PHREEQ C Modelling Tool Application to Determine the Effect of Anions on Speciation of Selected Metals in Water Systems within Kajiado North Constituency in Kenya

Carren Akinyi Nyapola
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DECLARATION

Declaration by the student

I hereby declare that this research thesis is my original work and has not been presented for the award of any degree, diploma, or credential at any institution.

Carren Akinyi Nyapola
SCT-352-001/2017

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

Approval by Supervisors
This thesis was conducted under our supervision and submitted for examination with our approval as university supervisors.

1. Dr. Martin Magu
   Department of Chemistry
   Faculty of Science and Technology

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

2. Prof. Anastasiah Ngigi
   Department of Chemistry
   Faculty of Science and Technology

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

DEDICATION

This thesis is dedicated to God Almighty, my Creator, Yahweh. He has served as my rock throughout this research. I likewise dedicate it to my late parents Mr. Nyapola(Japuonj) and Mrs. Pamela Nyapola, whose memories nevertheless influence my existence, in addition to my friend Eng. Paul Odongo, Smwel Alaro ,Joan Nyapola and Marion Nyapola who has backed me all step of the way and whose support has ensured that I finish what I have started and not forgetting Russell, Rufy, and Rugil (Shalom), who have been impacted by this journey in every form possible.

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The Various parameters used to identify and quantify toxicants in water, were pH, temperature electrical conductivity, metal ions, and anions. The results of the analysis are outlined and presented in Tables (4.1, 4.2, and 4.3). The parameters were viewed against the limits of the standards as prescribed by the World Health Organization(WHO) which is given in Table 2.1 398

LIST OF EQUATIONS

LIST OF ABBREVIATIONS/ACRONYMS AND SYMBOLS

AAS…………..Atomic Absorption Spectrometry

AES….…........Atomic Emission Spectrometry

ASV................Anodic Stripping Voltammetry

ATSDR…….. Agency for Toxic Substances and Disease Registry

CICAD……….Concise International Chemical Assessment Document

EC……............Electrical Conductivity

IC…………......Ion Chromatography

ICP-OES…......Inductively Coupled Plasma - Optical Emission Spectrometry

KEBS…………Kenya Bureau of Standards

NEMA………..National Environment Management Authority

ROS ………….. Reactive oxygen species

SPADNS……..Sodium 2-(Parasulfophenylazo)-1,8-Dihydroxy-3,6-Naphthalene Disulfonate

UNEP…….…United Nations Environmental programme

ABSTRACT

Heavy metals and anions in water pose a significant risk to living organisms, including humans, and must therefore be carefully monitored. There are numerous approaches and methods of analysis to choose from. Using the PHREEQ C chemical modeling technique, this study looked at the effect of certain anions on the speciation of selected metals in the water environment of Kajiado North. Twenty-five sampling points were used in the study, which covered five Kajiado North election wards. Samples were taken twice during the dry and rainy seasons, in November 2019 and March 2020. Using standard methods, physicochemical characteristics were analyzed, concentrations of selected heavy metals using the (ICP-OES) 7000 series, and selected anions using a multi parameter photometer, their concentration values compared to the specified maximum contaminant level and speciation analysis done using the Computer-based technique PHREEQ C. The range observed for pH, temperature, electrical conductivity, sulphate, chloride, fluoride, nitrate and carbonates was 7.43-9.30, 23.0 -28.0oC, 335-1265µS/cm, 4.54-361.41mgL-1, 5.19-184.6 mgL-1, 0.01-2.90 mgL-1, 0.1-8.6 mgL-1, and 3.18-55.19 mgL-1 respectively. The range observed for heavy metals was 0.06-1.08 mgL-1 , 0.00 -0.05082 mgL-1, 0.01-0.02597 mgL-1, 0.01-0.01610 mgL-1, 0.00 -0.0327 mgL-1, 0.00-42.7842 mgL-1, and below detection limit, for Fe, Mn, Cu, Zn, Pb, Mg, and Cd respectively. The findings revealed that Cd, Zn, Cu, Cl-, NO2-, and eElectrical cconductivity concentrations were below the WHO levels. At certain sampling points, however, SO42-, F-, Pb, Fe, and Mn were above WHO limits. In some water systems, traces of SO42-, F-, Cu, Fe, Cd, and Mn were found to pose significant health risks, according to PHREEQ C speciation analysis. Anion concentrations, pH, temperature, and metal concentrations are all important variables in modeling. Metals formed anion complexes and the total abundance of metal species was classified at the highest levels as Fe(OH)3, PbCO3, Zn(CO3)2, Cu(CO3)2, Mn+2, MgF-, and Mg+2. At a water system temperature of 25oC without anions, it was found to have the highest chemical species. CuCO3, CuNO3, and CuOH+ complexes are also formed at low pH. Based on the data for different metal species at different pH values, the bioavailability of metal species definitely depends on pH.

CHAPTER ONE
INTRODUCTION

A. Background of the Study

Water is fundamental to the endurance of plants, animals, and persons, and it is plentiful, top about three-cottage of the soil's surface. Agreement to the World Health Organization (WHO), most of the globe's society, or nearly 1.1 billion public, lacks access to reliable water for consumption, with Africa making up the largest number (WHO, 2017b). Four out of five Kenyans lack access to cleanand safe water, with shallow wells, shallow rivers, and ponds as their only sources, while another half lack fundamental cleanliness (GOK, 2016). When considering household water supply, water quality and safety are key concerns. Water is from two distinct natural sources; surface water and groundwater (Melegy et al., 2014). Water, being polar, makes it be thought of as clean because it absorbs, dissolves, or be in suspended compounds (WHO, 2007). Worldwide, there are large amounts of water sources available, but the vast majority of them are inappropriate for human use due to adulteration (WHO, 2022).

One of the most significant preventable health burdens in the world is associated with unsafe drinking water and inadequate sanitation. A survey by the World Health Organization (WHO, 2022), reveals further that 3.4 million populace die year after year from able to be averted water-connected ailments that can be averted. A contributing factor is the desire of states in developing countries to reach economic development standing while also broadening their state expansion objectives (Kiithia, 2012). A great deal of attention is paid to the impact of unsafe water and inadequate sanitation on the Millennium Development Goals (MDGs) (GOK, 2016) access to safe water as one of the goals. This illustrates the detrimental effects of poor sanitation and contaminated water. According to Kenya's constitution, every individual has the right to drink water that is safe and clean in adequate quantities (GOK, 2005).

The usage of polluted water in industries and household by humans is unfit (Budambula & Mwachiro, 2006). A variety of sources contribute to water pollution, including agricultural, municipal, industrial, and landfill drainage waters. These pollutants can be organic, nutrient-based, or heavy metal-based pollutants, as a result, they damage natural ecosystems and, in the long run, humans. A large focus has been placed on heavy metals as potential pollutants due to their toxicity at low concentrations (Marcovecchio, 2007; Nyapola & 2022).

To lessen well-being concerns induced by water contamination, it is decisive to monitor the presence of heavy metals in water systems constantly. Since it is evidenced that diverse decomposition states of trace metals have different classes of toxicity, it is important to determine the speciation of these metals (ODEBUNMI, 2014). While metal concentrations in the Kajiado North Constituency have been considered, their speciation is yet to be investigated, their full concentrations as well as their chemical species are taken into account to reduce the dangers of chemical contamination and manage the exposure to trace metals. Using a combination of metal absorption levels and chemical species as well as examining anions' effects to assess water quality in identified waterways, this study examined the water quality in these systems. With the aid of a multiparameter photometer, Fluoride (F^-), nitrite (NO_2^-), nitrate (NO_3^-), and sulphate (SO_4^{2-}), were measured, while chloride (Cl^-), carbonate (CO_3^{2-}), and hydrogen carbonate (HCO_3^-), by titrimetry and Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES) was used to study heavy metals (Cu, Fe, Pb, Mn, Mg, Cd, and Zn) and their speciation, which was then applied to the PHREEQC to demonstrate the importance of providing dependable water in Kajiado North constituency.

B. Water Sources in the Research Area and Environmental Issues

The Oloolaiser Water and Sewerage Company are supposed to provide water to residents of Kajiado North Constituency, but the service has proven to be insufficient over time (Kazungu, 2011). Rainwater, aquifers, dams, and boreholes are some of the water sources available for household use in the region. Underground water is known to be far more reliable and free of contamination than surface water. However, in the study region, inadequate waste disposal management of agricultural effluents, market effluents, open household sewage, and noxious anthropogenic waste disposal in local water systems causes water adulteration and has therefore lowered the water quality (Ochiba,2020Ochiba N.K, 2020). The effects of the aforementioned practices on water quality were confirmed in a study by (Obiefuna & Orazulike, 2010) in Yola waters.

➤ *Concerns about Heavy Metals and Anion Leakage*

Water contamination is known to be a serious issue that causes many diseases worldwide (UNDP, 2009). Cumulative toxins from heavy metals and anions such as Pb, Mn, Cd, NO_2^-, SO_4^{2-}, NO_3^-, F^-, and Cu populate the environment due to non-treatment, human and livestock waste contamination, and are the basis for environmental and highly toxic hazards (Jim McGeer, 2002). Certain heavy metals are irreversibly bound to inorganic anions or organic compounds (WHO, 2022). Therefore, these heavy metals when consumed tend to accumulate in the human body through various processes, leading to adverse effects. Insufficient waste management results in heavy metals building up in water supplies. Thus, in addition to other household wastes, water systems are negligently polluted with man-made excreta from open sewers, such as the Mbagathi river (Figure 1). Unfortunately, in determining how safe it is, public health studies highlight the study of chemical properties such as heavy metal content and anions in water, but little focus is put on the role of selected anions in metal speciation. According to mapping from the (KEBS, 2010), Kajiado County has at least 50% of its region where fluoride and metal in the underground water are higher than the recommended limit for drinking

water. High pollution of groundwater by solid waste inwater systems located in areas near septic tanks was found in a water analysis in Ongata Rongai (Ochiba N.K, 2020). No research on the effects of anions on metal speciation has been conducted so far in this region.

Fig 1: Pollution of water in Mbagathi River at Maasai Lodge - Bangladesh Bridge

➢ *Effects of Water Contamination*

It is very key to note that any contamination of the water can have devastating ramifications for human beings and other lives on earth, regardless of whether it is the result of inappropriate waste disposal and unsatisfactory treatment way in city centers or an oil leak or farm overflow that finds its way into water systems. Humans, mammals, and plants may suffer negative effects from water contamination in the following manners: Contaminated water sources that date back centuries have contributed to the scarcity of safe drinking water, with well-nigh one-quarter of the globe's population being unable to access clean water (WHO, 2022). No country is immune to befouled drinking water, even the highly developed ones. Flint, Michigan, USA, experienced dangerous levels of lead invasion in its water supplies in 2014, culminating in exposure to over 100,000 people and the end of life of 12 (Ruckart et al., 2019); (Hanna-Attisha et al., 2015). Contaminated water systems likewise influence the feeding relationships among organisms this ability seem to be minor, but chemicals, heavy metals, and other pollutants can poison microorganisms, disorganizing their ordinary functions. These are in turn consumed by larger creatures, which progressively leads to pollution in the feeding relationships among organisms (Hanna-Attisha et al., 2015). The worlds mammals and plants could both be impacted by water pollution, as there are countless species of plants and animals that rely on solely on the water for survival, making them the most vulnerable to water contamination. Several endangered fowls, turtles, aquatic creatures, and unquantified fish and invertebrates were adversely afflicted by the 2010 Deep Horizon oil discharge (Frasier et al., 2020). A large number of water systems around the world are seriously impacted by metallic contaminants (UNEP, 2017). Heavy metal contaminants have been linked to numerous infections associated with groundwater use (Vetrimurugan et al., 2017). Metals in water can cause DNA damage, activate different pathways that lead to tumor development, and promote pain and swelling (Chen et al., 2019). In 2004, cadmium was formally classified as a Class I human alveolus carcinogen founded on epidemiological studies (Chen et al., 2019). Cadmium too plays an outstanding role in the prostate, renal, liver, pouch, and stomach cancers (Chen et al., 2019). In addition to these effects, heavy metals in water are capable of damaging different organs, not to mention the nervous system. This can induce behavioral difficulties, learning disadvantages, mental disorders, concentration shortfalls, and low intellectual accomplishment in children (Dietert et al., 2004). For instance, lead causes an irreversible downturn in cognitive ability (Dietert et al., 2004). Disproportionate manganese exposure during the time of puberty induces hyper-activeness and learning disorders (CICAD, 2004). Furthermore, metal contamination of water influences the level of glucose in blood absorption since iron in excess is linked to insulin resistance, hyperglycemia, and raised risks of type 2 diabetes mellitus, some metals lower the levels of blood glucose for instance magnesium and zinc. There is, as a result, demand for adequate quality drinking water to meet up the fundamental human requirements, development, wellness, and well-being of people, again being all over acknowledged human rights.

➢ *Chemical Speciation of Metals*

In the environment, metals occur in countless diverse physical and chemical forms, for instance as an element (rare), as a metal component, as a free cation dissolved in water (e.g. Cd^{2+}), or bound to organic or inorganic molecules either in solid or in dissolved form (Allen, 1993). The distribution of diversified chemical forms (as mentioned above) of metal in any environmental model are noted as speciation. Metal speciation is influenced by the characteristics of the metal and environmental conditions such as pH and temperature. Identification of major reactions and environmental factors that influence metal speciation can help us to model metal speciation. Existing adaptive evolution approaches exploit an array of methods to isolate various metal forms (Reeder et al., 2005).

The objective of a speciation model is to resolve whether metal ions are "free" (only associated with water molecules) or have anions that replace water molecules in solution in the metal ion's hydration sphere (USEPA, 2003); (Jim McGeer, 2002). Several chemical modelling has been developed and adapted in speciation studies such as: MINTEQA2, WATEQ4F, and PHREEQ C .These are few models of computer-based investigative tools for chemical speciation that have been developed (Jeske-Kaczanowska, 2014). Chemical speciation modeling can be conducted by adopting PHREEQ C software that utilizes an ion-association aqueous model to carry out reduced-temperature aqueous geochemical computations. It also can determine metal adaptive evolution.

C. Problem Statement

Every metropolitan and rural advancement that performs vulnerable waste disposal approaches of household discharge treatment like septic tanks soil absorption methods, and pit latrines, generates a risk of groundwater pollution (Graham & Polizzotto, 2013). The escalating urbanization and the haphazard disposal of agrochemicals, industrial effluents, and household wastes into water systems are both contributing elements to the contamination of water systems (NEMA, 2015). There are still new neighbourhoods that rise every day in Kajiado North Constituency, but land parcels are noticeably smaller and that connotes more discharge from households. Metals such as Pb, Cd, and, Cu are aggregate poisons, which cause ecosystem hazards, and, are widely known to be highly poisonous. Oxidative nervous tension arises in the cells owing to their presence and is involved in the etiology of some afflictions in human beings. In Kajiado County, there is little or no control over borehole drilling, and metropolitan authorities are currently incapable of appropriately governing enormous amounts of generated solid waste, which is a crucial setback. Residents of the Kajiado North Constituency rely on groundwater for household purposes, in addition to drinking. To avert water pollution, heavy metals must be checked in water systems. In the Kajiado North Constituency, no studies have been conducted to evaluate water quality through chemical modeling of the effects of anions on metal speciation. The most common method of determining water quality status is to measure evaluated Physico-chemical and organic determinants using standard guidelines. This method is only convenient for identifying contamination sources and determining whether they meet water quality guidelines. It does not provide overall water quality monitoring in terms of predictive trends and contamination intensity,information on the levels of chosen metals and anions contaminants in water systems, as well as their speciation tendencies. The findings will aid in the development and implementation of control measures to protect water quality, accordingly contributing to the realization of Kenya's Vision 2030.

D. Justification

As with other areas that border Nairobi Cosmopolitan, Kajiado North Constituency and its environs have experienced increased population growth and population influx that has resulted in rapid and unplanned urbanization, without a proper sewerage management system. Environmental deposition of anthropogenically derived chemicals is a major source of heavy metals in water. Heavy metals are very harmful because of their non-biodegradability, long biological half-lives, and their potential to accumulate in different body parts. The major sources of household water in this region are at risk of heavy metals exposure. There is a possibility of water pollution through discharge or leaching. These are the contributing factors to water contamination, as the pollutants permeate into the water systems. Also, the area is located within the greater Rift valley, which is characterized by huge fluoride deposits. Metals and anions in water systems form metal ions and complexes that enter the ecosystem thus leading to pollution. The metals and selected anions at above certain levels become harmful and hazardous forming carcinogenic and non-carcinogenic related human problems. Some studies have been done in the waters in this region, For example, a study that mostly considered selected anions and heavy metals in groundwater systems in the region (machuma, 2014), and another study assessed only physical parameters and the heavy metal concentrations levels in the groundwater systems in the region by considering their location and in zones near septic tanks in Ongata Rongai (machuma, 2014; Nyapola & 2022; Ochiba N.K, 2020) in all these studies anions and heavy metals were determined separately, and no study has so far considered chemical modeling of the heavy metal and effect of the anions. Therefore, there is a need to evaluate the water quality of water sources in the Kajiado North Constituency and assess the risks associated with the contaminants to allowable limits by recognized regulatory bodies. Thus greater emphasis was given to the determination of the effect of anions on metal speciation in water systems by use of a chemical modeling tool PHREEQ C. The modeling helps to simulate costly and risky experiments, saving time, and reducing costs as a result.. As a result, using the PHREEQ C interactive computer-based tool to perform chemical speciation of selected anions, and their effects on metal in a given pH and temperature setting, this study provided more information on water quality in water systems and identified the abundance of species and their existing varieties in definite water structures. Metal speciation is well-considered crucial to determining how metals behave and their impact on any ecological system (Jim McGeer, 2002). As a result, chemical speciation is a greater concern than ever before, and it is now done regularly to control the quality of the environment's resources (Jim McGeer, 2002).

E. Hypotheses

- In the water systems of Kajiado North Constituency, anions have no impact on metal speciation.
- The metal speciation in Kajiado North Constituency water systems is unaffected by environmental factors like temperature and pH.

F. Objectives

➢ *Main Objective*

To determine the effect of anions, pH, and temperature on metal speciation using a chemical aqueous model in selected water systems in the Kajiado North Constituency in Kenya.

➢ *Specific Objectives*

- To analyze the physical parameters (pH, Temperature, Electrical Conductivity) in existing water systems (boreholes, dams, and rivers) in Kajiado North Constituency.
- To determine the levels of selected metals (Cu, Fe, Pb, Mn, Mg, Cd, and Zn) and level of anions (F^-, Cl^-, SO_4^{2-}, HCO_3^-, CO_3^{2-}, NO_2^-, and NO_3^-) in existing water systems (boreholes, dams, and rivers) in Kajiado North Constituency and compare them to regulatory limits.
- To determine metal speciation and bioavailability using chemical modeling tool PHREEQ C ..
- To simulate the effect of pH, Temperature & anions on the speciation of analyzed metals in existing water systems (boreholes, dams, and rivers) in Kajiado North Constituency.

CHAPTER TWO
LITERATURE REVIEW

A. Heavy Metals in Water and Exposure Routes

According to (Jarup, 2003), heavy metals are elements with atomic weights ranging from 63 to 200, as well as a density of more than 5 g/cm³. The different forms of heavy metals in water are colloidal, particulate, or dissolved (Denaix et al., 2001; Gautam et al., 2014). Both natural and anthropogenic processes introduce heavy metals into the environment (Ochieng et al., 2009). Natural weathering of the earth's crust and variations in sediment mineralogy with changes in trace metal amounts are some of these sources (EA Ochungo, 2019), point and non-point sources (Figure 2), soil degradation, industrial discharge, urban runoff, wastewater, plant-related pest or disease control agents, air pollution fallout, and many others (Yu, 2005).
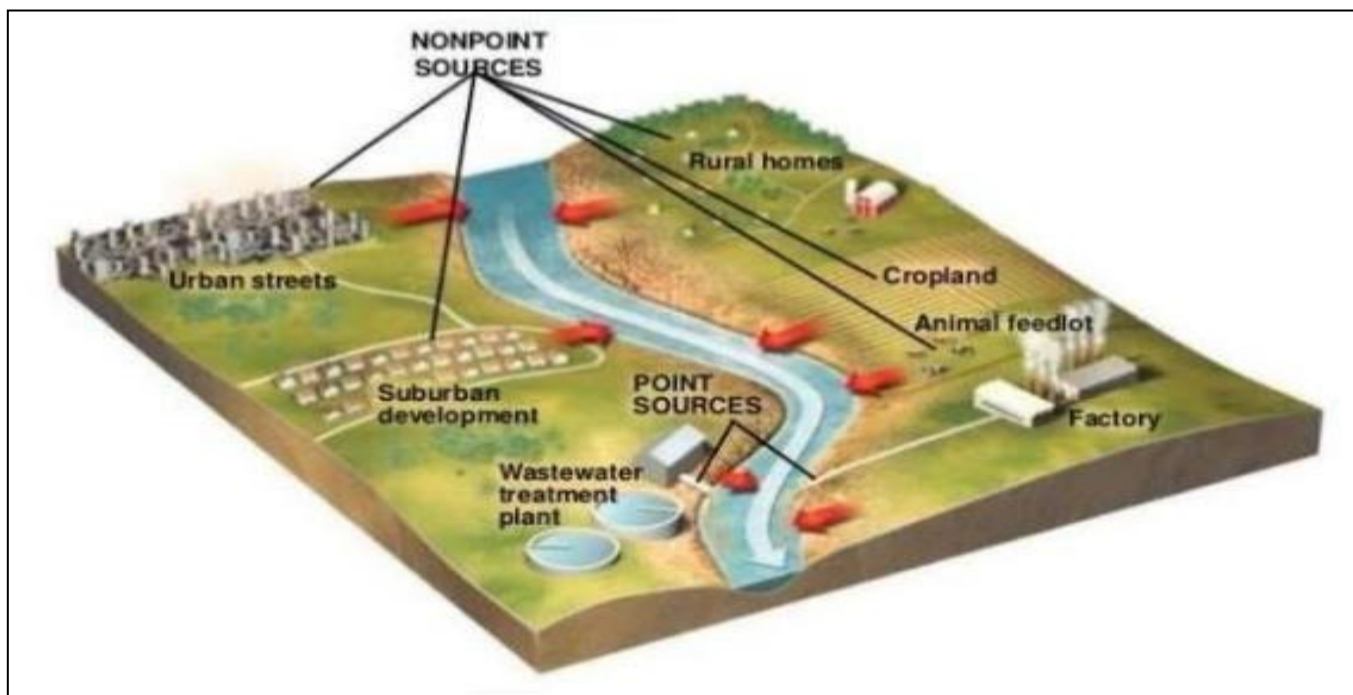
Fig 2: Sources of Water Pollution
Source (Arefin & Mallik, 2017)

In water, heavy metals are affected by the suspended sedimental constituents, the main sediment constituents, and the water chemistry. Adsorption which removes the metals from the water and desorption which does return the metals to the water system is regulated by the water chemistry (Jaishankar et al., 2014). Cadmium, copper, lead, and zinc are the most common heavy metals found in water systems, and they all pose health and surroundings risks (Jaishankar et al., 2014).

Colloidal and suspended forms of metal particles possibly contain an assortment of metal complexes, such as hydroxide, sulfide oxide, silicate, or organic matter bound to metal ions through absorption or ion exchange (Domingos et al., 2014). The form, features, and other kinetic and thermodynamics, of metal in solution (Namieśnik & Rabajczyk, 2010), can also influence its solubility. In an aqueous solution, Fe(II) dissolves quickly, but Fe(III) cannot be disintegrated. Metal ions in water are typically free metal ions or hydroxyl ions which are hydrated metal ions that succeed in their hydrated match (Domingos et al., 2014). In the presence of Cl^- and/or SO_4^{2-} ions, to a degree, either Cd or Zn forms a string of compounds (Namieśnik & Rabajczyk, 2010). Aqua-aggregates, free ions, and elementary complexes are all terms used to define dissolved species in water. When a cation and an anion or neutral molecule connect, a complex is constituted (van Leeuwen et al., 2005). Speciation and environmental conditions such as pH and temperature, influence metal solubility (Ochieng et al., 2009). The total analytical absorption of a metal in water is tallied by accumulating the concentrations of its free ion and complexes, as well as any metal accompanying suspended solids, whether natural or mineral.

The total molar absorption of lead, EPb, in water, for instance, maybe equal to:

$$EPb = mPb^{2+} + mPbOH^+ + mPbCO_3 + mPbHCO_3^+ + mPbSO_4 + mPb \text{ (suspended solids)}.$$

The concentration of free lead ions, mPb^{2+}, in most natural waters is lesser than the total of its aggregates, which in this circumstance are lead composites with hydroxyl, carbonate, bicarbonate, and sulfate ions (Namieśnik & Rabajczyk, 2010). Other metals that are chiefly found as complexes in place of free ions in natural waters are Cu^{2+} and Fe^{3+}.

B. Selected Heavy Metals and Anions Properties

➢ *Cadmium*

Cadmium occurs naturally in rocks and soils (Wang et al., 2004), as an accessory element in zinc ore (sphalerite, ZnS) (largest industrial source) and CdS, and as $CdCO_3$ (rare). It is one of the toxic metals (Tchounwou et al., 2012). It usually enters the human body through anthropogenic sources, which include industrial wastes (batteries, electroplating, pigment manufacture, video/fluorescent tubes, galvanized pipes, and roadside soils (vehicle use). Cadmium has carcinogenic properties as well as a long biological half-life (ATSDR, 2012; Orisakwe et al., 2010). leading to unceasing consequences as an upshot of buildup in the liver and renal cortex (Wang et al., 2004), bringing about kidney, liver, and pancreas functions to deteriorate or become completely ineffective (ATSDR, 2012; Sall et al., 2020). It also damages red blood cells by destroying DNA (Hanna-Attisha et al., 2015). During weathering processes, the Cd^{2+} ion is rapidly mobilized and bound to the humic material at pH 8 as Cd^{2+}, (ATSDR, 2012). when the water pH rises $[Cd(OH)]^+$ forms the complexes $Cd(OH)_2$ while $[Cd(OH)_4]_2$ will be formed in a highly basic environment. In the acidic environment these are formed: Cd^{2+}, and $CdSO_4$, while in the alkaline environment, Cd^{2+}, and $CdCl^+$ are prevalent (Hanna-Attisha et al., 2015; Kubier et al., 2019).

➢ *Copper*

Copper is an essential heavy metal for the proper functioning of organisms as well as the small-scale processing of several enzymes (ATSDR, 2020; Singh et al., 2011). Copper can be found in a variety of places, including wastewater (Shrivastava, 2009). Cu^+> Cu^{2+}> inorganic copper> organic copper, in that order Cu^+ is the most toxic form, with toxicity reducing in different forms (Cuppett et al., 2006). Copper is ingested, and a soaring level of copper in a human can cause gastrointestinal leakage, intravascular hemolysis, and acute renal failure (Sall et al., 2020). Cu^{2+} ions and the $CuCO_3(aq)$, $[Cu(HCO_3)_2]$,$[Cu(OH)_2]$, and$[Cu(OH)_4]_2$ complexes are found in waters with high absorption of hydrogen carbonates.

➢ *Lead*

Lead occurs in three varieties of inorganic, chemical, and metallic lead compounds that are widely recognized (Keil et al., 2011). Pb (0), Pb (II), and Pb (IV) have also been observed in these three oxidation states. Primary sources of lead include natural processes such as rock weathering, as well as anthropogenic sources such as unknowingly ingesting lead-contaminated water. The most common basis of lead in the human body may be water networks with lead pipes (Rabin, 2008; Zietz et al., 2008). Because of its poor solubility, the lowest lead levels are found in waters with a pH of 9.0-10.0 and an appropriate amount of hydrogen carbonates. In addition to Pb^{2+} and $[Pb(OH)]^+$, other soluble sources of lead include $[Pb_4(OH)_4]^{4+}$, $[Pb_6(OH)_8]^{4+}$and $[Pb(OH)_3]$ (Dietert et al., 2004; Jurgens et al., 2019). In dissolved form, anionic, cationic, or molecular complexes can be found in water as Pb^{2+} and $[PbCO_3]_{aq}$ based on pH as Pb^{2+} ions, and also as $[Pb(CO_3)_2]^{2-}$, $[Pb(OH)_2]_{aq}$, and $[Pb(OH)]^+$ in an alkaline environment, among others.

➢ *Manganese*

Municipal wastewater discharges of sewage sludge, fossil fuel burning, and fuel additives are the anthropogenic origins of manganese (CICAD, 2004). It is used in a variety of industries, including the manufacture of iron and steel alloys, batteries, glass, fireworks, cleaning products, fertilizers, varnish, fungicides, cosmetics, and livestock feeding supplements (CICAD, 2004). Manganese enhances neurotoxicity in humans and animals when consumed in water contaminated with metal (Institute of Medicine Panel on, 2001). The current guideline for maximum manganese levels in drinking water is 0.4 mg/L for human health (Table 1). Manganese is released into the groundwater as a result of a decrease in dissolved oxygen (Homoncik et al., 2010; WHO, 2020); and Mn (IV) is chemically reduced to the soluble form of Mn(II) under these conditions.

➢ *Zinc*

Zinc is an integral factor and plays an important function in organisms' biological processes (Frassinetti et al., 2006). The factors that can cause zinc toxicity in aquatic environments are water hardness (Ca, Mg content), alkalinity, and humic material content. Zinc is phytotoxic at concentrations over 100 ppm (Galceran et al., 2007; Institute of Medicine Panel on, 2001). While certain workers are more likely to be exposed to these substances at work, the most common route of exposure is through food and water for most people (Jaishankar et al., 2014). In drinking water, the permissible limit for zinc is 5.0 mg/L. In hypogenic conditions, Zn(II) arises when the Zn^{2+} ionic species create inorganic complexes that are basic of the type: $[Zn(OH)]^+$ $Zn(HCO_3)]^+$, $[Zn(OH)_3]^-$ (Krężel & Maret, 2016).

➢ *Iron*

Iron is an abundant cation and is easily found on the earth's crust, and if in higher amounts could stain laundry, utensils, and fixtures reddish-brown (Fitsanakis et al., 2009). It is used in building and piping water as a material and its oxides serve as pigments in the production of paints and plastics. Iron concentrations are higher in countries that use galvanized iron, brass, and cast iron in water distribution pipes, according to the WHO, and are generally found to be less than 0.3 mg/L(WHO, 2017b). The primary cause of iron toxicity is iron species bound to other compounds that are prevalent in river waters, which can be consumed through drinking water and food (Lieu et al., 2001; WHO, 2017b). In the presence of Cl, Fe(II) exists as soluble hydrogen carbonate bound to humic substances. This form is commonly known as $[FeCl]^{2+}$, and other $[FeCl_2]^+$ compounds that are readily soluble in pH 7 water (Rabajczyk et al., 2014).

➢ *Chloride*

The sources of chloride in water are natural, sewage, and agricultural waste, municipal drains full of de-icing salt, and overflowing salines (Mostafa et al., 2017). Depending on the alkalinity of the water, too much chloride concentration will increase the rate of metal degradation in the supply chain. This can contribute to higher metal supply concentrations. For chloride in drinking water, no health-based guide benefit is indicated. Chloride amounts above 250 mg/L will, on the other hand, give rise to a detectable taste in water (WHO, 2017b).

➢ *Fluoride*

Though this might seem to be a basic element of humanity, its nature has not been explored (Aoun et al., 2018). However, there is an indication that fluoride is a beneficial ingredient in the prevention of decay of teeth (Aoun et al., 2018; Horst et al., 2018). The ultimate source of fluoride is majorly the minerals of the gneissic bedrock (Aravinthasamy et al., 2020; Dharmagunawardhane et al., 2016). also fluoride-bearing minerals like apatite, fluorite, and biotite, along with hornblende (Aravinthasamy et al., 2020; Mukherjee & Singh, 2018). Weathering and transportation of these rock minerals through seepage reinforce the build-up of fluoride in groundwater. Agricultural fertilizers and bitumen flaming are anthropogenic inceptions of fluoride. Fluoride in groundwater emerges as :$[MgF_2]$ sellaite, $[CaF_2]$ fluorite or fluorspar, $[Na_3AlF_6]$ cryolite, $[3Ca^3 (PO_4)^2 Ca (F, Cl_2)]$ fluorapatite (Aravinthasamy et al., 2020).

➢ *Nitrate and nitrite*

Nitrate is a vital plant nutrient that is found naturally in the atmosphere. It is a component of the nitrogen cycle and is present in all plants at unsteady concentrations. Nitrite reduction is largely responsible for nitrate toxicity in humans. The involvement of nitrite in the oxidation of normal hemoglobin (Hb) to methemoglobin (metHb) is the most significant biological effect of nitrite in humans (ATSDR, 2013; Thamdrup & Dalsgaard, 2002), which leads to the inability to transport oxygen to the tissues. The two ions are readily soluble in water and ionically permeable. Excessive exposure to nitrate and nitrite via drinking water may cause severe illness in infants due to their interference with the oxygen-carrying potential in the blood (ATSDR, 2013). Because nitrite is in an extra steady oxidation state, it is rarely found in significant concentrations outside of reducing environments (Thamdrup & Dalsgaard, 2002). It can be made in vitro by microbial nitrate reduction and in vivo by reducing nitrate that has been consumed. At some point during the stagnation of nitrate, Nitrosomonas bacteria can produce nitrite chemically in distribution pipes (Thamdrup & Dalsgaard, 2002).

➢ *Bicarbonate*

Between the pH ranges of 4.4 and 8.2, bicarbonate is in equilibrium with carbon dioxide, and between the pH ranges of 8.2 and 9.6, it is in equilibrium with carbonate (Faiyad & Hussien, 2016). HCO_3^- ion concentration in groundwater could be derived from areas covered by igneous rocks with plagio clase feld spars and quartz, as in the Kajiado North Constituency.

➢ *Sulfates*

Sulfates are not naturally occurring but their presence in water could be as a result of contamination (WHO, 2014); (WHO, 2020). Sulfates and sulfuric acid products are used in the production of fertilizers, chemicals, dyes, glass, paper, soaps, textiles, fungicides, astringents, and emetics. They can be discharged into the waters from mines, wood pulp, metal, and plating industries, and from the sewage and, leather processing industries. Aluminum sulfate (alum) is used as a sedimentation agent in drinking water treatment. High sulfate concentrations above 200mg/L create a nasty taste in water for domestic use (USEPA, 2003; WHO, 2017b).

➢ *Carbonate*

Carbonate is the divalent anion produced by the total neutralization of carbonic acid. Within waters, it is an inactive balance with carbon dioxide gas, carbonic acid, bicarbonate anion, and solid types of unsolvable carbonate minerals mostly calcium carbonate. No drinking water standard has been established (WHO, 2017a). Bicarbonate and carbonate are known to increase alkalinity in water. Bicarbonates of calcium and magnesium putrefy in steam boilers forming scales and, liberating corrosive carbon dioxide gas (Faiyad & Hussien, 2016).

C. Heavy Metals and Anions Toxicity

Toxicity refers to the feature of a chemical to alter the continuity, progress, and duplication of a creature (Tchounwou et al., 2012). The form of transmission (diffusion, bodily contact, or swallowing), the amount of substance consumed, and the intensity of contact are a few of the factors that can affect the toxicity of heavy metals (Tchounwou et al., 2012). Due to their non-degradability and long-term persistence in the environment, heavy metals are difficult to deal with (Guangming et al., 2017). One of the main ways that heavy metals become toxic is through biochemical processes, such as their ability to suppress or imitate the effects of other necessary metals on how they interact with body proteins. For instance, high lead suppresses calcium in the human skeleton binding with the biological molecules in the process interfering with their function. They cause toxicity in the human body by forming complexes with proteins that contain carboxylic acid (–COOH), amine (–NH₂), and thiol (–SH) groups. Heavy metals furthermore become toxic when they compete with essential metallic cations for binding sites thus binding to protein sites not intended for them. Therefore, heavy metals remove natural metals from their natural binding sites, resulting in cells failure and eventually have toxicity, protein structure, and catalytic properties are both hampered in the process. Heavy metal binding to DNA and nuclear proteins causes oxidative deterioration of biological macromolecules, according to previous research (Mittal & Mehta,

2008). The process alters biological molecules, causing them to lose their ability to function as they should, resulting in cell malfunction or death. The toxin also produces harmful radicals, which cause biological molecules to oxidize. Different oxidation states of trace metals produce varying degrees of toxicity (Jaishankar et al., 2014). Copper can cycle between two oxidation states, it is potentially toxic given that superoxide, as well as hydroxyl radicals, can be produced. Cadmium along with zinc have similar oxidation states, and for this reason cadmium is capable of substituting zinc there in metallothionein, in so doing restraining it from standing in as a free radical hunter within the cell and altering its transport. Heavy metals bound to anions (SO_4^{2-}, F^-, Cl^-, CO_3^{2-}, and NO_3^-) exist as chemical species during chemical speciation processes, and when combined, they are less portable and toxic than free metal ions (Cu^{2+}, Fe^{3+}, and Mn^{2+}), which are equally toxic because they participate in the formation of toxic compounds with other ions. (Lenntech 2004). Reactive oxygen species (ROS) are produced as a result of lead toxicity, resulting in oxidative stress (Valko et al., 2005). The development of various diseases and abnormal conditions is linked to oxidative stress in organisms.

➤ *Effects of Toxic Heavy Metals and Anions on Human Health*

When toxic metals are present at greater concentrations, they are much more dangerous because higher levels can pose a threat to the organism (Galceran et al., 2007). Toxic metals like Cd and Pb have no known vital or beneficial effects on organisms, and their accumulation in the bodies of animals over time can result in serious illnesses (Jaishankar et al., 2014); (WHO, 2020). Pb poisoning can result in cancer, abdominal pain, and skin lesions, among other health problems (WHO, 2020). Pb exposure is linked to a lower IQ in children (Institute of Medicine Panel on, 2001) Pb is also said to be dangerous at low concentrations of less than 0.01 mg/L according to the world health organization. Heavy metals such as Cd and Pb deplete the major antioxidants of cells, particularly antioxidants and enzymes having the thiol group (-SH). Such metals may increase the generation of reactive oxygen species (ROS) like hydroxyl radical (HO˙), superoxide radical ($O_2^˙$), and hydrogen peroxide (H_2O_2) (Valko et al., 2005). Increased generation of ROS can devastate the inherent antioxidant defenses of cells and lead to a condition called "oxidative stress" (Valko et al., 2006). Heavy metals are nephrotoxic, especially in the renal cortex (Oord, 2017). Relatively higher concentrations of toxic heavy metals, Cd and Pb, have been established in patients with cancer and diabetes weighed to those normal persons in Lahore city, Pakistan (Salman et al., 2011). Some metals are essential and their deficiency in the human body could be detrimental e.g Cu deficiency is linked to food poisoning symptoms like headache, nausea, vomiting, and diarrhea, and in malnourished children, long-term intake of below-required levels can cause neutropenia, anemia, and bone demineralization (Institute of Medicine Panel on, 2001). Cu is also toxic when a species consumes high doses and is unable to control its unwarranted absorptions, which can result in acute renal failure, intravascular hemolysis, and oliguria (Gupta et al., 2018). The chemical form of the heavy metals is important in toxicity, for example, Copper toxicity largely depends on Copper speciation (Cuppett et al., 2006; Obiefuna & Orazulike, 2010). After Cu^+, Cu^{2+} is the copper ion with the highest toxicity, Copper hydroxyl complexes are toxic as well, albeit in smaller amounts (Namieśnik & Rabajczyk, 2010). Manganese pneumonitis (fever, cough, and malaise), liver damage, neurotoxicity, chronic respiratory tract inflammation, stillbirth, and birth defects (such as cleft lip, heart defects, imperforate anus, and deafness) are all health implications from high Mn concentrations (Etzel, 2003; WHO, 2017b). In excess of Fe, the body is disrupted, because the metals Cu, Zn, and Mn are exchanged, leading to enzyme dysfunction, swelling, and joint infection that may last for a very long time (Fitsanakis et al., 2009; Lieu et al., 2001). Diabetes, cancer, and nervous system diseases are just a few of the illnesses linked to Fe toxicity here (Lynch et al., 2018).

When F^- levels that exceed the WHO recommended limit are consumed, it causes fluorosis and teeth pitting (DenBesten & Li, 2011; KEBS, 2010). SO_4^{2-} consumption that exceeds the WHO limit causes diarrhea, risking diarrhea in infants, and male adults exposed to high concentrations may experience cathartic effects (USEPA, 2003; WHO, 2014). High concentrations of NO_3^- may cause methemoglobinemia (Fewtrell, 2004). Although individual metals show different signs of toxicity, the following symptoms have been linked to Cd, Pb, Fe, Zn, and Cu poisoning: when inhaled, vapour and fumes can cause gastrointestinal (GI) disorders, such as diarrhea, stomatitis, tremor, hemoglobinuria (a rust-red color in the stool), ataxia, paralysis, vomiting, and convulsions, as well as depression and pneumonia (Duruibe et al., 2007).

➤ *Safe Limits of Selected Metals, Selected Anions, pH and Conductivity*

Safe limits of selected metals and anions, and given environmental settings like pH and Electrical conductivity as endorsed by the World health organization are presented below.

Table 1: Recommended Maximum Limit of pH, Electrical Conductivity and Concentrations of
Various Metals ions and Anions (WHO, 2017)

Parameters	Chemical Symbol/formula	Limits in mg /L
Lead	Pb	0.015
Cadmium	Cd	10
Manganese	Mn	50
Iron	Fe	0.3
Zinc	Zn	3
Copper	Cu	1.5
Magnesium	Mg	150
Sulphate	SO_4^{2-}	400

Nitrate	NO_3^-	10
Nitrite	NO_2^-	3
Fluorine	F^-	1.5
Chlorine	Cl^-	250
Carbonate	CO_3^{2-}	Nil
Hydrogen carbonate	HCO_3^-	380
pH	pH scale	6.5-8.5
Conductivity (25ºC)	µs/cm	2500

D. Chemical Speciation

To comprehend chemical toxicity, bioavailability, and environmental destiny and transport, the full speciation of a chemical are necessary for envisioning its performance in a structure (Namieśnik & Rabajczyk, 2010). Chemical "speciation" is the evaluation of the individual concentrations of various chemical forms of an element that, when combined, constitute the total absorption of that component in a given form. It is essential to determine the individual chemical species, principally when these species have different effects and actions. By transforming the forms in which these components arise, changes in environmental conditions, either natural or anthropogenic, can have an exceedingly critical influence on their conduct. The pH, temperature, and the availability of anions that bring about complex creation as well as particle surfaces for adsorption and colloidal matter are a few of the more outstanding controlling determinants. Among these are the usual pH, temperature, and appearance of anions, which influence the oxidation state of a few metals and may likewise influence their bioavailability and toxicity. Metals comparatively Fe(II) and Mn(II), for instance, are solvable in reduced-oxygen natural waters but precipitate at higher oxidation states, free ionic forms of metals like Cu, and, Cd, are customarily great poisons to human beings. In alternative cases, temperature, and changes in pH may shift the evenness. The goal of speciation research is still important to maintain facts about the bioavailability and toxicity of the elements, which depend on the chemical combination, concentration, type of element, and also on the species in a given system (Namieśnik & Rabajczyk, 2010; Obiefuna & Orazulike, 2010).

E. Methods used in Chemical Speciation Studies

Typically, analytical chemistry methods alone are inadequate to establish a speciation analysis. A plurality of approaches is conceived to identify concentrations of free metal ions (Zeng et al., 2003) or metal concentrations in total (Wang et al., 2004). Traditional scientific methods that measure direct speciation call for loads of work and are oftentimes hyphenated (Moldovan M., 2004). The first concept of speciation was projected by (Florence & Batley, 1977). By passing samples through a 0.45m filter, the method divided dissolved and particulate metals. Anodic stripping voltammetry (ASV) was used to calculate the disintegrated portion, that detached the ASV-labile and non-ASV-labile fractions. UV emission was used to illuminate the samples before they were passed through chelating resins. Since then, a variety of speciation designs have been developed (Bjornsdottir, 1996). Chemical modeling, which uses popular thermodynamic connections among chemical forms to envision the overall evenness dispersion, and direct measurement of diverse forms of the target material in the laboratory are both used to establish speciation study. Chemical evaluation can only establish certain forms and modeling is used to foresee the additional forms having to do with the measured forms, a consolidation is used in several cases. Inductively Coupled Plasma Mass Spectroscopy (ICP-MS), Atomic Absorption Spectroscopy (AAS), Neutron Activation Analysis, and X-ray spectroscopy, amid additional means, are conceivably used to determine the absorption of metal ions in the laboratory. Fluorescence methods can be used to discover the number of free metal ions present (Zeng et al., 2003), additionally, microelectrode-based electroanalytical approaches have been used in combination with classical analytical techniques, such as anodic stripping voltammetry (ASV) to determine the concentration of a wide range of analytes, especially metal ions (Galceran et al., 2007). The most more often than not used chromatographic methods for separation are ion chromatography (IC), liquid chromatography (LC), and gas chromatography (GC), in addition to capillary electrophoresis (CE), which are consistently used in conjunction with atomic emission spectrometry (AES), atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectroscopy (ICP-AES), or (ICP-MS). To establish the absorption of each species present in a given constituent, chemical speciation modeling relies on thermodynamics and mass balance. Mass balances are purported to be equal to the analytically determined concentration of each factor in the model, and mass performance equations are explicit by balance constants. Thus the mass balance is outlined as;

$$M_j = \sum_{j=1}^{Nc} A_{ij} \frac{\chi_i}{\gamma_i} \gamma i \qquad 2.2$$

Where A_{ij} is the stoichiometric coefficient that gives the mole number of component j in class i; M_j is the total size of component j; γ_i is the activity interdependent of class i; χ_i is the action of the liquid species i and Nc is the number of units. The size operation comparison is outlined as;

$$Xi = \beta i \prod_{Cj}^{Nc} Aij \qquad 2.3$$

Where: βi shows the total balance creation constant for species i (**Vanbriesen**, **2010**)

Aij is the stoichiometric coefficient of the master class, j, is the corporation half-response for exchange class i,
Xi is an equilibrium constant especially reliant on temperature, and j ranges over all master class.

There are various geochemical models developed for metal speciation studies, for instance, EQ3NR, WATEQ4F, PHREEQC, Visual MINTEQ, MINTEQA, MINEQL+, and JESS among others. These models are outfitted with a standard thermodynamic collection of data (Appelo, 2013). PHREEQC program has established its convention in various statuses that involves chemical adaptive evolution and surface water. For example, (Elena & Constantin, 2010), used the PHREEQC program to complete activity an investigation of the chemical speciation of heavy metals in surface waters contaminated by anthropogenic activities. The determination of the distribution of the analyzed parameter was established in that study. PHREEQC adaptive evolution model was used to perform some metal ions' speciation in Yola's groundwater. The results founded on model calculations designated the presence of dominant anions in water (Obiefuna & Orazulike, 2010). Heavy metal adaptive evolution in Qaraauon reservoir water was performed by (Korfali & Jurdi, 2011). The ICP-MS technique was used to determine the total absorption of metals, and the AQUACHEM computer program blend alongside PHREEQC geochemical computer model was used to carry out adaptive evolution evaluation. Speciation was likewise done in South Africa in a study of metal contaminants appearing in several water structures (Magu et al., 2016). ICP-OES analytical approach was used to resolve the total aggregation of the metals, and AQUACHEM software geochemical modeling program PHREEQC application, the results revealed uprisen levels of metal species in the water systems. In Kenya nevertheless, there isn't much information on metal adaptive evolution, metal toxicity, and application of the above methods. PHREEQC was used in this study as a result of its expansive range of modeling proficiencies, along with the ability to use multiplex databases and mix new data into existent databases.

F. Methods in the Determination of Metals and Anions in Water

➢ *Inductively Coupled Plasma-Optical Emission Spectrometry*
This approach has existed and been enforced in both routine research and more itemized investigations since 1974. It's a means that uses inductively coupled plasma and a spectrometer to establish the basic distributions of largely water-dispersed samples. ICP's main advantage over other excitation methods is its ability to vaporize, atomize, excite, and ionize a wide range of elements in different sample matrices with high reproducibility. The excitation temperature of air-acetylene flame gauges between 2000K and 3000K in atomic absorption spectrophotometers, while the excitation temperature of argon in ICP-OES is weighted 5000K to 7000K, hence it competently excites a lot more elements. Its working principles are as briefly described: A peristaltic pump pushes the sample solution into a spray chamber through a nebulizer bringing about a fine mist that is guided to a plasma, and the encounter atomizes the analytes in the sample. In the torch, excitation takes place and releases energy as photons, as the molecule drops to the ground state light is discharged and enters ICP-OES. The ICP-OES is composed of gratings and prisms that separate the diverse wavelengths of light so that the wavelengths are distinct when they reach the detector (Figure 3)
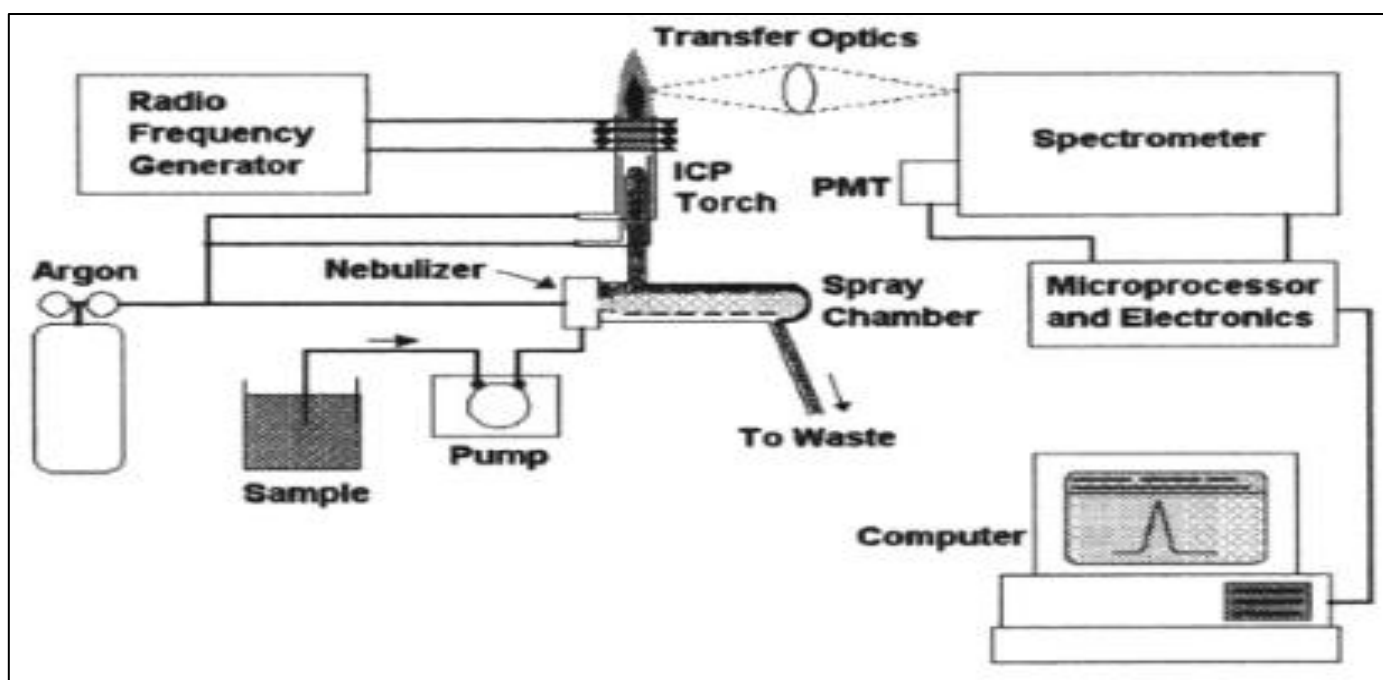
Fig 3: Schematic of a Typical Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) System
(Sneddon & Vincent, 2008)

➢ *Multiparameter Bench Photometer*

It is a photometer that uses the Beer-Lamberts law that states that the samples absorption is linearly proportional to the samples line distance for a likely material is equivalent to the absorbance of the light. Expressed as: Lambert-Beer Law;

$$A = \varepsilon\lambda \, Lc$$

Where: A is the amount of light absorbed for a well-known wavelength by the sample,

$\varepsilon\lambda$ is the molar extinction coefficient at the wavelength,

c is the molar concentration of the substance and,

Lis the distance covered by the light through the solution.

The optical order of the Multiparameter photometer (Hanna, HI 83099, USA). is restricted to definite subminiature tungsten lamps and narrow-band impedance filters to guarantee jointly extreme execution and reliable outcomes. With a light source of tungsten narrow band interference filters, silicon photocell as light detection and microprocessor-controlled special tungsten lamp emits radiation that is optically constrained before being beamed through the sample in the cuvette. (Figure 4)
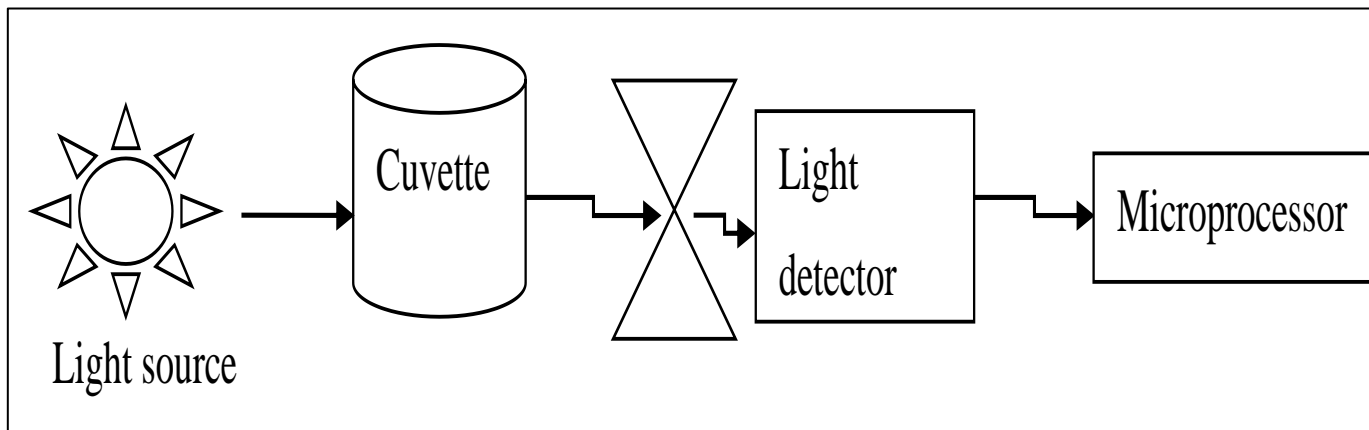
Fig 4: The Optical Layout of Multiparameter Photometer

➢ *Multiparameter Bench Photometer*

CHAPTER THREE
MATERIALS AND METHODS

A. Description of the Study Area

The research was executed in Kajiado North constituency, in Kajiado County. Kajiado County is bordered to the North by Nairobi County, Southwest by the Republic of Tanzania, Southeast by Taita-Taveta County Eastern side by Machakos and Makueni Counties, Northern by Kiambu County, and to the West by Narok County. It is placed middle of two points longitudes 36° 5" and 37° 5" E, and 1° 0" and 3° 0" S. It has a populace of 687,312 and covers a territory of around 21,909.9 square kilometers (KNBS, 2000). Ongata Rongai, Ngong, Nkaimurunya, Olkeri, and Oloolua are the five wards that make up Kajiado North constituency, from the most densely populated to the least densely populated.

➤ *Climate, Geology and Soils*

The average annual temperature in Kajiado North Constituency is 18.3°C, with annual rainfall ranging from 300 to 800 millimeters. "Short rains" are experienced from September to December, and "long rains" from March to May. From East to West across Kajiado County, the rainfall distribution between the two seasons has steadily changed. The Kajiado North Constituency is located in Kenya's semi-arid region, which has experienced prolonged droughts with little or no rainfall in recent years (Oord, 2017). Due to a scarcity of permanent surface water supplies, many small dams have been built and numerous boreholes have been drilled (Geology of Kajiado Region, 2014). According to the geophysics report, there are shallow aquifers between 20 and 40 meters below ground level, as well as deeper aquifers between 100 and 150 meters (Geology of Kajiado Region, 2014). Volcanic deposits of basalts, trachytes, phonoliths, and tuffs, all overlain by dense layers of clay soil, make up the geological makeup of this region. It has a low soil structure because it is mostly black cotton and rocky (Oord, 2017). This explains why, after heavy rains, the open earth drains and the surrounding area floods for a few hours.

B. Site Selection and Sampling

The sample site selection criterion was randomized based on the selected water resource system and its proximity to sources of pollution. Field trips to the study area were conducted for planning purposes, which include identification and acquisition of topographic maps, acquaintance with authorities, determination of the necessary equipment and general investigation, as well as determination of the actual resources needed, the time required, data collection techniques and all the facts risks associated with conducting this study.

➤ *Sampling at the Sites*

The water samples were taken in November 2019, for the duration of the rainy season, and February 2020, for the period of the dry season. Samples were randomly drawn from 25 selected water resource systems on basis of nearness to pollution sources throughout Kajiado North Constituency in both the dry and the wet seasons for the analysis of seven selected metals and anions. At each sampling point, duplicate samples were taken for metal and anion analysis on separate containers. During the study's duration, a total of 100 samples (50 samples during the wet season and 50 samples during the dry season) were taken from the sampling sites. These included 76 samples from 19 boreholes, 8 samples from 2 dams, and 16 samples from 4 surface water systems across Kajiado North Constituency. A plot locator Application from an android phone was used to obtain sampling site coordinates from Google maps at the sampling sites (Table 3.1). Water sampling was done according to the APA method (APHA, 2005) Grab samples were collected in 1L plastic containers that had been thoroughly cleaned by using 10% (v/v) nitric acid, followed by a number of rinses with deionized water, and then a final rinse with sample water before collection. The pH, temperature, and electrical conductivity parameters (EC) were recorded *in situ* immediately after sampling using calibrated standard instruments (Hanna, HI 9813-6, USA). The samples, taken in duplicate at each sampling point, were labeled for each corresponding anion or metal analysis, sampling site and the collection date indicated. The notable environmental features within each sampling site were also recorded (Table 3.1). All the metal samples were treated with a few drops of concentrated nitric acid to pH < 2 to dissolve the metal and inhibit microbial growth. Afterward, the samples were packed in a cooler box and taken to the laboratory.

Table 2: Locations of the Study Areas, the Samples Represented, the Coordinates, and the Physical Description of the Site

Sampling Site	Type of sample	Coordinates	Physical description of the site location
QWK001	Surface water	1°23′02.3″S 36°43′13.4″E	Silt, household effluents, and open sewers
QWK002	Surface water	1°23′10.1″S 36°41′56.3″E	Silt
QWG003	Surface water	1°23′28.1″S 36°46′51.1″E	Silt, an open sewer, a residential neighborhood, and a car wash
QWN004	Surface water	1°23′38.6″S 36°46′30.1″E	Silt
QWS005	Dam water	1°26′13.9″S 36°41′45.6″E	Silt and river water, the reservoir
QWS006	Dam water	1°26′13.9″S 36°41′56.7″E	Silt, the reservoir
QWK007	Borehole water	1°29′40.4″S 36°37′28.4″E	Market waste and car wash waste
QWG008	Borehole water	1°23′47.7″S 36°44′29.6″E	Residential area
QWG009	Borehole water	1°23′34.8″S 6°46′28.6″E	Residential area
QWG010	Borehole water	1°23′45.8″S 36°44′59.5″E	Market

Sampling Site	Type of sample	Coordinates	Physical description of the site location
QWG011	Borehole water	1º23′49.8"S 36º45′06.1"E	In a residential area, there is an open sewer.
QWG12	Borehole water	1º23′46.6"S 36º43′29.1"E	Open sewer
QWA013	Borehole water	1º23′30.5"S 36º44′21.8"E	Busy county Market, open sewer, Market landfill, carwash
QWG014	Borehole water	1º23′45.2"S 36º44′59.5"E	Residential area
QWG015	Borehole water	1º23′46.7"S 36º44′50.0"E	Car wash and garage
QWA016	Borehole water	1º23′17.4"S 36º44′35.9"E	Busy Car wash, open drainage
QWL017	Borehole water	1º21′42.2"S 36º39′11.6"E	Busy business center, carpet, and car wash
QWL018	Borehole water	1º20′19.5"S 36º40′42.2"E	Residential area
QWL019	Borehole water	1º20′11.3"S 36º40′48.6"E	Populated public school
QWL020	Borehole water	1º20′17.8"S 36º40′49.4"E	Residential and business center
QWO021	Borehole water	1º21′37.4"S 36º39′22.8"E	Busy public residential area
QWO022	Borehole water	1º23′34.2"S 36º41′00.3"E	Populated public institution
QWO023	Borehole water	1º21′43.8"S 36º38′53.4"E	Busy Bus station
QWO024	Borehole water	1º22′09.6"S 36º39′27.6"E	Church, Residential area
QWO025	Borehole water	1º21′29.1"S 36º39′25.0"E	Busy Shopping mall, Residential area

C. Materials

Analytical grade chemicals and reagents used were purchased from Sigma Aldrich through Kobian Company (Nairobi, Kenya); Concentrated HNO_3 acid, sodium nitrite, sulfanilamide, 1-naphthylethylenediamine, hydrazine sulphate, sodium hydroxide, sulfate indicator reagent, 1,8-Dihydroxy-2-(4-sulfophenylazo)naphthalene-3,6-disulfonic acid trisodium salt, SPADNS fluoride reagent solution, potassium chromate, silver nitrate, sodium chloride (98 % purity). HDPE bottles (with caps) were obtained from Safe Pack (Nairobi, Kenya), Multielement CertiPUR® Reference Material for Inductively Coupled Plasma (ICP) elemental analysis and ICP Magnesium Reference Standard (1.004 ± 5 mg/L) were acquired from Merck (Darmstadt, Germany). The metal elements contained in the certified multi-element reference material were as follows: $999 ± 5$ mg L^{-1} Cd, $1.000 ± 2$ mg L^{-1} Cu, $1.000 ± $ mg L^{-1} Fe, $1.002 ± $ mg L^{-1} Mn, $998 ± $ mg L^{-1} Pb, and $998 ± 5$ mg L^{-1} Zn.

The study utilized the following instruments; Ohaus top pan Weighing balance, Hot plate, Alcohol thermometer 100^0C, PTFE 10mm magnetic stirrer, pH and conductivity meters, Multiparameter photometer (Hanna, HI 83099, USA), and ICP-OES (700 series, Agilent Technologies Victoria Australia).

D. Sample Treatment and Analysis

In the laboratory, the well-labeled samples marked for analysis of anions (F^-, Cl^-, SO_4^{2-}, HCO_3^-, CO_3^{2-}, NO_2^- and NO_3^-) and the selected metals: cadmium, copper, iron, manganese, lead, Magnesium, and Zinc, were homogenized and filtered through 0.45 mm pore cellulose filters using vacuum suction pump into one-liter polyethylene bottles. Whereas 40 mg $HgCl_2$ L^{-1} was added to samples marked for anion analysis and stored at 4°C, those for trace metal analysis were acidified using nitric acid. 10 mL of concentrated nitric acid was added to 50 ml of the sampled water in a 250 ml conical flask, the mixture was evaporated to half its volume on a hot plate after which it was allowed to cool and finally diluted with double-deionized water in 50ml volumetric flask then stored at 4°C. for the ICP-OES analysis.

➢ *Analysis of Total Metal Concentrations*

The concentrations of the seven metals (Magnesium, Zinc, Copper, Iron, Lead, Iron, and Manganese) were determined using inductively coupled plasma optical emission spectrometry (ICP-OES 700 series, Agilent Technologies Victoria, Australia), system alongside the Expert 11 operating system.

The following ICP-OES instrument frameworks were used: cool flow CFT-7517.2°C refrigerated circulator, transfer optics, input module, UV/vis detector, argon gas, plasma gas flow of 15L/min, auxiliary gas flow of 0.2L/min, and nebulizer gas flow of 0.8L/min, power watts, peristaltic pump flow rate of 1.5mL/min, plasma axial view and equilibration delay of 15 seconds. Each sample scan was performed in triplicate.

The instrument was optimized according to manufacturer recommendations and calibrated using certified stock solutions. Dilution of stock solution (1 mg/mL in 2 percent HNO_3^-) with MilliQ water was used to make working standard solutions for each element. The mean value was calculated after each element's measurement was done (in triplicate) at its most sensitive spectral line, assuming that the line was free of interference from other elements in the sample. The limit of detection (LOD) and the limit of quantification (LOQ) were evaluated (Table 3.2) using a linear regression method based on the standard deviation and slope as presented in equations 3.1 and 3.2, respectively. Where s is the standard deviation of the response and y is the slope of the calibration curve (ALENA, 2014)

LOD = 3.3 (sy/s)　　　　　　3.3
LOQ = 10 (sy/s)　　　　　　3.4

Table 3: LOD, LOQ, and Equipment Parameters in the Analysis of Metals and Anions

Analyte	Wavelength (λ nm)	LOD (mgL^{-1})	LOQ (mgL^{-1})
Cadmium	214.438	0.0130	0.9140
Copper	324.754	0.2232	0.6764
Iron	259.940	0.1864	0.6017
Lead	220.353	0.0429	16.094
Magnesium	279.553	5.6877	18.949
Manganese	257.610	0.0138	0.9160
Zinc	213.856	0.0408	0.1236
Sulphate	466.000	0.1236	0.3756
Nitrate	525.000	0.0250	0.7576
Fluoride	575.000	0.0963	0.2918
Nitrite	525.000	0.0450	0.1365

➢ *Determination of Anions*

The concentration of Nitrite, Nitrate, sulfate, and Fluoride were determined by utilizing a multiparameter photometer (Hanna, HI 83099, USA) following the instructions from the manufacturer. For Nitrite evaluation, the Diazotization method was used at a wavelength of 525 nm where the reaction between nitrite and the reagent causes a pink tint. For Nitrate determination, the cadmium reduction method at a wavelength of 525nm was used, while, for sulfate determination, the sulfate method at a wavelength of 466 nm was used. The sulfate ions in the sample respond to barium in the sulfate reagent to form insoluble barium sulfate; emanating turbidity developed is directly equivalent to the sulfate aggregation (Hach, 2013). Fluoride was determined by the SPADNS method at a wavelength of 575nm. Fluoride combines with part of the Zirconium in the SPADNS reagent to form a colorless complex that bleaches the red color in a few that is equivalent to the fluoride concentration (Hach, 2013). For chloride determination, the EPA Method 9253 (titrimetric, silver nitrate) (EPA, 1994; Hach, 2013) was used. Carbonate in the samples was determined by direct titration with sulphuric acid using phenolphthalein as an indicator and endpoint marked by the disappearance of the pink colour, and bicarbonate was determined by back titration using methyl orange indicator until the straw yellow colour changes to rose red using Method 8221 (Hach, 2013). Certified reference reagents were used for the preparation of calibration standards for calibration curve plots, which was done following the process described by (Hach, 2013) as particularized in the sections below.

• *Determination of Sulphate*

Solutions of 10, 20,30,40,50, 60, and 70 mg/L SO_4^{2-} were prepared by appropriate dilution of 1000 mg/L sulfate standard solution. These solutions, in addition to sulfaVer 4 Sulfate Reagent were used for calibration using the filled cuvettes with 10 mL of unreacted sample (until the mark). The sulfate ions in the sample react with Barium in the sulfaver reagent to form insoluble barium sulfate, the amount of turbidity formed is proportionate to the sulfate aggregation (Hach, 2013).

Interferences that may be a result of calcium (as $CaCO_3$) above 20000 mg/L, chloride (as Cl-) above 40000 mg/L, magnesium (as $MgCO_3$) above 10000 mg/L, silica (as SiO_2) above 500 mg/L. Neither of these factors was present, since the concentrations were much lower than the concentrations that could interfere with the precipitation of barium sulfate, and the samples were already filtered.

• *Determination of Nitrite*

The Diazotization method was used in the determination of nitrite. Solutions of 1, 2, and 3 mgL$^-$ together with NitriVer 3 Nitrite Reagent were used to calibrate the photometer. 10.0 mL of the sample was put into a round sample cell followed by contents in one NitriVer 3 Nitrite Reagent powder pillow. The spectrophotometer was allowed to run for 20 minutes at a wavelength of 525nm. A pink color developed if nitrite was present. Another sample cell was filled with 10.0 ml of the sample (this was the blank), and it was used to zero the spectrophotometer. The prepared water sample was then placed into the cell holder, and the results were read in mgL^{-1} NO_2-N (Hach, 2013).

Interference that may be caused by high levels of nitrate (above 100 mgL^{-1}) could yield falsely high readings due to a minute amount of reduction to nitrite that could occur at these levels but the nitrate levels were considerably lower than above interference levels in all the samples.

• *Determination of Nitrate*

The concentration of nitrates (NO_3^-) was established at a wavelength of 525nm. Standard concentrations of 2 mgL^{-1} and 20 mgL^{-1} were transferred into separate beakers and nitrate buffer ((NH_4)$_2SO_4$) 1 ml was added to each. A volume of 50 ml of sample was added into a beaker, likewise to 1.0 ml of nitrate buffer. Nitrate readings of the sample were read at a maximum wavelength 525 nm and recorded.

- *Determination of Fluoride*

SPADNS method was employed in the determination of fluoride at a wavelength of 575nm. The reaction between fluoride and the liquid reagent brings about a red tint in the sample; Fluoride mixes with a component of the Zirconium in the SPADNS reagent resulting in a colorless complex that bleaches the red color in the quantity that is in proportion to the fluoride concentration (Hach, 2013). The photometer was calibrated using 0.5, 1.0, 1.5, and 2.0 mgL^{-1} of fluoride standard solution, alongside the SPADNS reagent. 10.0 mL of the water sample was pipetted into a dry round sample cell and 10.0 mL of distilled water was pipetted into a second dry sample cell (this was the blank). 2.0 mL of SPADNS reagent was pipetted into sample cells containing the sample and the blank. The spectrophotometer was set to run for 1 minute at a wavelength of 570nm. The blank was used to zero the spectrophotometer. The prepared water sample was put into the cell holder, and the concentrations of fluorides were determined in mgL^{-1} (Hach, 2013).

Interferences could be caused by alkalinity (as $CaCO_3$) above 5000 Iron, ferric above 10 mgL^{-1}, and chloride above 700 mgL^{-1} but these were way below the interference concentrations.

- *Determination of Chloride*

The reagents for the investigation of chloride levels were prepared as outlined below:

✓ ***Potassium chromate solution****: 50 g of neutral potassium chromate was dissolved in 50.0 mL of distilled water; silver nitrate was then added to the solution to produce a slight red precipitate and was left to stand for one night after which, it was filtered, and the resulting filtrate diluted to one-liter volume with distilled water.
✓ ***Silver nitrate solution****: 2.4 g of silver nitrate ($AgNO_3$) was dried at 105°C and dissolved in one liter of distilled water.
✓ ***Sodium chloride solution****: 16.48 g of NaCl was dried at 105°C and dissolved in one liter of distilled water, this was the stock solution.

The working solution was prepared by diluting 100 mL of stock solution to one liter with distilled water. Distilled water was used to prepare the blank solution and 50ml of the sample was measured into a beaker and 1 ml Potassium chromate (K_2CrO_4) indicator was added. This was titrated against 0.0141N Silver Nitrate ($AgNO_3$) until the color changed to pink-yellow. The amount of titrant used was recorded. More concentrated samples as indicated by the conductivity were diluted using distilled water. The calculation is as shown below;

✓ $$\mathbf{Cl}(\boldsymbol{ppm}) = \frac{\{(\boldsymbol{A-B})\mathbf{x}\boldsymbol{N}\mathbf{x35450}\}}{\mathbf{Vol.}} \qquad\qquad 3.5$$
✓ Or
✓ $\mathbf{Cl}(\mathbf{ppm}) = (\mathbf{A} - \mathbf{B})\mathbf{x\ 10}$ (**Standard formula when 50 ml of sample is used**).. 3. 6

Where: A - Volume of titre used, and

✓ B- Volume of titer for blank
✓ N- Normality of Silver nitrate.

E. Speciation Analysis

A geochemical model was necessary to predict metal speciation in water structures as a function of climatic changes, ionic intensity, and dispersion. The PHREEQ C computational chemistry tool was used to perform chemical modeling and simulations of concentration limits also including metal speciation, in addition to the consequence of preferred contaminants in water under real-time environmental circumstances like pH and temperature.

➢ *PHREEQC*

This is an acronym for pH Redox Equilibria in C. It's a Computer based- program that can perform a variety of weakened-climate aqueous geochemical estimations. The PHREEQC model, which is largely an ion-association liquid model, handles speciation analysis, as well. This study used PHREEQC adaptation 3.2.0-9820 (Parkhurst, 2013). To simulate an expansive range of chemical reactions and processes in a water system by utilizing laboratory data. It is enabled by an input file where the key factor is precise in KEYWORDS and allied data as temperature, pH, and concentrations of Pb, Mn, Cu, Fe, Zn, Cd, NO_3^-, NO_2^-, HCO_3^-, CO_3^{2-}, Cl^-, F^- and SO_4^{2-} were added to accomplish speciation analysis.

F. Chemical Modelling

Based on the total concentrations of the elements obtained from the laboratory analysis, the speciation distributions were determined in agreement with the aggregation and abundance of each chemical species. The speciation was executed to comprehend in what way or manner a given pH and given climatic conditions such as temperature could alter the concentrations of the distinct metal variety. The pH, Temperature, and total concentration for each metal (in mg/L^{-1}) and anion (in mg/L^{-1}) were used as input data for the modeling.

➤ *Modeling the Effect of Varying Anions, pH, and Temperature*

Information gathered from water samples that were tested at various pH levels and the temperature was used to establish the speciation of heavy metals on account of a contest between contradictory metal aggregates, metal chelates, and free metal ions. Using pH values of between 4 and 10, the total amount of heavy metals in sampled water was determined. The temperature of (15 °C and 35 °C), and the inclusion of anions (chlorides, nitrates, nitrites, hydrogen carbonates, carbonates, and sulfates) were used to determine the consequence of each limit, while the other considerations remained fixed.

G. Data Presentation and Analysis

The mean and standard deviations for the examined parameters in the diversified water systems were computed utilizing the triplicate results. The findings of the study were presented in form of tables, curves, and graphs. Analyses were performed using Origin 8.5 (Northampton, USA) and Microsoft Excel 2016 (Microsoft Corporation, New York), to establish correlations throughout the studied seasons, this was done employing Spearman's correlation analysis. Statistical measures like kurtosis and correlation coefficient were used to test theories at a significance level of $\rho = 0$.

CHAPTER FOUR
RESULTS AND DISCUSSION

A. *The Various parameters used to identify and quantify toxicants in water, were pH, temperature electrical conductivity, metal ions, and anions. The results of the analysis are outlined and presented in Tables (4, 5 and 6). The parameters were viewed against the limits of the standards as prescribed by the World Health Organization(WHO) which is given in Table 2.14.1.1($\mu S/cm$), Physical parameters results and dicussions*

During the wet and dry seasons, the pH of the samples of water was above seven, indicating that the water was slightly alkaline (Table 4). From table 4 the EC varied had the lowest recording at (QWK002, surface water), and the highest at (QWG009, borehole water). Changes in the conductivity of sampling sites may be indicative of disturbances or a discharge that is responsible for a decrease in the relative condition of the water source. This could stem from the surface runoffs in the cases of surface water of ionic conducting minerals into the river. The pH and EC of all sampled water were within the recommended limits (WHO, 2017a) (Table 4). except for the pH of one sampled borehole, QWG012, which was recorded as the highest during the wet season (Table 4). The high pH could be due to open sewage effluents that may have included soaps, kitchen drains, and other household bleach used near the sampling point. The was slightly high in the wet season in all sampling sites except in QWS006(dam water),QWS007 and QWG015 (borehole water) the high Ph value for borehole water could have also resulted from dissolution of limestone in the aquifer formation thereby releasing $CaCO_3$. The temperature was observed lowest at 23°C and highest at 28°C. Temperature is important since it influences water chemistry. More so the rate of chemical reactions generally increases at a higher temperature. This could flow from the sampling times and dates, because the average weather for the time of year was slightly lower at 14°C, despite the sunny morning for the wet season, Observed high temperatures during a wet season could even be the result of a physical principle that favors serious precipitation since beneath ideal conditions and on the average everywhere the planet, the intensity of rain will increase by seven percent for every °C (GOI, 2021; Peleg et al., 2018).

Table 4: Mean variation of pH, Conductivity ($\mu S/cm$), and Temperature (oc) in the wet (w) and dry (D) seasons.

SITE	Season	pH	EC (μs/cm)	Temperature (°C)
QWK001	D	7.68	460	23
	W	7.89	986	26
QWK002	D	7.52	335	27
	W	7.68	951	24
QWK003	D	7.5	994	26
	W	7.94	961	24
QWK004	D	7.5	912	27
	W	7.68	460	23
QWN005	D	7.51	512	27
	W	8	339	24
QWS006	D	7.78	612	28
	W	7.7	975	24
QWS007	D	7.84	423	24
	W	7.74	400	24
QWG008	D	7.98	531	26
	W	8.12	989	24
QWG009	D	7.68	635	25
	W	7.9	1265	23
QWG010	D	7.5	960	27
	W	7.84	965	23
QWG011	D	7.74	985	24
	W	8.22	786	26
QWG012	D	7.65	965	25
	W	9.3	970	25
QWA013	D	7.84	949	27
	W	7.74	861	24
QWG014	D	7.62	963	28
	W	7.65	965	25
QWG015	D	7.68	951	24
	W	7.62	336	28
QWA016	D	7.65	987	26

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	W	8.23	983	25
QWL017	D	7.85	942	27
	W	8.37	866	25
QWL018	D	7.94	961	24
	W	7.46	950	28
QWL019	D	7.61	963	26
	W	7.65	957	28
QWL020	D	7.69	952	25
	W	7.69	952	25
QWO021	D	7.65	953	28
	W	8.02	959	26
QWO022	D	7.46	957	28
	W	7.9	960	24
QWO023	D	7.52	975	24
	W	8	870	27
QWO024	D	7.43	983	25
	W	7.65	877	24
QWO025	D	7.89	986	26
	W	8.03	980	25

> *Anions Results and Discussions*

Table 5: Calibration Parameters for Various Analytes

Analyte	Equation	R^2
Magnesium	Y=0.0026x	0.9900
Copper	Y=0.0011x	0.9916
Manganese	Y=0.0014x	0.9932
Cadmium	Y=0.0050x	0.9924
Lead	Y=0.0026x	0.9934
Iron	Y=0.0013x	0.9916
Zinc	Y=0.0052x	0.9848
Flouride	0.148x+0.006	0.9935
Sulphate	0.0067x-0.0081	0.9958
Nitrate	Y=0.0047x-0.002	0.9915

The water samples recorded varying amounts of anions, which depended on sampling sites and the season of sampling (Table 6). Generally, the concentration of anions was higher during the dry season compared to the wet season. This is mainly due to dilution from rainwater, surface runoffs into surface water systems and dam water, and increased ground discharge into boreholes. There was no observable trend for the determined levels of the various anions with respect to the source, i.e., surface, dam, and borehole water. The frequency of detection of the determined anions followed the order $Cl^- = F^- = SO_4^{2-} = NO_3^- > CO_3^{2-} > HCO_3^-$. NO_2^- was not detected in any of the samples.

All the water samples had chloride content within the recommended maximum limit of below 250 mg L^{-1}, the maximum limit for domestic use. Natural causes, sewage, agricultural waste, municipal drainage full of salt, and saline contamination are all sources of chloride in water systems (Mostafa et al., 2017). This explains the observed high Cl^- levels in the borehole water system at QWO023 for both dry and wet seasons. This particular borehole is located near a busy bus station (Table 2) and observed Cl^- levels are indicative of the heightened anthropogenic activities around this area.

The water system QWO017 borehole recorded the highest concentration of F^-. The fluoride concentration was found to be above the recommended limit of 1.5 mg L^{-1} in 19 of the sites sampled during the dry season, comprising 3 surface water, 2 dams, and 14 boreholes. This represents a 76 % frequency of F^- above recommended limit during the dry season. During the wet season, a total of 3 boreholes recorded F^- above the recommended limit; QWO015, QWO017, and QWO019. The high F^- in these sites could be as a result of the weathering of the fluoride-bearing minerals such as apatite, fluorite, biotite, and hornblende rocks (Aravinthasamy et al., 2020; Mukherjee & Singh, 2018). and their permeation that strengthens their accumulation in groundwater, surface runoffs of minerals high in fluoride, and possible contamination by fertilizers, animal wastes, and household effluents including open sewers (Mukherjee & Singh, 2018). The site QWL017 with the highest recorded fluoride concentration is located within the proximity of a highly populated business center, busy carpet, and car wash that could be a point source (Table 2). Potential

health effects of long-term exposure to elevated fluoride concentrations include dental and skeletal fluorosis (DenBesten & Li, 2011).

The concentration of sulfates was higher in the wet season in comparison to the dry season (Table 6). Sulfates are not naturally occurring but their presence in water could be a result of contamination. High sulfate concentrations that are higher than 200 mg/L create a nasty taste in water for domestic use (USEPA, 2003; WHO, 2014). This could be attributed to the surface runoff whenever it rained from soils that are rich in sulfate minerals. The lowest sulfate concentrations were recorded at the dam water system QWS006 which is the reservoir and the highest value at the borehole water system QWA013. This might be caused by a point source of pollution since its located in a very busy county market, with an open sewer and improper solid waste disposal (Table 2) in the study area that also has a car wash. Market wastes contain sulfates and detergents used in a car wash are also causal agents for high sulfate values (USEPA, 2003). This point is also susceptible to rising sulfate levels above the recommended limit by WHO. In the presence of magnesium or sodium, high levels of sulfate (SO_4^{2-}) in water can cause gastrointestinal irritation (WHO, 2020).

The highest recorded amounts of nitrates were from the borehole, QWA016, during the dry and wet seasons. High concentrations of nitrates may be a consequence of different pollution sources including, septic tanks, open wastewaters, fertilizers, and the application of agricultural pesticides. However, all nitrate levels were found to be within the acceptable limits of a maximum value of 10 mg L^{-1}. This is an indication of minimal agricultural activities in the area, hence a low application of ammonium and nitrate fertilizers in the study area The site QWA016 is close to open drainage and a busy car wash (Table 2), hence susceptible to the observed slightly higher levels of NO_3^- as compared to the other sites.

Table 6: Mean and Standard Deviations of Anions in the Two Seasons.

SITE	SEASON	SO_4^{2-}	NO_2^-	NO_3^-	Cl^-	F^-	CO_3^{2-}	HCO_3^-	
		mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	
SURFACE WATER									
QWK001	D	42.56±0.01	n.d	2.69±0.01	32.54±0.01	2.07±0.01	30.60±0.01	n.d	
	W	43.66±0.01	n.d	1.36±0.00	30.54±0.01	1.40±0.00	33.60±0.02	n.d	
QWK002	D	60.47±0.03	n.d	4.28±0.01	75.91±0.02	2.00±0.01	n.d	126.24±0.09	
	W	64.58±1.87	n.d	3.15±0.00	71.91±0.02	0.91±0.01	n.d	130.00±0.02	
QWK003	D	58.67±0.47	n.d	3.02±0.01	71.00±0.01	1.70±0.01	3.18±0.01	n.d	
	W	60.96±0.02	n.d	2.50±0.01	69.00±0.01	1.10±0.01	3.55±0.05	n.d	
QWN004	D	51.18±0.09	n.d	4.07±0.02	72.66±0.02	1.45±0.01	6.58±0.05	n.d	
	W	53.52±0.02	n.d	3.00±0.01	70.66±0.01	0.69±0.02	7.60±0.07	n.d	
DAM									
QWS005	D	72.96±0.17	n.d	4.89±0.01	71.06±0.09	2.33±0.02	3.94±0.01	n.d	
	W	75.19±0.12	n.d	3.91±0.03	69.06±0.09	0.62±0.01	4.01±0.01	n.d	
QWS006	D	4.14±0.05	n.d	6.10±0.01	7.51±0.08	2.21±0.01	n.d	14.44±0.01	
	W	4.55±0.01	n.d	5.40±0.02	6.51±0.07	1.39±0.00	n.d	13.86±0.03	
BOREHOLE									
QWK007	D	10.27±0.04	n.d	3.03±0.02	68.87±0.01	1.70±0.01	7.40±0.02	n.d	
	W	11.76±0.04	n.d	2.49±0.02	65.87±0.01	1.11±0.01	8.20±0.03	n.d	
QWG008	D	9.59±0.05	n.d	0.62±0.01	23.37±0.02	2.42±0.02	25.20±0.05	n.d	
	W	10.56±0.01	n.d	2.25±0.01	6.51±0.02	1.38±0.01	25.90±0.06	n.d	
QWG009	D	7.99±0.02	n.d	1.40±0.01	15.86±0.01	2.01±0.02	11.10±0.01	n.d	
	W	8.88±0.04	n.d	0.91±0.01	12.86±0.01	1.23±0.01	12.90±0.03	n.d	
QWG010	D	9.65±0.01	n.d	1.89±0.00	32.19±0.01	1.20±0.02	21.80±0.02	n.d	
	W	9.87±0.02	n.d	0.49±0.01	28.19±0.02	0.69±0.01	22.90±0.03	n.d	
QWG011	D	32.26±0.01	n.d	1.41±	29.88±0.04	1.51±0.01	12.40±0.02	n.d	
	W	32.81±0.02	n.d	0.39±0.00	27.88±0.03	0.80±0.02	13.50±0.01	n.d	
QWG012	D	60.10±0.02	n.d	2.80±	13.90±0.02	1.79±0.06	11.00±0.02	n.d	
	W	61.19±0.02	n.d	2.11±0.02	11.90±0.02	0.41±0.01	12.00±0.01	n.d	
QWA013	D	360.21±0.02	n.d	1.93±	15.03±0.04	1.75±0.07	12.60±0.02	n.d	
	W	361.41±0.03	n.d	1.20±0.01	15.0±0.01	0.61±0.01	13.00±0.04	n.d	
QWG014	D	53.31±0.03	n.d	4.33±0.00	20.41±0.01	2.50±0.02	55.20±0.03	n.d	
	W	53.76±0.02	n.d	3.49±0.00	19.41±0.01	2.11±0.08	56.00±0.02	n.d	
QWG015	D	9.58±0.21	n.d	1.22±0.00	2.19±0.05	2.50±0.02	18.40±0.03	n.d	
	W	10.45±0.01	n.d	0.85±0.00	5.19±0.05	1.53±0.09	19.00±0.05	n.d	
QWA016	D	86.21±0.02	n.d	9.21±0.00	49.76±0.02	2.80±0.04	28.10±0.02	n.d	
	W	86.79±0.03	n.d	8.64±0.00	48.26±0.02	1.50±0.09	29.50±0.02	n.d	
QWL017	D	81.17±0.02	n.d	1.02±0.00	25.86±0.02	2.93±0.06	28.50±0.05	n.d	
	W	81.73±0.02	n.d	0.79±0.00	20.86±0.01	1.80±0.02	29.00±0.00	n.d	
QWL018	D	8.20±0.02	n.d	2.30±0.00	25.21±0.01	2.16±0.03	13.60±0.02	n.d	
	W	8.56±0.02	n.d	1.60±0.00	24.11±0.02	1.35±0.01	13.99±0.02	n.d	
QWL019	D	11.99±0.03	n.d	0.30±0.00	31.00±0.03	1.87±0.01	12.50±0.02	n.d	
	W	12.52±0.03	n.d	0.11±0.01	28.00±0.02	1.55±0.02	13.01±0.01	n.d	
QWL020	D	13.20±0.02	n.d	2.50±0.00	33.52±0.02	1.80±0.02	13.30±0.03	n.d	
	W	13.57±0.03	n.d	1.62±0.00	32.72±0.01	0.52±0.02	13.92±0.04	n.d	

SITE	SEASON	SO_4^{2-}	NO_2^-	NO_3^-	Cl^-	F^-	CO_3^{2-}	HCO_3^-	
		mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	
QWO021	D	25.22±0.01	n.d	1.69±0.00	67.51±0.02	2.11±0.01	35.70±0.04	n.d	
	W	25.64±0.02	n.d	1.21±0.00	65.51±0.02	1.52±0.01	37.20±0.01	n.d	
QWO022	D	51.98±0.02	n.d	2.85±0.00	97.00±0.03	0.52±0.00	25.40±0.01	n.d	
	W	52.11±0.02	n.d	1.79±0.00	96.50±0.02	0.13±0.00	25.79±0.02	n.d	
QWO023	D	82.36±0.03	n.d	1.22±0.00	185.00±0.03	2.86±0.09	n.d	242.46±0.01	
	W	82.74±0.02	n.d	0.73±0.08	184.60±0.04	1.51±0.01	n.d	240.30±0.08	
QWO024	D	71.37±0.03	n.d	1.54±0.00	162.18±0.03	0.52±0.00	6.08±0.03	n.d	
	W	71.87±0.03	n.d	0.21±0.00	160.18±0.00	0.09±0.01	6.66±0.04	n.d	
QWO025	D	52.39±0.02	n.d	1.29±0.00	131.00±0.02	1.18±0.01	44.60±0.04	n.d	
	W	53.10±0.01	n.d	0.69±0.00	130.70±0.02	1.22±0.01	45.03±0.00	n.d	

➤ *D and W Represents Dry and Wet Season Respectively and n.d not Detected*

Carbonate concentration was higher during the wet season as compared to during the dry season with borehole water system QWG014 showing the highest recorded concentration. No drinking water standards have been established for carbonates (WHO, 2017a).

Bicarbonate had only three sites with detectable concentrations in the dry season; one dam QWS006, which was the reservoir, one surface water system (QWK002), and one borehole QWO023) (Table 6). These levels were below the recommended maximum limit of 380 mg L^{-1} for bicarbonate. This could only mean the sites are covered by granitic rocks, especially silicate minerals (Faiyad & Hussien, 2016) suggested that HCO_3^- ion concentration in groundwater could be derived from areas covered by igneous rocks that comprise plagio clase feld spars and quartz as in the study area.

➤ *Metal Results and Discussion*

Individual cation values obtained from the different sample sources did not show any discernible trend. The frequency of metal ion detection rose in the following order: Cd (not detected), Zn, Cu, Pb, Mn, Fe, and Mg. The maximum and minimum concentrations of cadmium recorded were below the detection limit in the two seasons (Table 7), however, zinc which is the least harmful and necessary element in the human diet, as is required for a healthy immune system function, recorded values below the set WHO limits of below 0.005 mg L^{-1} in the two seasons, except for one dam and one borehole in the two seasons. This implies that cadmium could not have occurred as an accessory or partner element of zinc ore, sphalerite (MEC, 2022). The noticeable values recorded for zinc (Table 7) from the dam and borehole may be attributed to the low depth of the dam and the borehole, and pollution due to persistent leaching along with the top layers of the soil. The concentration of zinc was found to be very low this could also be attributed to mineralogy and weathering. For the other metal ions, the concentrations were generally higher (varying degrees) in the wet season compared to the dry season, except for a few observed cases where the levels were higher in the dry season (Table 7).

Iron was detected in eight sampling sites; one from dam water, three from surface water, and the remaining four from borehole water, representing a detection frequency of 32 %. It recorded concentrations above the permissible limits recommended for domestic water use of 0.1mg/L^{-1} in the two seasons: 3 surface water, 1 dam, and 2 borehole water systems (Table 7). This could be due to the leaching of iron from open sewers, other non-point sources such as storm runoff in the cases of surface waters, disposal of metal in the case of dam water systems, and leachates from market landfills for the cases of borehole QWA013, which recorded the highest amount.

The frequency of detection of Cu at 28% was slightly lower than that of Fe, as it was detected in 7 sampling sites (two surface water, one dam, and four boreholes) out of a total of 25 sites (Table 7). All the detected amounts of Cu were below the recommended limit of 1.5 mg L^{-1} for domestic water in all the water systems over the two seasons. The wet season had slightly higher (not significant) levels of Cu compared to the dry season, except for one surface water source, QWK002, where the values were the same. Detected levels of Cu could be linked to anthropogenic activities, industrial effluents, and also to mineralogy and weathering (Reeder et al., 2005; Shrivastava, 2009). The slightly noticeable higher values recorded during the wet season as compared to the dry season might be attributed to the persistence of copper complexes that dissolves when the volume of water increases during the rainy season (Cuppett et al., 2006).

Contrary to Zn, Cu, and Fe, the metal ion Pb was detected in all sampled surface water, one dam site, and eleven boreholes, giving a frequency of detection of 64 %. A total of 5 water systems comprising 1 surface and 4 borehole sampling points in both seasons recorded lead concentrations (Figure 7) above the recommended limit guidelines of 0.015 mg L^{-1} in the order QWG015 > QWA013 > QWG012 > QWG011 > QWA013 for both the dry and wet season, except for QWA012 where the high level was for the wet season. The five sites represented 31 % of the sites with Pb detection. Borehole water system QWG015 had the highest recording in the two seasons which might be linked to effluents from the garage and car wash situated close to the water resource (Jurgens et al., 2019; Zietz et al., 2008).

Manganese was detected in 10 sites (three surface water, one dam, and six boreholes), with a 40% detection frequency. All determined Mn concentrations were below the recommended maximum limit of 50 mg L^{-1} for domestic water. These concentrations varied with QWA013 recording the highest amounts. The highest concentration of manganese could be as a result of landfill leachates leaching into the water system since it was near a busy market center and in direct contact with the open sewer, landfill, and also due to runoff from the nearby garage and car wash (Homoncik et al., 2010). The element magnesium was the most frequently detected (96 %) among all determined metal ions. All the concentrations were below the recommended limit of 50 mg L^{-1}. Sixteen out of the twenty-four sites had levels in the wet season slightly higher (not significant) than in the dry season. For the rest of the 8 sites, all boreholes had levels higher in the dry season compared to the wet season, which was significant ($\rho = 0.05$). This included QWA016, QWL017, QWL018, QWL019, QWLO20, QWO021, and QWO023.

Table 7: Mean and Standard Deviations of Metals in the Two Seasons.

SITE	SEASON	Zn	Cd	Fe	Cu	Pb	Mn	Mg
		Mg L^{-1}						
SURFACE WATER								
QWK001	D	n.d	n.d	n.d	n.d	0.00±0.00	0.00±0.00	12.07±0.02
	W	n.d	n.d	n.d	n.d	0.01±0.00	0.02±0.01	12.12±0.05
QWK002	D	n.d	n.d	0.50±0.01	0.00±0.00	0.00±0.00	0.00±0.00	9.70±0.05
	W	n.d	n.d	0.51±0.01	0.00±0.00	0.01±0.00	0.01±0.00	9.71±0.07
QWK003	D	n.d	n.d	0.17±0.02	n.d	0.00±0.00	n.d	9.66±0.10
	W	n.d	n.d	0.21±0.01	n.d	0.01±0.00	n.d	9.67±0.10
QWN004	D	n.d	n.d	0.79±0.02	0.02±0.00	0.00±0.00	0.02±0.00	9.76±0.03
	W	n.d	n.d	0.80±0.01	0.03±0.00	0.01±0.00	0.03±0.01	9.77±0.02
DAM								
QWS005	D	n.d	n.d	0.20±0.01	n.d	0.00±0.00	n.d	9.70±0.04
	W	n.d	n.d	0.22±0.01	n.d	0.01±0.00	n.d	9.73±0.08
QWS006	D	0.01±0.00	n.d	n.d	0.05±0.00	n.d	0.01±0.00	0.11±0.06
	W	0.02±0.01	n.d	n.d	0.06±0.00	n.d	0.02±0.00	0.12±0.05
BOREHOLE								
QWK007	D	n.d	n.d	n.d	n.d	0.00±0.00	0.00±0.00	2.50±0.02
	W	n.d	n.d	n.d	n.d	0.01±0.00	0.01±0.00	2.51±0.02
QWG008	D	n.d	n.d	n.d	n.d	0.01±0.00	n.d	1.45±0.09
	W	n.d	n.d	n.d	n.d	0.02±0.00	n.d	1.50±0.04
QWG009	D	n.d	n.d	0.06±0.00	0.01±0.00	0.02±0.00	0.00±0.00	2.46±0.05
	W	n.d	n.d	0.07±0.01	0.02±0.00	0.01±0.00	0.01±0.00	2.56±0.02
QWG010	D	n.d	n.d	0.11±0.01	0.00±0.00	0.00±0.00	0.01±0.00	1.67±0.06
	W	n.d	n.d	0.10±0.01	0.01±0.00	0.01±0.00	0.00±0.00	1.68±0.01
QWG011	D	n.d	n.d	n.d	0.00±0.00	0.01±0.00	n.d	3.37±0.04
	W	n.d	n.d	n.d	0.01±0.00	0.02±0.00	n.d	3.36±0.03
QWG012	D	n.d	n.d	n.d	n.d	0.01±0.00	0.00±0.00	1.81±0.06
	W	n.d	n.d	n.d	n.d	0.02±0.00	0.01±0.00	1.82±0.08
QWA013	D	n.d	n.d	1.09±0.08	n.d	0.01±0.00	0.00±0.00	n.d
	W	n.d	n.d	1.08±0.07	n.d	0.02±0.00	0.05±0.01	n.d
QWG014	D	n.d	n.d	n.d	n.d	0.01±0.00	n.d	0.96±0.06
	W	n.d	n.d	n.d	n.d	0.03±0.00	n.d	0.97±0.06
QWG015	D	n.d	n.d	0.06±0.00	n.d	0.03±0.00	n.d	1.55±0.09
	W	n.d	n.d	0.05±0.00	n.d	0.04±0.01	n.d	0.05±0.00
QWA016	D	n.d	n.d	n.d	n.d	0.02±0.00	n.d	19.80±0.02
	W	n.d	n.d	n.d	n.d	0.03±0.00	n.d	0.05±0.00
QWL017	D	n.d	n.d	n.d	n.d	0.01±0.00	n.d	10.28±0.03
	W	n.d	n.d	n.d	n.d	0.02±0.00	n.d	0.01±0.00
QWL018	D	n.d	n.d	n.d	n.d	n.d	n.d	2.01±0.01
	W	n.d	n.d	n.d	n.d	n.d	n.d	0.01±0.00
QWL019	D	n.d	n.d	n.d	n.d	n.d	n.d	0.75±0.09
	W	n.d	n.d	n.d	n.d	n.d	n.d	0.01±0.01
QWL020	D	n.d	n.d	n.d	n.d	n.d	n.d	0.62±0.01
	W	n.d	n.d	n.d	n.d	n.d	n.d	0.01±0.00
QWO021	D	n.d	n.d	n.d	n.d	n.d	n.d	1.11±0.01
	W	n.d	n.d	n.d	n.d	n.d	n.d	0.00±0.00
QWO022	D	n.d	n.d	n.d	n.d	n.d	n.d	0.01±0.00
	W	n.d	n.d	n.d	n.d	n.d	n.d	0.01±0.00
QWO023	D	n.d	n.d	n.d	n.d	n.d	n.d	4.06±0.04
	W	n.d	n.d	n.d	n.d	n.d	n.d	0.01±0.00
QWO024	D	n.d	n.d	n.d	n.d	0.01±0.00	n.d	42.78±0.04
	W	n.d	n.d	n.d	n.d	0.00±0.00	n.d	43.04±0.01
QWO025	D	0.15±0.00	n.d	n.d	0.00±0.00	0.00±0.00	0.01±0.00	0.00±0.00
	W	0.14±0.01	n.d	n.d	0.01±0.00	0.01±0.01	0.03±0.00	0.01±0.00

> *D and W Represents Dry and Wet Season Respectively and n.d not Detected*

The presence of underground mineral deposits may be the cause of the high concentration of magnesium observed at borehole QW0O24 during the dry season and the lower-than-expected detection limit at QWA013might be a result of higher iron concentrations, which lowered magnesium values.

B. Correlations of Ions in the Water System

The Correlations between ions were carried out using Spearman's correlation analysis between pH-F⁻, pH-Zn, Cl⁻-HCO₃⁻, Cl⁻-Mg, Fe-Mn, SO_4^{2-}-Fe, and SO_4^{2-}-Mn and recorded as positive correlations with r^2 values of 0.44, 0.44,0.56, 0.57,0.67, 0.70, and 0.76 respectively, (Table 8, and Table 9). This proposes that the variation in water composition could be measured by these factors or constraints (Odukoya et al., 2013). The correlation between SO_4^{2-}-Fe ($r^2 = 0.70$) and SO_4^{2-}-Mn ($r^2 = 0.76$) gives a clue that domestic effluents, open sewers, poor sanitation, and generally point and non-point pollution in the study area could be a greater source of sulfates, iron, and manganese through surface runoffs and leaching into the water systems resulting in these limits. The much stronger positive correlations between Fe-Mn, ($r^2 = 0.67$) HCO₃⁻-Cl, ($r^2 = 0.56$) Mg-Cl⁻ ($r^2 = 0.57$) additionally point out the comparable source of these ions in the water samples studied. The weak positive correlation could suggest that some other reliable sources account for their concentration in the water system in the studied area.

Table 8: Correlation Matrix during the wet season

	pH	Conductivity	Temp.	Cl [mg/L]	SO_4^{2-} [mg/L]	NO_2^- [mg/L]	NO_3^- [mg/L]	F⁻ [mg/L]	CO_3^{2-} [mg/L]	HCO₃[mg/L]]	Zn [mg/L]	Cd [mg/L]	Fe [mg/L]	Cu [mg/L]]	Pb [mg/L]]	Mn[mg/L] Mg[mg/L]
pH	1															
Conductivity	-0.1378	1														
Temp.	-0.2084	0.07275	1													
Cl[mg/L]	-0.4414	0.17298	0.07376	1												
SO_4^{2-} [mg/L]	0.1065	0.13033	0.25437	0.06	1											
NO_2^- [mg/L]	0.00	0.00	0.00	0.00	0.00	1										
NO_3[mg/L]	-0.1281	-0.16109	0.30953	-0.03	0.107	0.00	1									
F[mg/L]	0.4435	-0.12772	-0.37175	-0.29	-0.333	0.00	-0.105	1								
CO_3^{2-} [mg/L]	0.2427	0.28551	0.276	-0.14	-0.05	0.00	0.009	0.1338	1							
HCO₃⁻[mg/L]	-0.2584	-0.11285	-0.17819	0.56	0.085	0.00	-0.006	0.1219	-0.3532	1						
Zn[mg/L]	0.4494	-0.04393	-0.01727	0.02	0.049	0.00	-0.013	0.0434	0.0907	-0.1666	1					
Cd[mg/L]	0.2398	0.12619	-0.2146	0.1	0.048	0.00	-0.096	0.0093	0.0944	-0.062	-0.039	1				
Fe[mg/L]	-0.0578	-0.28815	0.33698	-0.07	0.707	0.00	0.1646	-0.313	-0.2995	0.0433	-0.007	-0.234	1			
Cu[mg/L]	-0.0223	-0.50059	-0.0647	-0.12	-0.122	0.00	0.0641	0.0571	-0.2245	-0.0391	0.2178	-0.256	0.4202	1		
Pb[mg/L]	0.1809	-0.00806	-0.12796	-0.4	0.205	0.00	-0.007	0.1451	0.175	-0.2947	0.0496	-0.125	0.2854	0.0978	1	
Mn[mg/L]	0.2513	-0.09638	0.04872	-0.29	0.763	0.00	-0.079	-0.2	-0.1752	-0.0885	0.2097	0.1385	0.689	0.1193	0.207	1
Mg[mg/L]	-0.2234	0.02639	-0.06286	0.57	0.086	0.00	0.1617	-0.227	-0.0159	-0.0292	0.0905	-0.039	-0.06	0.045	0.06	-0.211

Table 9: Correlation Matrix During the Dry Season

	pH	Conductivity	Temp.	Cl [mg/L]	SO$_4^{2-}$ [mg/L]]	NO$_2^-$ [mg/L]	NO$_3^-$ [mg/L]	F$^-$ [mg/L]	CO$_3^{2-}$ [mg/L]	HCO$_3^-$ [mg/L]	Zn [mg/L]	Cd [mg/L]	Fe [mg/L]	Cu [mg/L]	Pb [mg/L]	Mn [mg/L] Mg [Mg/L]
pH	1															
Conductivity	0.1624	1														
Temp.	-0.0954	-0.13245	1													
Cl[mg/L]	-0.0877	0.06648	-0.08755	1												
SO$_4^{2-}$ [mg/L]	0.0248	0.01247	-0.19848	0.06	1											
NO$_2^-$ [mg/L] [mg/1]	0.00	0.00	0.00	0.00	0.00	1										
NO$_3^-$ [mg/L]	0.0183	-0.08123	-0.28821	0.01	0.109	0.00	1									
F$^-$ [mg/L]	0.1341	-0.08138	0.37845	-0.34	-0.004	0.00	0.1559	1								
CO$_3^{2-}$ [mg/L]	0.0989	0.31362	0.10266	-0.15	-0.051	0.00	-0.028	-0.02	1							
HCO$_3^-$ [mg/L]	-0.0295	0.02136	0.18574	0.55	0.084	0.00	-0.062	0.295	-0.3567	1						
Zn [mg/L] [mg/l]	0.2813	-0.03892	-0.0849	0.01	0.05	0.00	-0.015	-0.006	0.1028	-0.1717	1					
Cd [mg/L]	0.2087	-0.1319	0.09798	0.04	-0.018	0.00	-0.245	-0.035	-0.2315	-0.2629	0.1572	1				
Fe [mg/L]	-0.1566	-0.28847	-0.34976	-0.07	0.7	0.00	0.2023	0.0089	0.3111	0.0468	0.0136	-0.144	1			
Cu [mg/L]	0.0426	-0.28564	-0.23329	-0.12	-0.12	0.00	0.0757	0.137	-0.224	-0.0394	0.2203	0.0162	0.4229	1		
Pb [mg/L] [mg/l]	0.1993	-0.09163	-0.05037	-0.42	0.205	0.00	0.0203	0.1037	0.1753	-0.2961	0.0958	-0.092	0.2618	0.0913	1	
Mn [mg/L]	-0.0932	-0.17175	-0.21323	-0.29	0.764	0.00	-0.07	0.0086	-0.1715	-0.0881	0.2068	0.0939	0.679	0.1216	0.195	1
Mg [mg/L]	0.0863	-0.18049	-0.31389	0.03	-0.027	0.00	0.3918	0.0521	-0.2762	0.0439	0.0826	-0.202	0.3834	0.389	0.095	-0.091

C. Effect of Anions on Speciation and Bioavailability

All the metal species found in the water systems were cationic and anionic. The majority of these species were metal hydroxides. Anions quickly connect with metals in the available water to form a type of class, as illustrated; $P^{+m} + Q^{-n} \leftrightarrow P_n Q_m$

where: P and Q refers to the metal(s) and the anion(s) respectively and, accompanying the metal's and non-valences metal's denoted by +m and -n, individually. As a result, several series of lead species were created, which includes the following: $Pb(OH)^{3-} > Pb_2(OH)^{+3} > Pb(OH)^{2+} > PbOH^+ > Pb^{+2}$

➢ Surface Water Systems

In QWK001, QWK002, QWK003, QWK004 Magnesium, lead, and manganese were found to be the most dominant metal species without anions, accounting for nearly 100 percent of the total. During the wet season, however, anions introduced into the system resulted in higher speciation of magnesium, lead, and manganese compounds than during the dry season.

The most abundant species were $MgSO_4$, Mg^{2+}, $Mg(HCO_3)_2$, MgF_2, $MgCO_3$, $PbCO_3$, $Mn(CO_3)_2$, and $Mg(OH)_2$, $Fe(OH)$, $Fe(HCO_3)_2$, and $Mn(HCO_3)_2$ in these surface waters QWK001, QWK002, QWK003, and QWK004 (Table 10). This could be explained by the high concentration of anions available to form compounds with metals. However, in QWK002, this location contained traces of metal ion species, Fe^{+2}, while the iron was found in two forms, Fe(111) and Fe(11). This could be due to the high concentrations of iron recorded in the input data over the two seasons.

In QWK003 manganese(11) was observed, which is more soluble and more bioavailable than other forms of manganese (CICAD, 2004; Homoncik et al., 2010).

In QWK004. Chemical species such as F^-, and Fe^{+2} were recorded. Fe(11) also existed in two oxidation states. This could be due to significantly higher concentrations of iron recorded in the input data in the two seasons.

➢ *Dams Water Systems*

As a result of the chemical speciation of metals without anions at locations at QWN005, and QWS006, the chemical species Mg^{2+}, Cu(2), and $Cu(OH)_3$, Fe(11), Fe(111), $Fe(OH)_3$, and Pb^{+2} predominated (Table 10). After the introduction of anion in both the wet and dry seasons, fluorides, hydroxyl, carbonates, hydrogen carbonates, and sulphates were found to produce compounds with the highest speciation results. The most abundant chemical species were $MgSO_4$, Mg^{2+}, $Mg(HCO_3)_2$, $FeSO_4$, $Fe(OH)_3$, $Fe(HCO_3)_2$, MgF_2, and $MgCO_3$ (Table 10). This may be explained by the elevated concentrations of anions found at the sampling points during the two seasons, as well as the low concentrations of other heavy metals, resulting in only a small percentage of anions forming metal-anion compounds and the rest remaining free. Traces of ions species were also recorded at QWN005 locations such as NO_3^-, F^-, Fe^{2+},Fe(11), and Cu(1). This could be due to considerably higher concentrations of these anions and metals recorded in the input data in the two seasons.

In location QWS006 the species formation could be attributed to the high pH and high temperature of 28℃ recorded, which may have triggered the speciation of fluorides ion species in the two seasons and low concentrations of other heavy metals at the sampling point, resulting in only a small percentage of anions forming metal-anion compounds and the rest remaining free. Traces of ions species also existed in this location with Mg^{2+}, and F^-, taking the lead, iron species also existed in two oxidation states of Fe(11) and Fe(111) this could be due to considerably higher concentrations of iron recorded in the input data of (0.203 mg L^{-1}) in the two seasons. Under mild oxidizing conditions, iron exists in a +3 oxidation state as an insoluble precipitate, Fe_2O_3 undergoes a reduction and is transformed to +2 valence states as the soluble Fe^{2+} cation. Iron concentrations in water samples could rise due to the re-dissolution of previously produced unsteady precipitates or the discharge of iron from the bordering rocks.

➢ *Borehole Water Systems*

Chemical species were recorded in borehole water systems before and after anion introduction in (Table 10). In location QWS007 traces of other ion species were observed in this location, including, F^-, Fe(11), and Fe(111) this could be due to considerably higher concentrations of fluoride and iron recorded in the input data in the two seasons.

At sites QWG008, QWG009, QWG010, and QWG011 had Other ion species recordings such as CO_2 and NO_3^-, the low iron concentration might have triggered the speciation of nitrates, and the low concentration of other metals at the sampling point, and therefore only a small percentage of anions formed compounds with metals and the rest were free. CO_2 could have been triggered by the hydrogen carbonate in the waters. QWG010 had Cu (11) ion it is evident that at pH 7.5 copper exists in the majority at oxidation state II. Cu^{2+} is the second most toxic form of copper (Jones & Bolam, 2007) this was present in the waters.

At QWG012 speciation heavy metal concentrations without anions recorded dominance in this order Mg^{2+}, Mn^{+2}, Mn(11), Fe(11), and $Pb(OH)_2$ while by the introduction of anions the same metal species were dominating by forming compounds with anions. Carbonates, Hydrogen carbonates, and Sulphates were noted to have speciated and created compounds with the highest speciation molality values in both the wet season and the dry season. The Abundant species in the wet season were HCO_3^-, NO_3^-, CO_3^{2-}, F^-, and dry season $Mg(HCO_3)_2$, $PbCO_3$ $MgCO_3$, $MgSO_4$, Mg^{2+}, F^-, the percentage abundance in the two seasons of Magnesium hydrogen carbonate was found to be close. The most abundant chemical species were $MgSO_4$, Mg^{2+}, F^-, NO_3^-, MgF_2, NO_3^-, $Mg(HCO_3)_2$, $MgCO_3$, and $CuCO_3$ in that order respectively. A high concentration of anion ions and low concentration of other heavy metals at the sampling point and therefore only a small percentage of anions formed compounds with metals and the rest were free. Traces of ions species also existed in this location with Mg^{2+}, NO_3^-, F^-, and Cl^- taking the lead.

In location QWA013 speciation of heavy metals concentrations without anions recorded dominance in this order Fe(111), $Fe(OH)_3$, $Fe(OH)^{2+}$, Mn^{2+}, Mn(11), Pb^{+2}, , and $Pb(OH)^+$ while by the introduction of anions the same metal species were dominating by forming compounds with anions. Fluorides, hydroxyl, Carbonates, and Sulphates were noted to have speciated created compounds with the highest speciation molality values in both the wet season and the dry season. the percentage abundance in the two seasons was closely associated with Magnesium and Iron which were also predominant metal species forming species with anions of sulphate, hydrogen carbonate, carbonate, and hydroxyl ions. The most abundant chemical species were $MgSO_4$, Mg^{2+} $Mg(HCO_3)_2$, $Fe(OH)_3$, MgF_2, and $MgCO_3$ in that order respectively. This might be attributed to the high levels of sulphate ions recorded from this site's high pH since that might have triggered the speciation of sulphate ions, iron, and manganese. Anions Cl^-, HCO_3, NO_3^-, and F^- species also existed in this location.

At QWG014, chemical speciation of heavy metals recorded predominance in this order Mg^{2+}, Pb(11), and $Pb(OH)^+$, while after the introduction of anions, metal and anions formed compounds with Sulphates and hydrogen carbonate, carbonate, and hydroxyl ions. The most abundant chemical species were SO_4^{-2}, HCO_3^-, Cl^-, NO_3^-, F^-, $Mg(HCO_3)_2$, $MgCO_3$, $Pb(HCO_3)_2$, and $PbCO_3$ respectively. This could be due to the high pH, which may have resulted in low speciation of sulphates, hydrogen carbonate, and fluorides ion species in the two seasons, as well as low concentrations of other heavy metals at the sampling points, resulting in only a small proportion of anions produced by metal compounds and the rest is free. Traces of metal ion species also existed at this

position of Mg^{2+}, F^-, Cl^- taking lead, iron species also existed in two oxidation states of Fe(11) and Fe(111), which may be attributed to slightly higher iron concentrations reported in input data during the two seasons.

At QWG015, the chemical speciation of heavy metals without anions displayed predominance in this order Pb^{2+}, $Pb(OH)^+$, Mg^{2+}, Fe(111), Fe(11), and Fe(OH), although the same metal species dominated the formation of anion metal compounds after the incorporation of anions. Sulphates and Fluoride were reported to have highly speciated leading to the formation of compounds with the highest speciation molality values of anion lead during the two seasons with SO_4^{-2}, F^-, and Cl^- leading. The most abundant chemical species were SO_4^{2-}, F^-, Cl^-, $MgSO_4$, $Mg(HCO_3)_2$, MF^+, $Fe(OH)^3$, $Pb(HCO_3)_2$, and $PbCO_3$ respectively.

At position QWA016, anion-free concentrations of heavy metals reported predominance in this order Mg^{2+}, Pb^{2+}, $Pb(OH)^+$, and $Pb(OH)^2$. Although the introduction of anions occupied heavy metal species through the development of anion metal compounds. Sulfates, chlorides, and hydrogen carbonates were stated to have been strongly speciated. SO_4^{2-} was the most abundant chemical species. In that order, Cl^-, HCO_3^-, $MgSO_4$, $Mg(HCO_3)_2$, $Pb(HCO_3)_2$, $PbCO_3$

At position QWL017, anion-free concentrations of heavy metals reported predominance in this order Mg^{2+}, Pb^{2+}, $Pb(OH)_2$, and $Pb(OH)^+$ while anion-free concentrations dominated the same metal species through the formation of anion compounds. Sulfates were the most common chemical species, followed by HCO_3^-, Cl^-, F^-, and NO_3^-, respectively, forming metal complexes in the order of $MgSO_4$, $Mg(HCO_3)_2$, $Pb(HCO_3)_2$, $PbCO_3$

At position QWL018, heavy metals recorded predominance in this order Mg^{2+} and $Mg(OH)_2$, whereas after the introduction of anions the same metal species dominated by forming compounds with anions. Anion and metal species abundance formation was recorded with $MgSO_4$, $Mg(HCO_3)_2$, $Pb(HCO_3)_2$, and $PbCO_3$ in that order, the other metal species were comparatively low in abundance.

Chemical Speciation of heavy metals without anions in position QWL019 reported dominance in this order Mg^{2+} and $Mg(OH)_2$, the same metal species dominated by forming anion compounds after the incorporation of anions. Hydrogen carbonate, chlorides, hydroxyl, carbonates, and sulphates are reported to have speciated contributing to the formation of compounds $MgSO_4$, $Mg(HCO_3)_2$, and $Pb(HCO_3)_2$, $PbCO_3$ were the most common chemical species in order of abundance. This could be due to the high pH and high temperature of 28°C, which could have caused the speciation of fluoride ion species in the water system during the two seasons and the low concentration of other heavy metals recorded in the water system leading to only a small percentage of species produced by anions and the rest were free. Traces of metal ions species also existed in this location with Mg^{2+}, and F^-, taking the lead, iron species also existed in two oxidation states of Fe(11) and Fe(111) this could be due to considerably higher concentrations of iron recorded of (0.204 mg L^{-1} mg/L) in the two seasons.

In this order, speciation of heavy metal concentrations without anions reported dominance in position QWL020. Mg^{2+} and $Mg(OH)_2$ whereas the same metal species is dominated by forming compounds with anions after the incorporation of anions. Chloride was the most abundant followed by sulfates, hydrogen carbonate, nitrate, and fluoride of other chemical species such as $MgSO_4$, Mg $Mg(HCO_3)_2$, MgF_2, and $Mg(OH)_2$ were below 1 percent, respectively.

At position QWO021, anion-free species of heavy metals reported predominance in this order Mg^{2+} and $Mg(OH)_2$, Hydrogen carbonate was the most prevalent followed by sulphates followed by fluorides, and nitrates. Other chemical species were $MgSO_4$, and $Mg(HCO_3)_2$, which may be due to the low concentration of other heavy metals at the sampling points and that only a limited percentage of anions were produced with metals, to formation of complexes.

At the site of QWO022 speciation, the concentrations of heavy metals without anions displayed predominance in this order of Mg^{2+} and $Mg(OH)_2$, whereas the same metal species dominated the formation of anion compounds through the incorporation of anions. Chloride was the most prevalent followed by sulphates, hydrogen carbonate, and nitrates. Other chemical species in this order were $MgSO_4$, $Mg(HCO_3)_2$, and $MgCO_3$.

At position QWO023, anion-free concentrations of heavy metals documented predominance in this order Mg^{2+} and $Mg(OH)_2$, while anion-free concentrations dominated the same metal species by the formation of anion compounds, hydrogen carbonate was the most abundant than sulfates and carbonates. $MgSO_4$, Mg^{2+}, and $Mg(HCO_3)_2$, in that order, were other chemical species.

Table 10: Most Abundant, Similar, and Dissimilar Chemical Species before and after Anion Introduction at the Sampling Site

Site	Most abundant Chemical species before anions introduction	Most abundant Chemical species after anions introduction	Most abundant similar chemical species	Most abundant dissimilar chemical species
Surface				
QWK001	Mg^{2+}, Fe(11), Fe(111), $Fe(OH)_3$, Pb^{2+} Mn^{2+}, and Mn(11),	$MgSO_4$, Mg^{2+}, $Mg(HCO_3)_2$, MgF_2, $MgCO_3$, $PbCO_3$, $MnCO_3$, and $MgOH^+$	MgF^+,$MgSO_4$,Mg^{2+}, $Mg(HCO_3)_2$ and $MgCO_3$	$PbCO_3$, $MnCO_3$, and $MgOH^+$,$Mn(HCO_3)_2^+$, $Fe(OH)_3$, $FeHCO_3^+$, MgF^+,
QWK002	Mg^{2+}, Mn^{2+}, Mn(11), Fe(11), and $Pb(OH)_2$	$MgSO_4$, Mg^{+2}, $Mg(HCO_3)_2$, Fe(OH), $FeHCO_3^+$, MgF^+, and $MgCO_3$,		
QWK003	Mg^{2+}, Mn^{2+}, Mn(11), Fe(11), and Pb(OH)	Mg^{2+}, $MgSO_4$, $Mg(HCO_3)_2$, MgF_2, $MgCO_3$, $PbCO_3$, $MnCO_3$, $MgOH^+$, and $Mn(HCO_3)_2$		
QWK004	Mg^{2+}, Pb(OH), and Pb^{2+},Fe(111) , $Fe(OH)_3$	$MgSO_4$, Mg^{+2}, $Mg(HCO_3)_2$, $Fe(OH)_3$, $FeHCO_3^+$, MgF_2, and $MgCO_3$		
Dam				
QWN005	Mg^{2+}, Cu(11), Fe(111), and $Cu(OH)_3$	$MgSO_4$, Mg^{2+}, $Mg(HCO_3)_2$, $FeSO_4$, $Fe(OH)_3$, $FeHCO_3^+$, MgF^+, and $MgCO_3$, Others, F^-, Mg^{+2}, and Fe^{+2}	$MgSO_4$, Mg^{+2}, $Mg(HCO_3)_2$, $Fe(OH)_3$, MgF^+, and $MgCO_3$	$FeSO_4$, F^- ,$FeHCO_3^+$, Fe(11) and Fe(111)
QWS006	Mg^{2+}, Fe(11), Fe(111), $Fe(OH)_3$, and Pb^{2+}	$MgSO_4$, Mg^{2+}, $Mg(HCO_3)_2$, $Fe(OH)_3$, MgF^+, and $MgCO_3$		
Borehole				
QWS007	Mg^{2+}, Mn^{4+}, Zn^{2+}, Cu^{2+}	$MgSO_4$, Mg^{+2}, $Mg(HCO_3)_2$, MgF^+ $Fe(OH)_3$, Fe(11) and Fe(111)	$MgSO_4$, Mg^{2+}, $Mg(HCO_3)_2$, MgF_2	Cu(11), $CuCO_3$,Fe(11), Fe(3), $Fe(OH)_3$, $^+$, NO_3^-, $PbCO_3$, $Pb(HCO_3)_2$, $MgCO_3$, and $PbSO_4$
QWG008	Mg^{2+}, Pb(OH), and Pb^{2+}	$MgSO_4$, Mg^{2+}, MgF^+, NO_3^-, $PbCO_3$, $Pb(HCO_3)_2$, $MgCO_3$, and $PbSO_4$		
QWG009	Mg^{2+}, Mn^{2+}, Mn(11), Fe(11), and Pb(OH)	$MgSO_4$, Mg^{+2}, MgF^+, NO_3^-, $PbCO_3$, $PbHCO_3^+$, $MgCO_3$, and $PbSO_4$		
QWG010	Mg^{2+}, Fe(111), Fe(11), Mn(11), and Pb(OH)	$MgSO_4$, Mg^{2+}, NO_3-, MgF^+, $PbCO_3$, $Pb(HCO_3)_2$, $MgCO_3$, Cu(2)		
QWG011	Mg^{2+}, Cu(OH), Mg(OH)+, and Pb(OH)	$MgSO_4$, Mg^{2+}, F^-, NO_3^-, $MgF^{+,}$ NO_3^-, $Mg(HCO_3)_2$, $MgCO_3$, and $CuCO_3$		
QWG012	Mg^{2+}, Mn^{2+}, Mn(11), Fe(11), and Pb(OH)	$MgSO_4$, Mg^{+2}, F^-, NO_3^-, MgF_2, NO_3^-, $Mg(HCO_3)_2$, $MgCO_3$, and $CuCO_3$		
QWA013	Fe(111), $Fe(OH)_3$, $Fe(OH)^{2+,}$ Mn^{2+}, Mn(11), Pb(11), and $Pb(OH)^+$	$MgSO_4$, Mg^{2+}, $Mg(HCO_3)_2$, $Fe(OH)_3$, MgF_2, and $MgCO_3$		
QWG014	Mg^{2+}, Pb(11), and $Pb(OH)^+$	SO_4^{-2}, HCO_3^-, Cl^-, NO_3^-, F^-, $Mg(HCO_3)_2$, $MgCO_3$, $Pb(HCO_3)_2$, and $PbCO_3$	$Mg(HCO_3)_2$, $MgSO_4$, $PbCO_3$, $Pb(HCO_3)_2$	MgF_2, MgOH, SO_4^{-2}, HCO_3^-, Cl^-, NO_3^-, F
QWG015	Pb^{2+}, $Pb(OH)^+$, Mg^{2+}, Fe(111), Fe(11), and Fe(OH),	SO_4^{2-}, F^-, Cl^-, $MgSO_4$, $Mg(HCO_3)_2$, MgF_2, $Fe(OH)^3$, $Pb(HCO_3)_2$, and $PbCO_3$		
QWA016	Mg^{2+}, Pb^{2+}, $Pb(OH)^+$, and $Pb(OH)^2$	Cl^-, HCO_3^-, $MgSO_4$, $Mg(HCO_3)_2$, $Pb(HCO_3)_2$, $PbCO_3$		

QWL017	Mg^{2+}, Pb^{2+}, $Pb(OH)^+$, and $Pb(OH)^2$	$MgSO_4$, $Mg(HCO_3)_2$, $Pb(HCO_3)_2$, $PbCO_3$		
QWL018	Mg^{2+} and $Mg(OH)^+$,	$MgSO_4$, $Mg(HCO_3)_2$, $Pb(HCO_3)_2$, and $PbCO_3$		
QWL019	Mg^{2+} and $Mg(OH)^+$,	$MgSO_4$, $Mg(HCO_3)_2$, $Pb(HCO_3)_2$, and $PbCO_3$		
QWL020	Mg^{2+} and $Mg(OH)^+$,	$MgSO_4$, $Mg(HCO_3)_2$, MgF_2, and $MgOH$	$MgSO_4$, $Mg(HCO_3)_2$	MgF_2, Mg^{2+}, $Pb(HCO_3)_2$, $PbCO_3$, $MgOH$, $Zn(HCO_3)_2$, and $ZnCO_3$,
QWO021	Mg^{2+} and $Mg(OH)^+$	$MgSO_4$, $MgHCO_3$, Mg^{+2},		
QWO022	Mg^{2+} and $Mg(OH)^+$	$MgSO_4$, Mg^{2+}, and $Mg(HCO_3)_2$,		
QWO023	Mg^{2+} and $Mg(OH)^+$	$MgSO_4$, Mg^{2+}, and $Mg(HCO_3)_2$		
QWG024	Pb^{2+}, $Pb(OH)^+$, and $Pb(OH)_2$	$MgSO_4$, Mg^{2+}, $Mg(HCO_3)_2$, $Pb(HCO_3)_2$, and $PbCO_3$,		
QWO025	Pb^{2+}, $Pb(OH)^+$, and $Pb(OH)_2$	$MgSO_4$, Mg^{+2}, $Mg(HCO_3)_2$, $Zn(HCO_3)_2$, and $ZnCO_3$,		

Speciation of heavy metal without anions at QWG024 reported dominance in this order Pb^{+2}, $Pb(OH)^+$, and $Pb(OH)_2$ when the same metal species dominated by forming anion compounds by the introduction of anions. Speciation has been reported, and SO_4^{2-} was abundant with chlorides. The other chemical species were $MgSO_4$, Mg^{2+}, $Mg(HCO_3)_2$, $Pb(HCO_3)_2$, and $PbCO_3$, respectively, in that order.

In position QWO025, Zinc and lead-forming compounds with the hydroxyl ion were found to be dominant in heavy metal concentrations without anions, whereas the same metal species dominated by forming compounds with anions by the incorporation of anions. Species were reported as abundant with chlorides SO_4^{2-} and hydrogen carbonate. The other chemical species were $MgSO_4$, Mg^{2+}, $Mg(HCO_3)_2$, $Zn(HCO_3)_2$ and $ZnCO_3$, respectively. This can be due to the low concentration of other heavy metals at sampling points and that only a limited proportion of anion compounds are produced by metals and the remainder are free.

D. Effects of Temperature on Speciation
Decreased temperatures from 35°C to 15 °C appeared to favor metal speciation, leading to a high metal abundance. There was a maximum metal abundance observed at 28°C. Sites QWL018, QWL019, QWO025, and QWO022, showed Mg^{+2} all at different temperatures and then a drastic decrease at 15°C as was seen at site QWK004. Site QWO025 and QWA013 showed Zn^{+2}, $Zn(OH)_2$, $Fe(3)$, $Fe(OH)^{2+}$, Mn^{+2}, and $Pb(OH)^+$ dominance after increasing the temperature and raising pH to 10 (Appendix1.4),. Hydroxyl metal complexes were formed when increasing the pH range from 9-11. With the dissolution of $Pb(OH)_2$ to form $Pb(OH)_3$ complexes at high pH values $Fe(3)$, $Fe(OH)_3$, $Fe(OH)^{2+}$, Mn^{+2}, $Mn(2)$, $Pb(2)$, and $Pb(OH)^+$ .At fixed pH and absorption, the impact of temperature as well as metal species affluence is inversely proportionate.

E. Effects of pH on Speciation
It acknowledged pH is a key constraint that manipulates the metal ions speciation, and for that reason influences the abundance of species. Copper chemistry as a function of pH has been reported by (Cuppett et al., 2006), and the distribution of copper ions, which might be related to common anions in pure water. Copper divalent ion (Cu^{2+}) is dominating in the pH range 1-7. and $CuCO_3$, $CuNO_3$, and $CuOH^+$ complexes are also formed at low pH values site QWN005, QWS007, QWG011, and QWG012 had copper dominating at a pH below 8 leading to the formation of $CuOH^+$, $CuOH^+$, $Cu(11)$, and Cu^{2+} increasing the pH to 10 for example at QWN005(Appendix1.4), the amount of Cu^{2+} decreased and other chemical complexes as $CuOH^+$, $CuOH^+$ dramatically disappeared when increasing the pH to 10, this could be because of $Cu_2(OH)_2^{2+}$ and $Cu_3(OH)_4$ which were formed. On the other hand, in the case of, Iron, Manganese, zinc, and lead, at high pH values, the precipitation begins to dissolve as a hydroxyl complex, and the optimal pH is within the range of pH 3-10.

F. Abundant Chemical Species in the Water in the Study Region
As regards heavy metals and anions and evidence from PHREEQ C, the abundance of these metals species varied from one water system to the other. It was noted that metals formed anion complexes and the total abundance of metal species was classified at the highest levels as $Fe(OH)_3$, (Figure 5), $PbCO_3$, (Figure 6), $Zn(CO_3)_2$, (Figure 7), $Cu(CO_3)_2$, (Figure 8), Mn^{+2}, (Figure 9), and Mg^{+2} (Figure 10), in each group of heavy metal species. Overall the most dominant chemical species in the study area during the two seasons is Magnesium Fluoride (MgF^+) (Figure 11) this could only mean that Magnesium is generally found at a higher concentration that easily connects with the available fluoride forming the MgF^+.
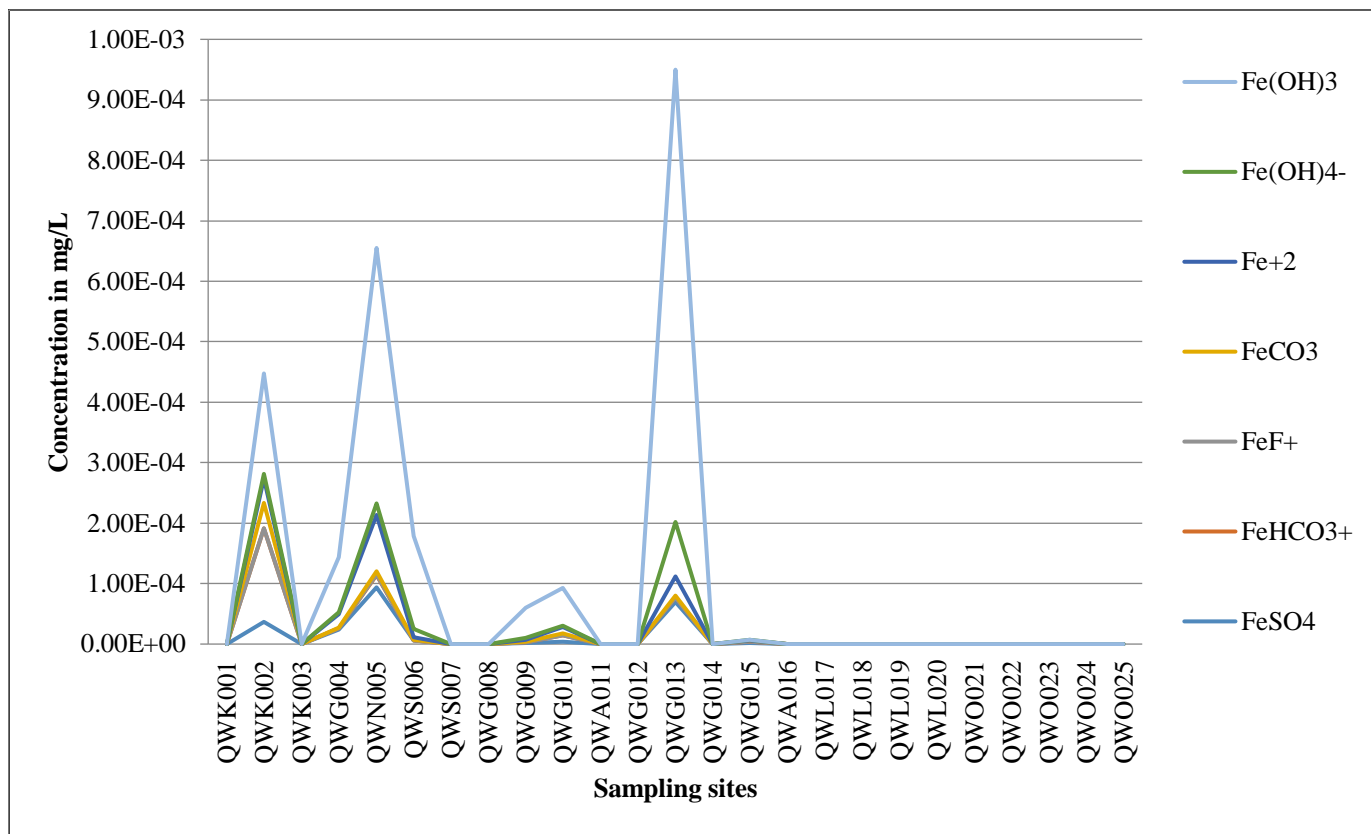
Fig 5: The abundant Iron Species in the Sampling Sites
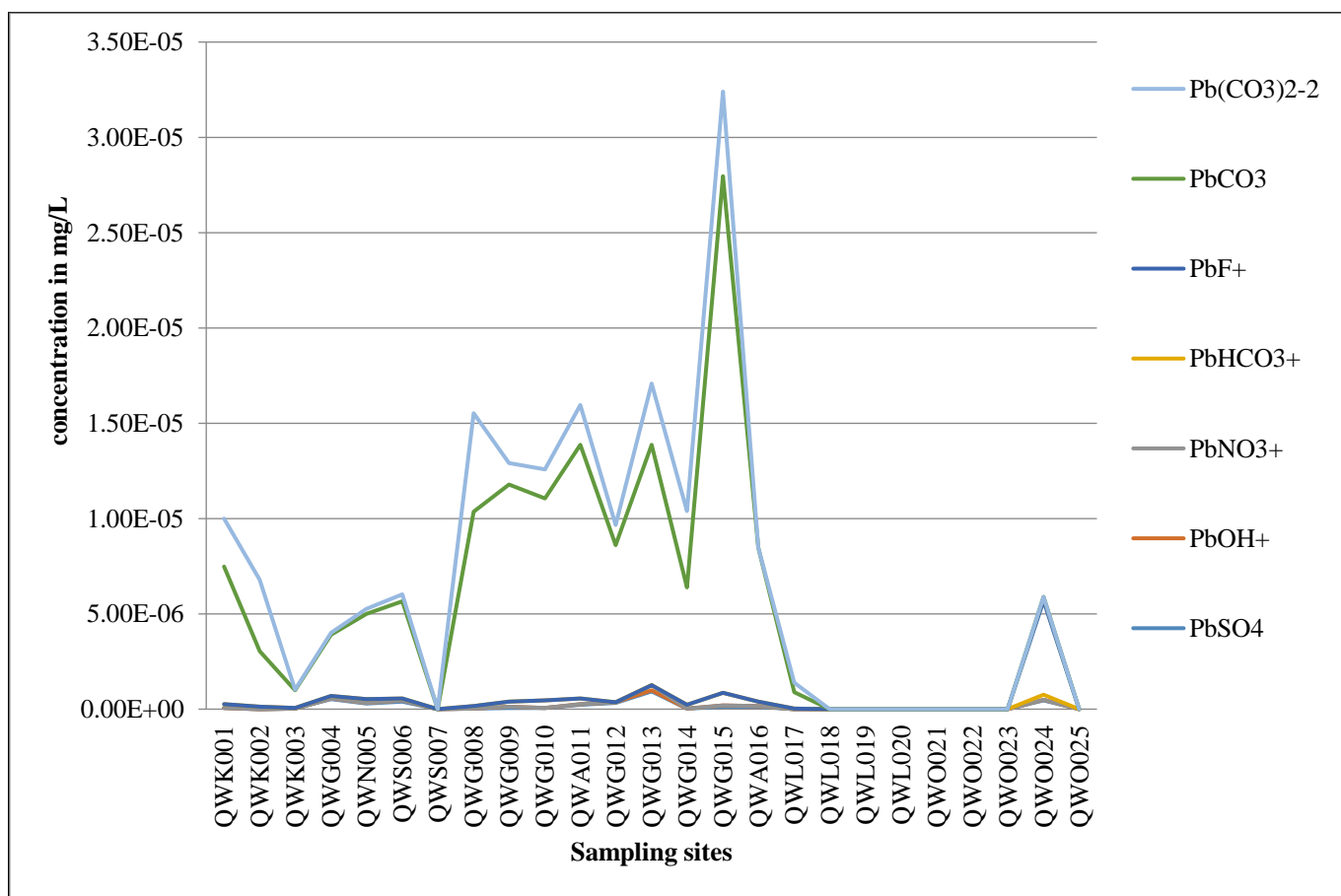
Fig 6: The Abundant Lead Species in the Sampling Site
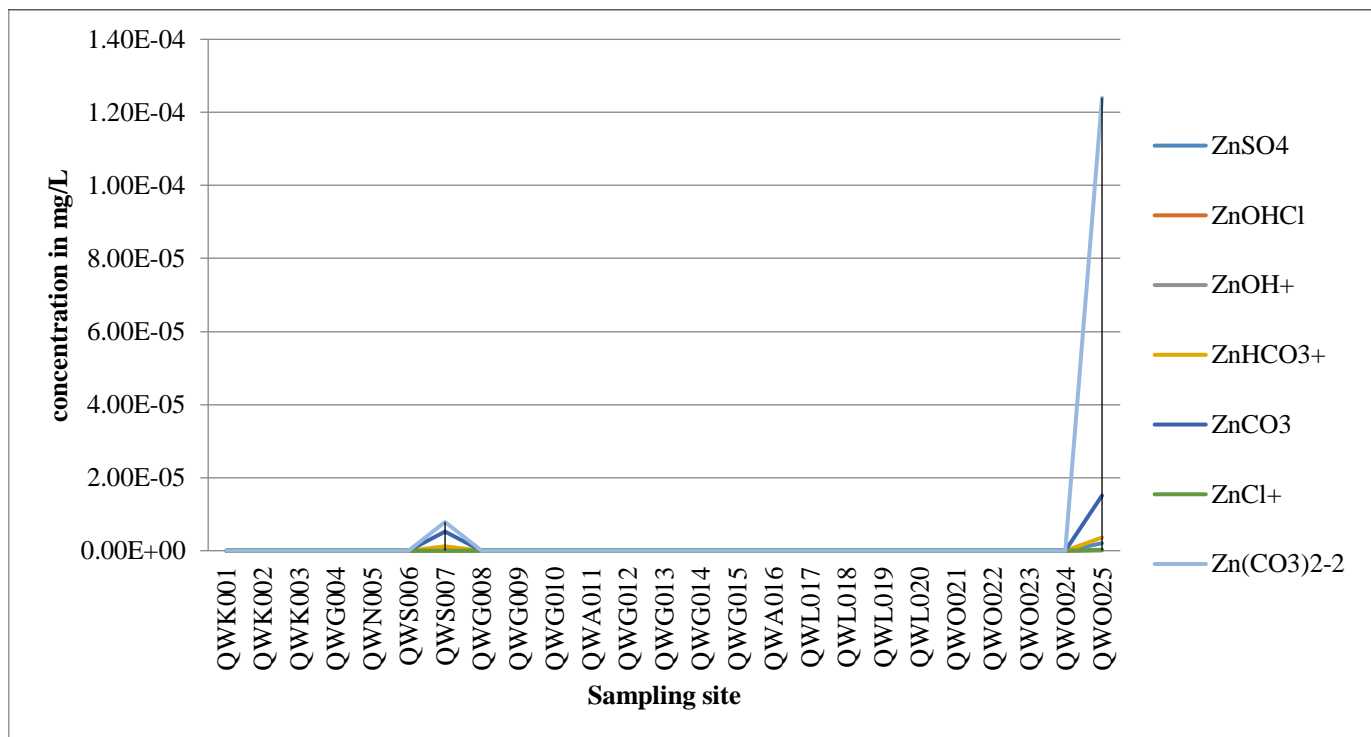
Fig 7: The Abundant Zinc Species in the Sampling Area
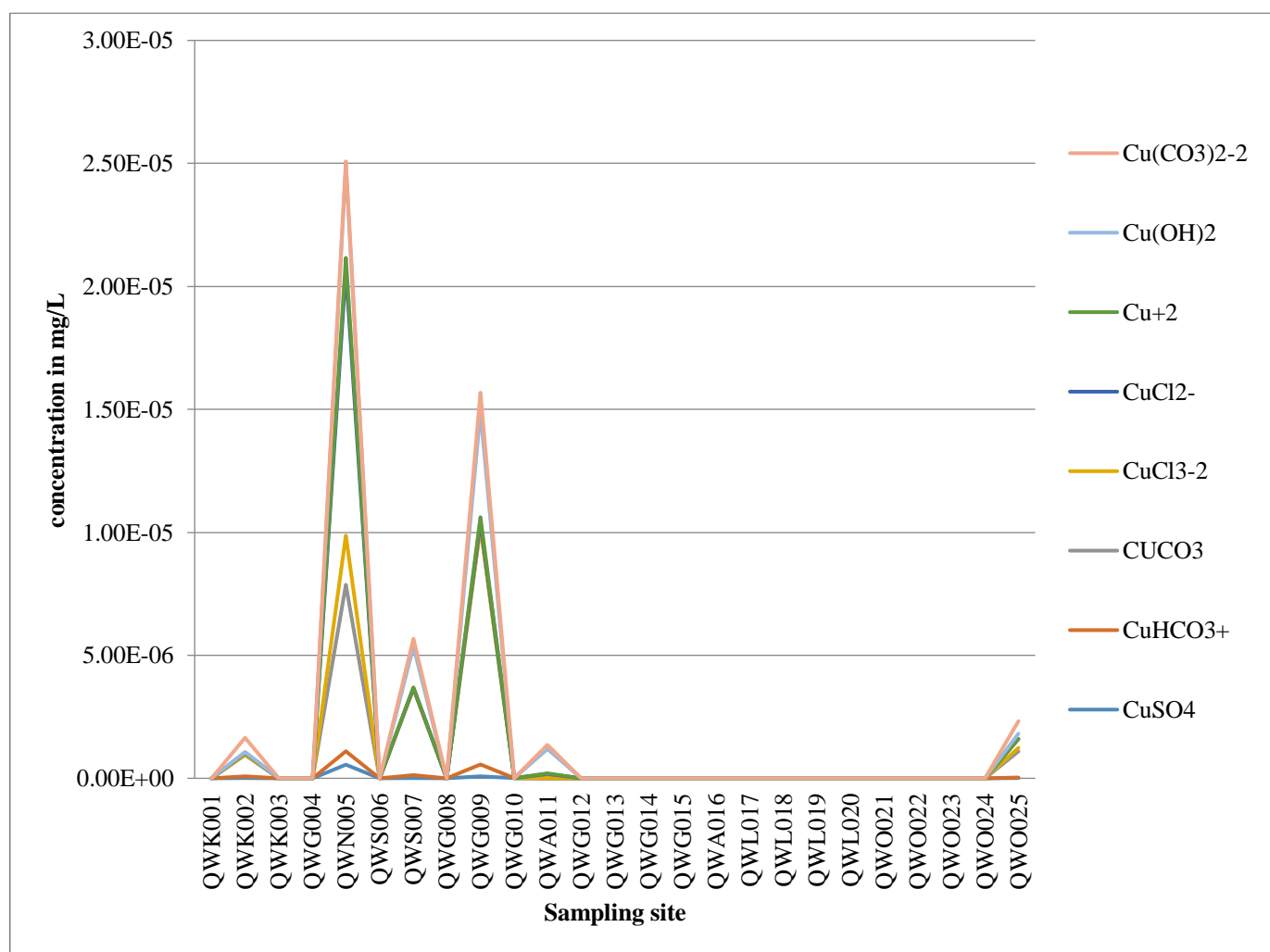
Fig 8: The Abundant Copper Species in the Sampling Site
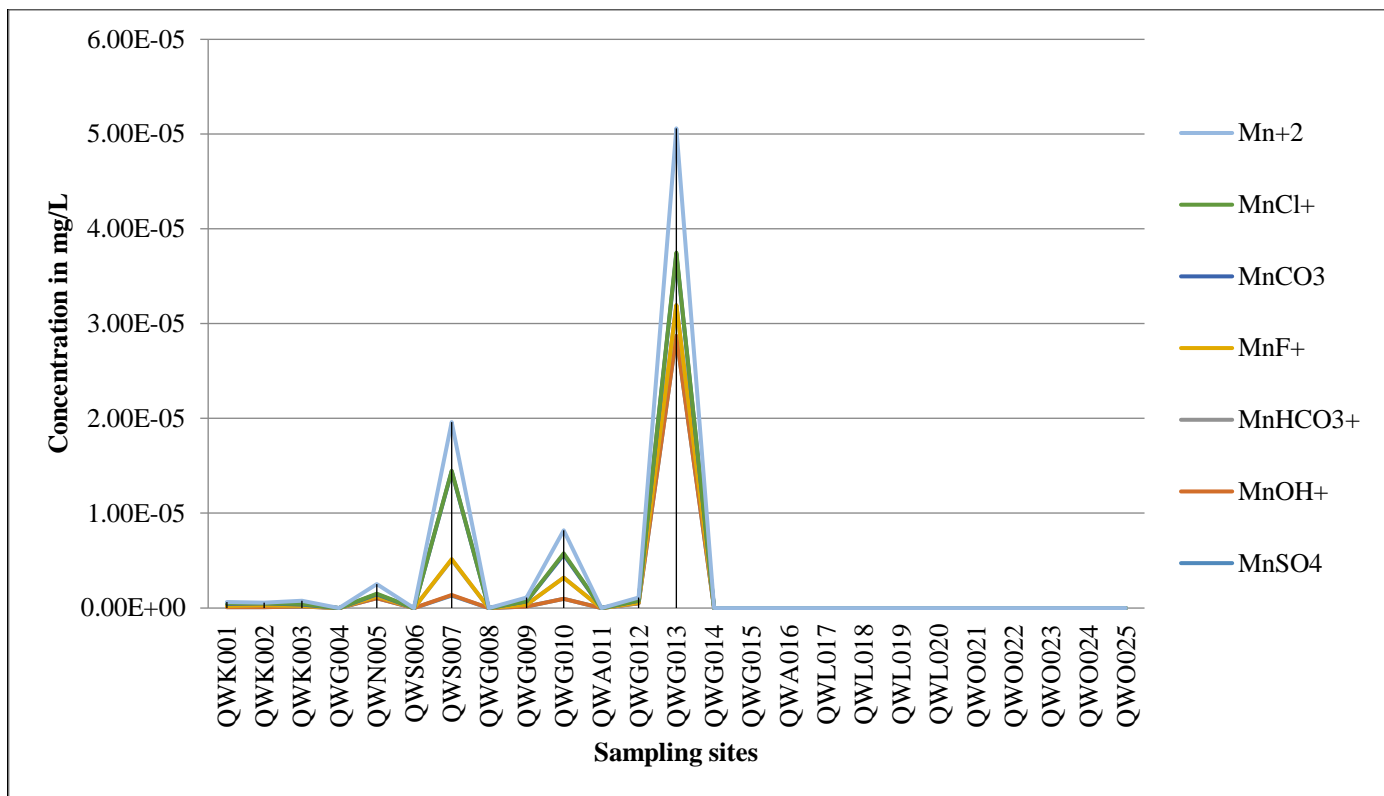
Fig 9: The Abundant Manganese Species in the Sampling Site
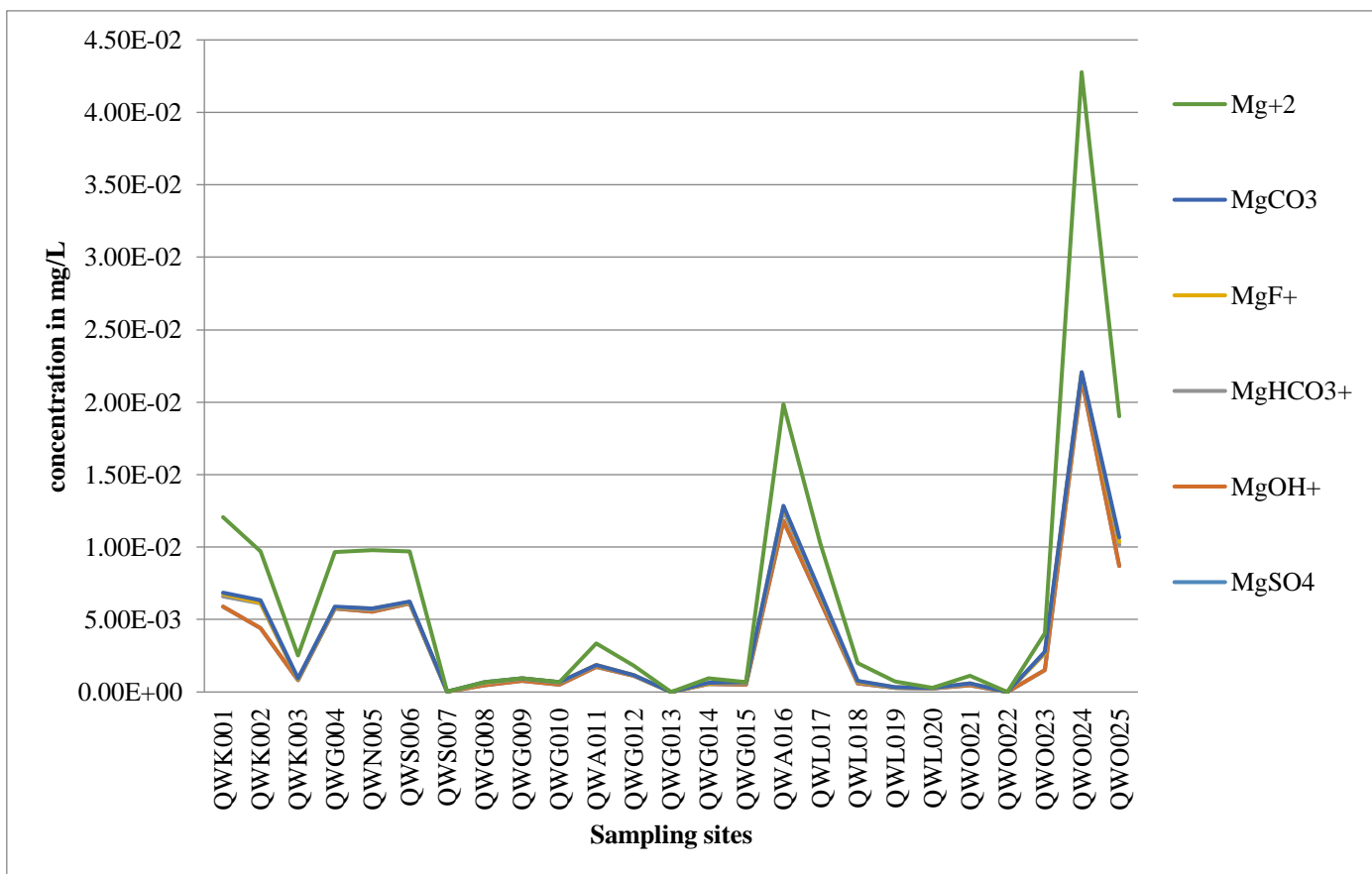
Fig 10: The Abundant Magnesium Species in the Sampling Sites
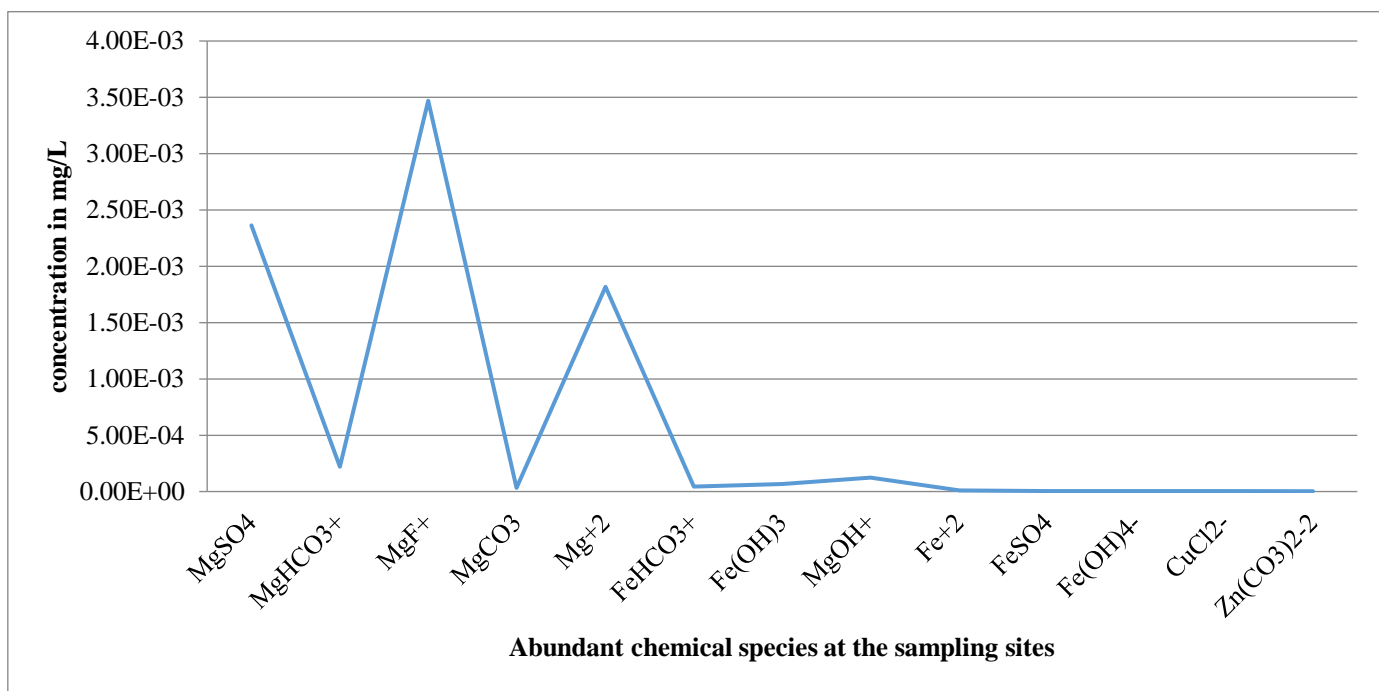
Fig 11: The Abundant Chemical Species in Sampling Sites

G. The Use of Temperature and pH in Simulations and Modeling

Simulation of the chemical species was undertaken using the lowest pH of 4, the highest pH of 10, the lowest temperature of 15°C, and the highest temperature of 35°C. The simulation was run for all the water systems data and output was tabulated in form of curves for all the water systems in the two seasons and comparison for each water system in the two-season done independently by way of curves. As a result, metal adaptive evolution and abundance are affected by determinants like pH, temperature, as well as anion concentrations.

➢ *Modelling the Variation of Concentration of Pollutants Over Varying Conditions of pH and Temperature*

Most simulation models are accustomed to foreseeing the shift of chemical elements through diversified modes such as soil, groundwater, and air in given real-time environmental conditions. Chemical speciation involves an element's steadfastness ahead of the complex formation line, when in fact real-time environmental conditions affect the constituent's ability to form compounds. The concentration of the abundant chemical species in the water systems in given environmental conditions of Temperature and pH was captured into concern in this model. The chemical species in this model were ideal as they formed on their abundance in each water system at a given environmental condition of Temperature and pH.

The x-axis characterizes the varying environmental conditions of pH and temperature set up in the water systems while the y-axis illustrates the pollutants concentrations in the water systems over the modeling duration.

➢ *Simulation based on different pH and Temperature Conditions of Surface, Dam, and Borehole Water Systems*

Surface water pollutant levels are highest during the high-temperature dry season (DS/HT) Figure 12 and lowest during the low pH wet and dry seasons (WS/LP) (DS) Figure 12 Pollutant concentrations in dam water systems are highest during the dry season (DS) and lowest during the wet season (WS) (WS) Figure 12. Contaminant concentrations in the borehole water system are higher during the dry season (DS) but are higher in all water systems during the wet season low-temperature (WS/LT) Figure 12.
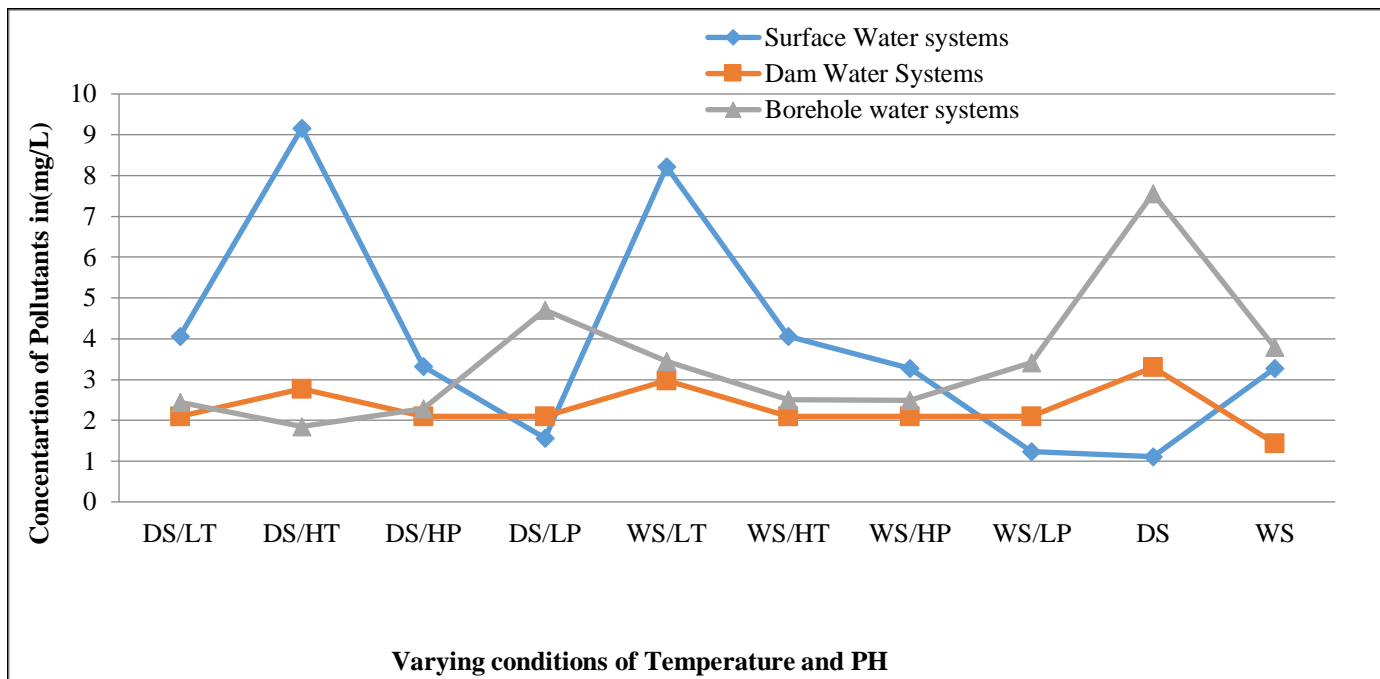
Fig 12: Simulation based on Different pH and Temperature Conditions of the Surface, Dam, and Borehole Water Systems

Figure 12, and Figure 13 WS/LT means wet season-low temperature, WS/HT stands for wet season High-temperature, WS/HP stands for wet season-high pH and WS/LP stands for Wet season Low pH, DS/LT means Dry season-low temperature, DS/HT stands for Dry season High-temperature DS/HP stands for Dry season-high pH and DS/LP stands for Dry season Low pH.

➤ *Simulation based on Different Temperature and pH Conditions in the Sampling Sites.*
    Wet season low temperatures (WS/LT) and a dry season high temperatures (DS/HT) both recorded the highest levels of contamination in the study area (Figure 13), suggesting that these seasons may be times when all water resources are severely polluted. Wet season low pH (WS/LP) may be a time when water systems are less dangerous.
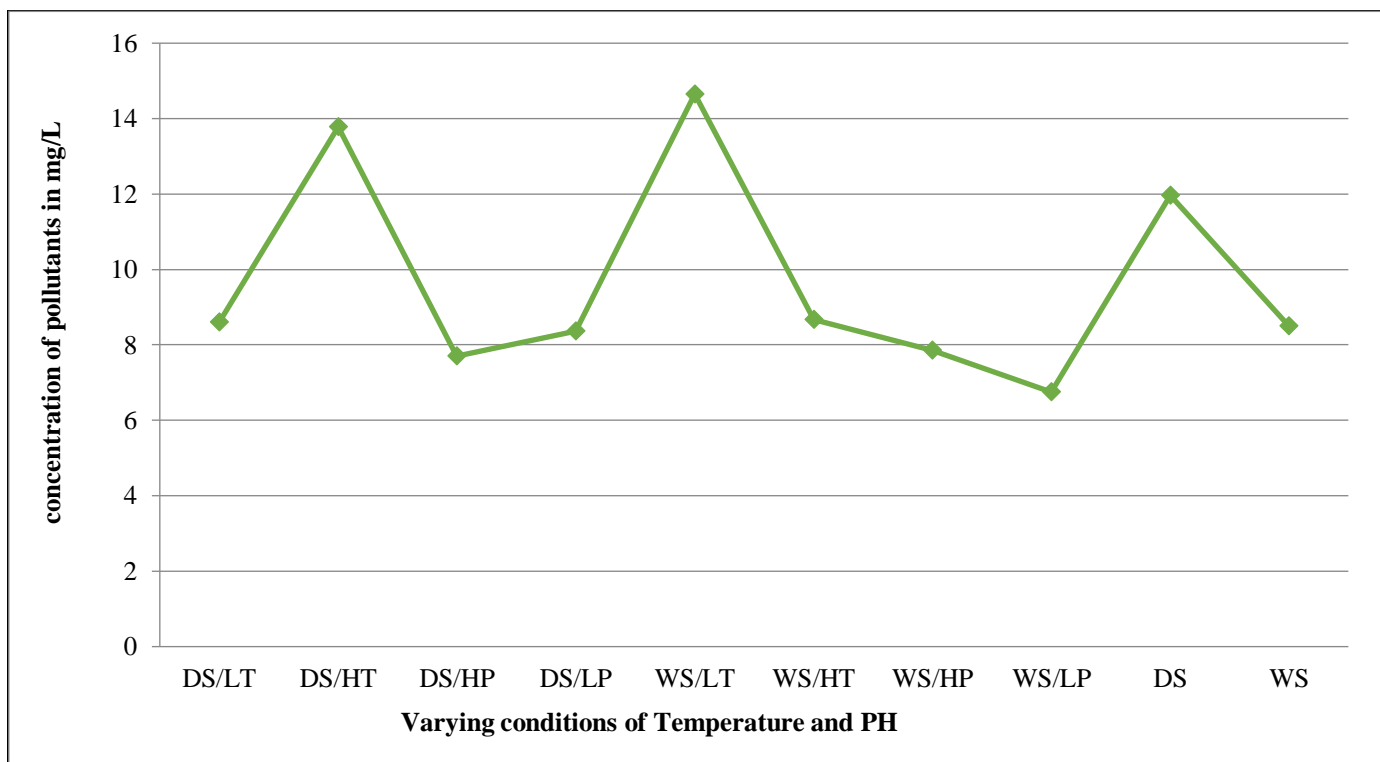
Fig 13: Simulation based on Different pH and Temperature Conditions in the Sampling Area

CHAPTER FIVE
CONCLUSIONS AND RECOMMENDATION

A. Conclusion

The study found that the water's conductivity, temperature, and pH were all within acceptable ranges for naturally occurring water, except for the pH of one borehole (QWG012, during the wet season). The dry season had slightly higher anions concentrations than the wet season, but NO_2^- was not detected. The majority of the determined anions were found to be within recommended limits as compared to F^-, which had 76% dominance in the studied region in the two seasons with exception of only four boreholes that recorded allowable limit (QWG010, QWO022, QWO024, and QWO025) in both seasons. Although the water was found to be soft because the CO_3^- levels were below 60 mg L^{-1}, the presence of slightly elevated levels of F^- is extremely concerning. While Fe was present at above allowable levels in three sites (QWK002, QWN004, and QWA013), Cu, Mn, and Mg had values that were below the maximum recommended limits; Pb was found to be above the maximum allowable limits in five borehole sites (QWG008, QWG011, QWG012, QWA013, QWG015), and Cd was not detected. In light of the parameters, it can be concluded that only four sampling sites (QWG010, QWO022, QWO024, and QWO025) have quality water.

Speciation analysis revealed that in the absence of anions, metal ions easily formed hydroxides. The addition of anions resulted in the formation of chemical species containing chloride, nitrite, carbonates, hydroxyl ions, hydrogen carbonate, and sulfate ions. Water system temperatures of 25 °C without anions produced the highest percentage abundance of chemical species as observed in (e.g QWK001, QWN005). Different metal species at various pH values showed that metal bioavailability is extremely affected by pH (e.g QWN005). Fe, Mn, Zn, Pb, Cd, and Mg were present as free ions as well as several other species, according to speciation studies. However, there is less likely that the water in the study area will become contaminated because of the low concentrations of these metals and the presence of inhibiting chemical operations (sulphate, fluoride, chloride, carbonate, and nitrite). Water systems were simulated using the most common chemical species at ambient temperature and pH for two seasons, with the lowest and highest temperatures being 15 ^{0}C, 35°C, and the lowest and highest pH of 4.0, and 10 respectively. Iron sulfate, magnesium sulfate, magnesium hydrogen carbonate, and lead carbonate compounds were the most prevalent species. Most of the locations had the Fe^{2+} (including all the surface and dam water systems); it is highly soluble its toxicity is related to its bioavailability and signifies a health risk in those water systems. During the wet season, Mn^{2+} was found in many places. Mn^{2+} is immobile posing no problem in the study area. Zn and Pb were divalent elements that mostly formed compounds with carbonates and sulphates. Pb^{2+} emerges to be mobile but on the other hand, causes no concern of pollution as Pb is found to be low (mean below 0.05 mg/L), and furthermore $PbCO_3$ will curb its mobility. Even though some heavy metal concentrations were higher than recommended, the vast majority of them were bound to anions (sulphate, fluoride, chloride, carbonate, and nitrite), which when combined are less portable and toxic than free ions. Nonetheless, traces of free metal ions render the water unfit for domestic and agricultural use. The water systems were more affected by high pH than by high temperatures, which could lead to the waters becoming more acidic, and the presence of more toxic-free metal ions. On the other hand, temperature, and pH are important physicochemical parameters to consider when modeling.

B. Recommendations

PHREEQ C has proven to be a powerful computer-based program for performing speciation analysis, and it is thus recommended for use in this field.

- Speciation analysis should be performed more frequently to get a better understanding of the chemical speciation of heavy metals in any given environment.
- Water quality guidelines should include metal speciation analysis because it provides additional information on heavy metal toxicity and mobility.

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APPENDICES

Appendix 1.1: Showing the PHREEQ C Results for input data Without anions for each of the 25 locations.

Site 1	WET SITE 1	Abundance (%)	DRY SITE 1	Abundance (%)
Mg	1.21E-02	49.9911999	1.21E-02	49.9963536
Mg^{+2}	1.21E-02	49.9911999	1.21E-02	49.99635357
$MgOH^+$	2.44E-06	0.01008087	1.15E-06	0.00475172
Mn(2)	1.82E-06	0.00751934	6.15E-07	0.002541137
Mn^{+2}	1.81E-06	0.00747802	6.15E-07	0.002541137
QWK002	**WET SEASON**	**Abundance (%)**	**DRY SEASON**	**Abundance (%)**
Cu(2)	1.65E-06	0.00826819	4.10E-09	2.00811E-05
$Cu(OH)_2$	1.57E-06	0.00786731	1.64E-06	0.008032437
Cu^{+2}	5.52E-08	0.00027661	1.51E-06	0.00739572
$CuOH^+$	1.81E-08	9.07E-05	1.11E-07	0.000543659
$Cu_2(OH)_2^{+2}$	1.71E-10	8.5689E-07	2.52E-08	0.000123425
Fe(2)	2.78E-05	0.13930654	3.46E-17	1.69465E-13
Fe^{+2}	2.75E-05	0.13780323	4.30E-05	0.210606589
$FeOH^+$	2.64E-07	0.00132291	4.27E-05	0.20913724
$Fe(OH)_2$	8.60E-11	4.3095E-07	3.53E-07	0.001728933
$Fe(OH)_3^{3-}$	1.74E-13	8.7192E-10	1.03E-10	5.04476E-07
$Fe(OH)_3$	3.89E-04	1.94928933	4.57E-04	1.15404E+26
$Fe(OH)^{2+}$	7.55E-05	0.3783325	3.56E-04	1.74362664
$Fe(OH)^{4-}$	1.87E-05	0.0937062	8.78E-05	0.430029267
$FeOH^{+2}$	7.39E-09	3.7031E-05	1.34E-05	0.06563089
Mg	9.70E-03	48.6069576	9.70E-03	47.50892812
Mg^{+2}	9.70E-03	48.6069576	9.70E-03	47.50892812
$MgOH^+$	1.05E-06	0.00526158	9.45E-07	0.004628447
Mn(2)	7.97E-07	0.00399379	5.97E-07	0.002924003
Mn^{+2}	7.96E-07	0.00398878	5.97E-07	0.002924003
Pb	4.29E-06	0.0214973	4.74E-06	0.023215703
Pb^{+2}	4.29E-06	0.0214973	4.74E-06	0.023215703
$PbOH^+$	2.66E-06	0.01332933	2.03E-06	0.00994259
$Pb(OH)_2$	4.29E-08	0.00021497	2.26E-08	0.000110691
QWK003	**WET SEASON**	**Abundance (%)**	**DRY SEASON**	**Abundance (%)**
Mg	2.51E-03	49.9567673	2.51E-03	49.9676249
Mg^{+2}	2.51E-03	49.9567673	2.51E-03	49.9676249
$MgOH^+$	5.82E-07	0.0115836	2.53E-07	0.00503658
Mn(2)	9.99E-07	7.23913043	7.99E-07	0.01590603
Mn^{+2}	9.97E-07	0.01984339	7.98E-07	0.01588612
$MnOH^+$	1.66E-09	3.3039E-05	5.66E-10	1.1268E-05
$Mn(OH)^{3-}$	1.66E-09	3.3039E-05	3.22E-19	6.4102E-15
Mn(3)	3.69E-28	7.3442E-24	3.96E-28	7.8833E-24
Mn^{+3}	3.69E-28	7.3442E-24	3.96E-28	7.8833E-24
Mn(6)	0.00E+00	0	0.00E+00	0
$MnO4^{-2}$	0.00E+00	0	0.00E+00	0
Mn(7)	0.00E+00	0	0.00E+00	0
$MnO4^-$	0.00E+00	0	0.00E+00	0
Pb(2)	5.26E-07	0.01046903	3.47E-07	0.00690787
$PbOH^+$	7.11E-07	0.0141511	7.08E-07	0.01409445
Pb^{+2}	5.26E-07	0.01046903	3.47E-07	0.00690787
QWK004	WET SEASON	Abundance (%)	DRY SEASON	Abundance (%)
Fe(2)	1.39E-05	0.08438345	1.66E-05	0.08438345
Fe^{+2}	1.38E-05	0.083875115	1.65E-05	0.083875115
FeOH+	1.23E-07	0.000665918	1.31E-07	0.000665918
Fe(3)	2.00E-04	0.787917752	1.55E-04	0.787917752
$Fe(OH)_3$	1.60E-04	0.61000084	1.20E-04	0.61000084

$Fe(OH)^{2+}$	3.25E-05	0.15758355	3.10E-05	0.15758355
$Fe(OH)^{4-}$	7.39E-06	0.021858363	4.30E-06	0.021858363
Mg	9.66E-03	49.10506762	9.66E-03	49.10506762
Mg^{+2}	9.66E-03	49.10506762	9.66E-03	49.10506762
$MgOH^+$	9.51E-07	0.004569923	8.99E-07	0.004569923
Pb(2)	3.00E-06	0.016165022	3.18E-06	0.016165022
Pb^{+2}	3.00E-06	0.016165022	3.18E-06	0.016165022
$PbOH^+$	1.86E-06	0.006608342	1.30E-06	0.182072829
$Pb(OH)_2$	3.01E-08	7.06584E-05	1.39E-08	7.06584E-05
Pb_2OH^{+3}	2.15E-10	8.13334E-07	1.60E-10	8.13334E-07
QWN005	**WET SEASON**	**Abundance (%)**	**DRY SEASON**	**Abundance (%)**
Cu(1)	7.28E-09	3.43417E-05	6.51E-08	0.000307431
Cu^+	7.28E-09	3.43417E-05	6.51E-08	0.000307431
Cu(2)	2.55E-05	0.120290444	2.52E-05	0.119005632
$Cu(OH)_2$	2.51E-05	0.118403535	2.28E-05	0.107671762
Cu^{+2}	2.02E-07	0.000952889	1.76E-06	0.008311504
$CuOH^+$	1.39E-07	0.000655701	3.90E-07	0.001841754
$Cu_2(OH)_2^{+2}$	9.99E-09	4.71256E-05	1.07E-07	0.000505302
Fe(2)	5.25E-06	0.02476568	7.18E-05	0.339071602
Fe^{+2}	5.15E-06	0.024293952	7.12E-05	0.336238135
$FeOH^+$	1.03E-07	0.000485879	5.75E-07	0.002715406
Fe(3)	7.90E-04	3.72664512	7.14E-04	7.338129496
$Fe(OH)_3$	6.62E-04	3.122834265	5.54E-04	2.616234926
$Fe(OH)^{4-}$	6.65E-05	0.313698608	1.40E-04	0.6611424
$Fe(OH)^{2+}$	6.15E-05	0.290112247	2.03E-05	0.095865648
$FeOH^{+2}$	2.89E-09	1.36329E-05	1.82E-08	0.657039711
Mg	9.77E-03	46.08775041	9.77E-03	46.13829463
Mg^{+2}	9.77E-03	46.08775041	9.77E-03	46.13829463
$MgOH^+$	2.20E-06	0.010377999	9.28E-07	0.00438243
Mn(2)	2.74E-06	0.012925326	2.54E-06	0.011995012
Mn^{+2}	2.74E-06	0.012925326	2.54E-06	0.011995012
Pb(2)	2.90E-06	0.01368009	1.63E-06	0.007697587
$PbOH^+$	3.74E-06	0.017642598	3.92E-06	0.018511987
Pb+2	2.90E-06	0.01368009	1.63E-06	0.007697587
QWS006	**WET SEASON**	**Abundance (%)**	**DRY SEASON**	**Abundance (%)**
Fe(2)	1.06E-05	0.053237496	2.79E-06	0.014012511
Fe^{+2}	1.05E-05	0.052735256	2.74E-06	0.013783389
$FeOH^+$	1.05E-07	0.000527353	4.45E-08	0.000223854
Fe(3)	2.09E-04	1.049682713	2.01E-04	1.011117224
$Fe(OH)_3$	1.69E-04	0.8487865	1.67E-04	0.84008247
$Fe(OH)^{2+}$	3.14E-05	0.157703527	2.17E-05	0.109160417
$Fe(OH)^{4-}$	8.52E-06	0.042790893	1.19E-05	0.059862164
Mg	9.73E-03	48.86800383	9.73E-03	48.94612233
Mg^{+2}	9.73E-03	48.86800383	9.73E-03	48.94612233
$MgOH^+$	1.10E-06	0.005524646	1.88E-06	0.009457216
Pb(2)	3.97E-06	0.019938949	3.56E-06	0.017908345
Pb^{+2}	3.97E-06	0.019938949	3.56E-06	0.017908345
$PbOH^+$	2.57E-06	0.012907582	2.77E-06	0.013934302
$Pb(OH)_2$	4.35E-08	0.000218475	5.62E-08	0.00028271
QWS007	**WET SEASON**	**Abundance (%)**	**DRY SEASON**	**Abundance (%)**
Cu(1)	4.86E-09	0.001545934	2.96E-09	0.000951885
Cu^+	4.86E-09	0.001545934	2.96E-09	0.000951885
Cu(2)	5.88E-06	1.870389562	5.68E-06	1.826589762
$Cu(OH)_2$	5.73E-06	1.822675542	5.58E-06	1.794431491
Cu^{+2}	9.83E-08	0.031268587	6.04E-08	0.019423595
$CuOH^+$	5.09E-08	0.016190957	3.94E-08	0.012670359

Mg	1.16E-04	36.8988417	1.15E-04	36.98201102
Mg^{+2}	1.16E-04	36.8988417	1.15E-04	36.98201102
$MgOH^+$	2.17E-08	0.006902628	2.49E-08	0.008007409
Mn(2)	1.98E-05	6.298250566	1.96E-05	6.303021009
Mn^{+2}	1.98E-05	6.298250566	1.96E-05	6.303021009
$MnOH^+$	2.63E-08	0.008365858	3.02E-08	0.009711798
Zn(2)	1.48E-05	4.707783251	1.43E-05	4.598632675
Zn^{+2}	1.48E-05	4.707783251	1.43E-05	4.598632675
$ZnOH^+$	8.38E-07	0.266562322	9.46E-07	0.304217238
$Zn(OH)_2$	5.18E-07	0.164772414	7.95E-07	0.25565825
$Zn(OH)^{3-}$	9.19E-11	2.92328E-05	1.77E-10	5.69201E-05
QWG008	**WET SEASON**	**Abundance (%)**	**DRY SEASON**	**Abundance (%)**
Mg	1.50E-03	49.65056063	1.50E-03	49.63719453
Mg^{+2}	1.50E-03	49.65056063	1.50E-03	49.63719453
$MgOH^+$	5.49E-07	0.018172105	4.76E-07	0.015751536
Pb(2)	4.82E-06	0.159543801	5.94E-06	0.19656329
$PbOH^+$	1.04E-05	0.344243887	9.23E-06	0.305434204
Pb^{+2}	4.82E-06	0.159543801	5.94E-06	0.19656329
$Pb(OH)_2$	4.99E-07	0.016517087	3.23E-07	0.010688543
$Pb_3(OH)_4^{+2}$	2.37E-08	0.000784479	1.65E-08	0.000546009
Pb_2OH^{+3}	1.42E-09	4.70025E-05	1.56E-09	5.16227E-05
$Pb(OH)^{3-}$	8.03E-10	2.65796E-05	3.76E-10	1.24424E-05
QWG009	**WET SEASON**	**Abundance (%)**	**DRY SEASON**	**Abundance (%)**
Cu(2)	1.56E-05	0.305349349	1.54E-05	0.301294524
$Cu(OH)_2$	1.54E-05	0.301434614	1.48E-05	0.289555776
Cu^{+2}	1.56E-07	0.003053493	4.14E-07	0.008099736
$CuOH^+$	1.00E-07	0.001957368	1.60E-07	0.003130333
Fe(2)	8.63E-07	0.016892083	2.58E-06	0.050476615
Fe^{+2}	8.48E-07	0.016598477	2.55E-06	0.049889678
Fe(3)	6.70E-05	1.311436306	6.72E-05	1.314739742
$Fe(OH)_3$	5.65E-05	1.105912705	5.50E-05	1.076051872
$Fe(OH)^{2+}$	6.49E-06	0.127033159	9.61E-06	0.188015609
$Fe(OH)^{4-}$	4.06E-06	0.079469125	2.59E-06	0.050672261
$FeOH^{+2}$	3.32E-10	6.49846E-06	7.58E-10	1.483E-05
Mg	2.46E-03	48.15124346	2.46E-03	48.12886555
Mg^{+2}	2.46E-03	48.15124346	2.46E-03	48.12886555
$MgOH^+$	4.75E-07	0.009297496	3.43E-07	0.006710651
Mn(2)	1.31E-06	0.025641516	1.11E-06	0.021716683
Mn^{+2}	1.30E-06	0.025445779	1.10E-06	0.021521037
Pb(2)	5.81E-06	0.113723059	5.51E-06	0.107800833
$PbOH^+$	7.18E-06	0.140538995	7.40E-06	0.144777888
Pb^{+2}	5.81E-06	0.113723059	5.51E-06	0.107800833
QWG010	**WET SEASON**	**Abundance (%)**	**DRY SEASON**	**Abundance (%)**
Cu(1)	6.09E-11	1.68936E-06	3.04E-11	8.41079E-07
Cu+	6.09E-11	1.68936E-06	3.04E-11	8.41079E-07
Cu(2)	1.13E-07	0.003134612	1.20E-08	0.000332005
$Cu(OH)_2$	1.11E-07	0.003079132	1.11E-08	0.000307104
Cu^{+2}	1.42E-09	3.93907E-05	6.81E-10	1.88413E-05
$CuOH^+$	8.17E-10	2.26635E-05	1.79E-10	4.95241E-06
Fe(2)	1.90E-06	0.05270587	8.45E-06	0.23378674
Fe^{+2}	1.87E-06	0.051873672	8.37E-06	0.231573374
$FeOH^+$	2.94E-08	0.000815554	8.07E-08	0.002232733
Fe(3)	1.03E-04	2.857212931	1.02E-04	2.822041117
$Fe(OH)_3$	8.61E-05	2.388408091	8.00E-05	2.213365582
$Fe(OH)^{2+}$	1.12E-05	0.310687231	1.92E-05	0.53120774
$Fe(OH)^{4-}$	5.33E-06	0.147853834	2.66E-06	0.073594406

$FeOH^{+2}$	6.38E-10	1.76981E-05	2.05E-09	5.67175E-05
Mg	1.68E-03	46.6030847	1.68E-03	46.48067722
Mg^{+2}	1.68E-03	46.6030847	1.68E-03	46.48067722
$MgOH^+$	2.92E-07	0.00810006	1.91E-07	0.00528441
Mn(2)	8.02E-06	0.22247425	8.22E-06	0.227423314
Mn^{+2}	8.01E-06	0.22219685	8.22E-06	0.227423314
$MnOH^+$	1.01E-08	0.000280173	6.53E-09	0.000180666
$Mn(OH)^{3-}$	3.50E-17	9.70898E-13	3.43E-18	9.4898E-14
Pb(2)	6.02E-06	0.166994387	4.27E-06	0.118138388
$PbOH^+$	6.71E-06	0.186134939	8.39E-06	0.232126715
Pb^{+2}	6.02E-06	0.166994387	4.27E-06	0.118138388
Pb(OH)2	1.69E-07	0.004688048	4.92E-08	0.00136122
$Pb_3(OH)_4^{+2}$	2.93E-09	8.1278E-05	1.04E-09	2.87738E-05
Pb_2OH^{+3}	1.16E-09	3.21783E-05	6.28E-10	1.73749E-05
QWG011	**WET SEASON**	**Abundance (%)**	**DRY SEASON**	**Abundance (%)**
Cu(1)	3.73E-10	5.51802E-06	3.08E-09	4.55569E-05
Cu+	3.73E-10	5.51802E-06	3.08E-09	4.55569E-05
Cu(2)	3.72E-06	0.05503227	3.52E-06	0.052065019
Cu(OH)2	3.70E-06	0.054736398	3.41E-06	0.050437987
CuOH+	1.17E-08	0.000173085	7.54E-08	0.001115256
Cu+2	8.98E-09	0.000132847	3.24E-08	0.000479235
Mg	3.37E-03	49.85450284	3.37E-03	49.8463389
Mg+2	3.36E-03	49.70656663	3.36E-03	49.69842691
MgOH+	1.73E-06	0.025592964	4.77E-07	0.007055402
Pb(2)	4.40E-06	0.065091932	7.20E-06	0.106496629
PbOH+	1.10E-05	0.162729831	8.71E-06	0.128831339
Pb+2	4.40E-06	0.065091932	7.20E-06	0.106496629
Pb(OH)2	6.48E-07	0.009586266	1.41E-07	0.002085559
Pb3(OH)4+2	4.93E-08	0.000729326	3.42E-09	5.05859E-05
Pb2OH+3	1.53E-09	2.26342E-05	1.99E-09	2.94345E-05
QWG012	**WET SEASON**	**Abundance (%)**	**DRY SEASON**	**Abundance (%)**
Mg	1.82E-03	49.59654032	1.82E-03	49.68940161
Mg+2	1.80E-03	49.05152339	1.82E-03	49.68940161
MgOH+	1.08E-05	0.29430914	2.43E-07	0.006634354
Mn(2)	1.35E-06	0.036788643	1.15E-06	0.031397149
Mn+2	1.29E-06	0.035153592	1.15E-06	0.031397149
MnOH+	5.48E-08	0.001493346	1.09E-09	2.9759E-05
Pb	1.85E-05	0.504140657	1.01E-05	0.275748877
PbOH+	9.82E-06	0.267603311	5.85E-06	0.159715934
Pb(OH)2	7.13E-06	0.194298534	4.19E-06	0.114394831
Pb3(OH)4+2	3.59E-07	0.009783054	6.81E-08	0.001859257
Pb+2	3.07E-07	0.00836601	7.13E-10	1.94662E-05
QWA013	**WET SEASON**	**Abundance (%)**	**DRY SEASON**	**Abundance (%)**
Fe(2)	2.67E-05	1.16925754	7.85E-06	0.341022835
Fe^{+2}	2.63E-05	1.151740573	7.66E-06	0.332768779
$FeOH^+$	4.01E-07	0.017560759	1.85E-07	0.008036844
$Fe(OH)_2$	1.69E-10	7.40092E-06	1.27E-10	5.51718E-06
$Fe(OH)^{3-}$	3.47E-13	1.5196E-08	3.39E-13	1.4727E-08
Fe(3)	1.05E-03	45.98203807	1.08E-03	46.91779136
$Fe(OH)_3$	8.76E-04	38.36215748	9.19E-04	15090.31199
$Fe(OH)^{2+}$	1.32E-04	5.780599072	9.62E-05	4.179158823
$Fe(OH)^{4-}$	4.30E-05	1.88307394	6.39E-05	2.775969322
$FeOH^{+2}$	7.95E-09	0.00034815	4.10E-09	0.000178114
Fe^{+3}	2.60E-14	1.1386E-09	8.86E-15	3.849E-10
Mn(2)	5.08E-05	2.224654794	5.06E-05	2.19818541
Mn^{+2}	5.08E-05	2.224654794	5.05E-05	2.19384117

MnOH$^+$	6.25E-08	0.002737026	1.00E-07	0.00434424
Pb(2)	9.10E-06	0.398510997	7.89E-06	0.342760531
PbOH$^+$	9.22E-06	0.403766087	1.01E-05	0.438768234
Pb^{+2}	9.10E-06	0.398510997	7.89E-06	0.342760531
Pb$_3$(OH)$_4^{+2}$	6.71E-09	0.000293847	1.75E-08	0.000760242
Pb$_2$OH^{+3}	2.02E-09	8.84607E-05	1.91E-09	8.2975E-05
QWG014	**WET SEASON**	**Abundance (%)**	**DRY SEASON**	**Abundance (%)**
Mg	9.67E-04	49.5159179	9.65E-04	49.57151324
Mg^{+2}	9.66E-04	49.46471219	9.65E-04	49.57151324
MgOH$^+$	1.36E-07	0.006963976	1.65E-07	0.008475958
Pb(2)	7.15E-06	0.366120799	6.09E-06	0.312839913
Pb^{+2}	7.15E-06	0.366120799	6.09E-06	0.312839913
PbOH$^+$	5.38E-06	0.275486699	4.27E-06	0.219347525
Pb(OH)$_2$	8.90E-08	0.004557308	6.59E-08	0.003385246
Pb$_3$(OH)$_4^{+2}$	1.30E-09	6.65674E-05	9.46E-10	4.85955E-05
Pb$_2$OH^{+3}	1.05E-09	5.3766E-05	7.08E-10	3.63696E-05
QWG015	**WET SEASON**	**Abundance (%)**	**DRY SEASON**	**Abundance (%)**
Fe(2)	1.17E-06	0.758461789	2.39E-06	0.073227999
Fe+2	1.15E-06	0.74549663	2.36E-06	0.072308819
FeOH+	1.84E-08	0.011927946	2.78E-08	0.000851773
Fe(3)	4.55E-05	29.49573622	5.41E-05	1.657587756
Fe(OH)3	3.77E-05	24.4393243	4.42E-05	1.354258389
Fe(OH)2+	6.22E-06	4.032164381	7.95E-06	0.243582674
Fe(OH)4-	1.63E-06	1.056660441	1.97E-06	0.06035948
Mg(2)	5.05E-06	3.273702592	1.55E-03	47.49096159
Mg+2	5.05E-06	3.273702592	1.55E-03	47.49096159
MgOH+	9.73E-10	0.000630755	2.06E-07	0.006311702
Pb(2)	1.81E-05	11.7334687	1.81E-05	0.554571874
Pb+2	1.81E-05	11.7334687	1.81E-05	0.554571874
PbOH+	1.43E-05	9.270088528	1.41E-05	0.432014554
Pb(OH)2	2.30E-07	0.149099326	2.46E-07	0.007537275
Pb3(OH)4+2	3.41E-08	0.022105596	2.17E-08	0.000664873
Pb2OH+3	6.00E-09	0.003889548	7.29E-09	0.000223361
Pb(OH)3-	1.11E-10	7.19566E-05	1.44E-10	4.41206E-06
Pb(OH)4-2	1.09E-14	7.06601E-09	1.90E-14	5.82147E-10
QWA016	**WET SEASON**	**Abundance (%)**	**DRY SEASON**	**Abundance (%)**
Mg	4.49E-06	18.37828953	1.98E-02	49.97801851
Mg+2	4.49E-06	18.37828953	1.98E-02	49.97801851
MgOH+	2.73E-09	0.011174327	2.12E-06	0.005351182
Pb(2)	2.82E-06	11.54271191	3.83E-06	0.009667465
PbOH+	9.18E-06	37.5752111	7.58E-06	0.019132999
Pb+2	2.82E-06	11.54271191	3.83E-06	0.009667465
Pb(OH)2	6.03E-07	2.468175631	5.50E-08	0.000138828
Pb3(OH)4+2	2.35E-08	0.096189266	1.34E-09	3.38235E-06
Pb(OH)3-	1.18E-09	0.004829929	6.21E-10	1.56749E-06
Pb2OH+3	5.90E-10	0.002414965	3.41E-11	8.60733E-08
Pb(OH)4-2	4.67E-13	1.91151E-06	6.01E-15	1.51701E-11
QWL017	**WET SEASON**	**Abundance (%)**	**DRY SEASON**	**Abundance (%)**
Mg	6.46E-06	43.66103649	1.03E-02	49.98987671
Mg+2	6.46E-06	43.66103649	1.03E-02	49.98987671
MgOH+	5.42E-09	0.036632015	2.12E-06	0.010289179
Pb(2)	2.70E-07	1.824842082	6.56E-07	0.003183821
PbOH+	1.22E-06	8.245582742	7.24E-07	0.003513852
Pb+2	2.70E-07	1.824842082	6.56E-07	0.003183821
Pb(OH)2	1.10E-07	0.743454182	1.56E-08	7.57128E-05
Pb(OH)3-	2.98E-10	0.002014085	1.87E-11	9.07583E-08

Pb3(OH)	7.52E-11	0.000508252	1.47E-11	7.13448E-08
Pb2OH+3	7.47E-12	5.04873E-05	5.51E-12	2.67422E-08
Pb(OH)4-2	1.62E-13	1.09491E-06	3.63E-15	1.76178E-11
QWL018	**WET SEASON**	**Abundance (%)**	**DRY SEASON**	**Abundance (%)**
Mg	5.50E-06	49.99661387	2.01E-03	49.99410517
Mg+2	5.50E-06	49.99661387	2.01E-03	49.99410517
MgOH+	7.45E-10	0.006772269	4.74E-07	0.011789655
QWL019	**WET SEASON**	**Abundance (%)**	**DRY SEASON**	**Abundance (%)**
Mg	5.99E-06	49.99478352	7.47E-04	49.99641927
Mg+2	5.99E-06	49.99478352	7.47E-04	49.99641927
MgOH+	1.25E-09	0.010432968	1.07E-07	0.007161468
QWL020	**WET SEASON**	**Abundance (%)**	**DRY SEASON**	**Abundance (%)**
Mg	4.98E-06	49.9956028	6.19E-04	49.99604232
Mg+2	4.98E-06	49.9956028	6.19E-04	49.99604232
MgOH+	8.76E-10	0.008794407	9.80E-08	0.007915367
QWO021	**WET SEASON**	**Abundance (%)**	**DRY SEASON**	**Abundance (%)**
Mg	3.64E-06	49.98969992	1.11E-03	49.99547338
Mg+2	3.64E-06	49.98969992	1.11E-03	49.99547338
MgOH+	1.50E-09	0.020600151	2.01E-07	0.009053234
QWO022	**WET SEASON**	**Abundance (%)**	**DRY SEASON**	**Abundance (%)**
Mg	5.01E-06	49.99346393	1.11E-39	7.2549E-27
Mg+2	5.01E-06	49.99346393	5.55E-40	3.62745E-27
MgOH+	1.31E-09	0.001110169	1.53E-11	100
QWO023	**WET SEASON**	**Abundance (%)**	**DRY SEASON**	**Abundance (%)**
Mg	5.24E-06	50.03700255	4.06E-03	49.99790649
Mg+2	5.23E-06	49.94151209	4.06E-03	49.99790649
MgOH+	2.25E-09	0.021485354	3.40E-07	0.004187017
QWGO024	**WET SEASON**	**Abundance (%)**	**DRY SEASON**	**Abundance (%)**
Pb	6.85E-06	99.20489804	2.19E-06	14.14590421
Pb(OH)2	5.44E-08	0.787846198	6.65E-06	42.954458
Pb2OH+3	2.60E-10	0.003765441	5.27E-06	34.04060055
Pb3(OH)4+2	2.13E-10	0.003084765	1.36E-06	8.784671111
Pb(OH)3-	2.80E-11	0.000405509	1.11E-08	0.071698419
Pb(OH)4-2	2.90E-15	4.19992E-08	4.13E-10	0.002667698
QWO025	**WET SEASON**	**Abundance (%)**	**DRY SEASON**	**Abundance (%)**
Cu(1)	5.58E-10	0.000176202	1.18E-09	3.07924E-06
Cu+	5.58E-10	0.000176202	1.18E-09	3.07924E-06
Cu(2)	2.53E-06	0.79890842	2.33E-06	0.006080194
Cu(OH)2	2.51E-06	0.792592938	2.27E-06	0.005923623
CuOH+	1.14E-08	0.003599825	3.55E-08	9.26382E-05
Cu+2	1.12E-08	0.00353667	1.70E-08	4.43619E-05
Cu2(OH)2+2	5.89E-11	1.85991E-05	1.98E-10	5.16686E-07
Mg	8.97E-07	0.283249349	1.90E-02	49.58098178
Mg+2	8.97E-07	0.283249349	1.90E-02	49.58098178
MgOH+	3.30E-10	0.000104205	3.56E-06	0.00928991
Mn(2)	2.97E-07	0.093784901	9.71E-08	0.000253385
Mn+2	2.96E-07	0.093469127	9.70E-08	0.000253124
Pb	7.62E-06	2.406198482	7.42E-06	0.019362678
PbOH+	4.92E-06	1.553608469	3.89E-06	0.010151054
Pb+2	2.49E-06	0.786277457	3.44E-06	0.008976767
Pb(OH)2	2.01E-07	0.06347059	8.60E-08	0.000224419
Zn	1.47E-04	46.41878961	1.49E-04	0.388819278
Zn+2	1.18E-04	37.26134132	1.36E-04	0.354895449
Zn(OH)2	1.59E-05	5.020807856	7.66E-06	0.019988964
ZnOH+	1.31E-05	4.136640434	5.24E-06	0.013673913

Appendix 1.2: PHREEQ C Results for Dry Season (DS) and Wet season(WS) with variations of Temperature and pH

QWK001										
	DS/LT	DS/HT	DS/HP	DS/LP	WS/LT	WS/HT	WS/HP	WS/LP	DS	WS
C(4)	3.06E-02	3.06E-02	3.06E-02	3.06E-02	4.37E-02	3.06E-02	3.06E-02	3.06E-02	5.91E-03	6.00E-03
HCO3-	2.84E-02	2.86E-02	1.80E-02	2.39E-02	3.84E-02	2.88E-02	1.42E-02	2.08E-02	5.21E-03	5.00E-03
CO2	1.23E-03	2.86E-02	8.39E-03	6.46E-03	3.25E-02	6.88E-04	1.15E-02	9.50E-03	1.24E-03	6.77E-04
MgHCO3+	7.60E-04	2.86E-02	3.81E-03	1.65E-04	3.25E-02	6.41E-04	4.63E-03	2.34E-04	6.96E-04	2.38E-04
CO3-2	1.01E-04	2.86E-02	3.04E-04	2.60E-06	3.06E-02	2.19E-04	2.09E-04	3.05E-06	1.58E-04	1.53E-04
MgCO3	6.70E-05	2.86E-02	9.62E-06	9.32E-07	2.88E-02	1.46E-04	9.83E-06	1.88E-06	8.82E-05	6.21E-06
PbCO3	7.58E-06	2.86E-02	6.54E-06	2.87E-07	1.21E-02	6.30E-06	3.03E-06	7.34E-07	7.22E-06	3.77E-06
Pb(CO3)2-2	2.03E-06	2.86E-02	5.97E-07	2.12E-07	5.75E-03	3.67E-06	1.78E-06	5.33E-07	2.50E-06	1.82E-06
PbHCO3+	2.71E-07	2.86E-02	4.30E-07	6.44E-08	5.23E-03	8.13E-07	3.20E-07	2.60E-07	6.15E-07	8.27E-07
MnCO3	1.78E-07	2.86E-02	4.18E-09	9.42E-10	1.88E-03	3.41E-07	7.25E-09	6.52E-09	3.72E-07	7.55E-07
MnHCO3+	1.56E-07	2.86E-02	1.23E-10	7.12E-10	7.54E-04	1.08E-07	5.32E-11	3.67E-09	2.04E-07	3.38E-07
Cl	3.05E-02	2.86E-02	3.05E-02	3.05E-02	2.23E-04	3.25E-02	3.25E-02	3.25E-02	2.03E-07	3.33E-07
Cl-	3.05E-02	2.86E-02	3.05E-02	3.05E-02	1.71E-02	3.25E-02	3.25E-02	3.25E-02	1.43E-07	2.99E-07
PbCl+	1.04E-08	2.86E-02	3.12E-10	5.68E-07	1.12E-04	1.70E-08	7.34E-10	5.19E-07	1.40E-07	1.02E-07
MnCl+	7.43E-09	2.86E-02	9.55E-12	1.65E-08	1.02E-05	5.73E-09	6.04E-12	3.94E-08	1.22E-07	3.19E-08
PbCl2	3.61E-10	2.86E-02	2.31E-12	1.35E-08	6.81E-06	1.70E-10	5.72E-12	1.51E-08	6.51E-08	2.67E-08
MnCl2	5.63E-11	2.86E-02	2.67E-13	3.96E-10	3.10E-06	1.36E-10	1.68E-13	3.93E-10	3.40E-08	2.21E-08
PbCl3-	8.11E-12	2.86E-02	1.95E-14	1.04E-10	1.82E-06	4.37E-12	5.13E-14	3.22E-10	2.74E-08	1.66E-08
MnCl3-	4.74E-13	2.86E-02	6.40E-15	9.18E-12	7.32E-07	1.22E-12	4.37E-15	9.98E-12	2.49E-08	1.25E-08
PbCl4-2	1.75E-13	2.86E-02	1.52E-16	8.76E-13	3.91E-07	1.10E-13	1.14E-16	2.88E-12	1.32E-08	8.63E-09

QWK002										

QWK003										
	DS/LT	DS/HT	DS/HP	DS/LP	WS/LT	WS/HT	WS/HP	WS/LP	DS	WS
C(4)	7.40E-03	7.40E-03	7.40E-03	7.40E-03	7.40E-03	7.40E-03	7.40E-03	7.40E-03	5.55E+01	1.60E-03
HCO3-	6.84E-03	6.93E-03	5.44E-03	6.28E-03	7.11E-03	7.12E-03	3.85E-03	5.00E-03	6.59E-02	7.64E-04
CO2	4.76E-04	3.87E-04	1.53E-03	1.11E-03	3.00E-03	1.49E-04	2.90E-03	2.38E-03	1.10E-02	7.64E-04
MgHCO3+	6.33E-05	5.98E-05	3.90E-04	9.85E-06	3.00E-03	6.11E-05	6.26E-04	2.09E-05	6.92E-03	7.52E-05
CO3-2	1.40E-05	1.98E-05	3.97E-05	1.03E-07	2.51E-03	5.30E-05	2.48E-05	2.13E-07	2.50E-03	6.11E-05
MgCO3	3.95E-06	6.06E-06	3.06E-06	3.06E-08	1.72E-03	1.55E-05	1.11E-06	1.75E-07	1.59E-03	1.55E-05
PbCO3	9.10E-07	9.22E-07	8.47E-07	2.72E-08	1.70E-03	1.07E-06	9.60E-07	1.48E-07	1.05E-03	1.07E-06
MnHCO3+	1.16E-07	1.17E-07	7.43E-07	2.33E-08	1.63E-03	3.14E-07	8.04E-07	6.03E-08	8.08E-04	3.85E-07
MnCO3	9.26E-08	1.07E-07	2.09E-07	9.73E-09	6.49E-04	1.50E-07	1.44E-07	5.34E-08	3.91E-04	3.14E-07
PbHCO3+	4.66E-08	4.82E-08	6.92E-09	2.52E-10	6.49E-04	1.10E-07	3.39E-09	1.72E-09	6.00E-05	2.53E-07

QWK004										
	DS/LT	DS/HT	DS/HP	DS/LP	WS/LT	WS/HT	WS/HP	WS/LP	DS	WS
C(4)	3.18E-03	3.06E-02	3.18E-03	3.18E-03	3.18E-03	3.18E-03	3.18E-03	3.18E-03	5.55E+01	5.50E-03
HCO3-	2.92E-03	2.86E-02	2.09E-03	2.65E-03	2.97E-03	3.00E-03	1.86E-03	2.47E-03	6.90E-02	3.98E-03
CO2	1.86E-04	9.97E-04	7.35E-04	5.18E-04	6.36E-05	1.05E-04	9.09E-04	6.96E-04	6.10E-02	1.38E-03
MgHCO3+	5.70E-05	6.74E-04	3.09E-04	8.74E-06	6.04E-05	5.15E-05	3.76E-04	1.21E-05	5.52E-02	1.31E-04
FeHCO3+	7.36E-06	1.42E-04	3.39E-05	1.46E-06	5.71E-05	1.50E-05	3.09E-05	2.52E-06	5.76E-03	1.24E-04
CO3-2	7.32E-06	9.67E-05	2.92E-06	9.82E-08	5.71E-05	6.48E-06	3.39E-06	1.43E-07	5.76E-03	5.20E-05
MgCO3	3.20E-06	7.08E-06	1.50E-06	2.42E-08	5.37E-05	3.76E-06	1.41E-06	4.91E-08	3.79E-03	4.43E-05
PbCO3	2.95E-06	2.67E-06	1.07E-06	1.81E-08	5.37E-05	1.81E-06	6.57E-07	3.40E-08	3.00E-03	3.17E-05
FeCO3	1.45E-06	2.11E-07	6.08E-10	7.98E-09	2.32E-05	6.97E-07	4.09E-10	1.48E-08	2.96E-03	2.05E-05
PbHCO3+	1.64E-07	1.84E-07	1.58E-11	3.96E-09	1.16E-05	1.49E-07	1.25E-11	9.51E-09	6.41E-04	2.00E-05

QWN005										
	DS/LT	DS/HT	DS/HP	DS/LP	WS/LT	WS/HT	WS/HP	WS/LP	DS	WS
C(4)	6.58E-03	1.31E-01	6.58E-03	6.58E-03	7.27E-02	6.58E-03	6.58E-03	6.58E-03	5.55E-03	5.35E-02
HCO3-	5.97E-03	1.23E-01	4.29E-03	5.46E-03	7.27E-02	6.25E-03	2.74E-03	6.20E-03	4.02E-03	4.82E-02
CO2	3.74E-04	5.72E-03	1.52E-03	1.08E-03	5.35E-02	1.15E-04	2.65E-03	3.67E-04	4.23E-04	9.77E-03
MgHCO3+	1.25E-04	1.70E-03	6.79E-04	1.98E-05	4.87E-02	1.05E-04	1.14E-03	6.86E-06	3.07E-04	6.58E-03
FeHCO3+	6.77E-05	4.95E-04	7.21E-05	1.48E-05	9.77E-03	6.41E-05	4.30E-05	5.26E-06	1.26E-04	6.25E-03
CO3-2	1.51E-05	1.54E-04	4.45E-06	2.70E-07	6.58E-03	3.05E-05	5.90E-06	1.17E-07	1.10E-04	5.32E-03
FeCO3	1.37E-05	1.54E-04	2.19E-06	1.74E-07	6.22E-03	7.06E-06	2.52E-06	5.76E-08	9.38E-05	4.90E-03
MgCO3	7.24E-06	4.20E-05	2.16E-06	6.87E-08	4.90E-03	5.47E-06	8.12E-07	1.57E-08	9.35E-05	4.14E-03
CuCO3	5.57E-06	3.74E-06	1.10E-06	4.15E-08	4.90E-03	1.91E-06	4.45E-07	8.64E-09	8.12E-05	1.73E-03
PbCO3	4.33E-06	2.91E-06	6.29E-07	4.13E-08	4.76E-03	1.55E-06	2.20E-07	4.27E-09	2.15E-05	7.75E-04

	DS/LT	DS/HT	DS/HP	DS/LP	WS/LT	WS/HT	WS/HP	WS/LP	DS	WS
C(4)	1.31E-01	1.33E-01	9.46E-02	7.11E-01	1.30E-01	1.29E-01	8.99E-02	5.44E-01	3.39E-03	4.18E-03
HCO3-	1.23E-01	1.23E-01	6.33E-02	5.85E-01	1.23E-01	1.22E-01	5.40E-02	4.18E-01	1.70E-03	3.47E-03
CO2	5.72E-03	7.15E-03	2.61E-02	1.24E-01	7.59E-02	4.09E-03	3.04E-02	1.24E-01	1.66E-04	1.71E-03
MgHCO3+	1.70E-03	1.92E-03	4.57E-03	1.75E-03	7.59E-02	1.71E-03	4.93E-03	1.77E-03	1.54E-04	2.86E-04
CO3-2	4.95E-04	3.54E-04	5.14E-04	3.33E-04	6.46E-02	6.71E-04	4.22E-04	3.42E-04	1.54E-04	2.25E-04
FeHCO3+	1.54E-04	2.85E-04	2.91E-05	5.00E-06	6.09E-02	2.04E-04	1.78E-05	6.81E-06	6.24E-05	2.19E-04

MgCO3	1.54E-04	1.07E-04	6.69E-06	4.73E-06	9.71E-03	1.20E-04	6.90E-06	4.58E-06	5.13E-05	2.04E-04
FeCO3	4.20E-05	5.66E-05	1.38E-06	1.58E-06	4.82E-03	4.46E-05	1.28E-06	2.11E-06	4.20E-05	1.35E-04
PbCO3	3.74E-06	3.43E-06	5.84E-07	1.18E-06	4.30E-03	4.38E-06	7.83E-07	1.55E-06	4.03E-05	1.20E-04
Pb(CO3)2-2	2.91E-06	3.14E-06	9.93E-08	9.05E-07	4.30E-03	2.52E-06	8.83E-08	1.27E-06	3.69E-05	5.34E-05

QWS006									
	DS/LT	DS/HT	DS/HP	DS/LP	WS/LT	WS/HT	WS/HP	WS/LP	DS	WS
C(4)	3.94E-03	7.40E-03	3.94E-03	3.94E-03	3.94E-03	3.94E-03	3.94E-03	3.94E-03	7.52E-02	2.13E-03
HCO3-	3.71E-03	6.93E-03	1.99E-03	2.83E-03	3.70E-03	3.72E-03	2.24E-03	3.01E-03	6.91E-02	1.81E-04
CO2	1.22E-04	3.87E-04	1.42E-03	1.09E-03	2.30E-03	1.22E-04	1.23E-03	9.17E-04	6.91E-02	1.72E-04
MgHCO3+	6.63E-05	5.98E-05	4.93E-04	1.64E-05	2.13E-03	5.76E-05	4.26E-04	1.43E-05	6.91E-02	1.41E-04
CO3-2	1.85E-05	1.98E-05	2.83E-05	3.21E-06	1.66E-04	2.03E-05	3.32E-05	3.03E-06	9.73E-03	1.22E-04
MgCO3	6.93E-06	6.06E-06	4.97E-06	2.43E-07	1.66E-04	7.41E-06	4.96E-06	2.15E-07	6.11E-03	5.76E-05
FeHCO3+	5.86E-06	9.22E-07	1.33E-06	1.15E-07	1.43E-04	5.09E-06	1.54E-06	7.78E-08	6.11E-03	3.88E-05
PbCO3	4.89E-06	1.17E-07	5.16E-07	7.71E-08	1.27E-04	2.03E-06	7.33E-07	4.99E-08	5.40E-03	3.18E-05
FeCO3	2.16E-06	1.07E-07	2.83E-10	2.87E-08	9.25E-05	8.05E-07	4.26E-10	1.84E-08	5.40E-03	2.03E-05
Pb(CO3)2-2	2.38E-07	4.82E-08	2.23E-12	1.66E-08	6.63E-05	2.72E-07	1.07E-11	1.20E-08	3.94E-03	1.89E-05
QWS007									
	DS/LT	DS/HT	DS/HP	DS/LP	WS/LT	WS/HT	WS/HP	WS/LP	DS	WS
C(4)	1.48E-02	3.18E-03	1.08E-02	5.57E-02	1.50E-02	2.52E-02	1.11E-02	6.55E-02	4.62E-04	9.98E-08
HCO3-	1.43E-02	2.96E-03	7.14E-03	4.12E-02	1.43E-02	2.44E-02	7.87E-03	5.11E-02	1.19E-04	6.08E-08
CO2	4.89E-04	1.51E-04	3.50E-03	1.44E-02	6.03E-04	3.47E-04	3.15E-03	1.44E-02	5.02E-05	5.12E-08
CO3-2	5.22E-05	4.96E-05	4.85E-05	7.64E-06	4.31E-05	2.57E-04	4.49E-05	7.45E-06	3.63E-05	4.95E-08
MnCO3	8.18E-06	1.04E-05	1.92E-05	7.19E-06	7.63E-06	1.18E-04	1.94E-05	7.21E-06	1.02E-05	4.95E-08
MgHCO3+	7.80E-06	4.53E-06	1.55E-05	6.84E-06	7.25E-06	4.66E-05	1.56E-05	6.86E-06	5.17E-06	3.96E-08
Zn(CO3)2-2	6.46E-06	3.21E-06	2.22E-06	3.34E-06	5.75E-06	9.31E-06	2.76E-06	3.51E-06	1.84E-07	3.30E-08
ZnCO3	5.63E-06	2.29E-06	2.02E-06	9.83E-07	5.45E-06	6.30E-06	2.51E-06	8.33E-07	1.25E-07	2.69E-08
MnHCO3+	4.32E-06	6.19E-07	2.58E-07	6.90E-07	4.71E-06	8.62E-08	3.34E-07	5.65E-07	2.39E-08	2.69E-08
CuCO3	3.26E-06	1.30E-07	2.00E-07	2.98E-07	3.66E-06	2.34E-02	2.25E-07	2.41E-07	1.70E-08	2.06E-08
QWG008									
	DS/LT	DS/HT	DS/HP	DS/LP	WS/LT	WS/HT	WS/HP	WS/LP	DS	WS
C(4)	2.52E-02	6.58E-03	2.52E-02	2.52E-02	2.52E-02	1.11E-02	2.52E-02	2.52E-02	1.31E-06	1.50E-03
HCO3-	2.43E-02	6.09E-03	1.32E-02	1.66E-02	2.44E-02	1.06E-02	1.29E-02	1.48E-02	1.13E-06	8.33E-04
CO2	5.74E-04	3.07E-04	1.11E-02	8.53E-03	2.34E-02	2.56E-04	1.14E-02	1.03E-02	8.39E-07	6.00E-04
CO3-2	1.41E-04	1.10E-04	8.49E-04	4.53E-05	2.34E-02	9.88E-05	8.89E-04	5.43E-05	4.80E-07	4.37E-04
MgHCO3+	1.28E-04	2.15E-05	2.85E-05	5.76E-06	1.06E-02	6.33E-05	2.32E-05	6.11E-06	4.79E-07	3.47E-04
MgCO3	2.48E-05	2.06E-05	1.50E-05	4.78E-06	1.02E-02	2.42E-05	1.53E-05	5.58E-06	3.97E-07	2.57E-04
PbCO3	1.12E-05	1.04E-05	2.47E-06	6.49E-07	2.40E-03	1.11E-05	1.58E-06	1.05E-06	3.37E-07	1.18E-04
Pb(CO3)2-2	4.12E-06	6.76E-06	5.12E-07	1.41E-07	2.34E-03	8.23E-06	4.49E-07	2.18E-07	2.76E-07	6.13E-05
PbHCO3+	1.84E-07	5.73E-06	6.42E-11	8.12E-09	1.50E-03	1.83E-06	4.27E-11	1.68E-08	2.08E-07	4.66E-05
Cl	2.14E-02	4.49E-06	2.14E-02	2.14E-02	9.07E-04	6.81E-07	2.34E-02	2.34E-02	2.00E-07	9.31E-06
QWG009									
	DS/LT	DS/HT	DS/HP	DS/LP	WS/LT	WS/HT	WS/HP	WS/LP	DS	WS
C(4)	1.11E-02	3.94E-03	1.11E-02	1.11E-02	1.11E-02	2.18E-02	1.11E-02	1.11E-02	4.62E-04	9.98E-08
HCO3-	1.04E-02	3.74E-03	7.49E-03	8.84E-03	1.06E-02	2.10E-02	6.34E-03	7.85E-03	1.19E-04	6.08E-08
CO2	5.02E-04	9.83E-05	2.77E-03	2.20E-03	8.88E-03	5.67E-04	3.79E-03	3.18E-03	5.02E-05	5.12E-08
MgHCO3+	1.05E-04	5.67E-05	7.49E-04	2.20E-05	8.24E-03	1.22E-04	8.88E-04	3.12E-05	3.63E-05	4.95E-08
CO3-2	2.82E-05	2.60E-05	4.92E-05	5.49E-06	2.46E-03	1.17E-04	3.78E-05	7.43E-06	1.02E-05	4.95E-08
PbCO3	1.15E-05	9.63E-06	1.14E-05	3.07E-06	2.00E-03	2.53E-05	1.20E-05	3.61E-06	5.17E-06	3.96E-08
MgCO3	1.05E-05	5.08E-06	2.96E-06	2.63E-06	1.91E-03	9.68E-06	1.54E-06	2.94E-06	1.84E-07	3.30E-08
FeHCO3+	1.00E-05	7.07E-07	1.58E-06	1.28E-06	1.61E-03	3.80E-06	1.28E-06	2.38E-06	1.25E-07	2.69E-08
CuCO3	8.76E-06	3.58E-07	1.07E-06	5.37E-07	1.40E-03	2.98E-06	1.21E-06	9.49E-07	2.39E-08	2.69E-08
FeCO3	3.43E-06	3.49E-07	8.33E-07	7.78E-08	1.40E-03	2.40E-06	5.78E-07	1.82E-07	1.70E-08	2.06E-08
QWG010									
	DS/LT	DS/HT	DS/HP	DS/LP	WS/LT	WS/HT	WS/HP	WS/LP	DS	WS
C(4)	2.18E-02	1.47E-02	2.18E-02	2.18E-02	2.18E-02	1.24E-02	2.18E-02	2.18E-02	4.62E-04	1.50E-03
HCO3-	2.02E-02	1.42E-02	1.66E-02	1.86E-02	2.09E-02	1.20E-02	1.34E-02	1.60E-02	1.19E-04	8.33E-04
CO2	1.44E-03	3.91E-04	4.55E-03	3.20E-03	9.87E-03	1.81E-04	7.58E-03	5.77E-03	5.02E-05	6.00E-04
MgHCO3+	1.27E-04	7.24E-05	6.30E-04	2.04E-05	9.46E-03	1.28E-04	8.10E-04	3.66E-05	3.63E-05	4.37E-04
CO3-2	3.86E-05	9.53E-06	6.10E-05	1.13E-05	1.90E-03	8.91E-05	4.11E-05	1.80E-05	1.02E-05	3.47E-04
FeHCO3+	3.58E-05	8.18E-06	1.17E-05	3.52E-06	1.90E-03	4.18E-05	1.23E-05	4.49E-06	5.17E-06	2.57E-04
PbCO3	1.09E-05	7.36E-06	9.39E-06	9.86E-07	1.68E-03	1.08E-05	7.89E-06	2.52E-06	1.84E-07	1.18E-04
MgCO3	8.17E-06	5.13E-06	8.00E-06	7.38E-07	1.20E-03	5.18E-06	3.61E-06	1.21E-06	1.25E-07	6.13E-05
FeCO3	7.88E-06	3.66E-06	9.78E-07	8.18E-08	1.17E-03	1.34E-06	6.13E-07	3.04E-07	2.39E-08	4.66E-05
MnHCO3+	2.46E-06	3.58E-06	7.17E-08	3.48E-08	1.09E-03	3.23E-07	3.54E-08	1.11E-07	1.70E-08	9.31E-06
QWG011									
	DS/LT	DS/HT	DS/HP	DS/LP	WS/LT	WS/HT	WS/HP	WS/LP	DS	WS
C(4)	1.24E-02	2.52E-02	1.24E-02	1.24E-02	1.24E-02	1.10E-02	1.24E-02	1.24E-02	1.31E-06	9.98E-08

HCO3-	1.18E-02	2.44E-02	7.74E-03	9.50E-03	1.20E-02	9.02E-03	6.99E-03	6.34E-03	1.13E-06	6.08E-08
CO2	4.60E-04	4.62E-04	3.91E-03	2.91E-03	3.37E-03	1.82E-03	4.33E-03	6.04E-03	8.39E-07	5.12E-08
MgHCO3+	9.96E-05	1.97E-04	7.17E-04	2.25E-05	1.68E-03	1.33E-04	1.08E-03	4.52E-05	4.80E-07	4.95E-08
CO3-2	4.48E-05	1.18E-04	4.64E-05	2.51E-06	1.50E-03	2.48E-05	2.18E-05	4.56E-06	4.79E-07	4.95E-08
PbCO3	1.35E-05	3.72E-05	1.46E-05	1.08E-06	1.50E-03	1.53E-05	1.53E-05	3.39E-06	3.97E-07	3.96E-08
MgCO3	1.05E-05	1.01E-05	2.50E-06	2.99E-07	1.50E-03	7.67E-06	8.21E-07	9.44E-07	3.37E-07	3.30E-08
CuCO3	1.84E-06	5.24E-06	1.41E-06	1.43E-07	1.45E-03	3.16E-06	4.47E-07	5.05E-07	2.76E-07	2.69E-08
Pb(CO3)2-2	1.61E-06	1.22E-07	2.24E-07	6.30E-08	1.40E-03	1.18E-06	8.56E-08	3.33E-07	2.08E-07	2.69E-08
PbHCO3+	4.08E-07	2.14E-02	4.30E-08	3.53E-08	1.40E-03	1.95E-08	9.18E-09	2.27E-07	2.00E-07	2.06E-08

QWG012

	DS/LT	DS/HT	DS/HP	DS/LP	WS/LT	WS/HT	WS/HP	WS/LP	DS	WS
C(4)	1.10E-02	1.11E-02	1.10E-02	1.10E-02	1.24E-02	1.26E-02	1.10E-02	1.10E-02	4.62E-04	1.50E-03
HCO3-	1.05E-02	1.05E-02	7.36E-03	8.72E-03	1.20E-02	1.21E-02	1.00E-02	1.01E-02	1.19E-04	8.33E-04
CO2	4.80E-04	4.08E-04	3.40E-03	2.31E-03	3.37E-03	2.87E-04	5.02E-04	8.52E-04	5.02E-05	6.00E-04
CO3-2	3.57E-05	9.88E-05	2.34E-04	6.84E-06	1.68E-03	1.02E-04	4.76E-04	2.96E-05	3.63E-05	4.37E-04
MgHCO3+	3.56E-05	3.96E-05	1.90E-05	9.05E-07	1.50E-03	2.10E-05	7.55E-06	2.08E-05	1.02E-05	3.47E-04
PbCO3	8.27E-06	1.61E-05	9.09E-06	3.09E-07	1.50E-03	1.27E-05	1.28E-06	1.46E-05	5.17E-06	2.57E-04
MgCO3	2.89E-06	1.14E-05	2.76E-06	1.05E-07	1.50E-03	8.10E-06	9.22E-07	1.64E-06	1.84E-07	1.18E-04
Pb(CO3)2-2	7.84E-07	9.78E-06	1.06E-06	3.66E-08	1.45E-03	4.28E-06	2.83E-07	9.59E-07	1.25E-07	6.13E-05
PbHCO3+	3.21E-07	1.31E-06	1.00E-06	8.51E-09	1.40E-03	3.43E-06	3.95E-09	8.04E-07	2.39E-08	4.66E-05
MnCO3	1.51E-07	1.17E-06	7.72E-09	5.09E-10	1.40E-03	2.41E-06	2.10E-10	1.58E-07	1.70E-08	9.31E-06

QWA013

	DS/LT	DS/HT	DS/HP	DS/LP	WS/LT	WS/HT	WS/HP	WS/LP	DS	WS
C(4)	1.26E-02	2.18E-02	1.26E-02	1.26E-02	1.26E-02	5.52E-02	1.26E-02	1.26E-02	4.62E-04	9.98E-08
HCO3-	1.21E-02	2.05E-02	6.62E-03	8.08E-03	1.21E-02	5.28E-02	6.80E-03	8.82E-03	1.19E-04	6.08E-08
CO2	2.74E-04	1.17E-03	5.88E-03	4.47E-03	1.90E-03	2.00E-03	5.70E-03	3.73E-03	5.02E-05	5.12E-08
CO3-2	9.64E-05	1.20E-04	4.32E-05	2.94E-05	1.90E-03	2.42E-04	4.27E-05	2.52E-05	3.63E-05	4.95E-08
FeHCO3+	5.21E-05	5.46E-05	1.69E-05	1.39E-06	1.80E-03	8.32E-05	1.69E-06	1.21E-06	1.02E-05	4.95E-08
FeCO3	1.96E-05	1.26E-05	1.38E-06	7.73E-07	1.80E-03	9.87E-06	1.60E-06	6.59E-07	5.17E-06	3.96E-08
PbCO3	1.25E-05	1.06E-05	1.06E-06	5.01E-07	7.61E-04	7.49E-06	1.60E-06	3.12E-07	1.84E-07	3.30E-08
MnCO3	4.66E-06	1.06E-05	2.60E-07	3.63E-07	4.38E-04	4.82E-06	3.43E-07	2.32E-07	1.25E-07	2.69E-08
MnHCO3+	3.82E-06	3.21E-06	2.95E-10	1.51E-07	4.38E-04	2.27E-07	4.56E-10	9.72E-08	2.39E-08	2.69E-08
Pb(CO3)2-2	2.26E-06	2.48E-06	2.11E-11	2.32E-08	3.36E-04	2.04E-02	8.92E-11	1.52E-08	1.70E-08	2.06E-08

QWG014

	DS/LT	DS/HT	DS/HP	DS/LP	WS/LT	WS/HT	WS/HP	WS/LP	DS	WS
C(4)	5.52E-02	1.24E-02	5.52E-02	5.52E-02	5.52E-02	1.84E-02	5.52E-02	5.52E-02	1.31E-06	1.50E-03
HCO3-	5.24E-02	1.19E-02	3.69E-02	4.40E-02	5.38E-02	1.75E-02	3.68E-02	4.37E-02	1.13E-06	8.33E-04
CO2	2.55E-03	3.72E-04	1.78E-02	1.12E-02	5.33E-02	8.07E-04	1.80E-02	1.15E-02	8.39E-07	6.00E-04
CO3-2	1.70E-04	8.74E-05	4.15E-04	1.81E-05	5.26E-02	5.42E-05	4.14E-04	1.90E-05	4.80E-07	4.37E-04
MgHCO3+	9.38E-05	6.29E-05	3.40E-05	3.26E-06	2.04E-02	2.77E-05	3.46E-05	4.01E-06	4.79E-07	3.47E-04
MgCO3	7.02E-06	1.49E-05	1.40E-05	1.11E-06	2.04E-02	3.91E-06	1.34E-05	1.37E-06	3.97E-07	2.57E-04
PbCO3	6.91E-06	1.32E-05	1.02E-05	5.00E-07	4.30E-03	3.28E-06	1.24E-05	5.19E-07	3.37E-07	1.18E-04
Pb(CO3)2-2	3.11E-06	2.21E-06	2.16E-07	2.31E-08	4.30E-03	1.27E-06	2.61E-07	2.38E-08	2.76E-07	6.13E-05
PbHCO3+	2.90E-07	2.05E-06	6.61E-11	1.47E-09	2.34E-03	7.87E-07	7.87E-11	1.90E-09	2.08E-07	4.66E-05
Cl	1.94E-02	2.90E-07	1.94E-02	1.94E-02	1.90E-03	2.98E-07	2.04E-02	2.04E-02	2.00E-07	9.31E-06

QWG015

	DS/LT	DS/HT	DS/HP	DS/LP	WS/LT	WS/HT	WS/HP	WS/LP	DS	WS
C(4)	1.84E-02	1.10E-02	1.84E-02	1.84E-02	1.84E-02	1.84E-02	2.81E-02	1.84E-02	4.62E-04	9.98E-08
HCO3-	1.73E-02	1.06E-02	1.29E-02	1.47E-02	1.74E-02	1.36E-02	2.73E-02	1.50E-02	1.19E-04	6.08E-08
CO2	8.34E-04	3.88E-04	4.79E-03	3.62E-03	1.05E-02	4.75E-03	5.24E-04	3.35E-03	5.02E-05	5.12E-08
MgHCO3+	9.99E-05	5.04E-05	6.12E-04	2.08E-05	1.04E-02	3.03E-05	2.59E-04	9.63E-06	3.63E-05	4.95E-08
CO3-2	4.77E-05	3.03E-05	4.21E-05	1.01E-05	2.50E-03	5.89E-06	7.26E-06	4.91E-06	1.02E-05	4.95E-08
PbCO3	2.78E-05	8.24E-06	3.01E-05	6.60E-06	2.50E-03	2.43E-06	5.31E-06	3.72E-06	5.17E-06	3.96E-08
FeHCO3+	1.18E-05	3.98E-06	5.09E-06	4.11E-06	2.19E-03	1.99E-06	1.66E-07	1.08E-07	1.84E-07	3.30E-08
MgCO3	9.94E-06	1.11E-06	2.40E-06	1.25E-07	2.19E-03	1.39E-07	7.08E-08	5.93E-08	1.25E-07	2.69E-08
FeCO3	4.01E-06	2.33E-07	6.04E-10	3.12E-08	1.20E-03	6.50E-10	4.40E-08	2.08E-08	2.39E-08	2.69E-08
Pb(CO3)2-2	3.45E-06	1.80E-07	2.25E-11	2.96E-08	1.20E-03	1.27E-11	4.98E-02	1.04E-09	1.70E-08	2.06E-08

QWA016

	DS/LT	DS/HT	DS/HP	DS/LP	WS/LT	WS/HT	WS/HP	WS/LP	DS	WS
C(4)	2.81E-02	1.26E-02	2.81E-02	2.81E-02	2.81E-02	2.85E-02	2.81E-02	2.81E-02	1.31E-06	1.50E-03
HCO3-	2.59E-02	1.22E-02	1.54E-02	2.18E-02	2.74E-02	2.76E-02	1.88E-02	1.45E-02	1.13E-06	8.33E-04
CO2	1.13E-03	2.20E-04	8.12E-03	6.12E-03	9.20E-03	7.08E-04	9.30E-03	1.36E-02	8.39E-07	6.00E-04
MgHCO3+	8.72E-04	1.37E-04	4.22E-03	1.83E-04	9.20E-03	1.92E-04	1.24E-05	3.56E-06	4.80E-07	4.37E-04
CO3-2	9.87E-05	1.26E-05	3.55E-04	1.98E-06	2.80E-03	1.03E-06	1.63E-06	2.88E-06	4.79E-07	3.47E-04
MgCO3	6.63E-05	7.63E-06	1.09E-05	6.61E-07	2.80E-03	5.55E-07	8.56E-07	2.82E-06	3.97E-07	2.57E-04
PbCO3	8.54E-06	5.39E-06	5.40E-06	3.14E-07	4.10E-04	2.42E-07	2.56E-07	8.95E-08	3.37E-07	1.18E-04
Pb(CO3)2-2	2.20E-06	3.93E-06	5.17E-07	2.21E-07	3.06E-04	1.45E-07	3.78E-08	2.63E-08	2.76E-07	6.13E-05
PbHCO3+	3.47E-07	3.23E-06	1.57E-10	5.45E-10	1.27E-05	3.29E-09	2.10E-11	3.95E-10	2.08E-07	4.66E-05

Cl	4.98E-02	3.21E-06	4.98E-02	4.98E-02	6.46E-06	2.59E-02	4.98E-02	4.98E-02	2.00E-07	9.31E-06

QWL017

	DS/LT	DS/HT	DS/HP	DS/LP	WS/LT	WS/HT	WS/HP	WS/LP	DS	WS
C(4)	2.85E-02	1.26E-02	2.85E-02	2.85E-02	2.85E-02	1.36E-02	2.85E-02	2.85E-02	4.62E-04	9.98E-08
HCO3-	2.70E-02	1.22E-02	1.39E-02	1.96E-02	2.77E-02	1.27E-02	2.08E-02	1.68E-02	1.19E-04	6.08E-08
CO2	7.54E-04	2.20E-04	1.16E-02	8.71E-03	2.59E-02	8.40E-04	7.65E-03	1.16E-02	5.02E-05	5.12E-08
MgHCO3+	4.60E-04	1.37E-04	2.90E-03	1.29E-04	2.59E-02	2.81E-05	2.58E-06	4.38E-06	3.63E-05	4.95E-08
CO3-2	1.58E-04	1.26E-05	1.47E-04	7.01E-07	2.90E-03	2.57E-07	1.57E-06	6.16E-07	1.02E-05	4.95E-08
MgCO3	5.66E-05	7.63E-06	3.06E-06	3.01E-07	2.90E-03	2.27E-08	5.16E-07	3.57E-07	5.17E-06	3.96E-08
PbCO3	9.51E-07	5.39E-06	1.35E-06	2.59E-07	1.00E-03	2.52E-02	4.27E-08	1.51E-07	1.84E-07	3.30E-08
Pb(CO3)2-2	3.95E-07	3.93E-06	4.45E-08	1.65E-07	1.00E-03	2.52E-02	2.89E-08	7.11E-09	1.25E-07	2.69E-08
PbHCO3+	2.41E-08	3.23E-06	8.28E-12	3.05E-10	5.55E-04	2.20E-03	1.70E-12	9.36E-10	2.39E-08	2.69E-08
Cl	2.09E-02	3.21E-06	2.09E-02	2.09E-02	2.27E-04	2.20E-03	2.59E-02	2.59E-02	1.70E-08	2.06E-08

QWL018

	DS/LT	DS/HT	DS/HP	DS/LP	WS/LT	WS/HT	WS/HP	WS/LP	DS	WS
C(4)	1.36E-02	1.84E-02	1.36E-02	1.36E-02	2.30E-03	1.25E-02	1.36E-02	1.36E-02	1.31E-06	1.50E-03
HCO3-	1.31E-02	1.75E-02	7.50E-03	9.32E-03	2.30E-03	1.20E-02	1.09E-02	1.17E-02	1.13E-06	8.33E-04
CO2	3.42E-04	6.76E-04	5.19E-03	4.23E-03	2.20E-03	5.02E-04	2.67E-03	1.84E-03	8.39E-07	6.00E-04
MgHCO3+	1.05E-04	9.23E-05	8.57E-04	3.39E-05	2.20E-03	4.27E-05	6.81E-06	4.30E-08	4.80E-07	4.37E-04
CO3-2	6.69E-05	6.69E-05	3.27E-05	2.77E-07	9.78E-04	2.32E-07	1.54E-06	3.86E-08	4.79E-07	3.47E-04
MgCO3	1.87E-05	2.69E-05	1.62E-06	9.11E-08	2.18E-05	3.11E-08	1.56E-07	3.89E-11	3.97E-07	2.57E-04
Cl	2.52E-02	1.49E-05	2.52E-02	2.52E-02	5.50E-06	3.10E-02	2.52E-02	2.52E-02	3.37E-07	1.18E-04
Cl-	2.52E-02	4.70E-06	2.52E-02	2.52E-02	3.60E-06	3.10E-02	2.52E-02	2.52E-02	2.76E-07	6.13E-05
F	1.40E-03	1.74E-06	1.40E-03	1.40E-03	1.40E-06	1.90E-03	2.20E-03	2.20E-03	2.08E-07	4.66E-05
F-	1.35E-03	8.12E-07	1.37E-03	1.34E-03	1.40E-06	1.90E-03	2.20E-03	2.19E-03	2.00E-07	9.31E-06

QWL019

	DS/LT	DS/HT	DS/HP	DS/LP	WS/LT	WS/HT	WS/HP	WS/LP	DS	WS
C(4)	1.25E-02	2.81E-02	1.25E-02	1.25E-02	1.25E-02	0.00E+00	1.25E-02	1.25E-02	4.62E-04	9.98E-08
HCO3-	1.18E-02	2.62E-02	9.13E-03	1.02E-02	1.19E-02	0.00E+00	8.95E-03	1.00E-02	1.19E-04	6.08E-08
CO2	6.53E-04	9.16E-04	3.14E-03	2.26E-03	1.90E-03	0.00E+00	3.55E-03	2.48E-03	5.02E-05	5.12E-08
MgHCO3+	3.13E-05	7.53E-04	2.08E-04	5.70E-06	1.90E-03	0.00E+00	3.55E-06	9.43E-08	3.63E-05	4.95E-08
CO3-2	2.91E-05	1.39E-04	1.61E-05	7.45E-08	5.87E-04	0.00E+00	1.79E-06	4.88E-08	1.02E-05	4.95E-08
MgCO3	2.59E-06	9.31E-05	4.07E-06	7.52E-09	3.00E-04	0.00E+00	1.20E-07	7.46E-11	5.17E-06	3.96E-08
Cl	2.80E-02	8.04E-06	2.80E-02	2.80E-02	3.00E-04	0.00E+00	3.10E-02	3.10E-02	1.84E-07	3.30E-08
Cl-	2.80E-02	2.93E-06	2.80E-02	2.80E-02	3.33E-05	0.00E+00	3.10E-02	3.10E-02	1.25E-07	2.69E-08
F	1.60E-03	2.38E-07	1.60E-03	1.60E-03	5.99E-06	0.00E+00	1.90E-03	1.90E-03	2.39E-08	2.69E-08
F-	1.58E-03	4.98E-02	1.58E-03	1.57E-03	3.67E-06	0.00E+00	1.90E-03	1.89E-03	1.70E-08	2.06E-08

QWL020

	DS/LT	DS/HT	DS/HP	DS/LP	WS/LT	WS/HT	WS/HP	WS/LP	DS	WS
C(4)	1.33E-02	2.85E-02	1.33E-02	1.33E-02	3.27E-02	1.33E-02	1.33E-02	1.33E-02	1.31E-06	1.50E-03
HCO3-	1.27E-02	2.72E-02	9.25E-03	1.05E-02	3.27E-02	1.28E-02	9.39E-03	1.05E-02	1.13E-06	8.33E-04
CO2	5.78E-04	6.08E-04	3.84E-03	2.78E-03	1.36E-02	4.85E-04	3.91E-03	2.78E-03	8.39E-07	6.00E-04
CO3-2	3.84E-05	3.91E-04	1.91E-04	5.75E-06	1.36E-02	5.09E-05	3.49E-06	1.11E-07	4.80E-07	4.37E-04
MgHCO3+	2.73E-05	2.22E-04	1.28E-05	1.10E-07	1.33E-02	2.00E-07	1.52E-06	4.49E-08	4.79E-07	3.47E-04
MgCO3	2.70E-06	7.81E-05	3.45E-06	8.75E-09	1.27E-02	2.91E-08	1.02E-07	6.83E-11	3.97E-07	2.57E-04
Cl	3.27E-02	8.60E-07	3.27E-02	3.27E-02	2.50E-03	3.27E-02	3.27E-02	3.27E-02	3.37E-07	1.18E-04
Cl-	3.27E-02	5.03E-07	3.27E-02	3.27E-02	2.50E-03	3.27E-02	3.27E-02	3.27E-02	2.76E-07	6.13E-05
F	5.00E-04	1.59E-08	5.00E-04	5.00E-04	1.80E-03	1.80E-03	1.80E-03	1.80E-03	2.08E-07	4.66E-05
F-	4.95E-04	2.09E-02	4.96E-04	4.93E-04	1.80E-03	1.80E-03	1.80E-03	1.80E-03	2.00E-07	9.31E-06

QWO021

	DS/LT	DS/HT	DS/HP	DS/LP	WS/LT	WS/HT	WS/HP	WS/LP	DS	WS
C(4)	3.57E-02	1.36E-02	3.57E-02	3.57E-02	3.57E-02	3.57E-02	3.57E-02	3.57E-02	4.62E-04	9.98E-08
HCO3-	3.39E-02	1.31E-02	2.39E-02	2.82E-02	3.48E-02	3.48E-02	1.86E-02	2.22E-02	1.19E-04	6.08E-08
CO2	1.60E-03	2.75E-04	1.13E-02	7.45E-03	2.50E-02	5.82E-04	1.71E-02	1.35E-02	5.02E-05	5.12E-08
CO3-2	1.09E-04	9.79E-05	4.81E-04	2.00E-05	2.50E-02	3.44E-04	2.72E-06	1.36E-06	3.63E-05	4.95E-08
MgHCO3+	9.59E-05	9.33E-05	3.51E-05	3.30E-07	2.10E-03	2.91E-07	2.01E-06	1.19E-07	1.02E-05	4.95E-08
MgCO3	8.03E-06	2.85E-05	8.78E-06	2.85E-08	2.10E-03	8.44E-08	6.71E-08	3.72E-10	5.17E-06	3.96E-08
Cl	6.55E-02	2.52E-02	6.55E-02	6.55E-02	1.70E-02	6.75E-02	6.75E-02	6.75E-02	1.84E-07	3.30E-08
Cl-	6.55E-02	2.52E-02	6.55E-02	6.55E-02	1.70E-02	6.75E-02	6.75E-02	6.75E-02	1.25E-07	2.69E-08
F	1.50E-03	1.40E-03	1.50E-03	1.50E-03	6.85E-04	2.10E-03	2.10E-03	2.10E-03	2.39E-08	2.69E-08
F-	1.48E-03	1.34E-03	1.49E-03	1.47E-03	2.69E-04	2.10E-03	2.10E-03	2.10E-03	1.70E-08	2.06E-08

QWO022

	DS/LT	DS/HT	DS/HP	DS/LP	WS/LT	WS/HT	WS/HP	WS/LP	DS	WS
C(4)	2.54E-02	1.25E-02	2.54E-02	2.54E-02	9.65E-02	2.54E-02	2.54E-02	2.54E-02	1.31E-06	1.50E-03
HCO3-	2.37E-02	1.19E-02	1.90E-02	2.15E-02	9.65E-02	2.47E-02	1.37E-02	1.72E-02	1.13E-06	8.33E-04
CO2	1.65E-03	5.29E-04	6.39E-03	3.88E-03	5.21E-02	5.18E-04	1.18E-02	8.18E-03	8.39E-07	6.00E-04
CO3-2	5.48E-05	4.10E-05	1.04E-05	1.27E-07	5.21E-02	2.07E-04	2.83E-06	6.78E-07	4.80E-07	4.37E-04
Cl	9.65E-02	2.87E-05	9.65E-02	9.65E-02	2.54E-02	2.22E-07	1.71E-06	7.57E-08	4.79E-07	3.47E-04
Cl-	9.65E-02	3.86E-06	9.65E-02	9.65E-02	2.47E-02	4.60E-08	8.38E-08	1.58E-10	3.97E-07	2.57E-04

H(0)	1.86E-26	2.80E-02	1.59E-30	1.60E-22	2.90E-03	9.65E-02	9.65E-02	9.65E-02	3.37E-07	1.18E-04
H2	9.28E-27	2.80E-02	7.94E-31	7.97E-23	2.90E-03	9.65E-02	9.65E-02	9.65E-02	2.76E-07	6.13E-05
N(5)	1.80E-03	1.60E-03	1.80E-03	1.80E-03	6.09E-04	2.18E-27	2.17E-31	2.19E-23	2.08E-07	4.66E-05
NO3-	1.80E-03	1.58E-03	1.80E-03	1.80E-03	1.62E-04	1.09E-27	1.09E-31	1.09E-23	2.00E-07	9.31E-06

QWO023

	DS/LT	DS/HT	DS/HP	DS/LP	WS/LT	WS/HT	WS/HP	WS/LP	DS	WS
C(4)	2.55E-01	1.33E-02	1.84E-01	1.35E+00	2.44E-01	2.43E-01	1.52E-01	5.92E-01	4.62E-04	9.98E-08
HCO3-	2.40E-01	1.28E-02	1.26E-01	1.11E+00	2.38E-01	2.36E-01	9.02E-02	3.50E-01	1.19E-04	6.08E-08
CO2	1.30E-02	4.68E-04	5.58E-02	2.41E-01	1.85E-01	3.52E-03	6.19E-02	2.42E-01	5.02E-05	5.12E-08
MgHCO3+	1.25E-03	5.39E-05	2.30E-03	1.17E-03	1.85E-01	3.07E-03	8.54E-06	3.35E-05	3.63E-05	4.95E-08
CO3-2	7.79E-04	2.51E-05	3.14E-04	1.03E-05	8.27E-02	1.38E-06	3.62E-06	1.47E-06	1.02E-05	4.95E-08
MgCO3	6.36E-05	4.01E-06	5.53E-05	8.86E-07	8.27E-02	3.14E-07	1.52E-07	3.65E-09	5.17E-06	3.96E-08
Cl	1.85E-01	3.27E-02	1.85E-01	1.85E-01	4.17E-03	1.85E-01	1.85E-01	1.85E-01	1.84E-07	3.30E-08
Cl-	1.85E-01	3.27E-02	1.85E-01	1.85E-01	2.90E-03	1.85E-01	1.85E-01	1.85E-01	1.25E-07	2.69E-08
F	1.50E-03	5.00E-04	1.50E-03	1.50E-03	2.90E-03	2.90E-03	2.90E-03	2.90E-03	2.39E-08	2.69E-08
F-	1.47E-03	4.95E-04	1.48E-03	1.46E-03	2.40E-03	2.90E-03	2.90E-03	2.90E-03	1.70E-08	2.06E-08

QWO024

	DS/LT	DS/HT	DS/HP	DS/LP	WS/LT	WS/HT	WS/HP	WS/LP	DS	WS
C(4)	6.08E-03	3.57E-02	6.08E-03	6.08E-03	1.62E-01	6.08E-03	6.08E-03	6.08E-03	1.31E-06	1.50E-03
HCO3-	5.19E-03	3.42E-02	3.11E-03	5.14E-03	1.62E-01	5.84E-03	4.01E-03	4.76E-03	1.13E-06	8.33E-04
MgHCO3+	4.81E-04	1.29E-03	1.74E-03	8.71E-04	7.19E-02	2.09E-04	2.05E-03	1.32E-03	8.39E-07	6.00E-04
CO2	3.70E-04	1.53E-04	9.73E-04	7.41E-05	7.19E-02	2.98E-05	5.74E-06	2.73E-07	4.80E-07	4.37E-04
MgCO3	2.17E-05	8.65E-05	2.50E-04	2.24E-07	6.08E-03	5.32E-06	1.44E-06	8.65E-08	4.79E-07	3.47E-04
CO3-2	1.22E-05	1.18E-05	4.72E-06	5.15E-08	5.81E-03	4.11E-07	1.08E-06	6.74E-08	3.97E-07	2.57E-04
PbCO3	4.68E-06	6.55E-02	1.87E-06	4.36E-08	1.50E-03	1.68E-07	3.41E-10	1.52E-11	3.37E-07	1.18E-04
PbHCO3+	3.19E-07	6.55E-02	1.83E-06	2.72E-08	1.50E-03	1.62E-01	1.62E-01	1.62E-01	2.76E-07	6.13E-05
Pb(CO3)2-2	1.48E-07	1.50E-03	9.59E-10	3.08E-12	2.45E-04	1.62E-01	1.62E-01	1.62E-01	2.08E-07	4.66E-05
Cl	1.60E-01	1.48E-03	1.60E-01	1.60E-01	2.31E-05	2.18E-07	6.40E-10	1.56E-06	2.00E-07	9.31E-06

QWO025

|	DS/LT	DS/HT	DS/HP	DS/LP	WS/LT	WS/HT	WS/HP	WS/LP	DS	WS
C(4)	4.46E-02	2.52E-01	4.46E-02	4.46E-02	1.31E-01	4.46E-02	4.46E-02	4.46E-02	4.62E-04	9.98E-08
HCO3-	4.12E-02	2.39E-01	1.87E-02	2.97E-02	1.31E-01	4.31E-02	2.46E-02	2.69E-02	1.19E-04	6.08E-08
MgHCO3+	1.62E-03	1.04E-02	1.71E-02	1.43E-02	5.31E-02	6.58E-04	1.96E-02	1.77E-02	5.02E-05	5.12E-08
CO2	1.04E-03	1.12E-03	8.09E-03	5.40E-04	5.31E-02	5.08E-04	1.46E-04	3.01E-05	3.63E-05	4.95E-08
CO3-2	2.68E-04	1.09E-03	3.90E-04	2.88E-05	4.46E-02	1.30E-04	7.50E-06	2.38E-06	1.02E-05	4.95E-08
MgCO3	2.16E-04	9.23E-05	1.48E-04	2.36E-06	4.31E-02	1.15E-05	2.89E-06	2.09E-06	5.17E-06	3.96E-08
Zn(CO3)2-2	1.14E-04	1.85E-01	7.25E-06	1.38E-06	1.30E-03	4.32E-06	8.62E-07	1.88E-06	1.84E-07	3.30E-08
ZnCO3	1.92E-05	1.85E-01	3.79E-06	1.25E-06	1.30E-03	3.23E-06	4.46E-07	1.73E-06	1.25E-07	2.69E-08
ZnHCO3+	6.14E-06	1.50E-03	7.59E-07	1.22E-06	1.20E-03	2.05E-06	2.93E-07	8.10E-08	2.39E-08	2.69E-08
PbCO3	4.27E-06	1.46E-03	3.89E-07	1.15E-06	1.20E-03	1.09E-06	2.69E-07	7.69E-08	1.70E-08	2.06E-08

Appendix 1.3:Calibration Curves For The Analytes
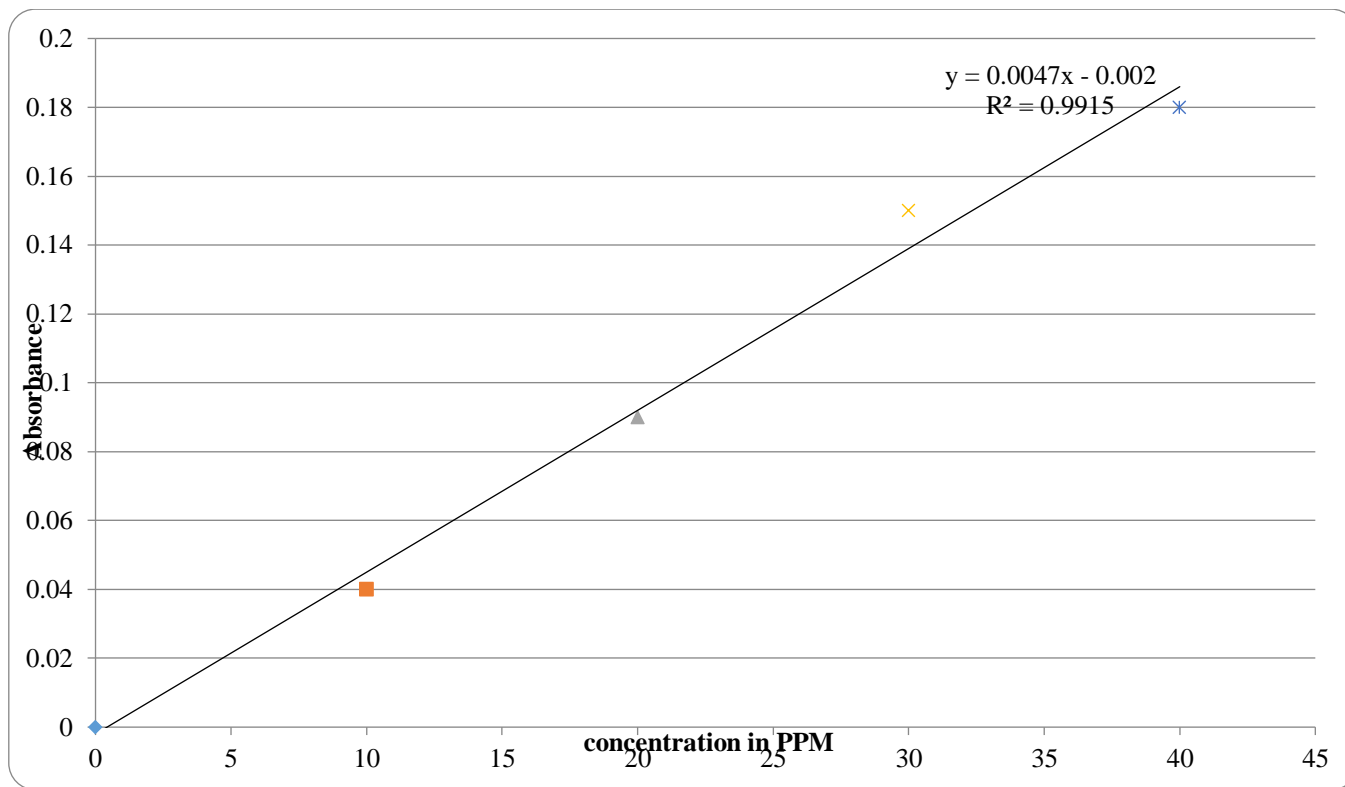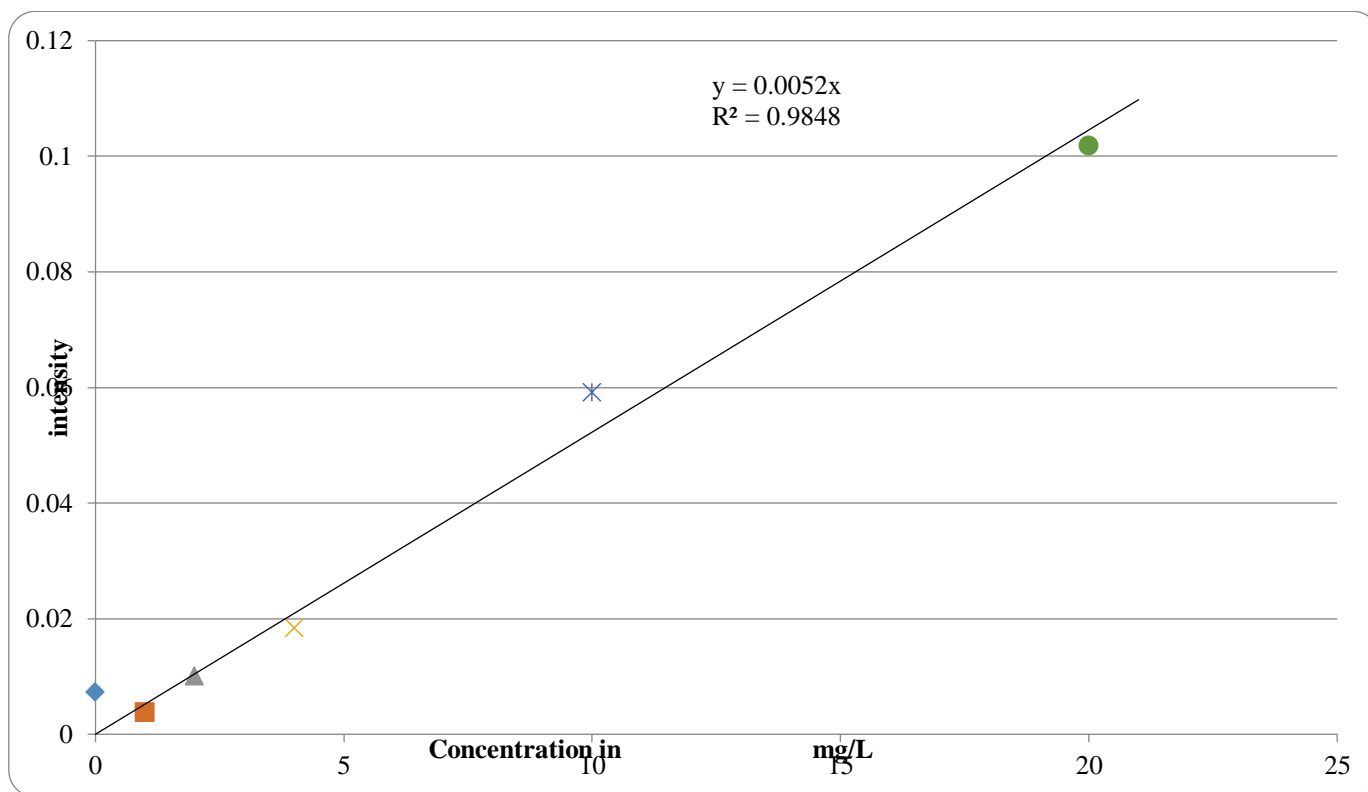

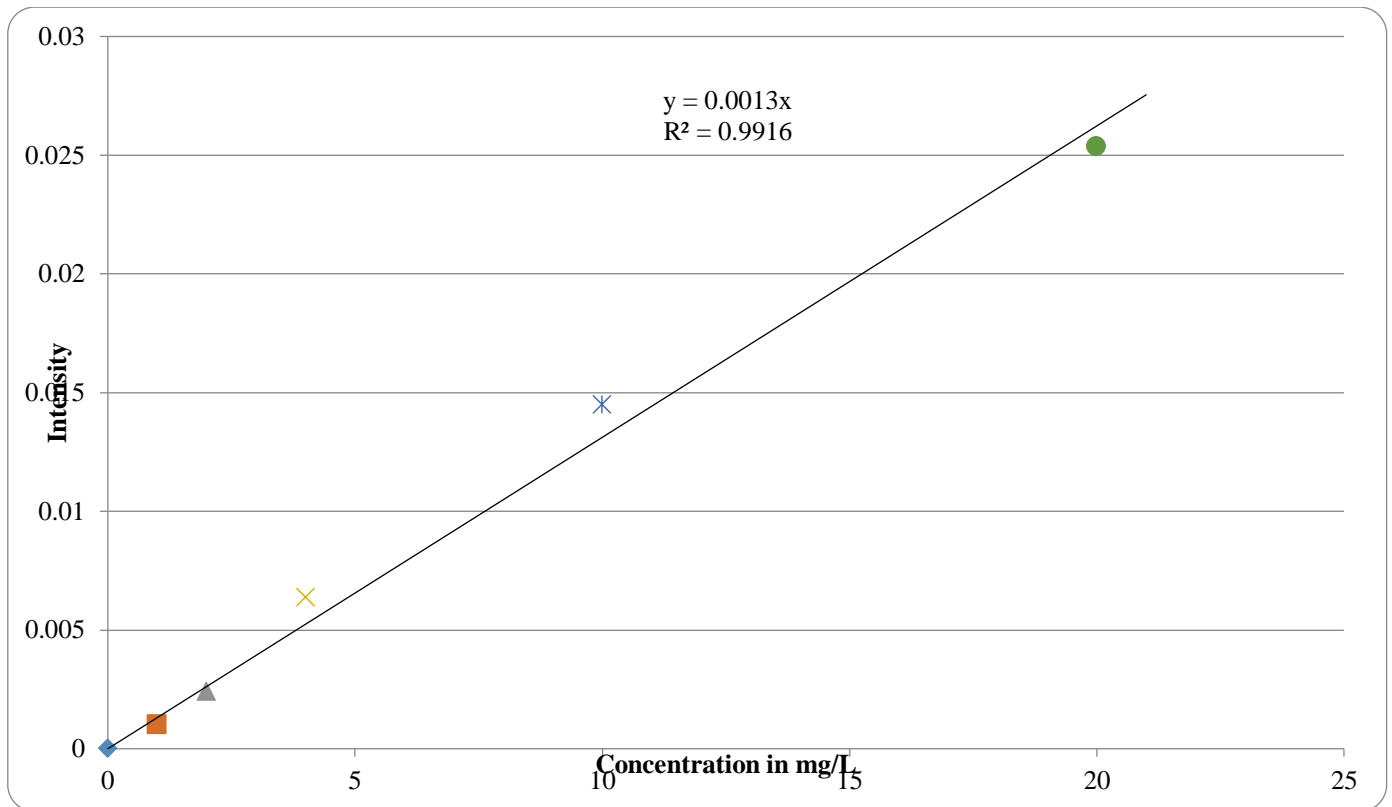Appendix 1.3.1: Calibration curve for Nitrate
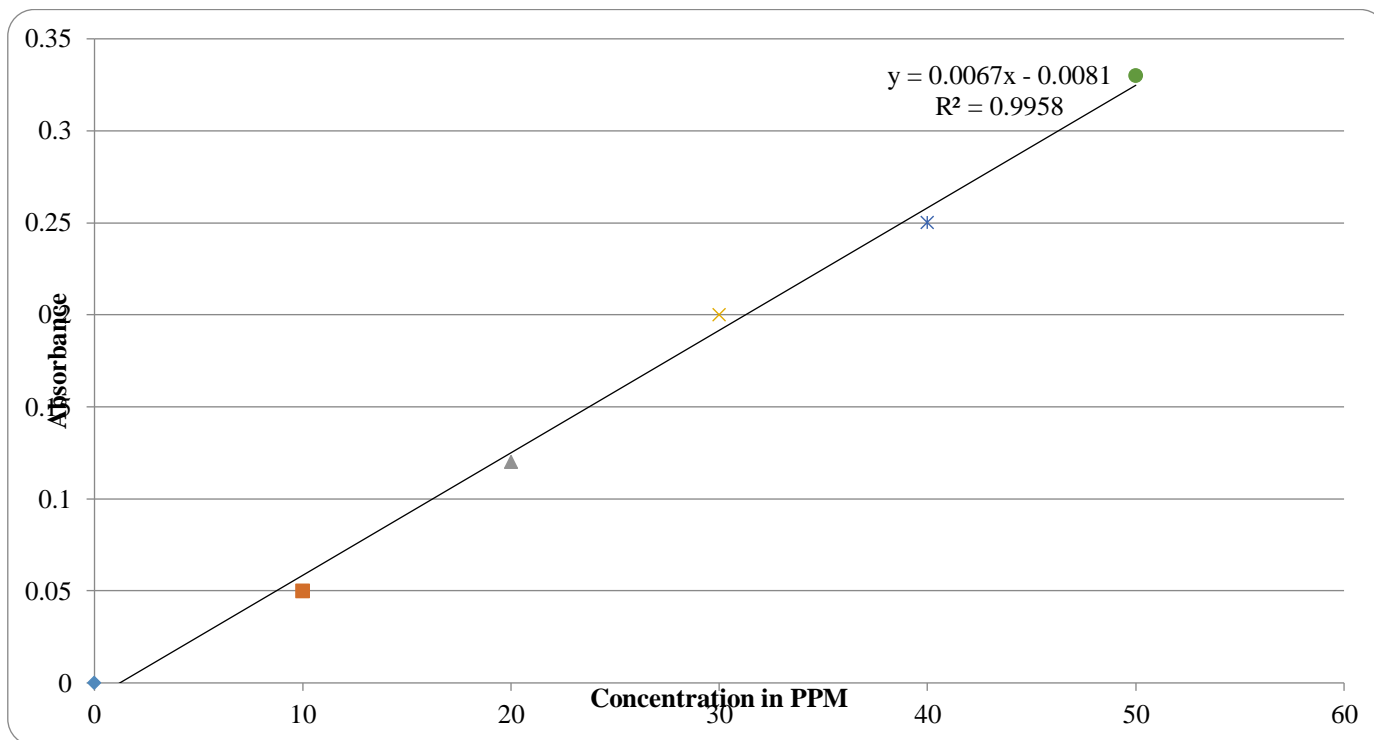
Appendix 1.3.2: Calibration curve for sulphate
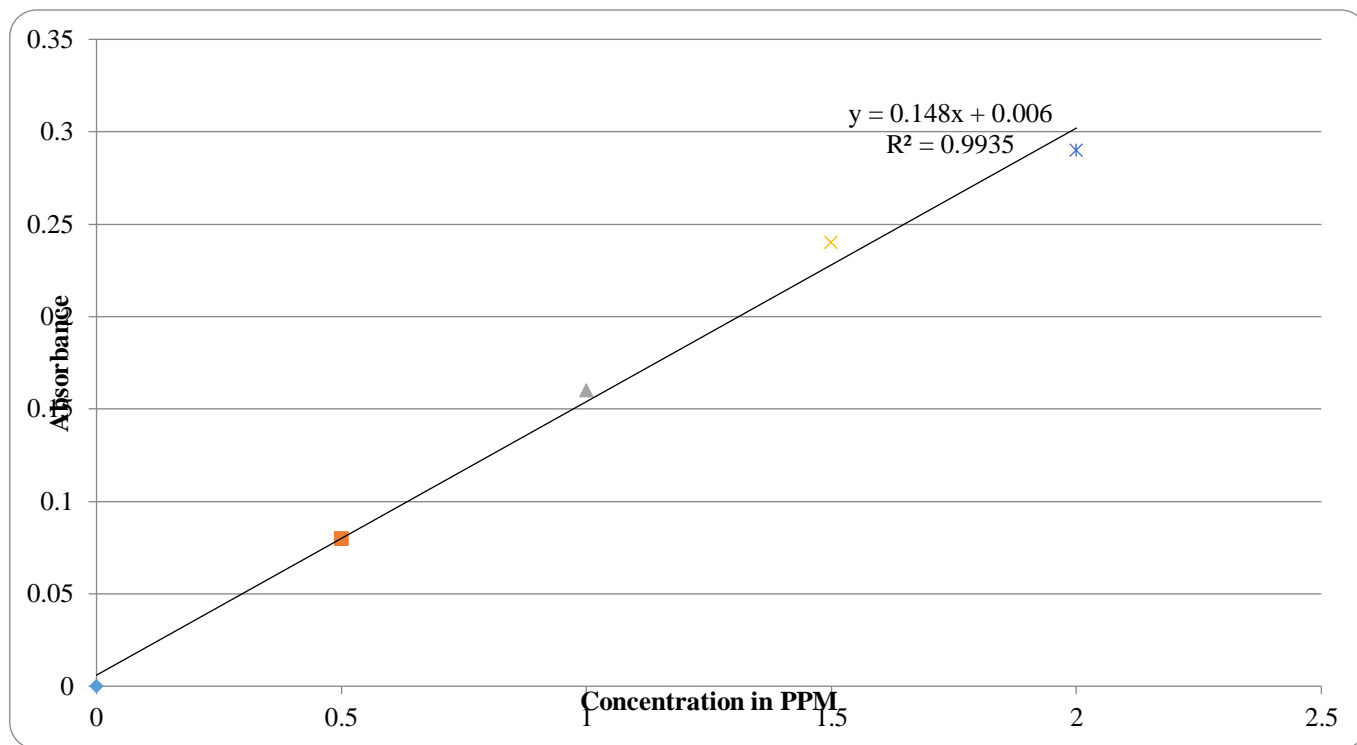
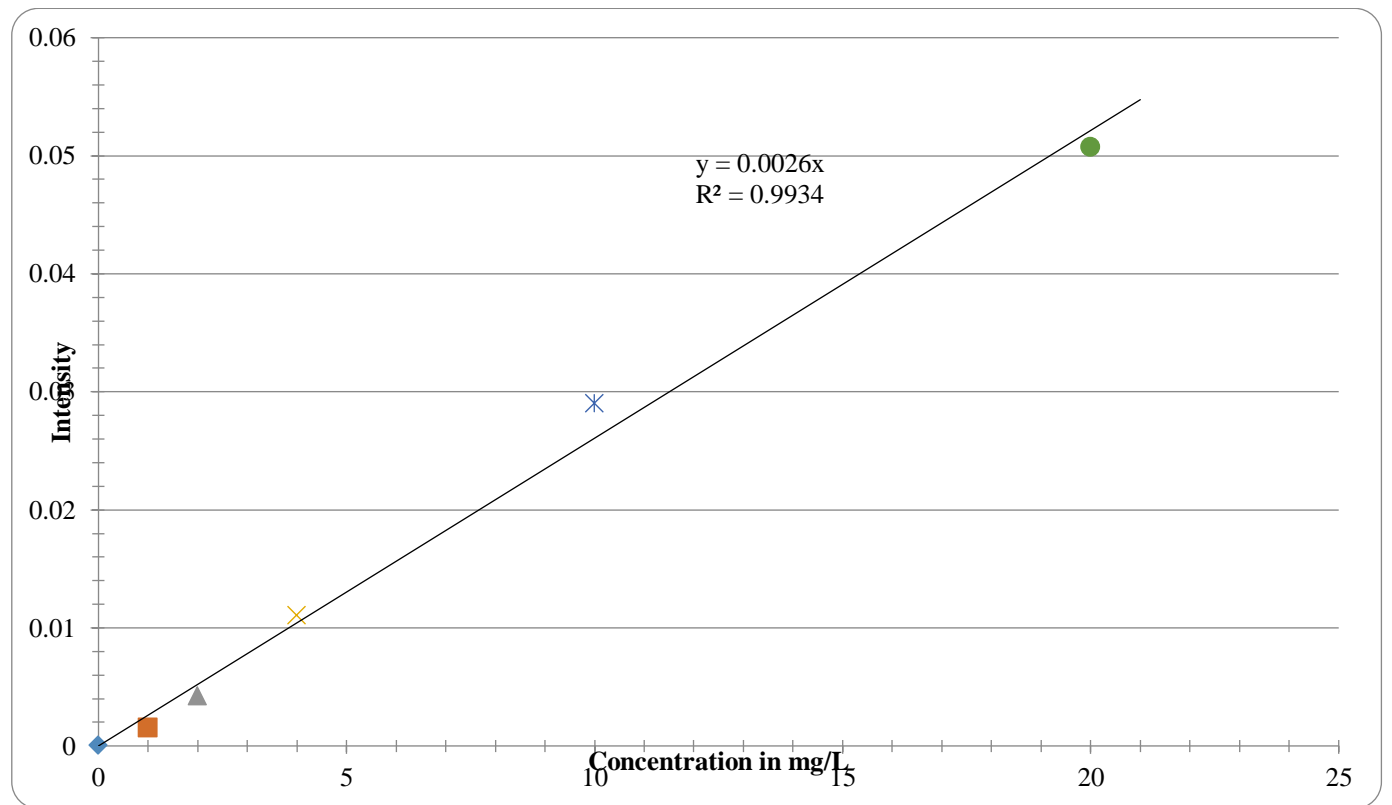Appendix 1.3.3: Calibration curve of fluoride

Appendix 1.3.4: Calibration curve of Zinc

y = 0.0013x
R² = 0.9916

Concentration in mg/L

Intensity

Appendix 1.3.5: Calibration curve of Iron

y = 0.0026x
R² = 0.9934

Concentration in mg/L

Intensity

Appendix 1.3.6: Calibration curve of Lead

$y = 0.0050x$
$R^2 = 0.9924$
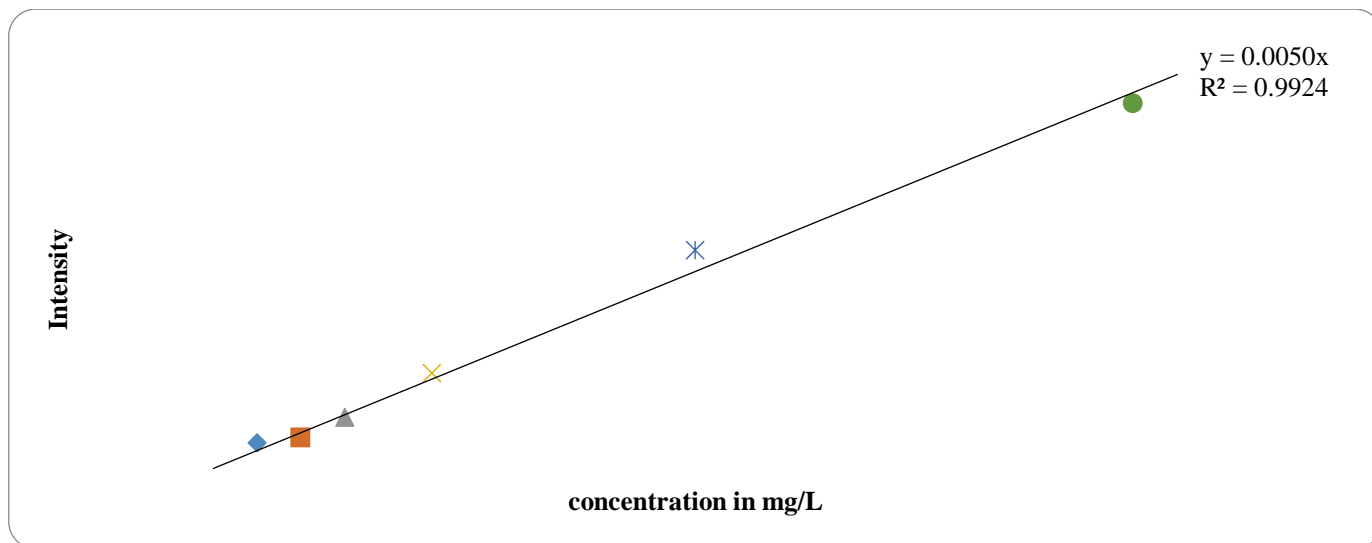
Appendix 1.3.7: Calibration curve of Cadmium

$y = 0.0013x$
$R^2 = 0.9932$
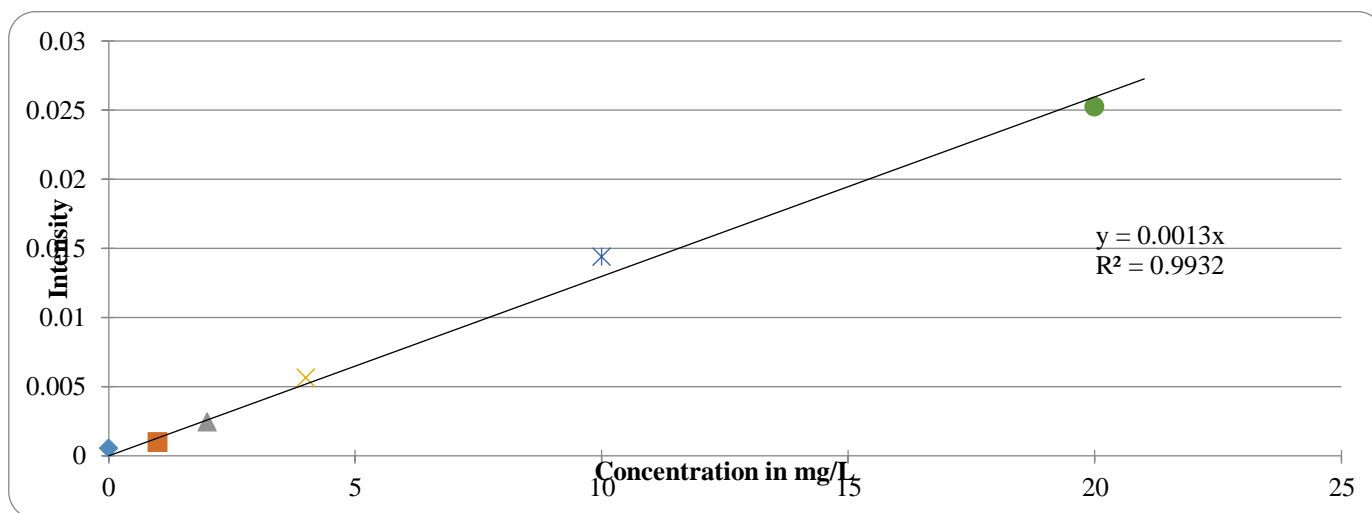
Appendix 1.3.8:Calibration curve of Manganese

$y = 0.0011x + 0.9927$
$R^2 = 0.9916$
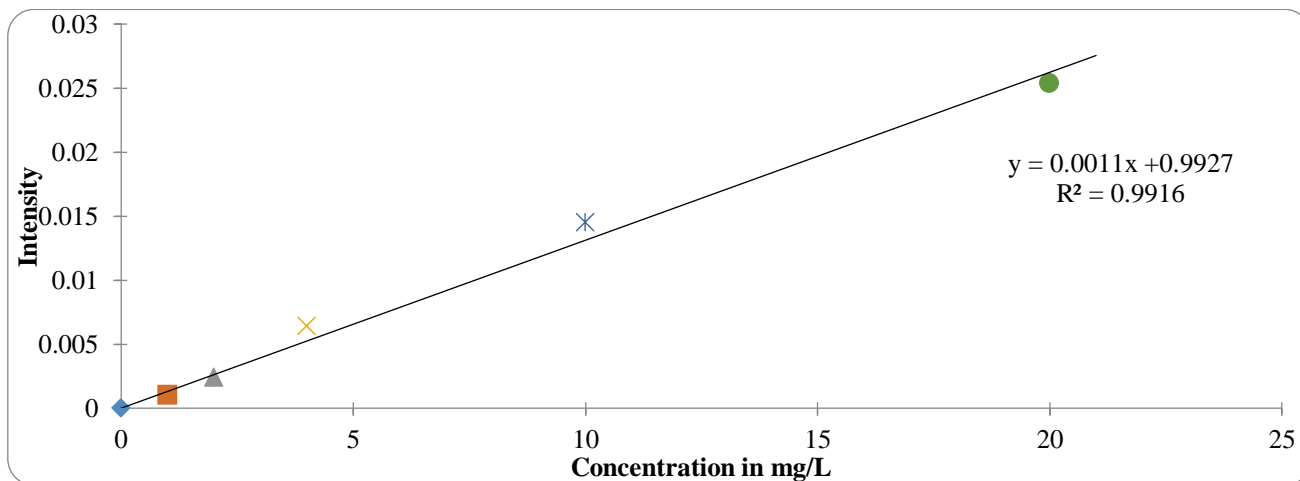
Appendix 1.3.9: Calibration curve of copper
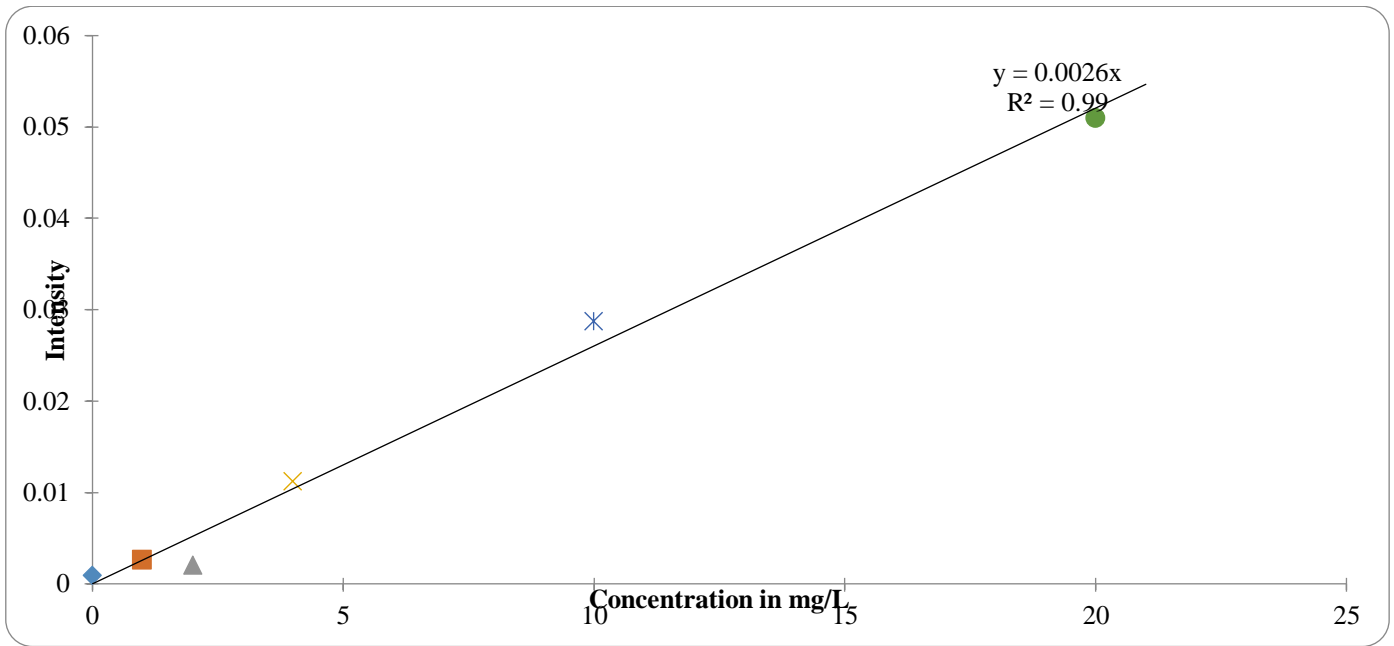
Appendix 1.3.10: Calibration curve of Magnesium

Appendix 1.4: Sampled PHREEQ C Output Data

Sample PHREEQ C output

Before the introduction of any Anion into the program.(A)

Species	Molality
OH-	9.782e-07
H+	1.460e-08
H2O	5.551e+01
H(0)	2.314e-27
H2	1.157e-27
Mg	1.207e-02
Mg+2	1.207e-02
MgOH+	2.439e-06
Mn(2)	1.815e-06
Mn+2	1.812e-06
MnOH+	2.592e-09
Mn(OH)3-	8.874e-18
Mn(3)	1.143e-27
Mn+3	1.143e-27
Mn(6)	0.000e+00
MnO4-2	0.000e+00
Mn(7)	0.000e+00
MnO4-	0.000e+00
O(0)	1.284e-38
O2	6.422e-39
Pb	1.015e-05
Pb+2	5.093e-06
PbOH+	4.919e-06
Pb(OH)2	1.271e-07
Pb3(OH)4+2	2.215e-09
Pb2OH+3	1.021e-09
Pb(OH)3-	1.323e-10

Species	Molality
OH-	8.790e-07
H+	1.347e-08
H2O	5.551e+01
C(4)	5.007e-04
HCO3-	4.824e-04
CO2	1.317e-05
MgHCO3+	2.310e-06
CO3-2	2.062e-06
MgCO3	6.740e-07
PbCO3	4.392e-08
MnCO3	3.226e-09
MnHCO3+	1.022e-09
PbHCO3+	5.672e-10
Pb(CO3)2-2	2.283e-10
Cl	9.178e-04
Cl-	9.178e-04
MnCl+	8.879e-11
PbCl+	5.538e-11
PbCl2	7.182e-14
MnCl2	3.233e-14
PbCl3-	5.269e-17
MnCl3-	8.170e-18
PbCl4-2	2.565e-20
F	1.105e-04
F-	1.076e-04
MgF+	2.945e-06
HF	2.016e-09
MnF+	1.767e-11
PbF+	2.829e-12
HF2-	8.391e-13
PbF2	5.644e-15
H2F2	1.022e-17
PbF3-	4.399e-18

Sample PHRREQ C output after anions introduction into the program (B)

H(0)	2.326e-27
H2	1.163e-27
Mg	4.966e-04
Mg+2	4.905e-04
MgF+	2.945e-06
MgHCO3+	2.310e-06
MgCO3	6.740e-07
MgOH+	1.315e-07
Mn(2)	3.304e-08
Mn+2	2.863e-08
MnCO3	3.226e-09
MnHCO3+	1.022e-09
MnCl+	8.879e-11
MnOH+	5.392e-11
MnF+	1.767e-11
MnCl2	3.233e-14
Mn(NO3)2	3.183e-15
MnCl3-	8.170e-18
Mn(OH)3-	1.847e-19
Mn(3)	1.271e-29
Mn+3	1.271e-29
Mn(6)	0.000e+00
MnO4-2	0.000e+00
Mn(7)	0.000e+00
MnO4-	0.000e+00
N(5)	1.928e-04
NO3-	1.928e-04
PbNO3+	4.214e-12
Mn(NO3)2	3.183e-15
O(0)	1.291e-38
O2	6.457e-39
Pb	4.898e-08
PbCO3	4.392e-08
PbOH+	2.348e-09
Pb+2	1.790e-09
PbHCO3+	5.672e-10

Appendix 1.4.1: Sampled PHREEQ C Output of Anions Effect on Chemical Speciation

Sampled PHREEQ C output data for QWO025

At low temperatures 15°C

C(4)	3.055e-02
HCO3-	2.843e-02
CO2	1.185e-03
MgHCO3+	7.458e-04
CO3-2	1.068e-04
MgCO3	7.115e-05
PbCO3	7.506e-06
Pb(CO3)2-2	2.131e-06
PbHCO3+	2.551e-07
MnCO3	1.832e-07
MnHCO3+	1.528e-07
Cl	3.054e-02
Cl-	3.054e-02
PbCl+	1.027e-08
MnCl+	7.252e-09
PbCl2	3.428e-10
MnCl2	5.497e-11
PbCl3-	7.808e-12
MnCl3-	4.626e-13
PbCl4-2	1.710e-13
F	1.400e-03
F-	1.249e-03
MgF+	1.511e-04
HF	2.398e-08
MnF+	5.015e-10
PbF+	2.414e-10
HF2-	1.079e-10
PbF2	3.485e-12

at High Temperatures 35°C

C(4)	4.459e-02
HCO3-	4.135e-02
MgHCO3+	1.373e-03
CO2	7.792e-04
CO3-2	4.335e-04
MgCO3	3.689e-04
Zn(CO3)2-2	1.284e-04
ZnCO3	1.319e-05
Pb(CO3)2-2	3.913e-06
PbCO3	3.420e-06
ZnHCO3+	2.690e-06
CuCO3	1.052e-06
Cu(CO3)2-2	6.030e-07
PbHCO3+	5.054e-08
MnCO3	4.913e-08
CuHCO3+	3.173e-08
MnHCO3+	1.797e-08
Cl	1.307e-01
Cl-	1.307e-01
CuCl2-	3.267e-07
ZnCl+	2.755e-07
CuCl3-2	1.208e-07
ZnOHCl	1.175e-07
ZnCl2	1.916e-08
PbCl+	9.711e-09
ZnCl3-	3.082e-09
MnCl+	2.478e-09
CuCl+	8.558e-10
PbCl2	8.507e-10

Appendix1.4.2: Sampled PHREEQ C output on effects of Temperature on speciation

Sampled PHREEQ C for QWN005

at Low PH 4 | at High PH 10

	Low PH 4			High PH 10
CuCl+	3.679e-08			
PbCl2	6.062e-09			
MnCl2	1.689e-09			
CuCl2	7.524e-10			
PbCl3-	3.443e-10	OH-		1.444e-04
MnCl3-	3.294e-11	H+		1.304e-10
PbCl4-2	1.976e-11	H2O		5.551e+01
CuCl3-	2.003e-13	C(4)	1.578e-01	
FeCl+2	1.801e-13	CO3-2		8.938e-02
FeCl2+	1.711e-14	HCO3-		6.550e-02
CuCl4-2	1.221e-16	MgCO3		2.807e-03
FeCl3	6.542e-17	MgHCO3+		1.288e-04
Cu(1)	1.287e-05	CO2		9.378e-06
CuCl2-	1.084e-05	Cl	1.846e-01	
CuCl3-2	2.012e-06	Cl-		1.846e-01
Cu+	1.332e-08	F	1.500e-03	
Cu(2)	1.241e-05	F-		1.485e-03
CuCO3	6.764e-06	MgF+		1.457e-05
Cu(OH)2	3.728e-06	HF		1.252e-10
CuSO4	5.552e-07	HF2-		7.892e-13
CuHCO3+	5.437e-07	H2F2		4.721e-20
Cu+2	4.933e-07	H(0)	1.283e-31	
Cu(CO3)2-2	1.936e-07	H2		6.416e-32
CuOH+	7.706e-08	Mg	4.061e-03	
CuCl+	3.679e-08	MgCO3		2.807e-03
Cu2(OH)2+2	5.201e-09	MgSO4		5.648e-04
CuF+	2.584e-09	Mg+2		5.386e-04
CuCl2	7.524e-10	MgHCO3+		1.288e-04
Cu(OH)3-	9.857e-12	MgF+		1.457e-05
		MgOH+		7.253e-06
		N(5)	7.000e-04	

Appendix 1.4.3: Sampled PHREEQ C output with effects of PH on Speciation.

Appendix 1.5: Types of equipment Used

Appendix 1.5.1: Showing image of Multiparameter Photometer

Appendix 1.5.2: Showing Images of Conductivity Meter

Appendix 1.5.3: Displaying images of 1 and 2, which are ICP-OES and laboratory preparation of samples for further analysis, respectively.

Appendix 1.6: Some of the sampling sites

Appendix 1.5.1: Photos of two(1,2) Dam Sampling Sites and (3 and 4)Representation of Two Surface Water Sites (5,6,7,8 9 and 10)are a Representation of the Borehole Water Sampling Sites