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IMPACT OF FARMING ACTIVITIES ON THE WATER QUALITY OF THE PRATU RIVER AND ITS TRIBUTARIES IN THE MUNI-POMADZI WETLAND

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DECLARATION

This thesis is the result of research work undertaken by Stella Tiakor in the Department of Nuclear Sciences and Applications, School of Nuclear and allied Sciences, University of Ghana, under the supervision of Dr. T. T. Akiti and Dr. J. R. Fianko

No part of this research work has been presented, in whole or in part, to any other university or institution for the award of a degree or diploma.

Works by other people, cited in this thesis have been duly acknowledged under references.

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Stella Tiakor	Dr. T. T. Akiti
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(Co – Supervisor)

Date……

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DEDICATION

This work is dedicated to my unborn child Macarios Kwabena Amponsah Asiedu whom I carried in my womb throughout this research work. May the Good Lord make you great and favour you before all whom you meet.

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To God be the Glory for the Great Things He has done. I am most grateful to God for the strength given me to complete this work even during pregnancy. I wish to express my heartfelt appreciation to my supervisors Dr, T.T. Akiti and D. J. R. Fianko as well as all lecturers in my department for their coaching, guidance and supervision. Also a special appreciation goes to Dr. Gyampo who provided his car and assistance for all my sampling trips as well as Mr. David Saka for his assistance during the sampling period.

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To colleague classmates, I am most grateful to you all. We are not only mates but now a big family. I ask the Lord's Blessings for all in all endeavours.

INTEGRI PROCEDAMUS

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ABSTRACT

The Muni-Pomadze wetland in the Central Region of Ghana is one of five internationally-recognised coastal wetlands (Ramsar sites) in Ghana under the Convention on Wetlands of International Importance. The wetland is known for its rich variety of biodiversity and unpolluted ecosystem and is fed by a main river called Pratu along with its tributaries (Ntakofa and Muni Rivers) that flows into the Muni lagoon. However, the need to produce enough food to feed the ever increasing population has led to the extensive use of land especially along the banks of the rivers that feed the wetland for farming activities. This disturbing issue coupled with other anthropogenic activities has led to an increasing level of pollution in the wetland resulting in water quality degradation in the river catchment. This has consequently diminished both the local and international significance of the wetland. In this light, this research sought to assess the impact of farming and other anthropogenic activities along the Pratu River and its tributaries and consequently the Muni lagoon in the wetland by determining the source, types and level of pollution existing in the river basin. Water samples from the Pratu River, Ntakofa River and the Muni lagoon were analysed for physico – chemical parameters (pH, Temperature, Electric Conductivity, Salinity, Total Dissolved Solids, Alkalinity, Dissolved Oxygen, Biological Oxygen Demand, Chemical Oxygen Demand and Total Hardness) using titrimetry, Hach Sension 5 Conductometer and Hach pH Meter; trace metals (Iron, Copper, Zinc, Lead, Cadmium, Cromium and Mercury) using the Atomic Absorption Spectrometer; ions (Na, Ca, K, Mg, Cl^-, SO_4^{2-}, NO_3^- and PO_4^{3-}) using the Flame Photometry, UV-Visible Spectrophotometry and titrimetry. Pesticide residues (Organochlorines, Organophosphates and Synthetic Pyrethroids) were also

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analysed using the Gas Chromatography–Electron Capture and Pulse Flame Photometric Detections. Results of the physical analysis showed high concentration of EC (20655.77 µS/cm, 16822.32 µS/cm and 55600 µS/cm respectively), TDS, (13761.77 mg/L, 10775.89 mg/L and 33333.33 mg/L respectively) and salinity (14.95, 11.79 and 37.33 respectively) depicting a high level of dissolved ions in the basin. High levels of total hardness were 3833.85 mg/L, 2942.222 mg/L and 6933.333 mg/L respectively and COD were 10.35 mg/L, 14.31mg/L and 13.8mg/L respectively. This may be attributed to the high levels of dissolved ions and anthropogenic activities involving farming practices, illegal gold mining operations, domestic effluents and other chemical effluents that enter the river through surface run-off. Major cationic dominance pattern for the basin was Na>Ca>K>Mg and that of the anions were Cl >SO_4^{2-} > NO_3^- > PO_4^{3-}. The observed pattern shows that Na and Cl concentrations are dominant in the basin. This condition may be attributed to the effect of aerosols from the sea and Na and Cl ions which may be present in the soils close to the river banks (evidenced by salt-like precipitates on the soil surface). Results of trace metals and pesticide analysis in the sediment of the river basin showed that, most of the metals and the pesticides found were all adhered to the soil sediment in low concentrations hence may not pose a threat to the river's quality. Sodium Adsorption Ratio (SAR) was measured in the basin. 21.02, 29.44 and 51.02 respectively for the three parts of the basin showed that the river is not suitable for irrigation (results were >13). However continual use of the river as a source of irrigation may cause stunted growth of the crops resulting in low yield. This may necessitate increased fertilizer use and consequently impact the river by eutrophication. Based on these findings, it is recommended that further water quality analysis be conducted on the river on an annual

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basis in order to ascertain the pollution progress of the river and its impact on the wetland. Secondly, SAR measurements should be conducted on the soils of the farmlands to give more detailed information on the degree of sodicity of the soil. This will help the farmers make an informed decision on best farming practices.

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CHAPTER ONE

INTRODUCTION

1.1 Background

The township of Winneba has a vast variety of natural resources including forests, precious minerals and water systems. The Muni-Pomadzi wetland is one of Winneba's major sources of natural resource that has received a growing amount of attention from different groups of people with the general aim of preservation and maintenance. Among the elements of the Muni-Pomadzi wetland are gold, salt (NaCl) and rivers. The rivers have tributaries that flow into the Muni lagoon; the major tributary being the Pratu and Ayensu rivers. These tributaries are very important in the maintenance of the flora and fauna in the wetland.

Quality water is of great significance to life. It is a requirement by every creature for their survival without which, living becomes nearly impossible. Water makes up about 70% of the earth's surface but only 2.53% is fresh water whereas the remaining percentage is salty water (UNESCO, 2003). Without adequate fresh water in its appropriate quantity and required quality, sustainable maintenance of development will not be possible (Adeyeye and Abulude, 2004).

However, anthropogenic activities such as farming along the banks of rivers, flow of domestic effluents into rivers, small scale industries located close to rivers and other human activities are beginning to impact on these tributaries leading to changes in water quality (Hill, 1999). As a result, there is widespread catchment erosion and subsequent

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river sedimentation, water shortage, pollution and other physico-chemical impacts not only on the tributaries but also on the wetland (Ansah – Asare, 1995).

Agriculture is an important aspect of the global economy. Appelgren (1994) stated that, "agriculture is the single largest user of freshwater resources, using a global average of 70% of all surface water supplies. However, the pressure to produce sufficient food has had a worldwide impact on agricultural practices". In many countries including Ghana, over 60% of the population depends completely or incompletely on agricultural land for a livelihood (Udo, 1978). This pressure has developed into the need to expand into lands close to rivers in order to maintain a seemingly constant source of water for irrigation. Farming activities therefore play an important role in the changes in water quality among many river basins including the Pratu and its associated tributaries that feed the Muni wetland.

One way farming affects the quality of rivers is pollution. According to Dix (1981), 'A river may be said to be polluted when the water in it is altered in composition or condition, directly or indirectly as a result of the activities of man, so that it is less suitable for all or any of the purposes for which it would be suitable in its natural state'. Rivers are among the most vulnerable water bodies to pollution because of their role in carrying wastes, chemical loads and run-offs from agricultural lands into their very large drainage sinks (UNESCO, 2003).

Generally, in many countries, all types of pollution that is sourced from agricultural activities and land use are regarded as a non-point source. The main nature of non-point sources of pollution is that they are difficult to measure or control entirely (and therefore

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are very hard to regulate) (Ackefors and Enell, 1992). According to Andreoli (1993), "agriculture is only one of a variety of non-point sources of pollution". However, it is generally regarded as the largest contributor of pollutants of all the varieties. Non-point source pollution, no matter the source, is carried overland and through the soil by surface run-off. Consequently, these contaminants settle in groundwater, rivers and lakes and, finally, into oceans, usually as sediment and chemical loads. The percussion of these contaminants range from simple inconvenience substances to extremely serious ecological percussions including flora and fauna, and on human health (Avcievala, 1991). FAO (1990a) made it quite clear that, "... *appropriate steps must be taken to ensure that agricultural activities do not adversely affect water quality so that subsequent uses of water for different purposes are not impaired."*

1.2 Problem Statement

The Muni-Pomadzi wetland is one of the five internationally – recognised coastal wetlands (Ramsar sites) in Ghana under the Convention on Wetlands of International Importance (Gyasi *et al.,* 1995). Being one of the major tourist attractions in Ghana, the wetland was an undisturbed ecosystem full of rich biodiversity supported by the tributaries that kept the wetland alive with healthy flora and fauna both in the terrestrial and the aquatic habitats. The wetland is particularly important to the people of Winneba, serving as their traditional hunting grounds for fish and terrestrial vertebrates.

According to Ryan and Attuquayfio (2000), the previously diverse aquatic fauna of the aquatic ecosystem has dwindled, with some of the animals (e.g. deer and antelopes),

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presumed locally extinct or existing in very low numbers. Research results (Ntiamoa-Baidu and Gordon, 1991; Ryan and Ntiamoa-Baidu, 1998) indicate that pollution may be evident in the area and this could be largely attributable to neglect and unsustainable human activities over the years.

The need to produce enough food to feed the ever increasing population has led to the extensive use of agrochemicals in farming activities which may enter the river body when surface flow and erosion occurs (Appelgren, 1994).

The Muni wetland and biosphere reserve struggle with challenges such as waste management especially plastics and sustainable resource utilization that beset the wetland. The main challenges induced by human activity in Muni wetland and Biosphere Reserve are habitat modification for agriculture evidenced by farming along the banks of the rivers feeding the wetland, illegal mining operations, small scale industries (block making factories, generator repairs), fish pond farming, flow of domestic effluents into the river and bushfires.

These disturbing situations, if allowed to continue, are likely to result in water quality degradation in the river catchment, consequently diminishing both the local and international significance of the wetland (Amatekpor, 1994).

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1.3 Research Objectives

1.3.1 Main Objective

The main objective of this study is to assess the quality of water in the Pratu River and its tributaries by focusing on the impact of farming activities along the river catchment and the Muni lagoon.

Specific Objectives

i. To determine the different sources of pollutants in the Pratu river and the Muni lagoon
ii. To determine the types of pollutants existing in the river and the lagoon
iii. To determine the level of pollution in the river and the lagoon

1.4 Justification

The sources of pollution that impact the Pratu water resource and its tributaries can develop at different scales if not managed promptly. Identification of source, types and levels of pollution is a prerequisite to assessing the risk of the pollution being created to both the aquatic systems and through that system, to humans and the environment. With the knowledge of the principal sources of the pollution, the appropriate mitigation strategy can be identified to reduce the impact on the Pratu water resource.

The challenge of how to improve water quality by protection of streams, rivers, reservoirs, wetlands and related surface water bodies is a growing national concern. However, surface water pollution risks, particularly in developing countries, remain relatively widespread. Therefore a valuable step in identifying the nature and extent of

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water quality impacts linked to pollution is to investigate and analyze the various pollutants that find their way into the water catchments.

Agrochemicals used in excess obviously pollute the river when erosion occurs. Within this framework, surface water quality assessment has important ecological health implications not only for the Pratu river catchment and the Muni Wetland but for the social welfare of the entire Municipality within its catchment since a good number of the population in the area are farmers. This means that, surface water resource assessment becomes an important issue of research interest in order to help the inhabitants of the area know the effect of their activities on the quality of surface water and environmental health.

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CHAPTER TWO

LITERATURE REVIEW

2.1 Water Quality

Diersing, (2009), defines water quality as the chemical, physical, biological, and radiological characteristics of water. Johnson *et al.* (1997) also states that it is a measure of the condition of **water** relative to the requirements of one or more biotic species and or to any human need or purpose. Water quality is a topmost priority for good river wellbeing. This is because it is fundamental to continuous ecological processes that supports the vast ecosystem and hence biodiversity such as fish populations, vegetation, wetlands and all other aquatic fauna and flora. Similarly, many anthropogenic uses depend on water quality that is reliable for irrigation, watering stock, drinking, fishing and recreation, and to meet psychological needs stemming cultural to spiritual needs (NSW Environment and Heritage, 2014).

Water is important to the health of human life the environment. It comprises marine, estuarine, freshwater (river and lakes) and groundwater catchments that stretch across coastal and inland areas since its worth cannot be overemphasized (Florida Keys National Marine Sanctuary, 2011). Water has two parameters that cannot be overlooked: quantity and quality. A healthy environment is one in which the water quality supports a rich and varied community of organisms and protects public health.

Water quality in a body of water influences the way in which communities use the water for activities such as drinking, swimming or commercial purposes. More specifically, the water may be used by the community for:

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- drinking
- recreation (swimming, boating)
- irrigating crops and watering stock
- industrial processes
- navigation and shipping
- production of edible fish, shellfish and crustaceans
- protection of aquatic ecosystems
- wildlife habitats
- scientific study and education

Water quality is almost always affected by the surrounding environment and land use. Other than in its vapour form, water is never in its pure state and is affected by anthropogenic uses such as agriculture, urban and industrial use, and recreation. The modification of natural stream flows by dams can also affect water quality (Belsare, 2006). The weather, too, can have a major impact on water quality, particularly in a dry region like the northern, upper east and west which is periodically affected by irregular rainfall patterns.

Generally the water quality of rivers is best in the western and coastal regions, where rainfall is often abundant. Water quality often declines as rivers flow through areas where land and water use are intense and pollution from intensive agriculture, large towns, industry and recreation areas increases (Yogesh and Pendse, 2001). Of course, there are exceptions to the rule and water quality may improve downstream, behind dams and weirs, at points where tributaries or better quality groundwater enter the main stream, and

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in wetlands (DFID, 1999). Rivers may act as channels for pollutants by assembling and transporting wastewater from catchments and, finally, releasing it into the ocean. Storm-water, which can also carry heavy loads of nutrients, organic matter and pollutants, finds its way into rivers and oceans, mostly through the storm-water drain network (Belsare, 2006)

According to Abdul-Razak *et al.* (2009), indicators of the quality of water are mainly linked to the presence of contaminants and the features of water. These water quality indicators can be categorised as biological (bacteria and algae), Physical (temperature, salinity, dissolved solids, conductivity, hardness), Chemical (pH, dissolved oxygen, biological and chemical oxygen demand, nutrients (including nitrogen, sulphates and phosphorus), organic and inorganic compounds (including pesticides and petroleum) and finally radioactive (alpha, beta and gamma radiation emitters).

Measurements of these indicators can be used to assess, and monitor changes in, water quality, and determine whether it is suitable for the health of the natural environment and the uses for which the water is required (Danquah, 2010)

According to UNESCO (2003), the design of water quality monitoring programs is a complex and specialized field. The different types of indicators that can be measured and analysed are of a wide range and other indicators may be adopted in the future. The cost of a monitoring schedule to assess them all would be near impossible, so resources are often geared towards assessing contaminants that are of significance to the local environment or for a specific use of the water (UNICEF, 2008). This water quality information can then be used to develop management programs and action plans to ensure that water quality is protected.

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With reference to the thesis of Gajendran (2011), on the subject of Water Quality Assessment And Prediction Modelling of Nambiyarriver Basin, Tamil Nadu, India, there is the topmost challenge on the environment concerning the sustainability of river water quality.. Monitoring diverse sources of contaminant load into the river basin is quite a difficult and costly process which sometimes leads to errors in analysis. The main objective of his study was to develop a model to assess and predict the water quality changes of the Nambiyar River Basin, in Tamil Nadu, India, using Neural Network and GIS techniques, and to compare the results through the statistical method. Hydro-geochemistry of groundwater in Nambiyar River basin was the method used to assess the quality of groundwater for determining its portability for drinking and agricultural purposes. The cations such as Ca, Mg, Na, K and anions like HCO_3, CO_3, Cl, SO_4 and NO_3 were analysed in the laboratory. By this study it was found that a strong correlation exists between SO_4 and COD. Similarly, in the second phase of his work, a correlation and regression analysis on the ground water quality showed the linear relationship among the different water quality parameters. His results showed a high correlation coefficient observed from TDS with Cl, Ca, SO_4 and Na; from Cl with Ca; and from SO_4 with Ca. In the third phase of his study, water quality indices of the basin were analysed. The physico-chemical parameters such as pH, DO, TDS, NO_3, BOD, COD, Total Alkalinity, Total hardness, Ca, Mg, Cl, SO4 and F of the basin were used in the determination of the nature of the basin's quality. The results revealed that the major part of the basin had moderate to poor surface water quality for drinking purpose and, in general, the surface water quality of the basin decreases from Northwest to Southeast. Most of the

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groundwater quality index for the pre- and post-monsoon seasons lied between good and excellent. It was also observed that the basin water had high concentrations of Hardness that resulted in the majority of people suffering from kidney related health problems.

Holm (2004) stated in her report on The Water Quality of the Wood River and the Effects of Land Use that, the purpose of her study was in three folds. First, to evaluate the water quality of the Wood River and compare it to similar river systems. Second, to evaluate the effects of nutrients on the pelagic phytoplankton in the river to determine the biological responsiveness to nutrient additions which might occur as a result of agricultural land use and municipal waste water effluent. Lastly to propose mitigative measures that could help to reduce the potential threat of increased nutrients.

To determine the effect that agricultural land use and municipal waste water effluent was having on river water quality, nutrient and chlorophyll levels in the river were examined. Nitrogen (N) and phosphorus (P) levels were high in the Wood River when compared to similar systems. The mean total phosphorus concentration for the Wood River over the two years of this study was 474 µg/L while the mean ammonia concentration was 223 µg/L. These concentrations exceeded water quality guidelines. Algal biomass and nutrient concentrations were higher at sites where nonpoint source pollution from agriculture or point source pollution from sewage effluents was present. Nutrient enrichment bioassays also indicated that the algal population in the Wood River was responsive to additions of nutrients; therefore, increases in nutrients will increase algal biomass in the river. The bioassays also revealed that at the sites where agriculture and municipal waste water were present, the algal population was Nitrogen limited indicating an excess of Phosphorus in the river. The municipal point source of pollution had a great

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effect on algal biomass and these effects lasted for about three weeks after the release. Different land use patterns and municipal waste water effluent were potentially having a negative effect on the water quality of the Wood River.

The Yamuna River, a tributary of the Ganga River, is one of the most polluted rivers in India and especially in urban centres like Delhi is of a critical water quality. The discharge of untreated waste water is the main reason of the decrease in water quality. But also diffuse sources like dumping of waste material, religious offering of flowers or food, immersion of idols, holy baths, clothes washing or cattle bathing lead to pollution. The rapid growth and the high population density in India makes the situation worse very fast. Although there are many investigations, e.g. the Yamuna Action Plan, an improvement is hardly noticeable. As per Central Pollution Control Board (CPCB) the water quality of River Yamuna is of the category E which makes it fit only for irrigation, industrial cooling and controlled waste disposal. Vaishali and Prachi (2014), conducted a research titled "Water quality analysis of river Yamuna – the Delhi stretch" and the test results confirmed a bad water quality, thus zero dissolved oxygen, normally 4 mg/L, and a BOD of 17 mg/L, 3 mg/L in a good condition, was determined.

The Narmada, also called Rewa is a river in central India and the fifth largest river in the Indian subcontinent. The bank of Narmada River is covered by tribal people, and their daily wastes are drained into this holy river, which alters the Physico-chemical parameters of the river. Sharma *et al.* (2012) also conducted a research on the Evaluation of Physico- chemical parameters of Narmada River, MP, India. The study was carried out for a period of one year from August 2009 to July 2010 to enumerate the various Physico-chemical parameters of Narmada River.

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Water samples were taken from sampling stations every month and were analyzed as per standard methods prescribed in limnological literature. Temperature, Transparency, pH, Dissolved Oxygen were determined at the site while Biochemical oxygen demand, Chloride, Phosphate, Nitrate, Alkanity, Sulphate, Total Hardness were determined in the laboratory. The Physico- Chemical parameters were determined by standard methods of Golterman (1991), Welch (1998) and APHA (2002). The results indicated that most of the Physico- chemical characteristics of Narmada water samples were within the WHO recommended guidelines.

Narrowing down to Africa, specifically at the western part, the country of The Gambia, has little information regarding the status of the country's groundwater and surface water quality. In an attempt to fill this information gap, research thesis undertaken by Healey (2014), conducted a baseline study of water quality on The Gambia River pertaining to human and ecosystem health. The data collected at each of the 29 sampling locations indicated that specific areas of the Gambia River, such as those located further downriver, had inferior water quality, with respect to irrigation and consumption, due to the presence of salt water, anthropogenic disturbances, and effluents. The entire river was deemed unfit for consumption by humans due to high salt levels, from the mouth of the river to site 12, and the presence of coliform bacteria at all sites. However, with reference to the findings of the research, the river water is widely used, ecosystem health appears to be good, and the upper reaches are suitable for agricultural purposes. The lower areas of the river, though unsuitable for irrigation due to its brackish nature, have a more diverse fish fauna (Albaret *et al.* 2006). The upper reaches of The Gambia River (approximately 250 kilometers or more upriver) are freshwater and are valuable for rice and groundnut

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production due to the freshwater swamp area (Carney, 1998). There is no tidal (salt water) influence and the growing conditions are ideal for these crops. The quality of water here is sufficient for human consumption, if treated, and for irrigation.

The CSIR Water Research Institute of Ghana undertook water quality monitoring and assessment of the Southwestern and the Coastal Rivers Systems of Ghana from 2005 to 2008 for the Water Resources Commission of Ghana (WRC) under proximately 30% of the total drainage basins of Ghana. A total of 19 surface water stations were selected for the monitoring programme. The Adapted Water Quality Index (WQI) was to be used as a tool to classify the overall ambient water quality at the 19 different stations. The index classified water quality into one of four categories: good (Class I, >80), fairly good (Class II, 50 - 80), poor (Class III, 25 - 50), and grossly polluted (Class IV, <25). Their paper presented the Water Quality Index approach to the assessment of water quality of the waters in the different stations during the period of study. These ten water quality parameters were used to determine the water quality index (WQI): Dissolved Oxygen (DO % Saturation), Biochemical Oxygen Demand (BOD), Ammonium Nitrogen (NH4-N), Faecal Coliform (FC), pH, Nitrate as Nitrogen (NO_3-N), Phosphate as Phosphorus (PO_4-P), Total Suspended Solids (TSS), Conductivity and Temperature. Evaluation of the waters with the WQI indicated that most Ghanaian waters are currently in Class II, the fairly good water quality state, but with variations in this range within the seasons and stations, and from one water body to the other. A 4-year study from 2005 to 2008 of surface waters in the Southwestern and Coastal Rivers Systems of Ghana revealed that the annual water quality decreased in the order: 2005>2007>2006>2008.

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Research was undertaken by Monney *et al*. (2014) on Urbanization and Pollution of Surface Water Resources in the Two Largest Cities in Ghana. Water samples from specific locations of the Aboabo river in Kumasi and the upper reaches of the Korle Lagoon in Accra were collected and analysed for their physico-chemical and microbial quality during their study period. The results from the study pointed out that the upper reaches of the Lagoon was rendered anaerobic during the dry season and with appreciably low DO even during the wet season. Drastic depreciation in DO levels in the Aboabo River as it flows through highly populated areas (Aboabo, Moshie Zongo and Anloga) were depicted through the study. Elevated BOD (upper reaches of the Korle Lagoon: 27.7 mg/L – 200 mg/L; Aboabo river: 38.25 mg/L – 260 mg/L) and E. coli (upper reaches of the Korle Lagoon: 5.0x106 - 2.8x109 CFU/100 mL; Aboabo river: 4.0x106 CFU/100 mL - 1.3x108 CFU/100 mL) levels were also recorded in both water bodies generally attributed to disposal of organic wastes and fecal matter into them.

Sisa River is one of the major rivers in one of the sub-catchments in Kumasi, Ghana. It is located in the Asokwa Sub-Metro in the eastern part of Kumasi. Water resources in the peri-urban area around Kumasi including Sisa are losing their values due to pollution. According to Agyeman (2012), since the particular pollution situation at specific areas of Sisa River had not yet been documented, his project had two main objectives, which were: to identify specific existing or emerging water quality problems as a result of the presence of different potential pollution sources and their particular waste-water management along the banks of Sisa River and to gather information to design specific pollution prevention or remediation programs

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The results revealed that there is a clear deterioration of water quality of Sisa River from the more rural (upstream of Kumasi) to the more urban-affected (within and downstream of Kumasi) sub-catchments. The following obtained on Sisa River supported this. The taste and odour of the water were offensive and objectionable to the people. There were low levels of Dissolved Oxygen which makes it difficult for many species of fishes to thrive well in the water. Conductivity levels were far higher than EU recommended levels. Nitrites level exceeded EU recommendations. There was widespread coliform contamination

Water quality assessment conducted in the Densu basin of Ghana between July 2003 and March 2004 by Karikari and Ansa-Asare (2004), identified human, animal and agricultural activities as the main sources of pollution. The pH of the water was neutral (pH range 7.20–7.48) and was unaffected by seasonal variation. The river waters were moderately soft to slightly hard (range of hardness 91.2–111 mg/L $CaCO_3$) with high turbidity due to poor farming practices, which resulted in large quantities of topsoil ending up in the river after rains. High nutrient loads observed in the basin were due to domestic, agricultural and industrial activities. The waters exhibited a general ionic dominance pattern of Na > Ca > Mg > K and HCO_3> Cl> SO_4, a pattern which is an intermediate between fresh and sea water systems. There was a dominance of chloride over sulphate which was probably due to domestic activities resulting from household effluents, fertilizer use and other anthropogenic point sources. Trace metal levels were low suggesting low metal contamination of the river. However, the microbial quality of the river water was poor due to direct contamination by animal and human excreta and

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other activities such as swimming, washing of clothes, etc. The river water cannot be used for domestic purposes without any form of treatment.

The water quality of the Weija Reservoir was assessed by Asante et al. (2008) and the various sources of contaminants were identified in order to provide scientific basis for finding appropriate remedies to the contamination problems that may confront the Reservoir. Monthly water samples were taken from three sampling stations in the Weija Reservoir and analysed for physico-chemical parameters in the laboratory. The mean pH values of the sampling sites were within the recommended range of 6.5–8.5 for potability and sustenance of aquatic life. The ionic dominance pattern observed was Na > Ca > Mg > K and HCO_3 > Cl > SO4, indicating partial cationic characteristics of sea water and anionic characteristics intermediate between fresh water and sea water. Dissolved oxygen (DO) levels were 102.5%, 81.5% and 82.7% saturation for Weija Intake, Machigani and Galilea, respectively. Thus, the oxygen conditions in the Weija Reservoir were sufficient to support fish and other aquatic life. Maximum BOD level was 8.1 mg/L at Weija Intake. Compared with previous studies on the Weija Reservoir, results of the study show a slight increase in nitrate, ammonia, sulphate and phosphate levels. Generally, the levels of nitrate, sulphate, phosphate, trace elements (e.g. manganese and iron) and BOD were moderately high. Anthropogenic activities, such as stone quarrying, dumping of domestic wastes, as well as run-offs from agricultural activities and the occurrence of algae, are some of the sources of contamination identified in the study.

Danquah *et al.* (2011) studied the Anthropogenic Pollution of Inland Waters: the Case of the Aboabo River in Kumasi, Ghana. This study assessed the quality of the Aboabo River and examined the anthropogenic factors that lead to river pollution. Water quality

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analyses were carried out on water samples collected in December 2008 and January, 2009 (Dry season). Parameters that were examined include Temperature, Color, Electrical Conductivity, Hardness, pH, Dissolved Oxygen (DO), Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Total Dissolved Solids (TDS), Total Suspended Solids (TSS), Sulphate, Nitrate, Calcium, Magnesium and Faecal coliform. This study established that the Aboabo River was bacteriologically polluted. Excessive faecal coliform counts revealed pollution from anthropogenic activity. These anthropogenic activities included indiscriminate dumping of refuse into the Aboabo River, channelling of raw sewage into the Aboabo River, open defecation along the banks of the Aboabo River and discharge of untreated effluents into the Aboabo River by the small scale industries. The direct anthropogenic activities were the result of the interplay of factors such as population growth, and institutional constraint.

2.2 Physical Parameters

2.2.1 pH

pH is the amount of the hydrogen ion concentration in water as ranked on a scale of 1.0 to 14.0. The lower the pH of water, the more acidic it is and the higher the pH of water, the more basic, or alkaline, it is. The pH scale measures the logarithmic concentration of hydrogen (H^+) and hydroxide (OH^-) ions, which make up water ($H^+ + OH^- = H_2O$). When both types of ions are in equal concentration, the pH is 7.0 or neutral. Concentrations below 7.0, implies that the water is acidic. However, a pH concentration above 7.0 usually implies that the water is alkaline, or basic. Since the scale is logarithmic, a drop in the pH by 1.0 unit is equal to a 10-fold increase in acidity. This

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means that a sample of water with a pH of 5.0 is 10 times as acidic as one with a pH of 6.0, and pH 4.0 is 100 times as acidic as pH 6.0 (Gallogher, 2011).

pH has an impact on many chemical and biological systems in the water and varying organisms have their specific range of pH within which they survive comfortably. The majority of fishes and other aquatic organisms survive between a pH of 6.0 - 8.0. pH that deviates from this range reduces the biodiversity in the stream because the physiological systems of most of these fauna is stressed and can decrease reproduction. Low pH concentrations can peak the solubility of trace metals (USGS, 2007). As the hydrogen ion concentration rise, cations of metal origin such as aluminum, lead, copper and cadmium are discharged into the water rather than being adsorbed to the water's sediment. As the levels of trace metals rise, their levels of lethality also progresses. Aluminum for example, can cut down on growth and reproduction while mortality rates increase at levels as low as 0.1-0.3 mg/L. In addition to this, the dissolved trace elements can be consumed by organisms as they respire, resulting in physiological damage (Osmond *et al.*, 1995). This is specifically dangerous to aquatic species such as rainbow trout (USEPA, 2012). On the other side of the pH range, high pH concentrations can be detrimental to the gills and skin of aquatic fauna and cause death at concentrations over 10.0.

There are a variety of circumstances that can affect pH in water, which can be classified into natural and man-made factors. Most changes that occur by reason of nature can be attributed to interactions with surrounding geology. pH can also remain unstable with the effect of rainfall, wastewater or mining effluents (USEPA, 2012). In addition, CO_2 levels can affect pH levels when photosynthesis, respiration and decomposition occur.

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However, the gravity of these influences depends on the alkalinity of the water. Carbonate materials and limestone are two elements that can buffer pH changes in water. Calcium carbonate ($CaCO_3$) and other bicarbonates can combine with either hydrogen or hydroxyl ions to neutralize pH (Utah State University, 2013).

Human induced causes of pH changes are usually connected to pollution. A common cause is point source pollution which can either increase or decrease pH depending on the pollutants involved (Utah State University, 2013). These pollutants can originate from agricultural and industrial runoff as well as wastewater discharge. Coal mining operations can result in acid runoff and seepage of acid into the groundwater if the buffering capacity of the soil surrounding the groundwater is poor (Osmond *et al.*, 1995). Detergent and soap based containing wastewater products can result in a water source becoming too basic.

The alkalinity of water may fluctuate due to the presence of dissolved salts and carbonates, as well as the mineral composition of the surrounding soil. Conventionally, when alkalinity levels rise, pH also rises and the opposite implies for low alkalinity; that is, the pH will also decrease (Murphy, 2007). The recommended pH range for most fish is between 6.0 and 9.0 with a minimum alkalinity of 20 mg/L, with ideal $CaCO_3$ levels between 75 and 200 mg/L (Wurts and Durborow, 1992).

2.2.2 Temperature

Brown (1999) defines Water temperature as a physical property that gives an indication of how hot or cold water is. According to him, temperature can further be defined as a

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measurement of the average thermal energy of a substance. Temperature measures the mean kinetic energy of the atoms and molecules. This energy can be transported between molecules as heat flow. Heat transfer, whether from natural sources such as air, sunlight, another water source or others such as thermal pollution can alter the temperature of water.

Temperature is an important element to analyse when determining water quality. Apart from its own effects, temperature affects many other parameters and is capable of changing the physical and chemical characteristics of water. Therefore, water temperature should be evaluated when determining (Wilde, 2006):

– Metabolic rates and photosynthesis production

– Compound toxicity

– Dissolved oxygen and other dissolved gas concentrations

– Conductivity and salinity

– Oxidation reduction potential (ORP)

– pH

– Water Density

Water temperature can affect the metabolic rates and biological activity of aquatic organisms (Wetzel, 2001) because it mostly affects the chosen habitats of the wide variety of aquatic fauna (USEPA, 2012). Aquatic organisms such as aquatic flora particularly survive in warmer temperatures, while some fishes such as trout or salmon prefer colder streams (USEPA, 2012).

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Temperature can also reduce plant respiration and photosynthesis (Wetzel, 2001). Conventionally, algal photosynthesis will rise with temperature increase, though a variety of species possess varying peak temperatures for optimum photosynthetic activity (Wetzel, 2001). Above and below this peak temperature, photosynthesis may reduce. Increased water temperatures can increase the level of solubility and consequently the lethality of heavy metals (Washington State Department of Ecology, 1996) including cadmium, zinc and lead as well as compounds like ammonia. In one study on labeo bata fish, the 24 hour 50% lethal concentration (LC50) at 15°C was 540 mg/L, while at 30°C, the LC50 dropped to 210 mg/L (Bhadja and Vaghela, 2013). This occurs because tissue permeability, metabolic rate and oxygen consumption all increase with increased water temperature (Bhadja and Vaghela, 2013).

Water temperature can be affected by many ambient conditions. These elements include sunlight/solar radiation, heat transfer from the atmosphere, stream confluence and turbidity. Shallow and surface waters are more easily affected by these factors than deep water (Pasquero, 2008). Man-made influences on water temperature may include thermal pollution, runoff, deforestation and impoundments.

2.2.3 Conductivity, Salinity and Total Dissolved Solids

The USEPA (2012) defines conductivity as a measure of water's ability to pass electrical flow. This is directly proportional to the concentration of ions in the water. Ions that conduct electricity usually originate from dissolved salts and inorganic substances which include alkalis, chlorides, sulphides and carbonate compounds (Miller *et al*., 1988). Compounds that dissolve into ions are also known as electrolytes (Milliequivalents

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(Powerpoint) *et al*., (n.d.)). The more ions found in the water, the higher the level of conductivity. The opposite is also true for lower levels of conductivity, that is, the fewer ions that are in the water, the less conductive it is. Deionized water can act as an insulator due to its near to negligible conductivity value (Perlman, 2014). Sea water, however, has a very high conductivity. Ions are able to conduct electricity because of their positive and negative charges (USEPA, 2012). When electrolytes dissolve in water, they divide into positively and negatively charged elements known as cations and anions respectively. As these combined cations and anions divide in water, the concentrations of each of their charges remain equal. This means that although the conductivity of water rises when more ions are added, it still maintains its electrically neutral state (Perlman, 2014). Conductivity is usually measured in micro- or millisiemens per centimeter (µS/cm or mS/cm).

As a basic definition from Wetzel (2001), salinity is the total concentration of all dissolved salts in water. These electrolytes form ionic particles as they dissolve, each with a positive and negative charge. Hence, salinity contributes strongly to conductivity. Even though the salinity can be measured by a complete chemical analysis, the method is difficult and time consuming (American Public Health Association *et al.*, 1999). For example, the seemingly simple process of evaporating seawater into dry salt mass is near to impossible since the chloride ions may be lost during the process. (Stewart, 2004). More often, salinity is derived from conductivity measurement instead of direct measurement and this is called practical salinity. Wagner (2006) stated in his report that "these derivations compare the specific conductance of the sample to a salinity standard such as seawater". When salinity is measured based on conductivity values, the unit of

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measurement is usually unitless, but are often followed by the notation of practical salinity units (psu) (Sommer and Spitzer, 2004).

There are a variety of dissolved salts that contribute to the salinity of water. The major contributing ions in seawater (with a practical salinity of 35) are: chloride, sodium, magnesium, sulphate, calcium, potassium, bicarbonate and bromine (Sommer and Spitzer, 2004). Freshwater sources also have these ions present in them, but in smaller concentrations (Wetzel, 2001). The surrounding environment is a contributing factor to the ionic composition of most inland water sources such as lakes and rivers which possess alkali and alkaline earth metal salts, with calcium, magnesium, sodium, carbonates and chlorides making up a high percentage of the ionic composition (Wetzel, 2001). According to Paytan (2006), "freshwater usually has a higher bicarbonate ratio while seawater has greater sodium and chloride concentrations". Salinity units of measurement are unstable because of its application and reporting procedure. Parts per thousand or grams/kilogram (1 ppt = 1 g/kg) used to be the standard (NSIDC, 2013). In some freshwater sources, this is reported in mg/L (Wetzel, 2001; Scannell and Jacobs, 2001). Salinity values are now reported based on the unitless Practical Salinity Scale (sometimes denoted in practical salinity units as psu) (NSIDC, 2013).

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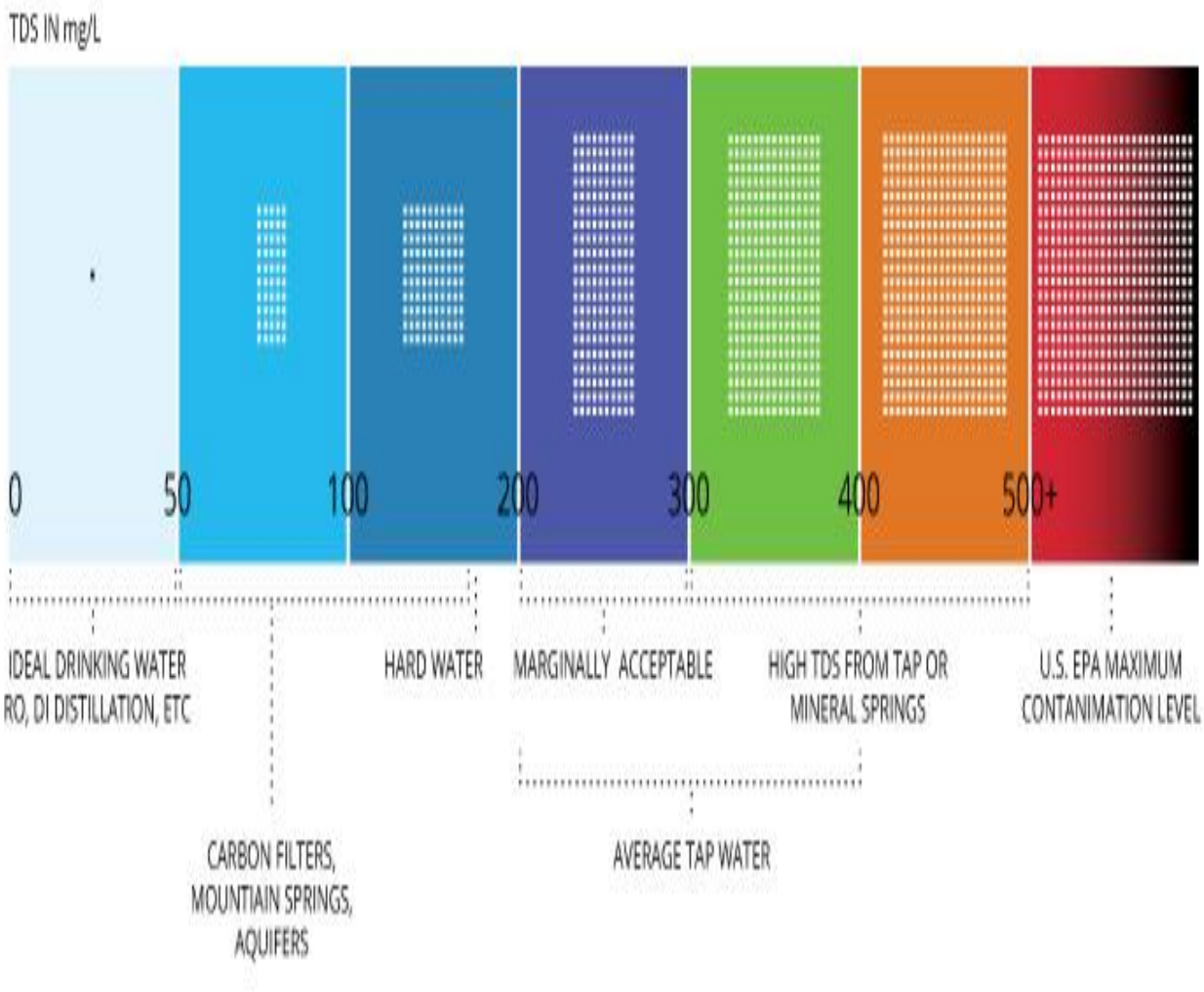

Fig 2.1: The USEPA, USPHS and AWWA recommend an upper limit of 500 mg/L TDS, though this is exceeded in some regions with little ill effect (Hem, 1985).

USEPA (2012) states that, total dissolved solids (TDS) combine the sum of all ion particles that is smaller than 2 microns (0.0002 cm). According to Thompson *et al.* (2006), "this includes all of the disassociated electrolytes that make up salinity concentrations, as well as other compounds such as dissolved organic matter. In "clean" water, TDS is approximately equal to salinity". Thompson *et al.* (2006) again stated that

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"in wastewater or polluted areas, TDS can include organic solutes (such as hydrocarbons and urea) in addition to the salt ions".

While TDS measurements originate from conductivity, some states, regions and agencies often set a TDS maximum instead of a conductivity limit for water quality (Scannell and Jacobs, 2001). At most, freshwater can have 200 mg/L of total dissolved solids and most sources should have much less than that (American Public Health Association *et al*., 1999). Depending on the ionic properties, excessive total dissolved solids can produce toxic effects on fish and fish eggs. Salmonids exposed to higher than average levels of CaSO4 at various life stages experienced reduced survival and reproduction rates (Scannell and Jacobs, 2001). When total dissolved solids ranged above 2200-3600 mg/L, salmonids, perch and pike all showed reduced hatching and egg survival rates (Scannell and Jacobs, 2001). Dissolved solids are also important to aquatic life by keeping cell density balanced; for example in deionized water, water will flow into an organism's cells, causing them to swell (USEPA, 2012). In water with a very high TDS concentration, cells will shrink hence, an organism's ability to move in a water column becomes affected, causing it to float or sink beyond its normal range (USEPA, 2013). TDS can also affect the taste of water, and often is a signal of high alkalinity or hardness (Thompson *et al*., 2006)

Conductivity, is one of the most useful and commonly measured water quality parameters (Miller *et al*., 1988). In addition to being the basis of most salinity and total dissolved solids calculations, conductivity is an early indicator of change in a water system. Most bodies of water maintain a fairly constant conductivity that can be used as a baseline of comparison to future measurements (USEPA, 2012). Significant change, whether it is due

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to natural flooding, evaporation or man-made pollution can be very detrimental to water quality. Conductivity and salinity have a strong correlation (Miller *et al*., 1988). As conductivity is easier to measure, it is used in algorithms estimating salinity and TDS, both of which affect water quality and aquatic life.

Salinity is important in particular as it affects dissolved oxygen solubility. The higher the salinity level, the lower the dissolved oxygen concentration. Oxygen is about 20% less soluble in seawater than in freshwater at the same temperature (Miller *et al*., 1988) . This means that, on average, seawater has a lower dissolved oxygen concentration than freshwater sources. Most aquatic organisms can only tolerate a specific salinity range (SWRCB, 2002). The physiological adaption of each species is determined by the salinity of its surrounding environment. Most species of fish are stenohaline, or exclusively freshwater or exclusively saltwater (Myers, 1949). However, there are a few organisms that can adapt to a range of salinities.

A sudden increase or decrease in conductivity in a body of water can indicate pollution. Agricultural runoff or a sewage leak will increase conductivity due to the additional chloride, phosphate and nitrate ions (USEPA, 2012). An oil spill or addition of other organic compounds would decrease conductivity as these elements do not break down into ions (LCRA, 2014). In both cases, the additional dissolved solids will have a negative impact on water quality. Conductivity and salinity vary greatly between different bodies of water. Most freshwater streams and lakes have low salinity and conductivity values. The oceans have a high conductivity and salinity due to the high number of the dissolved salts present. In streams and rivers, normal conductivity levels come from the surrounding geology. Clay soils will contribute to conductivity, while

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granite bedrock will not (USEPA, 2013). The minerals in clay will ionize as they dissolve, while granite remains inert. Likewise, groundwater inflows will contribute to the conductivity of the stream or river depending on the geology that the groundwater flows through. Groundwater that is heavily ionized from dissolved minerals will increase the conductivity of the water into which it flows. Discharges such as pollution can also contribute to salinity and TDS, as wastewater effluent increases salt ions and an oil spill increases total dissolved solids (USEPA, 2012).

Despite the lack of standards and the effects of the surrounding environment on conductivity, there are approximate values that can be expected based on source (American Public Health Association *et al*., 1999; SWRCB, 2002):

Table 2.1: Different water sources and their equivalent range of electric conductivity (SWRCB, 2002)

TYPE OF WATER	**µS/cm**
Distilled Water	0.5 – 3
Melted Snow	2 – 42
Tap Water	50 – 800
Portable Water in the USA	30 – 1500
Freshwater Streams	100 – 2000
Industrial Wastewater	10000
Seawater	55000

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Freshwater has a wide conductivity range due to geology effects. Freshwater that runs through granite bedrock will have a very low conductivity value (LCRA, 2014). Clay and limestone soils can contribute to higher conductivity values in freshwater (LCRA, 2014). Some saline lakes exist due to a restricted outflow (Wetzel, 2001). The conductivity of these lakes is dependent on the specific ionic composition present (Wetzel, 2001).

Once a history of conductivity measurements has been conducted, it is easy to see an established range for a particular body of water (USEPA, 2012). This range can be used as a baseline to evaluate measurements as expected (and unexpected) values (USEPA, 2012).

Unusual conductivity and salinity levels are usually indicative of pollution (USEPA, 2012). In some cases, such as excessive rainfall or drought, they can be connected to extreme natural causes. Regardless of whether the result was caused by manmade or natural sources, changes in conductivity, salinity and TDS can have an impact on aquatic life and water quality.

2.2.4 Alkalinity

A water body's capability to go through the process of buffering is termed as alkalinity. It is the measurement of water body's capacity to redress acids and bases resulting in the maintenance of a fairly stable pH (Thompson et al., 2006). Compounds including carbonates and bicarbonates as well as hydroxides are constituents of water that is a good buffer. These compounds function by combining with H^+ ions also existing in the water thereby raising the pH of the water to be basic. Without this buffering ability, any acid added especially to a fresh water source would immediately alter its pH (Talley, 2000).

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Alkalinity is commonly derived from rocks and soils, salts, specific plant processes, and specific industrial wastewater effluents (detergents and soap-based effluents are alkaline). If the geology of an area has embedded in it large amounts of calcium carbonate or limestone, the water bodies on which they flow tend to be more alkaline than usual. Granite bedrock however does not have that capacity to buffer acidic inputs because of its deficiency in alkaline ions and compounds (Larson, 2013). Additions of lime as a soil amendment to decrease acidity in home lawns can runoff into surface waters and increase alkalinity.

The USEPA developed 6 categories to describe alkalinity status of lakes and ponds. As the concentration of $CaCO_3$ increases, the alkalinity increases and the risk of acidification decreases.

The U.S. E.P.A. category Concentration of $CaCO_3$(mg/L) are as follows:

Acidified	=	< 1 and pH < 5
Critical	=	< 2
Endangered	=	2 – 5
Highly Sensitive	=	5 – 10
Sensitive	=	10 – 20
Not Sensitive	=	> 20

2.2.5 Dissolved Oxygen and Biological Oxygen Demand

According to Talib and Amat (2012). Dissolved oxygen (DO) is basically oxygen measured in its dissolved state. If the oxygen is expended more than is yielded, dissolved

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oxygen concentrations decrease and some sensitive organisms migrate, become weak, or die.

DO concentrations vary in seasons and even during the day (over a 24-hour period). They fluctuate along with water temperature and altitude. Roelofs (1991) stated in his report that, “cold water holds more oxygen than warm water and water holds less oxygen at higher altitudes”. Thermal effluents, including water used to cool equipments in a manufacturing or power plant, increases the temperature of water hence decreasing its oxygen volume. Lowered DO levels affects most aquatic organisms especially at dawn on hot sunny days when the flow of streams decrease, water temperatures increase and aquatic flora’s ability to produce oxygen has not been met by sunset.

Biochemical oxygen demand, or BOD, is the measurement of the bulk of oxygen absorbed in stream water by microorganisms in decomposing organic matter (Talib and Amat, 2012). BOD is also the measurement of the removal of oxygen from a water body through a chemical reaction. Usually, an experiment is used to quantify the concentration of oxygen expended by these organisms during a particular period of time (usually 5 days at 20°C). The rate of oxygen absorption in a stream or river is often influenced by a number of parameters: temperature, pH, the presence of certain species of microorganisms, and the type of biological and non-biological material in the water (APHA, 1992).

BOD directly proportional to dissolved oxygen in rivers and streams. In other words, BOD has a great influence on dissolved oxygen in every aquatic medium. When BOD increases, oxygen is depleted rapidly in the stream. This will ultimately make less oxygen

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available to higher forms of aquatic life. The effects of high BOD are the same as those for low concentrations of dissolved oxygen: aquatic organisms become stressed, suffocate, and die (Hach *et al.*, 1997).

According to Sarfo- Afriyie (1999), "BOD is evident when substances such as leaves and woody debris; dead plants and animals; animal manure; effluents from pulp and paper mills, wastewater treatment plants, feedlots, and food-processing plants, failing septic systems and urban storm-water runoff are present in the water body".

2.2.6 Chemical Oxygen Demand

The ability of water to absorb oxygen during the breakdown of organic substances and the oxidation of inorganic compounds such as ammonia and nitrite is known as Chemical oxygen demand (COD) (Talib and Amat, 2012). COD calculations are often conducted on samples of waste waters or of natural waters polluted by domestic and/or industrial wastes. COD is calculated as a standardized laboratory assay where a sample of water which is closed is allowed to brood with a strong chemical oxidant under a specific mode of temperature and for a particular time frame (APHA, 1992). A commonly used oxidant in COD assays is potassium dichromate ($K_2Cr_2O_7$) and it is mostly in combination with boiling sulfuric acid (H_2SO_4). COD has a strong relationship with biochemical oxygen demand (BOD) which is another standard test for ascertaining the strength of oxygen-demand of waste waters. However, BOD only calculates the concentration of oxygen absorbed by oxidation of microbes and is most significant to waters abundant in organic materials (Boyles, 1997a). It is crucial to understand that COD and BOD do not necessarily calculate the same types of rate of consumption of oxygen. For example,

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COD does not measure the oxygen-consuming potential associated with certain dissolved organic compounds such as acetate but acetate can be degraded by microorganisms and would therefore be detected in an experiment of BOD. On the other hand, the rate at which oxygen is consumed by cellulose is not measured during a short-term BOD experiment, but it is measured during a COD test (Boyles, 1997b). The dichromate reflux method has been preferred choice of assay procedure over other methods using other oxidants because of its high oxidizing ability with different types of samples, and ease of management (APHA, 1992).

2.2.7 Total Hardness

When water passes through or over mineral deposits such as limestone, the levels of Ca^{2+}, Mg^{2+}, and HCO_3^- ions present in the water greatly increase and cause the water to be classified as hard water (Perlman, 2014). This term results from the fact that calcium or magnesium ions in water combine with soap molecules, forming a sticky scum that interferes with soap action and makes it "hard" to get suds. One of the most obvious signs of water hardness is a layer of white film left on the surface of showers. Since most hard-water ions originate from calcium carbonate, levels of water hardness are often referred to in terms of hardness as $CaCO_3$ (Bennet and Di Santo, 2011)

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2.3 Major Ions

2.3.1 Anions ($NO_3^-, PO_4^{3-}, SO_4^{2-}, Cl^-$)

2.3.1.1 Nitrate (NO_3^-)

Nitrate ion which is commonly found in natural waters is known as one of the frequently combined form of nitrogen in aquatic habitat. Plant and animal debris, igneous rocks and land drainage are common sources of nitrate especially in surface water. However, human induces activities which involve leachates from land fill sites, sewage effluence and waste water from industries and municipal communities as well as the use of inorganic fertilizers can contribute to significant levels of nitrate in surface water (Stute, 2015).

Natural unpolluted water will have nitrate levels not exceeding 0.1 mg/L. Nevertheless, influenced by human activities, nitrate concentrations can have a limit between 1mg/L NO_3-N – 5 mg/L NO_3-N. However, concentrations are mostly less than 1 mg/L. If the surface water is hit by extreme pollution such as fertilizer run off or human and animal waste, concentrations usually exceed 5 mg/L and can rise up to 200 mg/L in the case of very extreme pollution (Finlayson *et al.*2000).

2.3.1.2 Phosphorus (PO_4^{3-})

Phosphorus in an aquatic habitat is an essential nutrient and usually occurs as particulate species and dissolved compounds. However, increase in phosphorus concentrations usually due to anthropogenic activities is the major cause of eutrophication (Stute, 2015).

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Phosphorus usually occurs as orthophosphates and polyphosphates as well as organically bound phosphates in natural and waste waters. Due to decomposition and synthesis of organic bound forms, changes between the forms of phosphorus continuously occur. Anthropogenic pollution such as fertilizer run-off, industrial effluents and domestic waste water especially those containing detergents does elevate phosphorus levels in surface water.

Even though phosphorus rarely occurs in high concentrations in freshwater due to the constant uptake by plants there can be elevated values occurring as seasonal fluctuations control the concentrations in surface water. Most natural waters have phosphorus concentrations ranging from 0.005-0.020 mg/L PO_4-P. saline waters may have as high as 200 mg/L PO_4-P whereas pristine waters may have low concentrations of 0.001 mg/L

2.3.1.3 Sulphate (SO_4^{2-})

Sulphate arises from decomposition of oceanic aerosols and the leaching of sulphur compounds, either sulphate minerals such as gypsum or pyrite from sedimentary rocks. It occurs naturally in surface waters as SO_4^{2-} and is readily soluble in water. It is also a stable oxidant from sulphur. Industrial discharges can also be a major contributing factor to the amount of SO_4^{2-} in surface water. It is used by bacteria as a source of oxygen and thereby converting sulphate to Hydrogen Sulphide (H_2S) under anaerobic conditions (Stute, 2015).

In natural waters sulphate may range from 2-80 mg/L even though it may be greater than 1000 mg/L especially in areas which are close to industrial discharges or where sulphate

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minerals such as gypsum is present. When sulphate concentrations hit amounts >400mg/L, it may be unpleasant to drink (Finlayson *et al.*, 2000).

2.3.1.4 Chloride (Cl^-)

Chloride, (which mostly occurs as Cl^- in solution) finds its source in surface water from industrial and sewage effluents, agricultural run-off, weathering of sedimentary rocks whicih contain salt deposits and sometimes from atmospheric deposition of oceanic aerosols. High concentrations of chloride may cause the water to be unpalatable and therefore unsuitable for drinking purposes both for humans and livestock (Sytsma, 2009).

Pristine freshwaters usually contain chloride concentrations lower than 10 mg/L and sometimes less than 2 mg/L. Higher concentrations may however occur near sewage and other waste outlets, irrigation drains, salt water intrusions and arid and wet coastal areas. Chloride is frequently associated with sewage and therefore may be a good indicator in the assessment of the possible extent of dispersion of sewage discharges in water bodies (Watershed Action Plan Development Guidebook, 2001).

2.3.2 Cations (Ca^{2+}, Mg^{2+}, Na^+, K^+)

2.3.2.1 Calcium (Ca^{2+})

Calcium which is present in all waters finds its source from calcium rich minerals especially as carbonates and sulphates such as limestone and gypsum. Calcium together with magnesium salts is mainly responsible for hardness in water. Anthropogenic activities also contribute to increased calcium concentrations in surface waters (Sytsma, 2009).

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Since calcium is an essential element for all organisms, it can be found incorporated in the shells and bones of invertebrates and vertebrates respectively. Natural waters contain Ca^{2+} concentrations of < 15 mg/L whereas waters with carbonate rich rocks may reach concentrations of 30 – 100 mg/L. salt waters however may reach concentration levels of several hundred mg/L or more. Ca^{2+} can be determined by a titrimetric method using EDTA or by Atomic Absorption Spectrometry (Finlayson *et al.*, 2000).

2.3.2.2 Magnesium (Mg^{2+})

Along with calcium, magnesium which occurs mostly in common natural waters as Mg^{2+} is the main source of water hardness. Magnesium finds its source mostly from ferromagnesium minerals and from some carbonate rocks which releases magnesium ions as a result of rock weathering (Talley, 2000). Magnesium can also be found in organic matter and organometallic compounds since it is a necessary element for use by most living organisms.

Magnesium concentrations in the natural fresh water state may range from 1 to > 100 mg/L depending on the geology within the catchment area. Magnesium is greatly used in the industrial sector however the industries contribute little to the total prevailing concentrations of magnesium in surface water (USEPA, 2013).

Magnesium is usually analysed using the EDTA method or the Atomic Absorption Spectrometer. Magnesium concentrations can also be estimated by evaluating the difference between total hardness and calcium concentrations (USEPA, 2012).

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2.3.2.3 Sodium (Na^+)

Sodium salts are highly water soluble, very abundant in the earth and is found in all natural waters. It is also found plant and animal matter as well as in an ionic form. Anthropogenic activities may however increase Na^+ concentrations in natural waters. Intrusion from sea water mat also result in high concentrations in coastal aquatic habitats (Keiden, 1999).

Sodium concentrations vary depending on its source, whether geological or anthropogenic. Concentrations values can range from 1 mg/L or less to 10 mg/L or more in natural salt waters. Many surface waters, including those receiving wastewaters, have concentrations well above 50 mg/L (APHA, 1992)

2.3.2.3.1 Sodium Adsorption Ratio (SAR)

Where water is to be used for agricultural purposes especially irrigation and for drinking, sodium is commonly measured. Restricted water movement and stunted plant growth may result from high concentrations of Na^+ which causes soil degradation. SAR is therefore used in the evaluation of water's suitability for irrigation. The SAR gives information as to how much sodium can be adsorbed by the soil. This therefore means that, high SAR will indicate that Na^+ may substitute Calcium and Magnesium concentrations in the water thereby causing soil degradation (Water Analysis Guide, 2004). The formula for calculating SAR for irrigation water is defined as;

$$\text{SAR} = \frac{Na^+}{\sqrt{(Ca^{2+} + Mg^{2+})/2}} \qquad 2.1$$

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Where ion concentrations are measured in milliequivalents per litre (meq/L)

Table 2.2 shows an interpretative guideline on SAR results

Table 2.2: Interpretative guideline for SAR results (Water Analysis Guide, 2004)

SAR HAZARD LEVELS

Application	**None**	**Increasing**	**Significant**	**High**	**Severe**	**Very Severe**
Most Production Systems	<1	1-2	2-4	4-5	5-12	>13

2.3.2.4 Potassium (K^+)

Potassium salts are widely used industries and in the manufacture of agriculture fertilizers even though they occur in small amounts in natural waters because of the resistibility of potassium rich rocks to weathering. These industrial and agricultural products increase the level of K^+ in water when discharges and run-off occurs (Keiden, 1999).

Potassium is highly soluble and often occurs in its ionic form. It is also found in most aquatic biota and mineral structures. Natural water concentrations usually occur less than 10 mg/L. However, salt waters and hot springs can have high concentrations of 25,000 mg/L and 100 mg/L respectively

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2.4 Metals, Pesticides and Herbicides, Organics

Metals, petroleum products, and organic contaminants, including solvents, electrical insulators, lubricants, herbicides, fungicides, and pesticides, can accumulate in aquatic environments and cause toxic effects on aquatic life and increase health risks of drinking water. These chemicals are at very low concentrations in the natural environment, and they are typically introduced to surface waters as waste from human activities. Some of the metals of concern for human and aquatic health are cadmium, lead, copper, mercury, selenium, and chromium (Taylor, 1997).

Cadmium is widely used in industry and is often found in solution in industrial waste discharges. Cadmium replaces zinc in the body, and long term consumption of cadmium may lead to bodily disorders. Cadmium is toxic to both humans and fish and seems to be a cumulative toxicant. Small salmon fry have been killed from concentrations of 0.03 mg/L (APHA *et al.*, 1999).

Lead sources are batteries, gasoline, paints, caulking, rubber, and plastics. Lead can cause a variety of neurological disorders. In children, it inhibits brain cell development. Lead also prevents the uptake of iron, so people ingesting lead often exhibit symptoms of anemia including pale skin, fatigue, irritability, and mile headaches (Keiden, 1999).

Metal plating, electrical equipment, pesticides, paint additives, and wood preservatives are sources of copper. Copper is also toxic to juvenile fish. Other toxicants that are associated with industrial effluent are mercury and silver (Davies and Mazunda, 2003).

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Mercury and silver affect fish in ways similar to cadmium, copper, lead and zinc. When fish are exposed to either of these at certain concentrations, gill tissues are damaged and death by asphyxiation can occur (Donald *et al.,* 1999).

Pesticides and herbicides are found in streams and rivers draining agricultural and residential areas, usually during periods of extended wet weather or intense precipitation when overland flow is most likely (Donald *et al.,* 1999). These substances are toxic to many aquatic organisms and they may act as mutagens for human beings. Since water treatment plants are not designed to remove these substances, it is important to prevent their introduction to drinking water supplies (USEPA, 2012).

There are a wide variety of organic chemicals, including chlorinated hydrocarbons that are used as solvents, cleaners, lubricants, insulators, and fuels in many industries. Many of these chemicals are believed to be cancer-causing agents. Since these are organic chemicals, most of them are biologically active to some degree. This means that bacteria in the environment often degrade these substances into byproducts. Unfortunately, some of these byproducts are more toxic than the original substance (APHA *et al.*,1999).

The EPA regulates concentrations of literally hundreds of these chemicals in drinking water and groundwater. These chemicals are often found in association with each other, and the inter-actions of these chemicals as mutagens are poorly understood. Because they are suspected cancer-causing agents, regulatory levels for many of these chemicals are in the parts per billion range, which means that analytical techniques for these chemicals are rigorous, time-consuming, and expensive. False positive measurements for these chemicals are quite common (USEPA, 2013).

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CHAPTER THREE

METHODOLOGY

3.1 The Study Area

The Muni wetland is situated in the Central Region of Ghana. It lies between longitudes 0°38'20" and 0° 42'00" West and latitudes 5° 20'00" and 5°25'30" North (Fig. 3.1). It approximately covers an area of 9500 ha and has an altitude ranging from 0-290 m above mean sea level (Hawthorne and Abujuam, 1995).

Specifically, the study area is situated to the west of the coastal town of Winneba, approximately 55 km west of Accra. It encompasses over 90 km² of the Muni lagoon watershed. The northern part comprises two protected areas, Yenku A and Yenku B Forest Reserves, (covering 10% of the site), while the traditional hunting areas of the Efutu people make up another 15% (Amatekpor, 1994). Also included is the catchment of three seasonal rivers, the Pratu, the Ntakofa and the Muni, which drain into Muni lagoon. This lagoon, its surrounding flood-plains and the adjacent sandy beach, constitute the southern part of the site. It is a shallow, saline, closed, coastal lagoon, with a surface area of about 300 ha. Reports indicate that during the rains the lagoon fills up completely and spills over to flood the surrounding area about once every 10 years. At such times, the villagers dig a canal to open the entrance to the sea and the excess water is released (Wuver and Attuquayefio, 2006).

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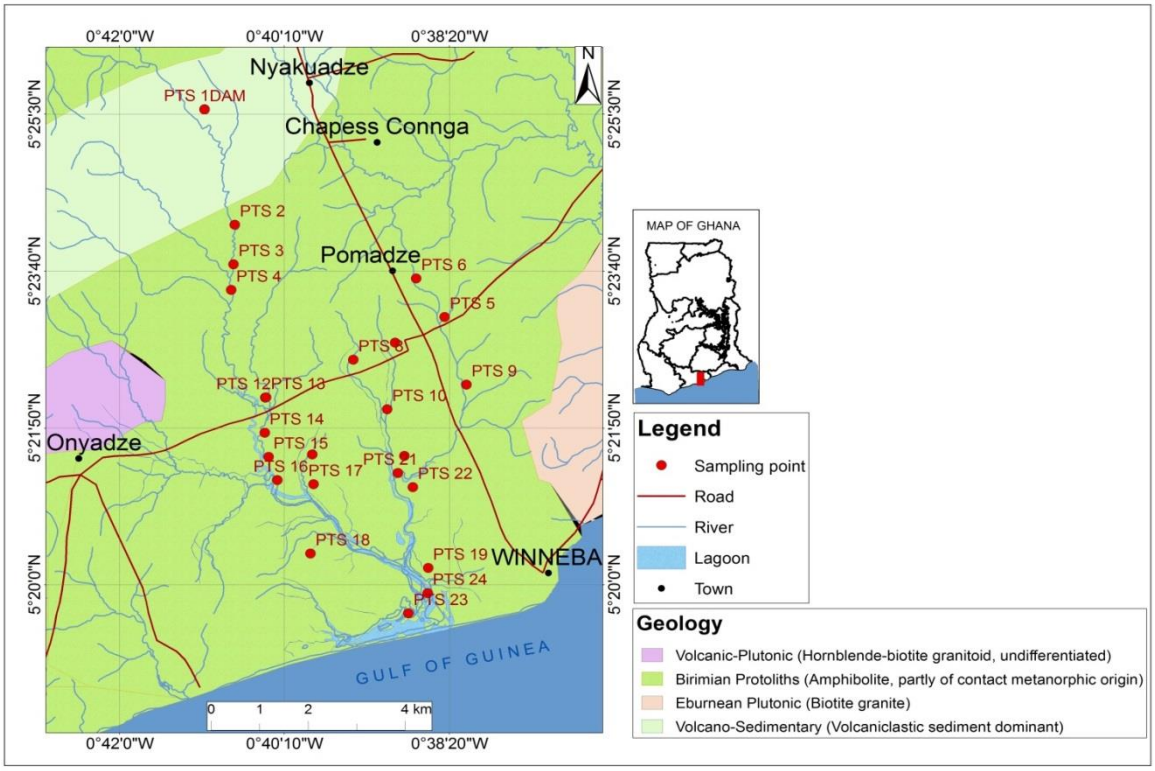

Fig 3.1: Map of the study area showing the various sampling points and geology on the Pratu River, its tributary and the Muni Lagoon

3.1.1 Geology

The geology of the area is made up of volcanic plutonic rocks with hornblende-biotite granitoid minerals that are undifferentiated along the Onyadze area of Winneba. Majority of the Winneba municipality, however, is made up of the Birimaian Protoliths which originate from amphibolites, partly of contact to metamorphic origin. Other parts of the area are made up of the Ebumean Plutonic originating from the biotite granite and upstream at Nyakuadze are the volcanic sedimentary rocks (Kesse, 1985).

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3.1.2 Climate

The area falls within the coastal savanna vegetation zone of Ghana, characterized by a mean annual bimodal rainfall of about 854mm. The major rainy season starts from March/April to July/August with peak rainfall in June. The minor rainfall season runs from September to November. The main dry season runs from December to March, with the minor dry season running from August to September. The mean annual temperature ranges from 24 °C in August to 29 °C in March and relative humidity (RH) ranges between 75 and 80% (Hawthorne and Abujuam, 1995).

3.1.3 Vegetation

The vegetation of the wetland is southern marginal forest, comprising mainly of grassland, thicket islands and savanna trees (Hall and Swaine, 1981). Dominant grass species include *Andropogon gayanus, Hetero-pogon contortus, Panicum maximum* and *Sporobolus pyramidalis*. About 40% of the area was converted into *Eucalyptus, Azadirachia indica* (neem) and teak plantations when parts of the area were designated as forest reserves (Yenku A and B). The lagoon shoreline is covered with *Sesuvium portulacastrum*, *Paspalum vaginatum* and *Sporolobus virginicus*, successively, up the sides of the dunes. The sand dunes themselves are planted with coconut-palm *Cocos nucifera*. The vegetation in the northern part of the wetland includes mangroves, with *Typha australis*, *Ludwigia erecta* and other typical freshwater hydrophytes occurring further inland.

The major human activities in the wetland are farming and artisanal fishing (marine and lagoon). Other activities include hunting, sand-winning, charcoal burning, crafts, salt and

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clay mining, alcohol distillation, quarrying and trading, illegal gold mining operations, block making factories and generator repairs shops (Wyllie, 1968). Maize, plantain and cassava are the main cultivated crops as well as vegetables such as okra, green pepper, tomatoes, red pepper and fruits including mangoes and bananas. There are human settlements in the wetland, the largest being Winneba with a population of approximately 27000 people (Grimble et al., 1998)

3.2 Choice of Sampling Points

The sampling area that was captured for this research included three main parts of the Pratu River namely; the Pratu River which forms the main river into which the tributaries flow, the Ntakofa River which is a tributary of Pratu River and the Muni lagoon into which the Pratu River flows.

Twenty five (25) sampling points were chosen to study the impact of farming and anthropogenic activities on the water quality of the Pratu River and its tributaries. The sampling points included 5 points from the surrounding villages on the road to Agona Swedru town (Nyarkuadze and Chapess Connga including a sample taken from a dam which is presumed to be the source of the main river), 6 points from along the main Winneba Junction to the Apam Junction road which houses a number of towns such as Onyadze and Bewadze; two points were taken behind the Winneba Senior High School where the tributary Ntakofa flows and three taken from an area still located at the Winneba Senior High School but has been taken over by intensive vegetable farming activities. Six points were taken from the Pomadze town and three samples taken from the Muni lagoon itself.

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3.3 Sampling Procedure Employed

Both water and sediment samples were collected following stratified sampling procedure (Yogesh, 2006). This is a probability sampling which involves dividing the population into smaller homogenous groups (strata). Within these smaller strata random samples are drawn. In this work, the Pratu and Ntakofa Rivers as well as the Muni lagoon was divided based on the assumption that pollution may be occurring due to the population size and the sort of activities going on in that area. Stratified sampling is a good representative of the population because it is objective and can be used for inferential purposes. It is also a very important technique for sampling because:

i. It follows systematic grouping of the river into different regions based on mainly consideration of human activities (e.g. small scale industries, human settlements and population size)

ii. This method is also statistically good because it optimizes the number of samples required. Thus the amount of bias introduced during sampling decreases.

Combining the above sampling strategy and a topographical map of the area, the Pratu River, its tributary (Ntakofa) and the Muni lagoon were divided into a total of 25 surface water and 17 sediment sampling points. Each of these parts of the river catchment has its own specific characteristics which are:

- **Pratu River**: 13 sampling points were earmarked on the Pratu River. A dam is situated the river and serves as the main source of water for rivers PTS1 – PTS4. PTS1 – PTS4 drains small surrounding villages with various farmlands scattered around the area. PTS1 especially houses a galamsey operation site just about a

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kilometer away from the river PTS12 and 13 are located very close to a local settlement along the main Cape Coast road. There is a fish pond sited just a few meters away from PTS12. PTS14 to PTS18 are located in a local settlement also called Pomadze and is dominated mainly by cattle grazing and a few farmlands.

- **Ntakofa River**: This is a tributary of Pratu River and is sourced in a town called Pomadze. PTS5, 6, 7 and 8 are located at the heart of Pomadze town surrounded by various local industries including block making factories, human settlements and a school (primary and JHS). PTS9 is located at a new settlement and has a local domestic sewage flowing through that part of the river. PTS10, 20, 21 and 22 are located behind the Winneba Senior High School where intensive vegetable farming prevails. That part of the river is mainly used as a major source of irrigation.
- **Muni lagoon**: Muni lagoon is surrounded by a local township just along the shore at the lagoon. Thus, human waste (both faecal and domestic) is visibly seen along the shores of the lagoon. There is also a salt winning site and a cattle farm located along the lagoon banks. Harvesting of shell fishes is one of the major activities of the inhabitants residing there.

3.4 Sample Collection

Both water and sediment samples were collected for the study. Global Positioning System (GPS) was used to exactly mark the locations of the sampling points.

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3.4.1 Collection of Water Samples

Water samples were collected in a 330ml polyethylene bottles. They were all soaked in detergent solution for 24 hours, rinsed with tap water, followed by soaking in 10% v/v nitric acid (HNO_3) for another 24 hours. The bottles were then rinsed with distilled water and then dried. Grab sampling method, which is a single volume of water taken at one time from a single point was found to be more appropriate for the study (APHA, 1998). This method was thus employed to collect the surface water from the Dam through to the Muni lagoon.

At each sampling point, the river water was used to rinse the inside and outside of each bottle three times before filling it up. This was done to prevent mixing of rinsing water with the final sampling specimen. The water was collected by tilting the bottle against the direction of the flow of the river. Labelling of each water sample was done appropriately as described in Appendix A. The samples were then stored in a thermally insulated container with ice packs with the intention of maintaining an optimum temperature of 4°C. This technique conserves the concentration of the compounds in the water at the time between collection and analysis.

3.4.2 Sediment Sampling

About 1 kg of sediment sample was taken at each of the sampling points where the water samples were taken and labelled accordingly from PTSS1 – PTSS24. Sediment samples from the Dam were not taken because the water depth was too deep to sample and there were no available divers to help with the sampling.

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The sediment from each sampling point was collected with an acid pre-cleaned plastic shovel. The shovel was washed with the river water where the sediment was collected between successive sampling points. After collection, the sediment was transferred from the shovel to clean hermitically closed polyethylene bags (zip lock) and stored in a thermally insulated container with ice packs. All sediments and water samples were then transported to the Laboratory at the Ghana Atomic Energy Commission (GAEC).

On arrival at the laboratory, sediment samples were divided into two equal parts. The first part were freeze dried with the CHRIS ETA 1 – 16 for 96 hours, then the clods in the samples were crushed and each was pulverized with the FRITSCH Pulverisette 2 into a fine texture in a dust free room. With the help of Retsch AS 20 shaker, at 10mm/g amplitude, the pulverized samples were sieved through 500 µm or 0.5 mm metric test sieve. The sieved samples were individually packed into clean transparent hermitically closed polyethylene bags and labeled appropriately for further laboratory analysis.

The second portion of the sediment samples were stored at room temperature in the laboratory to be transferred to the Ghana Standards Authority (GSA) for pesticide residue analysis.

3.5 Analysis of Samples

3.5.1 Physico-Chemical Parameters

Water temperature, pH, Electrical Conductivity (EC), Salinity, Total Dissolved Solids (TDS) and Alkalinity were measured in the field. These were done according to the protocol prescribed by Standards methods for Examination of Water and Wastewater

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(APHA, 1998). Measurement were done by inserting the probe of an already calibrated Hach Sensions 5 Conductometer and Portable Hach pH Meter (calibrated with buffers of 4, 10 and 12.) into a collected amount of the surface water in a beaker at every sampling point. Readings were taken after the readings stabilized. The probe of the conductometer and pH meter was completely cleaned with deionized water after use at each site.

3.5.2 Alkalinity

The Alkalinity Test Kit was used for the alkalinity analysis in the field. All equipment was rinsed with deionized water before the test began. 5 mL of the water sample was measured into the portable polyethylene beaker and one drops of bromophenol indicator was added to the sample. The beaker was then covered with a plastic cap and shaken gently. About 1 ml of 0.01 M HCl was measured using a portable syringe and inserted into the beaker through a small cavity provided on the cap of the beaker.

Titration of the samples with HCl was done a pale yellow end point. The titre value was then recorded and put into the equation 3.1 to calculate the alkalinity concentration.

$$\text{Alkalinity} = \frac{A\,x\,[HCl]x\,5000}{v} \qquad 3.1$$

Where

A = Titre Value in mL

[HCl] = Concentration of HCl (0.02 M)

V = Volume of Water Sample (5 mL)

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3.5.3 Dissolved Oxygen

Dissolved oxygen (DO) analysis was carried out in two phases: DO1 which refers to DO analysis performed on the first day and DO5 which is dissolved oxygen analysis performed on the fifth day. For DO1, 1 ml of Winkler 1 and 1 ml of Winkler 2 solutions were added to the water sample at each sampling point. After rigorously shaking the sample, 5 mL of sulfuric acid were added to the water sample and shaken again. The addition of sulfuric acid was done to dissolve the precipitate formed from adding the Winkler 1 and 2. The solution turned deep yellow after this.

About 25 mL of the water sample was then pipetted into a conical flask and titrated against 0.025 M sodium thiosulphate solution till it turned pale yellow. About 2 drops of starch indicator was then added to the water sample which turned deep blue. A final titration was done again with sodium thiosulphate solution till the colour turned from deep blue to colourless. The titre value was then recorded and put into equation 3.2 to obtain the DO concentration.

$$\text{DO (mg/L)} = \frac{Titre\ value\ of\ Sodium\ Thiosulphate\ x\ 101.6}{Volume\ of\ sample} \qquad 3.2$$

DO5 analysis was performed on water samples incubated at 20 ^{0}C for five days using the same procedure as DO1. Biological oxygen demand (BOD) was recorded by subtracting the concentration of DO5 from that of DO1.

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3.5.4 Chemical Oxygen Demand (Cod)

Surface water sample (25 mL) was measured into a glass tube and 1.5 mL of potassium dichromate ($K_2Cr_2O_7$) solution added to it. About 3.5 mL of sulphuric acid reagent was then carefully added to the mixture which formed a yellow solution. Distilled water (25 ml) was also taken though the same procedure. The tubes were then closed and kept in a COD digester at 150°C for about 2 hours. After digestion, both solutions were removed and placed on the laboratory table to cool to room temperature. The solutions were then transferred into two conical flasks after the cooling. Two drops of ferroin indicator was then added to both samples which turned the solution green. Titration of the solutions was done against Ferrous Ammonium sulphate solution till the green colour turned reddish brown showing the endpoint of titration. The titre values of both samples were then used to calculate the concentration of COD using equation 3.3:

$$\text{COD (mg/L)} = \frac{(A-B)x\ N\ x\ 8\ x\ 1000}{Volume\ of\ sample\ taken} \qquad 3.3$$

Where A = Blank (Distilled water titrant)

B = Sample Titrant

N= Concentration of Ferrous Ammonium Sulphate (0.1M)

3.5.5 Total Hardness

Total hardness concentration was determined using the titrimetric method. About 25 mL aliquot of the water sample was pipetted into a conical flask. 2 mL of ammonia buffer was then added to the sample and then two drops of EBT indicator was also added which

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changed the colour of the sample to pinkish red. Titration of the sample was then done against EDTA solution till the colour of the sample turned steel blue indicating the endpoint of the titration. Total hardness was then calculated using equation 3.4:

$$\text{Total Hardness (mg/L)} = \frac{Volume\ of\ EDTA\ x\ N\ x\ 50\ x\ 1000}{volume\ of\ sample\ taken} \qquad 3.4$$

Where:

N = Concentration of EDTA (0.002M)

Volume of EDTA = Titre value of EDTA

3.6 Major Ions

Water samples used for major ion analyses were subjected to filtration through suction into cleaned 330 mL polyethylene bottles.

3.6.1 Cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+})

3.6.1.1 Sodium and Potassium

The flame photometer was used for the sodium and Potassium analysis. The Flame Photometer, (Sherwood Flame Photometer Model 420), was switched on for 15 minutes before use to achieve optimum operation of the equipment. The machine was calibrated with distilled water which served as a blank and a mixed sodium and potassium standards solution (100 mg/L). The calibrated solution was prepared by adding about 2 mL of

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lithium standard (100 mg/L) to 5 mL of the blank (distilled water) and 5 mL of the mixed sodium and potassium standard. After the calibration, 5 ml each of the filtered water samples was analyzed by adding 2 mL of the lithium standard to the various samples and aspirated through the photometer to record the corresponding values of sodium and potassium.

3.6.1.2 Calcium

Calcium analysis was done using the EDTA complexometric method. 25 mL of the field sample was pipetted into a conical flask. 2 mL of NaOH solution was added to the sample and a pinch of Ammonium purpurete was also added. This action turned the sample pink. The solution was then titrated against the EDTA solution till it turned purple which indicated the endpoint of the titration. Concentration of calcium was determined using equation 3.5:

$$\text{Calcium Hardness (mg/L)} = \frac{Volume\ of\ EDTA\ x\ N\ x\ 50\ x\ 1000}{Volume\ of\ sample} \qquad 3.5$$

Where:

N = Concentration of EDTA (0.002M)

Volume of EDTA = Titre value of EDTA

The result obtained from this formula was used to determine the actual calcium present in the sample using the formula below:

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Ca^{2+}, present in sample = $\frac{Ca^{2+}\ hardness\ in\ mg/L\ x\ Molecular\ weight\ of\ Ca}{Molecular\ weight\ of\ CaCO_3}$ 3.6

Where:

Molecular weight of Ca = 40.078 g

Molecular weight of $CaCO_3$ = 100 g

3.6.1.3 Magnesium (Mg^{2+})

Magnesium analysis was performed using the Atomic Absorption Spectrometer (AAS). This was done by putting 1 mL of each filtered sample in the test tube and aspirated through the AAS. Readings were recorded appropriately.

3.6.2 Anions ($NO_3^-, PO_4^{3-}, SO_4^{2-}, Cl^-$)

3.6.2.1 Nitrate, Phosphate and Sulphate

The nitrate, phosphate and sulphate concentrations were determined using the following official methods according to the Association of Official Analytical Chemists (AOAC).

3.6.2.1.1Nitriate (NO_3^-)

3.6.2.1.1.1 Principle and Calibration

Nitrate was determined using AOAC Official method 973.50 (AOAC, 1995). Nitrate ion is made to react with brucine sulphate in H_2SO_4 solution at 100 °C. The complex produces a yellow colour which was measured at a wavelength of 410 nm.

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In the process of calibration, 5 mL of each of the calibrant solution (0 – 0.5 mg/L) was pipetted into separate 20 mL test tubes. 1 mL of 30% NaCl solution followed by 5 mL, 6.5 M H_2SO_4 was added to each of the test tubes. To ensure thorough mixing of the reagents, the test tubes were shaken well. About 0.5 mL of brucine sulphanilic acid was added to the content of each test tube with exception to the blank sample. The tubes were then placed in a test tube rack and lowered into a water bath set at 95 °C for 25 minutes. After this, the rack holding the test tubes was removed from the water bath and immersed in ice. An appropriate aliquot of the yellow coloured calibrant solutions was transferred into a 1 cm cell. The cell was then placed in the spectrophotometer and the absorbance of the solution measured at a wavelength of 410 nm. A standard graph of absorbance of standards against concentration of standards was plotted as seen at Appendix C

3.6.2.1.1.2 Measurement of Nitrate levels in water samples

Succeeding the calibration process, 5 mL aliquot of water samples were transferred into separate 20 mL test tubes and the same procedure used for the establishment of the calibration graph. This was done to obtain the absorbance of each of the samples at a wavelength of 410 nm on the UV-Visible Spectrophotometer. The concentration of NO_3^- in the sample was deduced from the calibration graph and calculated using equation 3.7:

$[NO_3^-]$ = [Calibration] x Df **3.7**

Where: $[NO_3^-]$ = concentration of nitrate

[Calibration] = concentration from calibration graph

Df = Dilution factor

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3.6.2.1.2 Phosphate (PO_4^{3-})

3.6.2.1.2.1 Principle and calibration

The ascorbic acid method (Official Method 4500) was used to determine the levels of phosphate in water samples APHA, 1992).

Ammonium molybdate and potassium antimonyl tartrate react in acid medium with orthophosphate to form an antimonyl-phosphomolybdate complex, which is reduced to intensely coloured molybdenum blue ascorbic acid. The absorbance of the molybdenum blue is measured at a wavelength of 880nm on the UV-Visible Spectrophotometer.

To calibrate the UV-Visible Spectrometer, 10 mL aliquot of the calibrant solutions (0 – 0.5 mg/L) were transferred into separate 20 mL test tubes. To each test tube, 2 mL of the combined reagent was added to each test tube and left to stand for about 5 minutes. During this period, the blue colour of antimonyl – phosphomolbdate complex was developed in each test tube. Appropriate aliquot of each blue coloured calibrant solution was transferred into a 1 mL cuvette; the cuvette was inserted into the spectrophotometer and the absorbance measured at a wavelength of 880 nm against a reagent blank. A calibration graph of absorbance against concentration of PO_4^{3-} in each calibrant solution was plotted. The concentration of PO_4^{3-} in the sample was deduced from the calibration graph.

3.6.2.1.2.2 Phosphate Analysis of Water Samples

For PO_4^{3-} analysis, 10 mL aliquot of ach sample was transferred into a 20 mL test tube and the same procedure as used for the establishment of the calibration graph was

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followed to obtain the absorbance of each sample at a wavelength of 880 nm on the UV-Visible Spectrophotometer.

3.6.2.1.3 Sulphate SO_4^{2-}

3.6.2.1.3.1 Principle and Calibration

The turbidimetric method (Official Method 4500) was used to determine sulphate. In principle, there is a reaction of SO_4^{2-} with barium chloride ($BaCl_2$) under acidic conditions to precipitate barium sulphate ($BaSO_4$), the absorbance of $BaSO_4$ suspension is measured at a wavelength of 420 nm on the UV-Visible Spectrophotometer.

To calibrate the spectrometer, 10 mL of the standard SO_4^{2-} solutions (0 – 25 mg/L) were quantitatively transferred into separate test tubes. 1 mL of the acid salt solution, 0.5 mL glycerol solution (Conc.) and 0.5 g of $BaCl_2$ were added to each test tube, shaken for 50 seconds and left to stand for 5 minutes. The solution turned cloudy. A given aliquot of the cloudy solution was then transferred into a 1 cm cell and the absorbance of the coloured solution measured at a wavelength of 420 nm on the UV-Visible Spectrophotometer. The absorbance of each calibrant solution was plotted against concentration of the calibrants. The concentrations of the water samples were deduced from the straight line graph of after measurement of the absorbance for each sample.

3.6.2.1.3.2 Sulphate Analysis of water samples

About 10 mL aliquot of each water sample was transferred into a 20 mL test tube and the same procedure as used for the establishment of the calibration graph was followed to

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obtain the absorbance at a wavelength of 420 nm on the UV-Visible Spectrophotometer. The concentration of SO_4^{2-} in each of the water samples was obtained from the calibration graph.

3.6.2.2 Chloride (Cl^-)

The Mohr Method which makes use of Silver nitrate was used for the analysis of Chloride in the laboratory. It is a titrimetric method in which 25 mL of the sample was measured into a conical flask. After this, 1 mL of Potassium Chromate indicator was added to visualize the endpoint.

Titration of the sample was then done against the standard silver nitrate solution to pinkish yellow endpoint. The volume of titrant used was then recorded and used in the determination of chloride concentration through formula 3.8

$$\text{Chloride concentration (mg/L)} = \frac{(A \; x \; N \; x \; 35.45) x \; 1000}{Volume \; of \; Sample} \qquad 3.8$$

Where:

A = Volume of titrant used

N = Concentration of silver nitrate (0.0141M)

3.7 Trace Metals Analysis

3.7.1 Digestion of Water and Sediment Samples for Metal analyses

Digestion of water samples is a way of taking care of interfering species by way of nullifying them. It is done to reduce interference by organic matter and it also converts

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the metals in the water samples to a form (usually the free metal) that can be determined by AAS.

Therefore, 25 mL of the water sample was accurately pipetted into pre-cleaned conical flasks. 6 mL of concentrated nitric acid, 3 mL of HCl and 0.25 mL of 30% hydrogen peroxide were added sequentially to the water sample in the fume hood. This is a least rigorous method which provides complete and consistent recovery compactible with the analytical method and the metals being analysed. The digestion process was completed by placing the conical flask containing the solutions onto a hot plate set at a temperature of about 100 ^{o}C for 3 hours. After digestion, the sample solutions were cooled in a water bath for 30 minutes to reduce the temperature and pressure build up within the conical flasks. The mixture was then quantitatively transferred into a volumetric flask after filtration, diluted to 50 mL volume using deionized water and transferred into labeled test tubes and capped. A blank was also prepared in similar fashion but without the analyte.

For sediment samples, 2.0 g of the sieved samples were weighed into the conical flasks. The same reagents and digestion process was used for the analysis as with the water samples. A reagent blank and soil standards were also prepared in similar fashion. To ensure the reliability of analytical method used during digestion and sample preparation, blank samples were also digested along with each set of samples and analysed through the same procedure.

After going through the same procedure after digestion as with the water samples (sediment solutions were however diluted to 30 mL volume), both set of samples were

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taken to the AAS laboratory for analysis. In the AAS laboratory, iron, magnesium, copper, zinc, lead, cadmium, chromium and mercury were analysed.

Trace metal concentrations were obtained by plotting an appropriate standard solutions prepared with the components of the extraction. All determinations were done in duplicates. Calculations for the concentration of trace metals in each set of samples were done as follows:

$$\text{Final concentration (mg/L)} = \frac{AAS\ reading\ x\ Nominal\ Volume}{Sample\ Weight} \qquad 3.10$$

Where : Nominal volume of water sample = 50 mL

Nominal volume of sediment sample = 30 mL

Sample weight for water sample = 5.0 g

Sample weight for sediment sample = 2.0 g

3.8 Pesticide Analysis

Pesticide residues (organochlorines, synthetic pyrethroids and organophosphates) in sediment samples were analysed at the Pesticide Residue Laboratory of the Ghana Standards Authority. The Varian CP-3800 Gas Chromatograph (GC) with a CombiPAL Autosampler, Electron Capture Detector and a Pulse Flame Photometric Detector was used for the analysis. Before the GC analysis was done, the following procedures were followed:

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3.8.1 Extraction

About 10.0 g ± 0.1 g of the sediment samples were weighed into a 100 mL separating flask. 10 mL acetonitrile was added to the sample and the separating flask was then corked and sonicated for 5 minutes using the Clifton SW 3H Ultrasonic Bath. After that, 10 mL acetonitrile was further added and the flask was corked again, placed on the Horizontal Ika – Werke HS 501 Digital Mechanical Shaker and set to shake continuously for 30 minutes.

The mixture was then transferred into plastic test tubes and placed in an electronic centrifuge for about 6 minutes to separate the mixture into its layers. An aliquot of the organic phase (top layer) was pipetted (about 10 mL = 5.0 g) into a 50 mL round bottomed flask. The organic phase was then evaporated to about 2 mL (RPE 35°C) for extract purification.

3.8.2 Extract Purification using Silica

About 1000 mg or 6ml of Silica cartridge was conditioned. It has 1 cm thickness layer of anhydrous magnesium sulphate on top with (10 ± 0.2 mL) of acetonitrile. The extract was loaded from 2 mL volume onto the cartridge and collected for evaluation into a 50 mL pear shaped flask. The cartridge was eluted with 10±0.2 mL of acetonitrile and the filtrate was concentrated below 40 °C on the Bibby, RE 200 and Buchi Ratovapor R-210 Rotary Film Evaporator just to dryness. The extract was then redissolved by pipetting 1 mL of ethyl acetate into the pear shaped flask. The extract was then transferred into a 2 mL standard opening vial prior to quantitation by the GC – ECD.

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Table 3.2 provides a summary of the chromatographic conditions used for the analysis of the organochlorines, synthetic pyrethroids and polychlorinated biphenyls pesticides.

Table 3.1: Summary of chromatographic conditions used for pesticide analysis

APPARATUS	
Instrument	**Description**
Gas chromatograph	Varian CP-3800 GC-ECD with a CombiPAL Autosampler
Analytical Column	30 m + 10 m EZ Guard x 0.25 mm internal diameter fused silica capillary
	coated with VF-5 ms (0.25 µm film)from Varian Inc.
TEMPERATURE	
Item	**Conditions**
Injector	Spitless mode, temperature 270 °C
Oven	70 °C/$2min^{25°C/min}$ 180 °C/$1min^{5°C/min}$ 300 °C
Detector - ECD	300 °C
GASES	
Gas	**Flow Rate**
Nitrogen (Carrier)	1 min/min constant flow
Make-up	29 mL/min

3.9 Quality Assurance For Analysis

Validation of any analytical technique is as essential as the analysis itself. Standard reference material (Fluka Analytical Standards) was used to ascertain the accuracy of the AAS used. A recovery test was conducted on each of the metals analysed to assess the accuracy and correctness of the analytical technique. Standard solutions in double distilled water of certified reference material (Fluka Analytical Standards) of the various metals was run. Thus a known amount of each of the metals was aspirated into the instrument and the metal level recorded. The analyser was rinsed by aspirating deionized

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water continuously to clear the system from any traces of trace metal assessed. Each recovery test was performed four times. The results of the test are illustrated in Appendix A.

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CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Physico-Chemical Parameters

Table 4.1 shows the results of the physico-chemical parameters of the surface water samples from the Pratu and Ntakofa rivers as well as the Muni lagoon'

Table 4.1: Physico-chemical parameters of the surface water samples from the Pratu River.

	PHYSICO-CHEMICAL PARAMETERS FOR PRATU RIVER				
Sample Code	**Cond µS/cm**	**Temp. °C**	**pH**	**TDS mg/L**	**Salinity**
DAM	5830	30.4	7.95	3490	3.2
PTS 1	4630	32.7	7.4	2780	2.5
PTS 2	5460	29.1	7.74	3280	3
PTS 3	5280	28.4	7.99	3170	2.9
PTS 4	5180	28.7	8.1	3100	2.8
PTS 11	1655	29.1	7.39	993	0.8
PTS 12	8980	32.2	7.29	5390	5.1
PTS 13	5360	30.2	7.41	3210	2.9
PTS 14	14650	24.9	7.47	8790	8.5
PTS 15	54700	27	7.6	32800	36.3
PTS 16	53000	28.5	7.93	37700	42.6
PTS 17	52300	28.5	8.12	37300	42.1
PTS 18	51500	29.6	8.25	36900	41.6
MEAN	20655.77	29.17692		13761.77	14.94615
ST. DEV.	22562.36	2.022026		15694.85	17.98247

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Table 4.2: Physico-chemical parameters of the surface water samples from the Ntakofa River.

PHYSICO-CHEMICAL PARAMETERS FOR NTAKOFA RIVER					
Sample Code	**Cond µS/cm**	**Temp. °C**	**pH**	**TDS mg/L**	**Salinity**
PTS 5	925	27.3	7.12	556	0.4
PTS 6	5100	27.9	7.5	3060	2.8
PTS 7	306	27	7.1	184	0.2
PTS 8	96	31.1	8.14	58	0.1
PTS 9	926	30.2	7.06	556	0.4
PTS 10	948	26.1	7.01	569	0.4
PTS 20	40500	31.4	8.3	24500	26.1
PTS 21	50300	30.8	8.52	30200	33.3
PTS 22	52300	33	8.44	37300	42.4
MEAN	16822.32	29.42222		10775.89	11.78889
ST. DEV.	23418.58	2.391536		15284.16	17.12246

Table 4.3: Physico-chemical parameters of the surface water samples from the Muni lagoon

PHYSICO-CHEMICAL PARAMETERS FOR MUNI LAGOON					
Sample Code	**Cond µS/cm**	**Temp. °C**	**pH**	**TDS mg/L**	**Salinity**
PTS 19	57700	29.1	8.135	34600	38.7
PTS 23	54300	32.4	8.38	32600	36.4
PTS 24	54800	36	8.45	32800	36.9
MEAN	55600	32.5		33333.33	37.33333
ST. DEV.	1835.756	3.451087		1101.514	1.209683

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The temperature of the water samples analysed ranged between 24.9 °C – 32.7 °C for the Pratu River, 26.1 °C – 33 °C for Ntakofa River and 29.1 °C – 36 °C for the Muni Lagoon with mean values of 29.2 °C, 29.4 °C and 32.5 °C respectively. With reference to the mean values, temperature regimes among the three parts of the river were fairly stable. However, fluctuating temperatures occurring in the sampling area may be due to the ambient air temperature during sampling. According to Brown, (1999), heat transfer, whether from the air, sunlight, another water source or thermal pollution can change the temperature of water.

The Pratu River was found to be alkaline in nature. The pH recorded at the dam site was 7.95. pH levels from PTS1(7.4) increased to PTS4 (8.1). From PTS12 to PTS18, pH recorded an increase from near neutral to alkaline in ascending order (7.29-8.25). This could be due to the presence of living organisms and plants in the water which go through daily photosynthesis, respiration and decomposition processes. Coupled with the shallow nature of the river, these may have had an effect on the pH of PTS1 due to the buffering effect of the comparatively high pH level arising from the dam. According to Bialkowski (2008), photosynthesis, respiration and decomposition all contribute to pH fluctuations due to their influences on CO_2 levels which is a common cause of acidity in water. pH levels rose from near neutral to alkaline from PTS1 – PTS4. This may be due to the increase in eutrophication effects as the river moves down (from PTS1-PTS4). According to Craig and Louis (2008), when plants or algae are growing rapidly, more carbon dioxide is removed each day by photosynthesis than is added each night by respiration. As a result, pH may rise to abnormal levels of alkalinity. The steady increase in the alkaline nature of pH from PTS12 through to PTS18 may be due to the influence of

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anthropogenic activities occurring around the area. This is because a large portion of that part of the river is located in a comparatively large populated town from whose houses domestic effluents may flow into the river. However the sharp increase from PTS4 to PTS12 may be influenced by the presence of a fish pond which is located just about two meters away from PTS12. The fish pond may be introducing more nutrients into the river thereby increasing algae growth and resulting in nearly alkaline pH levels.

Ntakofa river revealed a stable pH trend. However, PTS 20, 21 and 22 showed alkaline pH levels. This may be due to the effect of agricultural run-off occurring from the vegetable farmland located at the bank of the river. Alkaline pH values (8.14, 8.38 and 8.45 respectively) were recorded at the Muni lagoon because of the high influence of the sea on it (the sea usually has a pH always above 8.0).

EC, TDS and Salinity results ranged between 1655 µS/cm – 54700 µS/cm, 96 µS/cm - 52300 µS/cm and 54300 µS/cm – 57700 µS/cm; 993 mg/L-37700 mg/L, 58 mg/L-37300 mg/L and 32600 mg/L – 34600 mg/L; 0.8 mg/L – 32.6 mg/L, 0.1 mg/L – 42.4 mg/L and 36.4 mg/L – 38.7 mg/L respectively for Pratu river, Ntakofa river and the Muni lagoon. The mean values of EC, TDS and salinity were 20655.77 µS/cm, 16822.32 µS/cm and 55600 µS/cm; 13761.77 mg/L, 10775.89 mg/L and 33333.33 mg/L; 14.95, 11.79 and 37.33 respectively for Pratu river, Ntakofa river and Muni lagoon.

Generally for all three parts of the river, EC, TDS and Salinity levels were observed to be high. This is because the conductivity of most fresh waters ranges from 10 to 1000 µS/cm (Chapman, 1992). Secondly, the values of TDS exceed the recommended level of 500 mg/L (US EPA, 2012) for aquatic life. Finally, highly saline water ranges from

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10000ppm to 35000ppm (Johnson et al., 1999). However at the Pratu River, the Dam site through PTS1 – PTS13 was observed to have comparatively low levels of EC, TDS and salinity except for PTS12 which had slightly high levels. This condition may be due to the influence of the fish pond (fig. 4.1) which is located very close to that part of the river due to its potentially high nutrient level and dissolved solids.

Fig 4.1: Fish pond sighted close to PTS 12

According to Pearlman (2014), effluents from sources such as fish ponds in addition to being high in nutrients, often has a higher concentration of dissolved solids that can influence conductivity. The low levels observed from the dam through PTS1 to PTS13 may due to the influence of the rains at the period of sampling which may have caused a dilution effect. According to South Carolina Oyster Restoration and Enhancement. (2015), heavy rainfall can decrease the conductivity of a body of water as it dilutes the

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current salinity concentration. From PTS14 through to PTS18, it was observed that EC, TDS and salinity levels were comparatively very high. This could be ascribed to the influence of the dry season during the time of sampling which may have reduced the river volume. Also, all along the banks of those areas, it was observed that salt precipitates were present. This may influence the levels of EC, TDS and salinity when run-off occurs. According to Fisheries and Aquaculture Department (2015), if a floodplain contains nutrient-rich or mineralized soil, previously dry salt ions can enter solution as it is flooded, raising the conductivity of water.

At Ntakofa River, from PTS5 to PTS10, EC, TDS and salinity levels were comparatively low except for PTS6 which was observed to have high values. This is with reference to the limits set by USEPA, (2012), Chapman, (1992) and Johnson *et al.* (1999). This condition may be due to the limited water flow through that area from preceding points which may have resulted in saturation of salts and dissolved minerals. PTS20 to PTS22 was observed to have very high EC, TDS and Salinity values. This may be due to the combined effect of agricultural run-off and aerosols that may have drifted into the river from the sea.

At the Muni lagoon high EC, TDS and Salinity values were observed (with reference to the limits set by USEPA, (2012), Chapman, (1992) and Johnson *et al*. (1999)). PTS19 was however observed to have the highest values of EC, TDs and Salinity. This may be due to, a large salt winning site located close to the bank of that part of the river. PTS23 and PTS24 were observed to have high EC, TDs and salinity levels mainly because of the influence of the sea on the lagoon. However the values seem to be lower than that of PTS 16, 17 and 18. According to Taylor (1997), the conductivity of water often decreases

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during a coastal flood. Seawater will pick up suspended solids and nutrients from the soil, but can also deposit its salts on land, decreasing the conductivity of the water. Therefore this salt depositing effect may be responsible for the comparatively low levels of EC, TDS and salinity at the Muni lagoon.

4.2 Chemical Parameters

Tables 4.4, 4.5 and 4.6 shows the results of the chemical parameters of the surface water samples from the Pratu and Ntakofa Rivers as well as the Muni lagoon.

Table 4.4: Chemical Parameters of the surface water samples from Pratu River

CHEMICAL PARAMETER OF SURFACE WATER FROM PRATU RIVER				
SAMPLING POINTS	**ALKALINITY**	**COD**	**TOTAL HARDNESS**	**BOD**
Dam Sample	90	10.2	2840	3.251
PTS_1	125	7.1	2120	2.235
PTS_2	90	9.6	2720	3.017
PTS_3	90	9.8	2600	3.032
PTS_4	88	10.4	2560	3.048
PTS_{11}	50	4.3	1200	1.064
PTS_{12}	90	13.5	3580	4.016
PTS_{13}	65	7.3	2740	2.001
PTS_{14}	69	11.9	3080	3.903
PTS_{15}	75	11.6	7200	3.871
PTS_{16}	90	11.7	7280	3.893
PTS_{17}	85	12.8	6640	4.267
PTS_{18}	90	13.8	5280	4.61
MEAN	84.38462	10.30769	3833.846	3.246769
ST. DEV.	17.64246	2.753017	2046.336	1.008607

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Table 4.5**:** Chemical parameters of the surface water samples from the Ntakofa River

CHEMICAL PARAMETERS OF SURFACE WATER FROM NTAKOFA RIVER					
SAMPLING POINTS	**ALKALINITY**	**COD**	**DO**	**TOTAL HARDNESS**	**BOD**
PTS_5	39	7.364	26.114	1400	2.438
PTS_6	73	6.789	26.982	320	2.032
PTS_7	59	3.857	27.186	660	1.219
PTS_8	23	8.735	27.499	200	2.845
PTS_9	32	2.479	25.598	1480	0.813
PTS_{10}	42	2.523	25.482	1220	0.813
PTS_{20}	100	29.18	24.234	5700	5.836
PTS_{21}	108	32.92	24.112	6200	6.584
PTS_{22}	130	34.905	24.426	9300	6.981
MEAN	**67.33333**	**14.30578**	**25.737**	**2942.222**	**3.28455**
ST. DEV.	**37.76242**	**13.76439**	**1.303797339**	**3273.506**	**2.50055**

Table 4.6: Chemical parameters of the surface water samples from the Muni Lagoon

SAMPLING POINTS	**ALKALINITY**	**COD**	**DO**	**TOTAL HARDNESS**	**BOD**
PTS_{19}	84	26.095	27.126	6400	5.219
PTS_{23}	100	38.49	25.729	6800	7.698
PTS_{24}	115	37.13	25.582	7600	7.426
MEAN	**99.66667**	**33.905**	**26.14566**	**6933.333**	**6.781**
ST. DEV.	**15.50269**	**6.79775**	**0.852169**	**611.0101**	**1.35955**

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In the Pratu river, total alkalinity and hardness values ranged from 50 mg/L – 125 mg/L and 1200 mg/L – 7280 mg/L respectively with mean values of 84.38 mg/L and 3833.85 mg/L respectively. With reference to the research of Karikari and Ansah Asare (2004), the values observed in table 4.4 were relatively high. At the Ntakofa river site, concentrations of total alkalinity and hardness measured between the ranges of 23 mg/L – 130 mg/L and 200 mg/L- 9300mg/L respectively whiles their mean values measured 67.33 mg/L and 2942.22 mg/L respectively. At the Ntakofa river, alkalinity and hardness concentrations were comparatively low from PTS5 to PTS10 whiles from PTS20 to PTS22, concentrations were very high. At the Muni lagoon, concentrations of alkalinity and Total hardness ranged from 84 mg/L – 115 mg/L and 6400 mg/L – 7600 mg/L with mean values of 99.67 mg/L and 6933.33 mg/L respectively. With reference to the mean values, total alkalinity and hardness concentrations were very high and may be due to the lagoon's close proximity to the sea.

Snoeyink and Jenkins (1980), stated in their report on water chemistry that alkalinity and hardness comes from rocks and soils, salts, certain plant activities and certain industrial wastewater discharges hence the variation in alkalinity and hardness may be attributed to the geology, anthropogenic activities in the study area.

The levels of BOD and COD at the Pratu river site ranged from 1.064 mg/L - 4.61 mg/L and 4.3 mg/L – 13.8 mg/L respectively with mean values of 3.25 mg/L and 10.35 mg/L respectively. According to Benedict *et al.,* (2003), water may be termed as unpolluted if it's BOD and COD concentrations are not more than 2 mg/L and 20 mg/L respectively. With reference to the mean concentrations observed for BOD and COD in the Pratu River, it may be generally unpolluted. However relatively high values observed at PTS12

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and PTS18 may be due to the presence of small scale industries and houses from where domestic and industrial waste flows which is in close proximity to those sampling points. PTS12 also has a fish pond located very close to its banks. This may also be a contributing factor to the high BOD and COD concentrations.

At the Ntakofa River, BOD and COD concentrations ranged from 0.813 mg/L – 6.981 mg/L and 3.857 mg/L – 34.91 mg/L with mean concentrations of 3.28 mg/L and 14.31 mg/L respectively. With reference to the report of Benedict *et al.*, (2003), it was observed that the Ntakofa River was generally unpolluted. However, high values occurring at PTS20 to PTS22 shows some level of pollution. This may be due to the influence of large scale vegetable farm activities and the use of petrochemically operated generators for irrigation purposes on the river.

High concentrations of BOD and COD were observed at the Muni Lagoon ranging between 5.219 mg/L – 7.698 mg/L and 4.3 mg/L and 13.8 mg/L with mean concentrations of 3.25 mg/L and 10.31 mg/L respectively. In accordance with the report of Benedict *et al.,* it may be said that the Muni lagoon is polluted. This may be due to the organic waste that is dumped close to the banks of the lagoon which may affect the lagoon when runoff occurs. Also, since the lagoon serves an aquatic sink; high COD concentrations may be due to the combined effect of all chemical discharges that flow into the lagoon right from the different points of the Pratu and Ntakofa rivers.

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4.3 Major Ions

Concentrations for sodium and potassium levels in the Pratu River ranged between 382 mg/L – 4070 mg/L and 501 mg/L – 750 mg/L respectively with mean values of 1486.92 mg/L for sodium and 195.92mg/L for Potassium (Fig. 4.2).

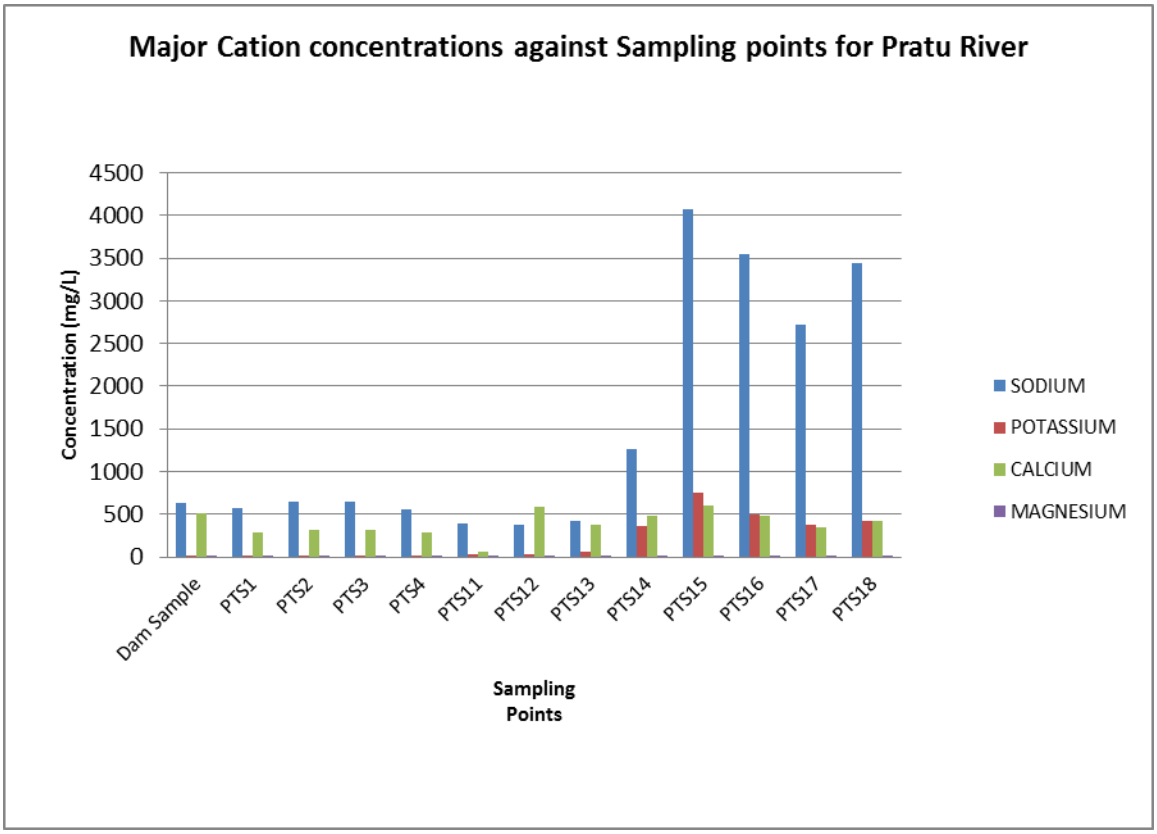

Fig 4.2: Major cation concentrations against the sampling points for Pratu River surface water

According to the research done on the Kpeshie lagoon by Apau et al., (2012), mean values of sodium and potassium were 15165.71mg/L and 672.86 mg/L respectively As observed, sodium levels are high as compared to the research of Apau et al., (2012) and the other cations measured. This condition may be due to the effect of sea aerosols the abundance of salt-like precipitates along the banks of the river which is presumed to be

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NaCl especially prominent from PTS14 through to PTS 18. The decreasing trend in sodium concentration from PTS14 to PTS17 may be due to increasing volume of river water as it travels towards the lagoon. However at PTS18, it is seen that, that point is closest to the lagoon and the salt winning site. This may contribute to the high level of sodium concentration observed there. Potassium levels are comparatively lower but prominent compared to the rest of the cations especially from PTS14 to PTS18. The low concentrations may be due to their uptake by organisms in the water and also its high solubility. However, high levels of potassium may be due to the influence of domestic sewage as well as agricultural runoff.

Concentrations of calcium and magnesium ranged from 65.73 mg/L – 609.19 mg/L and 13.5 mg/L – 17.56 mg/L respectively with mean values of 391.65 mg/L and 15.37 mg/L respectively. The concentration of calcium in freshwater is generally in the range of 0 to 100mg/L (Johnson et al., 1999). Therefore with reference to figure 4.3, it is observed that calcium concentrations were high. This may be due to the weathering of calcium carbonate rocks which may be present in the soil. At PTS11, it was observed that calcium concentrations were low and this may be because the organisms living in and around the river may be making good use of the calcium content for survival. Magnesium concentrations were however observed to be very low as compared to all the other cations. This condition may be attributed to its high intake by plants living around the river since magnesium is an essential element for photosynthesis (Chapman et al., 1992).

Chloride concentrations at the Pratu River ranged between 441.86 mg/L – 4208.69 mg/L with a mean value of 8412.62 mg/L (Fig. 4.3). The high chloride concentrations (Maximum level for fresh water aquatic life is 230 mg/L (US EPA, 1988)) may be largely

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attributed to the effect of sea aerosols which usually carry chloride compounds though drift. The presence of salt - like precipitates (NaCl) that occur on most of the river banks which when washed off by run-off into the river may have increased its chloride content may also be a contributing factor. Application if agricultural fertilizers on farmlands located close to the river banks may also be another factor.

Phosphate concentrations in the Pratu river ranged between 0.12 mg/L – 0.48 mg/L with mean a value of 0.23 mg/L. Plant growth can be stimulated by levels above 0.1mg/L (Johnson et al., (1999) and the natural background level of PO4 3- - P in waters usually ranges from 0.005 – 10 mg/L (WRC, 2003).The phosphate concentrations observed along the Pratu river may be largely attributed to the cattle and human waste as well as the fertilizer applications on the farmlands near the river banks. These find their way into the river through the effect of run-off. This condition is evident from PTS14 to PTS18 where domestic and cattle wastes have been observed to be quite prominent.

Sulphate concentrations in the Pratu river also ranged between 306.56 mg/L – 25222.33 mg/L with a mean value of 1176.87 mg/L. The recommended limit for sulphate (SO_4^{2-}) ion is 250 mg/l for water (US EPA, 2011). The high concentrations of sulphate ion in the Pratu River may be attributed to the presence of farmlands existing close to the river banks. Fertilizer application to these farmlands may have been washed off into the river through run-off thus increasing the river's sulphate content. High sulphate concentrations may also be due to the high salinity, Na and Cl concentrations in the river.

Nitrate concentrations in the Pratu river also ranged between <0.01 mg/L – 1.37 mg/L with a mean value of 0.47 mg/L. Generally, nitrate concentrations were low. This is

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because nitrate levels in freshwater are usually less than 1 mg/L but manmade sources of nitrate may elevate levels above 3 mg/L (Johnson et al., 1999). As compared to the other anions, the low levels may be due to the limited amount of Nitrate in the fertilizers used by the farmers which may have already been used up by the aquatic organisms once introduced into the river through run-off.

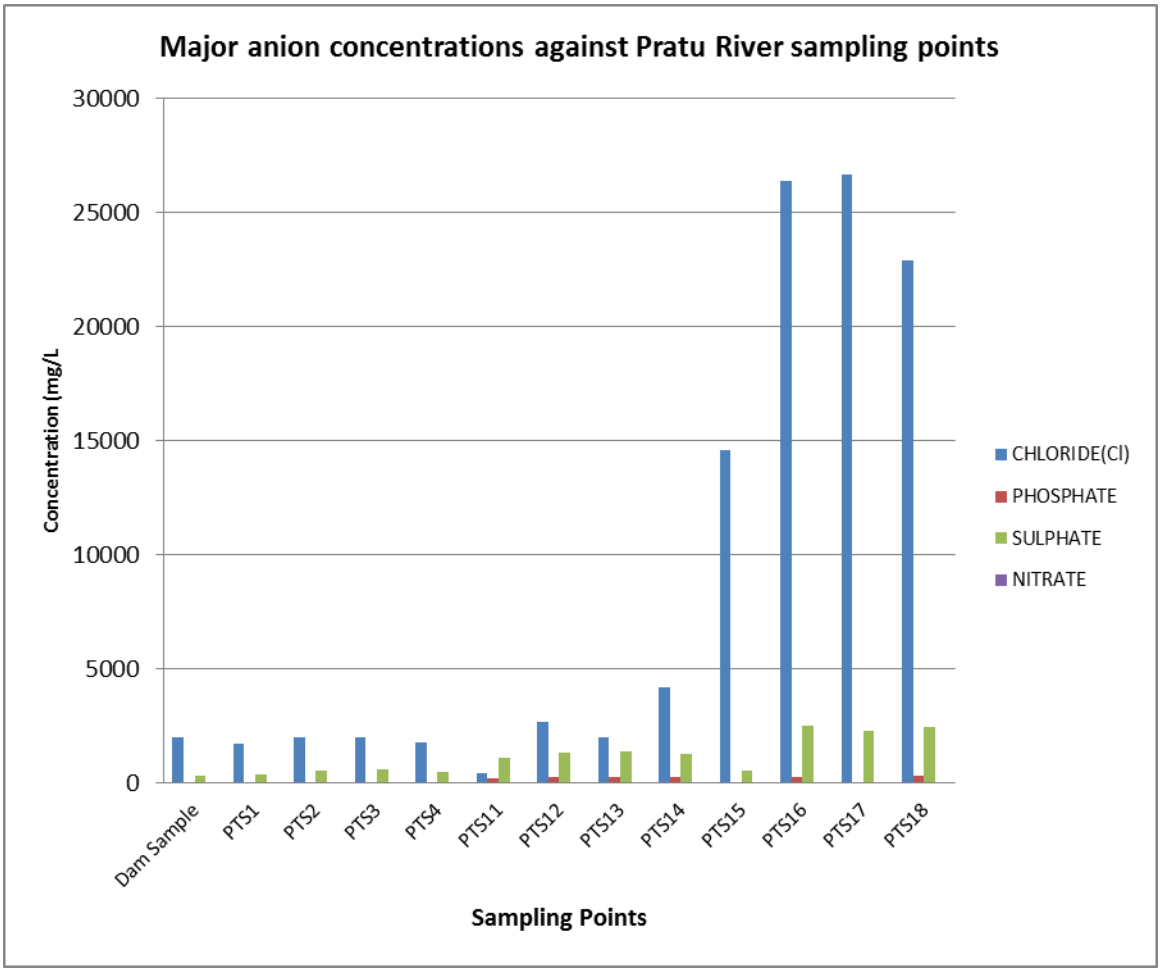

Fig 4.3: Major anion concentrations against the sampling points for Pratu River surface water

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Sodium and potassium concentrations in the Ntakofa river ranged between 111 mg/L – 5642 mg/L and 8.4 mg/L – 475 mg/L respectively (Fig. 4.4) with mean values of 2053.33 for sodium and 157.64 for potassium. Sodium concentrations were observed to be high at the Ntakofa river and are especially prominent at PTS20, 21 and 22. This condition may be due to the presence of salt-like precipitates (presumed to be NaCl) found along the river banks especially close to PTS20, 21 and 22. At these three points, it is also observed that their location was quite close to the lagoon and could be a contributing factor to the high sodium concentrations. PTS 8, 9 and 10 were observed to have relatively low concentrations of sodium. This may be due to the limited presence of salt-like precipitates along the banks of those points (Apau et al., 2012). With reference to fig. 4.4, potassium concentrations were generally low from PTS5 through to PTS10. However, potassium concentrations rose from PTS20 to PTS22. This may be largely attributed to the influence of the intensive farming activities that occur along the river banks of these points. Fertilizer application may be introduced into the river through agricultural run-off which may have increased the potassium content in the river (Gibrilla et al., 2010).

Calcium and magnesium concentrations in the Ntakofa river ranged between 11.22 mg/L – 945.84 mg/L and 14.09 mg/L – 17.05 mg/L respectively with mean values of 342.89 mg/L for calcium and 15.16 mg/L for magnesium. With reference to fig. 4.6, calcium concentrations in the Ntakofa river were generally low but exceptionally high at PTS20 to PTS22 and this condition may be attributed to the weathering of calcium carbonate rocks embedded in the river (Gibrilla et al, 2010). Magnesium concentrations are however low which may be due to its uptake especially by plants in the river.

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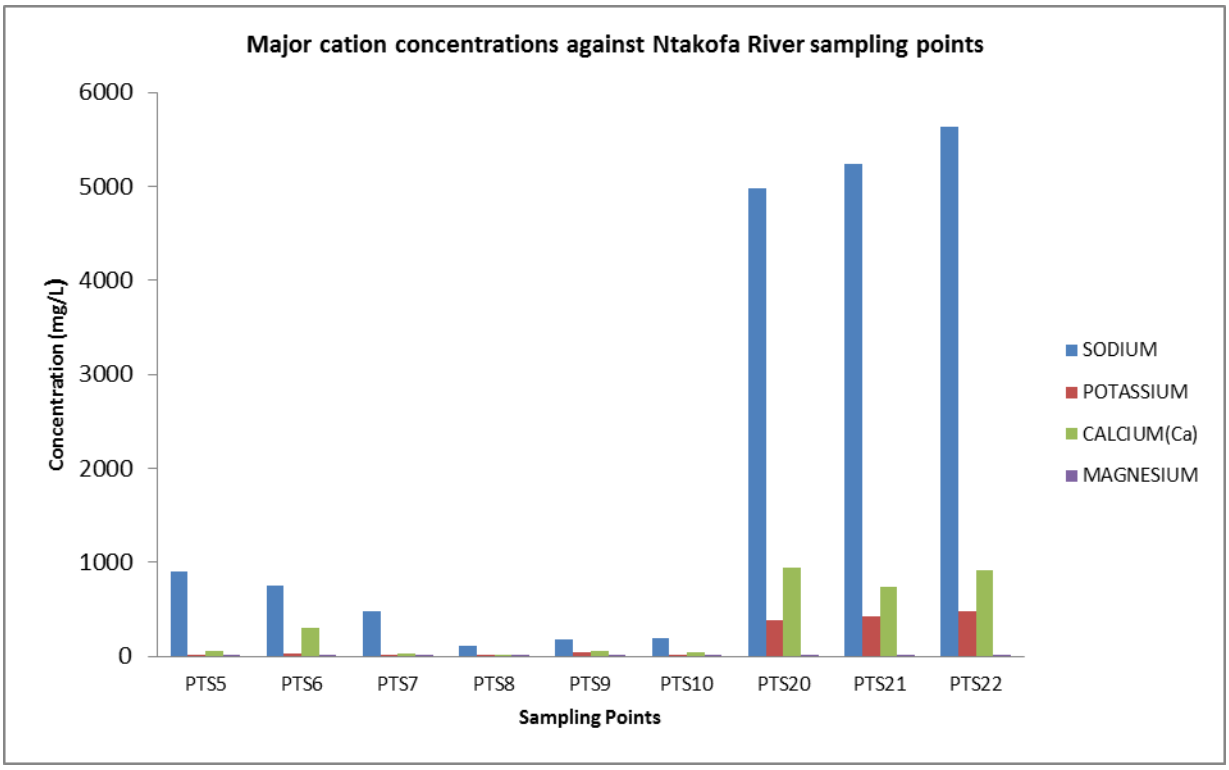

Fig 4.4: Major cation concentrations against the sampling points for Ntakofa River surface water

Chloride concentrations in the Ntakofa River ranged between 41.99 mg/L – 25687.28 mg/L (Fig. 4.5) with a mean value of 6755.02 mg/L. The observed high concentrations of chloride in the Ntakofa River may be largely attributed to the presence of salt-like (NaCl) precipitates found along the river banks. Its high prominence at PTS20, 21 and 22 may be due to the added influence of the lagoon which is quite close to those points (Apau et al., 2012).

Phosphate concentrations in the Ntakofa river ranged between 0.04 mg/L – 0.22 mg/L with a mean value of 0.15 mg/L. Phosphate concentrations were observed to be very low at the Ntakofa River. This condition may be due to the uptake of phosphate by the plants inhabiting the river and also the vegetable farm that exists along the banks of PTS 20, 21

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and 22 (Johnson et al., 1999). This condition is evident especially at PTS21 which has the lowest concentration of phosphate.

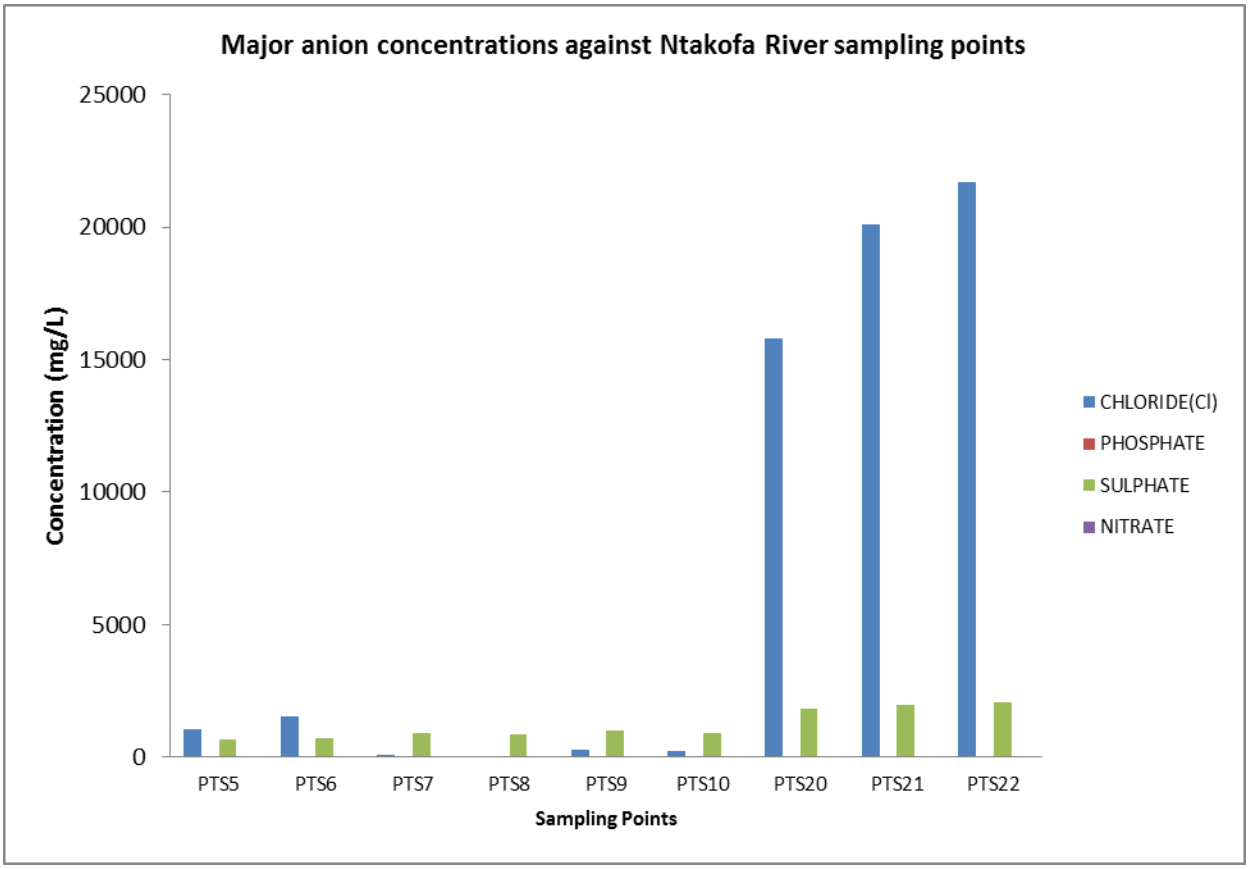

Fig 4.5: Major anion concentrations against the sampling points for Ntakofa River surface water

Sulphate concentrations also varied between 652.92 mg/L – 2068.00 mg/L with a mean value of 1217.62 mg/L. This condition is largely attributed to the application of fertilizer on the farmlands along the banks of the river which when washed off into the river through the effect of run-off may have increased the concentration of sulphate in the river (Apau et al., 2012).

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Nitrate concentrations varied between 0.03 mg/L – 1.35 mg/L. The mean value was 0.38 mg/L. The low nitrate level observed at the Ntakofa River may be attributed to its total usage by plants in the river and those along the river banks for survival. Nitrate compounds may have also adhered to the river sediment (Johnson et al., 1999).

Sodium and potassium concentrations in the Muni lagoon varied between 2920 mg/L – 6143 mg/L and 340 mg/L – 492 mg/L (fig. 4.6) respectively with their mean values of 4986.67 mg/L for sodium and 437.33 mg/L for potassium. Similar to the Pratu River and the Ntakofa river, sodium concentrations at the Muni lagoon were equally very high. The lagoon's closeness to the sea may be the main contributing factor to this effect. Secondly, since the lagoon serves as a sink to the Pratu River and its tributary, it may house most of the sodium cation that flows into it from the rivers (Johnson et al., 1999). Potassium concentrations were also high at the Muni lagoon and this could be due to the lagoon's property of acting as a sink to the rivers flowing into it.

Calcium and magnesium concentrations varied between 22782.94 mg/L – 35982.84 mg/L and 16.59 mg/L – 17.16 mg/L respectively with mean values of 30916.41 mg/L for Calcium and 16.85 mg/L for magnesium. The high concentrations observed for calcium in the Muni lagoon may be largely attributed to the close proximity of the lagoon to the sea thus its influence on calcium concentrations (Finlayson et al., 2000). Magnesium concentrations are however generally low in the lagoon because of the generally low concentrations that flow into the lagoon from the Pratu river and also the effect of dilution since the lagoon is a sink for the Pratu river.

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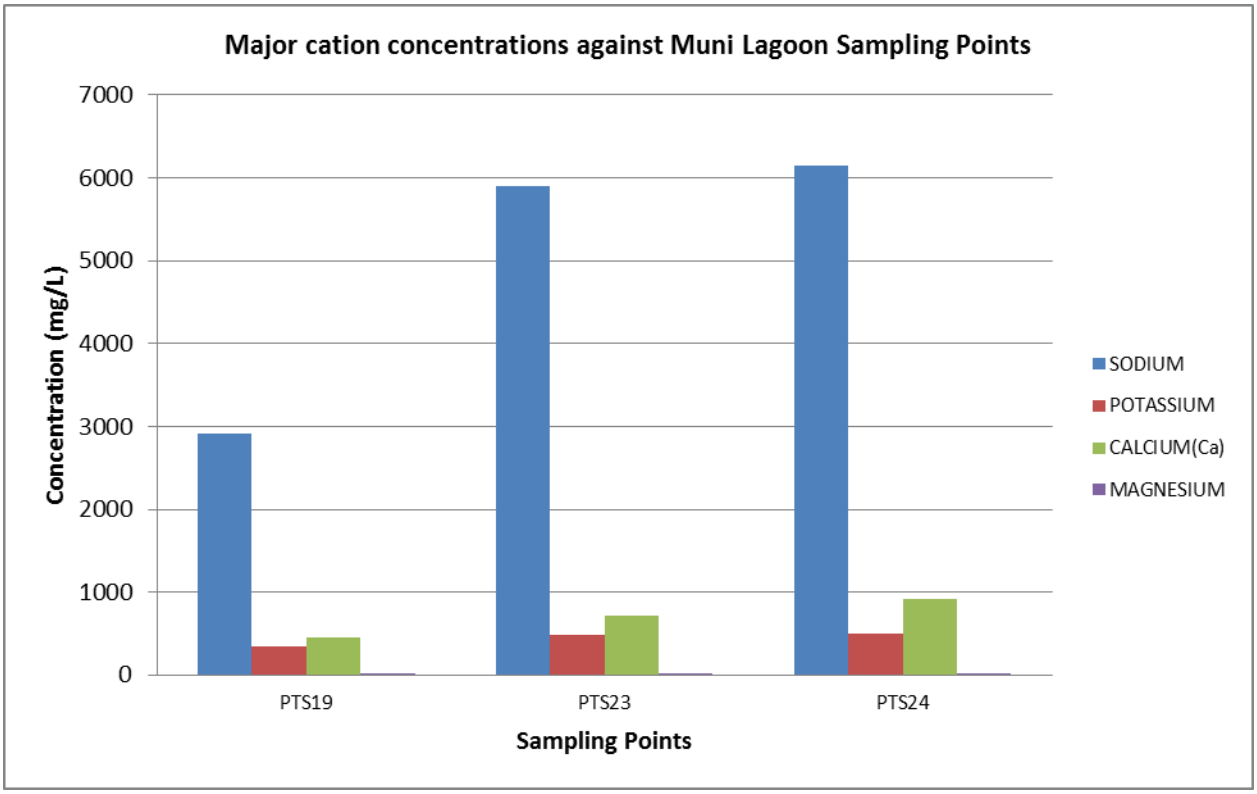

Fig 4.6: Major cation concentrations against the sampling points for Muni Lagoon surface water

Chloride concentrations in the Muni lagoon varied between 22782.94 mg/L – 35982.84 mg/L (fig. 4.7) with a mean value of 30916.41 mg/L. Similar to chloride concentrations in the Pratu and Ntakofa rivers, chloride concentrations were high. The lagoon is close to the sea and is also a sink to the Pratu river. These may be a contributing factor to the high chloride content in the lagoon (Lamptey et al., 2013).

Phosphate concentrations also varied between 0.04 mg/L – 0.19 mg/L with a mean value of 0.09 mg/L. The low concentration of phosphate observed in the muni lagoon may be due to its limited amount since organisms in the lagoon may have utilized it (Johnson et al., 1999). Phosphate ions may also be adhered to the lagoon's sediment and therefore may be present in limited amount in the aquatic medium (Lamptey et al., 2013).

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Furthermore, because the lagoon acts as a sink, the effect of dilution may be the reason for low phosphate concentration in the lagoon (Apau et al., 2012).

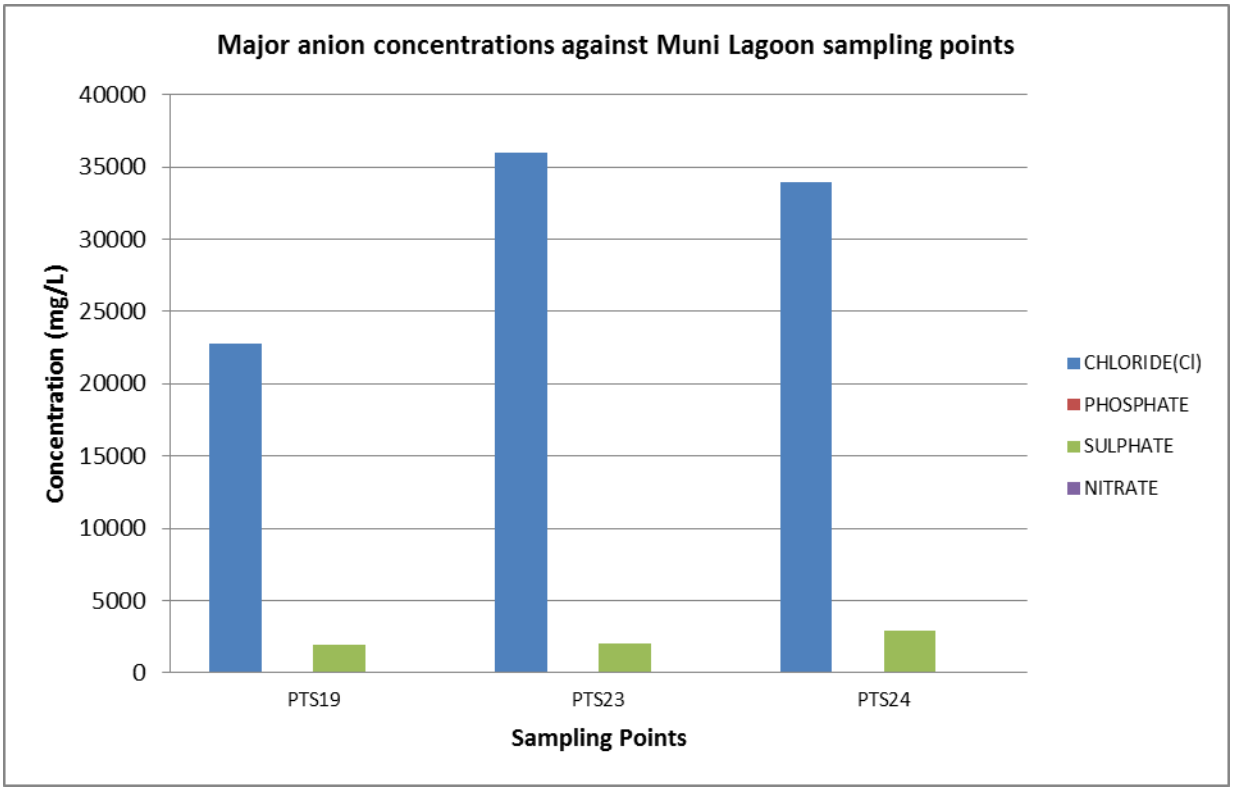

Fig 4.7: Major anion concentrations against the sampling points Muni Lagoon surface water

Sulphate concentration varied between 1883.99 mg/L – 2929.43 mg/L with a mean value of 2281.32 mg/L. Sulphate concentrations were observed to be high in the Muni lagoon. This effect may be due to the presence of domestic and faecal waste scattered along the banks of the lagoon (Apau et al., 2012). Secondly, since sulphate concentrations were high at the Pratu and Ntakofa rivers, the Muni lagoon acting as a sink to these rivers receives and accumulates the excess sulphate ions that flow into it thereby increasing its concentration (Lamptey et al., 2013).

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Nitrate ion concentration also varied between 0.28 mg/L – 1.31 mg/L with a mean value of 0.95 mg/L. nitrate concentration was generally low in both the Pratu and the Ntakofa rivers thereby the effect of dilution by reason of the lagoon serving as a sink may be the cause of the lagoon's low nitrate levels. Nitrate ions may have also adhered to the lagoon's sediment resulting in limited concentrations in the aquatic medium (Johnson et al., 1999).

Overall, the cationic and anionic dominance pattern of the three parts of the basin using their mean concentrations were Na>Ca>K>Mg and Cl>$SO_2 > NO_3 > PO_4$ respectively. This shows that sodium and chloride are dominant in the Pratu Basin hence there may be a high level of NaCl pollution.

4.4 Classification of The Quality of Surface Water Using The Sodium Adsorption Ratio (SAR).

In order to ascertain the Sodium Adsorption Ratio (SAR) of the Pratu and Ntakofa Rivers as well as the Muni lagoon, the mean values of magnesium, sodium and calcium ions were used for its calculation in the formula below:

$$SAR = \frac{Na^+}{\sqrt{(Ca^{2+} + Mg^{2+})/2}} \qquad 4.1$$

Where ion concentrations are measured in milliequivalents per litre (meq/L)

Table 4.7 shows an interpretative guideline on SAR results

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Table 4.7: Interpretative guideline for SAR results (Water Analysis Guide, 2004)

SAR HAZARD LEVELS						
Application	**None**	**Increasing**	**Significant**	**High**	**Severe**	**Very Severe**
Most Production Systems	<1	1-2	2-4	4-5	5-12	>13

The mean values of the measured Sodium, magnesium and calcium were used in the calculation of the Sodium Adsorption Ratio of the surface water samples of the Pratu and Ntakofa rivers as well as the Muni lagoon.

The results from the analyses (table 4.8) indicated that the SAR of the sampled surface waters highly exceeds the highest hazard level appropriated for irrigation water on most plant production systems (>13). This clearly shows that the Pratu and Ntakofa Rivers as well as the Muni Lagoon are not suitable for irrigation. It was observed in the field that most vegetables irrigated with water from these water sources have stunted growth.

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Table 4.8: Calculation of the Sodium Adsorption Ratio of the surface water samples of Pratu river, Ntakofa river and the Muni lagoon.

Sampling Point	Parameter	Mean (meq/L)	Calculated SAR	Inference
Pratu river	Sodium	64.65	20.02	Very Severe
	Magnesium	1.27		
	Calcium	19.58		
Ntakofa river	Sodium	89.28	29.44	Very Severe
	Magnesium	1.25		
	Calcium	17.14		
Muni Lagoon	Sodium	216.81	51.02	Very Severe
	Magnesium	1.39		
	Calcium	34.73		

4.5 Trace Metals

Fe concentration in the Pratu River varied between 0.48 mg/L – 8.49 mg/L with a mean value of 3.90 mg/L (Fig. 4.8). Fe concentrations were high especially from PTS15 to PTS18. This condition may be due to the weathering of Fe containing rocks over which the river passes over (Johnson et al., 1999).

Copper concentrations varied between <0.003 mg/L – 1.84 mg/L with a mean value of 0.73 mg/L. The presence of copper in the Pratu river was observed to be minute. However, copper concentration in the Pratu river could be attributed to the effect of agricultural fertilizer run-off and bush fires which usually occur around PTS14 to PTS18 during the dry season (Lamptey et al., 2013).

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Zinc concentrations in the Pratu river varied between <0.001 mg/L –0.14 mg/L with a mean value of 0.03 mg/L. Zinc concentrations were observed to be low in the Pratu river. This could be due to its adherence to the river's sediment. The concentrations observed in the river may be due to the effect of weathering of zinc containing rocks in the river (Gibrilla et al., 2000).

Lead concentrations in the Pratu river varied between <0.001 mg/L – 0.23 mg/L with a mean value of 0.04 mg/L. Lead concentrations in the Pratu river was generally low and only occurs at PTS 16 and 17. This condition may be attributed to lead's adherence to the river's sediment or its combination with carbonate compounds in the water thereby making it insoluble (Gibrilla et al., 2000). At PTS16 and 17, the release of lead containing waste into the river could be the cause of the observed lead concentrations.

Cadmium concentrations in the Pratu rover were found to be below the detection limit of the equipment used for its analysis (<0.002). This condition may be due to cadmium's adherence to the river's sediment thereby remaining undissolved in the river (Apau et al., 2012).

Chromium concentrations varied from <0.006 mg/L – 1.78 mg/L with a mean value of 0.59 mg/L. Chromium concentrations are also observed to be low and may be because of its adherence to the river's sediment. However, its occurrence from PTS14 to PTS18 suggests that, domestic waste channelled into the river may contain synthetic materials containing chromium.

Mercury concentrations in the Pratu river were observed to be below the detection limit of the equipment used for its analysis (<0.001). This condition may be attributed to

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mercury's adherence to the river's sediment or its adsorption by clay particles in the river.

The effect of agricultural fertilizer run-off in to the water, waste from galamsey operations and small scale industries as well as metal containing pesticides could also be a contributing factor to the level of metals in the study area.

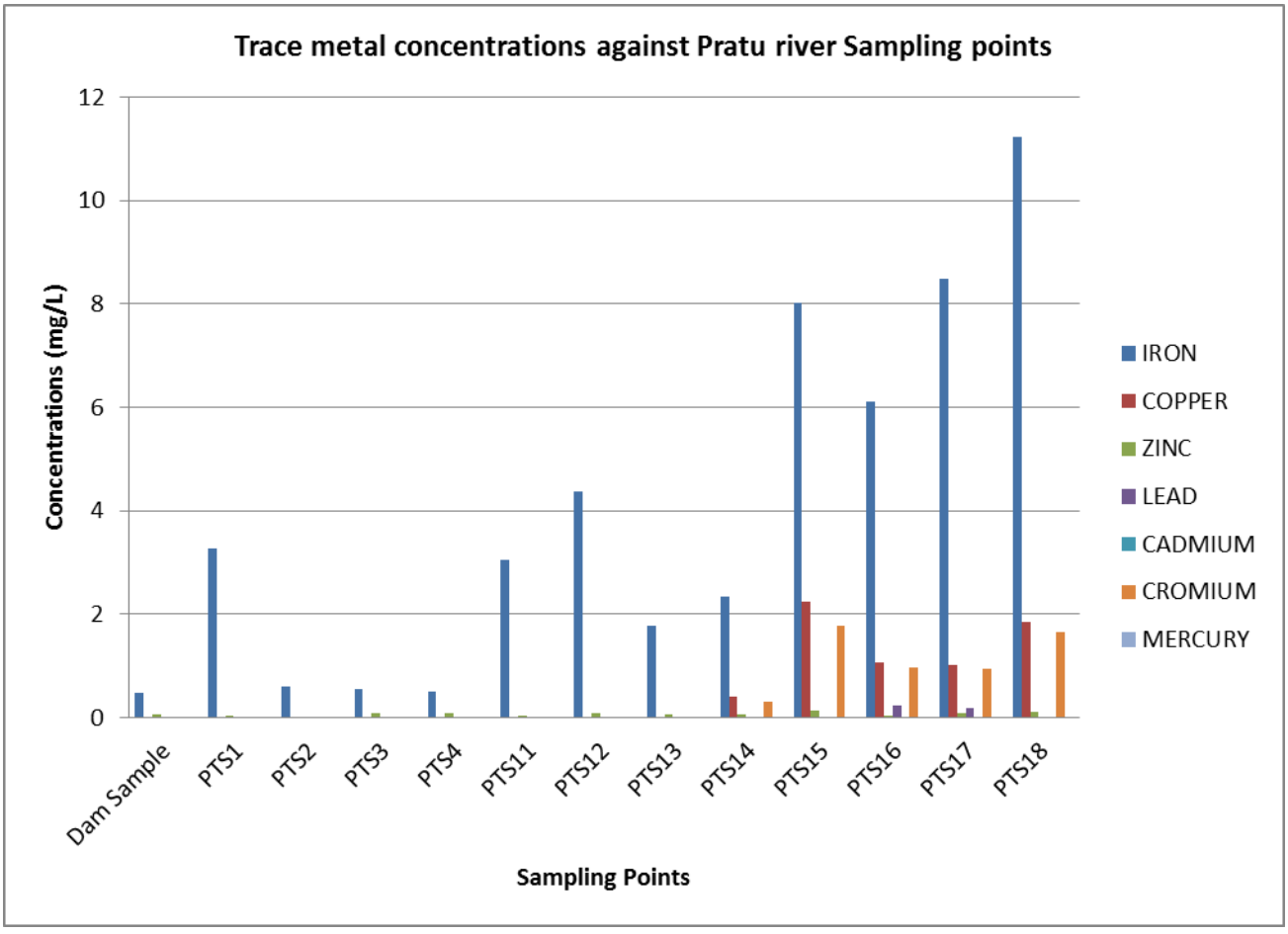

Fig 4.8: Variation of Trace Metals Concentrations at the Pratu river

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Fe concentrations in the Ntakofa river varied between 0.38 mg/L – 10.36 mg/L with a mean value of 3.63 mg /L (Fig 4.9). Fe concentrations were very high and rose from PTS5 through to PTS8, and then lowered at PTS9. It then rose again from PTS9 through to PTS22. This condition may be due to the fact that, PTS5 to PTS8 may be influenced by iron containing domestic waste since each point draws itself closer to relatively high population existing at that area. PTS9 however, was located at a point which receives inflows from other rivers such as the Ayensu River. Thus, its low concentration may be influenced by mixing and dilution from other river sources. PTS10 to PTS22 had the highest iron concentrations and this may be largely attributed to the on-going agricultural activities occurring around that area. Iron containing fertilizer applications, when washed off into the river through run-off may be the reason for the high Fe concentration. Also since petroleum generators are used for irrigation purposes, chemicals containing iron from the generator may seep into the river thus increasing its iron content (Johnson et al., 1999).

Copper concentrations at the Ntakofa river ranged between <0.003 mg/L – 1.08 mg/L with a mean value of 0.97. With reference to fig. 4.9, copper only occured at PTS20, 21 and 22. This may be largely attributed to the influence of the petroleum generators that are used for irrigation on the farmlands around that area as well as the washing off of copper containing fertilizers into the river (Lamptey et al., 2013) .

Zinc concentrations in the Ntakofa river ranged between 0.03 mg/L – 0.08 mg/L with a mean value of 0.047 mg/L. The low concentration of zinc in the Ntakofa river may be due to the effect of weathering of zinc containing minerals in the rocks of the river bed since zinc occurs naturally in river water (Gibrilla et al., 2000).

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Lead concentrations in the Ntakofa river ranged between <0.003 mg/L – 0.29 mg/L with a mean value of 0.17 mg/L. As observed from table 4.12, lead only occured at PTS20, 21 and 22. This condition may be due to the influence of the petroleum generators used for irrigation on the farmlands around that area (Gibrilla et al., 2000).

Cadmium concentrations in the Ntakofa river were observed to be below the detection limit of the equipment used for its analysis (0.002 mg/L). This condition may be due to cadmium's adsorption or adherence to the river's clay particles or river sediment respectively (Apau et al., 2012) .

Chromium concentrations varied between <0.006 mg/L – 0.99 mg/L with a mean of 0.91 mg/L. Chromium was also observed only at PTS20, 21 and 22. This condition may again be due to the use of petroleum generators for irrigation on the farmlands at that area. The chemicals in the generator containing chromium may have seeped into the river, thereby resulting in its occurrence.

Mercury concentrations were observed to be below the detection limit of the equipment used for its analysis (<0.001 mg/L). This condition may be due to the fact that, mercury may have adhered itself to the river's sediment or has been adsorbed by the clay particles in the river.

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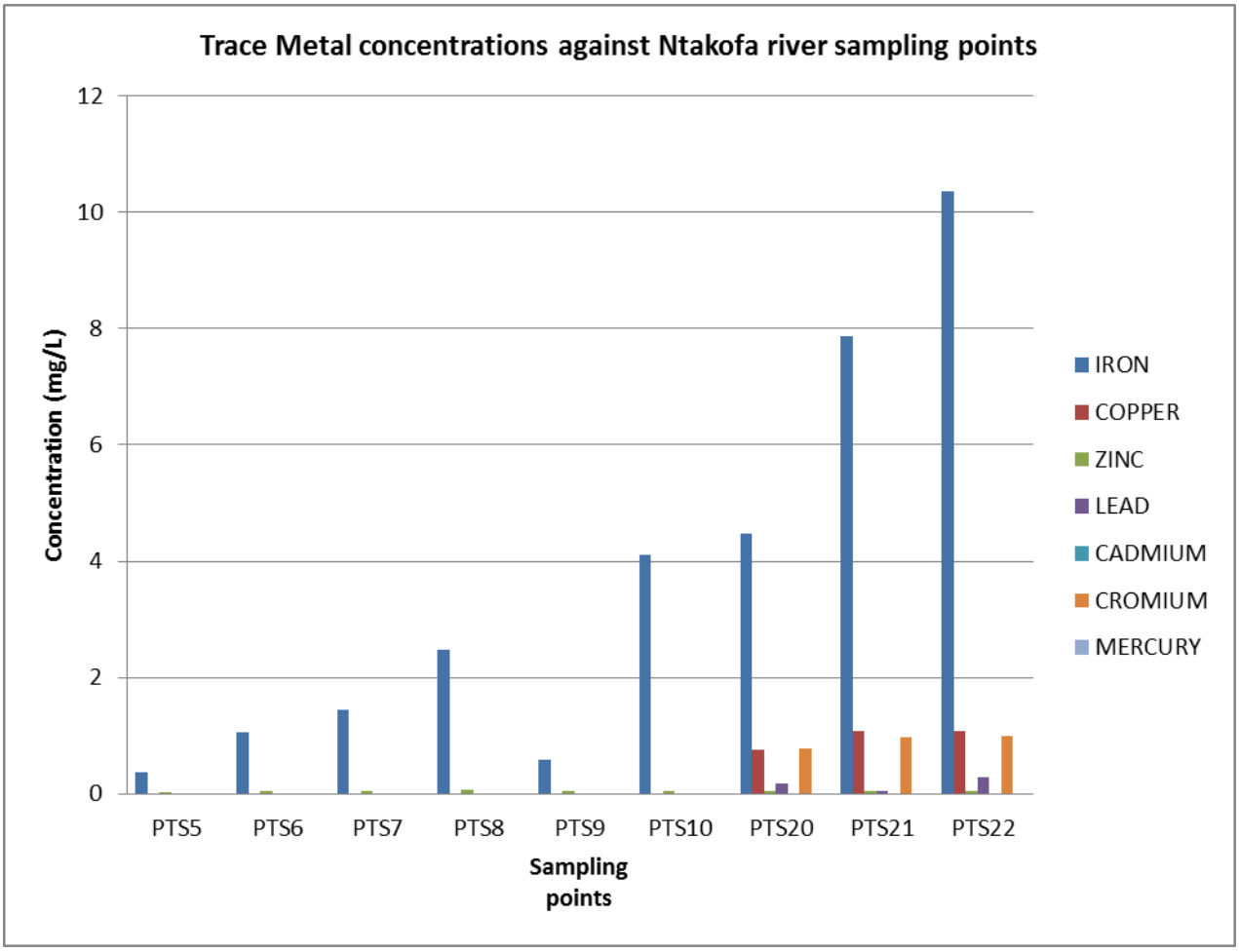

Fig 4.9: Variation of Trace Metal Concentrations at the Ntakofa River.

Fe concentrations in the Muni lagoon varied between 8.86 mg/L – 14.54 mg/L with a mean of 11.6 mg/L (Fig. 4.10). The high concentrations of iron observed at the Muni lagoon may be due to the lagoon's property of acting as a sink to the rivers flowing into it. Iron concentrations from the rivers flow into the lagoon thereby increasing its concentration. The sea also contains some amount of iron and may influence the lagoon's iron concentration since it is close to the sea (Johnson et al., 1999).

Copper concentrations in the Muni lagoon varied between 1.00 mg/L – 1.38 mg/L with a mean of 1.14 mg/L. The presence of copper in the Muni lagoon may be due to the

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combined effect of the rivers flowing into it which may contain some levels of copper. Since the lagoon acts as a sink, it resultantly houses most of the copper that flows into it (Lamptey et al., 2013).

Zinc concentrations in the Muni lagoon varied between 0.03 mg/L – 0.31 mg/L with a mean value of 0.19 mg/L. Zinc occurs naturally in water through the weathering of zinc containing minerals. Therefore Zinc concentrations in the Muni lagoon may be attributed to the weathering of zinc containing minerals. Also zinc concentrations in the rivers flowing into the lagoon may have influenced its concentration (Gibrilla et al., 2000).

Lead concentrations in the Muni lagoon varied between 0.13 mg/L – 0.2 mg/L with a mean of 0.19 mg/L. the lead concentrations observed in the Muni lagoon may be sourced from the Ntakofa river which is influenced by the usage of petroleum generators for irrigation. The Ntakofa river's flow into the lagoon may have carried some lead along with it thereby depositing it in the lagoon (Gibrilla et al., 2000).

Cadmium concentrations in the Muni lagoon were observed to be below the detection limit of the equipment used for its analysis (<0.002 mg/L). This condition may be attributed to cadmium's adherence to the lagoon's sediment or adsorption by the clay particles in the lagoon (Apau et al., 2012).

Chromium concentrations in the lagoon varied between 0,92 mg/L – 1.01 mg/L with a mean of 0.97 mg/L. This condition may be attributed to the effect of the use of petroleum generators in the Ntakofa river for irrigation. The chemicals in the generators, when they seep into the river may have been carried away into the lagoon which serves as a sink to the Ntakofa river.

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Mercury concentrations in the Muni lagoon were observed to be below the detection limit of the equipment used for its analysis (<0.001 mg/L). This condition may be due to mercury's adherence to the lagoon's sediment or its adsorption into the clay particles in the lagoon.

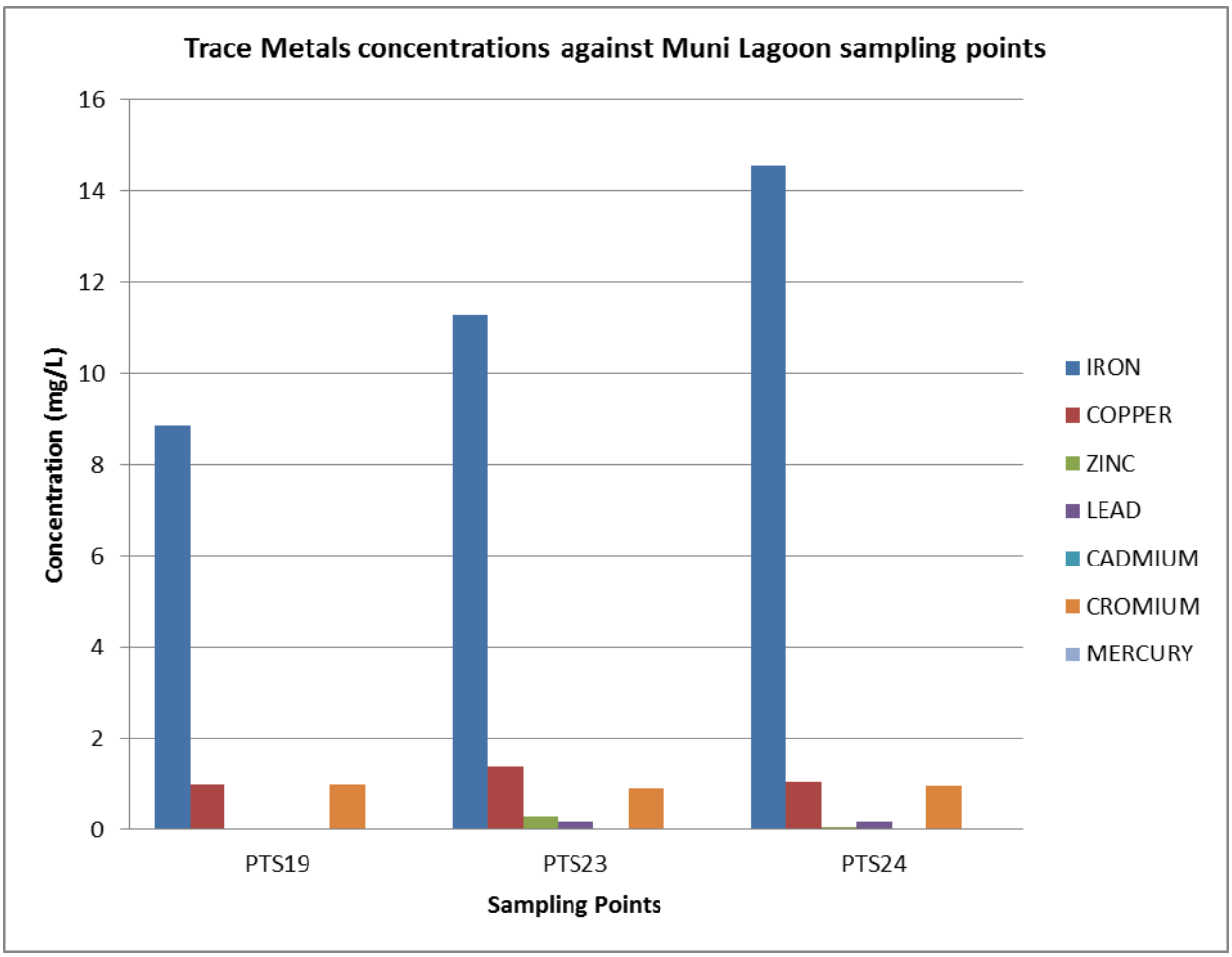

Fig 4.10: Variation of Trace Metal Concentrations at the Muni Lagoon

Heavy metal concentrations were higher in the sediment than in the water samples (Fig. 4.11). This may be due to the metals' adherence and absorbance to the river's sediment. It could also be due to deposition of the metal over a longer period of time. However, it was

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noticed that copper and chromium concentrations were predominant in the river than all the other metals especially at PTS1. This may be due to the influence of the galamsey operations evident at the bank of PTS1. Copper containing fertilizers as well as effluents from domestic waste could also be a contributing factor to the high copper and chromium concentrations (Johnson et al., 1999). Zinc concentrations were also quite evident in the river and its accumulation may be due to the influence of the galamsey operations as well as its natural occurrence in river (Lamptey et al., 2013). Iron and lead concentrations were comparatively low. This may be attributed firstly to iron's easy solubility in water. Lead containing domestic effluents may also be contributing to its concentrations in the sediment (Gibrilla et al., 2000). Cadmium and mercury concentrations were very low and below their respective detection limits. At the Pratu river this condition may be because of the constant recycling of the mercury for the small scale mining since it is expensive.

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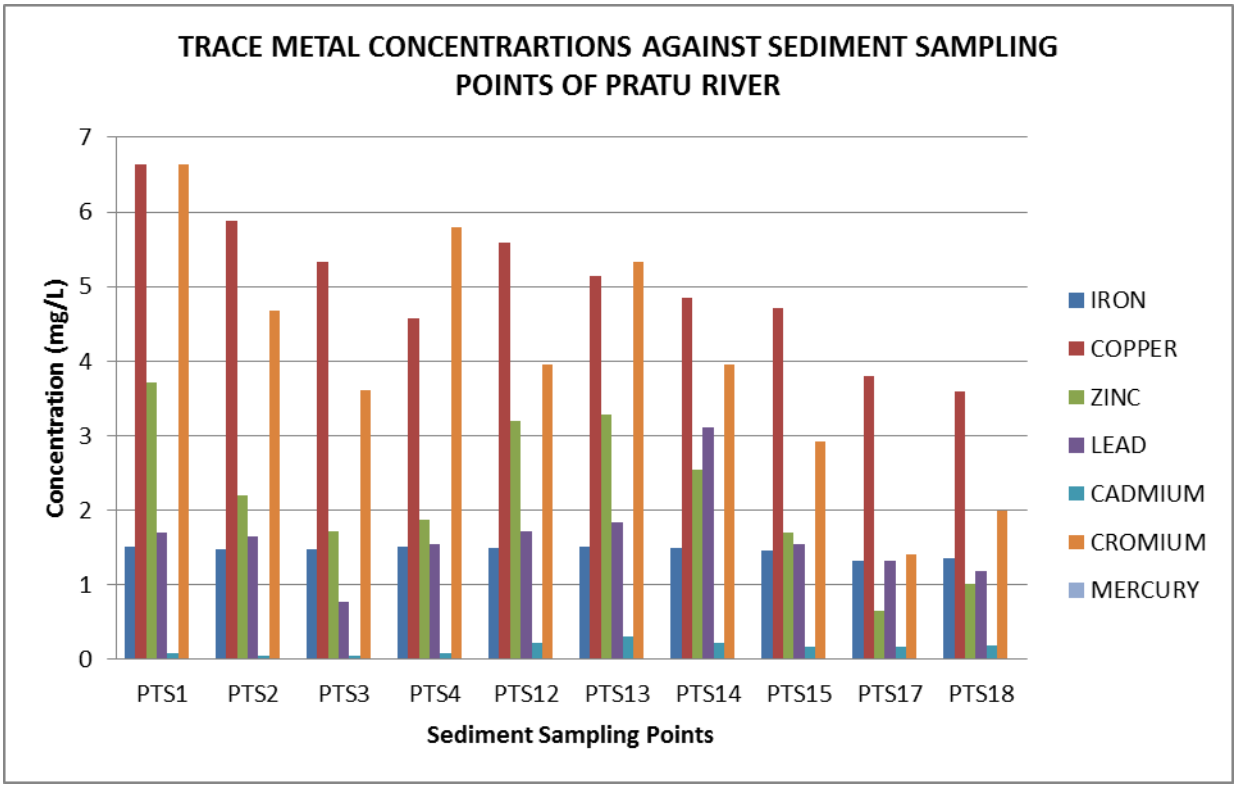

Fig 4.11: Variation of Trace metal concentrations from sediment samples at Pratu river.

At the Ntakofa River, copper concentrations were high as compared to the other metals. This condition was made very prominent at PTS20, 21 and 22. This may be largely due to the influence of petroleum generators for irrigation on the farms existing along the river banks as does the use of fertilizers containing these metals. At PTS 20, 21 and 22, it is observed from figure 4.12 that all the metals were in higher concentrations as compared to the other sampling points mainly due to the irrigation process and the influence of the farmlands which are extensive at those three points. Low concentrations of cadmium in the sediment samples may be due to leaching into the unsaturated zone (Lamptey et al., 2013). Mercury concentrations were found to be below detection limit (<0.001).

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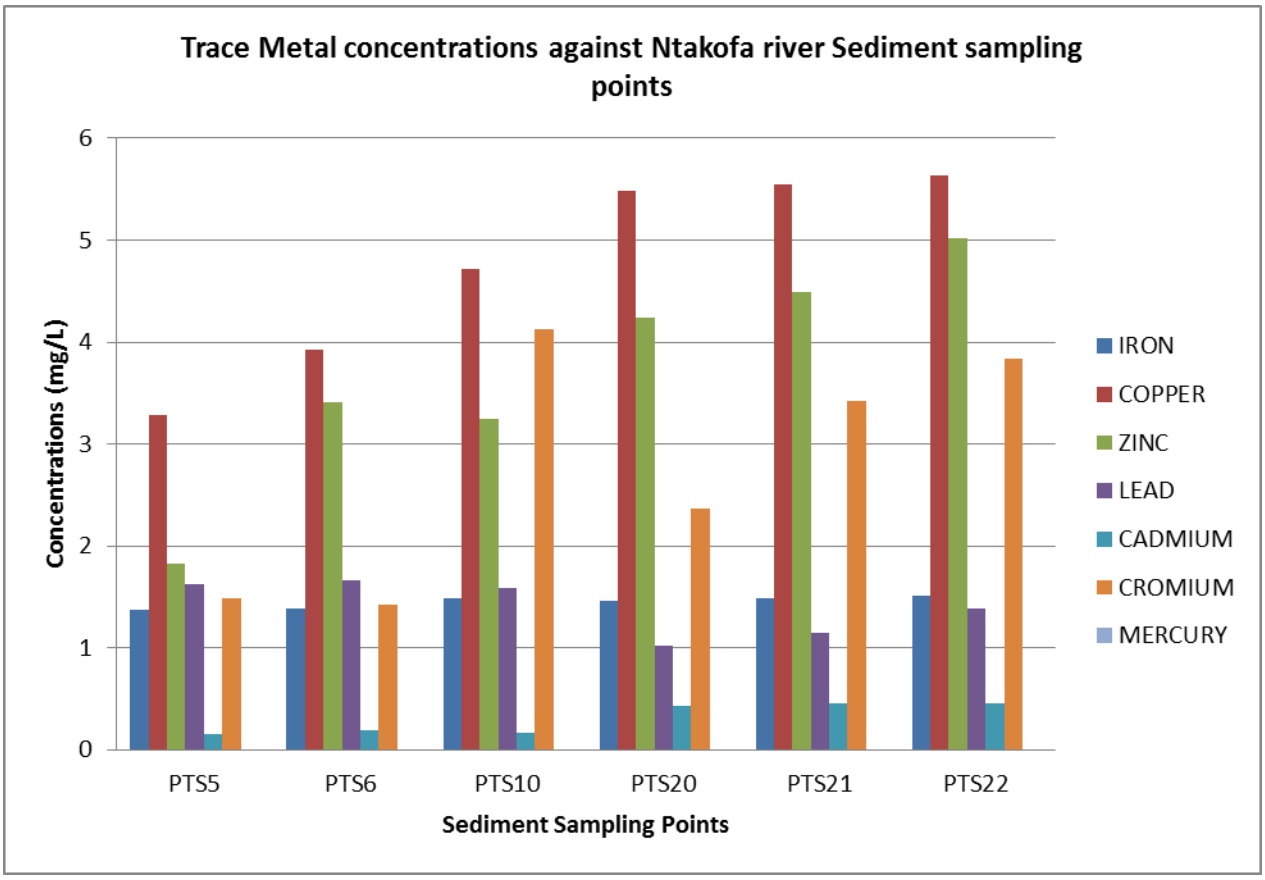

Fig 4.12: Variation of trace metal concentrations from sediment samples at the Ntakofa river.

Since the lagoon was too deep to sample sediments from, PTS19 was the only point on the Muni lagoon stretch from which results of trace metal concentrations were deduced. As seen in figure 4.13, copper dominated in its concentration as compared to the other metals just as it did in the Pratu and Ntakofa rivers. This may be attributed to the residual effect of copper concentrations from the two rivers that flow into the lagoon and consequently drop their metal contents (Gibrilla et al., 2000). The same can be said for lead, iron, chromium, zinc and cadmium. Domestic effluents that flow from the town close to the lagoon may also be contributing factors to the high concentrations observed

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at PTS19. Mercury concentrations were below detection limit. This may be because the same condition exists in both rivers that flow into the lagoon.

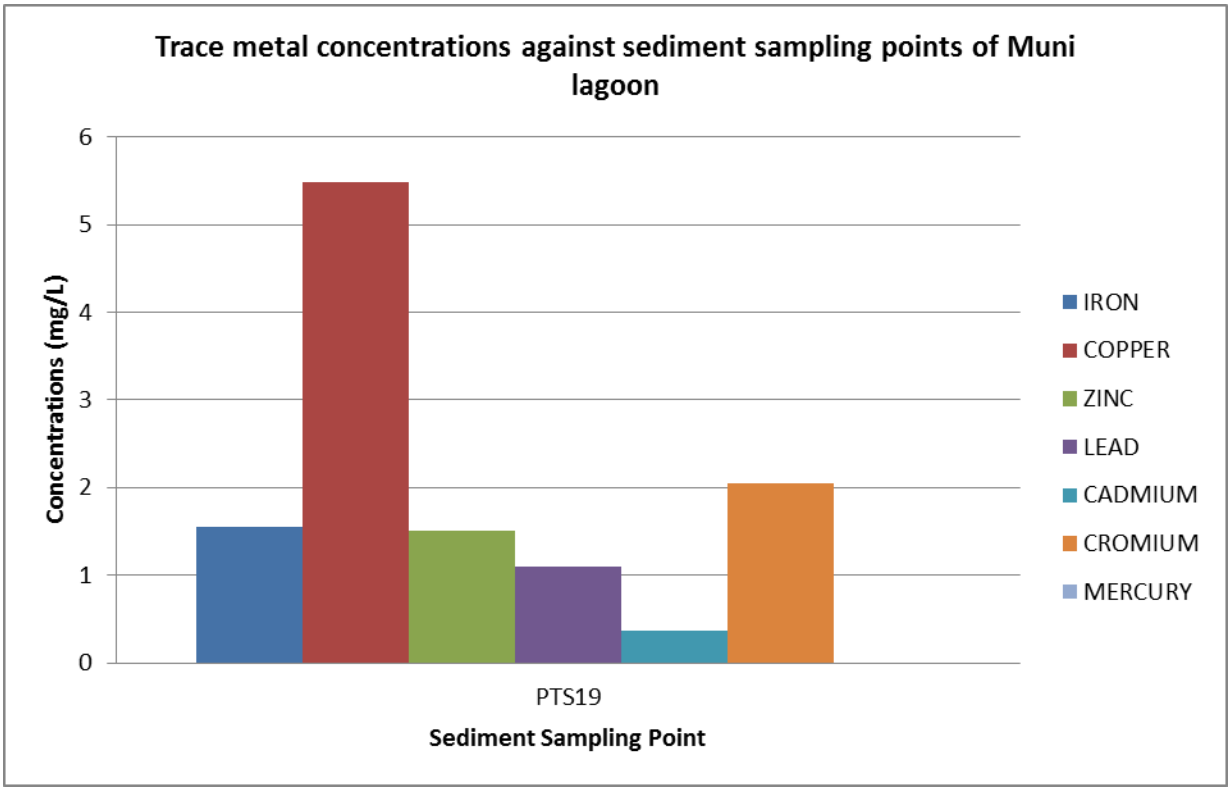

Fig 4.13: Variation of Trace metal concentrations from sediment samples at Muni Lagoon

4.6 Pesticides Residue Levels in Sediment Samples of The Pratu River, The Ntakofa River And The Muni Lagoon.

Amongst these pesticides residues analysed, four synthetic pyrethroids were observed to occur in the sediments of the Ntakofa river catchment in minute quantities. Pratu River and Muni Lagoon revealed pesticide levels below the detection limit of the equipment

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used in its analysis (.<0.005 for organochlorines; <0.010 for Organophosphates and <0.010 for Synthetic Pyrethroids). Figure 4.14 illustrates the concentrations of the various pesticides residues occurring at the Ntakofa River.

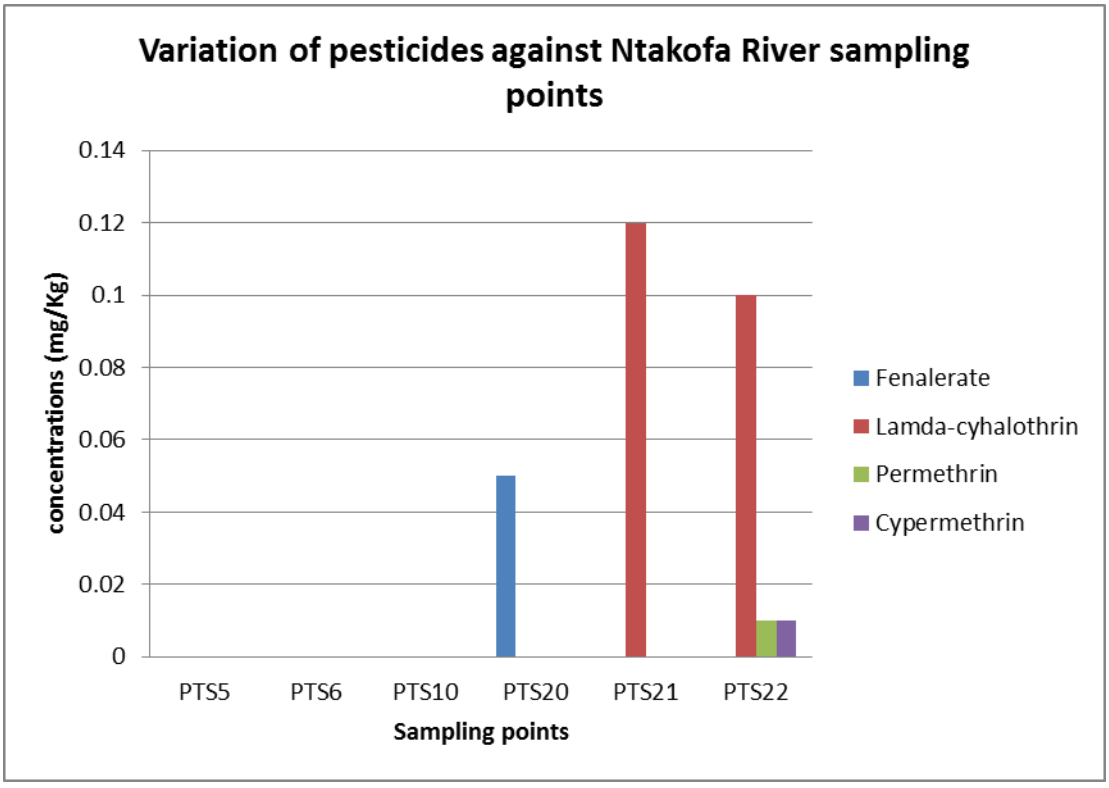

Fig 4.14: Concentrations of pesticides in the sediment samples of the Ntakofa River

At the Ntakofa River it was observed that, pesticide concentrations were predominant especially with the synthetic pyrethroids. This condition may therefore suggest that, farmers use more of synthetic pyrethroid containing pesticides more than the organochlorines or the organophosphates. The Muni lagoon was observed to have no trace of pesticides in its sediment. This condition may be due to the pesticides leaching effect into the unsaturated zone.

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CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The mean concentrations of all the parameters measured were highest in the Muni lagoon followed by the Ntakofa River and then the main Pratu River. Secondly the Ntakofa River was more influenced by the exclusive farming activities occurring there as compared to the influence of the farms along the Pratu River. Again, the Pratu River was more influenced by the varying anthropogenic activities that occur around its banks such as the illegal mining and small scale industries such as generator repairs and block making factories and the effluent of domestic waste coming from homes along the river.

With reference to the results, the mean concentrations of the EC, TDS, salinity, alkalinity and total hardness for Pratu River, Ntakofa River and the Muni Lagoon showed that there are high levels of salt in the water right from the Pratu River down to the lagoon. This means that the carbonate and bicarbonate related salts are in high concentrations in the river rendering it unsuitable for many domestic purposes according to the WHO standards. Mean temperature and pH values for the Pratu River, the Ntakofa River and the Muni lagoon were fairly stable except at the Muni lagoon which was high due to its closeness to the sea especially with reference to the pH. The BOD and COD concentrations with reference to the mean results showed that, the rivers were not greatly affected by the organic and inorganic pollution.

Average concentrations of anions and cations in the rivers showed a dominance pattern of Na > Ca > K > Mg for cations and Cl > SO_2 > NO_3 > PO_4 for anions in all three parts

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of the Pratu Basin. Na, Cl and sulphate levels were very high. Amongst the nutrients measured mean NO_3 in the three parts of the river shows that, concentrations may begin to promote eutrophication. Phosphate concentrations however are low. However the Pratu and Ntakofa rivers showed relatively high concentrations of nitrates and phosphates as compared to the Muni lagoon

Mean concentrations of trace metals measured both in the water and the sediments showed that the river may be unpolluted with trace metals. However the majority of the trace metals are adhered to the river's sediments.

Pesticides analysis on the three divisions of the basin showed that, synthetic pyrethroid based pesticides were mostly used on the farms by the farmers. Since traces of pesticides were only found in the Ntakofa river, it showed that pesticide use along the banks of the Ntakofa river may be more extensive than that of the Pratu river.

SAR calculations conducted on the three divisions of the Pratu Basin using sodium, calcium and magnesium concentrations revealed that all three parts of the river may not be suitable for irrigation. However, farmers continued to use the water from the rivers as a source of irrigation.

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5.2 Recommendations

a) In view of the research findings, there should be an annual water quality assessment of the Pratu Basin in order to ascertain the progress of pollution in the river especially with reference to nutrients associated with fertilizer application. This will give an informed decision on the right mitigation measure to take in conserving the quality of the rivers and consequently the importance of the wetland.

b) Further SAR investigations should be conducted on the soil of the farmlands in order to ascertain how affected the soil is by the water used for irrigation. This action may help farmers to be informed of the best irrigation practices in order to increase crop yield or better still seek for new farming grounds where portable irrigation water may be accessible.

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APPENDIX A

RESULTS OF RECOVERY TEST PRECEEDING WATER AND SEDIMENT ANALYSIS FOR TRACE METALS USING AAS.

	Fe	Cu	Zn	Pb	Cd	Cr	Mg	Hg
WATER								
STD1	1.959	2.006	0.249	1.919	0.499	0.967	0.094	0.022
STD1	1.959	2.003	0.249	1.962	0.492	0.965	0.101	0.022
STD1	1.970	2.004	0.249	1.982	0.498	0.957	0.101	0.021
STDQC1	4.937	5.001	0.501	4.941	1.989	1.966	1.191	0.040
SEDIMENT								
STD1	2.005	2.000	0.250	2.001	0.500	1.001	0.198	0.021
STD1	2.003	2.001	0.250	2.003	0.501	1.003	0.206	0.020
STD1	2.001	2.003	0.252	2.004	0.500	1.003	0.203	0.020
STDQC1	5.003	5.001	0.501	5.004	2.001	1.997	0.505	0.042

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APPENDIX B

GPS COODINATES FOR SAMPLING POINTS OF PRATU RIVER, NTAKOFA RIVER AND THE MUNI LAGOON

No.	Sample Code	Name of Sampling point	Coordinates		Altitude
			Latitude N/S DDMMSS.DD	Longitude W/E DDDMMSS.DD	(m)
1	PTS 1	PRATU	5.42599	0.68429	3
2	PTS 2	PRATU	05.40347	0.67864	4
3	PTS 3	PRATU	5.39579	0.67890	3
4	PTS 4	PRATU	05.39079	0.67932	3
5	PTS 5	NTAKOFA	5.385518	-0.639721	25
6	PTS 6	NTAKOFA	5.388338	-0.60862	32
7	PTS 7	NTAKOFA	5.380486	-0.648930	19
8	PTS 8	NTAKOFA	5.377155	-0.656656	20
9	PTS 9	NTAKOFA	5.372331	-0.635687	19
10	PTS 10	NTAKOFA	5.367512	-0.650372	19
11	PTS 11	PRATU	5.358674	-0.6642978	13
12	PTS 12	PRATU	-5.3698056	-0.6729722	
13	PTS 13	PRATU	-5.3698333	-0.6728611	9
14	PTS 14	PRATU	-5.3629444	-0.6731111	9
15	PTS 15	PRATU	05.35822	0.67239	11
16	PTS 16	PRATU	5.35371	0.67077	15
17	PTS 17	PRATU	5.35289	0.66404	10

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18	PTS 18	PRATU	05.33937	000.664592	6
19	PTS 19	MUNI	05.33657	000.64279	6
20	PTS 20	NTAKOFA	05.35839	000.64721	12
21	PTS 21	NTAKOFA	05.35507	000.64840	10
22	PTS 22	NTAKOFA	05.35233	000.64563	10
23	PTS 23	MUNI	05.32769	000.64643	18
24	PTS 24	MUNI	05.33168	000.64285	15
25	DAM	PRATU	-5.4259444	-0.6842778	

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APPENDIX C

PESTICIDE RESULTS OF SEDIMENT SAMPLES FROM TE PRATU AND NTAKOFA RIVERS AS WELL AS THE MUNI LAGOON.

TEST CONDUCTED	PTS1	PTS2	PTS3	PTS4	PTS5	PTS6	PTS10	PTS12	PTS13	PTS14	PTS15	PTS17	PTS18	PTS19	PTS20	PTS21	PTS22	IONS-US M
Methamidophos	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	0.03(Max)
Ethoprophos	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	0.05(Max)
Phorate	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	0.05(Max)
Dimethoate	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	0.03(Max)
Beta-HCH	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	0.03(Max)
Delta-HCH	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	0.03(Max)
Diazion	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	0.03(Max)
Fonofos	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	0.05(Max)
Lindane	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	0.04(Max)
Heptachlor	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	0.03(Max)
Pirimiphos-methyl	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	0.03(Max)
Fenitrothion	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	0.05(Max)
Malathion	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	0.05(Max)
Chlorpyrifos	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	0.03(Max)
Aldrin	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	0.04(Max)
Parathion	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	0.04(Max)
Chlorfeninphos	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	0.05(Max)
Allethrin	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	0.01(Max)
Gamma Chlordane	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	0.25(Max)
Profenofos	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	0.05(Max)
p,p'-DDE	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	0.04(Max)
Dieldrin	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	0.02(Max)
Endrin	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	0.04(Max)
Alpha-Endosulfan	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	0.05(Max)
Beta-Endosulfan	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	0.04(Max)
Endosulfan Sulfate	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	0.04(Max)
p,p'-DDT	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	0.05(Max)
p,p'-DDD	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	0.04(Max)
Beifenthrin	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	0.04(Max)
Fenpropathrin	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	0.02(Max)
Methoxychlor	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	0.05(Max)
Lambda-cychalothrin	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	0.12	0.1	0.02(Max)
Perethrin	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	0.01	0.10(Max)
Cyfuthrin	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	0.01	0.15(Max)
Cypermethrin	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	0.05(Max)
Fenvalerate	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	0.05	<0.010	<0.010	0.03(Max)
Deltamethrin	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	0.05(Max)

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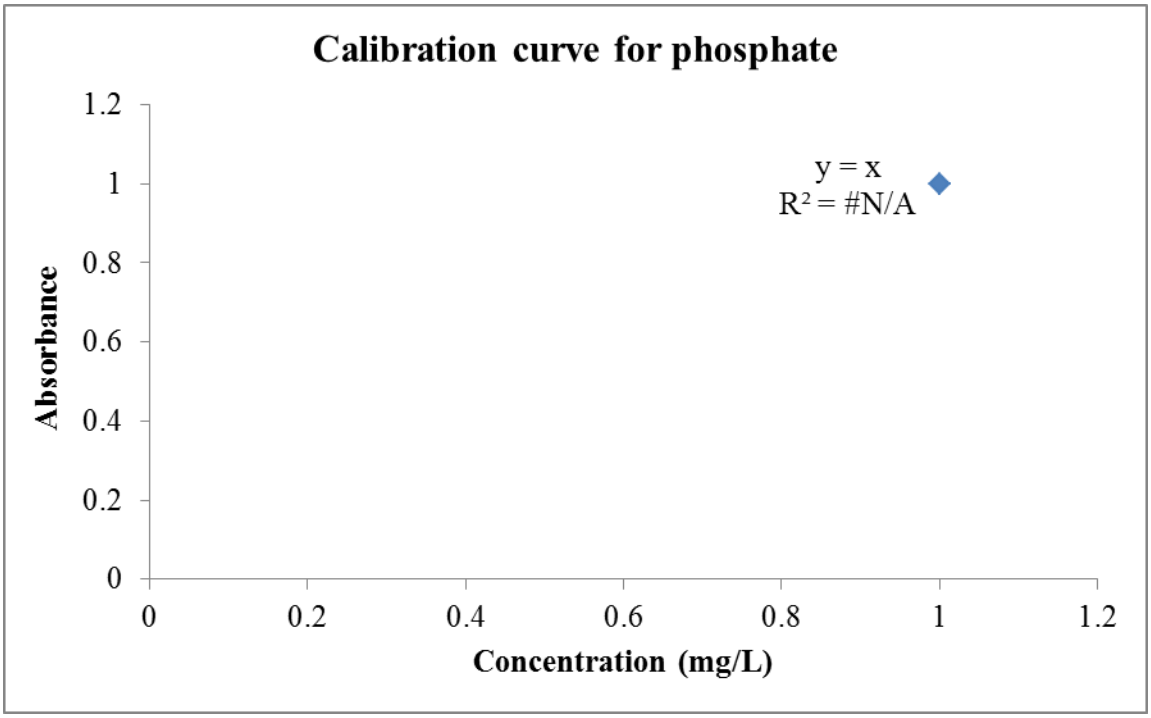
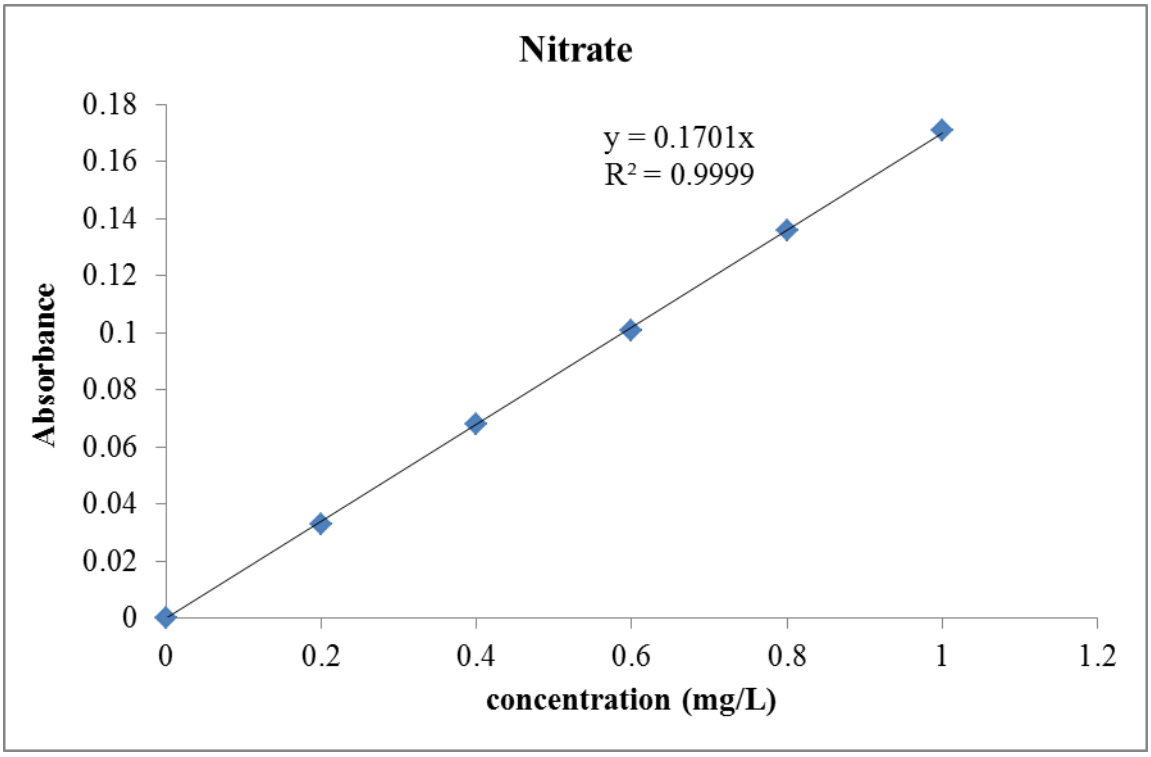
APPENDIX D

LINEAR REGRESSION LINES FOR CALIBRATION OF UV-VISIBLE SPECTROMETER





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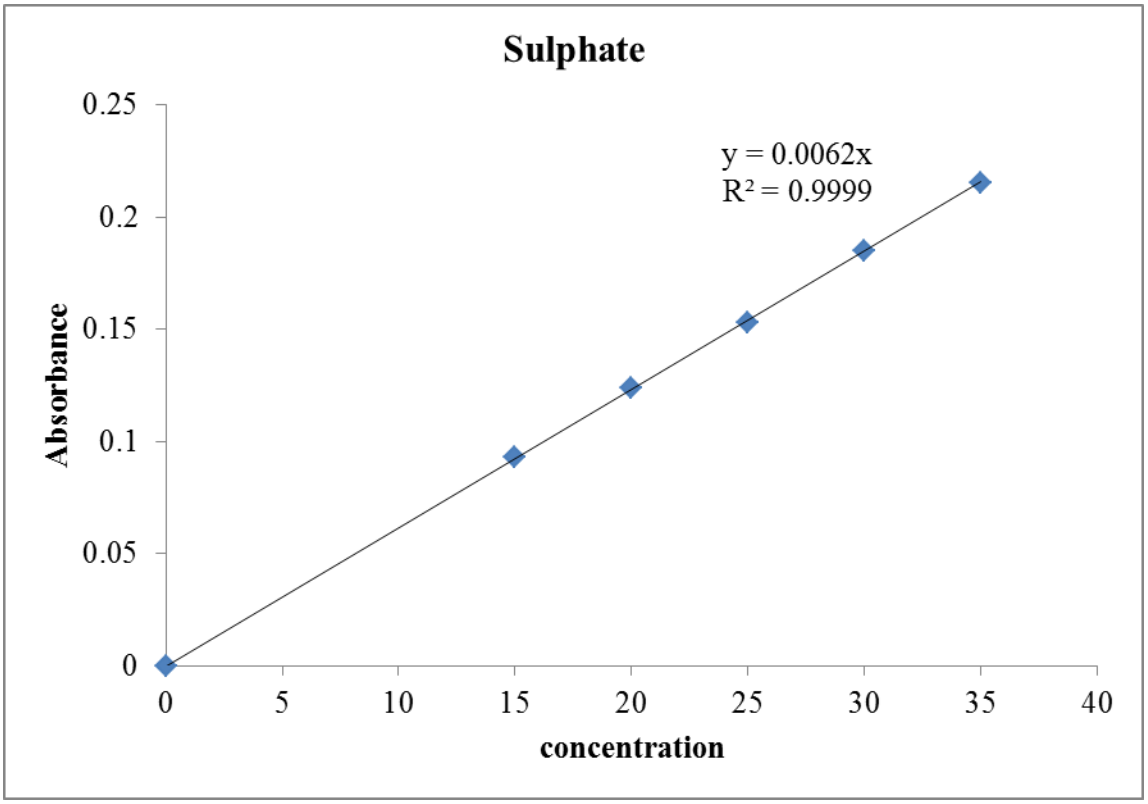

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APPENDIX E

REGRESSION LINE OF CALIBRATION OF FAAS FOR IRON (Fe) METAL