CONCENTRATION OF SELECTED NUTRIENTS AND HEAVY METALS IN SOILS IN TEA FARMS AND WATER FROM NYAMASOGOTA RIVER, KISII COUNTY, KENYA

OMWANCHA P. NYABOKE
156/CE/23828/2013

A Thesis Submitted in Partial Fulfillment of the Requirements for the Award of the Degree of Master of Science (Chemistry) in the School of Pure and Applied Sciences of Kenyatta University

JULY, 2017
DECLARATION

This thesis is my original work and has not been presented for any award of degree in any university or any other institution.

Omwancha P. Nyaboke
Kenyatta University

Signature ………………………………… Date…………………………..

Supervisors:

This thesis has been submitted with our approval as University supervisors:

Prof. Jane Murungi
Department of Chemistry
Kenyatta University

Signature ………………………………… Date…………………………..

Dr. Alphonse Wanyonyi Wafula
Department of Chemistry
Kenyatta University

Signature……………………………… Date………………………..
DEDICATION

This work is dedicated to my beloved husband Mr. Dominic Onderi, my son Johnson Onderi and other family members for the tireless encouragement, support and insightful ideas that made this work possible. May the almighty God bless them.
First, special thanks to God for giving me good health during the time of research.

I would also like to express my appreciation to Kenyatta University fraternity which includes School of Pure and Applied Sciences and the Department of Chemistry for unconditional support I was granted. In particular, special thanks go to my supervisors Prof. Jane Murungi and Dr. Alphonse Wanyonyi who began the journey of research with me and kept on encouraging and giving me directions until the work was accomplished.

I thank the laboratory technicians of Kenyatta University and the entire KIRD staff (laboratory) for technical support.

Finally, I thank my family for giving me the opportunity to gain access to higher education and for their full financial support during my study. My gratitude also goes to my colleagues at Maumba secondary school for their valuable advice and support accorded me during the time of research.
# TABLE OF CONTENTS

DECLARATION .................................................................................................................. ii
DEDICATION ..................................................................................................................... iii
ACKNOWLEDGEMENTS .................................................................................................... iv
TABLE OF CONTENTS ..................................................................................................... v
LIST OF TABLES ................................................................................................................. viii
LIST OF FIGURES .............................................................................................................. ix
ABBREVIATIONS AND ACRONYMS ................................................................................ x
ABSTRACT ........................................................................................................................ xi

## CHAPTER ONE .............................................................................................................. 1

INTRODUCTION ............................................................................................................... 1
  1.1 Background of the study .......................................................................................... 1
  1.2 Problem statement and justification ....................................................................... 8
  1.3 Hypotheses ............................................................................................................. 9
  1.4 Objectives ............................................................................................................. 9
    1.4.1 General objective ............................................................................................. 9
    1.4.2 Specific objectives ......................................................................................... 10
  1.5 Significance of the study ....................................................................................... 10
  1.6 Scope and limitation of the study ......................................................................... 10

## CHAPTER TWO ........................................................................................................... 11

LITERATURE REVIEW ..................................................................................................... 11
  2.1 Water and soil contamination ............................................................................... 11
  2.2 Contamination of soil with heavy metals ............................................................... 11
    2.2.1 Copper .......................................................................................................... 13
    2.2.2 Lead ............................................................................................................. 15
  2.3 Phosphates ........................................................................................................... 18
  2.4 Nitrates ................................................................................................................. 20
  2.5 Methods of analysis for heavy metals and nutrients ............................................... 21

## CHAPTER THREE ....................................................................................................... 24

MATERIALS AND METHODS ......................................................................................... 24
  3.1 Research design ................................................................................................... 24
  3.2 Study area ............................................................................................................. 24
  3.3 General Procedures ............................................................................................. 26
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3.1</td>
<td>Sample collection</td>
<td>26</td>
</tr>
<tr>
<td>3.3.2</td>
<td>Apparatus and reagents</td>
<td>27</td>
</tr>
<tr>
<td>3.3.3</td>
<td>Soil sampling</td>
<td>27</td>
</tr>
<tr>
<td>3.3.4</td>
<td>Water sampling and pre-treatment</td>
<td>28</td>
</tr>
<tr>
<td>3.3.5</td>
<td>Labeling of samples</td>
<td>29</td>
</tr>
<tr>
<td>3.4</td>
<td>Sample preparation</td>
<td>30</td>
</tr>
<tr>
<td>3.4.1</td>
<td>Water sample preparation</td>
<td>30</td>
</tr>
<tr>
<td>3.4.2</td>
<td>Soil sample preparation</td>
<td>30</td>
</tr>
<tr>
<td>3.5</td>
<td>Preparation of stock and standard solution</td>
<td>30</td>
</tr>
<tr>
<td>3.6</td>
<td>Determination of nutrients</td>
<td>31</td>
</tr>
<tr>
<td>3.7</td>
<td>Data management and statistical analysis</td>
<td>33</td>
</tr>
<tr>
<td>3.4</td>
<td>Sample preparation</td>
<td>30</td>
</tr>
<tr>
<td>3.4.1</td>
<td>Water sample preparation</td>
<td>30</td>
</tr>
<tr>
<td>3.4.2</td>
<td>Soil sample preparation</td>
<td>30</td>
</tr>
<tr>
<td>3.5</td>
<td>Preparation of stock and standard solution</td>
<td>30</td>
</tr>
<tr>
<td>3.6</td>
<td>Determination of nutrients</td>
<td>31</td>
</tr>
<tr>
<td>3.7</td>
<td>Data management and statistical analysis</td>
<td>33</td>
</tr>
<tr>
<td>4.1</td>
<td>Introduction</td>
<td>34</td>
</tr>
<tr>
<td>4.2</td>
<td>Validation of results</td>
<td>34</td>
</tr>
<tr>
<td>4.3</td>
<td>AAS calibration curves</td>
<td>35</td>
</tr>
<tr>
<td>4.4</td>
<td>Concentration of heavy metals in soils</td>
<td>37</td>
</tr>
<tr>
<td>4.4.1</td>
<td>Concentration of lead in soils</td>
<td>37</td>
</tr>
<tr>
<td>4.4.2</td>
<td>Concentration of copper in soils</td>
<td>38</td>
</tr>
<tr>
<td>4.5</td>
<td>Comparative mean levels of metals between wet and dry seasons</td>
<td>41</td>
</tr>
<tr>
<td>4.6</td>
<td>Concentration of nutrients (phosphates and nitrates) in tea soils</td>
<td>42</td>
</tr>
<tr>
<td>4.6.1</td>
<td>Concentration of nitrates in soils</td>
<td>42</td>
</tr>
<tr>
<td>4.6.2</td>
<td>Concentration of phosphates in soils</td>
<td>43</td>
</tr>
<tr>
<td>4.7</td>
<td>Concentration of heavy metals in river Nyamasogota water</td>
<td>45</td>
</tr>
<tr>
<td>4.7.1</td>
<td>Comparison of levels of copper and lead in river Nyamasogota with standard values</td>
<td>47</td>
</tr>
<tr>
<td>4.8</td>
<td>Concentration of nutrients in river Nyamasogota water</td>
<td>50</td>
</tr>
<tr>
<td>4.8.1</td>
<td>Comparison of nitrate and phosphate levels in river Nyamasogota water with standard values</td>
<td>52</td>
</tr>
<tr>
<td>4.8.1.1</td>
<td>Levels of nitrates in river Nyamasogota water</td>
<td>52</td>
</tr>
<tr>
<td>4.8.1.2</td>
<td>Levels of phosphates in river Nyamasogota water</td>
<td>53</td>
</tr>
</tbody>
</table>

**CHAPTER FIVE** ........................................................................................................... 54

**CONCLUSION AND RECOMMENDATIONS** ................................................................. 54

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1</td>
<td>Conclusion</td>
<td>54</td>
</tr>
<tr>
<td>5.2</td>
<td>Recommendations from the study</td>
<td>55</td>
</tr>
<tr>
<td>5.3</td>
<td>Recommendation for further studies</td>
<td>56</td>
</tr>
</tbody>
</table>

**REFERENCES** .................................................................................................................. 57
Appendix I: ANOVA for difference in means of Cu and Pb between dry and wet season..................................................................................................................... 68
Appendix II: Paired sample tests for difference in means of nitrates between seasons for AL, TF and UTF........................................................................................................................................ 68
Appendix III: Paired sample tests for difference in means of phosphates between seasons for AL, TF and UTF ........................................................................................................................................ 69
Appendix IV: Test for significant difference between mean of lead and standard value................................................................. 69
Appendix V: Test for significant difference between mean of copper and standard value........................................................................................................... 70
Appendix VI: Difference in levels of nitrates between dry and wet season in river Nyamasogota water...................................................................................... 70
Appendix VII: Difference in levels of nitrates between dry and wet season in river Nyamasogota water...................................................................................... 70
Appendix VIII: Test for significant difference between levels of nitrates and standard value........................................................................................................... 71
Appendix IX: Test for significant difference between levels of phosphates and standard value ................................................................. 71
Appendix XI: Standard curve for copper....................................................................................................................................................... 72
Appendix XII: Standard curve for Lead ...................................................................................................................................................... 73
Appendix XIII: Standard curve for nitrates .................................................................................................................................................. 74
Appendix XIV: Standard curve for phosphates ........................................................................................................................................ 75
LIST OF TABLES

Table 1.1: KEBS and WHO concentration for standards of heavy metals and nutrients .5
Table 3.1: Labeling of soils samples and river Nyamasogota water ..........................29
Table 4.1: Percentage recovery of copper, lead, phosphates and nitrates ..............35
Table 4.3: Concentration of copper in soil samples .................................................39
Table 4.4: Comparative mean levels of lead and copper between dry and wet seasons.41
Table 4.5: Concentration of nitrates in soil samples ...............................................42
Table 4.6: Concentration of phosphates in soils .....................................................44
Table 4.7: Concentration of lead and copper in river Nyamasogota water ............46
Table 4.8: Concentration of nitrates and phosphates in river Nyamasogota water ....50
LIST OF FIGURES

Figure 4.1: Calibration curve of Cu ................................................................. 36
Figure 4.1: Levels of copper and lead in river Nyamasogota water relative to std. values .................................................................................................................. 48
Figure 4.2: Levels of nutrients in river Nyamasogota water relative to standard values 52
### ABBREVIATIONS AND ACRONYMS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AAS</td>
<td>Atomic Absorption Spectrophotometer</td>
</tr>
<tr>
<td>AL</td>
<td>Adjacent Land</td>
</tr>
<tr>
<td>ANOVA</td>
<td>Analysis of Variance</td>
</tr>
<tr>
<td>APHA</td>
<td>American Public Health Association</td>
</tr>
<tr>
<td>AR</td>
<td>Analytical Reagent</td>
</tr>
<tr>
<td>ATSDR</td>
<td>Agency for Toxic Substances and Disease Registry</td>
</tr>
<tr>
<td>CL</td>
<td>Confidence Level</td>
</tr>
<tr>
<td>EPA</td>
<td>Environmental Protection Agency</td>
</tr>
<tr>
<td>IARC</td>
<td>International Agency for Research on Cancer</td>
</tr>
<tr>
<td>KEBS</td>
<td>Kenya Bureau of Standards</td>
</tr>
<tr>
<td>KIRD</td>
<td>Kenya Institute of Research Development</td>
</tr>
<tr>
<td>UNCHS</td>
<td>United Nations Centre for Human Settlements</td>
</tr>
<tr>
<td>UNEP</td>
<td>United Nations Environment Programme</td>
</tr>
<tr>
<td>UTF</td>
<td>Upper Tea Farms</td>
</tr>
<tr>
<td>WHO</td>
<td>World Health Organization</td>
</tr>
<tr>
<td>WT</td>
<td>Water Sample</td>
</tr>
</tbody>
</table>
ABSTRACT

The issue of water contamination and quality dilapidation in Kenya is more and more becoming a menace to the natural water resources due to modern methods of farming and industrialization which have resulted in water pollution especially in rivers. River Nyamasogota provides water for growing crops and for domestic purposes. The river passes through the areas that have many tea farms where fertilizers are heavily used and hence polluted by inorganic, organic and microbial substances. The waste effluents from tea factories also drain into the river. This research therefore aimed at establishing the levels of lead, copper, phosphates and nitrates in both river water and tea soils in comparison with the limits set by World Health Organization and Kenya Bureau of Standards. Variation of phosphates, nitrates, lead and copper were investigated in river Nyamasogota and adjacent farms during dry and wet seasons. Sampling was done at various points along the river Nyamasogota and randomly selected section of tea farms, upper tea farms and adjacent land in the months of February to April 2016. Water samples were filtered using whatman filter paper, digested and then analyzed while soil samples were dried, ground, sieved, digested using 30% hydrogen peroxide and then analyzed. Analysis using UV-VIS spectrophotometer was used to determine the levels of nitrates and phosphates while heavy metals were studied by Atomic Absorption Spectrophotometry technique. ANOVA, paired sample and one way sample t-tests were used for analysis. Results for two seasons ranges as follows: Pb in soils (0.139±0.026 to 0.279±0.024) mg/g. Pb in river Nyamasogota water (0.100±0.015 to 0.202±0.034) mg/l. Cu in soils (0.045±0.032 to 0.243±0.037) mg/g. Cu in river Nyamasogota water (0.127±0.016 to 0.312±0.013) mg/l. Nitrates in soil (0.031±0.025 to 0.626±0.022) mg/g. Phosphates in soils (0.045±0.021 to 0.231±0.017) mg/g. Nitrates in river Nyamasogota water (0.206±0.021 to 0.358±0.015) mg/l. Phosphate in river Nyamasogota (0.232±0.021 to 0.524±0.023) mg/l. From the results the mean values of copper and phosphates in river Nyamasogota during wet season were above those set by KEBS and WHO (p<0.05). Based on the findings, the farmers should dig terraces to prevent runoff from tea farms since the land is sloppy and also intensify water purification before drinking water from river Nyamasogota in Kisii County. Farmers should also be educated on the impact of applying excessive phosphate based fertilizers on water quality alternatively they can use organic ones.
1

CHAPTER ONE

INTRODUCTION

1.1 Background of the study
Majority of problems that mankind is confronting in the 21st century are identified with water amount and water quality. Before the 20th century, the greater part of the materials individuals utilized were chiefly regular and henceforth, when they were disposed of, the waste items contributed to less contamination. In any case, amid the 20th century, the improvement of plastics, composites, and other engineered materials has created another era of unusual materials that the environment is unable to break down (Mumba and McDonald, 2005).

Land dumping of urban and factory wastes, vehicles emanations, mining action, and uses of inorganic fertilizer and pesticides for farming have added to consistent gathering of heavy metals in soils (Tu et al., 2000; Selene et al., 2003; Nouri et al., 2008). The applications can contribute to the rise of heavy metals especially Cd, Pb, and Cu. High fertilizers applications and corrosive environmental accumulation, consolidated with inadequate liming, likewise cause a lessening in pH and therefore rise in lead and copper presence, infuriating the issue of worsening food quality, metal discharge, and effects on plants and animals (De Vries et al., 2002).

Agricultural practices can add to nutrient contamination when not appropriately controlled. Animal compost and fertilizer, which are equally rich in nitrogen and
phosphorus, are the essential origin of nutrient pollution from agricultural sources (WHO, 2006). Surplus nutrients can affect water quality when it downpours or when water and soil containing nitrogen and phosphorus wash-down into close-by waters or seep into underground water (EPA, 2015). Soil fertilized and animals can be important basis of gaseous, nitrogen-based compounds like ammonia and nitrogen oxides (Gomes et al., 2003). Ammonia can be detrimental to marine life if huge quantities are dumped to surface waters (EPA, 2015).

Globally, contaminant loads brought to surface water bodies are turning out to be strong to the point that aquatic ecosystems are degraded seriously (Scheuer, 2005). Freshwater environment for example, streams and lakes are progressively at danger from pollution influences on a worldwide scale with land based releases being the prevalent source (Greiner et al., 2000). Water problems in developed nations are as of now identified with protection of aquatic ecosystem, hazard based toxicity and outcome assessment at organism level, endocrine disturbance and the synergistic and cumulative impacts of harmful pollution (Rabeni and Wang, 2001; Gomes et al., 2003).

In most deprived nations, there is dependably episode of cholera and different sicknesses as a consequence of drinking water that is polluted (Yongsi, 2010). Several pollutants are carcinogenic in the body of humans and animals. Nutrients such as phosphates and nitrates make up a major group of potential environmental hazards especially in rural areas. Contamination by heavy metals has been associated with uncontrolled human
activities such as farming methods and industrial technologies (Clark and Richardson, 2002). The nature of water is worsening because of inorganic anions and cations being discharged from residential and modern effluent. By the year 2030, when Kenya will have achieved an industrial economy, manufacturing and domestic water will be a rare asset. The vast majority of the groundwater will be profoundly contaminated and a portion of the water bodies will be secured by vegetation as an outcome of eutrophication and render the water non-consumable (Kithiia and Khroda, 2011).

Chemical components having particular gravity of no less than five times the particular gravity of water are termed as heavy metal. Heavy metals are important in soil ecology so they are gaining attention as environmental pollutants. Every time heavy metals are accumulated up into the soil, they may move to the food chain and lead to dangerous health effects (Kashif et al., 2006).

Some of the heavy metals are essential for life in small quantities but problems arise when their quantity increases from certain limit called threshold limit (Saif et al., 2005). Metals with their specific character of being held up in the body proteins are constant threat as they can persist in body for long time (WHO, 2006). Through the soil, heavy metals are taken up by plants. Roots and foliar surface are two main paths by which elements are taken up or gathered up by plants (Sawidis et al., 2001). It is obvious from reports that there is a varying capacity of different plants to gather up heavy metals, so health risks are associated when food crops are consumed.
Studies showed that effluents from untreated waste water from many industries in Faisalabad city, Pakistan are highly polluted with heavy metals which made it unsuitable for agricultural use (Shakoor et al., 2013). Human activities are introducing heavy metals into the environment at high rate above their required standards (WHO, 2006). These are not confined to neighbourhood rather are dispersed over an extensive region through air, water and soil. At the point when the heavy metals are conveyed into the soil, they will collect there for a while and go into the environment or the food chain resulting in impairment of human health. Heavy metal pollution in soil has happened subsequent to ancient times; however, the degree of pollution has expanded immensely because of expanded rate of urbanization and a few anthropogenic actions (Riffat et al., 2016).

Water, a major requirement for human existence and modern advancement is being influenced by different actions of man which changes its arrangement physically, chemically or biologically. Contamination of seaside waters by heavy metals has been generally conveyed (Ndiokwere and Ezihe, 2010). Causes of pollution by trace metals comprise atmospheric discharge from fossil fuels burning, local sewage release, land run-off and discharge from industrial processes such as mining, canning and electroplating (Ayenimo et al., 2004).

According to World Health Organization (WHO, 2004) and Kenya Bureau of Standards (KEBS, 2007) a number of several water bodies have shown different levels of heavy metals but their recommended set limits are as shown in the table 1.1
Table 1.1: KEBS and WHO concentration for standards of heavy metals and nutrients

<table>
<thead>
<tr>
<th>Metal /nutrients</th>
<th>KEBS Concentration in mg/l</th>
<th>WHO Concentration in mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead</td>
<td>0.10</td>
<td>0.01</td>
</tr>
<tr>
<td>Copper</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Phosphates</td>
<td>0.025</td>
<td>0.025</td>
</tr>
<tr>
<td>Nitrates</td>
<td>0.50</td>
<td>2.00</td>
</tr>
</tbody>
</table>

KEBS, 2007, WHO, 2004

Public alertness on the threats connected with heavy metals has been slightly in charge of cautioning managements on the need to protect the well-being of the public by keeping consistent watch on levels of harmful poisons, finding a way to diminish them to satisfactory levels and guaranteeing control of discharge of contaminations into the environment by enactment (Ayenimo et al., 2004). Nevertheless, these targets are not being effectively followed in numerous second and third world countries, Kenya included (Omwoma et al., 2011).

Through expanded enhancement of industrialization and especially the broad usage of unrefined petroleum in Nigeria, particularly in the Niger-Delta district, the concentration of metal contaminations in the ecosystem has been stated to have risen (Egborge, 2009). River Warri, a notable river in Niger-Delta zone of Nigeria holds up significant business
activities, for example, delivery of unrefined petroleum, fishery and recreational fishing and prawning. The river has been implicated of pollution by heavy metals in the past (Ndiokwere and Ezihe, 2010).

River Nile contains heavy metals above the set limits (Gisbert et al., 2003). Through their study, serious and urgent intervention is required to remedy the situation by both countries where the river is essential to their daily lives (Kjellstrom et al., 2006). In western part of Kenya, major rivers flow into Lake Victoria and these include Nyando, Kibos, Nzoia and Kasat and it is reported by many researchers that they contain high levels of Cu, Pb and Cd (Mwamburi, 2000).

The origin of heavy metals in tea soil plantation in Magena area and river Nyamasogota in Kisii County comes from natural and artificial sources. Heavy metals which occur naturally in water and soils come mainly from sources such as rock weathering, soil leaching, dissolving of water, soluble salts and surface runoff. For lead it occurs everywhere. It is present in river waters including river Nyamasogota, tea soils, our residences, vehicles, our diet and even in our bodies. Lead has an average concentration of around 13 mg/kg (Gathumbi et al., 2013). Copper in specific is present in the Earth's crust at concentrations between 25-75 mg kg\(^{-1}\), with the abundances design that display the tendency for the concentration in mafic igneous rocks (60-120 mg kg\(^{-1}\)) and argillaceous deposits (40-60 mg kg\(^{-1}\)), but it is relatively excepted from the carbonate rocks (2-10 mg kg\(^{-1}\)) (Brewer, 2007).
Phosphate occurs mostly in insoluble form; only small part is soluble in nature and thus phosphate solubilizing microbes change the insoluble form of phosphate to solvable form. Heavy metal contamination in soils has happened compared to ancient times; however, the degree of pollution has increased due to geogenic rate of urbanization and a few anthropogenic activities in Magena area Kisii County. The human actions leading to increased pollution include, mineral excavation, extraction and purification operations, use of sewage slime and inorganic nutrients, compost and pesticides.

Nyamasogota river in Magena sub-county of Kisii County is exposed to inorganic pollutants in its upper course; a situation that could have been caused by extensive tea farming activities in this region coupled with other anthropogenic activities such as intensive usage of soaps which result into the production of various pollutants that finally find their way into this river.

In the upper lands, the major activities include animals play, garden weeding and spray, motor bike and car washing that contain high levels of heavy metals especially lead that are transported to the river water during rainy season (wet) as the land slopes towards Nyamasogota river. The human activities at the tea farms include weeding, application of fertilizers and spray. These are the major sources of lead and copper in the tea soils and Nyamasogota river. The land adjacent to Nyamasogota river has less human activities due to the fact that most farmers have planted tea almost near to the river. In Nyamasogota river fishing, car, motor bike washing and making of bricks are the major
human activities conducted near the river. This is possibly the main cause of pollution to river Nyamasogota.

1.2 Problem statement and justification

Water resources in Kenya are more and more being polluted by organic, inorganic and microbial matter (Kithiia, 2006). The effect of contamination on water resources is evident by the poor water quality which gives rise to water noxiousness to mammals and marine life; loss of aesthetic value by becoming unhealthy for recreational activities, waterborne illnesses, high charge of water purification, eutrophication, deoxygenation, acid rain and habitat modification. Research on the influences of land use for example, farming and anthropogenic activities on water quality, have been carried out in the last three decades mainly focusing on heavily polluted large rivers (Ding et al., 2015). In contrast, studies regarding relatively small rivers are somewhat limited although water quality in such rivers may be impacted by unacceptable levels of inorganic nutrients and heavy metals (Dassenakis et al., 2000). Omwoma et al. (2011) established that fertilizer residues notably nitrates and phosphates get washed into river Kuywa during rainy season posing danger to the community. Just like river Kuywa, Nyamasogota river is a permanent water body whose environmental exposures are similar hence need for the study.

Several agricultural and industrial activities conducted in Magena area contribute to high levels of heavy metals and nutrients in soil and river Nyamasogota. Phosphate based fertilizers applied to tea farms and the gardens may increase the levels of lead and copper
in soil and water. Heavy metals that have contaminated roadside soils, riverbanks and Magena urban center are amongst the greatest serious ecological threats in the region. Therefore, it is necessary to establish levels of heavy metals and nutrients in water from Nyamasogota river and tea soils in Magena area.

1.3 Hypotheses
i. There is no significant difference between the levels of $\text{PO}_4^{3-}$ and $\text{NO}_3^-$ during rainy and dry seasons in soils from tea farms, adjacent lands and water from Nyamasogota river.

ii. There is no significant difference between the levels of heavy metals during rainy and dry seasons in soils from tea farms, adjacent land and water from Nyamasogota river.

iii. The levels of $\text{NO}_3^-$, $\text{PO}_4^{3-}$, Pb and Cu are higher than recommended limits set by WHO and KEBS.

1.4 Objectives
1.4.1 General objective
To investigate the variation of $\text{NO}_3^-/\text{PO}_4^{3-}$ and Pb/Cu in soils from tea farms, adjacent lands and water from Nyamasogota river in Magena sub-county, Kisii County during dry and rainy seasons.
1.4.2 Specific objectives

i. To determine the levels of $\text{PO}_4^{3-}$ and $\text{NO}_3^-$ in soils from tea farms, adjacent lands and water from Nyamasogota river during rainy and dry seasons.

ii. To determine the levels of Pb and Cu in soils from tea farms, adjacent lands and water from Nyamasogota river during rainy and dry seasons.

1.5 Significance of the study

The results of the study are expected to be important to different individuals, organizations, agencies and to all stakeholders involved in environmental conservation programmes. This study may also create awareness to people living in Magena sub-county on the implications of using untreated water from Nyamasogota river. Other farmers and tea factories in other parts of Kisii County may learn the need to minimize the large application of fertilizers and pesticides which may contribute to water pollution and reduction of fish production in rivers and Lake Victoria. The study will add important literature that can be referred to by academicians who have interest in water and natural resources conservation.

1.6 Scope and limitation of the study

There exist many substances that may have been introduced in Nyamasogota river through human activities. However, only copper, lead, phosphates and nitrates were studied since they are major constituents of inorganic fertilizers and factory effluents (Shakoor et al., 2013). Magena sub-county, Kisii County was studied due to intensive tea farming activities which is practiced in the area because of reliable amount of rainfall received in the area.
CHAPTER TWO
LITERATURE REVIEW

2.1 Water and soil contamination
One of the most significant environmental problems is water pollution (Carson et al., 2002). Water contamination is the defilement of water bodies (for instance lakes, streams, seas, aquifers and groundwater). This type of ecological degradation happens when contaminations are straightforwardly or indirectly released into soil and water bodies with no satisfactory remedy to eliminate poisonous compounds (Goel, 2006). Related to the Carson’s findings, Boyd and Suzuki Foundation (2010), points out that there are more and more toxic chemical run off from agricultural activities dumped into water bodies every year. These affect directly the human’s health. Some of these pollutants include nitrates, nitrites, phosphates and heavy metals such as copper, cadmium and lead which are introduced into rivers through industrial effluents and agricultural run-off (Prabodanie et al., 2010).

2.2 Contamination of soil with heavy metals
Heavy metal pollution of soils has taken place from ancient times, although the degree of contamination has been accelerated through geogenic speed of development and industrialization and a number of human activities (Yaylalı-Abanuz, 2011). The human actions include mineral extractions, factory processes, use of sewage slime, inorganic nutrients, animal wastes and pesticides (Paramasivam et al., 2006). Anthropogenic pollution with heavy metals is a global issue which triggers immense water and soil contaminations (Caussy et al., 2003). Heavy metals that have polluted developed areas,
roadside soils, riverbanks, and metropolitan regions make up the utmost severe ecological risks (Magrisso et al., 2009).

Sewage lime, an inevitable byproduct of waste-water treatment, has high amounts of organic matter and plant nutrients (Gawdzik et al., 2015). The use of sewage lime enhances the physical and chemical attributes of soil and therefore are prescribed (Stabnikova et al., 2005). It has pollutants and too much salts, which can likewise be taken into account in its farming use (Paramasivam et al., 2006). According to Su and Wong (2003) heavy metals in sewage lime may go into the food chain through farm harvests and impact negatively on people’s health. The physicochemical impacts of the continued utilization of sewage lime in the modification of topical soils are still doubtful.

The accumulation of heavy metals in plants has been a grave environmental concern in light of the fact that their uptake by plants from polluted soils is the significant way by which heavy metals go into the food chain and afterward to mankind and animals and are generally harmful at concentrations a little above than those required for keeping up usual metabolic activities of the body (Chakraborty et al., 2004). The taking in of heavy metals to soils by plants relies upon their levels in soil, organic matter, soil clay content and on their particular geochemical attributes (Bansal, 2004).

Plants type vary in heavy metals' uptake as well as transition of metals to different plant organs which effect heavy metal levels in food chain and food substances (Kirkham,
The level of toxicity relies primarily on the type of species available. In this manner, organic lead is to a large extent more toxic than the inorganic type. The oxidation state of metals likewise assumes a critical part in such manner. In this way, the hexavalent chromium is more poisonous than its trivalent species (Benerji, 2007). Previous studies have shown considerable development of heavy metals in the outward sediments of the Pearl River Estuary (Liu et al., 2003). Heavy metals cannot be destroyed by biological degradation, and they are effectively adapted and capable of being bio-accumulated in marine creatures (Egborge, 2009). Immense quantity of heavy metals enters the aquatic ecosystem through regular procedures and human activities. These conceivably lethal contaminations can cause danger to human health by being included in the food chain (Wogu and Okaka, 2011). For instance, lead has no known function in the body. It is a potential protein inhibitor as it binds itself to sulphhydryl (SH) group (Stern, 2010). It inhibits the haemo-biosynthetic pathway, producing hematological effects and competes at the molecular level with calcium (ATSDR, 2008).

2.2.1 Copper
Copper occurs in the Earth's crust at levels between 30-80 mg kg\(^{-1}\), with the loads pattern that indicate the trend for the levels in mafic igneous rocks (60-120 mg kg\(^{-1}\)) and argillaceous sediments (40-60 mg kg\(^{-1}\)), but it is slightly left out from the carbonate rocks (2-10 mg kg\(^{-1}\)) (Kabata-Pendias and Pendias, 2007). Its levels usually range globally from 1 to 135 mg kg\(^{-1}\) subject to the type of the soil parent material.
For the Brazilian environmental legislation (Rossi, 2008), the maximum copper levels recommended for river water class II is at 0.02 mg k\(^{-1}\). Besides, the World Health Organization contemplates 1.5 mg L\(^{-1}\) as the maximum copper permissible level in public water (WHO, 2004). These elevated starting point values suggested for copper content in drinking or river water are in excess when contrasted with the small toxic levels for root development.

In soil, copper occurs both in compact and in solution which is almost entirely as the divalent cation Cu\(^{2+}\) and the reduction of Cu\(^{2+}\) to Cu\(^+\) and CuO is possible under reducing states. Copper links with sulfide in the solvable minerals, Cu\(_2\)S and CuS. Being very volatile in soil, copper is in all matrix components. Most of the colloidal soil material (clay minerals, oxides of Mn, Al, Fe, and organic matter) adsorb copper strongly, and progressively as the pH is raised (Araújo do Nascimento et al., 2006). This is an indication that tea soils in Magena area in Kisii County contain traces of copper. Copper deficit may be able to generate anemia-like symptoms, neutropenia, bone anomalies, hypo pigmentation, weakened growth, more incidences of infections and anomalies in glucose and cholesterol metabolism due to its role in enabling iron uptake (Mesias et al., 2012).

The human body grew to store additional copper to fuel crucial body activities in the event of life-threatening situations like hemorrhage or food crisis, however, its buildup throughout the years is harmful for the reason that copper takes part in the production of
reactive oxygen species (ROS) where oxidative damage is produced as a result of oxygen-dependent energy production which is proved to contribute to long-lasting illnesses and getting old (Brewer, 2007).

Copper is a natural component of soil and can be carried into rivers and canals in runoff by natural breakdown or anthropogenic soil disruption. These processes sum up to about seventy percent of effluents of copper into water. Runoff is the leading aspect contributing to higher copper levels in river water in the absence of specific industrial sources, (Nolte 1988). Copper in storm water runoff originates from the sidings and tops of constructions and houses, various emanations from automobiles, and wet and dry depositional activities (Davis et al., 2001). Storm water runoff usually adds about 2% to the entire copper discharged to waterways. Contrary to that, copper in runoff that is attained from the natural breakdown of soil or is discharged from disturbed soils make up 70% of the copper discharged to waterways (Georgopoulos et al., 2001).

2.2.2 Lead

Lead is a soft, grayish-white, naturally occurring metal that has been extracted since ancient times. Early Egyptians, Greeks and Romans used it for water pipes and in ceramic glazes and paint pigments (Smoots, 2011). In the eighteenth century, lead poisoning among Americans and the English was traced to cider vats made with lead (Gartley, 2002).
Early tinkers and printers were exposed to lead through their day-to-day work activities. Lead was a constituent in paints for a number of years since it created a strong, long-term coating when dry. Despite the fact that the risks of lead contamination have been known for nearly 2000 years, its usage continues to date mainly for manufacturing reasons (Rossi, 2008). It is still in use since it has attributes that make it a multipurpose, long lasting and inexpensive commodity.

Lead is universal. It’s existing in water, soil, our homes, our cars, our food and even in our bodies hence its presence in tea soils and Nyamasogota river cannot be doubted. It has an average concentration of around 13 mg kg\(^{-1}\) (Gathumbi et al., 2013). Actually, none other pollutant has amassed in humans to normal concentrations very near to those said to possibly be medically toxic. In uncontaminated soils, normally lead occurs in levels between 2 and 60 million mg kg\(^{-1}\). Over time, anthropological action has elevated the levels of lead in some soils to unacceptable levels.

A study has been conducted in Kirinyaga South District, to measure the levels of copper and lead in fish and soil sediment, from areas growing horticultural crops (Gathumbi et al., 2013). This study found out that most farmers apply large amounts of fertilizers and pesticides which contributes to elevated levels of lead and copper in the river water hence harmful to human consumption. However, no attempt has been made to conduct such studies in nyamasogota river despite the fact that it drains its waters to even larger rivers and lakes. While doing a study on impacts of fertilizer residues on river Kuywa.
In New England, pollution from lead is mainly as a result of three causes lead paint, exhaust from unleaded gasoline, and the usage of lead arsenate as a pesticide, mainly in old orchards. Their usage has, however, been gotten rid of, but lead is a constant pollutant and therefore will persist in the soil much for an indefinite period mainly because it is a mineral and will not decompose. Lead though can still, accumulate in plant tissues, (Hong and Bartlet, 2008).

Various researches dealing with polluted soil propose that physiochemical soil properties, for example pH, clay content and organic matter substance are the main aspects regulating heavy metal toxicity and bioavailability (Covelo et al., 2007). It was shown that dissolved Pb is bioavailable, while bound Pb is not (Magrisso et al., 2009). As a result of their enormous adsorption limit, organic matter and iron (II) oxide are equipped to take in a lot of Pb and not discharging noticeable Pb to solution, lessening the bioavailability of Pb (Sauve, 2002). The bioavailability of Pb relies upon the kind of the soil and the parts it contains (Nagajyoti et al., 2010). Dry and semi-arid soils that have huge quantity of carbonates and minimal organic matter will impact in a different way the solvency of Pb and thus its bioavailability compared with mild soils which more often do not have pedogenic carbonate yet have huge portion of organic matter (Vega et al., 2007).
Mwashote (2003) conducted a study to investigate the concentration and distribution of cadmium and lead in water, sediments and selected fish species in Makupa and Tudor creeks in Mombasa and established that Pb and Cd concentrations were low in the water column with a few incidents of elevated levels in sediments and some fish species, especially during the rainy season.

2.3 Phosphates
Phosphorus is an important element required by the living beings. It is highly reactive and is therefore found as either inorganic phosphate rock or organic phosphate. Phosphate occurs mostly in insoluble form; only small part is soluble in nature. In order to obtain phosphorus, the phosphate must be converted into soluble form. Phosphate solubilizing microbes aid in converting the insoluble form of phosphate to soluble form (Chakraborty et al., 2012; Sharma et al., 2012).

Phosphate solubilizing microbes consist of members of both bacteria and fungi. They help in the release of phosphorus from inorganic and organic phosphate through solubilization and mineralization. Soil phosphorus changing aspects is portrayed through physicochemical (sorption-desorption) and biological (immobilization-mineralization) forms. Key constituent in soil for mineral phosphate solubilization is lowering of soil pH by microbial generation of organic acids that dissolved phosphatic minerals and/or chelate cationic partners of the phosphate ions, directly thus, discharging phosphorus into soil. And the release of phosphorus from organic phosphate is by mineralization of organic phosphate with phosphatases (Khan et al., 2009).
Phosphatases are a group of enzymes kept as membrane bound lipoproteins or discharged as soluble periplasmic proteins. Phosphatases are typically able to dephosphorylate a wide range of structurally distinct organic phosphoesters (nucleotides, sugar phosphates, phytic acid among the many) to obtain inorganic phosphate and organic by-products (Gandhi and Chandra, 2012). Activities of soil phosphatases and phosphodiesterase are amid the key foundations of new organic phosphate inputs to soil (Deiss et al., 2016).

Phosphatase enzyme significantly accelerates the release of inorganic phosphate from organically bound phosphate and returns it to the soil (Phukan et al., 2011). Phosphatases are usually classified as neutral [EC 3.1.3.0], alkaline [EC 3.1.3.1] and acid [EC 3.1.3.2] based on pH optima (Akanji and Adesokan 2005; Raghav et al., 2011; Banerjee et al., 2012).

In India, phosphorus content in normal soil is 0.05%. Only 0.1% from the overall phosphorus forms is accessible to plant, remainder of the phosphorus forms turns into insoluble salt (Leahu et al., 2011; Nisha et al., 2014). Huge quantity of phosphorus used as fertilizer in form of superphosphate, NPK goes into the immobile pools through precipitation reaction with highly reactive aluminium (Al$^{3+}$) and iron (Fe$^{3+}$) in acidic, and calcium (Ca$^{2+}$) in calcareous or normal soils (Gyaneshwar et al., 2002; Hao et al., 2002; Devi et al., 2012).
The use of phosphate based fertilizers has affected water quality by introducing excess nutrients to the water leading to increased eutrophication (American Public Health Association, 1999). In majority of emerging countries, releases from point sources have expanded essentially as a consequence of industrialization and high living standards. Moreover, the nutrient loads to streams in these nations have been joined by untreated wastewater releases (Corcoran, 2010). High dosages of metal salts especially magnesium phosphate, causes cleansing or purging of the bowels, and magnesium sulfate or Epsom salts have been utilized as a laxative (Capasso and Gaginella, 2012).

2.4 Nitrates
Nitrates are naturally occurring ions that are a part of the nitrogen cycle. The nitrate particle is the steady type of combined nitrogen for oxygenated system. Though chemically unreactive, it can be reduced by microbial activity. Nitrates can be distributed to both surface water and groundwater due to farming activities (as well as excess use of inorganic nitrogenous composts and fertilizers), from wastewater treatment and from oxidation of nitrogenous waste products in human and creature excreta, including septic tanks (Yaron et al., 2012).

A three-year (2004, 2005 and 2006) study in tea plantation of Kenyan Rift Valley led by Maghanga et al. (2012) recognized absence of specific pattern between surface water, nitrate levels and the period of fertilizer applications in tea ranches; nevertheless, fertilizers application led to rise in nitrate levels. Unlike almost entirely other pollutant standards, the drinking water standard for nitrate has no margin of safety (WHO, 2003).
Exposure to nitrates all through infancy founded on studies conducted show that this leads to increases in cancer risk from N-nitroso compound by a factor of six. The conversion of nitrates to nitrites takes place in the presence of enzymes nitrate reductase which requires reduced coenzymes I (NADH) or coenzyme II (NADPH) (Hord, 2009).

2.5 Methods of analysis for heavy metals and nutrients

The methods used for heavy metal analysis include: Atomic Absorption Spectroscopy (AAS) (Alloway, 1996) Cold Vapor Atomic Absorption Spectroscopy (CVAAS), Graphite Furnace Atomic Absorption Spectrometry (GFAAS), Flame Atomic Absorption Spectroscopy (FAAS), Atomic Emission Spectrometry (AES), and X-Rays Florescence (XRF) among others (Borisova et al., 2002).

Concentration of heavy metals can be determined using the formula given in equation 2.1;

\[
\text{actual concentration} = \frac{\text{digested concentration (mg/g)} \times \text{volume digested (l)}}{\text{weight of the sample digested (kg)}} \ldots \text{equation 2.1}
\]

It’s assumed that the final volume can be the same as the original volume where sample is digested and there is no further dilution. Pollution index for each metal can be calculated, which is the ratio of mean level (mg/l) of heavy metal in water to recommended level heavy metals in drinking water (mg/l) by WHO and KEBS. The pollution index less or equal to one indicates drinking water is less polluted as in equation 2.2; the data obtained is presented graphically (Reza and Singh, 2010; Akpoveta et al., 2011);
\[ Pollution \ index = \frac{ML}{RL} \leq 1 \] equation 2.2

Where ML= mean level of heavy metal in water

RL=Recommended level of heavy metal in drinking water.

Diverse procedures for phosphate examination have been produced; phosphomolybdate method has been used because of its simplicity to its application. Spectrophotometric techniques depend on the development of yellow molybdophosphoric acid and its diminishment to a blue heteropoly compound, phosphomolybdenum blue (Meaney et al., 2002).

Ultraviolet spectrophotometric screening method of Eaton et al. (1995) is used to determine nitrate present in the water and soil samples. Measurement of UV absorption at 220 nm empowers quick determination of \( NO_3^- \). Since dissolved natural matter may likewise retain at 220 nm and \( NO_3^- \) does not absorb at 275 nm, a second measurement can be made at 275 nm to remedy the \( NO_3^- \) value. Sample filtration is done to do away with potential intrusion from suspended particles.

Magen area is located along the river Nyamasogota and is known as tea giant estate in Ogembo district Kisii county, Kenya. It produces 6 million kgs per year of green leaf taken to Ogembo tea factory which receives 15 million kgs of green leaf per year. Therefore, the study is designed to determine the phosphatases activity of both the soil and the phosphate solubilizing microbes of the rhizosphere soil.
There is an urgent necessity to look into overall distributions of heavy metals in top soils, which act as a crucial sink, to understand the general result of heavy metal contamination and related environmental risks in the region of Magena area, Kisii County. The results are also useful for control of environment in parts experiencing speedy industrial revolution.
CHAPTER THREE
MATERIALS AND METHODS

3.1 Research design
The study adapted an experimental design that involved sampling of soils and water during the dry and rainy seasons followed by sample treatment and analysis.

3.2 Study area
The study area was in the nucleus of Magena sub county, Kisii County (Figure 3.1). It is within Kenya’s large-scale tea estates. Water from river Nyamasogota is used for domestic and industrial purposes. It is a permanent river which floods during the rainy season and serves a population of approximately 30,000 people. The study area covers an area of 50 km². The length of Nyamasogota river is about 29 km from Kiango to river Gucha. The catchment drains South wards from Kebuko near Nyamache through (Mogonga) Gucha river down to Homabay and to Lake Victoria.
Figure 3.1: A Map showing the flow of river Nyamasogota and its study area.
3.3 General Procedures

3.3.1 Sample collection

Sampling was purposive whereby samples from each section were randomly selected since the distance between them was varying. This was specific to tea soils in the tea estates along Nyamasogota river.

Three factor completely randomized block design was used in sampling where land above the tea farms, tea farms, adjacent land and Nyamasogota river were considered as separate blocks. Three such blocks were formed within equal distances. In each block, three sampling points were created in each of the four sections (land above tea farms, tea farms, adjacent land and Nyamasogota river) at approximately 1 kilometer apart and 10 centimeters deep. Thus 12 samples were obtained at every visit. The number of samples were calculated using equation 3.1;

\[ N \geq \left[ \frac{ts}{u} \right]^2 \]  

Where \( N \) = number of samples
\( t \) = student t statistic for a given confidence level
\( s \) = overall standard deviation
\( u \) = acceptable level of uncertainty

For every season, samples were collected three times. A total of 72 samples which included tea soil and river water (0-15) cm, corresponding 36 subsurface (I) soil samples (15-30) cm and 36 subsurface (II) soil samples (30-36) cm were collected from the
different areas of the tea farms. The samples were then transported to the laboratory in Kenyatta University.

3.3.2 Apparatus and reagents
The reagents of analytical grade and apparatus that were used during the study included: 2 L plastic buckets, a wooden pole and 500 ml plastic bottles for sampling, Whatman 4.5µm glass micro-fiber filter paper and a filter funnel for filtration, 100 ml, volumetric flasks and a pipette for measuring the volume and standardization of samples. Beakers, heater and conical flasks were used during heating. Detergents and dilute nitric acid were used for general washing of plastics and glass wares, nitric acid (AR) and 30% hydrogen peroxide for digestion and preservation of samples, while distilled water for rinsing the apparatus and diluting samples up to 100 ml.

First, all test tubes and glassware were soaked overnight in a freshly prepared concentrated chromic acid. They were then cleaned using tap water and soap then nitric acid was used to rinse them. Later distilled water was used to wash off the acid. Finally, they were dried in an oven at 100 °C. As for the plastic containers, they were washed with soap and rinsed with 6 % nitric acid and again rinsed with distilled water to eliminate traces of the acid.

3.3.3 Soil sampling
The soil samples collection was done using soil auger. Three samples were collected from each sampling point in every visit of data collection and after that combined to
acquire a composite delegate sample. Soil samples were collected during dry season in the month of February, in light of the fact that not any inorganic nutrients or compost was applied throughout this month in the tea plantations near Nyamasogota river. Also, in the month of April soil samples and water samples were collected during rainy season.

The effective size reduction was done by coning and quartering method. The method involved pouring the sample so that it takes a funnel shape and afterward smoothing it out into a cake. The samples were then separated into quarters; the two quarters inverse to each other were disposed of, while the other two were mixed and constituted the reduced sample. The same procedure was sustained until a suitable size remained. Analysis was made concerning the samples left behind.

3.3.4 Water sampling and pre-treatment
River water was collected using 2 L plastic bucket, a wooden pole and 100 ml plastic bottle against the flow of water at about 50 cm below the water surface, this was done to prevent contamination of the samples. The distance from each sampling point was 200 m and from each section was 1 km. For heavy metals water samples were treated with 10 ml nitric acid to avoid precipitation of metals according to procedure reported by Kirkham (2006). Water samples for determination of nitrates and phosphates were not treated with concentrated nitric acid. This procedure was repeated for the other 12 samples of upper, middle and lower section of the Nyamasogota river during dry season in February 2016 and repeated in April 2016 during wet season. Water samples were then filtered using Whatman filter paper (0.45 μm pore size) for approximation of dissolved metals. The
containers were rinsed carefully with deionized water after being cleaned in dilute nitric acid.

Initial treatment of the soil samples after assembling, conservation and examination were done following standard procedures (Gupta, 2007). The total samples were 36 each for wet and dry season.

**3.3.5 Labeling of samples**

Table 3.1 shows the labeling of soils samples and river Nyamasogota water

**Table 3.1:** Labeling of soil samples and river Nyamasogota water

<table>
<thead>
<tr>
<th>Upper tea farms</th>
<th>UTF1</th>
<th>UTF2</th>
<th>UTF3</th>
<th>UTF4</th>
<th>UTF5</th>
<th>UT6</th>
<th>UTF7</th>
<th>UTF8</th>
<th>UTF9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tea farms</td>
<td>TF1</td>
<td>TF2</td>
<td>TF3</td>
<td>TF4</td>
<td>TF5</td>
<td>TF6</td>
<td>TF7</td>
<td>TF8</td>
<td>TF9</td>
</tr>
<tr>
<td>Adjacent land</td>
<td>AL1</td>
<td>AL2</td>
<td>AL3</td>
<td>AL4</td>
<td>AL5</td>
<td>AL6</td>
<td>AL7</td>
<td>AL8</td>
<td>AL9</td>
</tr>
<tr>
<td>Water samples</td>
<td>WT1</td>
<td>WT2</td>
<td>WT3</td>
<td>WT4</td>
<td>WT5</td>
<td>WT6</td>
<td>WT7</td>
<td>WT8</td>
<td>WT9</td>
</tr>
</tbody>
</table>

Where UTF= Upper Tea Farms

TF = Tea Farms
AL = Adjacent Land
WT= Water Sample
3.4 Sample preparation
3.4.1 Water sample preparation
20 ml of water sample from each sample was placed in 100 ml beaker. 5 ml of nitric acid was added and heated for 5 minutes and left to cool for 10 minutes. A few drops of 30% hydrogen peroxide was added and reheated until fumes ceases. The solution was then filtered into 100 ml volumetric flask. Distilled water was then added to the mark then the solution was ready for analysis. The same process was repeated for other samples.

3.4.2 Soil sample preparation
Soil for chemical analyses was dried by being spread out in a tray and put in a constrained air drying cabinet maintained at around 37 °C. For the dry soil to pass through a 2 mm sieve it was ground in a pestle and mortar. On account of wet soil, soil was sieved by carefully pushing through a sieve of cross section size of 4 – 6 mm. The soil which was excessively wet, such that it spread on the sieve, it was first partly air-dried and placed in an oven at a temperature of 60 °C for two days and then ground using pestle and mortar. Amid sieving, material, for example, grass and stones were selected and expelled together with anything that may have been alive at the time of sampling, for example, roots and earthworms.

3.5 Preparation of stock and standard solution
Accurately measured amount of metal salts of analytical grade were used to make 1000 mg/L of the stock solution using electronic balance. In each case, where a metal salt was used, the mass used to prepare the stock solution was obtained by dividing the formula mass of the salt by the mass number of the element to be analyzed. The resulting standard
solutions were diluted as per standard procedure to get working standard solution (Jackson, 1999).

Lead standards were prepared by carefully weighing 0.800 g of lead nitrate of analytical grade and dissolving it in deionized water to get a stock solution of 1000 cm$^3$. The solution was completely acidified with 10 ml nitric acid and further diluted to 500 cm$^3$ to get 500 mg/l standard then followed by diluting to 1 mg/l, 2 mg/l, 3 mg/l, 4 mg/l and 5 mg/l respectively.

Copper standards were prepared by weighing 1.901 g of copper nitrate of analytical grade and dissolved in deionized water. The resulting solution was completely acidified with 10 ml nitric acid and diluted to 500 ml to get 500 mg/l standard then followed by diluting to 1 mg/l, 2 mg/l, 3 mg/l, 4 mg/l and 5 mg/l respectively.

All standards were ran under the same conditions as the samples and used to prepare calibration curves of absorbance versus concentration which were used to determine the concentration of respective samples.

3.6 Determination of nutrients
Phosphates were determined using molybdenum method. A 100 ml of water sample was digested in a beaker at 150 °C with 1 ml of concentrated sulfuric acid (H$_2$SO$_4$) + 5 ml concentrated nitric acid (HNO$_3$) and evaporated to dryness. The residue was then leached with 5 ml 1N HNO$_3$ and transferred to a 50 ml volumetric flask. A volume of 5 ml of
10% ammonium molybdate was added followed by addition of 5 ml of 0.25% ammonium vanadate in 6 N HCl. The mixture was diluted to the mark with distilled water and left to cool for 10 minutes.

Nitrates were determined using sodium salicylate method. A 0.500 g of AR grade sodium salicylate was dissolved in distilled water and diluted to 100 ml mark volumetric flask. Also 400.001 g AR sodium hydroxide pellets and 16.002 g AR potassium sodium tartrate were dissolved using distilled water in a plastic beaker then nitrate stock solution was prepared using 1.370 g AR sodium nitrate which was dissolved in distilled water and topped to 1 L. Soil samples were leached overnight and then using distilled water calibration solutions were prepared from the standard solutions in the range 1.0, 3.0, 6.0, 9.0 and 12.0 mg/l in 50.0 ml mark volumetric flask then the solutions were then transferred to 100 ml flask beakers and then analyzed using UV-VIS spectrophotometer.

Atomic Absorption spectroscopy (AA 6300 Shimadzu) was used as the method of analysis for heavy metals because the method meets the prerequisite need of speed, simplicity, rapidity, safety, sensitivity, and selectivity, low cost and high pre-concentration factor.

Standard spiking of the sample was done by splitting the sample into five even aliquots in separate 50 ml volumetric flasks. 5 ml of lead standard was added to the first flask followed by 10 ml, 15 ml, 20 ml and 25 ml respectively. For copper, nitrates and
phosphates their standards were used and the same procedure was followed. Analysis was then done for the total amount of the constituent present. The difference between the analytical results for samples with and without the added constituent was calculated and then the percentage recovery was found.

3.7 Data management and statistical analysis

One-Way ANOVA at 95% level using SPSS 16 for windows assuming that there were significant differences among them when the statistical comparison gives p<0.05 was used for analysis. The paired sample test was used to compare the means in the levels of the copper, lead, nitrates and phosphates between dry and wet seasons and between the four sections of sample collection.

Whenever a significant difference existed the means were compared at p=0.05 significance level which accounts for errors, using paired sample test and one sample t test since a sample was used to represent a population (Salvador et al., 2007).
CHAPTER FOUR
RESULTS AND DISCUSSION

4.1 Introduction
This chapter discusses all the results for all obtained research work conducted in the entire study. To identify and understand the presence of nutrients and heavy metals present in tea soils and river water from Nyamasogota river, the samples collected were prepared and analyzed using appropriate apparatus. The result of analysis of the selected heavy metals and nutrients are presented in the following sections.

4.2 Validation of results
The procedure and method for analysis was validated by use of standard spiking, where a certain amount of the component being ascertained was mixed with the sample (spiked with a standard of 4.5 ppm); which was then analyzed for the aggregate sum of the component present. The distinction between the analytical results for samples with and without the additional component was ascertained, and afterward the percentage recovery was calculated from equation 4.1 (Erxleben, 2009);

\[
\% \text{ recovery} = \frac{F-\text{NP}}{A} \times 100
\]

Equation 4.1

Where

F = Spiked sample concentration
NP = Unspiked sample concentration
A = Concentration of analyte added to the spiked portion

The results of the validation are presented in table 4.1.
Table 4.1: Percentage recovery of copper, lead, phosphates and nitrates

<table>
<thead>
<tr>
<th>Heavy Metals and Nutrients</th>
<th>Unspiked sample in mg/L</th>
<th>Spiked sample in mg/L</th>
<th>% Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>1.86</td>
<td>6.83</td>
<td>99.2</td>
</tr>
<tr>
<td>Cu</td>
<td>0.88</td>
<td>5.82</td>
<td>99.1</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>0.14</td>
<td>5.03</td>
<td>99.4</td>
</tr>
<tr>
<td>PO₄³⁻</td>
<td>0.40</td>
<td>5.35</td>
<td>99.2</td>
</tr>
</tbody>
</table>

From table 4.1, the percent recovery was from 99.1 to 99.4 which indicates that the results obtained during analysis were accurate and the samples were well prepared, efficiently handled and without contamination. The AAS instrument used for analysis was also accurate since the percentage recovery was almost 100% (Mendham *et al.*, 2000).

4.3 AAS calibration curves

The heavy metals levels were determined by AAS (AA 6300 Shimadzu) Kyoto, Japan based on absorbance. Samples and standards for each metal were run under the same conditions and were used to prepare calibration curves of absorbance versus concentration which was used to determine the concentration of the metals. A linear plot of $y = 0.033x$ over the concentration range of 20-100 mg/l with a slope of 0.033 and a correlation coefficient of $(r^2) = 0.9962$ was obtained for copper. The calibration curve for
copper analysis is presented in Figure 4.1 and for other elements, the calibration curves are presented in appendices XII to XIV.

![Calibration curve of Cu](image)

**Figure 4.1**: Calibration curve of Cu

The absorbance reading and the concentration of standards were determined using coefficient ($r^2$) (Mendham et al., 2000). It can be observed that there is a linear relationship between absorbance and the concentration of the standards, this is because the $r^2$ value was almost 1 hence the performance of the AAS instrument gave accurate results (Erxleben, 2009).
4.4 Concentration of heavy metals in soils

The levels of copper and lead in tea soils were analyzed separately in each section which includes land above tea farms, tea farms, adjacent land and Nyamasogota river. The samples were collected in three different visits and the results are presented in the following section.

4.4.1 Concentration of lead in soils

The concentration of lead is presented in table 4.2

Table 4.2: Concentration of lead in soils

<table>
<thead>
<tr>
<th></th>
<th>Dry season</th>
<th>Wet season</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N</td>
<td>Mean±SD (mg/g)</td>
</tr>
<tr>
<td>AL</td>
<td>9</td>
<td>0.104±0.026</td>
</tr>
<tr>
<td>TF</td>
<td>9</td>
<td>0.162±0.023</td>
</tr>
<tr>
<td>UTF</td>
<td>9</td>
<td>0.133±0.042</td>
</tr>
</tbody>
</table>

From table 4.2, the levels of lead in soil in Magena sub-county during dry season ranged from 0.104±0.026 mg/g to 0.162±0.023 mg/g with tea farms having the highest and adjacent land having the least. The levels of lead in the wet season ranged from 0.119±0.021 mg/g in adjacent land to 0.179±0.024 mg/g in tea farms. The higher levels of lead in tea farms compared to other sections could be due to the location of tea farms down the slope thus heavy metals are deposited from the land above as a result of soil
erosion. Also in upper tea farms there are a number of activities which contribute to elevated levels of lead contamination and are carried out by people in Magena sub-conty like car washing, spraying of insecticides, painting of houses and contamination from municipal water piping. Tea farms also recorded higher levels during the wet season as compared to the dry season. This could be informed by the fact that during rainy season there is a lot of soil erosion. This is transported by runoff and underground seepage water and deposited into the lower lying tea farms leading to increased levels. It is confirmed that the heavy metals can penetrate the soil by various ways and their actions and effect in soils vary according to their origin and types. Accumulation of heavy metals in the soil system actually takes place from the moment they enter the soil (Rossi, 2008).

This study is in line with that conducted by Chitdeswari and Jegadeswari (2007) on hazardous issues of heavy metals. From their findings it reveals that, penetration and spread of heavy metals within a section is affected by wind, water and gravity. The movement of lead within soil mass will be primarily in the solution stage. The penetration of lead or possibly dangerous component in the soil raises concerns because of potential effect on nature as a result of pollution of ground water through infiltration.

### 4.4.2 Concentration of copper in soils

Table 4.3 shows the levels of copper in the three land sections for both dry and wet seasons.
Table 4.3: Concentration of copper in soil samples

<table>
<thead>
<tr>
<th>Section</th>
<th>Dry season</th>
<th>Wet season</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N</td>
<td>Mean±SD (mg/g)</td>
</tr>
<tr>
<td>AL</td>
<td>9</td>
<td>0.051±0.031</td>
</tr>
<tr>
<td>TF</td>
<td>9</td>
<td>0.104±0.024</td>
</tr>
<tr>
<td>UTF</td>
<td>9</td>
<td>0.125±0.029</td>
</tr>
</tbody>
</table>

From table 4.3, the mean concentration of copper in soils ranged from 0.051±0.031 mg/g in adjacent land to 0.125±0.029 mg/g in upper tea farms in the dry season. The levels recorded in the wet season ranged from 0.061±0.037 mg/g to 0.137±0.032 mg/g, the highest being recorded in above tea farms and the lowest in adjacent land. All the three sections (adjacent land, tea farms and upper tea farms) recorded higher levels of copper in the wet season than in the dry season. There was no statistically difference between the two means during wet and dry season in all sections of land as determined by one way ANOVA p=0.128. This can be explained by application of fertilizers in the wet season during planting, as well as deposition of copper from higher grounds by rain water. Upper tea farms recorded higher levels of copper relative to tea farms and adjacent land in both dry and wet seasons. One factor that contributed to this is domestic activities taking place in the area. Earlier researches show that copper in domestic waste water is the starting point or basis of considerable portion of the copper effluents into rivers (HazDat, 2004).
Another factor is the agricultural practices in the area. Raven and Loeppert (1997) found agricultural sources to be a major contributor of copper content in the soil. They analyzed levels of copper in inorganic nutrients, soil modifications and other farming ingredients and listed the following as causes of copper accumulation in the soil: urea, ammonium nitrate, ammonium sulfate, ammonium phosphate, potassium chloride, potassium-magnesium-sulfate, rock phosphate, calcite, maize leaves, manure and austenite. The findings were in line with those of Feng and Chen (2013) who determined a mean copper concentration of 0.046 mg/g in soils during the dry season and a mean of 0.051 mg/g during the wet season. Their values fall within a range of 0.045±0.032 to 0.128±0.031 mg/g in the dry season and 0.055±0.032 to 0.139±0.037 mg/g in the wet season found in the present study.

From the data, levels of copper in tea soils generally increased from the upper section to the middle then followed by slight decrease in the lower section except where their levels generally increased down sections during the dry season. The concentration of copper was higher in upper tea farms followed by tea farms and adjacent land. These observations are attributed to accumulation of waste as surface run-off and leaching which occur down the slope passing through agricultural farms and industrial areas. The accumulation of copper metal as one of the heavy metals being studied is facilitated by erosion (Nwankwoala et al., 2011).
4.5 Comparative mean levels of metals between wet and dry seasons

The concentrations of copper and lead in soil from all the three sampling sites during the wet and dry seasons were compared. The combined means for the three sections (upper tea farms, adjacent land and tea farms) are as presented in table 4.4

Table 4.4: Comparative mean levels of lead and copper between dry and wet seasons

<table>
<thead>
<tr>
<th>METAL</th>
<th>SEASON</th>
<th>N</th>
<th>Mean±SD</th>
<th>95% Confidence Interval for Mean</th>
<th>Min.</th>
<th>Max.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Lower Bound</td>
<td>Upper Bound</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lead</td>
<td>Dry</td>
<td>27</td>
<td>0.133±0.024</td>
<td>0.123</td>
<td>0.143</td>
<td>0.104</td>
</tr>
<tr>
<td></td>
<td>Wet</td>
<td>27</td>
<td>0.144±0.026</td>
<td>0.133</td>
<td>0.154</td>
<td>0.119</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>54</td>
<td>0.138±0.025</td>
<td>0.131</td>
<td>0.145</td>
<td>0.104</td>
</tr>
<tr>
<td>Copper</td>
<td>Dry</td>
<td>27</td>
<td>0.093±0.032</td>
<td>0.081</td>
<td>0.106</td>
<td>0.051</td>
</tr>
<tr>
<td></td>
<td>Wet</td>
<td>27</td>
<td>0.112±0.037</td>
<td>0.097</td>
<td>0.126</td>
<td>0.061</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>54</td>
<td>0.103±0.035</td>
<td>0.093</td>
<td>0.112</td>
<td>0.051</td>
</tr>
</tbody>
</table>

The mean for lead ranged from 0.104±0.024 mg/g to 0.162±0.024 mg/g in the dry season and from 0.119±0.026 mg/g to 0.179±0.026 mg/g in the wet season. Although the mean for the wet season (0.144±0.026 mg/g) was higher than the mean for the dry season (0.133±0.024 mg/g), the difference was not significant as determined by one-way ANOVA ($F (1, 53) = 2.430, p = 0.125$).

The mean for copper ranged from 0.051 ± 0.032 mg/g to 0.125 ± 0.032 mg/g during the dry season and from 0.061 ± 0.037 mg/g to 0.137± 0.037 mg/g during the wet season. There was no statistically significant difference between the two means as determined by one-way ANOVA ($F (2, 53) = 1.397, p = .054$). ANOVA results for both lead and copper are presented in appendix I.
4.6 Concentration of nutrients (phosphates and nitrates) in tea soils

The levels of nitrates and phosphates in tea soils were analyzed separately for each of the three sampling areas. The results are as presented in the following sections.

4.6.1 Concentration of nitrates in soils

Table 4.5 shows the concentration of nitrates in soil during dry and wet seasons.

**Table 4.5: Concentration of nitrates in soil samples**

<table>
<thead>
<tr>
<th></th>
<th>Dry season</th>
<th>Wet season</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N</td>
<td>Mean±SD (mg/g)</td>
<td>Variance</td>
<td>N</td>
<td>Mean±SD (mg/g)</td>
<td>Variance</td>
<td>P value</td>
</tr>
<tr>
<td>AL</td>
<td>9</td>
<td>0.287±0.022</td>
<td>0.000</td>
<td>9</td>
<td>0.041±0.019</td>
<td>0.010</td>
<td>0.002</td>
</tr>
<tr>
<td>TF</td>
<td>9</td>
<td>0.601±0.025</td>
<td>0.001</td>
<td>9</td>
<td>0.081±0.021</td>
<td>0.007</td>
<td>0.050</td>
</tr>
<tr>
<td>UTF</td>
<td>9</td>
<td>0.492±0.017</td>
<td>0.002</td>
<td>9</td>
<td>0.061±0.013</td>
<td>0.000</td>
<td>0.001</td>
</tr>
</tbody>
</table>

From table 4.5, the levels of nitrates in soils during the dry season ranged from 0.287±0.022 mg/g in adjacent land to 0.601±0.025 mg/g in tea farms. During the wet season, the levels of nitrates ranged from 0.041±0.019 mg/g in adjacent land to 0.081±0.021 mg/g in tea farms. The mean levels of nitrates in the dry season was higher than the mean obtained by Mesoppirr *et al.* (2015) who obtained a mean of 0.018 mg/g while studying soils in Narok county. However, for the wet season, the mean concentration of nitrates matched with their levels of a mean of 0.028 mg/g in the wet season. This was almost near to their minimum value of 0.031±0.023 mg/g obtained in adjacent land during the wet season.
Generally, the levels of nitrates in the dry season were significantly higher than those in the wet season as presented in appendix II. The mean of nitrates in the soil for adjacent land in the dry season was statistically significantly higher than the mean in the wet season \((t (8) = 4.349, p = 0.002)\). The dry season mean nitrate for tea farms was also statistically significantly higher than the wet season mean \((t (8) = 21.316, p< 0.05)\). Similarly, the dry season mean nitrate for upper tea farms was statistically significantly higher than the wet season mean \((t (8) = 21.316, p = 0.001)\). This was also in line with the results of Mesoppirr et al. (2015) who found a significant difference between the levels of nitrates in the dry and the wet season \((p<0.05)\).

The higher levels of nitrates in soils in the dry season as compared to the wet season was due to the effect of rainfall. Since nitrates are highly soluble, they dissolve in the rain water and are carried away as run off or percolate into the underground through leaching. Also, the water evaporates during the dry season leaving behind salts thus increasing concentration per unit mass of soil.

**4.6.2 Concentration of phosphates in soils**

The levels of phosphates in the three sections for both the dry and wet seasons are as presented in table 4.6.
Table 4.6: Concentration of phosphates in soils

<table>
<thead>
<tr>
<th></th>
<th>Dry season</th>
<th>Wet season</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N</td>
<td>Mean±SD (mg/g)</td>
</tr>
<tr>
<td>AL</td>
<td>9</td>
<td>0.056±0.015</td>
</tr>
<tr>
<td>TF</td>
<td>9</td>
<td>0.127±0.016</td>
</tr>
<tr>
<td>UTF</td>
<td>9</td>
<td>0.095±0.019</td>
</tr>
</tbody>
</table>

During the dry season, the levels of phosphates ranged from 0.056±0.015 mg/g in adjacent land to 0.127±0.016 mg/g in tea farms. During the wet season, the levels of phosphates ranged from 0.059±0.013 mg/g in adjacent land to 0.092±0.011 mg/g in upper tea farms. The values found in this research were higher than those found by Mesoppirr et al. (2015) in soils in Ntulele. They found that phosphates in soils ranged from 0.001 mg/g to 0.004 mg/g during dry season and from 0.004 mg/g to 0.002 mg/g during wet season. The tea soils were not phosphate-deficient since the means obtained from this study were higher than the critical value of 0.005 mg/g (Wani et al., 2011; Rajaskhekha et al., 2010).

The higher levels of phosphates in tea farms relative to other sections are due to more frequent application of phosphate fertilizers. Paired sample test showed that the levels of phosphates in the soils do not vary significantly between the seasons, as presented in appendix III. The mean difference between phosphate in the dry and wet seasons for adjacent land was not statistically significant (t (8) = -0.424, p = .683). The difference in
dry and wet seasons means for tea farms was also not statistically significant \((t (8) = 1.179, p = .272)\). Similarly, there was no statistically significantly difference in means for upper tea farms between dry and wet seasons \((t (8) = .160, p = .877)\). These findings differed with those of Mesoppirr et al. (2015) who found lower phosphate concentration during the dry season and a significantly higher concentration in the wet season \((p<0.05)\).

Observations in the present study were in accordance with the earlier observations made by Venkatesan and Senthurpandian (2006) where they found that the tea garden soils in South India contained high levels of phosphates, implying excessive use of phosphate fertilizers. Estimations on the global availability of phosphate rock and the rate of depletion vary (Schröder et al., 2010). A maintainable use of phosphorus is required to safeguard food supply in the years to come and to lower the harmful effects of waste of natural resources on the surroundings. These include: proper fertilization practices, reduction of imbalances in phosphate inputs and outputs to farming soils, recovery of phosphorus from sewage for fertilization.

### 4.7 Concentration of heavy metals in river Nyamasogota water

Table 4.7 shows the levels of lead and copper in river Nyamasogota water in the dry and wet seasons.
Table 4.7: Concentration of lead and copper in river Nyamasogota water

<table>
<thead>
<tr>
<th></th>
<th>Dry season</th>
<th>Wet season</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N</td>
<td>Mean±SD (mg/l)</td>
</tr>
<tr>
<td>Lead</td>
<td>9</td>
<td>0.109±0.016</td>
</tr>
<tr>
<td>Copper</td>
<td>9</td>
<td>0.142±0.011</td>
</tr>
</tbody>
</table>

From table 4.7, the levels of lead in river Nyamasogota water ranged from 0.100±0.015 mg/l to 0.169±0.017 mg/l with a mean of 0.109±0.016 mg/l in the dry season. During the wet season, the levels of lead ranged from 0.070±0.029 mg/l to 0.202±0.034 mg/l with a mean of 0.084±0.032 mg/l. Higher levels of lead in the dry than wet season can be explained by the principle of dilution. During the rainy season, water levels in the river increase at a higher rate than the rate at which metals are deposited. Therefore, although the levels of metals increase due to continuous deposition of effluents from the tea factories for instance Ogembo and Nyamache tea factories, low concentrations are detected due to dilution by the heavy rain water. However, the mean levels of lead in river Nyamasogota water were higher than the recommended levels of 0.01 mg/l (WHO, 2004).

Studies of water from Ikpoba and Nairobi rivers during the dry season recorded mean Pb levels of 0.035 mg/l and 0.100 mg/l that were comparable to the current study but above the recommended limit of 0.01 mg/l of Pb in drinking water (Kithiia, 2006; Oguzie and Izevbigie, 2009). During the wet season, lower Pb mean concentrations (0.05 mg/l) than
those reported by the current study were obtained. Wachira (2007) reported that the water from Nairobi river was unsuitable for domestic use and attributed the higher levels of lead and copper to discharge of untreated industrial and urban effluent to the river.

From table 4.7, the concentration of copper in river Nyamasogota water during the dry season ranged from 0.127±0.016 mg/l to 0.252±0.017 mg/l with a mean of 0.142±0.011 mg/l. During the wet season, the levels of copper in water ranged from 0.156±0.013 mg/l to 0.312±0.013 mg/l with a mean of 0.175±0.013 mg/l. Higher copper levels in river Nyamasogota in the wet season can therefore be attributed to accumulated sediments of soils from surrounding areas, including the industrial area of Magena town and also copper sulphate which is used as fungicides, pesticides, nutritional supplement in animal feeds and in fertilizers. These effluents are transported into the river by surface runoff.

4.7.1 Comparison of levels of copper and lead in river Nyamasogota with standard values
The levels of lead and copper in river Nyamasogota relative to the recommended values by WHO (2004) for drinking water are as shown in figure 4.2
From figure 4.2, the mean level of lead in water was $0.109 \pm 0.017$ mg/l during dry season in three visits of data collection, which was slightly higher than WHO (2004) recommended value of 0.1 mg/l. However, the level of lead fell to $0.084 \pm 0.032$ mg/l in the wet season which was below the recommended value. A one-sample t-test was run to determine whether the levels of lead were significantly different from the recommended value of 0.1 mg/l. The mean for the dry season was not statistically significantly different from the recommended value ($t(8) = -0.384, p = .835$). Similarly, the mean for the wet season was not statistically significantly different from the recommended value ($t(8) = 0.216, p = 0.711$). This implies that the levels of lead in the water remain within
acceptable limits during both seasons and is safe for domestic consumption. The T-test results are presented in appendix IV.

From figure 4.2, the mean levels of copper were 0.142±0.012 mg/l during the dry season and 0.175±0.013 mg/l during the wet season. Both means were higher than the WHO (2004) recommended value of 0.05 mg/l. A one-sample t-test was run to determine whether the levels of copper were significantly different from the recommended value of 0.05 mg/l. The mean for the dry season was not significantly different from the recommended value (t (8) = 2.273, p= .053). However, the level of copper in the wet season was higher than the recommended value of 0.05, with a statistically significant difference of 0.125 (95% CL, .013 to 0.24), t (8) = 2.581, p = .033). This implies that the level of copper in the wet season is a health hazard to the community in Magena division that depend on Nyamasogota river for drinking water. The T-test results are as presented in appendix V.
4.8 Concentration of nutrients in river Nyamasogota water

Table 4.8 shows the levels of nitrates and phosphates in river Nyamasogota water in both dry and wet season.

<table>
<thead>
<tr>
<th>Nutrient</th>
<th>Dry season</th>
<th>Wet season</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N</td>
<td>Mean±SD (mg/l)</td>
</tr>
<tr>
<td>Nitrates</td>
<td>9</td>
<td>0.248±0.010</td>
</tr>
<tr>
<td>Phosphates</td>
<td>9</td>
<td>0.288±0.024</td>
</tr>
</tbody>
</table>

Table 4.8: Concentration of nitrates and phosphates in river Nyamasogota water

From table 4.8, the levels of nitrates in river Nyamasogota water during the dry season ranged from 0.206±0.021 mg/l to 0.291±0.019 mg/l, with a mean of 0.248±0.010 mg/l. During the wet season, the levels of nitrates ranged from 0.216±0.019 mg/l to 0.358±0.015 mg/l with a mean of 0.256±0.019 mg/l. Although levels of nitrates in water during wet season were higher than in dry season, there was no statistically significant difference between the two means (t (8) = -.539, p = .605). The Paired Sample Test results are presented in appendix VI. The levels of nitrates in both seasons were lower than the recommended value of 0.5 mg/l.

The higher concentrations of nitrates in the river during the wet season was due to soil erosion and surface run-off which is associated with heavy rainfall. The rain had accumulated soils containing nitrates from different farms and different waste from industrial and agricultural activities in Magena area. This implies that there was high
change of mean due to downwards movement of nitrates due to surface run-off and low gravity since it is at the lower side of the slope.

This is in line with Khan and Mohammad (2014) who stated that soil concentrations of nitrates from different anthropogenic activities, for instance application of phosphate and nitrate fertilizers, animal excreta contribute to high concentration of nitrates. Yaron et al. (2012) also found that nitrates can move to both river water and underground water as a result of farming activity (as well as application of excess nutrients and composts), from wastewater and from oxidation of nitrogenous garbage products in organism waste, comprising septic tanks.

From table 4.8, the levels of phosphates in river Nyamasogota water during dry season ranged from 0.232±0.021 mg/l to 0.524±0.023 mg/l with a mean of 0.288±0.024 mg/l. During the wet season, the levels of phosphates ranged from 0.279±0.022 mg/l to 0.518±0.023 mg/l with a mean of 0.319±0.021 mg/l. Paired sample T-test showed that the levels of phosphates in water during the wet season were significantly higher than the levels in the dry season (t (8) = -2.370, p=0.045) as presented in Appendix VII. This is attributed by use of phosphate-based fertilizers during wet season when planting takes place.
4.8.1 Comparison of nitrate and phosphate levels in river Nyamasogota water with standard values

The Figure 4.3 shows the levels of nitrates and phosphates in river Nyamasogota water relative to the recommended values by WHO (2004) for drinking water. Mean levels for both dry and wet seasons are presented.

Figure 4.3: Levels of nutrients in river Nyamasogota water relative to standard values

4.8.1.1 Levels of nitrates in river Nyamasogota water

From figure 4.3, the levels of nitrates in water during both seasons were lower than the recommended standard of 0.5 mg/l. The means for nitrates in water were found to be statistically significantly lower than the recommended value (p<0.05) as presented in appendix VIII. The levels of nitrates in river Nyamasogota water therefore remained within acceptable standards in the dry and wet season. However, the presence of nitrates shows the possibility for negative effects on the environment, particularly upon water
quality. Although other sources can be of significance, in specific, unrefined municipal wastewater in Magena town increases the concentration of nitrates in Nyamasogota river and also the use of nitrogenous fertilizers like ammonium nitrates in the area.

4.8.1.2 Levels of phosphates in river Nyamasogota water

From figure 4.3, the mean level of phosphates in river Nyamasogota water was 0.288 ± 0.023 mg/l in dry season and 0.319 ± 0.024 mg/l in wet season. The levels of phosphates in water during wet season were found to be significantly higher than WHO (2004) recommended values with ($t (8) = 3.152, p = .014$) for the dry season and ($t (8) = 4.179, p = .003$) for the wet season as shown in appendix IX. The levels of phosphates in river Nyamasogota are therefore above the recommended standards and are a great health hazard to the surrounding community.

Phosphates pollute the water if they are more than the recommended level of 0.05 mg/l for rivers flowing into basins, and not more than 0.025 mg/l for basins (De Girolamo and Porto, 2012). Extreme discharges of nutrients to water increases eutrophication, categorised by the production of algal blossoms that are visually unpleasant and lessen the clearness of water (KEBS, 2007). Poisonous gases which pose a menace to community well-being may be produced through decay of algae under anaerobic environment and this is also due to the fact that algal blossoms frequently comprise poisonous cyanobacteria (WHO, 2006). Algal blossoms likewise are linked with the damage of ‘desirable’ plant and animal species. Effects of eutrophication on river ecosystems are recognized all over the biosphere as well as Kenya.
54

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion
From the study the results showed that all the two heavy metals were present in drinking water in Nyamasogota river in Magena area and the levels of copper significantly differed in Nyamasogota river during dry and wet seasons. 99.9% of the samples had the level of copper metal above the levels set by the national and international standards. 100% of the samples from Nyamasogota river had lead metal levels below the set standards by KEBS and WHO. Based on the tested two metals in river Nyamasogota, levels of lead were not significantly different during both dry and wet seasons thus lead levels do not have health implications to people. In the three soil sections the levels of copper and lead did not vary significantly however the levels increased from upper to the lower sections due to farming.

The results also showed that phosphate and nitrates were present in Nyamasogota river, Kisii County. 99% of samples contained phosphate levels which were significantly higher than the standard levels this reveals that the levels of phosphates in Magena sub-county is a health hazard to the community as far as phosphate is concerned. The levels of nitrates were below the permissible limit in Nyamasogota river. This shows that the levels of nitrates do not affect the entire population of Magena sub-county.
In all three sections of soil, the levels of nitrates did not vary significantly during wet season. During dry season the levels of nitrates differed significantly from those of wet season. Levels of phosphates in the three land sections did not vary significantly hence during wet seasons the levels of lead are higher than dry season.

5.2 Recommendations from the study

From the study, the following recommendations were made:

i. The area above tea farms recorded the highest levels of copper in the soil. It is recommended that farmers in tea farms, which lie down the slope, should dig terraces to prevent runoff water from depositing copper into their farms.

ii. Levels of copper in the river rose above the recommended standards during the wet season. It is recommended that the community purifies the water before drinking it in the wet season, or use alternative water sources such as harvesting rain water, wells and boreholes. Alternatively, farmers in the area should make terraces in sloppy areas to prevent erosion during rainy season.

iii. It is recommended that farmers should not apply excess of phosphates during heavy rainfall since much of them are washed away and drained into the river. This deprives plants of nutrients as well causing pollution in river Nyamasogota water.

iv. It is recommended that the farmers be educated on the impact of applying phosphates on water quality. The levels of phosphates in river Nyamasogota were higher than the recommended values during both seasons. There’s need for the
farmers to take initiatives to stop the excessive deposition of phosphates into the river by substituting inorganic fertilizers with organic ones.

5.3 Recommendation for further studies

i. The concentration of heavy metals and nutrients in tea soils in other divisions of Kisii County should be assessed to find out their concentration and compare with the recommended levels.

ii. Other toxic heavy metals such as mercury and cadmium should be studied.

iii. Levels of pesticides and their residuals in soil and river water should be studied.

iv. Studies should be conducted to ascertain which proportion of nutrients is transported through runoff water and which proportion is transported through underground seepage.

v. A study be conducted to establish the proportions various sources such as industrial effluents, sewage, runoff from tea farms and runoff from urban centers contribute to the levels of pollution in river Nyamasogota water.
REFERENCES


### APPENDICES

**Appendix I: ANOVA for difference in means of Cu and Pb between dry and wet season**

**ANOVA**

<table>
<thead>
<tr>
<th></th>
<th>Sum of Squares</th>
<th>Df</th>
<th>Mean Square</th>
<th>F</th>
<th>Sig.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Between Groups</td>
<td>.002</td>
<td>1</td>
<td>.002</td>
<td>2.430</td>
<td>.125</td>
</tr>
<tr>
<td>Within Groups</td>
<td>.033</td>
<td>52</td>
<td>.001</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>.034</td>
<td>53</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Copper</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Between Groups</td>
<td>.005</td>
<td>1</td>
<td>.005</td>
<td>3.879</td>
<td>.054</td>
</tr>
<tr>
<td>Within Groups</td>
<td>.061</td>
<td>52</td>
<td>.001</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>.065</td>
<td>53</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Appendix II: Paired sample tests for difference in means of nitrates between seasons for AL, TF and UTF**

**Paired Samples Test**

<table>
<thead>
<tr>
<th></th>
<th>Paired Differences</th>
<th>T</th>
<th>df</th>
<th>Sig. (2-tailed)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>Std. Error Mean</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AL (Dry-Wet)</td>
<td>.2460000</td>
<td>.0565685</td>
<td>4.349</td>
<td>.002</td>
</tr>
<tr>
<td>TF (Dry-Wet)</td>
<td>.5200000</td>
<td>.0243952</td>
<td>21.316</td>
<td>.000</td>
</tr>
<tr>
<td>ATF (Dry-Wet)</td>
<td>.4310000</td>
<td>.0816708</td>
<td>5.277</td>
<td>.001</td>
</tr>
</tbody>
</table>
Appendix III: Paired sample tests for difference in means of phosphates between seasons for AL, TF and UTF

<table>
<thead>
<tr>
<th>Paired Samples Test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paired Differences</td>
</tr>
<tr>
<td>Mean Difference</td>
</tr>
<tr>
<td>AL (Dry-Wet)</td>
</tr>
<tr>
<td>TF (Dry-Wet)</td>
</tr>
<tr>
<td>ATF (Dry-Wet)</td>
</tr>
</tbody>
</table>

Appendix IV: Test for significant difference between mean of lead and standard value

<table>
<thead>
<tr>
<th>One-Sample Test for Lead</th>
</tr>
</thead>
<tbody>
<tr>
<td>Season</td>
</tr>
<tr>
<td>t</td>
</tr>
<tr>
<td>Lower</td>
</tr>
<tr>
<td>Dry</td>
</tr>
<tr>
<td>Wet</td>
</tr>
</tbody>
</table>
### Appendix V: Test for significant difference between mean of copper and standard value

<table>
<thead>
<tr>
<th>Season</th>
<th>T</th>
<th>df</th>
<th>Sig. (2-tailed)</th>
<th>Mean Difference</th>
<th>95% Confidence Interval of the Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry</td>
<td>2.273</td>
<td>8</td>
<td>.053</td>
<td>.0900000</td>
<td>-.001313 - .181313</td>
</tr>
<tr>
<td>Wet</td>
<td>2.581</td>
<td>8</td>
<td>.033</td>
<td>.1250000</td>
<td>.013305 - .236695</td>
</tr>
</tbody>
</table>

### Appendix VI: Difference in levels of nitrates between dry and wet season in river Nyamasogota water

<table>
<thead>
<tr>
<th>Paired Differences</th>
<th>T</th>
<th>df</th>
<th>Sig. (2-tailed)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>.0148492</td>
<td></td>
<td>.605</td>
</tr>
<tr>
<td>Std. Error Mean</td>
<td>-.539</td>
<td>8</td>
<td></td>
</tr>
</tbody>
</table>

| Nitrates | -0.008 | .0148492 | -.539 | 8 | .605 |

### Appendix VII: Difference in levels of nitrates between dry and wet season in river Nyamasogota water

<table>
<thead>
<tr>
<th>Paired Differences</th>
<th>T</th>
<th>df</th>
<th>Sig. (2-tailed)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>.01308</td>
<td></td>
<td>.045</td>
</tr>
<tr>
<td>Std. Error Mean</td>
<td>-2.370</td>
<td>8</td>
<td></td>
</tr>
</tbody>
</table>

| Phosphates | -.03100 | .01308 | -2.370 | 8 | .045 |
Appendix VIII: Test for significant difference between levels of nitrates and standard value

<table>
<thead>
<tr>
<th>SEASON</th>
<th>T</th>
<th>Df</th>
<th>Sig. (2-tailed)</th>
<th>Mean Difference</th>
<th>95% Confidence Interval of the Difference</th>
<th>Lower</th>
<th>Upper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry</td>
<td>-11.879</td>
<td>8</td>
<td>.000</td>
<td>-.2520000</td>
<td>-.300918</td>
<td>-.203082</td>
<td></td>
</tr>
<tr>
<td>Wet</td>
<td>-6.766</td>
<td>8</td>
<td>.000</td>
<td>-.2440000</td>
<td>-.327160</td>
<td>-.160840</td>
<td></td>
</tr>
</tbody>
</table>

Appendix IX: Test for significant difference between levels of phosphates and standard value

<table>
<thead>
<tr>
<th>Season</th>
<th>t</th>
<th>Df</th>
<th>Sig. (2-tailed)</th>
<th>Mean Difference</th>
<th>95% Confidence Interval of the Difference</th>
<th>Lower</th>
<th>Upper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry</td>
<td>3.152</td>
<td>8</td>
<td>.014</td>
<td>.2630000</td>
<td>.070590</td>
<td>.455410</td>
<td></td>
</tr>
<tr>
<td>Wet</td>
<td>4.179</td>
<td>8</td>
<td>.003</td>
<td>.2940000</td>
<td>.131756</td>
<td>.456244</td>
<td></td>
</tr>
</tbody>
</table>

Sampling of soil in tea farms
Appendix XI: Standard curve for copper

\[ y = 0.033x + 0.000 \]

\[ R^2 = 0.9962 \]
Appendix XII: Standard curve for Lead

\[ y = 0.042x + 0.001 \]

\[ R^2 = 0.9956 \]
Appendix XIII: Standard curve for nitrates

\[ y = 0.011x + 0.005 \]

\[ R^2 = 0.9961 \]
Appendix XIV: Standard curve for phosphates

\[ y = 0.044x + 0.026 \]

\[ R^2 = 0.9991 \]