Surface Water Quality Assessment around Chania Catchment in Kenya and Determination of Metal Concentrations by TXRF Technique

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Abstract: Surface waters are prone to pollution especially from agriculture and other anthropogenic activities hence the need to establish the levels of pollution. This present work focuses on Chania catchment situated on the lower side of the Aberdares water tower of Kenya that supplies 95% of water to the capital Nairobi. The aim of this study was to determine the physico-chemical and microbial quality of surface water in the catchment and also establish the water quality after treatment during the wet and dry seasons. Water samples were randomly collected in triplicate from five strategic locations and analysed for heavy metals by Total-Reflection X-Ray Fluorescence (TXRF) Spectroscopy. Other water quality parameters tested include chloride, sodium, nitrates, phosphates, EC, pH, turbidity, TDS and Total Coliforms. The microbiological quality of the raw surface water was found to contain a high number microbial indicator counts implying that the water is not suitable for drinking without treatment. Generally, most of the physico-chemical parameters were within the allowable WHO recommended maximum contaminant levels (MCL) with the exception of wet season where water samples had values of turbidity higher than WHO guideline values. Results of heavy metal analysis revealed that surface water in some sampling points was polluted with Manganese, Iron, Nickel and Lead above WHO recommended levels with Thika River sampling point having higher levels of metal pollutants.

Keywords: Pollution, Physico-Chemical, Water Quality

1. Introduction

Before water can be described as potable it has to comply with certain physical, chemical and microbiological standards which are designed to ensure that the water is palatable and safe for drinking [1]. Nearly half of all people in developing countries have infections or diseases associated with inadequate water supply and sanitation [2]. It is estimated that 80% of all diseases and over one third of deaths in developing countries are caused by the consumption of contaminated water [3]. Source water quality is the primary driving factor in determining the level of treatment process sophistication necessary to achieve drinking water standards and goals. More degraded raw water quality can lead to higher capital costs to achieve treatment objectives, particularly as driven by the need to design for worst case water quality events [4]. Agriculture is the single largest user of freshwater resources, using a global average of 70% of all surface water supplies and is also a cause of water pollution through its discharge of pollutants and sediment to surface or groundwater, through net loss of soil by poor agricultural practices [5].

Kenya is classified by the United Nations as a chronically water-scarce country with an annual freshwater supply of about 647 m³ per capita, which is significantly below the 1000 m³ per capita set as the marker for water scarcity [6]. The same is characterized by high spatial and temporal variability and extremes of drought and floods. Catchment degradation is a major problem, which is undermining the limited sustainable water resources base in the country. The main causes of catchment degradation are poor farming methods, population pressure and deforestation [7].

Chania Catchment is characterized by steep hill sides and areas of wetlands that have been converted to agriculture, removing areas where runoff water and sediment would be stored and filtered naturally. As a result, run off and resultant flow of sediments into rivers and reservoirs is becoming a serious problem and increasing the costs for water treatment. Today, 60% of Nairobi’s residents are water insecure and the challenges to water security will likely grow as climate change brings increasingly unpredictable rainfall [8]. According to Nairobi City Water and Sewerage Company Limited strategic plan 2014/15 – 2018/19, Ng’ethu Water Works supplies water to Nairobi City County (NCC) and accounts for about 440,000 m³/day (85%) of all potable water supplied to the city [9]. Raw water is abstracted from Chania, Kiamu and Kimakia rivers and if this meets Ng’ethu water works demand, Thika reservoir (whose main feeder river is Thika River) is left to re-charge and only supplies water during the dry season when river water levels are low. Ng’ethu water works is a conventional water treatment that utilizes the sequential use of coagulation, flocculation, sedimentation, filtration, and disinfection. The water filtration is by rapid gravity sand filtration which is mechanical and does not employ adsorptive media such as
use of powdered activated carbon (PAC) or granular activated carbon (GAC) as a filter media at any stage. Currently there are no other technologies for the removal other pollutants being employed.

2. Methodology

2.1 Study Area

The study focuses on Chania, a Sub-catchment of the larger Upper-Tana catchment basin of Aberdare mountain ranges central Kenya. The rivers of interest are Chania and Thika River - which is the main recharge river for Thika Reservoir.

![Figure 1: Map – Upper Tana Catchment (Water Fund Business Case – [8].)](image)

The catchment is mainly agricultural, characterized by steep hillsides with tea as main crop and areas of wetlands that have been converted to agriculture.

2.2 Water Sampling & Preservation

Grab water samples were collected randomly in pre-cleaned plastic bottles in triplicates using 500 ml plastic sampling bottles which were thoroughly cleaned by washing in non-ionized detergent and rinsed with tap water and soaked in 10% HNO₃ for 24hrs and finally rinsed with de-ionized water prior to use. Water samples were collected from five strategic locations identified (table 1) in the study area during the wet and dry seasons of Oct – Dec 2015 and Jan – Feb 2016 respectively. A well-mixed sample was taken at least 10 cm below the water surface and away from the river edge. Water Samples for free residual chlorine were kept out of direct sunlight and analysis done within 10 minutes of sample collection. Water samples for microbiological analysis were preserved and stored on ice between 1°C and 4°C in a sterile plastic container within 5 minutes of collection with samples holding time of 6 hours +2 hours for lab processing. For treated water (with residual chlorine), 0.1mL of a 10% sodium thiosulfate (Na₂S₂O₃) solution was added to dechlorinate and neutralize residual halogen within the sample water and the bottles were filled leaving approximately 2.5 cm head space. Overall, care was exercised to ensure that the samples were representative of the actual water composition.

![Table 1: Samples collection sites](image)

<table>
<thead>
<tr>
<th>Sampling Point</th>
<th>TD</th>
<th>Coordinates-UTM ARC 1960 Zone 37S (Northing – Easting)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chania river (Mataara bridge)</td>
<td>A</td>
<td>9906122 - 255153</td>
</tr>
<tr>
<td>Thika river (feeder river to Thika Dam)</td>
<td>B</td>
<td>9911184 - 256230</td>
</tr>
<tr>
<td>Thika reservoir discharge(Kiama tunnel)</td>
<td>C</td>
<td>9908349 - 258909</td>
</tr>
<tr>
<td>Inflow to Ng’ethu Water works</td>
<td>D</td>
<td>9898032 - 266406</td>
</tr>
<tr>
<td>Treated water from plant (clear well)</td>
<td>E</td>
<td>9897855 - 266642</td>
</tr>
</tbody>
</table>

2.3 Water Quality Variables Analysis

The samples were analysed for heavy metals by Total-Reflection X-Ray Fluorescence (TXRF) Spectroscopy using S2 PICOFOX Spectrometer with Gallium as internal standard for elemental quantification. Heavy metals (Lead [Pb], Iron [Fe], Manganese [Mn], Chromium [Cr], Nickel [Ni], Titanium[Ti], Potassium [K], Calcium[Ca], Copper [Cu] and Zine [Zn]. Analysis for aluminium was carried out by Flame Atomic absorption Spectrometry (ASS). Portable TDS meter (TDS Meter 3-Hm Digital), Portable Electrical Conductivity meter (Lovibond SensoDirect Con200), Bench Top Turbidimeter (HACH 2100N) and Bench Top pH meter (HANNA HI 2211) were used after calibration to measure Total Dissolved Solids, Electrical Conductivity, Turbidity, and pH respectively immediately after sampling. Nitrates, Phosphates and chloride ions were analysed by spectrophotometry method according to the standard methods for the examination of Water and waste water (APHA, 1999) using UV-1800 UV-VIS Spectrophotometer (SHIMADZU) with 1 cm matched quartz cells. The microbiological quality of water was analyzed for Indicator micro-organisms *Escherichia coli* and Total Coliforms and using the standard method for analysis of water and waste water [10]. Free Residual Chlorine was determined by DPD Colorimetric method using Color Disc Test Kit (Lovibond® Comparator 2000º). The analytical data was subjected to statistical tests of significance using t-test (P<0.05) to determine whether there was any significant difference between the dry and wet seasons.

2.4 Data processing and analysis

The data collected were statistically analyzed using Microsoft Office Excel 2013. The values obtained observations were expressed as means and the standard deviation calculated. This was then subjected to statistical tests of significance where paired t-test was used to establish whether there existed any significant difference between concentration levels of various physico-chemical water quality parameters and heavy metal pollutants during the dry and wet seasons at the different sampling locations. A 95% confidence level (P<0.05) was considered statistically significant.
3. Results

Water samples from the sampling points in Chania Subcatchment were analysed for below mentioned parameters during the wet (Oct – Dec 2015) and dry (Feb – March 2016) seasons. The mean values of the various parameters were computed as shown in table 3 & 4 below and inferential statistical data analysis conducted.

The results showed that turbidity levels were above the recommended levels in the catchment during the wet season. However, during the dry season only Chania River recorded slightly higher levels above recommended standard. The highest mean turbidity was 107.89±5.85 NTU recorded during the wet season at Chania River sampling point. The turbidity levels were high during the wet season and this could be attributed to run – off water that erodes soils in farms, earth roads drainage and also emanating from quarry masonry stone sites. Turbidity levels in the Catchment Rivers ranged from 2.84 NTU– 7.70 NTU during the dry season and 33.00 NTU to 181.00NTU during the wet season. The high levels of turbidity during the wet season are attributed to high run-off with increased soil erosion. The turbidity levels at the storage facility in both wet and dry season were below maximum allowable levels with the highest mean level recorded being 1.30±0.42 NTU.

Table 2: Mean Values, standard deviations (± S.D; n=18 samples-maximum) analyzed at the five studied stations.

<table>
<thead>
<tr>
<th>Water Quality Variable</th>
<th>Desired limit</th>
<th>Season</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Turbidity (NTU)</td>
<td>5 NTU</td>
<td>Dry season</td>
<td>7.04±0.39</td>
<td>6.20 – 7.70</td>
<td>1.50±0.05</td>
<td>1.45 – 1.60</td>
<td>3.00±0.15</td>
</tr>
<tr>
<td>Wet Season</td>
<td>107.89±5.8</td>
<td>5</td>
<td>65.00 – 181.00</td>
<td>6.95±0.26</td>
<td>6.50 – 7.20</td>
<td>38.09±5.08</td>
<td>33.00 – 45.50</td>
</tr>
<tr>
<td>TDS (mg/L)</td>
<td>500 mg/L</td>
<td>Dry season</td>
<td>17.66±0.58</td>
<td>17.10 – 19.00</td>
<td>11.91±0.53</td>
<td>11.26 – 13.00</td>
<td>34.52±1.15</td>
</tr>
<tr>
<td>Wet Season</td>
<td>35.40±0.96</td>
<td>34.20 – 37.10</td>
<td>12.30±0.34</td>
<td>11.80 – 12.70</td>
<td>10.90±0.37</td>
<td>10.70 – 11.80</td>
<td>33.20±0.60</td>
</tr>
<tr>
<td>pH Value</td>
<td>6.5-8.5</td>
<td>Dry season</td>
<td>7.10±0.10</td>
<td>6.90 – 7.23</td>
<td>6.80±0.03</td>
<td>6.75 – 6.85</td>
<td>7.10±0.22</td>
</tr>
<tr>
<td>Wet Season</td>
<td>6.70±0.05</td>
<td>6.71 – 6.80</td>
<td>6.81±0.02</td>
<td>6.75 – 6.79</td>
<td>6.60±0.03</td>
<td>6.57 – 6.66</td>
<td>6.90±0.05</td>
</tr>
<tr>
<td>EC (μS/cm)</td>
<td>600 μS/cm</td>
<td>Dry season</td>
<td>27.30±1.60</td>
<td>26.00 – 31.00</td>
<td>16.90±0.25</td>
<td>16.60 – 17.50</td>
<td>53.10±2.65</td>
</tr>
<tr>
<td>Wet Season</td>
<td>52.32±1.15</td>
<td>51.10 – 54.10</td>
<td>18.77±0.29</td>
<td>18.40 – 19.20</td>
<td>16.64±0.40</td>
<td>16.20 – 17.30</td>
<td>48.94±0.62</td>
</tr>
<tr>
<td>Temp. (°C)</td>
<td>9°C</td>
<td>Dry season</td>
<td>20.0±0.10</td>
<td>19.8 – 20.1</td>
<td>20.0±0.09</td>
<td>19.8 – 20.1</td>
<td>19.0±0.05</td>
</tr>
<tr>
<td>Wet Season</td>
<td>18.9±0.17</td>
<td>18.7 – 19.1</td>
<td>19.6±0.37</td>
<td>19.0 – 20.0</td>
<td>18.1±0.21</td>
<td>18.0 – 18.5</td>
<td>18.3±0.35</td>
</tr>
<tr>
<td>MPN per 100 ml</td>
<td>Nil</td>
<td>Dry Season</td>
<td>1067±153</td>
<td>-</td>
<td>333±115</td>
<td>-</td>
<td>123±152</td>
</tr>
<tr>
<td>Wet Season</td>
<td>1900±625</td>
<td>-</td>
<td>667±153</td>
<td>-</td>
<td>123±152</td>
<td>-</td>
<td>667±153</td>
</tr>
<tr>
<td>Mean Sodium conc. (mg/L)</td>
<td>300 mg/L</td>
<td>Dry season</td>
<td>4.14±0.05</td>
<td>4.09 – 4.20</td>
<td>0.86±0.03</td>
<td>0.84 – 0.89</td>
<td>0.93±0.04</td>
</tr>
<tr>
<td>Wet Season</td>
<td>4.61±0.36</td>
<td>4.31 – 5.00</td>
<td>0.80±0.02</td>
<td>0.78 – 0.82</td>
<td>0.97±0.01</td>
<td>0.96 – 0.98</td>
<td>4.16±0.29</td>
</tr>
<tr>
<td>Mean Aluminium conc. (mg/L)</td>
<td>0.10 mg/L</td>
<td>Dry season</td>
<td>0.027±0.00</td>
<td>0.017 – 0.041</td>
<td>0.038±0.01</td>
<td>0.023 – 0.055</td>
<td>0.02±0.00</td>
</tr>
</tbody>
</table>

Figure 2: Turbidity levels during the wet and dry seasons.
Mean dry & wet season concentration of manganese in Thika River seasons where; wet season was 0.04±0.01 mg/L and 0.03±0.01 mg/L recommended level during the wet season only. Mean (0.16±0.04 mg/L) and wet season (0.17±0.01 mg/L) respectively. Chania River dry and wet seasons respectively, showing no significant difference between dry & wet season concentration of manganese in Thika River and reservoir discharge where; t_cal (4) = 1.729 < t_tab = 2.776,
P_cal = 0.058 > P_tab=0.05. The t-test results also indicated that there was a significant difference in levels of turbidity from reservoir discharge during the wet and dry season where Chania river between the dry and wet seasons was < 0.0001 < P_tab=0.05 and the mean concentration of manganese in treated water was found to be within recommended level during both dry and wet seasons.

The highest mean concentration of iron (Fig.3) in the catchment during the wet and dry seasons was recorded at Chania River with mean iron concentration of 3.78±0.17 mg/L and 1.35±0.01 mg/L respectively. Mean concentration of iron in Thika River during the wet and dry season was 0.26±0.07 mg/L and 1.16±0.17 mg/L while that from the reservoir discharge was 0.26±0.09 mg/L and 0.36±0.08 mg/L respectively. At 95% confidence level, the t-test results indicated that there was a significant difference between the wet and the dry season iron concentration in Chania River and Thika River where; t_cal (4) = 24.7 > t_tab = 2.776, P_cal = 0.001 < P_tab=0.05 and t_cal (4) = 8.479 > t_tab = 2.776, P_cal = 0.001 < P_tab=0.05 respectively. However, there was no observed significant difference between dry & wet season concentration level of iron from reservoir discharge where; t_cal (4) = 1.438 < t_tab = 2.776, P_cal = 0.023 > P_tab=0.05. The t-test indicated that there was a significant difference between dry & wet season means of Fe levels in treated water where t_cal (4) = 3.84 > t_tab = 2.776, P_cal = 0.018 < P_tab=0.05. Mean concentration levels of Fe in the treated water during dry and wet season was 0.12±0.02 mg/L and 0.39±0.12 mg/L respectively, showing iron levels in treated water during the wet season being above the recommended maximum concentration of 0.3 mg/L.
The mean concentration of Nickel in Thika reservoir were found to be 0.024±0.01 mg/L during the wet season, which is slightly above the recommended WHO concentration level of 0.02 mg/L. All the other sampling points recorded concentrations below 0.015 mg/L during both dry and wet seasons. There was no observed statistically significant difference between dry & wet season mean concentrations of Nickel from Thika reservoir; \( t_{cal} (4) = 1.559 < t_{tab} = 2.776, P_{cal} 0.1940 > P_{tab=0.05}. \)

The mean lead concentration levels in the catchment during the wet season were found to be above 0.01 mg/L, which is the WHO [11] recommended standard with the highest level being recorded in Thika reservoir of 0.04±0.01 mg/L. Mean lead concentration levels were below 0.01 mg/L, which is the S2 PICOFIX Spectrometer limit of detection in all sampling points during the dry season. Also, the mean concentration of lead in Chania River was below 0.01 mg/L during both dry and wet seasons. Lead is likely to be accumulating in Thika reservoir emanating from Thika River and its catchment, which recorded a mean lead level of 0.02±0.001 mg/L during the wet season. Treated water recorded mean lead concentration of 0.013±0.001 mg/L during the wet season, which was slightly above the recommended levels.

The mean concentration of Nickel in Thika reservoir were found to be 0.024±0.01 mg/L during the wet season, which is slightly above the recommended WHO concentration level of 0.02 mg/L. All the other sampling points recorded concentrations below 0.015 mg/L during both dry and wet seasons. There was no observed statistically significant difference between dry & wet season mean concentrations of Nickel from Thika reservoir; \( t_{cal} (4) = 1.559 < t_{tab} = 2.776, P_{cal} 0.1940 > P_{tab=0.05}. \) These result indicate that there is a likelihood that nickel, which is normally a constituents of inks, dyes and paints could be accumulating in Thika reservoir. The main source of nickel in the catchment would be likely the run-off from garages located upstream of Thika reservoir.
4. Discussion

This study demonstrates that pollution effects of natural and anthropogenic activities within the Chania catchment are prevalent. The high turbidity level in Chania catchment for the wet season was found to be far above the 5.0 NTU limit set for water meant for domestic use. These levels imply that there is high soil erosion resulting to suspended particles emanating from farmlands in the upstream catchment thus providing favourable climate for survival of micro-organisms and this explains the reason for high MPN of coliforms during the wet season.

Mean lead concentration levels in Thika reservoir during the wet season was found to be 0.04±0.01 mg/L, which was above 0.01 mg/L, the WHO recommended standard. Lead is likely to be accumulating in Thika reservoir emanating from Thika River which is the reservoir’s main feeder river which recorded a mean lead level of 0.02±0.001 mg/L during the wet season.

The mean concentration of Chromium in the catchment was found to be below 0.02 mg/L during the dry and wet seasons except in Thika river sampling point where the mean concentration level of 0.045 ± 0.001 mg/L was recorded during the wet season (NEMA allowable maximum for chromium level is 0.05 mg/L).

The mean concentration of Nickel in Thika reservoir were found to be 0.024±0.01 mg/L during the wet season, which is slightly above the recommended WHO concentration level of 0.02 mg/L. These result indicate that there is a likelihood that nickel, which is normally a constituents of inks, dyes and paints could also be accumulating in Thika reservoir.

Mean dry season EC concentration level recorded at Thika River was 53.10±2.65 μS/cm and wet season level was 16.64±0.40 μS/cm while the dry and wet season TDS levels for the same sampling point were 34.52±1.15 mg/L and 10.90±0.37mg/L respectively. Further scrutiny showed that Thika River had higher levels of heavy metal pollutants Zinc, lead and chromium emanating from the catchment than other sampling points. The possible reason for higher EC during the dry season is likely discharge of effluent into the river which is diluted during the wet season.

The main sources of chemical pollutants in Chania catchment are agricultural farms within the catchment that generate domestic waste and utilize the inorganic fertilizers and manure that finally finds its way into water bodies through surface run-off. Other likely sources include natural geophysical processes like weathering of rocks. Anthropogenic activities like riparian cultivation of horticultural crops, Livestock keeping, poultry keeping, tea plantations, roads construction, masonry rock quarrying and motor vehicle garage activities are also contributors of pollution and degradation of the catchment. From the findings, the concentration of the metal pollutant iron was not sufficiently removed to recommended standards after treatment and thus the water treatment method was not effective in removal of these inorganic pollutants.

5. Conclusion

Based on the findings of this study, the following is recommended;

As an adaptive measure, the water treatment method to be improved for instance by introducing chemical oxidation technology as a pre-treatment .e.g. use of chemical oxidants such Chlorine dioxide, potassium permanganate, chlorine or by adding oxygen through artificial aeration to lower concentration of inorganic pollutants iron and manganese to acceptable levels. Enhancing oxidation will assist convert the dissolved forms of these metals to solid form or precipitates so that they are removed through sedimentation and filtration.

Creation of awareness and guidance on recommended pollution prevention strategies to help communities living within Chania catchment to stop activities leading to pollution of the environment i.e. adoption of organic farming to curb use of chemicals and inorganic fertilizers, proper domestic waste disposal, soil conservation methods and proper handling of garage wastes in an environmentally sound ways such as being able to realize hazardous waste streams from their operations and reduce spills. It is also recommended that there should be proper monitoring of effluents into receiving water as an integral part of water management in the catchment to enable verification of whether or not imposed standards and regulations are met.

Sufficient information is key for assessing the safety of a drinking-water source and water pollution potential. This assessment requires a variety of information, relating to the hydrogeology, socioeconomic conditions and the range of anthropogenic activities present in the catchment which potentially release pollutants. Further research is therefore recommended to establish such an information inventory as a tool for developing a sound understanding of potential pollution sources and the likelihood with which pollutants may reach the Chania catchment in concentrations that are hazardous to human health.

References


Author Profile

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