the field or laboratory: Digital pH meter (model no.55, MARTINI instruments, USA); EC/TDS digital meter (model no. 59, MARTINI instruments, USA); Ascon Drying oven (OV/125), Weighing balance (Mettler

Toledo, PW 214), Microwave digester (MLS GmbH 640), Inductively coupled plasma optical emission spectrometer (ICP – OES, Perkin – Elmer Optima 5300 DV).

3.3 DESCRIPTION OF SAMPLING POINTS

Figure 4 is a map of Lake Chilwa catchment area showing location and distribution of sampling points and other features. The map was developed using a Geographical Information System (GIS) software, Arc Map version 10. The sampling coordinates were obtained in the field using a Global Positioning System (GPS) device, and this is provided in appendix 1. To ascertain the spatial variability in heavy metals, twenty three water samples were collected in triplicates from Lake Chilwa, Sombani, Phalombe, Thondwe, Likangala, Naisi, Domasi and Mulunguzi rivers. Samples were randomly selected to represent the upper, lower and wetland catchment areas. Sites P01, P05, P07 and P08 located in the upper catchment area constitute mountains, upland fields, and human settlements which are sparsely distributed. Sites P01 and P07 are located in the heart of the mountains within the forest reserve. These two points were selected to represent areas with less anthropogenic disturbance. Sites P02, P03, P06, P09, P10, P22, P23, P14, P13,P18, P15, P16,P04 and P11 lie in the lower catchment areas where human settlements, farming and other anthropogenic activities are prevalent. Sites P03, P12 and P17 are located within the wetland where rice, maize and vegetable cultivation are dominant. Three sites, P19, P20 and P21 were selected from the lake to understand levels of heavy metals in the lake. Both water and surface sediments were sampled from these three lake locations. Site P19 represent the harbor, where a majority of activities along the lake take place including, trading, boat loading and offloading among others.

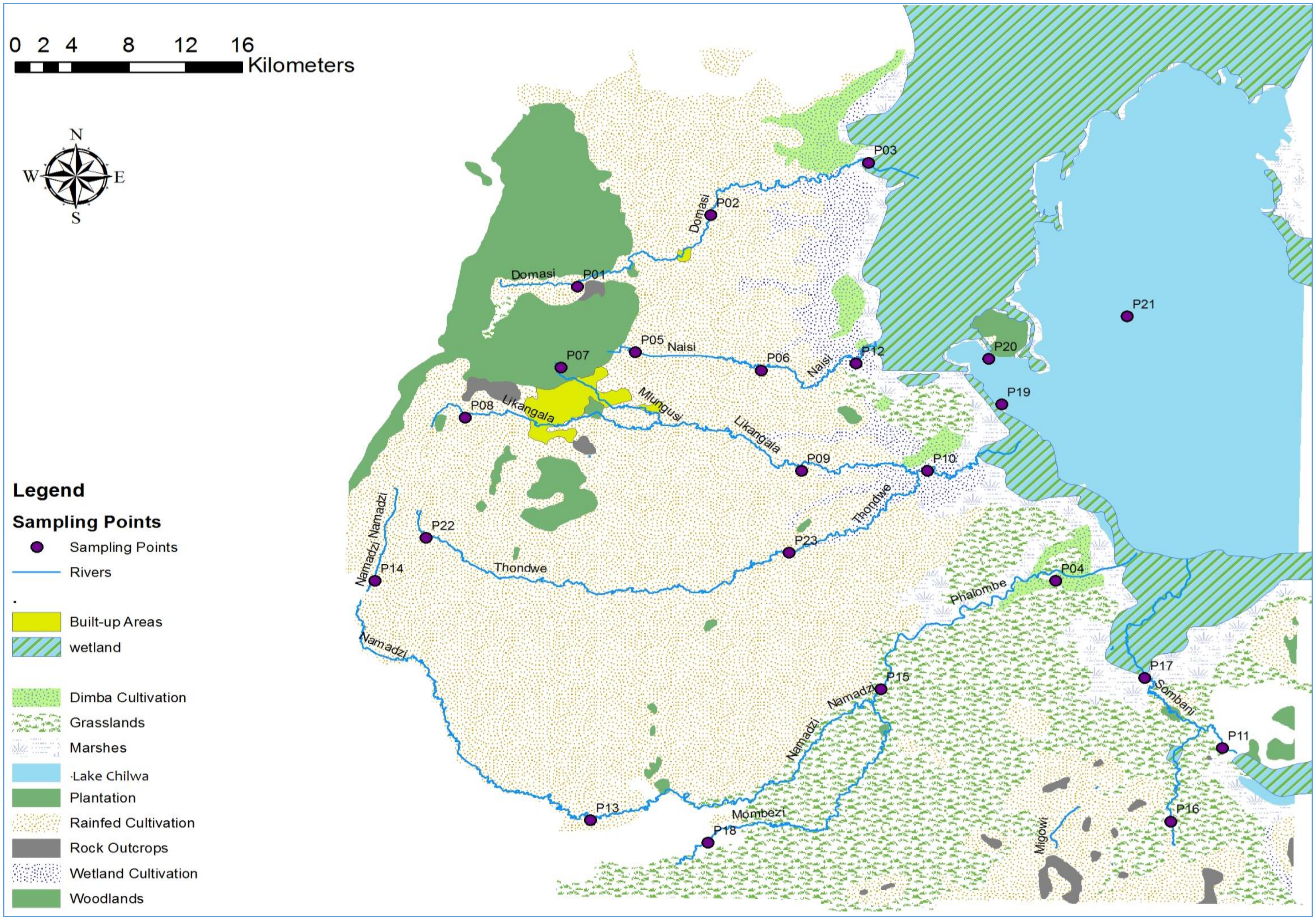

Figure 4: A description of the catchment and sampling point

3.4 WATER AND SEDIMENTS SAMPLING

High density polyethylene (HDPE) bottles were used to collect the water samples in triplicate. The bottles were first of all washed with dilute nitric acid (HNO_3), rinsed thoroughly with distilled water and finally washed thrice with the water to be collected before filling them up.

Sediment sampled were sampled using a sediment corer which was drilled through the sediment bed to a depth of 0 – 20 cm. The sediments were kept in the core and transported to the laboratory for analysis.

3.4.1 Treatment and preservation of water and sediment samples

Within a few hours after collection, the water samples were filtered through cellulose acetate membrane filters (0.45µm, Whatman) into an acid washed polyethylene 200 mL volume bottle. Preservation of the metals was done by acidifying the water samples to pH < 2, using nitric acid and stored at 4 ^oC until analysis. Surface sediments were dried in an oven at 105 ^oC and ground with a pestle and mortar. Digestion was performed by the aqua regia microwave digestion method, where approximately 1.0000 g of the ground sample was placed in a Teflon beaker, then 10 mL HNO_3 and 3 mL HCl were added then digested in a microwave digestion unit. Digested samples were then filtered and diluted to 100 mL with distilled water and kept in plastic bottles until metal analysis. Extraction was done in triplicate and blanks were included for quality control.

3.5 DETERMINATION OF PH AND CONDUCTIVITY

The pH and conductivity (EC) values of waters were measured on–site with a HANNA meter as described in (ALPHA, 1990). The pH was calibrated using two ready-made buffer solutions of pH 4.00 ± 0.02 and pH 7.00 ± 0.02 by Glassworld, SA. EC was calibrated using a ready-made standard solution M10031 (1413 uS/cm) by Glassworld, SA.

3.6 DETERMINATION OF HEAVY METALS

The metal elements (Cd, Pb, Zn, Cr, As, Hg, Ni and Cu) were analyzed by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) at University of Tubingen, Department of Geosciences, Germany following the instruments operating procedure.

3.6.1 Preparation of standard solutions

10 mL of the standard solution (1000 mg/L Zn, Cu, Cr, Cd, Pb and Ni) was transferred into a 100 mL volumetric flask, followed by dilution with distilled water. Serial dilutions were performed to produce 0.5, 1.0, 5.0, 10.0, 20.0 and 50.0 ppb solutions. Similarly standard solutions of Hg and As were prepared from their stock solutions. Calibration curves were prepared by plotting the absorbance versus concentration. Concentrations of each element in the samples were determined by referring directly to its calibration curve plotted.

3.7 HEAVY METAL POLLUTION INDEX (HPI)

Heavy metal pollution index (HPI) is a method of rating the heavy metal pollution proposed by Prasad & Bose (2001) that shows the composite influence of individual heavy metals on the overall quality of water. Based on the arithmetic mean method, the HPI indicates the total quality of water with respect to heavy metals. The water is considered not polluted if the HPI value is less than 100. This method is an effective tool to assess the water quality with respect to heavy metals.

The HPI method was developed by assigning a rating or weightage (Wi) for each chosen parameter. The rating is an arbitrary value between zero and one and its selection reflects the relative importance of individual quality considerations. It can be defined as inversely proportional to the standard permissible value (Si) for each parameter (Prasanna et al., 2012). In this study, the concentration limits (i.e., the standard permissible value (Si) and highest desirable value (Ii) for each parameter) were taken from the WHO 2008 standard (table 1). The uppermost permissive value for drinking water (Si) refers to the maximum allowable concentration in drinking water in absence of any alternate water source. The desirable maximum value (Ii) indicates the standard limits for the same parameters in drinking water.

The HPI, assigning a rating or weightage (W_i) for each selected parameter, is determined using the expression below:

$$HPI = \frac{\sum_{i=1}^{n} WiQi}{\sum_{i=1}^{n} Wi}$$

Where Q_i and W_i are the sub-index and unit weight of the *i*nth parameter, respectively, and n is the number of parameters considered.

The sub index (Q_i) is calculated by:

$$Qi = \sum_{1=1}^{n} \frac{\{Mi(-)Ii\}}{Si - li} x100$$

Where Mi, I_i, and S_i, are monitored metals, ideal and standard values of the *i*nth parameter, respectively. The sign indicates numerical difference of the two values, ignoring the algebraic sign (Prasanna et al., 2012).

Table 1: Referenced values used for computation of indices

Parameter	Standard Permissible Value (Si)	Unit Weightage (Wi)
Cd	3	0.333
Cr	50	0.02
Cu	2000	0.0005
Ni	20	0.05
Pb	10	0.1
Zn	5000	0.0002

Units for the concentrations = µg/L

3.8 STATISTICAL ANALYSES AND QUALITY ASSURANCE OF RESULTS

The data obtained was entered into Microsoft excel version 2010 to compute means and standard deviations. Pearson correlation coefficient (two tailed at 95%) was employed to detect relationships for the metals. To guarantee quality and reliability of the results, samples were collected and measured in triplicate.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1. RESULTS FOR SURFACE WATER QUALITY

4.1.1. pH and Conductivity

The pH of the water in the catchment was in the alkaline range (7.87 - 10.17) as shown in figure 5. Highest pH was observed in Lake Chilwa, ranging from 9.41 to 10.17 at points P19, P20 and P21. These findings are consistent with earlier studies in some parts of this catchment which also found pH within the alkaline range (Macuiane, Kaunda & Jamu, 2011; Saka, 2006).

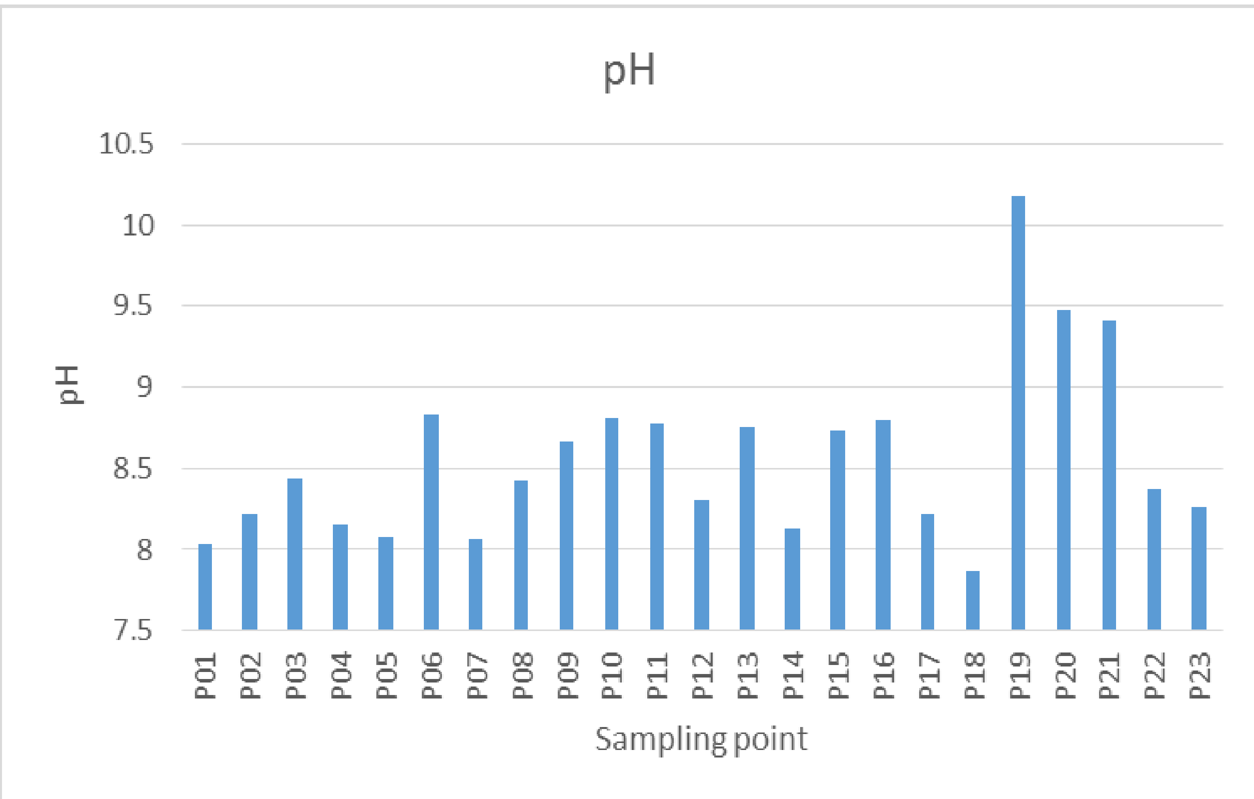

Figure 5: pH of the water from the lake and rivers

This high pH is attributed to high levels of sodium, carbonates and chlorides (Saka, 2006), from the underground hot springs, bedrock and soil composition that contains limestone ($CaCO_3$) through which the water flows (Chidya et al., 2011, Morgan & Kalk, 1970). High levels of these ions has an implication on heavy metal speciation. When pH is high, the competition between H^+ and the dissolved metals for ligands (e.g., OH^-, CO_3^{2-}, SO_4^{2-}, Cl^-, S^{2-}, and phosphates) becomes more and more significant. The adsorption abilities of the metals subsequently increase and then decrease the mobility of the heavy metals. Thus high pH will tend to fractionate the metals out of the water phase and favor precipitation and accumulation in the sediments (Korfali & Davies, 2004). This in turn reduces the levels of heavy metals in the water and increases the levels in the sediments.

Conductivity values followed a similar trend as pH (figure 6). High levels were observed in the lake waters compared to the rivers. The lake had conductivities ranging from 348–390 µS/cm, while the rivers had conductivities ranging from 97–260 µS/cm. The values observed from the lake are similar to those reported from an earlier study that recorded a conductivity of 383 µS/cm in the wet season (Macuiane et al., 2011). The elevated EC values in the lake, similar with pH, were attributed to dissolution of minerals like carbonatites and limestone as well as agricultural activities in nearby fields that make use of fertilizers that provide a direct source of ions (i.e. K, Ca, Mg, SO_4^{2-} and Fe^{3+}) (Chidya et al., 2011). The endorheic property of the lake allows concentration of the ions thereby increasing the ionic strength of the water which results in the high conductivity values observed. Kachulu harbor (P19) showed the highest conductivity of 390 µS/cm. A study by Pullanikkatil, *et al* (2015) cited this location as the most polluted point, mainly as a results of increased concentrations of calcium, potassium, nitrates, phosphates, Sodium, carbonates and sulfates from sewage and runoff from irrigated lands. Points located in the mountain areas, P07, P05 and P01 from Mulunguzi, Naisi and Likangala rivers respectively showed the lowest values of conductivity, while those in the downstream locations, P15, P10, P19 and P03 showed higher values. The highlands are characterized by less human activity with predominantly rural settlements while the lowland areas are dominated by farming and settlement activities. This could suggest that human activities such as farming activities dominating the low land areas have an impact on the ionic strength of the water bodies, similar to studies elsewhere (Cisse & JiWen, 2009, Amah-Jerry et al., 2017).

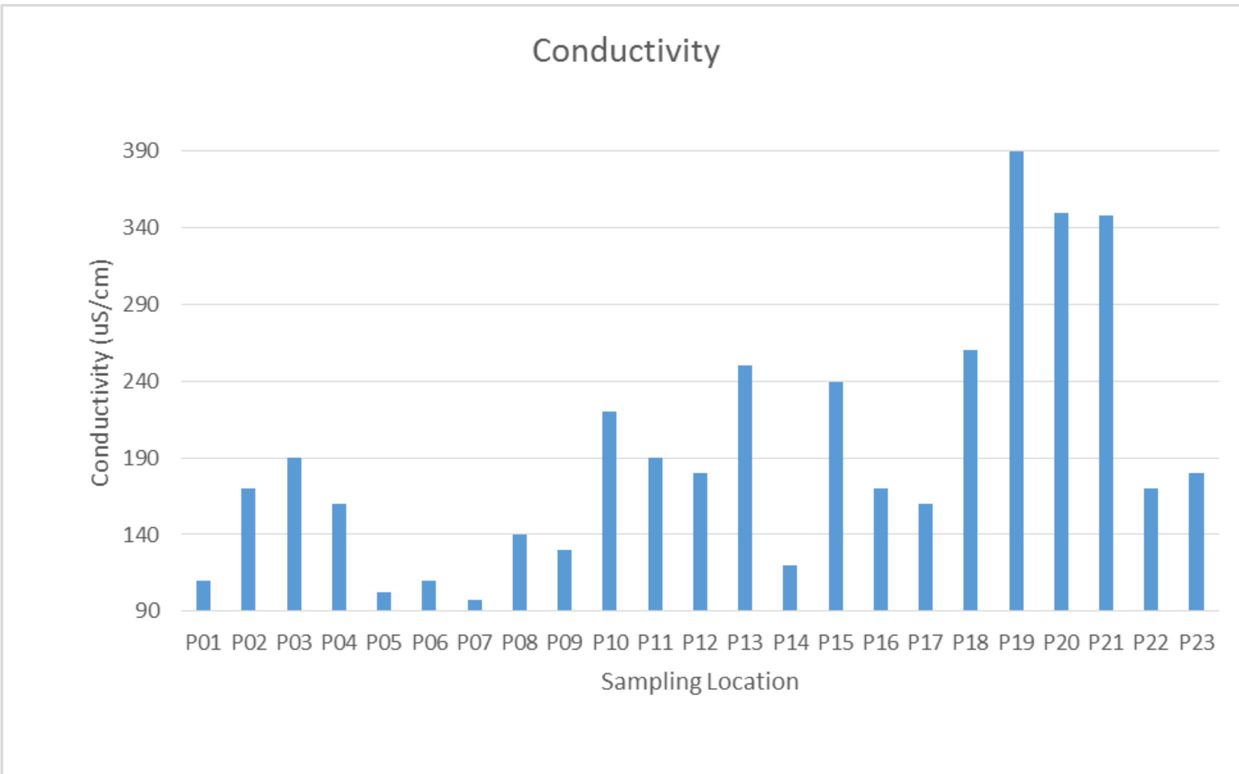

Figure 6: Conductivity values from the sampled points

4.1.2. Heavy metals

Six metal elements, in order of decreasing concentration, were detected in the waters (figure 7); Zn > Cu > Pb > Cr > Ni > Cd. Mercury and arsenic were not detected in all sampling locations.

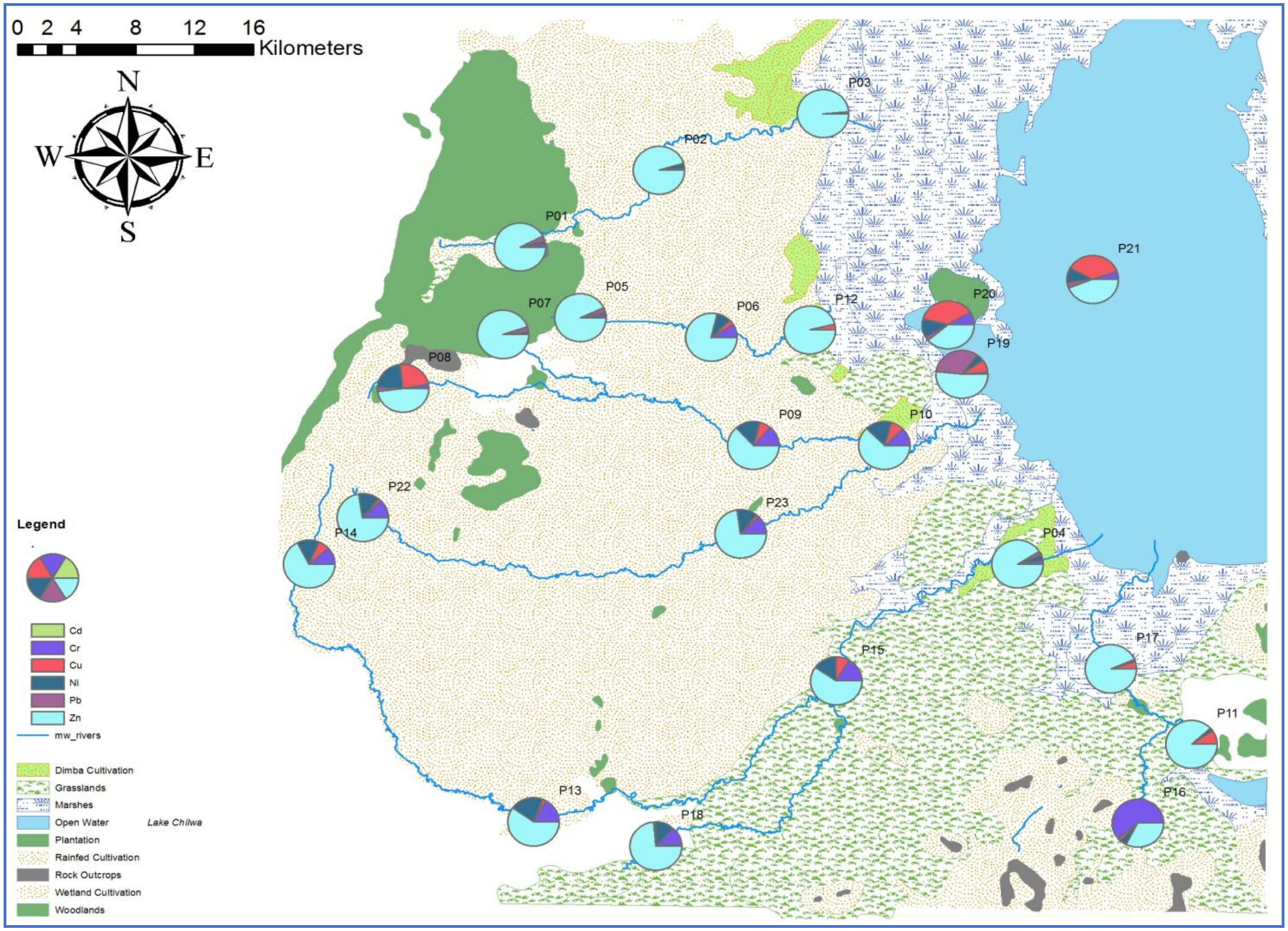

Figure 7: Variability of metal **concentrations with sample location**

4.1.2.1. Zinc

Zinc had the highest concentrations in all sampling stations with values ranging from 6.24 µg/L to 1168.70 µg/L at point P08 and point P12 respectively. Most of the sampling stations (> 80%, n = 23) had zinc concentrations above 50% of the total metal concentration, indicating that zinc is the dominating metal in this catchment. A study in Switzerland along a catchment drained by the river Kleine, similarly observed high levels of zinc compared to the rest, mainly attributed to agricultural activities within the catchment (Xue et al., 2003). Downstream locations along the marshy areas (P03, P12, P11 and P17) also showed high levels of zinc (figure 8).

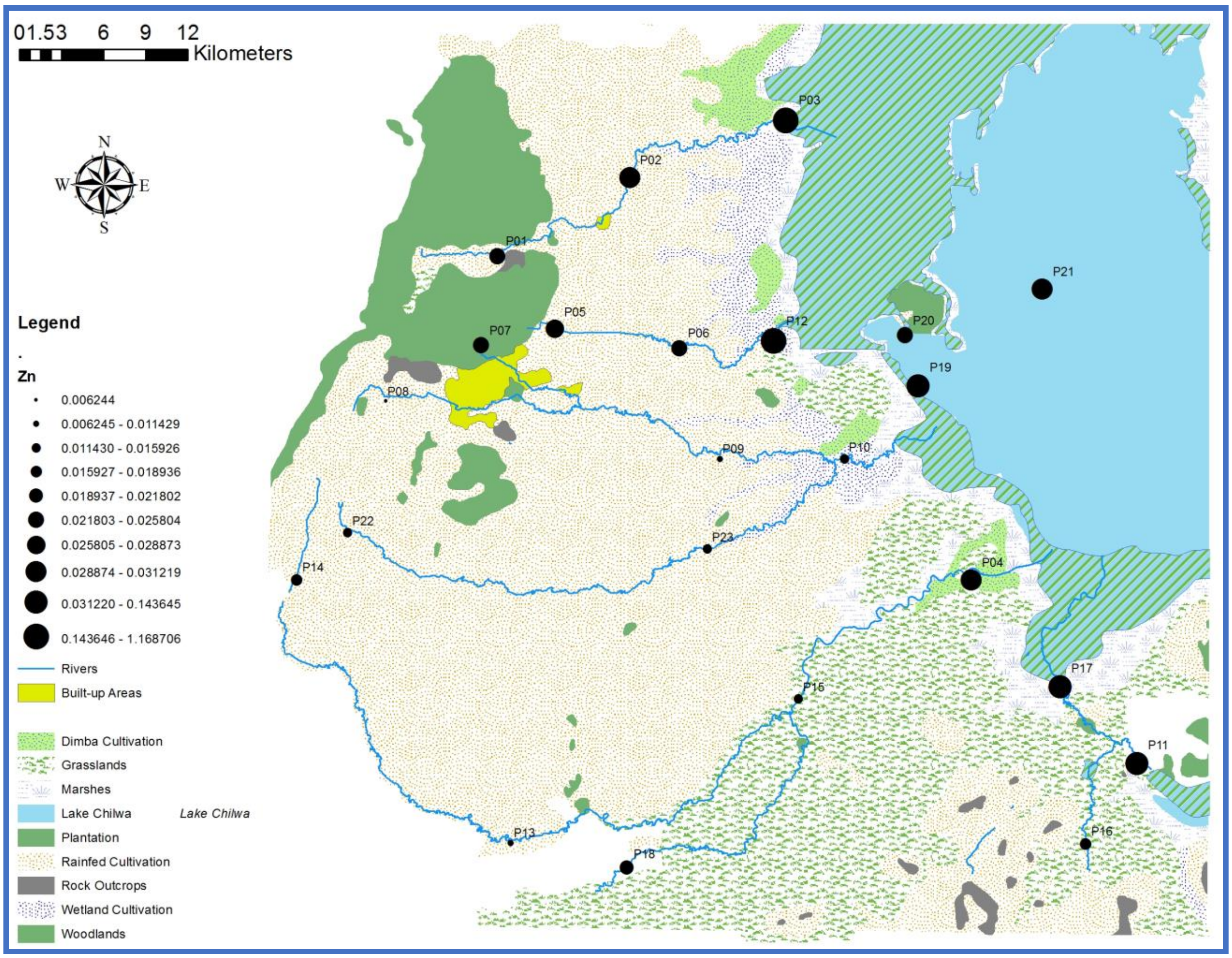

Figure 8: Variability of zinc concentration with sample location

The three rivers that originate from the mountains (Mulunguzi, Naisi and Domasi) had higher levels compared to the rest. Domasi river was observed to have an increasing trend from 25.8 µg/L in the upstream location in the mountain (P01) to 829.82 µg/L in the downstream location within the marshes of the lake, where agricultural activities dominate (P03). The high levels in the lake (P19, P20 and P21) are attributed to the closed nature of this lake which favors accumulation of the elements. Zinc concentrations along the Likangala river are similar to those reported by Chidya (2011), who detected levels between 0.00 mg/L to 0.03 mg/L. The observed levels of zinc are below the requirements of the Malawi Bureau of Standards (MBS) which recommends levels of 3 mg/L to 5 mg/L for drinking water (MBS, 2005).

4.1.2.2. **Copper**

Copper was found to be the second most abundant element in the catchment with an average of 7.11 µg/L (figure 9). Values for copper ranged from below detection limit (BDL) at point P02 within the midsection of Domasi river, to 47.83 µg/L at point P12, downstream of Naisi river. Highest levels were observed from points within the wetland (P03, P11, P12 and P17), where mainly rice and some maize farms were dominant. The lake waters also showed above average levels, attributed to its endorheic property which results in concentrations of the metal elements. Domasi and Thondwe rivers had an increasing concentration gradient with stream flow, while the rest did not show any pattern of change. The highlands, P01, P05 and P07, contrary to zinc, had the lowest concentrations of 0.06 µg/L, 0.03 µg/L and 0.05 µg/L respectively. This may indicate that concentrations downstream are as a result of the land use changes that include settlements and agriculture. A study in the Niger delta observed higher levels of copper within the waters ranging from 0.186 mg/L to 0.591 mg/L attributed to agricultural activities (Howard & Olulu, 2009).

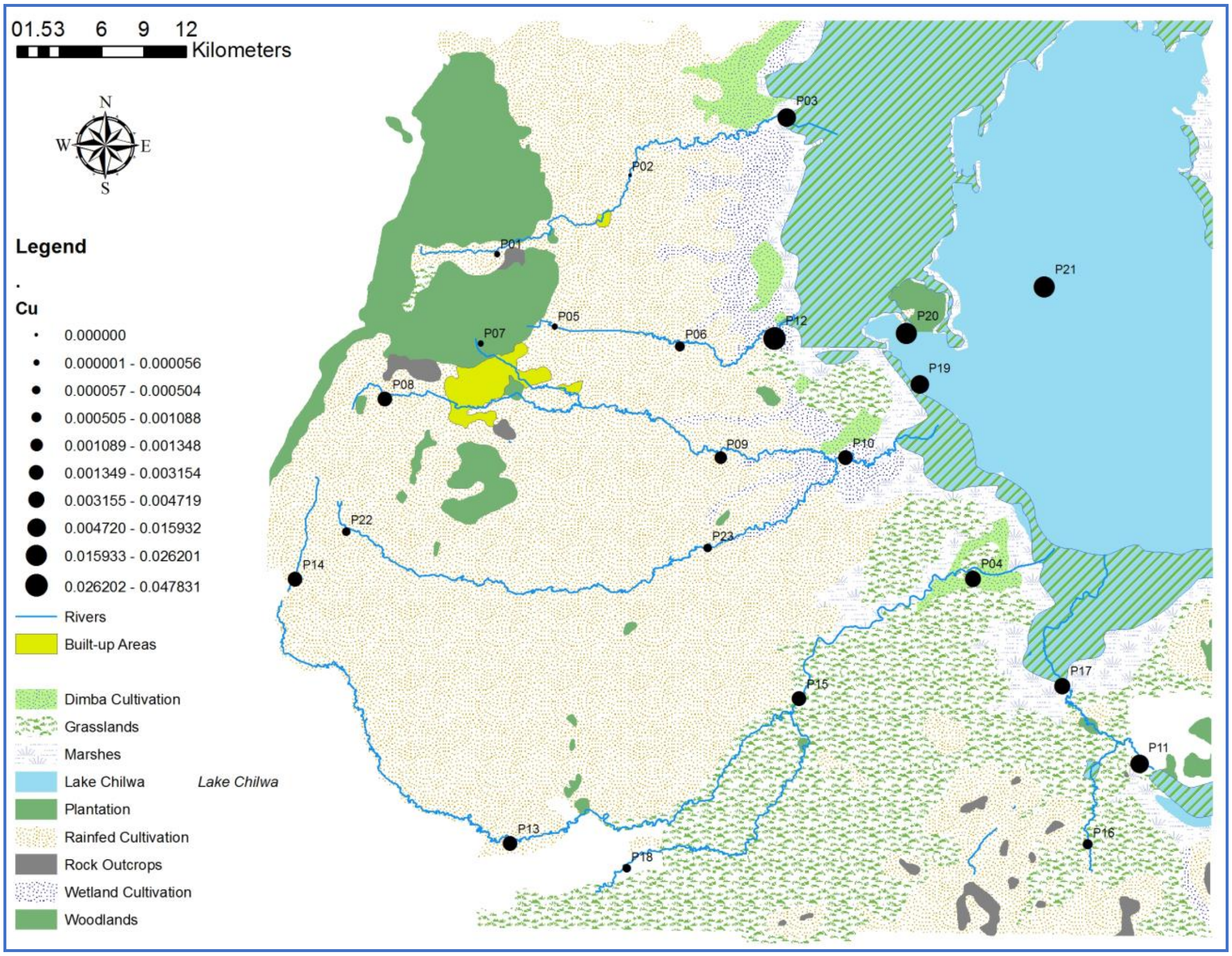

Figure 9: Variability of copper concentration with sample location

Similar results have also been reported by several studies done in the river Ganga in Asia (Paul, 2017). The World Health Organization (WHO) recommends a maximum level of 2 mg/L while the Malawi Bureau of Standards (MBS) recommends between 0.5 mg/L and 1.0 mg/L in drinking water. Values obtained in this study from all sampling locations fall below these standards, therefore the levels do not pose a serious health risk.

4.1.2.3. Lead

Concentrations of lead ranged from below detection limit (BDL) at points P06, P10, P13, P15 and P22, to 49.94 µg/L at Lake Chilwa harbor (P19). The harbor was recorded earlier as the most polluted site in the lake by an earlier study (Pullanikkatil et al., 2015). The other two points in the Lake, P20 and P21 also showed higher lead levels of 1.74 µg/L and 2.74 µg/L respectively. The downstream locations of Naisi and Domasi river had the highest concentrations among the river sampling sites. There was no significant pattern of change along the river courses, indicating that the concentrations are point specific. Variability of lead concentration within the catchment is shown in figure 10. The mountain areas (P07, P05 and P01) with less human activities had levels significantly greater than some points in the lowlands (0.97µg/L, 1.1µg/L and 1.01µg/L respectively). The results observed in the rivers are similar to those found in a study in India on Brahmani River and its tributaries (Reza & Singh, 2010). Chidya (2011) on reported higher lead levels ranging from 0.14 – 0.71 mg/L (Likangala river) during the dry season, which was mainly attributed to the lead bearing limestone and galena (PbS) and washing of leaded waste materials. Saka (2006) observed that some accumulation of lead occur along the roadsides in the municipality of Zomba and Likangala river as a result of deposition from vehicle exhausts. The world Health Organization (2008) and Malawi Bureau of standards (2005) stipulates a Lead level of 10 µg/L and 50 µg/L as the maximum allowable limit for drinking water respectively. The Chilwa harbor was observed to have a lead level above both standards for drinking water, there by posing a health risk to users of this water. This area is where most of the economic activities that include trading, offloading and loading of materials to the boats among others take place. All these activities have associated wastes that could be attributed to the high levels of lead at this site.

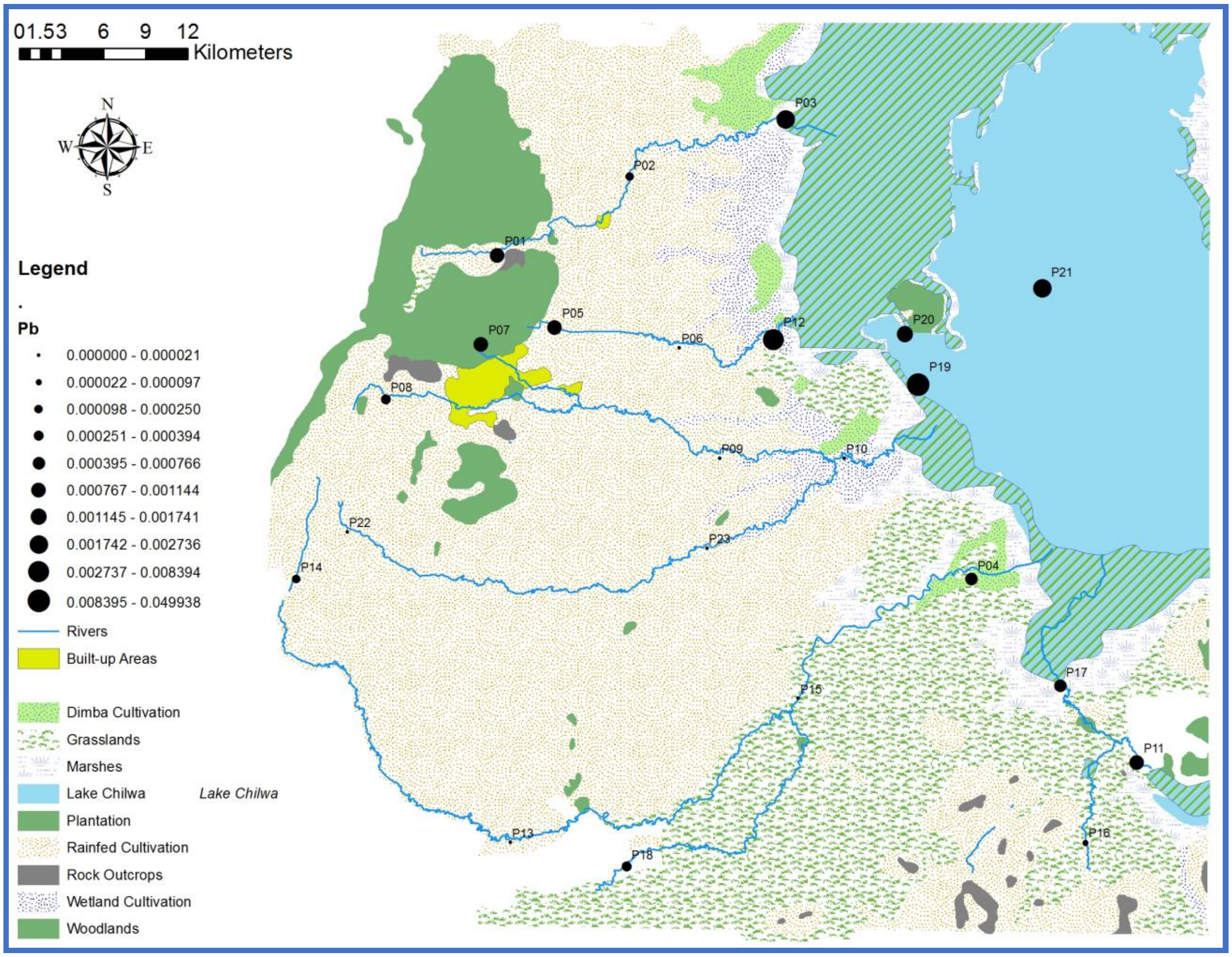

Figure 10: Variability of lead concentration with sample location

All other points fell below both limits posing no health risk to the users. However the point on the downstream location of Naisi, P12, had a value of 8 µg/ L close to the standards level.

4.1.2.4. Chromium

Similar to zinc, chromium was detected in all sampling stations with concentrations ranging from 0.22 µg/L on the upstream location of Mulunguzi (P07) to 33.05 µg/L on Sombani river within its midsection (P16). At this point (P16) chromium concentration dominated the proportion of metals (figure 7). There was no significant pattern of change along the river courses, except for

Domasi river which showed a decreasing trend from the upstream (0.69 µg/L) through its midstream point (0.39 µg/L) to the downstream point (0.27 µg/L). The downstream locations within the wetland (P17, P04, P12 and P03) had lower concentrations, contrary to Zn, Cu and Pb, than the upland and midstream courses of the rivers. Similarly upstream locations within the mountain areas (P08, P07 and P01) also showed lower concentrations. The lowland areas of the catchment within the midsections of the rivers had elevated levels. These areas are dominated by rain fed cultivation, mainly maize fields (figure 11). The lake had levels within 2.63 µg/L to 5.83 µg/L, lowest levels were observed on the harbor area, which was cited as the most polluted area by human activities, as earlier explained.

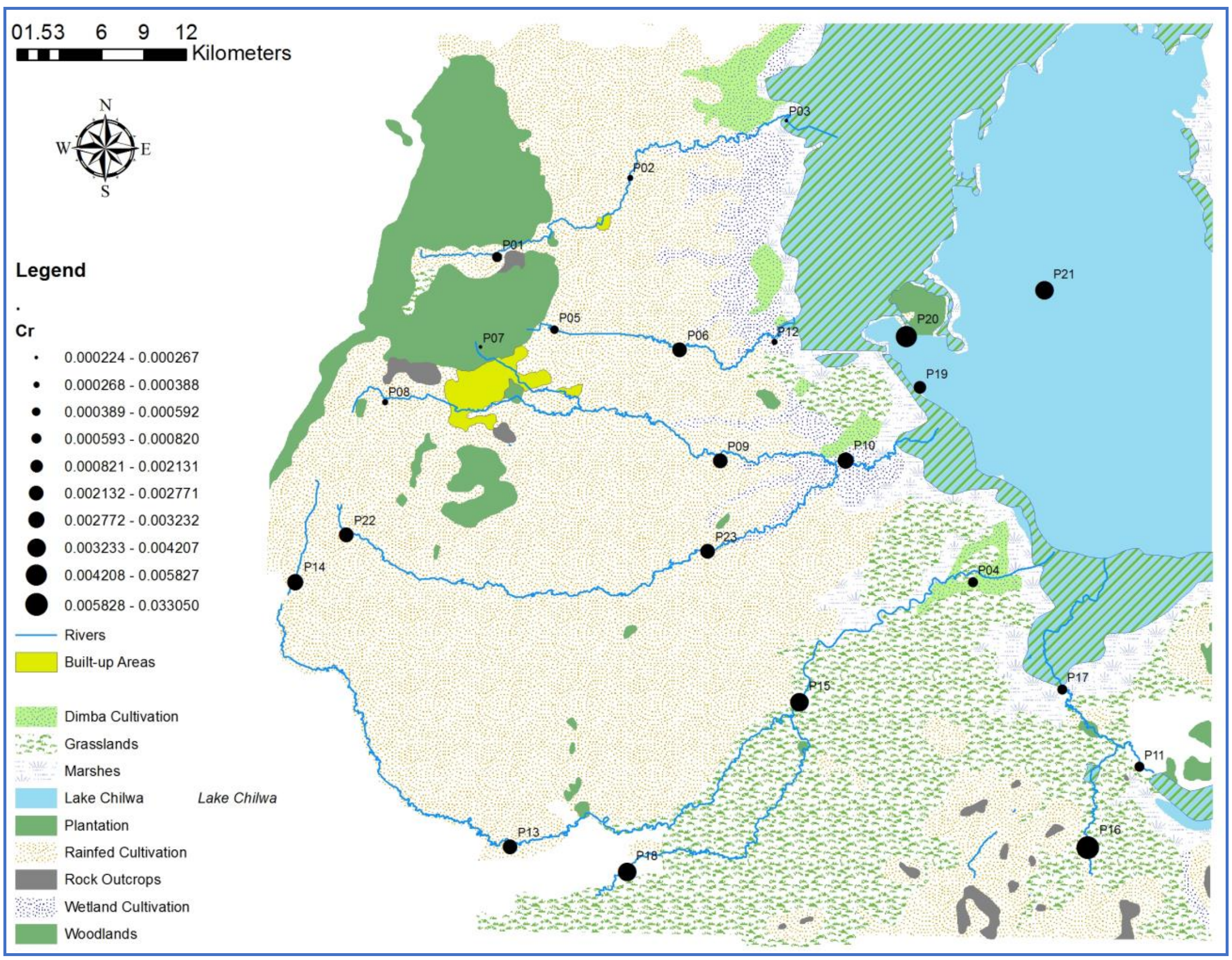

Figure 11: Variability of chromium concentration with sample location

A Study within Mudi river one of the rivers passing through the city of Blantyre, observed an average level of 0.22 mg/L higher than our observed value. The level of chromium was attributed to industrial waste from the manufacturing companies within the rivers catchment (Kumwenda et al., 2012). The values of chromium in this work are similar to those recorded in a study in the Malaysian aquatic environment. (Shazili et al., 2006). Higher levels of chromium (0.12 ppm) were observed in the waters of Harike Wetland in India and this was attributed to industrial waste (Brraich & Jangu, 2015). The world health organization (2008) gives a provisional limit of 50 µg/L which is higher than the observed levels, while the local standards by MBS (2005) give an upper limit of 10 µg/L. Two sampling stations (P16 and P20) were observed to have levels above the local standard, thereby posing a health risk to users of the water.

4.1.2.5. Nickel

Nickel was detected in all sampling stations with concentrations ranging from 0.40 µg/L at point P05, on the upstream location of Naisi, to 8.2 µg/L at P20 in Lake Chilwa (figure 12). The upstream locations of Mulunguzi (P07), Naisi (P05) and Domasi (P01) had the lowest levels of 0.42 µg/L, 0.40 µg/L and 0.48 µg/L respectively, while points in the lake, (P19, P20 and P21) showed the highest levels of 0.7.13 µg/L, 8.29µg/L and 6.98 µg/L respectively. Domasi river showed the lowest levels of nickel compared to the rest. In general there was no significant pattern of change across the river course. The maximum allowable limits of nickel in drinking water by the world health organization (2008) and Malawi Bureau of Standards (2005) are 0.07 mg/L and 0.05 mg/L respectively. Therefore the levels do not pose any serious health effects.

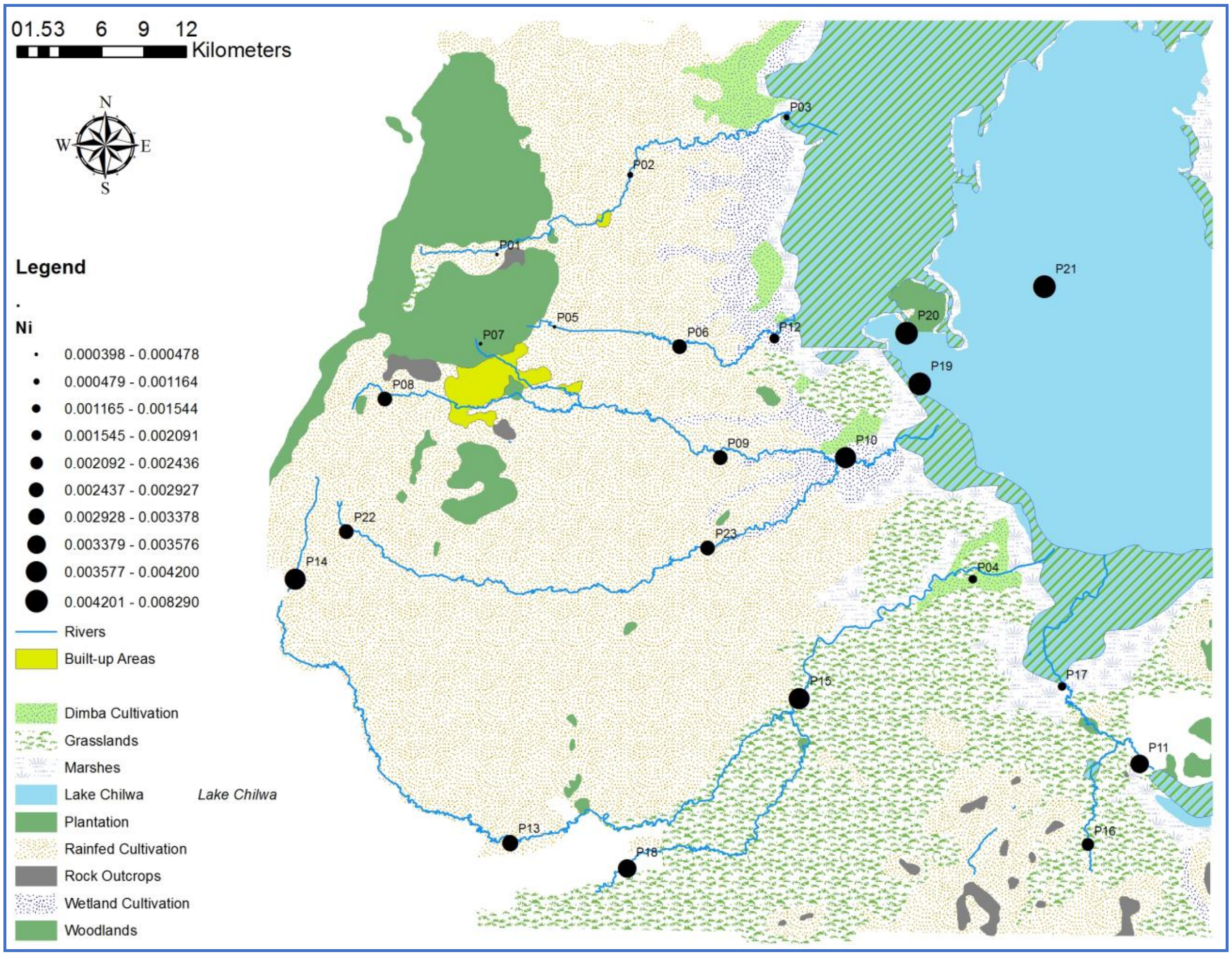

Figure 12: Variability of nickel concentration with sample location

4.1.2.6. Cadmium

Cadmium showed the lowest levels with concentrations ranging from undetected levels (BDL) (30%, n = 23) to 0.53 µg/L (figure 13). Locations within the highlands and the wetland (P01, P05 and P07) and (P03, P12, P04 and P17) respectively showed the lowest levels. Locations within the midsections of the river courses showed higher levels. The Harbor (P19) which is considered the most polluted area, (Pullanikkatil et al., 2015) showed the highest level of this metal. The other points within the lake (P20 and P21) contrary to the rest of the metals had lower values than those observed from the rivers. A study in Mudi river, passing through the industrial areas of Blantyre had an average level of 10 µg/L, higher than those observed in this catchment, attributed to industrial effluents (Kumwenda et al., 2012). The maximum allowable limit of cadmium in drinking water by the world health organization (2008) and Malawi Bureau of Standards (2005) are 3 µg/L and 5 µg/L respectively. Concentrations in this catchment are all below these standards, therefore the levels observed do not pose any serious health risk to the users in as far as cadmium is concerned.

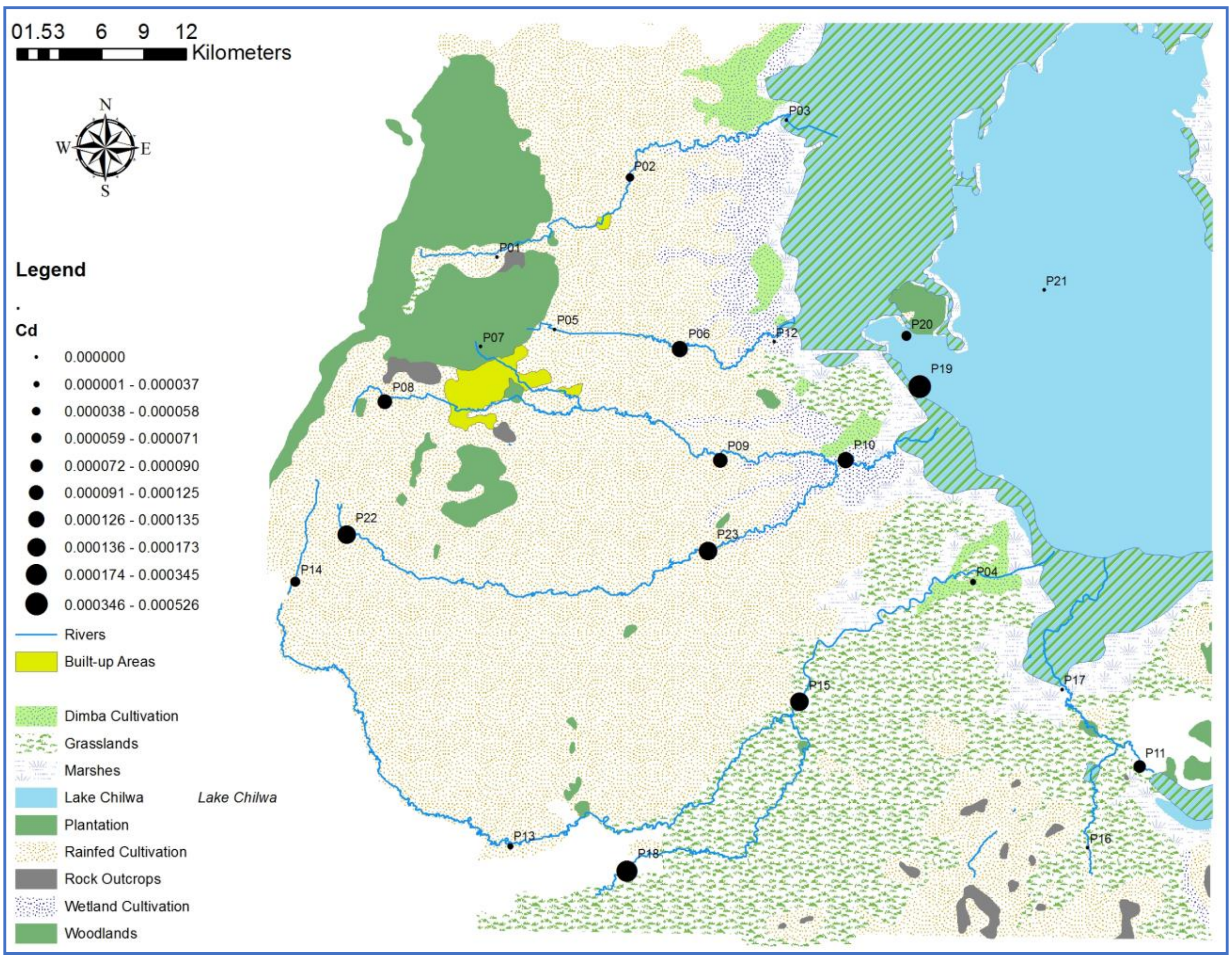

Figure 13: Variability of cadmium concentration with sample location

4.1.2.7. Mercury and Arsenic

Mercury and arsenic were not detected in all the sampled waters. Mercury is a volatile metal which easily escapes as a vapor to the atmosphere under normal surface temperatures. In natural waters concentrations are usually very small, rarely exceeding a few tenth of a microgram per liter (Hem, 1985). Arsenic has been used as a component of pesticides and thus may enter streams through waste disposal or agricultural drainage. This metal is insoluble in water especially under basic conditions, therefore concentrations are usually low in water (Hem, 1985).

4.1.3 CORRELATION STUDY OF THE METALS

Pearson's correlation (PC) matrix was computed to determine if some parameters correlated with each other and the results are presented in table 2. There was significant positive correlation between cadmium and lead (0.70), copper and zinc (0.70), cadmium and nickel (0.50) and lead and nickel (0.41). Chromium showed the least associations with the other metals.

Table 2: Correlation analysis for the measured parameters

	Cd (ppm)	*Cr (ppm)*	*Cu (ppm)*	*Ni (ppm)*	*Pb (ppm)*	*Zn (ppm)*
Cd (ppm)						
Cr (ppm)	-0.08526					
Cu (ppm)	-0.12068	-0.09907				
Ni (ppm)	**0.4769**	0.11986	**0.3956**			
Pb (ppm)	**0.6898**	-0.06838	0.25939	**0.41728**		
Zn (ppm)	-0.22121	-0.15884	**0.69865**	-0.20255	0.12139	1

Correlation analysis is used to understand inter elemental association which can be used to understand sources of the metal elements. The elemental association may signify that each paired elements has an identical source (Sekabira, Basamba, Mutumba & Kakudidi, 2010). Nickel and cadmium (r = 0.50) is used in rechargeable batteries. Used batteries discarded within the dumpsites could provide a source of the metals to the water resources. A study in Switzerland observed elevated levels of nickel and cadmium from soils within the vicinity of a waste dumping facility where used batteries were disposed (Lemann, Walder, & Schwyn, 1995). Lead and cadmium (r = 0.70) is used in vehicle acid batteries. Their disposal after use could release these metals into the environment. In Nigeria, high levels of Lead and cadmium were detected in Omilende stream. The levels were attributed to battery waste from a dumpsite located close to the stream (Afolayan, 2018). Copper and nickel (r = 0.40) are used in stainless steel products that include iron sheets and cooking utensils, cosmetcics and shampoos (Ngole & Ekosse, 2012). Improper waste management (figure 17) within the catchment facilitates the transport of these elements to water resources.

Figure 14: Waste bunker not properly used on the banks of Likangala River (Source R. Chidya 2011)

Copper and Zinc (r = 0.70) are often added to livestock feed due to their anti-microbial and growth promoting properties, with significant concentrations ending up in manure. The high association between copper and zinc could be attributed to manure usage within the agricultural fields (Mantovi, Bonazzi, Maestri & Marmiroli, 2003). Poor farming practices that include farming along the river banks exacerbate the transport of these metals to the water resources as shown in figure 15.

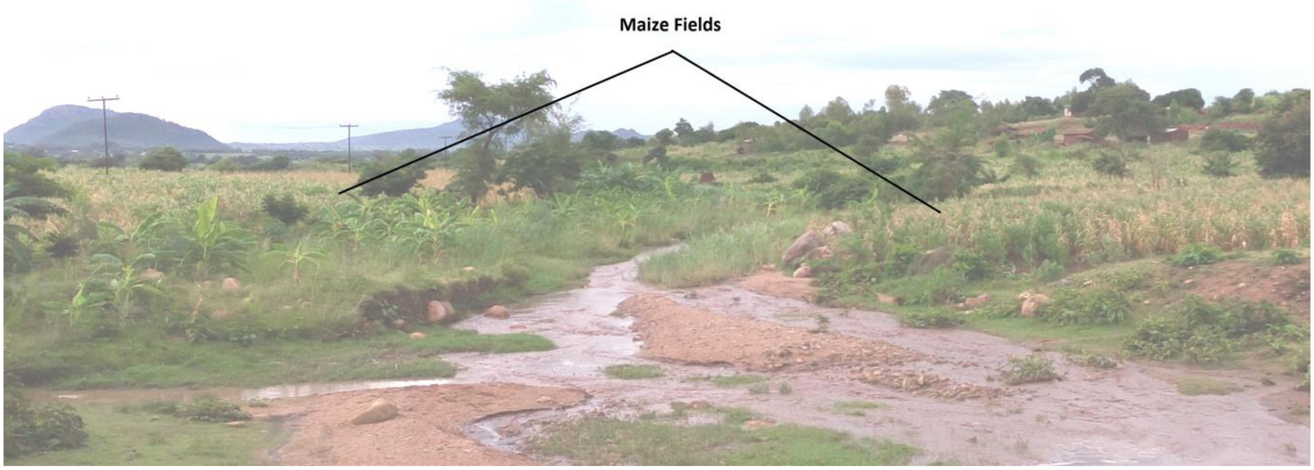

Figure 15: Cultivation along the banks of Phalombe River (source: Researcher 2016)

4.2. METALS IN SEDIMENTS

The following metals were detected in the sediments in order of decreasing concentration; Zn > Cr > Ni > Cu > Pb > As. Cd and Hg were below the detection limits of the instrument. Figure 16 shows the levels of the metals in the sediments from the two sampling stations. Levels of metals from the two points did not show any significant difference (P > 0.05). Zinc is the dominating element in this catchment, with the highest proportion in both water and sediments. The concetration of the elements observed followed a similar trend as that observed in the river

Ganga where zinc had the highest concentration and cadmium showed the lowest concentration (Paul, 2017). Arsenic which were absent in the water column was detected in the sediments, while cadmium which was detected in the water, was absent in the sediments. The absence of cadmium in sediments could be attributed to its low level detected and its high water solubility, similar to that observed in the Ebute Ogbo river in Nigeria (Adeniyi et al., 2011).

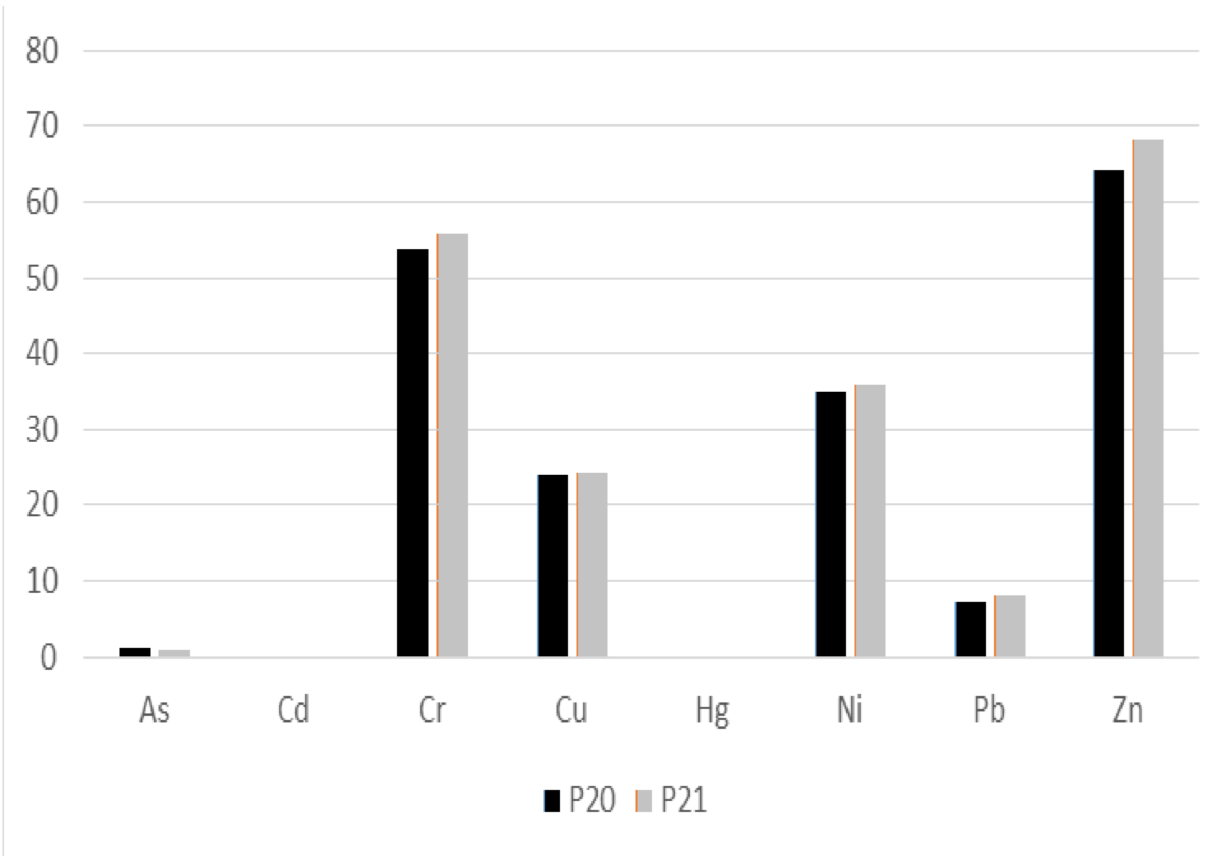

Figure 16: Concentration of metals in sediments

Arsenic is fairly insoluble, and tends to bind to particulates in the water and settle down to the sediment phase (Stumm & Morgan, 1984). This could explain why arsenic was only detected in the sediments and not in the water phase.

The sediments are the final repository of metals when conditions are favorable. The high pH of the waters favors fractionation to the sediments phase (Peltier et al., 2003). Thus, sediment processes could act to sequester permanently these elements, reducing their bioavailability and toxicity. However the levels in the sediments could pose a risk of secondary water pollution under sediment disturbance and/or changes in the geo-chemistry of sediments.

4.3. HEAVY METAL POLLUTION EVALUATION

4.3.1. Heavy metal pollution index

Values of the pollution index ranged from 2.24 (P17 and P02) to 114.45 (P19). All points except the harbor, had values below the critical level of 100, suggesting that the levels do not pose a health risk in as far as heavy metals are concerned. However, the harbor where most activities are taking place, showed the highest level (114.45), higher than the critical value of 100 indicating that the location is polluted. The highlands (P07, P05 and P01) had lower levels while points within the lake (P19, P20 and P21) had higher levels compared to the rest (figure 17). The middle and lowland areas of the catchment comprise cultivated lands that include estates, rice schemes, and subsistence maize farm lands. Settlements are also intensified in the middle and lowland areas. These demographic characteristics could be attributed to the increased levels of heavy metals. The endorheic property of the lake allows concentration of the metal elements resulting in an increase in the lake. If levels within the catchment are not controlled the lake could be at risk of concentrating the toxic elements.

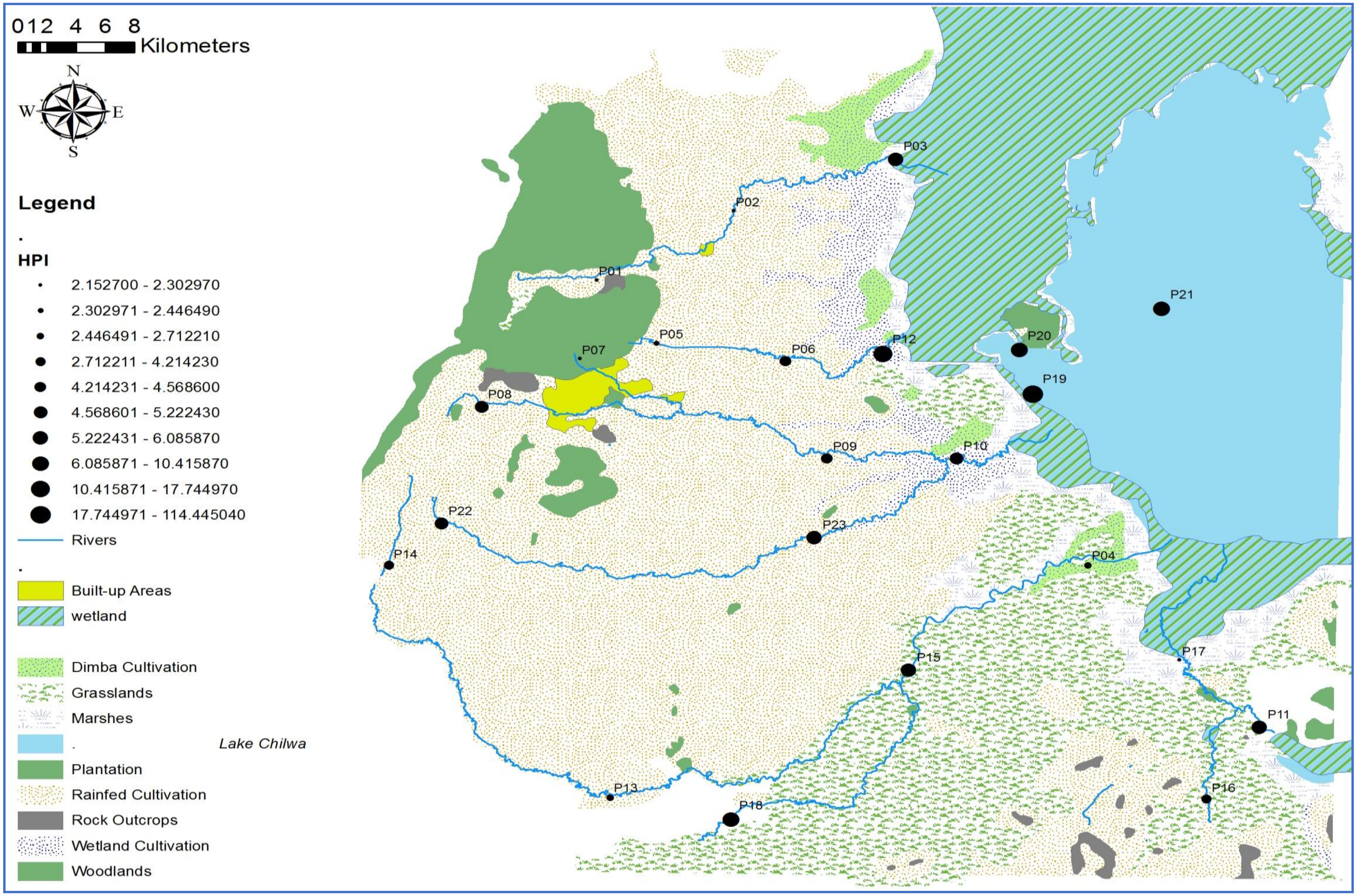

Figure 17: Variability of MPI with sample location

CHAPTER FIVE

CONCLUSION

This study intended to assess the levels and distribution of heavy metals in Lake Chilwa and its catchment. The results show that there is a widespread distribution of heavy metals in the catchment. However the levels observed were within acceptable limits, posing no health risk except at the harbor where levels of lead were above the WHO (2008) limits. Heavy metals bio-accumulate and are persistent, therefore the low levels now would pose a great threat in the near future if proper controls are not put in place. The high pH favors fractionation of the metals to the sediment phase and this explains why levels were low in the water column. Out of all the parameters (Zn, Cu, Cr, Cd, Pb, As, Hg and Ni) examined in this study, zinc was the dominating element in both water and sediments, while mercury was not detected in all samples. Arsenic and chromium were only detected in the sediments and waters respectively. Lake Chilwa waters had the highest overall concentrations of the metal pollutants, owed to its endorheic property. Metals washed from the catchment concentrate in the lake waters, hence the increased concentrations. The Lake harbor where most of the economic activities take place had the highest level of pollution.

Concentrations of most elements were low in the upstream locations located in the highlands and high in the lowland areas close to the lake. Most of the highlands are rocky areas, not suitable for cultivation and settlements as a result human induced changes in the waters are low compared to the lowland areas, comprising the cities and fertile lands where settlements and agricultural activities are practiced. The study therefore revealed that anthropogenic impacts including indiscriminate waste disposal and agricultural activities, could account for the increased levels of metals in the catchment.

The sediments being the ultimate sink, accumulated most of the metals received from the inflowing waters. The endorheic property of the Lake favored the concentration of these metal elements in the lake. The high pH favored fractionation from the water phase to the sediment phase.

Recommendations

The research therefore recommends that measures should be put in place to protect this catchment because the levels, though low now, if left unchecked could result in the accumulation of the metals to toxic levels and cause deleterious irreversible effects to the ecosystem. Based on the findings the following recommendations are therefore made:

- There is need for integrated management of land, water and waste to prevent accumulation of the metals in the catchment.
- Frequent water quality monitoring should be done to monitor the levels of these heavy metals. This will ensure generation of data for sound decision making on safe, sustainable use and management of the water resources.
- Proper waste management facilities should be employed in the area to avoid the indiscriminate disposal of waste that is common within the area.

Areas for further research

This study focused on metals in water and sediments, however heavy metals also accumulate in biota and increase in organisms high in the food chain. Another study should therefore be done to understand the levels in biota within the catchment to understand the level of bio magnification.

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APPENDICES

	GPS Location (UTM)		
Sampling Point	**Easting**	**Northing**	**Rivers and Lake**
P01	749845.5	8306620	Domasi River
P02	759263	8312213	Domasi River
P03	770392	8316327	Domasi River
P04	783600	8283567	Namadzi River
P05	753933.8	8301485	Namadzi River
P06	762821.6	8300057	Naisi River
P07	748688	8300270	Mulunguzi River
P08	741894.2	8296343	Likangala River
P09	765671	8292193	Likangala River
P10	774559.1	8292195	Likangala River
P11	795401.3	8270457	Mpoto Lagoon
P12	769497.7	8300603	Naisi River
P13	750763	8264806	Namadzi River
P14	735524.1	8283569	Namadzi River
P15	771292	8275075	Phalombe River
P16	791760	8264718	Sombani River
P17	789925	8275949	Sombani River
P18	759056.1	8263043	Mombezi River
P19	779816	8297378	Lake Chilwa
P20	778879.1	8300974	Lake Chilwa
P21	788677	8304276	Lake Chilwa

P22	739157	8286938	Thondwe River
P23	764798.1	8285771	Thondwe River

Appendix 1: Sampling locations, coding and descriptions

Appendix 2: HPI values from the sampling stations

Sampling point	Description	MPI
P01	Domasi Upstream	**2.30**
P02	Domasi Middle stream	**2.24**
P03	Domasi Downstream	**5.67**
P04	Namadzi Downstream	**2.67**
P05	Naisi Upstream	**2.45**
P06	Naisi Midstream	**4.57**
P07	Mulunguzi upstream	**2.15**
P08	Likangala Upstream	**4.84**
P09	Likangala Midstream	**4.38**
P10	Likangala Downstream	**5.22**
P11	Mpoto outlet	**6.09**
P12	Naisi Downstream	**17.74**
P13	Namadzi Mid-stream	**2.71**
P14	Namadzi Upstream	**4.21**
P15	Phalombe Midstream	**5.55**
P16	Sombani midstream	**4.03**
P17	Sombani Downstream	**2.24**
P18	Mombezi Upstream	**10.42**
P19	Lake Chilwa Harbor	**114.45**
P20	Lake Chilwa	**9.60**

P21	Lake Chilwa	**9.19**
P22	Thondwe Upstream	**4.97**
P23	Thondwe Midstream	**5.37**

Appendix 3: Mean concentration values for pH, Conductivity, Cd, Cr, Cu, Ni, Pb, Zn, As and Hg measured in the water

		Coordinates			Conductivity								
ID	Description	Easting	Northing	pH	uS/cm	Cd (ppb)	Cr (ppb)	Cu (ppb)	Ni (ppb)	Pb (ppb)	Zn (ppb)	As (ppb)	Hg (ppb)
P01	Domasi Upstream	749846	8306620	8.03	110	0.0000	0.6850	0.0560	0.4780	1.0130	25.8040	BDL	BDL
P02	Domasi Middle stream	759263	8312213	8.22	170	0.0580	0.3880	0.0000	1.1640	0.1780	31.1100	BDL	BDL
P03	Domasi Downstream	770392	8316327	8.44	190	0.0000	0.2670	10.7940	0.8260	2.6370	829.8150	BDL	BDL
P04	Namadzi Downstream	783600	8283567	8.15	160	0.0180	0.8200	4.2110	1.3880	0.7660	30.7060	BDL	BDL
P05	Naisi Upstream	753934	8301485	8.08	102	0.0000	0.5920	0.0320	0.3980	1.1090	28.8730	BDL	BDL
P06	Naisi Midstream	762822	8300057	8.83	110	0.1350	2.7270	1.0880	2.7740	0.0000	24.0120	BDL	BDL
P07	Mulunguzi upstream	748688	8300270	8.07	97	0.0000	0.2240	0.0470	0.4210	0.9700	25.4930	BDL	BDL
P08	Likangala Upstream	741894	8296343	8.43	140	0.1190	0.3310	3.1540	2.9270	0.3734	6.2442	BDL	BDL
P09	Likangala Midstream	765671	8292193	8.67	130	0.1250	2.4670	1.3480	2.8050	0.0210	11.4290	BDL	BDL
P10	Likangala Downstream	774559	8292195	8.81	220	0.1310	3.1580	2.0710	4.2000	0.0000	15.9260	BDL	BDL
P11	Mpoto outlet	795401	8270457	8.78	190	0.0900	0.6870	15.9320	3.5760	1.1440	143.6450	BDL	BDL
P12	Naisi Downstream	769498	8300603	8.31	180	0.0000	0.3880	47.8310	2.0910	8.3940	1168.7060	BDL	BDL
P13	Namadzi Mid-stream	750763	8264806	8.75	250	0.0370	2.7710	2.4120	3.3780	0.0000	9.7730	BDL	BDL
P14	Namadzi Upstream	735524	8283569	8.13	120	0.0680	3.2320	2.0120	3.9540	0.2500	18.9360	BDL	BDL
P15	Phalombe Midstream	771292	8275075	8.73	239	0.1480	4.2070	2.1130	3.9280	0.0000	14.9930	BDL	BDL
P16	Sombani midstream	791760	8264718	8.8	170	0.0000	33.0500	1.0020	2.4360	0.0970	17.5430	BDL	BDL
P17	Sombani Downstream	789925	8275949	8.22	160	0.0000	0.7360	4.7190	1.5440	0.7110	91.8630	BDL	BDL
P18	Mombezi Upstream	759056	8263043	7.87	260	0.3450	3.5970	0.2650	3.5160	0.3940	21.8020	BDL	BDL
P19	Lake Chilwa Harbor	779816	8297378	10.17	390	0.5260	2.1310	12.7450	7.1340	49.9380	76.9140	BDL	BDL
P20	Lake Chilwa	778879	8300974	9.48	350	0.0710	5.8270	24.5450	8.2900	1.7410	25.7080	BDL	BDL
P21	Lake Chilwa	788677	8304276	9.41	348	0.0000	3.7210	26.2010	6.9830	2.7360	31.2190	BDL	BDL
P22	Thondwe Upstream	739157	8286938	8.37	170	0.1530	2.6340	0.5040	2.7940	0.0000	15.5950	BDL	BDL
P23	Thondwe Midstream	764798	8285771	8.26	180	0.1730	2.6500	0.4400	2.6740	0.0080	15.3560	BDL	BDL

**BDL = below detection limit*

Appendix 4: Concentrations of Metals in sediments in mg/Kg

	P20	**P21**
As	1.2705±0.38	0.7274±1.02
Cd	0.00±0.0	0.0±0.0
Cr	53.7165±3.67	55.8917±9.31
Cu	24.0379±1.35	24.1596±0.44
Hg	0.00±0.0	0.00±0.0
Ni	35.0268±2.70	35.7387±6.83
Pb	7.3554±0.52	8.1318±0.74
Zn	64.1512±5.28	68.1052±10.35