ASSESSMENT OF KANGEMI SEWAGE TREATMENT WORKS EFFICIENCY AND THE IMPACT OF THE EFFLUENT ON WATER QUALITY OF CHANIA RIVER NYERI, KENYA

SAEED HASSAN KARIUNGA

A Thesis Submitted to the Graduate School in Partial Fulfillment of the Requirements of the Master of Science Degree in Limnology of Egerton University

EGERTON UNIVERSITY
October 2019
DECLARATION AND RECOMMENDATION

Declaration
I declare that this thesis is my original work and has not been presented for examination in any institution.

Saeed Hassan Kariunga
SM18/14492/15

Signature ___________________________ Date ___________________________

Recommendation
This thesis has been submitted with our approval as the university supervisors in accordance to Egerton University regulations.

Signature ___________________________ Date ___________________________

Prof. Nzula Kitaka
Egerton University

Signature ___________________________ Date ___________________________

Dr. A. W. Muia
Egerton University
COPYRIGHT
All rights reserved. No part of this thesis may be produced or transmitted in any form or by any means including photocopying, recording or any information storage or retrieval system without permission in writing from the author or Egerton University.

©2019 Saeed Hassan Kariunga
ACKNOWLEDGEMENTS

Gratitude upon whom if there were other deities beside him all will be ruined (Allah). I wish to thank Egerton University for the opportunity to study in their institution. I am sincerely very grateful to Florian from Rotary Club of Vienna through LWM office at Egerton University for awarding me a fellowship to undertake this study. I am particularly indebted to Prof. Nzula Kitaka who is also my supervisor and programme coordinator for LWM/RCV, together with Dr. Wairimu Muia for their thorough guidance and goodwill in making this thesis a success. I appreciate, LWM Programme and Biological Sciences Department for equipment and facilities offered to me especially in the LWM Water Quality Laboratory through my entire research period. My sincere thanks also go to all lecturers for any assistance and support given, Mr. Eddison for logistical support, Mr. Mungai for helping me on equipment acquisition and Ms. Priscilla who worked with me in the laboratory during analysis. I can't forget Mr. Ken Ochieng for his input on data analysis, and many others I cannot mention here who assisted me in one way or another. I appreciate the assistance of staff from Nyeri Water and Sewerage Company through Engineer Gathungu, for giving me an opportunity to do my data collection in their Kangemi Sewage Treatment Works. I extend further thanks to my colleagues in Limnology class at Egerton University for their great enrichment towards this work. In a special way, I acknowledge the patience and inspiration of my family saying, Thank You all!
DEDICATION
I dedicate this work to my wife and daughters for their exemplary patience, support and encouragement. The work is also dedicated to my entire family who gave me moral support, not forgetting my late dad and all others who assisted me in achieving this thesis.
ABSTRACT

Sewage treatment plants (WTPs) use a combination of physical, chemical and biological processes to reduce the pollutant loads in wastewater. The treated wastewater is then either discharged to surface water or is reused. Successive stages in wastewater treatment plants reduce the quantity of suspended solids, biological contaminants, organic matter content and nutrient constituents in sewage. Changes in the properties of the effluents can occur along the treatment process leading to reduction or little change in effluent quality based on the effectiveness of the treatment process. The discharge of inadequately treated sewage from ineffective WTPs into the rivers and other receiving water bodies are both potential health risk and environmental hazard to both adjacent and downstream communities. This study estimates the efficiency of Kangemi Sewage Treatment Works (KSTW) in pollutant removal and the impact of its effluent on water quality of Chania River (CR). For environmental quality assurance, the plant’s performance requires consistent monitoring to evaluate the impact of the effluents to the receiving waters. Key nutrients (Nitrogen and Phosphorus), total suspended solids (TSS) and biological oxygen demand (BOD₅) were determined using American Public Health Association (APHA, 2005) standard methods. Kruskal-Wallis test was run at p<0.05. Nitrogen, BOD₅ and TSS indicated a significant difference between the sites (P<0.05). Physico-chemical parameters varied significantly, however, no significant difference for TP (Kruskal Wallis, 4.515, P=0.341) and SRP (Kruskal Wallis, 2.160, P=0.696) respectively across sites in KSTW. Removal efficiency for BOD₅, TSS, NH₄ and TN were 60%, 85%, 59% and 54% respectively. The KSTW had high removal efficiency for N but low for P but it was a source of nitrate, nitrite and TP. Organic-N was the most dominant form of N in KSTW, while P was mostly inorganic. In CR, the confluence (S8) recorded highest concentrations for most parameters (N, P, BOD₅ and TSS). Inorganic-N in the CR was more than organic-N after effluent discharge point. Nitrate-N was the most common species of the dissolved nitrogen in CR. All parameters measured in CR showed a significant difference except TSS (Kruskal Wallis, P=0.733). Nutrients and organic matter in both the KSTW and Chania River indicated a strong correlation with temperature, DO and pH. Both for N and P, the organic form was dominating in CR. In conclusion, Pollution impact was highest at the KSTW point of effluent discharge (S8), with, the river indicating quick recovery downstream. In contrast, TSS indicated a progressive increase in concentration downstream from S8-S10. For recommendation, long-term surveys should be conducted to capture temporal efficiency and impact of KSTW effluent on Chania River.
TABLE OF CONTENTS

DECLARATION AND RECOMMENDATION ..........................................................II
COPYRIGHT ..................................................................................................................III
ACKNOWLEDGEMENTS ..............................................................................................IV
DEDICATION ....................................................................................................................V
ABSTRACT .....................................................................................................................VI
TABLE OF CONTENTS ..................................................................................................VII
LIST OF FIGURES .........................................................................................................X
LIST OF TABLES ............................................................................................................XI
LIST OF PLATES ...........................................................................................................XII
LIST OF ABBREVIATIONS AND ACRONYMS .........................................................XIII
CHAPTER ONE .............................................................................................................1
INTRODUCTION ............................................................................................................1
  1.1 Background Information .......................................................................................1
  1.2 Statement of the Problem ......................................................................................2
  1.3 Objectives ..............................................................................................................3
    1.3.1 General Objective ..........................................................................................3
    1.3.2 Specific Objectives .......................................................................................3
  1.4 Hypotheses ............................................................................................................4
  1.5 Justification ..........................................................................................................4
CHAPTER TWO .............................................................................................................6
LITERATURE REVIEW ...............................................................................................6
  2.1 Wastewater Treatment Processes in a Conventional Sewage Treatment Plant ..........6
    2.1.1 Preliminary Treatment of Sewage .................................................................7
    2.1.2 Primary Treatment of Sewage .....................................................................7
    2.1.3 Secondary Treatment of Sewage .................................................................7
    2.1.4 Tertiary (Advanced) Treatment .................................................................8
  2.2 Sources and Types of Wastewater Pollution ......................................................9
  2.3 Rivers as Receptacles for Sewage Disposal .......................................................10
  2.4 Self-Purification Potential of Rivers and Streams ...............................................12
  2.5 Parameters Affecting Wastewater and River Water Nutrient Dynamics .............13
    2.5.1 Effect of Temperature on Wastewater and Surface Water (Rivers) ............13
    2.5.2 pH Effects on Biochemical Reaction in Wastewater Treatment ....................14
2.5.3 Effects of Dissolved Oxygen in WTP Effluents to Receiving Waters ........................................ 14
2.5.4 BOD Classification and Biodegradation Processes in Wastewater ........................................ 15
2.5.5 Total Suspended Solids as Pollutant in River Systems ......................................................... 17
2.6 Nutrient Forms and Transformation in Wastewater and Rivers ............................................. 17
   2.6.1 Nitrogen Forms and Their Biochemical Processes ....................................................... 18
   2.6.2 Phosphorus Forms and their Biochemical Processes ..................................................... 20
2.7 Water Pollution as Environmental Hazard ............................................................................... 20
2.8 Nutrient Loading and their Impact in Lotic Systems .......................................................... 21
2.9 Surface Water Quality Status, Legislations and Standards in Kenya ...................................... 23

CHAPTER THREE .................................................................................................................. 25
MATERIALS AND METHODS ............................................................................................. 25
3.1 Study Area ......................................................................................................................... 25
3.2 Sampling Sites ..................................................................................................................... 26
   3.2.1 Sampling and Field Measurements .................................................................................... 27
   3.2.2 Determination of Nitrogen and Phosphorus in Water Samples ........................................ 28
   3.2.3 Total Suspended Solids (TSS) ........................................................................................ 29
   3.2.4 Biological Oxygen Demand in Wastewater and River ..................................................... 29
   3.2.5 Discharge Measurements for WTP and River ............................................................... 29
   3.2.6 Loading Rates Determination of N and P into Chania River .......................................... 29
   3.2.7 Wastewater Treatment Plant Efficiency Estimation ....................................................... 30
3.3 Data Analysis ...................................................................................................................... 30

CHAPTER FOUR .................................................................................................................. 31
RESULTS ............................................................................................................................... 31
4.1 Water Quality Parameters at Kangemi Sewage Treatment Works (KSTW) ........................... 31
   4.1.1 Temperature, pH and conductivity variation within the system .................................... 31
   4.1.2 BOD$_5$ and TSS Dynamics in Sites within KSTW ......................................................... 32
   4.1.3 Nutrients Concentrations within KSTW ........................................................................ 32
   4.1.4 Relationship between Wastewater Flow and Water Quality Parameters in KSTW ......... 34
4.2 Variability in Physico-chemical Parameters, Nutrients and Organic Matter in CR ............ 35
   4.2.1 Temperature DO, Conductivity and BOD$_5$ Variation along the sites in CR .................. 36
   4.2.2 Nutrients Concentration Spatial Variability along Chania River ..................................... 37
   4.2.3 Relationship of Discharge, Nutrients and Physico-chemical Variables in CR ............. 39
4.3 The Organic and Inorganic Components of N and P at KSTW and CR .............................. 40
4.3.1 Organic and Inorganic Fraction of N and P in KSTW ......................................................... 40
4.3.2 A Comparison of Inorganic and Organic (N and P) Composition of Sites in CR ............... 41
4.4 Nutrients and Organic Matter Removal Efficiencies of KSTW .............................................. 41
  4.4.1 Percentage Contribution of Nutrient Fraction at Influent and Effluent of KSTW .............. 42
  4.4.2 Kangemi Sewage Treatment Works Removal Efficiency of Nutrients and OM .............. 42
4.5 Nutrients and Organic Matter Loading Rates at KSTW ......................................................... 44
  4.5.1 Nutrient and Organic Matter Retention and Release in KSTW .................................. 44
  4.5.2 Removal of Pollutant Loads at Longitudinal Profile of Chania River ......................... 45

CHAPTER FIVE ................................................................................................................................. 47

DISCUSSION ................................................................................................................................. 47
5.1 Overview of KSTW efficiency and Impact of the Effluent on CR Water Quality ............... 47
5.2 Physico-Chemical parameters, Nutrient and Organic Matter Dynamics in KSTW ........... 47
5.3 Nutrient Transformation in Wastewater at KSTW ................................................................. 49
  5.3.1 Nitrogen Transformation in Wastewater ................................................................. 49
  5.3.2 Phosphorus Dynamics and Removal in KSTW ............................................................... 50
  5.3.3 Organic Matter Degradation in KSTW Wastewater Treatment Pathway ..................... 51
5.4 Nutrients and Organic Matter Removal Efficiencies of KSTW ........................................... 52
5.5 The Impact of KSTW Effluent Input in Physical & Chemical Characteristics, Nutrient and Organic Matter on the Water Quality of Chania River ........................................................................... 55
  5.5.1 Influence of Physical Variables on the Chania River ...................................................... 55
  5.5.2 Influence of Effluent from KSTW on Nutrients Loading in Chania River .................... 56
  5.5.3 Influence of Nutrient and Organic Loading and its Dynamics on River Chania .......... 58
  5.5.4 Self-purification Process in River Chania ...................................................................... 59

CHAPTER SIX ................................................................................................................................. 61

CONCLUSION AND RECOMMENDATIONS .................................................................................. 61
6.1 Conclusions ............................................................................................................................. 61
6.2 Recommendations .................................................................................................................. 62

REFERENCES .................................................................................................................................. 63

APPENDICES ................................................................................................................................... 83
LIST OF FIGURES

Figure 1: Schematic Diagram of a Conventional Wastewater Treatment Plant ......................... 6
Figure 2: A Map showing location of KSTW and the sampled sites in Chania River, Nyeri ........... 25
Figure 3: Schematic map showing sampling sites layout in both KSTW and CR .......................... 26
Figure 4: Mean ± SE levels of Organic Matter (a) BODs and (b) TSS at sites along KSTW ....... 32
Figure 5: Mean ± SE levels of nutrients. (a) Nitrite, (b) Nitrate, (c), Ammonium-N (d) TN, (e) TP and (f) SRP at sites along KSTW .................................................................................. 34
Figure 6: Mean ± SE levels of Organic Matter (a) BODs and (b) TSS at sites along Chania River (S8 being the KSTW effluent point into the river) ................................................................. 37
Figure 7: Mean ± SE concentration of nutrients, (a) Nitrite, (b) Nitrate, (c) Ammonium-N, (d) TN, along the Chania River ........................................................................................................ 38
Figure 8: Mean ± SE concentration of nutrients, (a) SRP and (b) TP at sites along Chania River ........................................................................................................................................... 39
Figure 9: Mean ± SE comparison of Organic-Inorganic (a) N and (b) P fraction in KSTW sites 41
Figure 10: Mean ± SE comparison of Organic-Inorganic (a) N and (b) P fraction across CR sites ........................................................................................................................................... 41
Figure 11: Fraction (%) of (a) IN, (b) ON, (c) IP and (OP) proportion of KSTW influent and effluent ....................................................................................................................................... 42
Figure 12: A graph showing retention/release of selected nutrient and organic matter in KSTW 44
Figure 13: The comparison of Nutrient Loading of (a) TN and Nitrate, (b) Nitrite and Ammonium-N, (c) TP and SRP and (d) Organic Matter (BODs) and (e) TSS along CR ... 46
LIST OF TABLES

Table 1: Limits of some physical chemical parameters for Discharge into Surface Water in Kenya ................................................................. 23
Table 2: Mean ± S.E values of physical-chemical variables at sites in KSTW, ..................... 31
Table 3: Kruskal-Wallis test of physico-chemical at KSTW......................................................... 32
Table 4: Kruskal-Wallis test of nutrients and organic matter along the Sites at KSTW .......... 33
Table 5: Correlation Analysis (2 tailed) of physico-chemical and nutrients variables at KSTW. 35
Table 6: Mean Physico-chemical Parameters in Chania River.................................................... 36
Table 7: Table showing Means of Nutrients and Organic Matter along Chania River Sites...... 37
Table 8: A Relationship of physico-chemical, nutrients and organic matter at CR ............ 40
Table 9: A Comparative Nutrient and Organic Matter Removal Efficiencies in (%) at KSTW .. 43
Table 10: Loading Retention and Release (%) Nutrient and OM in KSTW ............................. 44
Table 11: Removal and Release of loads (ton/yr) and (%) removal between sites S8 to S9 and downstream S9-S10 within Chania River................................................................. 45
LIST OF PLATES

Plate 1 (a-d): Photograph showing (a) site S1, (b) site 2, (c) site 3-5, (d) site 8 at KSTW .......... 27
Plate 2 (a-d): Photograph showing (a) site 6, (b) site 7 (c) site 9, (d) site 10 along Chania River 27
### LIST OF ABBREVIATIONS AND ACRONYMS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADF</td>
<td>Australian Defence Forces</td>
</tr>
<tr>
<td>BOD</td>
<td>Biological Oxygen Demand</td>
</tr>
<tr>
<td>CCME</td>
<td>Canadian Council of Ministers of the Environment</td>
</tr>
<tr>
<td>CR</td>
<td>Chania River</td>
</tr>
<tr>
<td>DO</td>
<td>Dissolved Oxygen</td>
</tr>
<tr>
<td>DWAF</td>
<td>Department of Water Affairs and Forestry</td>
</tr>
<tr>
<td>EBPR</td>
<td>Enhanced Biological Phosphorus Removal</td>
</tr>
<tr>
<td>EMCA</td>
<td>Environmental Management and Coordination Act</td>
</tr>
<tr>
<td>GF/C</td>
<td>Glass Fiber Filter</td>
</tr>
<tr>
<td>IEPA</td>
<td>Ireland Environmental Protection Agency</td>
</tr>
<tr>
<td>IN</td>
<td>Inorganic Nitrogen</td>
</tr>
<tr>
<td>IP</td>
<td>Inorganic Phosphorus</td>
</tr>
<tr>
<td>KNBS</td>
<td>Kenya National Bureau of Statistics</td>
</tr>
<tr>
<td>KSTW</td>
<td>Kangemi Sewage Treatment Works</td>
</tr>
<tr>
<td>LVEMP</td>
<td>Lake Victoria Environmental Management Project</td>
</tr>
<tr>
<td>MEA</td>
<td>Millennium Ecosystem Assessment</td>
</tr>
<tr>
<td>n.d</td>
<td>No Date</td>
</tr>
<tr>
<td>NEMA</td>
<td>National Environmental Management Authority</td>
</tr>
<tr>
<td>NH$_4$-N</td>
<td>Ammonium-Nitrogen</td>
</tr>
<tr>
<td>NO$_2$-N</td>
<td>Nitrite-Nitrogen</td>
</tr>
<tr>
<td>NO$_3$-N</td>
<td>Nitrate-Nitrogen</td>
</tr>
<tr>
<td>NWQMS</td>
<td>National Water Quality Management Strategy</td>
</tr>
<tr>
<td>NYEWASCO</td>
<td>Nyeri Water and Sewerage Company</td>
</tr>
<tr>
<td>OEPA</td>
<td>Ohio Environmental Protection Agency</td>
</tr>
<tr>
<td>ON</td>
<td>Organic Nitrogen</td>
</tr>
<tr>
<td>OP</td>
<td>Organic Phosphorus</td>
</tr>
<tr>
<td>SDGs</td>
<td>Sustainable Development Goals</td>
</tr>
<tr>
<td>SPSS</td>
<td>Statistical Package Social Sciences</td>
</tr>
<tr>
<td>SRP</td>
<td>Soluble Reactive Phosphorus</td>
</tr>
<tr>
<td>TEPA</td>
<td>Taiwan Environmental Protection Administration</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>TN</td>
<td>Total Nitrogen</td>
</tr>
<tr>
<td>Ton/yr</td>
<td>Tons per Year</td>
</tr>
<tr>
<td>TP</td>
<td>Total Phosphorus</td>
</tr>
<tr>
<td>TSS</td>
<td>Total Suspended Solids</td>
</tr>
<tr>
<td>USEPA</td>
<td>United States Environmental Protection Agency</td>
</tr>
<tr>
<td>W.H. O</td>
<td>World Health Organization</td>
</tr>
<tr>
<td>WTP</td>
<td>Wastewater Treatment Plant</td>
</tr>
</tbody>
</table>
CHAPTER ONE
INTRODUCTION

1.1 Background Information
Globally the generation of wastes from domestic and industrial sources has increased due to increase in human population coupled with urbanization and surface runoff from agricultural lands into the recipient waterbodies (Franchetti, 2009). Municipal waste that (includes both solid/liquid waste) and sewage (mixture of wastewater from households with industrial wastewater and/or run-off rain water) is disposed of indiscriminately into water systems such as streams and rivers posing a threat to surface water pollution (Jaji et al., 2007; Solomon, 2009). Domestic wastewater is usually generated from households, washrooms, laundries and kitchens. It also contains grey water made up of urine, excreta and flush water generated from toilets. All these when combined, and channeled through a sewerage system end up in a septic tank or sewage treatment plant as sewage (Obuobie et al., 2006).

Discharge of wastewater due to anthropogenic activities into aquatic systems has resulted to their degradation by frequent reception of domestic and industrial wastes. Consequently, this has led to pollution of these systems with excessive nutrients, organic wastes, dissolved ions and inorganic compounds. Therefore, exposing humans and aquatic biota to multiple health hazards (Bakare et al., 2003). Kithiia (2012) pointed out that surface water resources in Kenya are increasingly becoming polluted from both point and diffuse sources. This is caused by rapid industrialization, urbanization, intensive farming, and dumping of solid waste in aquatic ecosystems. Ruchira and Gawande (2016), maintained that treatment plants contribute N and P resulting to nutrient pollution, while noting human sewage is the most prevalent source of urban pollution.

Adeyemo, (2003) found that entry of nutrients into aquatics systems is mainly by storm water runoff and sewage discharge into streams resulting to pollution of receiving water systems. Therefore, sewage treatment plants are expected to stabilize sewage to meet chemical and physical standards that are acceptable, meet the regulatory limits, and would not cause any detrimental effects to public health and the environment. Increased nutrient concentrations, bacterial numbers and suspended matter are some of the major properties of degraded river water quality because of sewage input.
At the same time nutrients, organic matter and other contaminants removal in wastewater varies depending on level of contaminants in the effluents and the methods used in the treatment, which in turn determine the removal efficiency. For instance, N in untreated municipal wastewater comprises approximately 60% of ammonia, 40% organic nitrogen and some nitrates. Nitrogen levels in treated domestic sewage will vary depending on the method of treatment applied. Removal of nitrogen will depend on organic loading which affects nitrification process efficiency in the wastewater. In addition, the removal of nitrogen in most treatment facilities is through cell synthesis and solids elimination. Other factors that influence nitrification efficiency includes the specific hydraulic or organic loading of the trickling filter media, its surface area and the wastewater retention time (USEPA, 2000).

Ineffective control of surface water pollution compromises water quality, increases treatment costs of drinking water and is a potential health and environmental hazards. Boesch et al. (2001) suggested that discharging untreated or inadequately treated wastewater into surface waters, including rivers, can facilitate eutrophication due to increased nutrient levels and consequently resulting to algal blooms coupled with Dissolved Oxygen (DO) depletion. The main aim of this study therefore, was to investigate and understand the performance of KSTW in pollutant (nutrient and organic matter) removal. And further evaluate the effluent loading and impact of these pollutants on water quality of recipient Chania River.

1.2 Statement of the Problem
Emerging challenges in wastewater treatment and increased knowledge about the consequences from water pollution such as eutrophication; has led to common desire and need for better water quality. To maintain acceptable water quality standards, conventional wastewater treatment plants are required to meet both local and international standards, prior to discharge to reduce negative impacts into receiving river systems. Discharging of effluents that meet regulatory discharge standards subsequently, promote protection of diminishing freshwater resources. Kangemi Sewage Treatment Works (KSTW) is a conventional plant that was built with the intent of treating wastewater generated from Nyeri town prior to discharge into Chania River (CR). The plant (KSTW) rears fish in the wastewater plants’ maturation ponds as a primary biological indicator of the plants’ efficiency in wastewater treatment. However, it’s a good initiative, it can’t sufficiently reflect nutrient pollution magnitude and acceptable measure of discharge standards thus possible
eutrophication. Furthermore, fish may not indicate microbial and heavy metal response levels immediately hence posing threat to human and river water quality alike. Therefore, there is a need to employ other wastewater monitoring tools as indicators for water quality to supplement the existing primary water quality assessment indicator at the plant.

In the last two decades Kenya has experienced an increase in population, rapid urbanization and development of businesses/industries in urban centers. Therefore, a potential increase in demand for sewerage services to cater for the increasing population in urban areas such as Nyeri and other towns in Kenya. Therefore, there is a possible potential pressure on the existing plant capacity to handle wastewater influent, which may hinder effective wastewater treatment and efficiency of the plant in pollutants removal. Consequently, the effluent generated and discharged into Chania River may provide an indication of the KSTW treatment efficiency, which in turn could have an adverse effect the water quality of CR particularly if the treatment is not highly efficient. This study carried out a three-month monitoring of KSTW in nutrient and organic matter removal efficiency of KSTW to understand its performance in the removal of pollutants in the effluents discharged into Chania River. Thus, provide information on the performance of KSTW that will contribute to informed decision making in the management of the plant and prevent pollution of water resources of Chania River.

1.3 Objectives
1.3.1 General Objective
The general objective of the study was to determine efficiency of Kangemi Sewage Treatment Works and impact of the effluent on water quality of Chania River, Nyeri.

1.3.2 Specific Objectives
1. To determine spatial variability of selected physico-chemical parameters within KSTW and at selected sites before and after effluent discharge along Chania River.
2. To compare the removal efficiency of N, P and organic matter at different treatment stages within Kangemi Sewage Treatment Works.
3. To determine the loading rates of N, P and organic matter in Kangemi Sewage Treatment Works’ (KSTW) effluent discharged into Chania River from KSTW.
1.4 Hypotheses

1. There are no significant spatial variations in physico-chemical variables within KSTW and at selected sites before and after effluent discharge along Chania River.
2. There are no significant differences in the removal of N, P and organic matter at different treatment stages within Kangemi Sewage Treatment Works.
3. There are no significant differences in loading of N, P and organic matter at the Kangemi Sewage Treatment Works and Chania River from KSTW

1.5 Justification

Recently, most urban centers in Kenya have seen an increase in human population, industrialization, intensive agricultural practices and urbanization. These anthropogenic activities have led to increase in the amounts of wastewater or partially treated sewage entering both WTP and effluent getting into receiving river systems. This has affected the receiving rivers in terms of water quality and capacity to handle increased organic content. Currently, KSTW only determines water quality parameters that include pH, total dissolved solids (TDS), BOD and Chemical Oxygen Demand (COD). In addition, only two stations are sampled within the plant and one point along the river (50m after effluent) twice per month. Nutrient concentration in KSTW are never measured, despite the impact they would have on river water quality such as eutrophication and hypoxia. Therefore, input and output of nutrients in this system and their consequent impact on water quality of Chania River is not known. Therefore, this study determined the nutrients concentrations and loadings from the KSTW to Chania River and increased the sampling frequency and stations to ascertain the nutrient and organic matter removal efficiency of KSTW. This identified additional wastewater treatment quality assessment indicators for the plant. In addition, the study emphasized the need to identify variability in other physico-chemical water quality parameters (TSS, DO, discharge and electrical conductivity (EC), since these parameters help in understanding nutrient and organic matter dynamics both in KSTW and CR.

This study focused on sampling points within the plant, above and below the effluent discharge point in CR to assess the impact of the effluent discharge on water quality of CR as opposed to its status before the effluent discharge. Hence, understand the contribution of KSTW effluent to the physical and chemistry characteristics of CR. Chania River is used for diverse purposes downstream by the people for domestic and agricultural uses, hence, the need to evaluate the
loading of the effluent discharged into it. Determination of loading of effluent is useful in the prediction of pollutants accumulation or loss in the river over time thus helping in the mitigation and control measures. Pollutant loading exceeding rivers self-purification capacity will impair water quality and eco-biological function of CR. Therefore, findings obtained in this study are useful to NYEWASCO in establishing the efficiency of KSTW in nutrient and organic matter removal. It will also guide the company in conformity with nutrient and organic matter discharge standards from KSTW as set by NEMA (2016) in Kenya. The findings of the study will also provide an opportunity to identify management strategies for KSTW in improving its overall performance in removal of pollutants intended. The results of the research will serve as a baseline and reference to further research in assessing the efficiency of WTPs and in management and conservation water quality of effluent of CR and other rivers in Kenya.
CHAPTER TWO
LITERATURE REVIEW

2.1 Wastewater Treatment Processes in a Conventional Sewage Treatment Plant

The general process of wastewater treatment is divided into three ‘basic’ stages: preliminary (physical), primary (physical) and secondary (biological) treatment as shown in figure 1. When effluents from secondary treatment require further processing to meet regulatory standards, a tertiary treatment, is employed such as maturation ponds, ozonation, filtration and activated sludge or use of plants as biofilters in constructed wetlands.

Figure 1: Schematic Diagram of a Conventional Wastewater Treatment Plant (WEF, 2011)

Wetland systems with vegetation, the removal rate of TN is higher than non-vegetated systems (Taylor, 2005; Taylor, 2006). A study by (Njuguna et al., 2017) in Athi River (fourteen falls), Kenya showed that, *E. crassipes*, can assimilate NO₃. The findings recorded 104 μg/L-NO₃, in the rainy season, compared to an upstream of the river, which had 2382 μg/L without *E. crassipes*. This would be explained by the presence and role of the macrophytes in nitrate removal. In most eutrophic ecosystems, P is often the limiting factor. Fresh water P concentration above 0.02 mL/L accelerates eutrophication (Sharpley et al., 2003). Thus, wastewater should receive primary (physical removal/settling) and secondary (biological) treatment, before being discharge into the recipient waterbodies.
2.1.1 Preliminary Treatment of Sewage
At the preliminary stage coarse solids and other large materials such as sticks, and plastic bottles are removed from the wastewater. Preliminary stage usually involves course screening of large materials and removal of grit to prevent them from entering the next treatment stage (Aganga et al., 2005).

2.1.2 Primary Treatment of Sewage
Primary wastewater treatment comprises the second stage of treatment where suspended solids and grease are removed. The lighter particles such as fats and grease rise to the surface of the tank as scum. At the primary stage, removal of suspended matter is by gravity settling or sedimentation. Sedimentation takes place when heavier suspended particles settle down at the bottom of the primary sedimentation tank (USEPA, 2004). In scenarios where fine suspended matter in the wastewater column and dissolved forms cannot be removed by gravity sedimentation, because the finer particles are so small and light thus alum for coagulation/flocculation is used to enhance clumping together of fine suspended matter (Spellman, 2014). The sludge that accumulates in the bottom is removed for drying or other uses as required. This is important as reported by Australian Defence Force-ADF (2009) where removal of suspended solids ranges from 50-65% resulting to 30-40 per cent reduction of the five-day biochemical oxygen demand during the primary treatment.

2.1.3 Secondary Treatment of Sewage
Secondary treatment involves a biological process that removes biodegradable organic matter through microbial action that consumes dissolved substances and suspended matter producing carbon dioxide and other byproducts (Epstein, 2003; Dominica et al., 2009). This occurs in the secondary sedimentation tank. The microorganisms use the organic matter as their ‘food’ thus removes most of it from the wastewater (USEPA, 2004). Wastewater enters a sedimentation tank, where the flow rate gradually slows down, enabling the wastewater to sit in these settling tanks which have been designed to hold the wastewater for several hours. During this time, most of the heavy solids fall to the bottom of the tank forming primary sludge further reducing the suspended solid content of the wastewater. The remaining suspended solids decompose resulting to greatly reduction of the microbial load.

A variety of secondary treatment options are available that are categorized into; wastewater stabilization ponds, suspended growth systems or fixed film systems. In these processes, organic matter removal of approximately 90% is obtained (IEPA, 1997). Wastewater stabilization ponds
may be constructed either singularly or in parallel with the number of ponds increasing as the volume of waste being processed by the plant increases. These ponds are classified by the type of bacteria responsible for the decomposition process as well as the duration for which the waste will remain in the pond (Mara, 2004). Suspended growth systems are generally applied to smaller communities and consist of three main types: activated sludge, sequential batch reactor and aerated lagoons whilst fixed film systems involve the passage of raw wastewater onto a filter medium in which bacteria can attach, build up and accumulate in biomass which is subsequently removed (USEPA, 2017).

2.1.4 Tertiary (Advanced) Treatment

After secondary wastewater treatment, some dissolved and suspended substances may remain in effluents, thus the need to apply tertiary treatment prior to disposal into the recipient waterbody. In tertiary treatment, physical, chemical or biological treatment processes such as gravity settling, chemical precipitation and algal uptake are employed for further removal of pollutants (Environment Canada, 2001). Other processes like filtration or sand filters, de-ammonification through conversion of ammonia to nitrogen gas. De-ammonification is a two-step process that involves aerobic (nitrification) and anaerobic (denitrification) processes. Technically, organic-nitrogen is not converted directly to nitrate (NO₃); it must first be converted to ammonia (NH₄-N), and the ammonia (NH₄) converted to nitrite (NO₂) and then to nitrate (NO₃) by bacterial process. The nitrate is then converted to nitrogen gas in anaerobic conditions and released to the atmosphere (Hijnen et al., 2006).

In tertiary treatment, processes, such as the use of activated carbon, oxidation, ozonation, separation of impurities and demineralization using reverse osmosis or distillation are applied. According to Renuka et al. (2013); Liu and Vyverman (2015), during biological wastewater treatment in maturation ponds, microalgae are able to assimilate both inorganic N and P to low concentrations. Similarly, bacteria can remove nitrogen through assimilation and anaerobic ammonia oxidation (Annamox) (Yao et al., 2013; Fitzgerald et al., 2015). For instance, aerobic denitrifying bacteria enhance high N removal in aerobic conditions (Zhang et al., 2012; Guo et al., 2013). Other key Inorganic-N removal mechanisms include nitrification and denitrification (Daims et al., 2015). When the N/P ratio is low, nitrogen removing algae dominate in wastewater (Liu and Vyverman, 2015).
In tertiary stage of treatment, phosphorus is converted into particulate then removed by sedimentation, filtration, or some other solids removal process. Removal of the chemical or biological bound solid-phase phosphorus is critical in meeting effluent standards (Von Sperling, 2014). Additionally, phosphates can be precipitated at higher pH to form hydroxyapatite with magnesium and calcium ions (Lu et al., 2016). Hydrolysis of organic phosphorus can occur through enzymatic catalysis process which is further removed as inorganic form (Zhu et al., 2016). On the other hand, high abundance of microalgae significantly lower the nutrient availability and increase DO levels (Renuka et al., 2013).

Use of constructed wetlands and other aquatic systems macrophytes have played an important role, where they have been used in the removal and transformation of nutrients in the water column and sediments (Tangahu et al., 2011). Macrophytes leaves and root system can take up nutrients and hence remove it from the wastewater (Wang et al., 2014). For example, Canna indica has reportedly been used in TN removal (Cui et al., 2005). Eichhornia crassipes was found to efficiently remove NO$_3$ and heavy metals from contaminated water and soil (Sood et al., 2012; Subhashini and Swamy, 2014). Macrophytes have the capacity to take up nutrients like ammonia and nitrate and converting inorganic to organic nitrogen forms as building blocks for their tissues (Vymazal, 1995). Ammonium-N uptake is preferred by those macrophytes in limited nitrification environments where NH$_4$ is abundant (Garnett, et al., 2001). Ideal candidate plants that are desirable for nutrient assimilation in constructed wetlands must have fast growth, high nutrient tissue storage and ability to maintain a high-standing crop (Vymazal, 2002). The type of macrophytes in a constructed wetland has stronger influence on nitrogen removal than organic matter (Acratos et al., 2007). Common macrophytes used in constructed wetlands are reed, cattail and bulrush (Kadlec et al., 2000).

2.2 Sources and Types of Wastewater Pollution

Surface water pollutants can either be from point or non-point sources (Chinedu et al., 2011). Point sources discharge effluents such as wastewater through pipes, ditches and sewers into water bodies at specific locations. Some of the pollutants into rivers include industrial effluents that discharge chemicals, acid wastes and hot water into receiving water bodies. Raw sewage from domestic and business premises entering dysfunctional sewerage treatment plants can be a significant source of pollutant into receiving waters. Others are solid waste, organic matter and
inorganic waste from farmlands that find their way into rivers through surface runoff (Otieno, 1995). A report by NEMA (2004) indicates that, of the municipal waste generated in the urban centers in Kenya, 21% is from industrial sources and 61% from residential areas.

Wastewater can mainly be classified into domestic, industrial, agricultural and urban. Urban wastewater is defined as a combination of domestic and industrial wastewater and urban storm flow runoff. Whereas, agricultural wastewater consists of wastewater generated through agricultural activities such fertilizer and livestock (Hamdy et al., 2005). Agricultural wastewater is becoming important as source of water pollution; however, main focus is on domestic and industrial wastewater source which contribute to surface water eutrophication (DWA, 2011). Domestic wastewater contains food remains, fecal matter and black water derived from household activities e.g washing and bathing (TEPA, 2018).

In the developing world, sewage and animal wastes are important causes of anthropogenic pollution (Van der Struijk and Kroeze 2010). Nutrients (N and P) increase is a major problem in rivers, where nutrient increase is directly proportional to population increase and sewage inputs (Suwarno et al., 2014). A high population growth, industrialization and intensive agriculture in urban and peri-urban areas, have contributed to increased pollution of surface waters. These human activities have led to discharge of raw and improperly treated sewage, organic loads and wastewater into rivers and streams leading to deterioration of their water quality. According to Mwanzia and Kariuki (2003), it is projected that by 2020 more than half of African population, (Kenya included) will be living in urban areas. In addition, 0.2-0.5% of these urban dwellers will not have access to adequate water and sanitation services. This will translate to increased pressure on existing water resources and sewerage facilities.

2.3 Rivers as Receptacles for Sewage Disposal

In literature, studies on wastewater treatment plants (WTPs) have mainly focused on efficient resource use and technological function. Nevertheless, fewer studies have paid adequate attention to effectiveness of WTPs in controlling pollution of rivers (Katsoyiannis et al., 2004). Rapid urbanization and industrialization, has resulted to catastrophic use of rivers as sewage portals especially in the developing countries (Su et al., 2011). Increased input of raw and partially treated wastewater in rivers is a major threat to human health and the ecosystems (Pimpunchat et al.,
It is estimated that, over 80 percent of the sewage in developing countries is discharged untreated or partially untreated in receiving water bodies mainly rivers (UNWWAP, 2018). Pollution of rivers with organic waste from sewage effluent is one of the major global sanitation untreated sewage risks consequently, a variety of diseases and deaths when people consume water directly from rivers that receive raw or inadequately treated sewage. According to UNICEF and WHO (2019) it was estimated that as of 2017, nearly 4.5 billion people globally lacked safely managed sanitation.

Discharge of excess load of untreated sewage into rivers is detrimental to the health and integrity of the receiving waters. This is true especially when the river in question cannot handle the effluent volume being discharged into it. Every river has its maximum threshold to which they can receive sewage and other organic wastes. Research by Phiri et al. (2005) demonstrated that, most of the water bodies like lakes and rivers in developing countries end up as receivers of effluents discharged from industries and treatment plants, which significantly contribute to water pollution.

Excessive nutrient loading can lead to eutrophication and temporary oxygen deficiencies that ultimately alter ecological balance of biotic-abiotic relationship. Disruption of community structure and function usually occurs. Turbid effluent discharge can also result in the accumulation of organic debris in aquatic system, disrupting sediment characteristics and hindering natural water flows (Wakelin, 2008).

The physical detriments of the recipient waterbody include the foul odours of organic matter decomposition, solids and turbidity caused by dissolved and suspended matter. Chemical detriments consist of oxygen depletion in water, which is caused by high BOD through decaying of organic matter. An overload of organic and inorganic effluents from sewage plants into a river may overwhelm the innate biodegradation ability to handle high organic discharge (ADF, 2009). Thus, accumulation of organic pollutants in rivers is a threat to entire river ecosystem through oxygen depletion caused by high growth of bacteria in rivers (Sirota et al., 2013). For example, the water discharge of Nairobi River streams, which is about 23.6 m$^3$ s$^{-1}$ (36.7 X 10$^{6}$) m$^3$ yr$^{-1}$, is lower than the discharge of wastewater from both industrial and domestic effluents of the city of Nairobi (Kithiiia, 2012). This gives clear picture of how excess sewage discharge can be a potential enhancement factor to river quality degradation and thus any management approaches of the
wastewater treatment systems should adhere to ensuring to counter balance this effect. In a study of Nairobi River at Riara point a high BOD (24 mg/L) was recorded, which was attributed to domestic effluent and organic waste discharge. These results contrasted those of Lenana dam section of Nairobi River which had a BOD\textsubscript{5} of 17mg/L. However, the above sites concentrations were below NEMA (30mg/L) standards for both dry and wet seasons (Mbui \textit{et al.}, 2016).

\textbf{2.4 Self-Purification Potential of Rivers and Streams}

Rivers and streams have self-purification properties through degradation of organic matter by microorganisms in natural waters. It simply encompasses all processes that reinstate the polluted water body to close to its original status (Ellis \textit{et al.}, 1989). Self purification in rivers applies the same principle as in WTPs. Organic matter is degraded through microbial decomposition in the river to dissolved and mineral bound elements with consequent reduction in organic matter content in water (Brettar and Rheinheimer, 1991).

Research has shown that despite nutrient concentrations being greater near WTP effluent points, they decline with distance away from the discharge points (Murdock, \textit{et al.}, 2004). For instance, in Arkansas’ third order stream that received effluent from a WTP, it was found that SRP concentrations (9.9mg/L) were up to 50 times higher downstream immediately after the discharge point of the effluent of the plant. However, the concentrations declined (6 mg/L) further downstream of the discharge point (Haggard \textit{et al.}, 2005), although, the concentration was 30 times greater than the upstream reference site (0.06-0.17 mg/L). It is possible that downstream reaches of rivers after effluent discharge maintain high nutrient concentrations, even with in-stream mixing, dilution and denitrification processes. For instance, when there is very high effluent discharge from point source and the base flow is low in the river. In many studies along Nairobi River by (Kithiia, 2006; Okoth and Otieno, 2000; Mavuti, 2003) have shown that, there is a downstream trend of increase in water pollutant (sediments, nutrients and heavy metals) and degradation in water quality. This is the case especially due to increased human activities and land use changes downstream around the catchment. For instance, Kithiia, (2012) reported increase in TSS (255 mg/L), 564 µs/cm and TDS (290.9 mg/L) at a site in Outering and Mathare area of Nairobi River which were higher than most other sites in the study. In Sabaki River in Kenya, high nutrient concentration was attributed to agricultural activities upstream and sewage input into Athi River upstream (Ongore \textit{et al.}, 2013). The effect of pollution on water resources results to poor
water quality which is costly to treat, to suitable quality for use based on the regulatory specifications (UNWWAP, 2017).

2.5 Parameters Affecting Wastewater and River Water Nutrient Dynamics

Some of the physico-chemical variables which include temperature DO, pH, TSS, conductivity and nutrients are used in water quality monitoring. These parameters affect the existence and transformations of chemical and biological reactions in wastewater and surface waters. Their effects are discussed in details below.

2.5.1 Effect of Temperature on Wastewater and Surface Water (Rivers)

Temperature is a basic determinant factor for some wastewater properties (Khuzali et al., 2012). The temperature of wastewater whether from domestic or industrial sources is usually higher than the temperature of the receiving water due to additional impurities in wastewater that increase chemical reactions (USEPA, 2012). However, high wastewater temperature is significant for biodegradation of the organic matter and other biochemical reactions that are temperature dependent. Essentially, in the biological treatment of wastewater, microbial and chemical reactions increase with increase in temperature, a phenomenon which improves WTP system efficiency (Water Planet Company, n.d). For example, aerobic digestion of organic matter and nitrification processes halt beyond 50°C and at the same time, there is a notable sharp slowdown in nitrification when temperature falls below 2°C (Droste, 1997). Other processes such as BOD degradation and microbial processes are equally influenced by temperature changes in water.

Imoobe and Koye (2010), suggested that effluent from WTP discharge would influence the temperature of the receiving waters. When water with higher temperature is discharged in large quantities, it raises the temperature of receiving streams, which influences and disturbs ecological and biological functions; such as surge in metabolic activity and increase in DO demand for aquatic organisms. In addition, increase in temperature has been reported to increase toxicity of substances and their effects to organisms (DWAF, 1996). Ahipathy and Puttaiah, (2006) reported that temperature changes in polluted water systems have a significant effect on DO and BOD of water hence, affecting biochemical reactions of receiving waters. DO concentration levels of rivers/streams can be reduced with increased temperature due to entry of industrial chemical discharge, inhibiting nitrification and organic matter degradation by microbes (Smith et al., 2000). Eventually, reduced dissolved oxygen levels in wastewater will affect the microbial degradation
of organic matter because DO is needed by microbes as electron acceptor for decomposition. Hence, low DO conditions reduce microbial degradation activity and nutrient release, affecting wastewater treatment efficiency.

2.5.2 pH Effects on Biochemical Reaction in Wastewater Treatment

Generally, the wastewater bicarbonate buffer capacity prevents acidity and reduces the pH while, the carbon dioxide produced by microbial activity in wastewater controls high alkalinity levels in sewage (Hartley, 2013). The pH of most surface waters range between is 4 to 11, but well buffered freshwater systems may be between 6 to 8 (DWAF, 1996). Metabolic activities of aquatic organisms are dependent on pH whose variations affect their physiology (Wang et al., 2002). Thus, the optimal pH range for sustainable aquatic life ranges between 6.5 and 8.2 (Murdoch et al., 2001).

It has also been observed that the solubility of many toxic and nutritive chemicals is affected by water pH. For example, at pH 9 and above phosphorus can be precipitated to metal phosphates and ammonia is converted to ammonia gas; therefore, reducing the availability of these substances to aquatic organisms (Mosley et al., 2004). A high pH enhances the precipitation of P with metal ions and influence the algal growth rate and species composition in wastewater systems.

In sewage treatment algae can be utilized for tertiary wastewater treatment due to its potential to assimilate nitrogen and phosphorus for their metabolism (Travieso, 2004). pH range of 7.5-8.5 has been reported to be suitable for several species of algae such as *Chlorella sp.* for treatment of wastewater (Chisti, 2008), although, other species like duckweed have been reported to grow in higher pH conditions (Ogbonna et al., 2000).

2.5.3 Effects of Dissolved Oxygen in WTP Effluents to Receiving Waters

When the waste water or the effluent is discharged into a natural stream, the organic matter is broken down by bacteria to products such as ammonia, nitrates, sulphates and carbon dioxide. In this process of oxidation, the dissolved oxygen content of natural water is utilized. Due to this, deficiency of dissolved oxygen is created, resulting to production of gases like hydrogen sulphide (H$_2$S) (Walakira, 2011). DO decrease in rivers receiving sewage effluents has been linked to discharge of oxygen demanding wastes into rivers from both point and non-point sources (Dulo, 2008). The effect of DO depletion caused by organic waste accumulation in rivers and streams has
shown a proportional increase in decomposers like anaerobic bacteria and fungi. Bacteria and other microorganisms such as protozoa and fungi degrade organic matter by using atmospheric oxygen diffusing inside the spaces within the trickling filter media (USEPA, 2004).

In sewage systems that use facultative ponds, rate of organic matter degradation depends on additional oxygen produced by photosynthetic algae. The oxygen produced in the ponds is used as an oxidizing agent by bacteria to degrade organic matter releasing nutrients and gases such as methane and hydrogen sulphide and consequently reduce organic load in the wastewater (USEPA, 2002). Therefore, reduction in DO in secondary treatment processes limit effective removal of organic matter in sewage thus affecting the efficiency of WTP. The effluent from such a plant in turn affects the receiving rivers by adding partially treated wastewater with high BOD.

Dissolved Oxygen concentrations in both wastewater and rivers fluctuate with time in natural conditions depending on rates of turbulence and biochemical processes like photosynthesis and respiration (Dallas and Day, 2004). Therefore, the amount of oxygen available in the system will influence the rate of organic matter degradation through microbial processes. Thus, the higher the amount of oxygen available in the systems the higher the rate of OM degradation.

**2.5.4 BOD Classification and Biodegradation Processes in Wastewater**

Biological Oxygen Demand (BOD) is one of the major parameters used in determining organic content in wastewater (Grismer and Shephard, 2011). BOD is usually expressed in mg/L or parts per million for a given time and temperature. The BOD$_5$ of water, refers to the amount of DO needed by aerobic bacteria to oxidize organic matter in a sample after 5 days of incubation at 20°C in the dark (Vaishali and Punita, 2010). The BOD$_5$ is usually the commonly used standard of measuring BOD, but other alternatives such as BOD$_3$ and BOD$_7$ have been reported in literature.

BOD is removed in WTP by anaerobic processes in the sedimentation tanks and through aerobic oxidation of organic matter at the trickling filters (Naidoo and Olaniran, 2014). The organic matter is degraded by microbial processes in the water column whereby bacteria utilize the BOD as carbon and energy sources (Koottatep et al., 1999) resulting to production of nutrients compounds and gases such as methane and acids (ethanol). Increase in temperature up to its optimum, increases the rate of BOD removal. Also, the source of wastewater whether industrial, domestic or agricultural is a crucial factor as it will influence the removal rate of BOD.
The BOD₅ of water as an example, refers to the amount of DO needed by aerobic bacteria to oxidize organic matter in a sample within 5 days of incubation at 20°C in the dark (Vaishali and Punita, 2010). The BOD₅ is the standard measure of analysis used, but other alternatives are BOD₃ used when there is need for quick analysis. While BOD₇ is used for convenience; however, if almost all BOD measure is needed BOD₂₅ is used for analysis. At 20°C, only two-thirds of the totals BOD₅ for domestic sewage is achieved, with almost the entire BOD in 20-25 days at the same temperature of 20°C (Kaur et al., 2014). In untreated sewage BOD₅ has a range of about 100 to 300mg/L, and treated sewage should have a BOD₅ not exceeding 20 mg/L (WEF, 2010; Mara 2004). In Kenya, the maximum allowable BOD discharge into rivers is 30mg/L (NEMA, 2006).

In a research conducted by Wang et al. (2011), it was noted that Dandora WTP in Nairobi had BOD₅ levels of up to 1500 mg/L, which was about 70% final effluent removal efficiency. The BOD₅ discharge value was way above the WHO, EU and EMCA (2015) discharge standards of below 30mg/L. It’s important to note that, a higher BOD removal reflects a higher system efficiency, although removal of BOD will depend on the load and influent concentrations. Direct discharge of inadequately treated effluents into receiving waters of rivers leads to a high BOD due to increase in oxygen demanding pollutants in the effluent from point and non-point sources entering the river. Increased BOD is as a result of increased microbial activity (degradation and mineralization) due to increased concentration of assimilable organic matter. This in turn results to high oxygen demand for the microbes to degrade the organic matter further consequently depleting DO available for respiration by aquatic organisms (Imoobe and Koye, 2010).

A study conducted at Nairobi River reported a steady increase in BOD with increase of effluent discharge and organic waste content into the stream (Dulo, 2008). He reported a BOD increase sharply just below the point of discharge by Kariobangi Sewer Treatment Plant. Low BOD in water reduces the rate of DO consumption and depletion. Therefore, an indication that, water or wastewater with high BOD is discharged, which can deplete DO in receiving rivers leading to slowing down and eventually halting of biochemical reactions, hence slow nutrient cycling. Thus, a high BOD removal in wastewater treatment is a good system indicator and low BOD in rivers reflect good water quality.
2.5.5 Total Suspended Solids as Pollutant in River Systems

Total Suspended Solids (TSS), are solids in water that can be trapped by a filter. TSS comprises of a wide variety of material, such as silt, decaying plant and animal matter, industrial wastes and sewage. The unit for TSS is given as mg/L (APHA, 2005). Domestic wastewater usually has large amount of suspended solids, from both organic and inorganic in nature (Davies and Day, 1998). The cloudiness colour of untreated sewage is caused by suspended particles which can range from 100 to 350 mg/l and <30 mg/l) for treated effluents. The maximum allowable TSS discharge into surface water in Kenya is 30mg/L (NEMA, 2006, amended 2016).

In natural water bodies, excessive TSS loading can increase suspended solids therefore affecting stream ecology and processes like photosynthesis, by blocking light penetration. Reduced photosynthetic rate may result in low oxygen production in water. Low oxygen may limit organic matter biodegradation hence lowering nutrient cycling and other biological processes like decomposition and respiration (Paul and Bjourn, 1998).

Dulo (2008) recorded suspended solids varying from 4mg/l to of 320mg/l in Nairobi River. The observed surge in TSS increased in areas where there were input and deposition of organic matter and surface runoff along the river course. This was especially evident in the areas with high human activities such as car washing, ‘jua kali” technicians, commercial and industrial activities which includes Kariakor Bridge, Globe cinema, Gikomba market, Kibera and Industrial Area. The average suspended solid obtained in this study was 116.43 mg/l, which is higher than the 30mg/l set for Kenyan waters (Table 1), indicating a massive pollution entering the watercourse. It was observed in the same study that turbidity decreased as streams approached the CBD and a sharp surge, further downstream, at the discharge point of the Kariobangi Treatment plant. This is a good indication of inefficiency of the WTP consequently discharging high load of OM in in the natural system. Thus, TSS can be used efficiently as a good indicator to determine the efficiency of any WTP.

2.6 Nutrient Forms and Transformation in Wastewater and Rivers

In earlier years, water quality assessment studies in lotic systems was focused on Carbon enrichment from untreated sewage but current concerns on stream eutrophication, the focus has shifted mainly on N and P enrichment (Moore, 2003). Nutrients in water are in both inorganic and organic form, which are transformed from one form to another based on the physico-chemical and
biological status of the water. Nitrogen and phosphorus are the major nutrients that are found in water (Naidoo and Olaniran 2014). Nitrogen exists in various forms in water but the principal variants of nitrogen in wastewater include total and organic nitrogen, ammonia, nitrate, nitrite and TN which refers to the summation of the various components of nitrogen). Total Nitrogen concentration recorded in untreated municipal wastewaters ranges from 15 to 50mg/L (Reed and Brown, 1995). Phosphorus exists as orthophosphate (SRP) and total phosphorus (TP) in wastewater.

2.6.1 Nitrogen Forms and Their Biochemical Processes

Input of excess nitrates in water can cause hypoxia and dead zones, which can be toxic at higher concentrations (10 mg/L) (APHA, 2005). Excess input of nitrates in water cause algal blooms. Thus, nitrate is one of the components used in monitoring water quality in rivers and lakes (eutrophication) as an indicator of high nutrient enrichment in surface waters. Nitrates, sources in surface waters originate from surface runoff from diffuse sources such as agricultural catchments using nitrate fertilizer, WTPs and industries. Further, nitrates result from the nitrification process in the system through oxidation of nitrogen atom (Wolfgang et al., 2002).

Nitrates are used as oxidizing agents in the anaerobic ponds of a WTP as they are converted to ammonia and free nitrogen during organic matter decomposition. Nitrite is another N form that is easily converted to nitrate thus rarely available in water. The USEPA has set maximum levels of 1 mg/L for nitrite-nitrogen in water (Sawyer et al., 2003). For instance, Githuku (2009) analyzed the quality of wastewater effluent to Nairobi River and found high levels of nitrates (100 mg/L) which is beyond the acceptable standards (Table 1). This clearly shows an inefficient sewage treatment system. Decomposition of the organic matter lowers the dissolved oxygen level, which in turn slows the rate at which ammonia is oxidized to nitrite (NO₂) and then to nitrate (NO₃) through biological nitrification (Bozek, Navratil and Kellner, 2005).

Nitrification process is influenced by various factors that include DO concentrations, temperature, alkalinity and nitrifying bacterial numbers (USEPA, 2000). Bacterial nitrification in wastewater can be triggered by DO concentration above the range of 0.6-1.0 mg/L (Tchobanoglous et al., 1991) and inhibited when levels fall below 0.5 mg/L (Tchobanoglous et al., 2003). Temperature variation influences nitrification process. For example, the rate of nitrification is very slow at
temperatures below 10°C (Koottatep, 1999). Thus, if temperature of wastewater is below 20°C, nitrification process progresses at a slower rate. *Nitrosomonas* and *Nitrobacter* bacteria are actively involved in the nitrification process during wastewater treatment (Tchobanoglous *et al.*, 2003). Ammonium is nitrified to nitrite (NO$_2^-$) by the bacterium *Nitrosomonas* and then to NO$_3^-$ by *Nitrobacter*. The overall nitrification reaction is:

\[ \text{NH}_4^+ + 2\text{O}_2 \rightarrow \text{NO}_3^- + 2\text{H}^+ + \text{H}_2\text{O} \]

The NO$_3^-$ produced in the nitrification process, as well as a portion of the NH$_4^+$ produced from ammonification, can be assimilated by organisms to produce cell protein and other nitrogen-containing compounds. The NO$_3^-$ may also be denitrified to form NO$_2^-$ and then nitrogen gas. Several species of bacteria may be involved in the denitrification process, including *Pseudomonas*, *Micrococcus*, *Achromobacter*, and Bacillus. The overall denitrification reaction is

\[ 6\text{NO}_3^- + 5\text{CH}_3\text{OH} \rightarrow 3\text{N}_2 + 5\text{CO}_2 + 7\text{H}_2\text{O} + 6\text{OH}^- \]

Nitrogen gas may be fixed by certain species of cyanobacteria when nitrogen is limited. Nitrification favors acid production such as methanoic acid from microbial processes thus lowering the pH of the wastewater. The lowering of pH favours a decrease in alkalinity, which is buffered by liming from the wastewater. Alkalinity of at least 60 mg/L in the aeration tank or trickling filter of a WTP is required for proper buffering (Spellman, 2014).

Ammonia is another important nutrient in both freshwater and wastewater. In wastewater ammonification is a process that occurs when organic-nitrogen is converted to ammonium-nitrogen (NH$_4^+$) by microbial degradation of organic nitrogen compounds. Then, ammonia part is converted to (NO$_3^-$) by an aerobic biological process through nitrification. Finally, (NO$_3^-$) is converted to nitrogen gas biologically through bacterial processes. In low-oxygen conditions the process of denitrification and nitrate respiration takes place as shown in the general nitrification and denitrification equations above (WSDH, 2005). Denitrification is an anoxic process accomplished in the absence of dissolved oxygen such that the microorganisms utilizes nitrate as their electron acceptor in oxidation. Nitrogen is found in wastewater in the form of urea (Tchobanoglous *et al.*, 2003). During wastewater treatment, the urea is transformed into ammonia nitrogen. Because ammonia exerts a BOD and chlorine demand, high quantities of ammonia in wastewater effluents are undesirable. The process of nitrification is utilized to convert ammonia to nitrate (UNWWAP, 2017).
2.6.2 Phosphorus Forms and their Biochemical Processes

Sewage from domestic sources especially in urban setup has been found to be the major source and producer of P into the environment. This is usually because of the use of P-based detergents, both in domestic and industrial purposes. In rural areas sources of P might be due to human and animal in-stream activities and agriculture where phosphorus containing fertilizer is used (Crites et al., 2006). Phosphorus exists in various forms in wastewater; it may occur as soluble orthophosphate, organically bound phosphorus and other P compounds. The organic P forms originate from faecal, organic plant materials and food remains among other natural and anthropogenic sources. In general, phosphorus ranges from 6 to 20 mg/l in untreated wastewater (Gray, 2002). To lower the solubility of the metal phosphates, liming technique is used in tertiary stage to increase the pH of wastewater and hence lowering the solubility of metal phosphates to form calcium phosphate precipitate (Morse et al., 1998). Also, high pH conditions caused by increased oxygen and reduced carbon dioxide in sewage treatment lagoons can remove up to 50% of P through precipitation, whereas organic phosphate is assimilated as algal biomass.

2.7 Water Pollution as Environmental Hazard

Inadequately treated sewage is potentially harmful to the environment. According to NWQMS, (2012), there is a necessity after several decades for sewerage systems and WTP to be rehabilitated and expanded in order to protect water resources. Collaro (2015), quoted by the Millennium Ecosystem Assessment (M.E.A, 2005), suggested that if sources of wastewater aren’t properly managed, they can be sources of pollution in water systems hence, hazardous to human health and environment. The M.E.A report further showed that 60% of global ecosystem services are being degraded and this has a close connection to ecosystem integrity and human health. Water pollution not only reduces available freshwater, but also affects human health and ecosystem functioning at large (Montgomery, 2007).

Inadequate wastewater treatment can negatively affect human health through contaminated drinking water especially in urban areas (Feliciano et al., 2009). Drinking water with sewage contamination can carry pathogens that cause ailments like cholera, diarrhea and dysentery that are potentially life-threatening ailments (Davis, 2011). The level of impact of these illnesses depend on exposure time and level of contaminants in the drinking water sources that has been contaminated with polluted water or raw sewage (Salifu, 1997).
2.8 Nutrient Loading and their Impact in Lotic Systems

Several studies have shown that surface water have low nutrient concentrations compared to raw sewage (Dunne et al., 2013; Liu et al., 2016). For example, in rivers TN is usually about <10 mg/L and TP at <1.0 mg/L (USEPA, 2007). However, the said concentrations should be minimized to prevent eutrophication, hence maintain surface water quality (Hernández-Crespo et al., 2017). The volume of effluent from WTPs discharged into the receiving rivers is crucial for it can easily dominate the stream thus providing a continuous nutrient source. Notably, even effluents with low nutrient concentrations can deliver high nutrient loads depending on the total volume discharged into the stream from WTPs against the river discharge. The total river discharge received downstream after effluent will therefore; control the nutrient dynamics and fluxes within the river (Lewis et al., 2007). The nutrient fluxes effect may be prominent during low river flows when the river/effluent discharge ratio is high (Passell et al., 2005). According to Marti et al. (2004), streams in populated areas have enormous dissolved solutes that include N and P.

Similarly, significant nutrient loads are contributed by receiving waters from municipal and industrial WTPs point sources (Migliaccio et al., 2007). For instance, it is reported that, 50% of nutrient inputs in the urban United States streams and rivers come from point sources (Carpenter et al., 1998). Hence, these urban point sources are significant in the water quality and eutrophication status of such rivers. Eutrophication of water bodies occurs when excess nutrient enrichment results to algal blooms in surface waters particularly of large rivers. This in turn affects the water quality status of such waters causing odours, high turbidity and oxygen depletion (Carpenter et al., 1998). Nutrients known to have critical contribution to eutrophication are N and P, which find their way to aquatic system often from human activities (Vymazal, 1995; Murdoch et al., 2001).

Several scientific studies (Carey et al., 2007; Ohte et al., 2007) have suggested that lotic systems are affected by excess nutrients. For eutrophication to have profound effect on rivers, the nutrients must be bioavailable in water. Nutrients such as nitrates, ammonia are readily bioavailable in water; organic nitrogen may be available by conversion to ammonium nitrogen form. Beside discharge from WTP, organic matter from the catchment brought by surface runoff consists of the bulk of nitrogen entering receiving freshwater systems (Follett, 2001). The effect of pollution on water resources vary from poor water quality which is also costly to treat, to suitable water quality
for use based on the regulatory specifications e.g. EMCA, NEMA and WHO. Other effects of pollution of rivers include eutrophication and deoxygenation of water due to high organic waste input (Kithiia, 2012). In a similar study conducted in Nairobi River (Alukwe, 2015) found that the major polluters of nitrogen into the environment are non-domestic sources from industries and businesses. It was found that annually a load of 45,301 ton/year N is discharged into the freshwaters, including rivers, which was attributed to mostly from agro based industries in Nairobi. However, it was noted that agriculture consists of the major source of N and P pollution of surface water. In the Nairobi River, the wastewater from domestic and agricultural sources contribute about 2mg/L to 15mg/L to streams waste inputs.

For streams that receive high nutrient loads, a deep understanding of factors influencing nutrient dynamics is required for us to improve the status of such systems and achieve our objective of acceptable effluent quality standards (Table 1). For instance, Nyangores tributary of the Mara River in Kenya recorded SRP levels varied between 11.9 ± 1.6 and 65.0 ± 3.0 μg/L. This mainly varied with anthropogenic activities (fertilizers, grazing and domestic waste) in the catchment and seasons (Nyairo et al., 2015). Phosphate pollution is easily characterized by SRP concentrations in streams. If it exceeds 50.0 μg /L, then it leads to eutrophic natural waters (USEPA, 2014). The phosphate levels in Nyangores tributary were significantly different in the sites and season, but within and within acceptable NEMA limits except for the SRP at the confluence along the Nyangores tributary (65.0 ± 3.0 μg/L) of SRP in the dry season (Nyairo et al., 2015). Shivoga et al. (2007) reported that in River Njoro, phosphate levels rose in densely settled areas around Egerton University. a study in River Nile, it was observed that there was increased nutrient concentration in settlement areas (Shehata and Badr, 2010).

Similarly, high concentration of NO$_3$-N has been observed in mixed agricultural catchments, where nitrate concentrations increased with increasing agricultural activities. In River Isiukhu in Western Kenya, Shivoga et al. (2007) observed that application of both organic and inorganic fertilizer in the River catchment increased nutrient load in streams with increased human activities. Shineni and O’Reilly (2007) reported similar findings in tropical streams on the northeast of Lake Tanganyika, where loading of phosphorus into streams was accelerated by use of the watershed by humans, poor recovery of the nutrient from agricultural applications and detergent use. Meanwhile, the catchment within the Kakamega Rainforest recorded lower mean concentrations
of both NO₃-N and PO₄³⁻-P because of reduced human activities (Onyando et al., 2016). Therefore, is a clear indication that anthropogenic activities contribute highly to increased streams nutrient loading and low nutrient in streams in less impacted watershed (Wetzel, 2001).

2.9 Surface Water Quality Status, Legislations and Standards in Kenya

The location of a river in relation to sources of pollutants like wastewater discharge points and onsite sanitation from domestic, industrial and institutions exposes the river to pollution and degradation (Mbuligwe and Kaseva, 2005). River water pollution is a major health risk especially to many people in developing countries of the world who do not have access to treated piped water with many resorting to direct use of rivers for their domestic water supplies (WHO and UNICEF, 2010). In Kenya, freshwater resources are facing a major threat because of pollution from domestic and industrial wastes. A study of Dulo, (2008) in Nairobi River, reported an average of pH 7.04, which was within Kenya (NEMA) and W.H.O Standards (6.5-8.5) for watercourses. The EMCA 1999 (amendment, 2015): NEMA 2006 (amendment, 2016) provides for standards of various parameters and wastes discharged into stream and rivers as by the standard shown in table 1. The Kenya Water Act 2016 also emphasizes on water resources utilization, conservation and management in Kenya.

Table 1: Limits of some physical chemical parameters for Discharge into Surface Water Kenya,

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Discharge standards</th>
<th>Drinking water standards</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium nitrogen</td>
<td>mg/L</td>
<td>&lt;20</td>
<td>0.5</td>
</tr>
<tr>
<td>BOD (5 days at 20 °C) max.</td>
<td>mg/L</td>
<td>&lt;30</td>
<td>Nil</td>
</tr>
<tr>
<td>pH</td>
<td>O₂/L</td>
<td>6.5-8.5</td>
<td>6.5-8.5</td>
</tr>
<tr>
<td>Temperature, maximum</td>
<td>°C</td>
<td>±3 ambient temperature</td>
<td>-</td>
</tr>
<tr>
<td>Total Nitrogen</td>
<td>mg/L</td>
<td>2</td>
<td>-</td>
</tr>
<tr>
<td>Total Phosphorus</td>
<td>mg/L</td>
<td>2</td>
<td>-</td>
</tr>
<tr>
<td>TSS</td>
<td>mg/L</td>
<td>&lt;30</td>
<td>nil</td>
</tr>
<tr>
<td>NH₄⁺, NO₂ and NO₃ compounds</td>
<td>mg/L</td>
<td>&lt;100</td>
<td>-</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>mg/L</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>NO₂⁻</td>
<td>mg/L</td>
<td>3</td>
<td>0.01</td>
</tr>
</tbody>
</table>

However, the river had elevated pH downstream as opposed to upstream reaches, which was attributed to chemical industrial discharge downstream. Also, organic load input from domestic origin sources as it passed the settled areas of the city played a role. For example, according to a recent study (Njuguna et al., 2017) in Nairobi River, mean P concentration was between 1.5 and 2 mg/L, which may be attributed to a high organic matter content in water (Riemersma et al., 2006).

A study by Ombaka et al. (2012) in Naka River, Meru County, obtained ammonia concentration of 0.50 - 4.93 mg/L, and 1.15 to 27.48 mg/L nitrate concentration, which when combined as DIN (nitrate and ammonia compounds) were below the 100mg/L discharge standards for Kenya (Table 1). Although nitrite range varied between 0.00 to 0.78 mg/ L, but the levels were below the Kenya standards of discharge into surface waters especially during the wet season. The P concentration was between 1.56-191.31 mg/L. A high P concentration level is an indicator of pollution. The electrical conductivity was between 0.21 to 12.90 and μS/cm that was below the WHO guideline value prescribed for drinking purposes (1,500 μS/cm).

In a recent study by Kinyua et al., (2016) in Chania River (Nyeri), working on drinking water quality sources in Nyeri recorded mean NH₄⁺, NO₃, TP and orthophosphate concentrations of (0.43-1.05mg/L), (0.31-2.4mg/L), (0.01-1.2 mg/L and (0.004-0.6 mg/L) respectively. For physicochemical variables, temperature ranged from 21.4-22.0°C, pH (6.74-8.6) and conductivity (20.2-133.9 μS/cm). Phosphorus concentrations in Chania River were above the recommended Kenya standards for discharge into surface waters.
CHAPTER THREE
MATERIALS AND METHODS

3.1 Study Area

The study site, Kangemi Sewage Treatment Works (Figure 2), is located near Chania River at 0°25'S, 36°58'E in Nyeri County. It is situated 4 km from the town center and was commissioned in 1988 (NYEWASCO, 2007). The Nyeri Town population projection is 123,942 with an area of 183.10 Km² (KNBS, 2013). Chania River originates in the Aberdare range, which is the main source of water for Nyeri Town and it receives effluents from the KSTW in Kangemi area of Nyeri Town (Figure 2). The annual rainfall in the Chania River catchment ranges between 1,200 mm-1,600 mm during the long rains and 500 mm-1,500 mm during the short rains. Nyeri County lies between 3,076 meters and 5,199 meters above sea level with monthly mean temperature range between 12.8ºC to 20.8ºC (NCIDP, 2013).

Figure 2: A Map showing location of KSTW and the sampled sites along Chania River, Nyeri. (Inset: map of Nyeri County and Kenya). Source: (ILRI dataset) - Map Created with QGIS by Kariunga, 2019
3.2 Sampling Sites

Sampling was done both in the KSTW and in CR at selected sites for three months. Samples were taken at least thrice per point in both systems scheduled to capture spatial variability of the sampling parameters. The sampling layout illustrated in Figure 3 comprises of five (1-5) sampling points within the KSTW and five sampling points within Chania River. The river sampling stations are (S6 and S7) i.e. distance of 298 m and 131 m respectively before the effluent discharge point of KSTW. While site (S8) is at the confluence of effluent and Chania River, and a further two points (S9 and S10), which are about (143 and 250 m respectively) after effluent discharge in CR.

Figure 3: Schematic map showing sampling sites layout in both KSTW and CR (Kariunga, 2018)

The sampling design layout for KSTW is illustrated in figure 3. Sampling point S1 was situated at the primary sedimentation tank with S2 in the secondary sedimentation tank after trickling filters and just before the maturation pond. Sampling point S3 was at the outlet of maturation pond 1, S4 at outlet of maturation pond 2 and S5 at the effluent of KSTW as shown in plate 1 (a-d).
Plate 1 (a-d): Photograph showing (a) site S1, (b) site 2, (c) site 3-5, (d) site 8 Location at KSTW

Sampling in CR was done at sampling point S6 and S7 on the upper reach of the CR before KSTW effluent discharge point, S8 at the confluence of KSTW discharge point and CR and at S9 and S10 after the discharge respectively. Plate 2 (a-d) shows the sampling sites as described above.

Plate 2 (a-d): Photograph showing (a) site 6, (b) site 7 (c) site 9, (d) site 10 along Chania River

3.2.1 Sampling and Field Measurements

Sampling was done twice in a month for a total of three months in each site. Physico-chemical measurements of discharge, temperature, DO concentration, conductivity, pH, was taken in-situ using calibrated portable multi-meters (HACH, hq40d model) within KSTW and CR selected sites (Figure 2 and 3). Discharge was determined using the velocity-area method (Wetzel 2001) where river cross-sectional area in square metres was multiplied by river velocity in cubic metres per second. During the sampling period, water samples for nutrients (SRP, TP, NO₃-N, NO₂-N, NH₄-N, and TN) and TSS analysis were collected in triplicate using 500 ml acid-washed plastic bottles at each sampling points in KSTW and CR. For the BOD, Winkler bottles were filled during sampling with water samples from the KSTW and CR. BOD winkler bottles were wrapped with aluminium foil to prevent light penetration in the bottles. Then re-aeration through bubbling was
avoided, and initial oxygen concentration measured using (HACH 40QD) meter probes model. Then stored in a dark place in the laboratory at 20°C or at room temperature in a wooden cupboard to prevent temperature fluctuations. The water samples for nutrient analysis were transported in a cool box, at 4°C, for analysis to Egerton University LWM water quality laboratory. On arrival the samples were stored in a refrigerator before analyses within 24 hours of sampling. Nutrient analyses were done using the standard methods for water and wastewater for APHA, (2005).

3.2.2 Determination of Nitrogen and Phosphorus in Water Samples

Different forms of nitrogen were determined; (NH₄-N), (NO₃-N), (NO₂-N) and (TN) using procedures described in APHA (2005). The NH₄-N was determined using hypochloride procedure by adding 2.5 ml of sodium-salicylate solution and 2.5 ml of hypochloride solution to 25 ml of filtered water samples. NO₃-N was determined using sodium-salicylate method, whereby 1 ml of freshly prepared sodium salicylate solution was added to 20 ml of filtered water sample. NO₂-N was analyzed through the reaction between sulfanilamide and N-Naphthyl-(1) ethylendiamin-dihydrochloride. The colour complex formed and its absorbance read at a wavelength of 543 nm. Total nitrogen (TN) was determined through persulphate digestion for 90 minutes under high temperature and pressure. After digestion, the TN was reduced to constituent nitrate form, then it was analyzed using Korollef technique. This was done by cooling the digested samples and topping up with distilled water to 50ml, then adding 1ml of HCL. Samples are read at two absorbance including 220nm and 275nm for turbidity correction in sample.

Soluble reactive phosphorus (SRP) was analyzed using the ascorbic acid method (APHA, 2005). The ascorbic acid procedure was done by preparing a mixed solution of ammonium molybdate, sulphuric acid, ascorbic acid and potassium antimonyl-tartarte solutions in ratio of 2:5:2:1 respectively. Then 2.5ml of the mixed solution was added to the 25ml of the samples and absorbance read at 885nm. Total phosphorus (TP) was determined through persulphate digestion of unfiltered water to reduce the forms of phosphorus present into SRP. After the digestion, evaporated water was replaced and TP analyzed as SRP using ascorbic acid method. Standard curves for different nutrients were developed by plotting the absorbance obtained using GENESYS 10uv scanning spectrophotometer model against the concentration of working solution for determination of actual concentrations of samples.
3.2.3 Total Suspended Solids (TSS)

TSS was determined by filtering a known volume of water samples through pre-weighed Whatman GF/C filters of pore size 0.45 μm. The filter papers were then dried to a constant weight at 95 °C for 3 hours. The TSS in mg/L was calculated using APHA, (2005) as in formula 3 as follows:

\[
TSS \text{ (mg/L)} = \left[ (WC - Wf) \times 10^6 \right] \frac{V}{1}\tag{3}
\]

Where TSS is the Total Suspended Solids (mg/L), Wf is the Weight of dried filter paper in grams, WC is the constant weight of filter paper + residue in grams, V is the volume of water filtered (ml) and \(10^6\) is the conversion factor from grams to mg and litres to ml to give TSS in standard units.

3.2.4 Biological Oxygen Demand in Wastewater and River

The initial oxygen concentration was taken in situ before incubation. Then final oxygen concentration was taken using (HACH 40d) multi-meter probes after 5 days incubation period at 20 °C. The difference in oxygen concentration in the sample after 5 days was obtained BOD was calculated using APHA, (2005) formula 4 given below:

\[
BOD \text{ (mg L}^{-1}\) = \text{O}_S - \text{O}_E\tag{4}
\]

\text{O}_S \quad \text{Oxygen concentration in mg L}^{-1}\text{at the start of incubation (0day)}

\text{O}_E \quad \text{Oxygen concentration in mg L}^{-1}\text{at the end of incubation (5days)}

3.2.5 Discharge Measurements for WTP and River

Discharge of wastewater at influent and effluent sampling points of KSTW and before and after effluent sites along CR was determined using Velocity-Area method. A portable automatic flow meter (Flo-Mate, model 2000, Marsh McBirney) was used to measure the mean water velocity at 60% water depth across the channels and discharge calculated as in Wetzel (2001) formula 5 below:

\[
Q \text{ (m}^3\text{/s)} = \sum V_i A_i\tag{5}
\]

Where, Q is the discharge, \(V_i\) is the mean current velocity (m/s) and \(A_i\) is channel cross-sectional area (m²).

3.2.6 Loading Rates Determination of N and P into Chania River

Nutrient loadings or losses in both treatment facility and the Chania River were calculated as shown in the following formula 6

Nutrient loading/loss (Kg/d) = Discharge (L/s) x Concentration (mg/L) x 0.0864 \tag{6}
Where nutrient loading/loss (kg/day), discharge (L/s), nutrients concentration (mg/L) and 0.0864 is concentration time conversion factor from mgs\(^{-1}\) to kgd\(^{-1}\). Thus,

\[
\text{Nutrient loading/loss (\%) = \frac{\text{influent loading-effluent loading}}{\text{influent loading}}} \times 100
\]

(7)

The nutrient and organic matter loading per day from the KSTW effluent into CR was calculated for N, P, BOD\(_5\) and TSS in Kg/day then converted to tons per year. Loading was estimated based on the concentrations at S1 (Primary tank influent) and S5 (effluent) in the Plant.

### 3.2.7 Wastewater Treatment Plant Efficiency Estimation

The Total Suspended Solids (TSS), Biochemical Oxygen Demand (BOD\(_5\)) and nutrients removal efficiency were estimated using Jamwal et al. (2015) formula 8 as follows:

\[
\text{Efficiency (\%) = \frac{\text{IC (mg/L) - EC (mg/L)}}{\text{IC (mg/L)}} \times 100}
\]

(8)

Where: IC refers to Influent Concentration and EC, Effluent Concentration

### 3.3 Data Analysis

Descriptive statistical parameters such as mean and standard errors were calculated using SPSS version 24. Graphs were prepared using Sigma Plot Version 11 and Microsoft Excel 2016. Indicators of measurements of various variables in both KSTW and CR were used to calculate quantity average concentrations of the sampled parameters. A *Students’ t-test* was done to test mean differences in discharge between sites of KSTW and effluent along CR. Data was subjected to a normality and homogeneity of variance tests and all tests were carried out at \(p<0.05\) significance level. A \(p\) value of \(p< 0.01\) was also used for correlation. The median values at different sampling points in the KSTW and CR were tested using the Kruskal-Wallis test (ANOVA on ranks). This nonparametric test was chosen because of the skewness and heterogeneity of the variances of most variables. Spearman’s correlation was used to show the relationship between physico-chemical, nutrients, BOD and TSS. The organic forms of both N and P were calculated from subtracting the inorganic forms from the TN and TP respectively. In the plant, the percentage composition of organic and inorganic forms of N and P were calculated at influent (S1) and effluent (S5) of KSTW and before (S7) and after effluent (S9) sampling points of Chania River to show the most dominant form at each of the sites. Retention and release were calculated by the difference in loadings (ton/yr) in the S1 and S5 sampling sites of KSTW.
4.1 Water Quality Parameters at Kangemi Sewage Treatment Works (KSTW)

Physico-chemical parameters, nutrients and Organic matter results obtained for KSTW showed a significant difference (Kruskal Walls, P=0.05) in most parameters across the sites except for TP and SRP. The pH was within the neutral range of 7.0-7.9 throughout the system.

4.1.1 Temperature, pH and conductivity variation within the system

Water temperature in the KSTW ranged between 22.13 ± 0.26 and 24.23 ± 0.19 °C. The highest temperature was at S5 (24.23±0.19°C) at the outlet of the plant and lowest at primary sedimentation tank (S1) (22.13°C±0.26). Temperature differed significantly across the sites (Kruskal Wallis, P = 0.000). Temperature at sites S1 and S2 was significantly different from S3, S4 and S5, while sites S3 and S5 were also significantly different. Oxygen concentration also differed significantly (Kruskal Wallis, p = 0.000) across the sites with lowest DO concentration recorded at site S1 (0.26±0.02 mg/L) and highest at S3 (6.93±0.48 mg/L) as shown in Table 2 and 3. The DO measured in site S1 was significantly lower than all other sites in the treatment plant. DO at site S2 was also significantly different from S3 and S4.

Table 2: Mean ± S.E values of physical-chemical variables at sites in KSTW. (n=90),

<table>
<thead>
<tr>
<th>Site</th>
<th>Temperature °C</th>
<th>DO mg/L</th>
<th>Conductivity µS/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>22.13±0.26</td>
<td>0.26±0.02</td>
<td>1352.17±68.88</td>
</tr>
<tr>
<td>S2</td>
<td>22.69±0.3</td>
<td>4.01±0.33</td>
<td>865.17±34.86</td>
</tr>
<tr>
<td>S3</td>
<td>23.54±0.17</td>
<td>6.93±0.48</td>
<td>921.11±36.92</td>
</tr>
<tr>
<td>S4</td>
<td>23.86±0.2</td>
<td>6.05±0.33</td>
<td>875.44±33.86</td>
</tr>
<tr>
<td>S5</td>
<td>24.23±0.19</td>
<td>5.48±0.71</td>
<td>855.94±37.60</td>
</tr>
</tbody>
</table>

The pH of incoming wastewater ranged between 7.28-7.89. However, the highest pH range of (7.76-7.89) (0.61 units) was recorded in S5 while the lowest pH range of 7.28-7.48 (0.2 units) was recorded in S1. Site S1 at the primary sedimentation tank recorded the highest conductivity (1352.17±68.88 µS/cm) value that progressively decreased from S1 to S5 with the latter site having the lowest conductivity (855.94±37.60 µS/cm). There was a significant difference in conductivity among the sites (Table 3). A significant variation in conductivity was observed between site S1 and all other sites in KSTW.
Table 3: Kruskal-Wallis test (*P<0.05) of physico-chemical at KSTW. n=90, d.f =4

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Mean</th>
<th>H</th>
<th>P=Asymptotic sig. (2 tailed test)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>23.29</td>
<td>36.030</td>
<td>0.000*</td>
</tr>
<tr>
<td>Oxygen</td>
<td>4.33</td>
<td>50.441</td>
<td>0.000*</td>
</tr>
<tr>
<td>Conductivity</td>
<td>1076.31</td>
<td>27.820</td>
<td>0.000*</td>
</tr>
</tbody>
</table>

4.1.2 BOD$_5$ and TSS Dynamics in Sites within KSTW

The mean value of BOD$_5$ in all the sites was 68.7 mg/L with the highest mean BOD$_5$ of 111.21±7.76 mg/L at the primary sedimentation tank (S1) and the lowest was 45.3±7.87 mg/L at the effluent site (figure 4a). BOD$_5$ varied significantly across the sites during the monitored period (Kruskal Wallis, P<0.05). The results obtained showed that, BOD$_5$ at S1 site had a significant variation from the rest of the sites (S2-S5) in KSTW. The mean value of total suspended solids (TSS) in all the sites of the plant was 56.90 mg/L. The highest TSS was recorded at S1 (191.8±9.93 mg/L) and lowest (18.7±1.38 mg/L) at site S4 (figure 4b). The mean TSS increased slightly at S5 (26.9 mg/L). TSS concentration varied significantly among the sites. The mean TSS in S1 differed significantly from the rest of the sites in KSTW. Sites S2, S3 and S4 also varied significantly with site S5 in TSS concentrations within the treatment plant. Site S4 varied with sites S2 and S3 (Kruskal Wallis, P<0.05).

Figure 4: Mean ± SE levels of Organic Matter (a) BOD$_5$ and (b) TSS at sites along KSTW

4.1.3 Nutrients Concentrations within KSTW

The mean concentration of nitrite and nitrate at KSTW was 0.24 and 10.69 mg/L respectively as illustrated in Table 4. The highest nitrite was recorded at S4 and lowest at S1 as shown in figure 5a. The average value of nitrate nitrogen during the monitoring period in all the sites within the
The plant was 10.6 mg/L, with lowest concentration of NO$_3$-N at S1 (0.21±0.02 mg/L) and highest value at S3 (figure 5b). The nitrite and nitrate nitrogen in the sites studied varied significantly across the sites (Kruskal-Wallis, p< 0.05) (Table 4). The concentrations in KSTW for nitrite and nitrate indicated a significant variation between S1 and all other sites (Kruskal Wallis, P<0.05).

Table 4: Kruskal-Wallis test (*P<0.05) of nutrients and organic matter along the Sites at KSTW

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Mean (mg/L)</th>
<th>(H)</th>
<th>(P)=Asymptotic sig. (2 tailed test)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrite</td>
<td>0.24</td>
<td>42.987</td>
<td>0.000*</td>
</tr>
<tr>
<td>Nitrate</td>
<td>10.69</td>
<td>37.643</td>
<td>0.000*</td>
</tr>
<tr>
<td>Ammonia</td>
<td>2.82</td>
<td>18.751</td>
<td>0.001*</td>
</tr>
<tr>
<td>TN</td>
<td>48.9</td>
<td>80.668</td>
<td>0.000*</td>
</tr>
<tr>
<td>SRP</td>
<td>1.25</td>
<td>2.216</td>
<td>0.696</td>
</tr>
<tr>
<td>TP</td>
<td>1.57</td>
<td>4.515</td>
<td>0.341</td>
</tr>
<tr>
<td>BOD$_5$</td>
<td>67.04</td>
<td>26.223</td>
<td>0.000*</td>
</tr>
<tr>
<td>TSS</td>
<td>57.79</td>
<td>31.733</td>
<td>0.000*</td>
</tr>
</tbody>
</table>

The mean value of TN in all the sites sampled was 48.9 mg/L. The highest concentration for TN (67.90±1.76 mg/L) was recorded at S4 and lowest concentration 18.87± 0.76 at S5 as illustrated in figure 5c. TN varied significantly among the sites (table 4). The TN measured showed a significant variation between site S1 and all other sites in KSTW. The mean concentration of Ammonium-N at KSTW was 2.82 mg/L. The concentration was highest at S1 (4.2 ± 0.8 mg/L) and lowest concentration at S2 (1.5 ± 0.2 mg/L) as shown in figure 5d. There was a significant variation of Ammonium-N among the sites (Kruskal-Wallis, p < 0.01) as shown in table 4. For Ammonium-N, Site S2 was also significantly different from S5. The ratio of dissolved inorganic nitrogen (DIN) to dissolved organic nitrogen in KSTW was 0.38.

The average concentration of TP in KSTW during the monitored period was (1.57 mg/L). The highest TP was at S4 (1.63±0.02 mg/L) and lowest TP, 1.48mg/L was at S2 (figure 5e). The mean SRP was 1.25 mg/L, with the highest SRP recorded in S3 (1.3±0.02mg/L) and lowest at S1, 1.2±0.07 mg/L, (figure 5f). There was an increase in SRP from S4 to S5 although not significant, SRP and TP showed no significant variation among the sites (Kruskal-Wallis, p > 0.05) as shown in table 4. The obtained mean ratio of SRP/TP was 1:1.3.
4.1.4 Relationship between Wastewater Flow and Water Quality Parameters in KSTW

The average discharge at the influent and effluent were 0.03 m$^3$/s (3110 m$^3$/day) and 0.06 m$^3$/s (6040 m$^3$/day) respectively. The highest discharge obtained at the effluent was almost twice that...
of the influent discharge. As expected, there was a positive correlation of discharge with loading rate for all the nutrients at the effluent except for ammonia and TN. The loading of organic matter (TSS and BOD) at the effluent also showed a positive correlation with discharge. The mean discharge had a minimal change over the three months sampled. November, December and January recorded average discharge of 3532, 3338 and 3338 m$^3$/day respectively.

Table 5: Correlation Analysis (2 tailed) of physico-chemical and nutrients variables at KSTW.

<table>
<thead>
<tr>
<th>Spearman rho</th>
<th>Nitrates</th>
<th>Nitrates</th>
<th>Ammonia</th>
<th>SRP</th>
<th>TP</th>
<th>BOD$_5$</th>
<th>TSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>.540**</td>
<td>.115</td>
<td>-.554**</td>
<td>.169</td>
<td>.207</td>
<td>-.325**</td>
<td>-.548**</td>
</tr>
<tr>
<td>Oxygen</td>
<td>.282**</td>
<td>.540**</td>
<td>-.021</td>
<td>.198</td>
<td>.069</td>
<td>-.682**</td>
<td>-.494**</td>
</tr>
<tr>
<td>pH</td>
<td>-.251*</td>
<td>.132</td>
<td>-.124</td>
<td>.015</td>
<td>.334**</td>
<td>-.481**</td>
<td>-.068</td>
</tr>
<tr>
<td>Conductivity</td>
<td>-.430**</td>
<td>.067</td>
<td>.202</td>
<td>.169</td>
<td>-.011</td>
<td>.224*</td>
<td>.316*</td>
</tr>
</tbody>
</table>

* (P<0.05) and ** (P<0.01)

Findings showed temperature had a significant negative relationship with BOD$_5$, TSS and Ammonium-N (Table 5). However, a positive significant correlation of temperature was observed with nitrites. The pH, nitrates and P showed no significant correlation with temperature. Dissolved oxygen in the plant showed a significant, positive correlation with pH, temperature and nitrates. A significant, negative correlation of DO with BOD$_5$ and TSS was observed. However, a non-significant relationship was observed between DO and ammonia (P> 0.05). Further analysis Spearmans’ correlation showed that pH correlation with TSS, conductivity and nitrites were not significant (P>0.05). The relationship of pH with TP and BOD$_5$ indicated a positive and negative significant correlation respectively. Temperature, DO and nitrites showed a significant negative correlation with conductivity. The values for nitrites (Spearmans, 0.067, P>0.05) and TP (Spearmans, -0.011, P>0.05) were not significant.

4.2 Variability in Physico-chemical Parameters, Nutrients and Organic Matter in CR

Most of the variables measured in CR indicated a significant difference across the sites except the temperature and TSS which were not significantly different across the sites. There was a sharp spike for all the nutrient and BOD$_5$ concentrations at S8 (KSTW effluent receiving point) of CR. However, TSS continued to rise downstream even after the effluent-river confluence.
4.2.1 Temperature DO, Conductivity and BOD₅ Variation along the sites in CR

The mean water temperature in Chania River was 18.33 °C at all sites. The highest temperature was at site S8 (confluence) (18.5±0.36°C) and the lowest was recorded at site S6 (upstream of effluent point) (17.9±0.28°C) as shown in Table 6 below. There was no significant difference (Kruskal-Wallis P=0.609) in temperature among the sites (S6-S10). The mean DO was 8.53 mg/L. The highest DO of 8.64±0.05 mg/L was obtained in S6 and lowest at S10 (8.12±0.31 mg/L). There was a statistically significant difference in DO concentration across the sites (Kruskal-Wallis, P=0.00) as shown in Table 6 below. In Chania River, Dissolved Oxygen at site S10 was significantly different from S6 and S7. The mean conductivity in Chania River was significantly different across the sites (P<0.05). There was a significant variation in conductivity between site S8 and all other sites in CR (S6, S7, S9 and S10). While Site S6 was also significantly different from sites S8, S9 and S10 (Kruskal Wallis, P<0.05).

Table 6: Mean Physico-chemical Parameters in Chania River (Kruskal-Wallis, * (P<0.05), n=90)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Mean</th>
<th>H</th>
<th>P=Asymptotic sig. (2-sided test)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>18.33</td>
<td>2.702</td>
<td>0.609</td>
</tr>
<tr>
<td>Oxygen</td>
<td>8.53</td>
<td>10.046</td>
<td>0.040*</td>
</tr>
<tr>
<td>Conductivity</td>
<td>97.00</td>
<td>34.401</td>
<td>0.000*</td>
</tr>
</tbody>
</table>

The mean concentration of BOD₅ across the sites was 8 mg/L. The lowest BOD₅ was recorded at site S7, while S8 recorded the highest BOD₅ (figure 6a). However, most sites recorded at least 6 mg/L of BOD₅ before and after the effluent. BOD₅ varied significantly across the sites in CR (Kruskal-Wallis, P=0.000). Findings for BOD₅ in CR, had a significant difference between site S8 and all the other sites along the river. The highest TSS was recorded at S10 (43 mg/L) and lowest (26.9mg/L) at site S6 (figure 6b). In Chania River TSS indicated a non-significant variation (Kruskal-Wallis, P=0.000) across the sites.
Figure 6: Mean ± SE levels of Organic Matter (a) BOD$_5$ and (b) TSS at sites along Chania River (S8 being the KSTW effluent point into the river)

4.2.2 Nutrients Concentration Spatial Variability along Chania River

The mean nitrite concentration across sites in CR was 0.02 mg/L. The lowest concentrations were recorded at S9, (0.01±0.00 mg/L) and highest at S8 (0.03±0.01 mg/L) as shown in figure 7a. Nitrite concentration varied significantly across the sites (Kruskal-Wallis, P=0.00) (table 7). For nitrite in CR, site S8 was a significantly different from other sites in Chania. The average concentration of nitrate nitrogen during the monitoring period in all the sites in Chania River was 0.70 mg/L. The lowest nitrate concentration was 0.19±0.02 mg/L recorded at S7 and highest concentration at S8 (2.52±0.54 mg/L) (figure 7b). A notable significant difference was recorded between S8 and all the other sites in CR. Site S6 and S7 were also statistically significant from S8, S9 and S10.

Table 7: Table showing Means of Nutrients and Organic Matter along Chania River Sites

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Mean (mg/L)</th>
<th>H</th>
<th>P= sig. (2-sided test)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrites</td>
<td>0.02</td>
<td>29.308</td>
<td>0.000*</td>
</tr>
<tr>
<td>Nitrates</td>
<td>0.72</td>
<td>37.965</td>
<td>0.000*</td>
</tr>
<tr>
<td>Ammonia</td>
<td>0.16</td>
<td>14.202</td>
<td>0.007*</td>
</tr>
<tr>
<td>TN</td>
<td>4.85</td>
<td>21.798</td>
<td>0.000*</td>
</tr>
<tr>
<td>SRP</td>
<td>0.09</td>
<td>65.006</td>
<td>0.000*</td>
</tr>
<tr>
<td>TP</td>
<td>0.25</td>
<td>30.946</td>
<td>0.000*</td>
</tr>
<tr>
<td>BOD$_5$ (Organic matter)</td>
<td>8.49</td>
<td>29.236</td>
<td>0.000*</td>
</tr>
<tr>
<td>TSS</td>
<td>36.32</td>
<td>31.733</td>
<td>0.733</td>
</tr>
</tbody>
</table>

(Kruskal-Wallis, * (P<0.05), n=90, d.f =4)
The mean value of TN in all the sites sampled was 4.8 mg/L. The highest concentrations of TN (5.3±0.23 mg/L) was at S8 (figure 7c) and lowest concentration at S10 (4.43±0.20). Total Nitrogen varied significantly among the sites (table 6) where site S8 recorded a significant difference with sites 6, 7 and 10. There was also a significant difference in TN between sites S9 and S10 in Chania River. The mean concentration of ammonium across the sites was 0.2 mg/L with lowest and highest concentration at S6 and S8 respectively as shown in figure 7d. There was a significant variation of ammonium nitrogen among the sites Kruskal-Wallis (P=0.000). Ammonium-N at site S8 differed significantly from all other sites in CR Ration of Dissolved Inorganic Nitrogen (DIN) to Dissolved Organic Nitrogen in Chania River was 0.23

Figure 7: Mean ± SE concentration of nutrients, (a) Nitrite, (b) Nitrate, (c) Ammonium-N, (d) TN, along the Chania River
The mean concentration of TP at CR during the monitoring period was 0.25 mg/L. The lowest and highest TP concentrations were recorded respectively at S10 and S8 (Figure 8a). Total phosphorus indicated a significant difference (Kruskal-Wallis, P=0.000) at the sites sampled in Chania River (table 7). Across the CR sites TP was significantly different between site S8 and all the other site, also sites S7 and S9 showed significant variation of TP. Highest increase in SRP was recorded at S8 (0.2 mg/L), thus, the site with the highest SRP concentration (Figure 8b). Soluble Reactive Phosphorus indicated a significant difference across sites (Kruskal-Wallis, P=0.00) in Chania River. The SRP at sites S7 and S8 were statistically significant different from all other sites. The mean ratio of TN/TP ratio was high (19:1).

![Bar chart showing TP and SRP concentrations at various sites along the Chania River.]

**Figure 8:** Mean ± SE concentration of nutrients, (a) SRP and (b) TP at sites along Chania River

### 4.2.3 Relationship of Discharge, Nutrients and Physico-chemical Variables in CR

The average discharge along Chania River was 1.9 m$^3$/s. The discharge before and after effluent was 1.4 and 2.0 m$^3$/s respectively. There was a positive correlation of discharge with loadings after effluent of all nutrients, BOD$_5$ and TSS except for nitrite. The loading of organic matter (TSS and BOD$_5$) at the effluent also showed a positive correlation with discharge. There was a significant positive correlation of temperature with nitrites, SRP and TP (P=0.000) as shown in table 8. Dissolved oxygen and pH showed a negative significant correlation with SRP and TP (p<0.05). A negative significant correlation of DO with ammonia (Spearmans, -0.332, P=0.001) could be explained by nitrification which converts more of ammonia to nitrates and reducing ammonia. A weak negative correlation of DO with nitrates (Spearmans, -0.209, P=0.048) could indicate more DO is being used to convert nitrites to nitrates. pH showed a negative strong correlation with Ammonia, SRP and BOD$_5$ (P=0.001) as shown in table 8. Similarly, conductivity showed a
positive strong correlation with NO$_2$, NO$_3$, TP, SRP and BOD$_5$. There was a negative correlation between conductivity, ammonia and TSS (Table 8).

Table 8: A Relationship of physico-chemical, nutrients and organic matter at CR

<table>
<thead>
<tr>
<th>Spearman rho</th>
<th>Nitrite</th>
<th>Nitrate</th>
<th>Ammonia</th>
<th>SRP</th>
<th>TP</th>
<th>BOD$_5$</th>
<th>TSS</th>
<th>TN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>.415**</td>
<td>-.087</td>
<td>.100</td>
<td>.380**</td>
<td>.410**</td>
<td>.035</td>
<td>.056</td>
<td>-.016</td>
</tr>
<tr>
<td>Oxygen</td>
<td>-.170</td>
<td>-.209*</td>
<td>-.332**</td>
<td>-.338**</td>
<td>-.263*</td>
<td>-.072</td>
<td>-.090</td>
<td>-.015</td>
</tr>
<tr>
<td>pH</td>
<td>-.269*</td>
<td>.095</td>
<td>-.416**</td>
<td>-.191</td>
<td>-.341**</td>
<td>-.346**</td>
<td>-.119</td>
<td>.189</td>
</tr>
<tr>
<td>Conductivity</td>
<td>.445**</td>
<td>.710**</td>
<td>-.249*</td>
<td>.429**</td>
<td>.504**</td>
<td>.317**</td>
<td>-.021</td>
<td>.162</td>
</tr>
</tbody>
</table>

* (P<0.05) and ** (P<0.01)

4.3 The Organic and Inorganic Components of N and P at KSTW and CR

In both KSTW and CR the most dominant form of Nitrogen was the organic component. For P component, inorganic P was higher in KSTW than organic P, while for CR organic P surpassed the inorganic P in CR.

4.3.1 Organic and Inorganic Fraction of N and P in KSTW

In general, the organic nitrogen, (ON) was higher than the inorganic nitrogen (IN) concentration in all the KSTW sites except at site S5 as in (figure 9a). Site S4 and S5 had the highest and lowest organic-N respectively. For Inorganic-N, S3 site had the highest concentration and S1 had the lowest. In this study, organic nitrogen (ON) indicated highest concentration of N, followed by Ammonium-N with the oxidized forms of nitrogen (NO$_2$ and NO$_3$) having the lowest concentrations.

Phosphorus components in KSTW, composed of inorganic phosphorus (IP), being dominant across all the sites. The IP fraction was twice the OP component as shown in figure 9b. In general, P did not show much notable change at individual sites within KSTW. The lowest IP was at S1 and highest at S5, while OP did not vary between the influent and effluent. Site S1 recorded the highest Organic-P while S2 had the lowest OP.
4.3.2 A Comparison of Inorganic and Organic (N and P) Composition of Sites in CR

In Chania River most of N was composed of organic forms in all the sites. The mean ON/IN ratio for Chania is 4:1 (figure 10a). Site S8 recorded the highest ON and IN forms with a ratio of 0.9 ratio. Whereas, site S7 and S10 had the lowest concentrations of IP and OP respectively (figure 10b). The OP/IP ratio was 2.

4.4 Nutrients and Organic Matter Removal Efficiencies of KSTW

For organic nutrient (N and P), influent comprised of the highest percentage of organic contribution. Whereas, the effluent of KSTW comprised mostly of inorganic component of both N and P. Nitrate and nitrite increased in within the system compared to the influent. Ammonia reduced progressively down the treatment stages. There was a minimal change in P component in KSTW.
4.4.1 Percentage Contribution of Nutrient Fraction at Influent and Effluent of KSTW

There was about 24% of Inorganic-N fraction in site (S1) and 76% at (S5) site of KSTW respectively as shown in the figure 11a. Whereas, ON, consisted of 89% at the influent and 11% at the effluent of the plant respectively indicating 78% removal (figure 11b). About 48% of IP was recorded at the influent (S1) and 52% was leaving the plant as effluent which infers 4% input of inorganic form of P (figure 11c). The Organic-P constituted 60% entering the plant and about 40% leaving the plant as (figure 11d).

![Pie chart of IN](image)

![Pie chart of ON](image)

![Pie chart of IP](image)

![Pie chart of OP](image)

Figure 11: Fraction (%) of (a) IN, (b) ON, (c) IP and (OP) proportion of KSTW influent and effluent

4.4.2 Kangemi Sewage Treatment Works Removal Efficiency of Nutrients and OM

The removal efficiencies were calculated for nitrogen and phosphorus in KSTW which indicated high removal efficiency for nitrogen derivatives and low removal of phosphorus component as illustrated in Table 9. The overall efficiency for nitrite and nitrate was negative, but some removal
of nitrite at S4-S5 was noted, other points registered an increase in concentration. However, removal efficiency of 9.1% for nitrite between S4-S5 and 27.2% (S3-S4) for nitrate was recorded. In the different stages of the WTP ammonia removal was highest at S4-S5 and lowest S2-S3 (7.05%). Statistics showed significant NH$_4$-N removal between S1 and S4, whereas, TN revealed a significant removal between S1 and S5. Highest removal TN was recorded at site S4-S5 and lowest at S2-S3 (2%). The N components overall removal efficiencies are: ammonium (63.97%) and TN (54.16%). The removal efficiency of TN and Ammonium nitrogen in KSTW was significantly different (Kruskal Wallis P<0.05).

Table 9: A Comparative Nutrient and Organic Matter Removal Efficiencies in (%) at KSTW
{negative (-) and positive (+) values indicate release and retention respectively}

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Sites</th>
<th>Overall %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S1-S2</td>
<td>29.72</td>
<td></td>
</tr>
<tr>
<td>S2-S3</td>
<td>7.05</td>
<td></td>
</tr>
<tr>
<td>S3-S4</td>
<td>7.94</td>
<td></td>
</tr>
<tr>
<td>S4-S5</td>
<td>40.00</td>
<td></td>
</tr>
<tr>
<td>(S1-S5)- Overall</td>
<td>63.97</td>
<td></td>
</tr>
<tr>
<td>TN</td>
<td>-48.86</td>
<td></td>
</tr>
<tr>
<td>BOD$_5$</td>
<td>27.65</td>
<td></td>
</tr>
<tr>
<td>TSS</td>
<td>87.04</td>
<td></td>
</tr>
<tr>
<td>SRP</td>
<td>-2.9</td>
<td></td>
</tr>
<tr>
<td>TP</td>
<td>7.50</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-6.08</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-3.82</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.68</td>
<td></td>
</tr>
<tr>
<td>(S1-S5)- Overall</td>
<td>2.03</td>
<td></td>
</tr>
</tbody>
</table>

Total Phosphorus and SRP had low removal efficiency as shown in table 9 above. However, statistics showed that TP removal efficiency was significant (Kruskal Wallis, P<0.05). There was a significant removal of TP between S1 and S2 sites. The other sites were sources for SRP as the concentrations increased progressively compared to the preceding sites. There was notably very low removal efficiency for P at all stages of the treatment. In contrast, as illustrated in table 9, BOD (organic matter) removal efficiency was high at KSTW. The removal efficiency of BOD$_5$ and TSS in KSTW was significantly different (Kruskal Wallis P<0.05). For BOD$_5$, highest removal efficiency was observed at S2-S3 and the lowest (2.56%) was in site S3-S4. Computation showed that TSS was removed consistently between S1 to S4, where a notable surge was recorded between (S4-S5). Overall (S1-S5), BOD$_5$ recorded a 59% and TSS had (86%) removal efficiencies respectively. The highest and lowest removal efficiency for TSS was recorded between S1 and S2 (87.0%) and S2 and S3 (10.6%) respectively as indicated in Table 9. Statistics showed significant BOD$_5$ removal between S2 and S3. Whereas, TSS indicated a significant removal between S1-S4.
4.5 Nutrients and Organic Matter Loading Rates at KSTW

The selected nutrient and organic matter release and retention within KSTW effluent into CR was calculated for TN, TP, BOD$_5$ and TSS. There was no retention (source) for nitrite, nitrate and SRP in KSTW. The table 10 below shows, the inflow loading (ton/yr) into KSTW, retention in percentage (%) release/outflow (effluent) into Chania River.

Table 10: Loading Retention and Release (%) Nutrient and OM in KSTW

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Influent (ton/yr)</th>
<th>Retention (%)</th>
<th>Effluent (ton/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TN</td>
<td>47.1</td>
<td>54</td>
<td>21.6</td>
</tr>
<tr>
<td>Ammonia</td>
<td>4.9</td>
<td>30</td>
<td>3.4</td>
</tr>
<tr>
<td>TP</td>
<td>1.8</td>
<td>-90*</td>
<td>3.3</td>
</tr>
<tr>
<td>BOD$_5$</td>
<td>128.6</td>
<td>21</td>
<td>101.6</td>
</tr>
<tr>
<td>TSS</td>
<td>159.9</td>
<td>63</td>
<td>59.5</td>
</tr>
</tbody>
</table>

*bolded values indicate that KSTW is a source rather than sink

4.5.1 Nutrient and Organic Matter Retention and Release in KSTW

As illustrated in figure 12, KSTW showed that it was a source of nitrite, nitrates and TP. The tonnage release of these loadings (ton/yr) into Chania River are shown in table 10.

![Figure 12: A graph showing retention/release of selected nutrient and organic matter in KSTW](image-url)
There was however, a notable retention of TN, BOD$_5$ and TSS within KSTW, hence the plant acted as a sink for these parameters. The highest retention recorded was for TSS, with an estimated TSS retention was 159.9 ton/yr, and only 59.5 ton/yr of TSS was released as loading into CR.

### 4.5.2 Removal of Pollutant Loads at Longitudinal Profile of Chania River

There was a significant removal of pollutants in Chania River from S8-S10. However, some parameters recorded an increase in loading. The highest removal of nutrient and organic matter was between S8 and S9 as shown in table 11.

Table 11: Removal and Release of loads (ton/yr) and (%) removal between sites upstream, S6 to S8 and downstream S8-S10 within Chania River (- values indicate Release, + indicate Removal)

<table>
<thead>
<tr>
<th>River Sites</th>
<th>BOD$_5$</th>
<th>TSS</th>
<th>NO$_2$</th>
<th>NO$_3$</th>
<th>NH$_4$</th>
<th>SRP</th>
<th>TP</th>
<th>TN</th>
</tr>
</thead>
<tbody>
<tr>
<td>S6-S7</td>
<td>-116.3</td>
<td>-9.2</td>
<td>-0.2</td>
<td>-5.1</td>
<td>0</td>
<td>-1.8</td>
<td>-8.9</td>
<td>-87</td>
</tr>
<tr>
<td>(%)</td>
<td>(-36.4)</td>
<td>(-0.6)</td>
<td>(-16.7)</td>
<td>(-82.3)</td>
<td>(0.0)</td>
<td>(-120)</td>
<td>(-136.9)</td>
<td>(-40.2)</td>
</tr>
<tr>
<td>S7-S8</td>
<td>-600.7</td>
<td>-593</td>
<td>-0.7</td>
<td>-166.4</td>
<td>-8.3</td>
<td>-10.6</td>
<td>-14.2</td>
<td>-98.4</td>
</tr>
<tr>
<td>(%)</td>
<td>(-137.9)</td>
<td>(-36.2)</td>
<td>(-50.0)</td>
<td>(-1472.6)</td>
<td>(-97.6)</td>
<td>(-321.2)</td>
<td>(-92.2)</td>
<td>(-32.4)</td>
</tr>
<tr>
<td>S8-S9</td>
<td>510.2</td>
<td>-532.6</td>
<td>1.4</td>
<td>150.8</td>
<td>7.6</td>
<td>8.5</td>
<td>9.2</td>
<td>74.7</td>
</tr>
<tr>
<td>(%)</td>
<td>(49.2)</td>
<td>(-23.9)</td>
<td>(67.7)</td>
<td>(84.9)</td>
<td>(45.0)</td>
<td>(61.2)</td>
<td>(31.1)</td>
<td>(18.6)</td>
</tr>
<tr>
<td>S9-S10</td>
<td>131.9</td>
<td>-2115.8</td>
<td>-0.1</td>
<td>-2.6</td>
<td>1.6</td>
<td>-1.4</td>
<td>20.4</td>
<td>119.6</td>
</tr>
</tbody>
</table>

The BOD$_5$ recorded highest load removal of 510.2 ton/yr and nitrite recorded the smallest removal of 1.4 ton/yr between the two sites. In contrast, TSS load increased downstream between the two sites (S9 and S10). There was a notable increase of loads for TSS, NO$_2$, NO$_3$, and SRP between the same sites (S9 and S10). There was a cumulative removal of pollutant between S8 to S10 for other measured parameters except for TSS which registered an increase across the downstream gradient of Chania River. This is an indication of TSS release from other sources downstream. The corresponding percentage removal between the sites (S8-S9 and S9-S10) are also shown (bolded) in table 11.

An overall increase of loads downstream between site S6 (reference point) to S8 for all the parameters was determined in this study, where BOD, TSS, NO$_3$ and TN recoded the highest increase respectively. Nitrite, SRP and ammonia respective increase downstream from S6 to S8
are illustrated in (table 11). In addition, a longitudinal gradient of loadings of all nutrient and organic matter are presented in figure 13a-e, which shows peaks along the sites of Chania River.

Figure 13: The comparison of Nutrient Loading of (a) TN and Nitrate, (b) Nitrite and Ammonium- N, (c) TP and SRP and (d) Organic Matter (BOD$_5$) and (e) TSS along Chania River
CHAPTER FIVE
DISCUSSION

5.1 Overview of KSTW efficiency and Impact of the Effluent on CR Water Quality

The wastewater in KSTW revealed marked variations in the physico-chemical and nutrients concentrations along the sites. Physico-chemical parameters such as temperature, dissolved oxygen, conductivity and pH are known to have a profound effect on the nutrient cycling dynamics in both wastewater and freshwater. In KSTW, temperature was lowest at S1 and highest at effluent S5, which was attributed to ambient temperature and sampling time. This implies that S1 had lowest temperature because it was sampled in the morning hours and S5 had the highest temperature as it was sampled later in the afternoon. Dissolved oxygen was lowest at S1 but oxygen improved progressively especially at the maturation ponds due to reduced organic matter. The low organic matter content in the maturation ponds, reduced the DO demand needed by microbes for degradation and breakdown of organic matter in wastewater. This differs with low oxygen obtained at S1 mostly due to high oxygen demand to break down the high OM from the incoming raw wastewater before treatment. S1 had the highest conductivity while pH remained neutral throughout the KSTW system.

In Chania River, sites above the effluent (S6 and S7) had no direct influence from effluent of KSTW hence, S6 was considered a reference point, but the effect of the effluent is pronounced at the confluence (S8). As expected, the river should self-purify downstream through dilution and organic matter breakdown under normal circumstances. Thus, Chania River, demonstrated self-purification properties by reduction of most pollutants downstream of discharge (S9 and S10) except for TSS which increased progressively. Therefore, the water quality improved after the effluent discharge (S8) downstream.

5.2 Physico-Chemical parameters, Nutrient and Organic Matter Dynamics in KSTW

The lowest (23.3°C at S1) and highest (24.1°C at S5) temperatures measured in this study is and within the range for effective nitrification process, organic matter degradation and photosynthetic activity, which optimise at 30°C (USEPA, 2014). At temperatures below 20 °C nitrification, organic matter degradation by microbial activity and photosynthesis proceeds at a slower rate, although it still continues even at slightly less than 10°C (Hopcroft, 2015). The temperature variation obtained could be attributed to the influence of ambient air temperature (USEPA, 2015). Energy released in metabolic and biodegradation process influence temperature especially where biological
treatment processes apply within the system. On the other hand, time of sampling could have influenced the temperature, for example S1 with lower temperature was always sampled first in the mid-morning hours compared to S5, which was always sampled later in the day when ambient temperatures were warmer. However, due to high altitude in Nyeri, the ambient temperature was always low and did not exceed 30°C. However, it’s important to note that maturation ponds are biological systems, which operate under the influence of environmental conditions such as temperature, wind speed and light intensity (Gray, 2004). Therefore, variation in ambient temperature during the daytime could have been a major factor that contributed to longitudinal increase in wastewater temperature from S1 to S5 inferring that lowest temperature at S1 and highest temperature at S5 are due to differences in daytime temperature during sampling in KSTW. Increased (optimum) temperature, accelerates biochemical reactions through microbial activities. There is also a possibility of heat generation within the system such as breakdown of the OM by micro-organisms which influence the temperature due to energy production processes such as methanogenesis. However, this was unlikely cause of temperature increase in KSTW as the process usually occur in anaerobic systems as explained in Jenicek et al. (2012). However, between S1-S2 high organic matter breakdown was recorded. In S2 indicated improved DO conditions, reduced ammonium concentration and highest TSS removal compared to S1. On the other hand, S5 had lowest TSS and ammonium N and highest temperature with slightly reduced DO compared S4. Lippi et al. (2009) suggested that temperature has a very strong influence on solubility and oxygen saturation levels within treatment systems wastewater.

As expected, low dissolved oxygen levels were recorded at the sedimentation tank (S1). This is due to high organic load received and being the site where decomposition by bacteria actively occurs. The bacterial activity on the organic component in the wastewater is known to accelerate oxygen consumption leading to anoxic conditions hence favouring denitrification and volatilization of ammonia (Mara, 2004, WEF, 2010). This could explain why, extremely low DO and high NH₄ concentration were obtained site S1 (primary sedimentation tank) in this study. Oxygen levels improved at maturation ponds, due to, increased algal photosynthesis, wind mixing and corresponding reduction of organic matter in tertiary stages of treatment. Photosynthesis and mixing have been found to be an important process in aeration of wastewater (WEF, 2010; Spellman 2014).
The pH values in the studied sites ranged between (7.6 - 7.8) which was within the optimum range for bacterial activity (USEPA, 2000). The pH range variations can inhibit nutrient cycling if they fall below or above the optimum range of 6-8. Above and below this pH range would result to slowing down N and P removal. In this study, highest conductivity (1352 µS/cm) obtained at S1, and lowest (856 µS/cm) at S5, can be attributed to release of ions and nutrients into the water column from hydrolysis, leaching and mineralization especially in the anaerobic pond (S1). However, reduction in conductivity in the subsequent sites is an indicator of ionic removal which could be attributed to algal bio-uptake, precipitation, denitrification, adsorption and nutrient lock on substrates and sediments (WEF, 2010).

5.3 Nutrient Transformation in Wastewater at KSTW

The N and P recorded in KSTW wastewater, were mostly in organic forms in the influent of KSTW. Organic nitrogen was the most abundant compared to inorganic N form. Nitrite and nitrate increased down the treatment stages due to mineralization and nitrification of ammonium N, resulting to reduction in ammonia progressively towards the effluent. The P forms showed that inorganic phosphorus was higher than the organic P which indicates that there was mineralization of P within KSTW system.

5.3.1 Nitrogen Transformation in Wastewater

As expected NH₄-N concentrations declined from primary influent to the effluent consistently. This could be explained by hydrolysis and mineralization of NH₄-N. The increase in oxygen concentration in the subsequent treatment stages, is an indication of enhanced nitrification process, which consequently decreases ammonification through conversion of NH₄ compounds by microbial degradation. Studies on N conversion under low-oxygen conditions as indicated in S1 have shown that ammonia can skip the conventional nitrification process and be converted to dinitrogen (Hunt et al., 2005). Alternatively, under low-oxygen conditions, the production of nitrite from ammonia is favored over the production of nitrate, while increased DO will facilitate complete nitrification, hence conversion of ammonia to nitrite then nitrate (Bernet et al., 2001). The NH₄-N may also have been removed by volatilization as ammonia gas, and through uptake by microbiota or denitrification at anaerobic “dead” zones. In anaerobic conditions, organic nitrogen (ON) is hydrolyzed to NH₄-N especially when the hydraulic retention time is higher in the sewer or primary tank as explained in Von Sperling, (2013). As evident in this study, nitrates increased
progressively from S1 to S3, with the highest concentrations at S3, which coincided with the highest dissolved oxygen at the same site. This is further evidence of high mineralization of ON compounds, nutrient availability in the wastewater increased algal activity through active photosynthesis indicated by high DO at this site. Mara, (1992) and Kayombo et al. (2003) found that, algal concentration in waste stabilization ponds depend on nutrient loading, temperature and sunlight. Therefore, due to photosynthetic activities of these algae diurnal variation of DO is experienced in the facultative ponds of wastewater treatment plants increasing after sunrise (Kayombo et al., 2002). It has also been suggested that, the bio-uptake of IN by algae and their consequent sedimentation due to die offs, may largely influence ammonium and TN removal in WTP (Jia and Yuan, 2018). In this study at KSTW ammonia reduced progressively from S1 to S5 either through mineralization or sedimentation, while TN showed a significant removal between the input and effluent due to bio uptake, sedimentation or algal die offs.

The high organic-N at maturation pond 2 could be explained by semi processed N derived from previous stages of treatment or contribution from high algal biomass (Camargo et al., 2010). High ON indicates that the nature of suspended organic nitrogen in maturation ponds effluents is mainly contributed by algal biomass. Spellman (2014), Naidoo and Olaniran (2014) and Mara (2004) reported that organic-N and ammonium dominate other forms of nitrogen (nitrites and nitrates) in domestic wastewater treatment systems. Therefore, the oxidized N species of nitrate and nitrite are uncommon or present in minute concentrations (WEF, 2011), which was the case in this study at KSTW. In contrast, concentration of organic-N at effluent was about 4 mg/L which was higher than average concentration of 1 mg/L, reported by Pagilla et al. (2006). However, the average TN concentration obtained was within the acceptable values of 3-8 mg/L TN according to WEF (2011). Elsewhere, research conducted using bioassays and freshwater algae by Pehlivanoglu and Sedlak, (2004); Urgun-Demirtas et al. (2008) showed that up to 61% of organic-N in the effluents is, bio-available.

5.3.2 Phosphorus Dynamics and Removal in KSTW

The lowest TP values were observed at the raw influent owing to partial mineralization of the sewage reaching KSTW, but having a higher value of OP. Neutral pH has been reported to limit the solubility of phosphorus and subsequent precipitation resulting to most phosphorus remaining in water column hence inhibiting significant removal (Ford et al., 2001). On the other hand, elevated pH (above 8)
increases the solubility of metal phosphates however, phosphorus precipitates to metal ions at high pH values above 9 (Zimmo et al., 2003). In KSTW, the pH was largely neutral hence limiting P removal along the wastewater treatment pathway. The TN\TP ratio of 31:1 obtained in this study, would mean that P was limiting in the ponds (Guildford and Hecky, 2000) resulting to the low algal biomass in the maturation ponds.

Sedimentation and adsorption have been reported as another factor besides algal uptake for phosphorus removal, making it readily unavailable in water column (Kayombo et al., 2010). However, in KSTW system, presence of fish in the maturation ponds could have caused disturbance of the settled matter resulting to re-suspension of phosphorus to the water column from the sediments, consequently, lowering the net phosphorus removal from the wastewater. This possibility was further supported by a slight increase in TSS at S5 (outlet of maturation pond 3). Findings in the first maturation pond (S3) indicated a higher peak for dissolved oxygen, conductivity, nitrates and SRP than the other sites. This could be explained possibly by accumulation of fine sludge from sedimentation of the remnant suspended matter from secondary tank, since there was no routine de-sludging undertaken within KSTW for almost 10 years (Pers. com). There is a high possibility that accumulation of fine sludge over time could act as a nutrient or pollutant source. Other factors that have influence on the performance of maturation ponds are inflow, volume and surface area of the ponds (Faleschini et al., 2012).

5.3.3 Organic Matter Degradation in KSTW Wastewater Treatment Pathway

Generally, degradation and mineralization of organic matter along the KSTW treatment pathway resulted to the consistent decline of BOD$_5$ from S1 to S5. This can be attributed to increase in oxygen concentration from anaerobic conditions of S1 to improved oxygen levels in sites S2-S5. Increase in oxygen resulted to an enhanced organic matter breakdown by bacteria thus reducing the BOD$_5$ significantly in S5. However, there was a slight increase of BOD$_5$ at S4 which could be as a result of OM spike due high algal increase, caused by improved nutrient availability due to mineralization. Kaya, (2007) and Mara, (2004) suggested a possible increase in BOD in maturation pond due to production of algal biomass.

The highest TSS value, recorded at S1, is due to high organic load and suspended debris from the raw sewage despite screening and grit removal. The reduction in TSS between S4 and S5 can be
attributed to increased breakdown of organic matter by bacteria to readily available nutrients, substrate attachment and settling. The sedimentation of suspended matter may adsorb nutrients such as phosphorus which otherwise precipitates, thus becoming readily unavailable for biological uptake. Slight increase of TSS at S5, may be due to high algal productivity accelerated by readily mineralized available nutrients. Some studies in Dandora Sewage Plant, Kenya and other tropical developing countries have indicated that high-suspended solids in maturation ponds of sewage treatment are associated with presence of algae (Mara, 2004 and Kaya et al., 2007). Another possible phenomenon for TSS increase at KSTW could be the physical disturbance by fish in the maturation ponds. Also swimming birds and wild ducks frequenting these ponds may disturb water as they swim, thus creating a current which causes re-suspension of matter from the sediment. In addition, these stabilization ponds are shallow in depth which can easily be mixed by wind (Tebbutt, 1998; USEPA, 2011). Therefore, it is possible that increased TSS at maturation 3 (S5), could have been caused by water turbulence and wind action on the water column as water flows out of the pond (S5).

5.4 Nutrients and Organic Matter Removal Efficiencies of KSTW

High organic content and low nitrate concentration was observed at S1. These findings are similar to a research conducted by Mahapatra et al. (2013) which showed that influent (raw) sewage has low concentration of NO$_3$-N (0.2 mg/L) and NO$_2$-N due to low nitrification. Therefore, most of the influent consisted of hydrolysed ammonia. According to Faleschini et al. (2012), systems with higher organic load and algal productivity, NO$_3$ concentrations of greater than 10 mg/l have been recorded in the initial portion of the facultative lagoons, which was the same as concentrations found at site S3 (maturation pond 1) of KSTW. During this study, nitrates increased with increase in DO indicating favourable conditions for nitrification to take place, similar to results by Bodin, (2013) working in constructed wetlands. Similarly, nitrite nitrogen (NO$_2$-N) showed the lowest concentrations of all other N forms in KSTW. High nitrite concentration is closely associated with incomplete nitrification. As expected, the lowest concentration of nitrite nitrogen was recorded at S1, (0.01±0.00 mg/L) and highest at S3 (0.31±0.03 mg/L) (Figure 5a). However, this value was within the minimum discharge standards for nitrite allowed in Kenya (3mg/L) while, the mean nitrate concentration (10.6 mg/L) at KSTW was within the maximum effluent discharge limits in Kenya (10mg/L) by NEMA, 2006. However, at S5 (effluent) the nitrate concentration (12.5mg/L) was slightly above 10mg/L of the Kenya standards of discharge (Table 1) by NEMA, 2006
The findings of this study identify ammonia as the highest N form in KSTW, which contradicts Mahapatra, (2013) results who obtained ON as the most abundant N form in sewage. In current study ammonia dropped progressively from S1 to S5, which can be attributed to settling of organic part of sewage in tanks and subsequent degradation by microbes; including the effect of increase in oxygen concentration from S3. The same trend has been reported by Faleschini et al. (2012) who found out that drop in NH$_4^+$ along the treatment processes was associated with settling of particulate organic matter, higher microbial activity and the improved DO conditions in subsequent treatment stages. Methanotrophs that support nitrification have been reported to contribute to further ammonia removal in anaerobic conditions through denitrification (Valero et al., 2010). However, in this study, a non-significant relationship was observed between DO and ammonia, where probably other factors such as temperature may have played a greater role than DO in the NH$_4^+$ transformation at KSTW. This has been reported by Tuncsiper, (2007) who found that temperature was a more effective factor in NH$_4$ transformation than oxygen. The measured values for NH$_4$ did not exceed the allowable discharge standards (NEMA, 2006) which is 30 mg/L at the effluent, but exceeds the recommended limits of ammonia concentration for drinking water (1 mg/L) for USEPA (2011). The removal efficiencies for ammonia and TN were close to the results reported by Assunção and Von Sperling (2013) which showed 60 and 59% removal efficiencies respectively. Site S4 recorded the highest TN concentration which can be explained by a possible algal settling (immobilization) at the maturation pond bottom. The settled organics may further have been re-suspended diffusing back to water column as non-biodegradable fraction of N. Similar observation have been recorded in other studies (Mahapatra et al., 2011a, 2011b).

Several studies have suggested that phosphate removal, especially OP, were higher at the middle portions of the facultative pond, probably due to active mineralization followed by lowest values at the effluents of the maturation ponds. But the TP component can be higher at aerobic regions of maturation ponds (Mahapatra et al., 2013). However, during this study there was no significant removal of phosphorus (TP and SRP) in the system, which could probably be attributed to neutral pH which was evident throughout the system. Neutral pH inhibits P solubility; however, low pH results to release of P into the water column, which further increases its concentration (UNWater, 2015). It has also been reported that low TP removals are associated with wastewater treatment plants that do not practice enhanced biological phosphorus removal (WEF, 2011) same as the findings of this study. Craggs et al. (2012) reported fairly low removal efficiencies (<20%) for P
(especially OP) in WTP with low industrial effluent. The inorganic N and P exceeding the organic forms at effluent can be attributed to increased mineralization of the organic matter and release of nutrients in dissolved form within the KSTW before being released into CR. A research investigation on Dandora WTP (Wang, 2011) reported lower nutrient removal efficiencies (46%, and 36%, for NH$_3$-N, TN) than KSTW which registered above 50% efficiencies of NH$_4$ and TN.

The highest mean BOD$_5$ was 111.21±7.76 mg/L at the primary sedimentation tank (S1) with the lowest being 45.3±7.87 mg/L at the effluent site (S5) which is above the recommended effluent standards of 30mg/L in Kenya (NEMA, 2006). The mean TSS increased slightly at S5 (26.9 mg/L). The measured TSS values did not exceed the effluent discharge standards allowable in Kenya (30 mg/L) (NEMA, 2006). In a conventional WTP, the removal for BOD$_5$, TSS and TN have been reported as 80-95%, 70-80% and 20-30% respectively (Ahmed and Hazem 2001; Jung, 2006). The latter findings contradict the results of this study for BOD$_5$ (59%) and TN (54%) but consistent with TSS removal (85%).

Results obtained in this study showed low removal rates for nutrients (especially P), and high BOD$_5$ and TSS removal. These results were in consistence with similar findings reported by Mara, (2004) working in Dandora, Kenya. Camargo et al. (2010) suggested that the carbon fixation during algal growth may substantially cause a sharp rise in BOD and TSS concentrations in effluents of WTP. A rise in BOD$_5$ was clearly observed at maturation pond S4 in KSTW. This may be explained by increased bacterial activity which in turn increases with temperature. In this study, ammonia reduced along the treatment stages towards the effluent. NH$_4$-N, could have decreased due to increased nitrification in the maturation ponds as a result of improved oxygen and temperatures. On the other hand, increase in temperature to optimum (20-35°C), can accelerate DO availability hence conversion of ammonia to nitrates. This in turn reduce NH$_4$-N concentration in water, similar to findings reported in other studies such as by CCME, (2003).

There was a significant, negative correlation of DO with BOD$_5$ and TSS at KSTW, which can be explained by DO consumption by microbes as they degrade BOD and TSS during degradation of organic matter. Vymazal (1999) reported that microbial degradation significantly reduces DO in wastewater during decomposition processes. Buchari et al. (2001), also emphasized that a decrease in DO is directly related to increase in organic pollutants which consume it during decomposition.
5.5 The Impact of KSTW Effluent Input in Physical & Chemical Characteristics, Nutrient and Organic Matter on the Water Quality of Chania River

The discharge of effluent from KSTW into Chania River has potential impact on the ambient water quality characteristics of the River. The effluent if not treated well can result to increase in the nutrient concentrations and organic content that eventually alter the ecology and integrity of Chania River.

5.5.1 Influence of Physical Variables on the Chania River

Temperatures were slightly higher at the KSTW effluent recipient site (S8) than other river sites. Similar findings by Fu et al. (2009) and Zeilhofer et al. (2010), found out that wastewater have slightly higher temperatures than normal surface water. Within Chania River, there was a significant positive correlation of temperature with nitrites, SRP and TP meaning that as the temperatures increased degradation of organic matter by bacteria increased hence releasing more nutrients through mineralization (Truu et al., 2009).

Naturally, rivers have high dissolved oxygen, but it may vary depending on organic matter content in the water, temperature conditions and re-aeration processes (Effendi, 2003). During this study, the upstream site above KSTW effluent (S6) had lower water temperatures than downstream (Bhateria and Jain 2016). The lower temperatures in river water may also explain the slightly higher DO saturation at S6. As reported by Said et al. (2004), the colder the water the more oxygen it can hold and high DO increase pH in water. At the same time improved oxygen conditions enable bacteria to degrade organic matter thus releasing more nutrients. This is expected as saturation levels of oxygen decrease with increase in temperature (Von Sperling, 2007).

The highest conductivity was recorded at S8 in CR which could be explained by the input of ions by the effluent discharged from KSTW at this site. The increased dissolved ion concentration is mainly from organic and nutrient mineralization of the wastewater within the treatment plant. It is evident that although KSTW was slightly efficient in organic matter breakdown and nutrients removal but, the effluent had more dissolved inorganic nutrients which were discharged into CR thus spiking the conductivity at S8. Similar results were obtained by Bhateria and Jain, (2016). They noted that nutrient input significantly increases conductivity in rivers. Gupta and Paul (2010)
on the other hand explained that geological characteristics of the catchment may more influence river conductivity.

There was a slight increase in pH below the discharge site (S9). The spike in ionic concentration upstream could have altered bicarbonate buffer equilibrium of the river physico-chemical conditions or due to enhanced periphyton photosynthetic activities resulting to more oxygen in river water (Adey et al., 2013; Makaya, 2010). Another explanation for the higher pH could be water flow turbulence which enhances re-aeration of the water in the river. Bhateria and Jain, (2016) suggested that re-aeration of water would increase DO resulting to elevate pH similar to results obtained in site S9 in this study. Site S9 (plate 2) was a shallow site with fairly exposed rock substrate conducive for periphyton growth. Periphyton grow on wet rocky substrate such as S9 site of Chania River, produce oxygen through photosynthesis raising the pH. Similarly, a negative strong correlation was found between pH and ammonia that was attributed to increase in pH that transforms ionized NH$_4^+$ to non-ionized-NH$_3$ as reported by Camargo and Alonso, (2006).

5.5.2 Influence of Effluent from KSTW on Nutrients Loading in Chania River
There was a sharp rise (spike) for all the N components (TN, NH$_4$, NO$_3$ and NO$_2$) at S8, which could be explained by the effect of effluent discharge from KSTW plant into Chania River. Based on results obtained in this study, there was low removal of inorganic-N in CR especially nitrite and nitrate. This means higher loading N at the effluent site, implies the KSTW plant was a source rather than a sink of inorganic N. The KSTW effluent discharged into CR added more nutrients in both particulate and dissolved form. A relationship between river flow discharge and variation in nutrient concentrations has been observed in many studies (OEPA, 2016). In this study there was evident that nutrient and organic matter loading increased at effluent point/confluence and after the effluent in CR. Airsien et al. (2003) explained that the presence of high ammonia in surface waters may suggest untreated or partially treated sewage input into a water body. The nitrite concentrations in CR were within the range (0.001 to 0.06 mg/L) reported for natural waters according to the Canadian Council of Resources and Environment Ministers (Swer et al., 2004) and Kenya NEMA, 2006 as indicated in Table 1 above.

High nitrate concentrations in river systems have been associated with high human activities in a given area. In Chania River ON was the most abundant nitrogen form. Findings obtained in this
study are similar to those reported elsewhere, where ON was most dominant Nitrogen fraction in Yangtze River (Chai et al., 2009). Despite point sources of sewage input being a continuous source of pollution of surface waters, surface runoff may constitute a seasonal and a significant pollution source (Bhardwaj et al., 2010) especially during the rainy season. Site S6 upstream the KSTW effluent input site, had the lowest concentration of nutrients compared to other sites in CR. However, the low TN/TSS ratio suggests that there was a higher N yields from CR catchment. Similar findings have been reported by Hecky et al. (2003) and LVEMP, (2005) working in Lake Victoria basin rivers of Kenya, Uganda and Tanzania. Nitrate was the most dominant (>50%) of the inorganic nitrogen (IN) species at all sites, inferring that nitrification process was active in CR. The high inorganic-N in CR after effluent may clearly shows that, the effluent from KSTW was contributing nutrient input into the river through direct effluent or indirect ground seepage of wastewater resulting to more dissolved-N into Chania River. Von Sperling, (2007) observed that sewage contributes much higher N and P in rivers than other sources of urban pollutants.

Decrease in nutrient concentrations emanating from a point source could be attributed to dilution of the effluent by the stream water, hence reducing the pollutants concentrations in the River (Ling et al., 2016). As it was the case in Chania River, Ammonium-N showed a considerable decrease in concentration after effluent (S8) progressing downstream in site S9 and S10. However, loading for TSS and inorganic nutrient species increased downstream. This could indicate presence of another point or non-point source of nutrients into the river apart from KSTW. Suspended particles have been found to have a considerably large proportion of nutrients. For example, Chen (2012) found out that suspended particles could easily adsorb NH₄-N resulting to higher Ammonium-N proportion in TN. The high suspended solids recorded in S8 coincided with high dissolved nitrogen forms contributed by effluent from the KSTW effluent into the river.

Coleman and Niekerk, (2007); Environment Canada, (2014), reported that high concentration of phosphate in rivers could give an indication of nutrient pollution that could lead to eutrophication especially in receiving waters. In Chania River, OP was the dominating P derivative, which recorded more than 50% in most cases, while SRP had 20-47% proportion in various sites; with site S8 recording the highest and lowest at S10. The results from this study compare with a study in Huanghe River where Particulate-P was between 60-99% of the total P (Liu, 2015).
5.5.3 Influence of Nutrient and Organic Loading and its Dynamics on River Chania

Notably, there was removal of TN, ammonia, BOD$_5$ and TP after S8, but loading of nutrients in Chania River indicated an increase of nitrites, nitrate and SRP after effluent discharge (S8). The decrease of nutrients particularly TP, TN and organic loads as BOD$_5$ in CR after the effluent point could be as a result of river dilution, biological degradation and mixing. On the other hand, increase in pollutant loading in rivers can be explained by upsurge in effluent coupled with in-stream or catchment nutrient characteristics (McLeod et al., 2006). For instance, Nzoia river in Kenya recorded massive loads of TN, TP and TSS amounting to 5,414, 844 and 678,110 tons /year respectively, while North Awach River loads of the same parameters are 48, 7 and 6,938 respectively (LVEMP, 2005). Research has shown that increased nutrient loads from the Yangtze River had led to increased harmful algal bloom (Li et al., 2014).

As noted in site S9 to S10 load of nitrite decreased slightly after a spike increase between S8-S9, which could be due to dilution downstream, bio-uptake or adsorption into the sediment. In a study by Bowes, (2005) a negative correlation of nitrites with discharge was observed especially if there was excess input of effluent particularly during river base flow. Christensen et al. (2011) noted that, besides domestic sewage, human related activities such as agriculture and settlements are the major sources of pollution in rivers. For instance, along the CR banks, small scale vegetable farms were observed, near site S9 which could be applying fertilizers or organic manure. This could be a possible nonpoint source of nutrients such as nitrate into the river (Reutter, 2003).

The mean concentration of BOD$_5$ across the sites in Chania River was 8 mg/L which is categorized as doubtful river water quality according to Klein (1962) classification. Highest BOD load was recorded at S8 that originated from effluent at S5, however, a decrease in BOD$_5$ load from S8 downstream recorded in CR could be due to degradation of organic matter downstream. A high BOD in surface water results to DO depletion which in turn affects the water quality, self-purification ability of the river and eventually oxygen stress to aquatic organisms (Bhateria and Jain, 2016). BOD$_5$, Organic matter and TSS are closely related water parameters for example, high organic content leads to a higher BOD due to high oxygen demand. Similarly, high organic content originating from point or diffuse (catchment) sources increase TSS in the water. In this study, TSS loading increased consistently downstream of S8 towards S9 and S10 that could be explained by point and diffuse sources, suggesting pollution from catchment and nearby riparian zone. High
TSS in rivers is associated with nutrients loading and organic input (Wen et al., 2017). High TN increases after point source indicates an input from human activities in the catchment. Systems with low BOD₅/TN ratio, infers that denitrification process is highly impaired (Winkler, 2012). A study conducted in rivers in Indonesia (Ciambulawung River Effendi et al., 2016) recorded BOD between 1.54 - 3.84 mg/L, which was relatively lower compared to obtained in 6 mg/L Chania River in this study. A low BOD (below 5 mg/L) content in water is an indicator of reduced organic pollution or input in the river (Saksena et al., 2008). Malaj et al. (2014) identified wastewater or effluents from WTP and livestock farming as the main sources of organic pollution in rivers.

5.5.4 Self-purification Process in River Chania

In this study Chania River was able to recover downstream from the increased pollutant concentration and loads at S8, but other parameters (TSS, SRP, NO₂, and NO₃) indicated inconsistent fluctuations at different sites. A number of studies have observed that pollution of rivers at point sources like sewage plants effluents, have an impact at downstream reaches of rivers resulting in undesirable effects such as eutrophication. For instance, Chen et al. (2013) suggested that increased nutrient loads promote excess algal blooms in rivers. The impact of the pollutants as it is being transported downstream can affect the river ecosystem by reducing the DO concentration needed for biological processes, impairment of the biotic integrity and aesthetic value of the river. Nevertheless, the water quality of the river, survival of aquatic organisms and human livelihoods who depend on the river ecosystem services are affected mainly by odor, taste and increased cost for treating and improving the polluted river water. The level of these impacts depends on the bio-ecological interactions of the river as well as the hydrological regime. For example, Nutrient concentrations in River Isiukhu in Western Kenya fluctuated with changes in the amount of rainfall received in the catchment. High nutrient levels occurred during the rainy seasons and vice versa (Onyando et al., 2016).

Diminishing waste loads and degradation of pollutants downstream of point source (S8) in CR is attributed to stream water dilution, physical and biological processes (bacterial action) as mixing and re-aeration that provides required DO by microbes for organic matter degradation. McDonald et al. (2011) suggested that, river dilution bring about river self-purification. However, this phenomenon may be affected by global warming hence climate change especially in areas that experience prolonged dry weather. Water abstraction from rivers is a significant activity that may
affect river dilution capacity and consequently influence river self-purification processes. For instance, a study, in China’s Huanghe River, findings showed that low water discharge correlated positively to low nutrients loading in streams (Fekete et al., 2010).
CHAPTER SIX
CONCLUSION AND RECOMMENDATIONS

6.1 Conclusions
From objective 1 this study concluded that there was significant variation of physico chemical parameters across the sites in KSTW. In contrast, pH did not show significant variation among the sites. Nitrogen showed significant variation across the sites with most of nitrogen being removed in form of organic nitrogen. However, phosphorus did not show significant variation in the sites sampled. In Chania River, physico-chemical parameters varied across the sites of Chania River. Both nutrient and organic matter loadings increased after the KSTW effluent discharge into the river. The highest TSS loading was from diffuse sources compared to point source because TSS increased further downstream in sites below the effluent. There was more of organic nutrient loading from the river than the inorganic portion. Therefore, the null hypothesis there are no significant variations in physico-chemical variables within KSTW and at selected sites along Chania River before and after effluent discharge is rejected in this study.

From objective 2 this study concluded that, there was significant removal efficiency of nutrients and organic matter in KSTW. There was a high removal efficiency of nitrogen with low and variable removal efficiencies of phosphorus, nitrates and nitrites at the different treatment stages. However, there was a high BOD5 and TSS removal efficiency. Therefore, Kangemi Sewage Treatment Works was efficient in removal of TN, NH4-N and organic matter (BOD and TSS). However, KSTW was inefficient in removal of nitrite, nitrate and phosphorus. Hence, the second null hypothesis that states there are no significant differences in the removal of N and organic matter at different treatment stages within Kangemi Sewage Treatment Works is rejected in this study.

From this study it’s clear that there was significant difference in loading of nutrients and organic matter between sedimentation tank influent (S1) and the effluent of KSTW (S5). There was a general decrease in loading of nitrogen derivatives at the effluent of KSTW into the river. However, Nitrite loading decreased by half in CR after the effluent input. There was an increase in loading into the CR at the effluent point compared to upstream before effluent point which further reduced downstream after the effluent except for TSS which increased downstream after the effluent.
Therefore, the hypothesis that there is no significant difference in loading of N, P and organic matter at the Kangemi Sewage Treatment Works and Chania River is rejected.

6.2 Recommendations

For objective 1 and conclusion 1, it is recommended that, there is need for a longer period of data collection in order to clearly define the variations and water quality of Chania River both at spatial and temporal scales. This will enable the understanding of the contribution of pollutants from the point and non-point sources and their dynamics at different seasons and flows. Thus, regular monitoring and maintenance of KSTW and wastewater quality might improve and minimise the Chania Rivers pollutant loading.

For objective 2 and conclusion 2, it is recommended that, there is need for regular maintenance of the existing sewage treatment facilities to be focused to sustain their effectiveness. For the KSTW management it is important to integrate technologies such as Enhanced Biological Phosphorus Removal (EBPR), which should be adopted to make the system more effective in P removal. Similarly, regular desludging of maturation ponds should be done to improve the effectiveness of KSTW in nutrient organic matter removal.

For objective 3 and conclusion 3, it is recommended that, enforcement of national standards for wastewater to preserve environment and livelihoods which will ensure acceptable limits is discharged into the river to protect and conserve river water quality. Furthermore, data collection should form part of the system management strategies to promote effective monitoring and water quality control enhancing Goal 6 of SDGs. Riparian buffer should be restored and controlled farming activities near the Chania River banks, that could be contributing to TSS and inorganic nutrient loading downstream of effluent. Research should be done to identify possible sources and activities contributing to increased TSS in the stretch of Chania River.
REFERENCES


Bakare, A., Lateef, A., Amuda, O.S. and Afolabi, R.O. (2003). The Aquatic toxicity and characterization of chemical and microbiological constituents of water samples from Ob-


Dunne, E., Coveney, M., Marzolf, E., Hoge, V., Conrow, R., Naleway, R., Lowe, E., Battoe, L. and Inglett, P. (2013). Nitrogen dynamics of a large-scale constructed wetland used to


Feliciano, S., Florigna, N. and Mengsteab, H. (2009). “Waste Management in Developing Countries”. City and Regional Planning, California State University, San Luis Obispo. C.A


water engineers and suppliers, Environmental Protection Agencies and all those organizations involved in water quality monitoring (1st Edition). pp.43.


79


APPENDICES

Appendix 1: A map showing the Chania River Catchment, KSTW, and their location in Nyeri County (Kenya) Dataset Source: DEM (srtm.cgiar.org) - Prepared with QGIS by author 2019

Appendix 2: Photos showing selected nutrients a) nitrates, b) ammonium, c) nitrites samples before reading with d) spectrometer in the Egerton University, LWM Water Quality Laboratory and selected sites e) sludge drying beds and f) low rate trickling filter within KSTW.
Appendix 3: Pairwise Comparison (Kruskal Wallis, P=0.05) of selected Nutrients & OM for KSTW sites

Pairwise Comparisons of SITES

**Ammonia: KSTW**

<table>
<thead>
<tr>
<th>SITE</th>
<th>Test Statistic</th>
<th>Std. Error</th>
<th>Std. Test Statistic</th>
<th>Sig.</th>
<th>Adj. Sig.</th>
</tr>
</thead>
<tbody>
<tr>
<td>S5-S4</td>
<td>18.611</td>
<td>8.708</td>
<td>2.137</td>
<td>.033</td>
<td>.489</td>
</tr>
<tr>
<td>S5-S2</td>
<td>28.611</td>
<td>8.708</td>
<td>3.286</td>
<td>.001</td>
<td>.015</td>
</tr>
<tr>
<td>S5-S3</td>
<td>29.000</td>
<td>8.708</td>
<td>3.330</td>
<td>.001</td>
<td>.013</td>
</tr>
<tr>
<td>S5-S1</td>
<td>35.083</td>
<td>8.708</td>
<td>3.799</td>
<td>.000</td>
<td>.002</td>
</tr>
<tr>
<td>S4-S2</td>
<td>10.000</td>
<td>8.708</td>
<td>1.148</td>
<td>.251</td>
<td>1.000</td>
</tr>
<tr>
<td>S4-S3</td>
<td>10.389</td>
<td>8.708</td>
<td>1.193</td>
<td>.233</td>
<td>1.000</td>
</tr>
<tr>
<td>S4-S1</td>
<td>14.472</td>
<td>8.708</td>
<td>1.662</td>
<td>.097</td>
<td>1.000</td>
</tr>
<tr>
<td>S2-S3</td>
<td>-.389</td>
<td>8.708</td>
<td>-.045</td>
<td>.964</td>
<td>1.000</td>
</tr>
<tr>
<td>S2-S1</td>
<td>4.472</td>
<td>8.708</td>
<td>.514</td>
<td>.608</td>
<td>1.000</td>
</tr>
<tr>
<td>S3-S1</td>
<td>4.083</td>
<td>8.708</td>
<td>.469</td>
<td>.639</td>
<td>1.000</td>
</tr>
</tbody>
</table>

Pairwise Comparisons of SITES

**TSS: KSTW**

<table>
<thead>
<tr>
<th>SITE</th>
<th>Test Statistic</th>
<th>Std. Error</th>
<th>Std. Test Statistic</th>
<th>Sig.</th>
<th>Adj. Sig.</th>
</tr>
</thead>
<tbody>
<tr>
<td>S4-S3</td>
<td>6.375</td>
<td>7.057</td>
<td>.903</td>
<td>.366</td>
<td>1.000</td>
</tr>
<tr>
<td>S4-S2</td>
<td>9.833</td>
<td>7.057</td>
<td>1.393</td>
<td>.164</td>
<td>1.000</td>
</tr>
<tr>
<td>S4-S5</td>
<td>-10.625</td>
<td>7.057</td>
<td>-1.506</td>
<td>.132</td>
<td>1.000</td>
</tr>
<tr>
<td>S4-S1</td>
<td>36.708</td>
<td>7.057</td>
<td>5.202</td>
<td>.000</td>
<td>.000</td>
</tr>
<tr>
<td>S3-S2</td>
<td>3.458</td>
<td>7.057</td>
<td>.490</td>
<td>.624</td>
<td>1.000</td>
</tr>
<tr>
<td>S3-S5</td>
<td>-4.250</td>
<td>7.057</td>
<td>-.602</td>
<td>.547</td>
<td>1.000</td>
</tr>
<tr>
<td>S3-S1</td>
<td>30.333</td>
<td>7.057</td>
<td>4.298</td>
<td>.000</td>
<td>.000</td>
</tr>
<tr>
<td>S2-S5</td>
<td>-7.92</td>
<td>7.057</td>
<td>-1.12</td>
<td>.911</td>
<td>1.000</td>
</tr>
<tr>
<td>S2-S1</td>
<td>26.875</td>
<td>7.057</td>
<td>3.808</td>
<td>.000</td>
<td>.002</td>
</tr>
<tr>
<td>S5-S1</td>
<td>26.083</td>
<td>7.057</td>
<td>3.696</td>
<td>.000</td>
<td>.003</td>
</tr>
</tbody>
</table>

TSS was significantly in S1 and all other sites in KSTW
**BODs: KSTW**

Pairwise Comparisons of SITES

<table>
<thead>
<tr>
<th>SITE</th>
<th>Test Statistic</th>
<th>Std. Error</th>
<th>Std. Test Statistic</th>
<th>Sig.</th>
<th>Adj. Sig.</th>
</tr>
</thead>
<tbody>
<tr>
<td>S5-S4</td>
<td>4.944</td>
<td>8.708</td>
<td>.568</td>
<td>.570</td>
<td>1.000</td>
</tr>
<tr>
<td>S5-S3</td>
<td>7.583</td>
<td>8.708</td>
<td>.871</td>
<td>.384</td>
<td>1.000</td>
</tr>
<tr>
<td>S5-S2</td>
<td>20.528</td>
<td>8.708</td>
<td>2.357</td>
<td>.018</td>
<td>.276</td>
</tr>
<tr>
<td>S5-S1</td>
<td>39.167</td>
<td>8.708</td>
<td>4.498</td>
<td>.000</td>
<td>1.000</td>
</tr>
<tr>
<td>S4-S3</td>
<td>2.639</td>
<td>8.708</td>
<td>.303</td>
<td>.762</td>
<td>1.000</td>
</tr>
<tr>
<td>S4-S2</td>
<td>15.583</td>
<td>8.708</td>
<td>1.790</td>
<td>.074</td>
<td>1.000</td>
</tr>
<tr>
<td>S4-S1</td>
<td>34.222</td>
<td>8.708</td>
<td>3.930</td>
<td>.000</td>
<td>.001</td>
</tr>
<tr>
<td>S3-S2</td>
<td>12.944</td>
<td>8.708</td>
<td>1.487</td>
<td>.137</td>
<td>1.000</td>
</tr>
<tr>
<td>S3-S1</td>
<td>31.583</td>
<td>8.708</td>
<td>3.627</td>
<td>.000</td>
<td>1.000</td>
</tr>
<tr>
<td>S2-S1</td>
<td>18.639</td>
<td>8.708</td>
<td>2.141</td>
<td>.032</td>
<td>.485</td>
</tr>
</tbody>
</table>

BODs was significantly in S1 and all other sites in KSTW. Site S2 was also significantly different from S5.

**Appendix 4:** Pairwise Comparison (Kruskal Wallis, P=0.05) of selected Nutrients & OM for CR sites

**Ammonia: Chania River**

Pairwise Comparisons of SITES

<table>
<thead>
<tr>
<th>SITE</th>
<th>Test Statistic</th>
<th>Std. Error</th>
<th>Std. Test Statistic</th>
<th>Sig.</th>
<th>Adj. Sig.</th>
</tr>
</thead>
<tbody>
<tr>
<td>S10-S9</td>
<td>-3.306</td>
<td>8.706</td>
<td>-.380</td>
<td>.704</td>
<td>1.000</td>
</tr>
<tr>
<td>S10-S6</td>
<td>-3.667</td>
<td>8.706</td>
<td>-.421</td>
<td>.674</td>
<td>1.000</td>
</tr>
<tr>
<td>S10-S7</td>
<td>-3.917</td>
<td>8.706</td>
<td>-.450</td>
<td>.653</td>
<td>1.000</td>
</tr>
<tr>
<td>S10-S8</td>
<td>-28.417</td>
<td>8.706</td>
<td>-3.264</td>
<td>.001</td>
<td>.011</td>
</tr>
<tr>
<td>S9-S6</td>
<td>.361</td>
<td>8.706</td>
<td>.041</td>
<td>.967</td>
<td>1.000</td>
</tr>
<tr>
<td>S9-S7</td>
<td>.611</td>
<td>8.706</td>
<td>.070</td>
<td>.944</td>
<td>1.000</td>
</tr>
<tr>
<td>S9-S8</td>
<td>25.111</td>
<td>8.706</td>
<td>2.884</td>
<td>.004</td>
<td>.039</td>
</tr>
<tr>
<td>S6-S7</td>
<td>-.250</td>
<td>8.706</td>
<td>-.029</td>
<td>.977</td>
<td>1.000</td>
</tr>
<tr>
<td>S6-S8</td>
<td>-24.750</td>
<td>8.706</td>
<td>-2.843</td>
<td>.004</td>
<td>.045</td>
</tr>
<tr>
<td>S7-S8</td>
<td>-24.500</td>
<td>8.706</td>
<td>-2.814</td>
<td>.005</td>
<td>.049</td>
</tr>
</tbody>
</table>

For Ammonia in Chania River, site S8 statistically significant different from all the other site in Chania.
**BOD<sub>5</sub>: Chania River**

Pairwise Comparisons of SITES

<table>
<thead>
<tr>
<th>SITE</th>
<th>Test Statistic</th>
<th>Std. Error</th>
<th>Std. Test Statistic</th>
<th>Sig.</th>
<th>Adj. Sig. &lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>S10-S7</td>
<td>-.528</td>
<td>8.708</td>
<td>-.061</td>
<td>.952</td>
<td>1.000</td>
</tr>
<tr>
<td>S10-S6</td>
<td>-6.833</td>
<td>8.708</td>
<td>-.785</td>
<td>.433</td>
<td>1.000</td>
</tr>
<tr>
<td>S10-S9</td>
<td>-7.889</td>
<td>8.708</td>
<td>-.906</td>
<td>.365</td>
<td>1.000</td>
</tr>
<tr>
<td>S10-S8</td>
<td>-40.167</td>
<td>8.708</td>
<td>-4.613</td>
<td>.000</td>
<td>.000</td>
</tr>
<tr>
<td>S7-S6</td>
<td>6.306</td>
<td>8.708</td>
<td>.724</td>
<td>.469</td>
<td>1.000</td>
</tr>
<tr>
<td>S7-S9</td>
<td>-7.361</td>
<td>8.708</td>
<td>-.845</td>
<td>.398</td>
<td>1.000</td>
</tr>
<tr>
<td>S7-S8</td>
<td>-39.639</td>
<td>8.708</td>
<td>-4.552</td>
<td>.000</td>
<td>.000</td>
</tr>
<tr>
<td>S6-S9</td>
<td>-1.056</td>
<td>8.708</td>
<td>-.121</td>
<td>.904</td>
<td>1.000</td>
</tr>
<tr>
<td>S6-S8</td>
<td>-33.333</td>
<td>8.708</td>
<td>-3.828</td>
<td>.000</td>
<td>.001</td>
</tr>
<tr>
<td>S9-S8</td>
<td>32.278</td>
<td>8.708</td>
<td>3.707</td>
<td>.000</td>
<td>.002</td>
</tr>
</tbody>
</table>

For BOD<sub>5</sub> in Chania River, there was a significant different between site S8 and all the other site in Chania.

**TN: Chania River**

Pairwise Comparisons of SITE

<table>
<thead>
<tr>
<th>SITE</th>
<th>Test Statistic</th>
<th>Std. Error</th>
<th>Std. Test Statistic</th>
<th>Sig.</th>
<th>Adj. Sig. &lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>S10-S6</td>
<td>-13.750</td>
<td>9.174</td>
<td>-1.499</td>
<td>.134</td>
<td>1.000</td>
</tr>
<tr>
<td>S10-S7</td>
<td>-16.825</td>
<td>9.174</td>
<td>-1.834</td>
<td>.067</td>
<td>1.000</td>
</tr>
<tr>
<td>S10-S9</td>
<td>-25.100</td>
<td>9.174</td>
<td>-2.736</td>
<td>.006</td>
<td>.093</td>
</tr>
<tr>
<td>S10-S8</td>
<td>-41.075</td>
<td>9.174</td>
<td>-4.478</td>
<td>.000</td>
<td>.000</td>
</tr>
<tr>
<td>S6-S7</td>
<td>-3.075</td>
<td>9.174</td>
<td>-.335</td>
<td>.737</td>
<td>1.000</td>
</tr>
<tr>
<td>S6-S9</td>
<td>-11.350</td>
<td>9.174</td>
<td>-1.237</td>
<td>.216</td>
<td>1.000</td>
</tr>
<tr>
<td>S6-S8</td>
<td>-27.325</td>
<td>9.174</td>
<td>-2.979</td>
<td>.003</td>
<td>.043</td>
</tr>
<tr>
<td>S7-S9</td>
<td>-8.275</td>
<td>9.174</td>
<td>-.902</td>
<td>.367</td>
<td>1.000</td>
</tr>
<tr>
<td>S9-S8</td>
<td>15.975</td>
<td>9.174</td>
<td>1.741</td>
<td>.082</td>
<td>1.000</td>
</tr>
</tbody>
</table>

For TN in Chania River, there was a significant different between site S8 and sites 6, 7, 10. There was also a significant difference between S9 and S10 in Chania.