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Determination of Selected Heavy Metals in Some Creeks in a Tennessee City

A thesis
presented to
the faculty of the Department of Chemistry
East Tennessee State University

In partial fulfillment
of the requirements for the degree
Master of Science in Chemistry

by
Ann Ejimole Item
May 2011

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Keywords: heavy metals, creeks, water, temperature, location, weather

ABSTRACT

Determination of Selected Heavy Metals in Some Creeks in a Tennessee City

by

Ann Ejimole Item

Concentrations of Ni, Cu, Zn, Fe, Cd, and Pb were determined in six different creeks within a city in Tennessee using Atomic Absorption Spectrophotometer. Mean concentrations of Ni, Cu, Zn, Cd, Pb, and Fe in the sites examined reveal that they exceed the USEPA recommended limits. High concentrations of Cu (0.130 mg/L), Zn (13.7 mg/L), Ni (0.267 mg/L), and Cd (0.010 mg/L) were observed in site B and Fe (3.01 mg/L) in site E relative to other sites. The concentration of Pb (0.795 mg/l) was higher in site A. Higher concentrations of Cu, Zn, and Fe were detected in samples collected in the month of January and Cd in samples collected in the month of June. Pb and Ni concentrations did not show any significant difference with respect to dates of sample collection. Their presence in the environment on a particular day depends on the type and volume of human activities.

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CHAPTER 1

INTRODUCTION

Pollution is defined as the introduction of a contaminant into the environment as a result of human activities or from natural disasters [1]. The American College Dictionary defines it as, "to make foul or unclean" [2]. Three main types of pollution have been identified. They are land, air, and water pollution [1]. Studies [3] have shown that pollution of our land, air, and water influenced the quality of lives on this planet. Land pollution is the contamination of the earth's land surface by industrial, commercial, domestic, and agricultural activities. Air pollution results when hazardous substances build up in the atmosphere and endanger plants, animals, and humans. Water pollution occurs when chemical, biological, and physical matter is introduced into bodies of water, degrading the quality of life that lives in it and consuming it. Effects of pollution on plants, animals and humans can be devastating. It has led to the loss of large area of land to dumpsites and oil spills, made our rivers and lake water undrinkable and unsuitable to swim in, and caused health problems [1]. History of environmental pollution by human activities dates back to the beginning of the twentieth century, but the actual order of occurrence is not the same in all areas. It is a function of population growth and industrialization [4].

Water makes up about 70% of the earth's surface and is essential for everything on our planet [5]. However, we have been disregarding its importance by adding large amount of unwanted materials into it. Human activities have led to important changes in the aquatic environment during the last 150 years [6]. Point and non-point sources are two types of water

pollutants. Point sources of pollution often occur when harmful materials are discharged directly into a water body. An example was the oil spill along the Gulf of Mexico that happened in April 2010. Non-point sources introduce pollutants indirectly through environmental changes. An example is when fertilizer from a field is carried into a stream by rain and then affects aquatic life [5]. Though point sources have been successfully controlled over the past several decades, non-point sources have become the leading cause of water pollution [7]. In the U.S, almost 25% of the beaches are closed every year because of water pollution. About 1.2 trillion gallons of sewage, storm water, and industrial wastes are discharged into the waters, and over 2.2 billion pounds of pesticides that eventually runoff into the rivers and lakes are used annually [1].

The influence of these anthropogenic activities on marine environments can be ascertained by measuring various chemical markers that include nutrients, organic compounds, and toxic heavy metals in the water column, biota, and sediments [8, 9]. Heavy metals are among the most prevalent of the numerous pollutants originating from these activities [10, 11]. Though weathering of minerals is the main natural source of heavy metals in water [12], industrial wastes, geochemical structure, domestic wastes, water effluents, coal burning power plants, dumping sewage sludge, smelters, and steel plants are potential sources of heavy metal pollution in aquatic environment [13, 14]. Large amount of heavy metals are released into fluvial systems by smelting waste sites and carried along hydrologic gradients for several kilometers in a relatively short time [7]. In urban runoff, roadways and automobiles are the main sources of heavy metals [15]. Metal species released include lead, zinc, copper, iron, cadmium, chromium, nickel, and manganese [15].

Most heavy metals are firmly attached to surfaces of road dust or other particulates. During precipitation, the bound metals dissolve or are swept off the roadway with the dust [16]. The metals are then directed into a storm drain [16]. In coastal zones, metals can enter such waters mainly through deposits from the air, discharge from industries, and streams [17].

Metals exist as dissolved ions and complexes, suspended ions, and solids in sediments in aquatic systems [3]. They do not have decay mechanisms [18] and thus can build up in the environment [18]. The persistence of these heavy metals in the environment made them useful markers of environmental change [19]. In addition, metals have fairly well known and relatively simple chemistry [20].

Though small amounts of some heavy metals are actually necessary for good health, under certain environmental conditions they can build up to toxic concentration [21] and cause ecological damage [22, 23]. Heavy metal toxicity can result in damaged or reduced mental and central nervous function, lower energy levels, and damage to blood composition, lungs, kidney, liver, and other vital organs [24]. According to Lentech Water Treatment and Purification holding [25], the most important disaster with heavy metals occurred in Minamata, Japan when a sewage containing mercury was discharged by Chisso Chemical Works into Minamata bay in 1932. Then, the first incident of mercury poisoning was observed in the population of Minamata Bay in 1952 as a result of consumption of fish polluted with mercury [25]. Another incident was recorded in Sandoz, when water used to extinguish a major fire carried a fungicide containing mercury into the upper River Rhine in 1986 [25]. Fish were killed over a stretch of 100 km. Also, in 1998, toxic chemicals in water from a burst dam belonging to a mine

contaminated a nature reserve in southern Spain and experts estimated that Europe's largest bird sanctuary as well as Spain's agriculture and fisheries would suffer permanent damage from the pollution [25].

Concentration of metal ions in water strongly depends on biological processes, redox potential, ionic strength, pH, activities of organic and inorganic chelators, and scavenging processes [26]. The pH tends to be a critical variable in this whole process [16]. Low water pH favors the loading of heavy metals in solution [27] because hydrogen ions are attracted to the negative charges of the sediment particles and little room is left to bind metals [16]. As a result, more metals remain in the soluble phase and cause harm to the aquatic organisms that are in close and prolonged contact with the soluble metals [16].

Concentration of metals found in nature may cause less fatal, interactive, and indirect effects instead of direct fatal effects [28]. Long-term exposure may result in a gradual advancement of physical, muscular, and neurological degenerative processes that are similar to Alzheimer's disease, Parkinson's disease, muscular dystrophy, multiple sclerosis, and even cancer [29]. Determination of total concentration of metals in an area supplies data valuable to initiate prompt action to prevent the spread of pollutants [30]. The physicochemical data can reflect variation of chemical composition of water caused by discharges when comparing with background and established water quality criteria [31].

Among factors like traffic volume, land use, road maintenance practices, and drainage systems that influence the level of heavy metals in water, antecedent dry weather has an important influence on pollution levels. Metal concentrations have been found to be generally

higher both at base flow and in storms following long dry weather [6]. However, seasonal fluctuation of heavy metals concentration in water may be concealed by irregular variation in municipal and industrial waste discharges [32].

Heavy Metals

Heavy metals are chemical elements with a specific gravity that is at least 5 times that of water [33]. There are more than 20 elements in this group [34]. They are antimony, arsenic, bismuth, cerium, chromium, cobalt, copper, gallium, gold, iron, lead, manganese, mercury, nickel, platinum, silver, tellurium, thallium, tin, vanadium, and zinc [34]. Heavy metals often exist as positively-charged ions and can bind on to negatively charged organic molecules to form complexes [34]. While some are essential micronutrients for life processes in plants, animals, and humans, most of them like cadmium, chromium, and lead do not have any known physiological activity [35, 36]. They cause harmful effects at very low concentration when they are not metabolized by the body and bio-accumulate in the soft tissues like kidneys and hard tissues like bones [37]. These metals enter the human body through food, water, air, or absorption through the skin when they come in contact with humans in agriculture and in manufacturing, pharmaceutical, industrial, or residential settings [34]. Acute poisoning is more likely to result from inhalation or skin contact of dust, fumes or vapors, or materials [34]. The agency for toxic substances and disease registry (ATSDR) compiled a list of top 20 hazardous substances, and heavy metals like arsenic, lead, mercury, and cadmium top the list.

Effects of Heavy Metals on Humans

Certain heavy metals are found naturally in the body and are essential to human health. In minute quantities, some of them are known to prevent anemia and are cofactors in enzyme reactions [34]. Others such as molybdenum, manganese, cobalt, and copper have been known to improve human growth, development, and reproduction [34]. As trace elements, they help to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning. High concentration of zinc for instance can cause a deficiency of copper, another important metal required by the body [29]. Excess heavy metals in certain tissues and glands increase the risk of vascular blockages. They can also decrease hormone production that causes early aging, stress, decreased sex drive, increase in menopausal symptoms, neurological diseases, and aggravation of conditions like osteoporosis and hypothyroidism [34]. Diseases like edema of eyelid, tumor, congestion of nasal mucous membrane and pharynx, stuffiness of head, gastrointestinal and genetic malfunction have been also documented as being caused by excess heavy metal [38- 40].

Arsenic

Arsenic is found in nature at low levels. It forms compounds with oxygen, chlorine, and sulfur as inorganic arsenic compounds and with carbon and hydrogen in plants and animals as organic arsenic compounds [34]. It is the most common cause of acute heavy metal poisoning in adults and is number one on the ATSDR's top 20 list [37]. Arsenic enters the environment during the smelting process of copper, zinc, and lead and during the production of glass [37]. In the manufacturing of pesticides, arsine gas which contains arsenic is released as a byproduct.

Arsenic may be found in water supplies worldwide. Other sources are paints, rat poisons, fungicides, and wood preservative. Arsenic attacks organs like kidneys and the central nervous, digestive, and skin systems [34]. Symptoms of acute arsenic poisoning are sore throat from breathing, red skin on contact or severe abdominal pain, vomiting, and diarrhea often an hour after ingestion. Other symptoms are anorexia, fever, mucosal irritation, and arrhythmia. Cardiovascular changes are often difficult to detect in the early stages, but can progress to cardiovascular collapse [37].

Chronic or lower level of exposure can lead to progressive peripheral and central nervous changes such as sensory changes, numbness and tingling, and muscle tenderness. Neuropathy (inflammation and wasting of the nerves) is usually gradual and occurs over several years [37]. There may also be excessive darkening of the skin in areas that are not exposed to sunlight, excess formation of skin on the palms and soles (hyperkeratosis), or white bands of arsenic deposit across the bed of the fingernails. Birth defects, liver injury, and malignancy are possible. According to the Environmental Protection Agency (EPA) [41], drinking water limit for arsenic is 0.05 ppm and the Occupational Safety and Health Administration (OSHA) maximum permissible exposure limit for workplace air borne arsenic is $10 \mu\text{g}/\text{m}^3$. A high level of about 60 ppm of inorganic arsenic in food or water is deadly [34].

Lead

Lead occurs in nature as a bluish-gray metal in minute quantity in the earth crust [34]. It is number two on the ATSDR's top 20 list [37]. Lead is a soft metal used in pipes, drains, and soldering materials for many years. Many homes constructed before 1940 still contain lead,

leading to chronic exposure from weathering, flaking, chalking, and dust [37]. Every year, industries produce about 2.5 million tons of lead throughout the world. Lead is used most often in making batteries, cable coverings, plumbing, ammunition, and as fuel additives. Other uses are as paint pigments and in PVC plastics, X-ray shielding, crystal glass production, and pesticides [37].

In humans, exposure to lead can result in a wide range of biological effects depending on the level and duration of exposure. Various effects occur over a broad range of doses, with the developing fetus and infants being more sensitive than adults. Exposure to high concentration of lead causes toxic biochemical effects on the kidneys, gastrointestinal tracts, joints, and reproductive systems, results in problems in the synthesis of hemoglobin, and acute and chronic damage to the nervous system [25]. At intermediate concentration, lead can have small, elusive effects particularly on neuro-psychological development in children. Some studies suggest that there may be a loss of up to 2 IQ points for a rise in blood lead levels from 10- 20 $\mu\text{g}/\text{dL}$ in young children [25]. Lead in the air adds to lead levels in food through deposition of dust and rain containing the metals on crops and soil. According to EPA, limit in air should not exceed 1.5 $\mu\text{g}/\text{m}^3$ averaged over 3 months and limit in drinking water is 15 $\mu\text{g}/\text{L}$ [41].

Mercury

Mercury is number three on ATSDR's top 20 lists [37]. It is released into the environment from degassing of the earth's crust from volcanic emissions [33]. It exists in three forms: elemental, organic, and inorganic [37]. Substantial amount of mercury is produced

during mining operations, from chloroalkali plants, and from paper industries [46].

Atmospheric mercury is spread across the world by wind and it comes back to the earth in rainfall, building up in the aquatic food chains and fish in lakes [34]. Mercury compounds were included in paints as fungicides until 1990. Using such compounds today is prohibited. However, old paint supplies and surfaces painted with these old supplies are still in existence. Mercury is still being used in thermometers, thermostats, and dental amalgam [34].

Mercury has no known physiological or biochemical functions in the human body and does not occur naturally in living organisms. Inorganic mercury poisoning is connected with tremors, gingivitis and/or minor psychological changes, in addition to spontaneous abortion and congenital malformation. Monomethyl mercury causes injury to the brain and the central nervous system, while fetal and post natal exposure has led to abortion, congenital malformation, and developmental changes in children [25]. It has been reported that women who were occasionally exposed to mercury had complications in pregnancy and childbirth and menstrual disturbances [34]. According to the EPA and FDA, the level of mercury in drinking water should not exceed 2 ppb, and maximum permissible level of methyl mercury in seafood is 1 ppm [34].

Cadmium

Cadmium occurs as a natural element in the earth's crust. It may also exist in a combined state with other elements such as oxygen (cadmium oxide), chlorine (cadmium chloride), or sulfur (cadmium sulfate, cadmium sulfide) [34]. Cadmium is a byproduct of the mining and smelting of lead and zinc and is number 7 on ATSDR's list [37]. It is used in the

manufacturing of nickel cadmium batteries, PVC plastics, and paint pigments. It can be in soils because of pesticides, fungicides, sludge, and commercial fertilizers that contain cadmium used in agriculture. Cigarettes also contain cadmium. Less common sources of exposure are dental alloys, electroplating, motor oil, and exhaust. Breathing in cadmium constitutes about 15-50% of absorption through the respiratory system; 2-7% is absorbed in the gastrointestinal system. Cadmium is bio-persistent and once absorbed by an organism remains resident for many years although it is eventually excreted [34].

In humans long-term exposure to cadmium can lead to obstructive lung diseases like pneumonitis, bronchopneumonia, and even death due to severe lung damage [34]. Taking in food and water contaminated with high concentration of cadmium increases salivation and irritates the stomach resulting in vomiting and diarrhea. Other effects of prolonged exposure are kidney diseases, fragile bones, abdominal pain, choking, and tenesmus. Animals that consumed food or water contaminated with cadmium showed high blood pressure, iron deficient blood, liver disease, and nerve or brain damage. However, there is no evidence that humans can get these diseases from consuming cadmium [34]. According to the EPA, limit of cadmium in drinking water is 5 ppb. In addition, there is a limit to quantity of cadmium released into water bodies. Use of cadmium in making fertilizers has been banned by EPA [37].

Chromium

Chromium is a naturally occurring element found in rocks, soil, plants, animals, and volcanic dust. It normally exists as chromium (0), chromium (III), and chromium (IV) [34]. Chromium (III), which is the most stable, is a necessary nutrient in our diet in minute amounts.

It is essential for insulin molecule to bring glucose into the cells for glycolysis. Glycolysis is the first step in adenosine triphosphate (ATP) production. ATP is the basic energy unit of the cell necessary for cell duplication [34]. Chromium is used in metal alloys, paint pigments, cement, paper, rubber, and other materials. Low exposure can irritate the skin and causes ulceration. Long-term exposure can cause kidney and liver damage and damage to the circulatory and nerve tissues. Chromium often accumulates in aquatic life; adding to the danger of eating fish that may have been exposed to high levels of chromium. Long-term exposure to high or moderate concentration of chromium can damage the nose and lungs and increase the risk of non-cancer diseases [34]. Consuming food contaminated with high amount of chromium can cause stomach upsets, ulcers, convulsions, and even death [28]. EPA's maximum permissible level of chromium (III) and chromium (IV) in drinking water is $10 \mu\text{g}/\text{m}^3$. According to the National Research Council (NRC), dietary intake of chromium (III) should be between 50-200 $\mu\text{g}/\text{day}$ [34].

Copper

Copper occurs as a reddish brown metal found in the earth's surface [42]. It is often used as an electrical conductor in electrical industries because it is relatively inexpensive. Copper compounds can be used as pesticides in agriculture. In addition, they are used in batteries, electroplating, as well as in other industrial processes [43]. Corrosion of metallic parts of vehicles like the engine contributes a significant amount of copper into the environment [42].

Copper is an essential element to human life [44]. It is an important component in iron metabolism and also helps in enzyme metabolism [44]. Deficiency in copper may result in anemia, bone, and cardio-vascular changes. But in high doses it can cause liver and kidney damage, stomach and intestinal irritation, and even death [44]. At high concentration copper increases the rate at which reactive oxygen is being formed. Hence, it brings about oxidative damage [42]. People with Wilson's disease are at a greater risk of health effects from overexposure to copper. Copper normally enters drinking water from copper pipes as well as from additives designed to control algal growth. Report shows that copper competes with calcium for binding sites in tissues and glands. Sites with low concentration of copper had high calcium levels [42].

Nickel

Nickel is an abundant element found in soils and emitted from volcanoes [34]. It is often found combined with oxygen (oxides) or sulfur (sulfides). Nickel can be alloyed with iron, copper, chromium, and zinc and is used in making metal coins and jewelry. Nickel compounds are used for nickel plating, to color ceramics, to make batteries, and as catalysts [34]. A small amount of nickel is needed by the human body to produce red blood cells [34]. However, in excessive amounts it can become mildly toxic.

Nickel is often released into the environment in auto exhaust, fertilizers, hydrogenated fats-oils, industrial waste, stainless steel cookware, testing of nuclear devices, tobacco smoke, baking powder, combustion fuel oil, dental work, and bridges. The most common adverse effect of nickel in humans is an allergic reaction. Headache, dizziness, shortness of breath,

vomiting, and nausea are initial symptoms of overexposure, the delayed effects consist of chest pain, coughing, shortness of breath, bluish discoloration of the skin and in severe cases delirium, convulsions, and death [34]. Short term exposure to nickel is not known to cause any health problems. According to the EPA, limit of nickel in drinking water consumed by children must not exceed 0.04 mg/L [34]. Nickel can accumulate in aquatic life but its presence is not magnified along food chains [34].

Zinc

Zinc is found in air, soil, and water and is present in all foods [34]. It is an important component of some digestive enzymes and proteins. Deficiency of zinc in human diet often results in impaired reproduction, growth, and immunity with loss of hair. Excess amount in food can lead to heart disease in humans [44]. Recommended Dietary Allowance (RDA) is 15 mg/day for men; 12 mg/day for women; 10 mg/day for children, and 5 mg/day for infants [34].

Zinc is used as coating to prevent rust, in dry cell batteries, and combined with other metals to make alloys like bronze and brass. Zinc compounds are used in industries to make paints, rubber, dye, wood preservatives, and ointments. It is also used to make household utensils, castings, printing plates, building materials, railroad car linings, extracting gold by the cyanide process, purifying fats for soaps, bleaching bone glue, manufacture of sodium hydrosulfite, and as reagents in analytical chemistry. Potential sources of zinc in the environment come from mining, steel production, coal burning, and burning of waste. Zinc builds up in fish and other organisms but does not accumulate in plants [34].

Breathing in zinc fumes causes sweet taste, throat dryness, cough, weakness, aching, chills, fever, nausea, and vomiting. Taking in soluble zinc salts may cause nausea, vomiting, and purging. Consuming large amounts of zinc for a short time can cause stomach cramps, nausea, and vomiting. Prolonged consumption can cause anemia, pancreas damage, and lower levels of high density lipoprotein cholesterol-the good form of cholesterol. Limit in drinking water according to EPA should not exceed 5 ppm and releases of more than 1,000 pounds of zinc into the environment must be reported [36].

Iron

Iron is a silvery, lustrous metal found in substantial amount in the earth crust, the sun, and many kinds of stars [45]. It is often alloyed with carbon or other metals [37]. Iron is an important component of plants and animals. It is required as an electron carrier in energy metabolism and is an essential component of hemoglobin [44]. Sources of iron are drinking water, iron pipes, and cookware. Deficiency in iron leads to anemia, weakness, and reduced immunity. Daily requirement of iron for children, male adults, female adults, and pregnant women, are 6-10 mg/day, 10-12 mg/day, 15 mg/day, and 30 mg/day, respectively [46]. Taking in about 20 mg of elemental iron per Kg of body weight results in toxicity [47]. Symptoms of acute iron toxicity include vomiting, diarrhea, fever, hyperglycemia, and leukocytosis. Hypotension, metabolic acidosis, lethargy, seizures, and coma are signs of chronic toxicity. Hyperbilirubinemia and increase in liver enzymes is a sign of liver injury while proteinuria and appearance of tubular cells in urine suggest kidney injury [47]. Iron toxicity occurs when free iron not attached to transferrin is in the blood. The free iron forms free radicals that poison

cellular mitochondria and uncouple oxidative phosphorylation. This free iron damage blood vessels and produce vasodilation with increased vascular permeability [47]. Permissible level required in humans must not exceed 300 $\mu\text{g}/\text{L}$ [44].

CHAPTER 2

RESEARCH ON ANALYSES OF METALS IN WATER

Heavy metal pollution of water and soil has become a major concern to our industrial societies due to its negative impact on organisms that cannot be reversed [48-50]. Most heavy metals are toxic and carcinogenic. And when discharged into water, they represent a serious threat to living organisms [51]. The discharge of these heavy metals into water bodies and sources of drinking water is now closely monitored because most industries use them in making starting materials for other products [52]. According to Joo Hyon et al. [7], even though point sources have been successfully controlled over the past several decades, non point sources have become the leading cause of polluted water bodies.

Non-point source pollution is caused by diverse natural and anthropogenic pollutants that are delivered into receiving water ways and water bodies by means of over land flow, percolation or return flow, and urban runoff during both wet and dry weather [7]. Inefficiency in industrial production process or lack of proper techniques required to handle and manage industrial wastes have been acknowledged as pollution sources responsible for introducing a considerable amount of heavy metals into the environment [53, 54]. The presence of residual ash deposits from coal combustion process in an energy plant can be a possible source of metallic pollutants [55]. Trace of heavy metals such as cadmium, lead, and zinc can have their origins from combustion residues that can get into aquifers, interact, and dissolve into natural ground water [54, 56]. Such hydrogeochemical transport and interaction processes can affect

the constituents of local and regional waters and therefore have a direct effect on the ecosystem [55].

Effects of Weather on Water Pollution

In order to meet water quality regulations, controlling dry and wet weather runoffs has become a major concern for many municipalities [57, 58]. Dry weather runoff takes place without quantifiable precipitation, resulting from ground water inflow, permitted discharge, and human activities including car washing, irrigation, street washing, and construction activities involving the use of water [7]. On the other hand, wet weather urban runoff happens during storm events and is typically a source for a greater amount of pollutant due to an increase in flow energy that moves pollutant deposited on the urban catchment surfaces [7]. Urban storm runoff has been identified as a major cause of non-point source discharge of heavy metals, polycyclic aromatic hydrocarbons, nutrient, and other toxic compound of anthropogenic origins [59, 60]. In urban runoff, the major source of heavy metals is vehicle traffic and the metal species typically found include lead, zinc, iron, copper, cadmium, nickel, and manganese [59].

The characteristic and amount of urban storm runoffs depend on various factors that include rainfall intensity and duration, antecedent dry period (ADP), traffic volume, land use, road maintenance practices, drainage system configuration, and physiogeographic characteristics of the catchment [60-64]. Amongst these factors, ADP plays a major role in determining the quantity of pollutants that settle on the catchment surface ready to be washed off during storms [65-67]. The effectiveness with which pollutants are scrubbed from

catchment surfaces depends on rainfall depth, intensity, and duration [67-69]. Different land use activities may create different pollutant sources and runoff volumes [67].

Joo Hyon et al. [7] found that metal concentrations in water were generally higher during wet summer season and downstream of water bodies than in other seasons and upstream. But, dissolved aluminum, iron, and manganese showed relatively high concentration during the winter months. They stipulated that this may be due to increased metal discharge from storm runoffs in the summer. They also asserted that higher concentration of metals downstream may be as a result of their transport from upstream downward. Wet weather flow contributes a reasonable amount of heavy metals not only because of storm water runoff that washes metals off the catchment surface but also because of the increased stream flow that may effectively carry along particle bound metals deposited on the river bed into the water. According to Karamanis et al. [70], the observed metal concentrations were significantly correlated to water temperature, with maximum value at the maximum water temperature. However, no particular trend was observed in the distribution of metal species in different seasons. Metal concentrations were influenced by dilution effects, characteristic of a particular stream, and often by stream's specific condition of flow, climate, and geochemistry.

Analytical Techniques Used in Water Analyses

The determination of trace concentration of metals in water is important for the evaluation of the degree of pollution and toxicity level. Finding total metal concentration in an environmental sample is often accomplished by means of standard spectroscopic techniques such as atomic absorption spectrometry (AAS) [71, 72], atomic emission spectroscopy (AES),

inductively coupled plasma-AES [73, 74], and inductively coupled plasma – mass spectrometry (ICP-MS). Meng et al. [3] used a combination of graphite furnace atomic absorption spectrometry, flame atomic absorption spectrometry, and cold vapor atomic absorption spectrometry to determine concentrations of heavy metals in water samples. Joo-Hyon et al. [7] analyzed water samples with ICP-MS. Using electrochemical techniques is also quite appealing because of the sensitivity, portability, and low cost of the technique [75]. In order to increase the sensitivity and detection limits of these electroanalytical methods, stripping analysis has been developed as the most sensitive for the detection of heavy metals in trace concentration [76]. La Pera et al [77] showed that hydrochloric acid extraction followed by derivative potentiometric stripping analysis (PSA) was a rapid, sensitive, and precise method to determine simultaneously trace concentration of Cd (II), Cu(II), Pb(II), and Zn(II) in oily matrices using glassy carbon mercury-coated working electrode. Application of flow injection to the electrochemical determination of metals in water samples and adsorption behavior on adsorbents using a micro column by means of an automated, computerized system has been reported [78-80]. Increased sample throughput and selectivity of trace metal determination by combining such systems has been shown [51].

Oyuntseseg et al. [81] used particle induced X-ray emission (PIXE) technique in combination with concentration method to measure heavy metals at ppb levels. The results of the analysis contained random and systematic errors introduced at different stages of the analytical procedure. X-ray fluorescence (XRF) spectroscopy technique has also been employed to determine trace metals in water [70].

Many of these new and more complex techniques are very costly. Most laboratories can not afford to purchase them despite their efficiency [58]. To reduce cost and obtain faster, accurate, and highly sensitive results for the determination of metals at trace levels, Santoyo et al. [55] applied ion chromatography to determine the concentration of heavy metals as well as other inorganic ions. However, use of ion chromatography for heavy metal analysis still has its disadvantages due to matrix interference. Generally, low concentration of heavy metals in the presence of high concentration of alkali and alkali earth elements in geohydrological samples have been identified as one of the main factors responsible for these interferences. The improved ion chromatography methodologies use a rather complex instrumentation for achieving a better separation and detection of these elements as well as optimizing the analysis time.

Sampling and Sample Treatment

Most researchers collect water samples within a particular period. Kar et al. [82] collected water samples once every month during April 2004 to March 2005 from two sites at four monitoring stations. The samples were collected from a depth of one foot below the surface using Nansen type water sampler and kept in polythene containers with the addition of 2 mL concentrated nitric acid to preserve the metals and to avoid precipitation. Meng et al. [3] stored samples in glass bottles after acidification with 0.2 mol/L H_2SO_4 . To monitor metals in both wet and dry weather conditions, Joo-Hyon et al. [7] collected grab samples from water surfaces at upstream and downstream during storm events for at least 24 hours until stream flow normalized.

To analyze for total heavy metals (dissolved and suspended), Kar et al.[82], digested 200 mL of water samples with a 5 mL of 9:4 HNO₃:HClO₄ mixture on a hot plate, filtered by Whatman number 42 filter paper and made up to 50 mL with double distilled water for analysis of heavy metals . Mohammad et al. [83] simply filtered water samples through a 0.45 micro pore membrane before analysis. Samples were stored at 4⁰C prior to analysis [84].

Statistical Analysis

Joo-Hyon et al. [7] used a two way analysis of variance (ANOVA) to compare metal concentrations between two different point sources as well as between dry weather and wet weather flow. Log transformed metal concentration data were used for ANOVA to make sure data were normalized. The statistical analysis were performed using SYSTAT 10.2 (Chicago, IL USA) in which a probability of 0.05 or less was considered statistically significant.

Oyuntsetseg et al. [81] determined the standard deviation of individual samples around the mean as variance. For the variance analysis, two targets were prepared from each water sample to estimate the stability of the target preparation including the effect of addition of internal standard. Each of the targets was irradiated two times for reproducibility of analytical results for solution.

Grande et al. [84] used both cluster and discriminatory analysis to classify individuals into categories. The quantitative analysis of the possible relationship was carried out by applying correlative cluster analysis to a sample of several variables. This enabled them to observe characteristic shared by the different communalities. The program used for their analysis applied single linkage method also known as nearest neighbor method. It is a

hierarchical method that consists of grouping the items according to their similarities. In any step of the analysis, the distance between two clusters was the distance between their nearest points.

Karamanis et al. [70] performed statistical analysis with the Statistical package SPSS 12.0 and used general linear model multivariate analysis to reveal spatial and seasonal trends of natural radioactivity and heavy metals in river water. Appropriate Post –Hoc Game Howell test was performed to reveal statistically significant differences between sites and the four seasons. Differences were considered statistically significant when $p < 0.05$.

To determine the significant difference and correlation between concentrations of heavy metals and radioactivity in surface water and sediment of Hazar Lake, Ozmen et al. [17] used the one way analysis of variance and Pearson correlation coefficient. All calculations were carried out on Microsoft Excel program for Window XP 2002 and SPSS 10.0 statistical calculation program.

CHAPTER 3

ANALYTICAL TECHNIQUES

The determination of trace amount of heavy metals in environmental samples is often achieved by means of standard spectroscopic and electrochemical techniques. This chapter describes some of these techniques and the advantages and disadvantages associated with them.

Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

Inductively coupled plasma method was first employed in the early 1960s with the intention to improve upon crystal growing techniques. It is used in determining trace metals [85] in samples. The aim of using ICP is to get elements to emit characteristic wavelength of light that can be measured quantitatively. This is often achieved by resolving light into its component radiation by means of a monochromator and then measuring the light intensity with a photomultiplier tube at the specific wavelength for each element [85]. The intensity of the signal is compared to intensities of known concentrations of the element measured subsequently and the concentration is computed [85].

In theory, ICP-MS has the ability to identify and quantify all elements except argon because many wavelength of varied sensitivity are available for determination of any element. It is suitable for all concentration ranging from ultra trace levels to major concentrations. The detection limits are generally good for most elements. Multi-element analysis can be accomplished quite rapidly. In real situations, certain unstable elements require special

facilities for handling radioactive fumes of the plasma [85]. ICP-MS has difficulty handling halogens –special optics for the transmission of very short wavelength becomes necessary.

The efficiency of ICP in producing singly-charged positive ions for most elements makes it an effective ionization source for mass spectroscopy. ICP-MS can discriminate between the mass of various isotopes of an element where more than one isotope occurs. Isotope dilution in which a change in the isotope-ratio of two selected isotopes of an element of interest is measured in a solution after the addition of a known quantity of a spike of the enrichment of one of the isotopes permits calculation of the concentration of the elements [85].

In ICP-MS, the sample is aspirated through a nebulizer into a spray chamber and only a small fraction is swept by argon into the torch. For every analytical run, 1 mL of the sample is required and about 99% is wasted. Recently, high efficiency nebulizers have been employed to prevent this problem [85]. Also, detection limit and precision obtained with the high efficiency nebulizers are superior to conventional nebulizer. The most important advantage of ICP-MS is its multi-element capacity, high sensitivity, and the possibility to get isotopic information on the element determined. However, in the ICP-MS system, there may be isobaric interferences produced by polyatomic species arising from the plasma gas and the atmosphere. The isotopes of argon, oxygen, nitrogen, and hydrogen can combine with each other or other elements to produce isobaric interferences. ICP-MS is not useful in the detection of non-metals [85].

X-ray Fluorescence Spectroscopy (XRF)

X-ray fluorescence spectrometry is used for routine, relatively non-destructive chemical analysis of rocks, minerals, sediments, and fluids. The relative ease and low cost of sample

separation and the stability and ease of use of X-ray spectrometers make this technique one of the most widely used for analysis of major and trace elements in rocks, minerals, and sediments [86].

XRF is based on the interaction between electron beams and X-ray with samples. The behavior of atoms when they interact with radiation makes the analysis possible [86]. When materials are excited with high energy short wavelength radiation, they can be ionized. If the energy of the radiation is sufficient to dislodge a tightly held inner electron, the atom becomes unstable and an outer electron replaces the missing inner electron. When this happens, energy is released due to the decreased binding energy of the inner electron orbital compared with an outer one. The emitted radiation is of lower energy than the primary incident X-rays and is termed fluorescent. Because the energy of the emitted photon is characteristic of a transition between specific electron orbitals in a particular element, the resulting fluorescent X-rays can be used to detect the abundances of elements that are present in the sample [86].

X-ray fluorescence is limited to analysis of relatively large samples, typically one gram, materials that can be prepared in powdered form and effectively homogenized, whose compositions are almost the same, well characterized standards are available, and those containing high abundance of element for which absorption and fluorescence effects are reasonable well understood [86].

In theory, XRF has the ability to detect X-ray emission from virtually all elements, depending on the wavelength and intensity of incident X-ray. However, in practice, most commercially available instruments are very limited in their ability to precisely and accurately

measure the abundances of elements with atomic number less than 11 in most natural earth materials [86]. XRF analysis cannot distinguish variations among isotopes of an element, so these analyses are routinely done with other instruments. It also cannot distinguish ions of the same element in different valence states, so these analyses of rocks and minerals are accomplished with techniques such as chemical analysis or Moosbauet spectroscopy [86].

Proton Induced X-Ray Emission (PIXE)

This is an X-ray spectrographic technique used for non-destructive, simultaneous elemental analysis of solid, liquid, or aerosol filter samples [87]. With PIXE techniques, samples could be analyzed without necessarily digestion, minimizing the potential for error. The X-ray spectrum is initiated by energetic protons exciting the inner shell electrons in the target atoms. The expulsion of these inner shell electrons produces X-rays. The energies of the X-rays emitted when the created vacancies are filled again are uniquely characteristic of the elements from which they originate and the intensity of X-ray emitted is proportional to the mass of the corresponding element in the sample. For quantitative analysis, the total number of protons and the proton energy (measured in million electron volts) must be known for best results [87]. All samples may be placed in one of three categories. They are thin, intermediate, and thick targets. For thin samples ($1000 \mu\text{g}/\text{cm}^2$), proton energy loss through the target is not relevant and this simplifies calculation to the trivial case [87]. The instrument itself is calibrated with thin film standards. Therefore, the linear dynamic range may be between $10,000 \mu\text{g}/\text{cm}^2$ to less than $0.001 \mu\text{g}/\text{cm}^2$ for most practical applications using thin targets [87]. With thick targets, it is the opposite. Protons come to rest in the sample. Under this condition, the theory of X-ray

production can be used to correct for proton energy loss because limit of integration are known. Factors needed to make these corrections are non-linear dependent functions and therefore, the data reduction computer code must incorporate these corrections in order to achieve quantitative analysis [87].

Gravimetric standards of 72 elements in the form of thin films of evaporated metals or compounds are used to construct a calibration curve of X-ray counts versus atomic number normalized per unit mass and proton charge [87]. A complete calibration is performed periodically to check changing characteristic of the X-ray detector with aging and also to check the constancy of the geometric arrangement of the bombardment facility. As part of the quality control system, a gallium phosphide standard is run at least daily to correct for minor variations in calibration drift [87].

Because X-ray production cross sections decrease with increasing atomic number for a given electronic shell and detector efficiency decreases with increasing X-ray energy, higher atomic number elements produce fewer X-rays per unit proton charge than do low atomic number elements. To offset this effect and to achieve more uniform detection limits across the entire periodic table, a dual irradiation is carried out on each sample. In one position the detector directly views the X-ray emitted from the target. This allows the low atomic number elements to develop. The second position has an absorber placed between the sample and the detector to preferentially filter the emitted X-rays and provides balance in the spectrum. Variation in these irradiation lines allows control of the detection limits for each element in the spectrum [87].

Unlike thin target samples where simple comparison of elemental X-ray intensities with the calibration curve leads directly to the PIXE results, the analysis of thick target samples requires additional information about the proton energy loss within the target, X-ray absorption by the sample mass, secondary induced fluorescence, and other matrix corrections not encountered in thin samples [87].

Neutron Activation Analysis (NAA)

Neutron activation analysis is a sensitive analytical technique used for both qualitative and quantitative multi-element analysis of major and trace elements in samples. It was discovered in 1936, when Hevesy and Levi found that samples containing certain rare earth elements became highly radioactive after exposure to a source of neutrons. They recognized that employing nuclear reactions on samples followed by measurement of the induced radioactivity could facilitate both qualitative and quantitative identification of the elements present in the samples. Today, NAA is recognized as the reference method of choice when new procedures are developed because of its accuracy and reliability [88].

In carrying out an NAA analysis, there should be a source of neutrons, instrumentation suitable for detecting gamma rays, and a detailed knowledge of the reactions that occur when neutrons interact with target nuclei [88]. NAA is classified into two categories depending on the time of measurement [88]. In prompt gamma ray NAA, measurement is made during irradiation while in the delayed gamma ray neutron activation analysis, measurement follows radioactive decay [88]. Neutron energy distributions are quite broad and consist of three principal components (thermal, epithermal, and fast). The thermal neutron component

consists of low energy neutrons (energies below 0.5 eV) in thermal equilibrium with atoms in the reactors moderator. The epithermal neutron component consists of neutrons (energies above 0.5 eV to about 0.5 MeV) that have been only partially moderated. The fast neutron component of the neutron spectrum (energies above 0.5 MeV) consists of the primary fission neutrons that still have much of their original energy following fission. Fast neutrons contribute very little to the reactions but induce nuclear reactions where the ejection of one or more nuclear particles is prevalent [88].

To calculate the concentration of an element in the unknown sample, the sample together with a comparator standard containing a known amount of element of interest are irradiated in the reactor. Then, the difference in decay between the two is corrected when the same detector is used. One usually decay correct the measured counts for both samples back to the end of irradiation using the half life of the measured isotope [88]. The sensitivity for NAA depends upon the irradiation parameters (that is, neutron flux, irradiation, and decay times), measurement conditions (that is, measurement time, detector efficiency), and nuclear parameters of the element being measured (that is, isotope abundance, neutron cross section, half life, and gamma-ray abundance) [88]. Accuracy of individual NAA determination ranges between 1 to 10% of the reported value.

Ion Chromatography (IC)

Ion chromatography is a type of liquid chromatography used for water chemistry analyses, to measure concentrations of major anions such as fluorides, chlorides, nitrates, and

sulfates. It can also be used to measure concentrations of major cations such as lithium, sodium, ammonium, potassium, and magnesium ions in part per billion range [89].

In ion chromatography, concentrations of ionic species are measured by separating them based on their interaction with a resin. Ions separate differently depending on type and size. Sample solution passes through a pressurized chromatographic column where ions are absorbed by column constituents. As an ion extraction liquid known as eluent runs through the column, the absorbed ions begin separating from the column. The retention time for different species determines the ionic concentration in the sample. The column packing for ion chromatography consists of ion exchange resins bonded to inert polymeric particles. For cation separation, the cation exchange resin is usually a sulfonic or carboxylic acid, and for anion separation, anion exchange resin is a quaternary ammonium group [89].

Anodic Stripping Voltammetry (ASV)

Anodic stripping voltammetry is an analytical method that involves pre-concentration of a metal onto a solid electrode surface or into mercury at a negative potential and selective oxidation of each metal species during an anodic potential sweep [90]. The technique is useful for analysis of very dilute solutions of up to 10^{-11} M, part per billion and even part per trillion because of the pre-concentration of the metal [90]. ASV technique is very sensitive and reproducible (RSD<5%) for trace metal ion analysis in aqueous media. Approximately 12-15 metal ions can be analyzed by this method and stripping peak current and peak widths are a function of size, coverage, and distribution of the metal phase on the electrode surface. In fact, ASV is the most economical choice for ultra-sensitive measurements because it is relatively

inexpensive compared to atomic absorption systems and inductively coupled plasma systems [90]. However, accuracy is proportional to the way one calibrates one's sample [90].

Flame Atomic Absorption Spectroscopy (FAAS)

In 1802, the phenomenon of atomic absorption was first observed with the discovery of Fraunhofer line in the sun's spectrum. But it was not until 1953 that an Australian physicist, Sir Alan Walsh, showed that atomic absorption could be used as a quantitative analytical tool [91]. Today, the technique is used for determination of metallic elements in both trace and major concentration [91]. In principle, light absorbed by vaporized ground state atoms is measured and related to concentration. A detector measures the intensity of light transmitted by the sample and compares it to the intensity that originally passed through the sample. The incident light beam is attenuated by atomic vapor absorption according to Beer's law [91].

In using FAAS, it is necessary to produce a calibration curve in order to determine the concentration of a known element in a sample. For this process, a known wavelength is selected and the detector will only measure energy emitted at that wavelength. As concentration of the target atom in the sample increases, absorption will also increase proportionally. For a series of known concentrations of the standard, the corresponding absorbance is measured. A straight line is drawn between all of the data points. The concentration of the unknown is obtained from its absorbance by extrapolation of the line [91].

The use of spectral light sources and specific wavelength selection allows the quantitative determination of individual components of a multi-element mixture. The process of flame atomic absorption measurement involves the atomization of the sample in flame and

the absorption of radiation from a light source by free atoms [91]. Both instrumental and chemical parameters of the system are selected such that only neutral ground state atoms of the element of interest are produced for best results. Sample is aspirated in a liquid form into the flame through a nebulizer, then dispersed into fine spray, which is desolvated and vaporized into neutral atoms. The instrument parameter must be set such that light from the source (hollow cathode lamp) is directed through the region of the flame that contains the maximum number of neutral atoms. The light produced by the hollow cathode lamp is emitted from excited atoms of the same element that is to be determined. Therefore, the radiant energy corresponds directly to the wavelength that is absorbable by the atomized sample. This method is both sensitive and selective as other elements in the sample will not absorb the chosen wavelength and thus will not interfere with the measurement. Background interference is reduced by isolating wavelength of interest with a monochromator placed between the sample and the detector [91].

The idealized calibration curve is stated by Beer's law that absorbance is proportional to its concentration. However, deviation from linearity often occurs as concentration of metallic analyte changes due to several reasons that includes unabsorbed radiation, stray light, or disproportionate decomposition of molecules at high concentrations. Absorbance can be brought into optimum working range by sample dilution, using an alternative wavelength having a lower absorptivity, or reducing the path length by rotating the burner head [91].

Though flame atomic absorption methods are relatively free from inter-element spectral interference, and background effects can easily be corrected using a deuterium lamp, for some

elements, the temperature or type of flame used is critical [91]. If flame and analytical conditions are not properly used, chemical and ionization interferences can occur [91].

Graphite Furnace Atomic Absorption Spectrometry (GFAAS)

Graphite furnace atomic absorption spectrometry is also known as electrothermal atomic absorption spectrometry. Samples are analyzed based on the same principle as FAAS but an electrically heated furnace is used to atomize the analyte. GFAAS is more sensitive than FAAS because it confines atoms in the optical path for a longer time than FAAS. Only a few micro-liter of the sample is required for analysis. In addition, it has a lower detection limit than FAAS [92]. Ideally, analytes are not usually vaporized until a constant temperature is reached in the furnace. However, premature atomization may occur when sample is injected directly on the inside of the furnace before constant temperature is reached. Difficulty in injecting a very small volume of the sample makes the short-term precision range (0.5-5%) of GFAAS greater than FAAS. Several interferences may be encountered when using GFAAS. Background effect occurs when matrix components are vaporized and atomized at the same time as the analyte. This is usually corrected using either deuterium or Zeeman background correction. When temperature required to burn sample matrix also vaporize the analyte, matrix interference results. Matrix interference can be prevented using matrix modifiers that ensure analytes do not evaporate until matrix is completely burnt and desired temperature is reached. Using GFAAS requires expertise. A skilful operator determines the heating condition to effectively atomize a sample [92].

Objectives of Research

Heavy metals have comparatively simple chemistry and do not decay in the environment. Their availability in the environment in high concentration indicates the level of pollution due to anthropogenic activities. When concentrations of these heavy metals exceed certain limits, they are known to harm plants, animals, and humans. Hence, determination of total metal levels in an area provides valuable information to initiate prompt action to prevent their prevalence in the environment. Besides the contribution of human activities to pollution in an area, weather has been found to influence pollution levels. Reports show that metal concentration was higher at base flow and in storms following long dry weather. From the above literature review, the objectives of this research are to:

1. Determine the concentration of some heavy metals in water samples collected from different creeks.
2. Evaluate how seasonal variation can influence the distribution and abundance of heavy metals in water.
3. Determine the correlation of human activities on the level of heavy metals found in water samples.

CHAPTER 4

MATERIALS AND METHOD

Reagents and Solutions

Reagents used in this study were:

1. 1000 µg/mL stock solutions of zinc, copper, iron, nickel, lead, and cadmium from Leeman Lab, (Hudson, NH).
2. Concentrated nitric acid by Seastar Chemical from Fisher scientific (Pittsburg, PA)

Instrumentation

The samples were analyzed using the Shimadzu AA 6300 model flame atomic absorption spectrophotometer manufactured by Shimadzu Corporation, analytical and measuring instruments division, Japan.

Hollow cathode lamps of specific elements manufactured by Photonics K.K Electrode tube division, Japan were used to provide the line source required for maximum absorption of each of the selected metal.

For all the metals analyzed, the flame used was air-acetylene mixture. The burner angle and support gas flow rate were zero degree and 15.0 L/min respectively.

Specific wavelength, gas flow rate, slit width, and burner height for each metal are outlined in Table 1.

Table 1: Measurement parameters for heavy metals analyzed

Metal	Wavelength (nm)	Gas flow rate (L/min)	Slit Width (nm)	Burner Height (mm)
Zinc	213.9	2.0	0.7	7.0
Copper	324.8	1.8	0.7	7.0
Iron	248.3	2.2	0.2	9.0
Nickel	232.0	1.6	0.2	7.0
Lead	217.0	2.0	0.7	7.0
Cadmium	228.8	1.8	0.7	7.0

Data Treatment and Statistics

Microsoft Excel 2007 was used to calculate distributive statistics and the correlation between metals. Also, the statistical software SPSS was used to perform a two-way analysis of variance to statistically compare the metal levels in the different samples and with respect to time of sampling.

Sampling and Sample Treatment

Water samples were collected at chosen intervals from January 2010 to September 2010 from 6 different sites, based on the major activities going on around an area. Table 2 gives a summary of the different chosen sites. Samples were all collected shortly after rainfall except in January, when they were collected after snowfall. The highest amount of rainfall and warmest temperature for the sample collection occurred in the month of June.

Table 2: Description and characteristics of different sites sampled based on human activity and flow conditions of the stream

Site	Code	Location	Activities at site & condition of water flow
1	A	Creek running between ETSU Library and Culp center	Less vehicular activity low flow
2	B	Creek running through a large parking lot between ETSU CPA and State of Franklin Road	High vehicular activity moderate flow
3	C	Creek running between State of Franklin and Mullikan Flooring Company	High vehicular activity, industrial site, road construction high flow
4	D	Creek running through Carter & Carter Machinery	Moderate vehicular activity and industrial site moderate flow
5	E	Creek adjacent to General Shale Brick along Broadway Road	High vehicular activity and industrial site high flow
6	F	Creek running between King Spring Church & Dave Buck Road	Residential area, less vehicular activity low flow

The samples were obtained upstream from the surface of creeks and stored in polyethylene bottles rinsed several times with deionized water. 2 mL of concentrated nitric acid was added to all the samples to preserve the metals and to avoid precipitation. Water samples were filtered and stored in the refrigerator prior to analysis using the flame atomic absorption spectrophotometer.

Preparation of Standard Solutions

Working solutions were first prepared by dissolving 500 μL of each of the stock solutions into 50 mL volumetric flasks and made up to mark with de-ionized water. From these working solutions serial dilutions were made to prepare calibration solutions. Concentrations of 0.1, 0.2, 0.4, 0.8, and 1.0 $\mu\text{g}/\text{mL}$ were prepared by measuring 25 μL , 50 μL , 100 μL , 200 μL , and 250 μL , respectively, from the working solution into 25 mL volumetric flasks and made up to mark with de-ionized water.

Sample Analysis

Standard solutions were prepared immediately prior to analysis to prevent adsorption of metals by glass containers and their decomposition. Also, same instrumental conditions were maintained throughout every measurement for a particular metal.

Standard and sample solutions were aspirated into the nebulizer through a capillary tube where solutions were converted into fine mist before they were being atomized in the flame. The free atoms absorbed radiation from the hollow cathode lamp. The instrument then records the absorption by a given calibration concentration. A calibration curve was obtained by plotting absorbance against concentration. The least square fit regression equation of the calibration curves was used to determine concentration of the sample solutions.

CHAPTER 5

RESULTS AND DISCUSSION

The concentrations of Ni, Fe, Cu, Cd, Pb, and Zn were determined in six different creeks around Johnson City, Tennessee, to evaluate if they would reflect the source and volume of heavy metals associated with different activities within an area. The effect of weather on the concentrations of metals found in them was also determined. Concentrations of the metals were obtained from calibration curves for the metals determined and these calibration curves are shown in Appendix A. Linear curves were obtained for all the metals determined with concentration range between 0.2 mg/L- 1.0 mg/L. Figure 1 is a typical example of the calibration curve obtained.

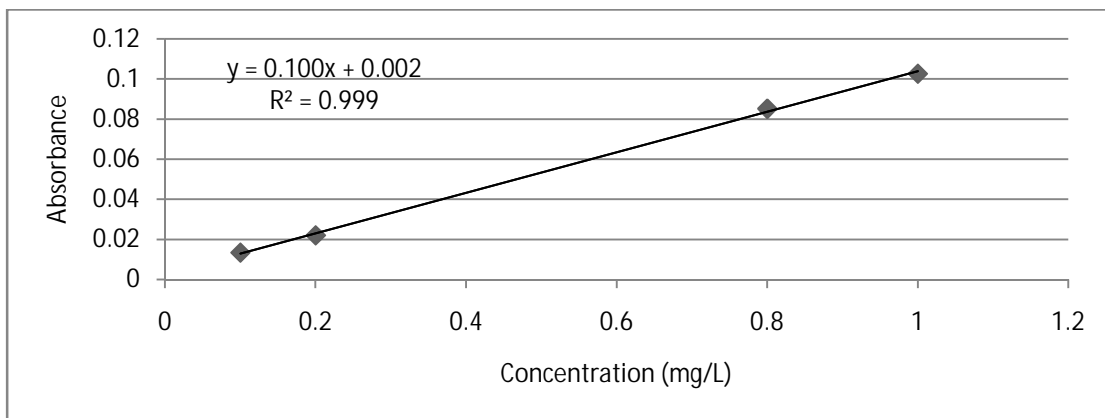


Figure 1: Calibration Curve for Zn used to determine concentration of Zn in samples collected from different creeks

For good precision and accuracy, all samples were analyzed in triplicates and the absorbance values of the calibration standards re-determined after samples measurement. Samples with concentrations of metals higher than 1.0 mg/L were diluted appropriately such

that the absorbance values fell within the linear dynamic range employed for the calibration curves.

Each site examined is characterized by different water flow conditions within the creek and different activities around their vicinities. Site A, located between the East Tennessee State University (ETSU) Library and Culp Center, is characterized by low flow throughout the sampling period. Besides the library and Culp Center, the creek is surrounded by office buildings, resident halls for students, and a small parking lot. Traffic volume is low and slow. Site B, also located within the ETSU campus, is characterized by moderate flow condition throughout the sampling period. The creek runs through a large parking lot adjacent to the State of Franklin Road. Some few miles away downstream from this creek are business centers, a gas station, and a mechanic workshop. Traffic density is high and fast. Site C, which runs along State of Franklin very close to a flooring company, is characterized by high flow throughout the sampling period. Not far away from this creek is a construction site, a gas station, and other business centers like Mc Donald's. Traffic density is also high and constant. Site D, which runs behind a metal coupling company, is characterized by moderate flow throughout the sampling period. Traffic density around this area is moderate. Site E, located opposite General Shale Brick Company on Broadway, is characterized by high and constant flow throughout the sampling period. Traffic density is high due to frequent loading and offloading from trucks and trailers in a transportation company in addition to normal vehicle traffic. Very few business centers are found around this area. Site F, located along Dave Buck Road within a residential area, is characterized by low flow. Traffic density around the area is low and slow.

In calculating the mean, concentrations below detectable limits were assigned zero.

The mean concentrations of the selected metals and the standard deviations found in water samples from the surfaces at different creeks are shown in Table 3. Each mean concentration tabulated was obtained by calculating the average concentration of each metal determined in triplicates at each site and also throughout the sampling period in each site.

Table 3: Mean concentrations and standard deviations of metals found in different sites along with the maximum EPA permitted chronic exposure values for an aquatic community

Mean concentrations (standard deviations) in mg/L of selected metals found in different sampling sites							EPA value
Metals	Site A	Site B	Site C	Site D	Site E	Site F	Chronic
Ni	0.073 (0.152)	0.262 (0.146)	ND	0.215 (0.033)	0.061 (0.079)	0.260 (0.105)	0.052
Cu	0.083 (0.140)	0.130 (0.032)	0.040 (0.046)	0.104 (0.114)	0.076 (0.055)	0.098 (0.040)	0.009
Cd	ND	0.010 (0.020)	ND	0.002 (0.005)	0.001 (0.002)	ND	0.00025
Fe	1.05 (1.30)	0.601 (0.240)	0.727 (0.364)	1.33 (0.750)	3.01 (3.29)	1.06 (0.701)	0.300
Zn	6.96 (13.1)	13.8 (23.7)	1.33 (2.48)	1.87 (2.66)	3.31 (3.92)	4.93 (8.62)	0.120
Pb	0.795 (2.31)	ND	ND	ND	0.040 (0.155)	ND	0.0025

The result shows that concentrations of different metals varied with sites. Cd was detected in only sites B, D, and E, with mean concentrations, of 0.010 mg/L, 0.002 mg/L, and 0.001 mg/L, respectively. Pb was below detectable limit in all the sites except in sites A and E, with mean concentrations of, 0.795 mg/L and 0.040 mg/L, respectively. Meanwhile, Ni, Cu, Fe, and Zn were detected in all the sites, except for Ni that was below detectable limit in site C.

The highest mean concentrations of Ni (0.262 mg/L), Cu (0.130 mg/L), and Zn (13.8 mg/L) were

observed in site B. Mean concentration of Fe (3.01 mg/L) was highest in site E. The mean concentrations of all these metals were observed to be much higher than the maximum permissible level of, 0.052 mg/L, 0.009 mg/L, 0.00025 mg/l, 0.300 mg/L, 0.120 mg/L, and 0.0025 mg/L, for Ni, Cu, Cd, Fe, Zn, and Pb, respectively, to which any aquatic organism community should be exposed to as recommended by the EPA [15].

The mean concentrations of the metals found in all the creeks examined at different time period are shown in Table 4. Each value was obtained by calculating the average of each of the triplicate determination of the metals observed in all the sites on each sampling date. The data were also subjected to statistical test to ascertain if there was a significant difference in the concentrations of the metals with sampling dates.

Table 4: Mean concentrations (standard deviations), in mg/L, of selected metals determined in triplicate samples collected from January 2010 to September 2010. Concentrations below detectable limits are represented with ND

Sampling Date	Ni	Cu	Cd	Fe	Zn	Pb
13-Jan	0.147	0.185	ND	2.22	17.2	0.015
12-Feb	0.163	0.103	0.001	1.89	3.16	ND
16-Apr	0.123	0.050	0.001	1.13	0.343	0.119
30-Jun	0.155	0.052	0.008	0.700	0.039	0.559
29-Sep	0.135	0.051	ND	0.580	6.11	0.004
Mean (Standard Deviation)	0.145 (0.144)	0.088 (0.084)	0.004 (0.009)	1.30 (1.68)	5.36 (12.2)	0.139 (0.964)

In general, for these metals that were determined, the average concentrations found over the different sampling dates were above the EPA recommended maximum values. Also

the standard deviations were large because the variation in amount of metals found at the different sites and at different periods together was quite large. This is reasonable as different sampling sites were chosen with the purpose of observing the correlation between activities occurring near the sites and how these activities affect the metal concentration found at these sites. Thus, some sites would be expected to have higher concentration of metals while others would have much less. These concentrations may increase over time resulting in elevated amounts of the metals in organisms that depend on the creeks for life. Heavy metals are non-degradable, bio-persistent, and bio-accumulative in nature. They tend to build up in the environment and the tissues of living organisms through the food chain. Chronic exposure to very high concentrations of these heavy metals may cause harm to aquatic life and humans.

Distribution of Metals in Samples From Different Sites

Nickel

A wide variation was observed in the distribution of Ni in the sites examined. Results for the concentrations of Ni found in the different sites at different sampling dates are shown in Table 5. These values are averages obtained from the triplicate measurements made for each sample. Mean concentrations of Ni varied from, 0.073 mg/L (0.152), 0.262 mg/L (0.146), 0.215 mg/L (0.033), 0.061 mg/L (0.079), and 0.258 mg/L (0.105) at sites A, B, D, E, and F, respectively. There was no detectable concentration of Ni for samples at site C at all time periods. Analysis of variance showed that there is a significant difference in ($p=0.000$) the concentration of Ni among the different sites ($p<0.05$) but no significant difference ($p=0.111$) with respect to dates of sample collection as seen in Table 6.

Table 5: Mean concentrations of Ni (standard deviations) in mg/L determined in samples collected from different sites at different periods of the year

Concentration of Ni in the different Sites (mg/L)						
Date	Site A	Site B	Site C	Site D	Site E	Site F
13-Jan	0.366	0.073	ND	0.226	0.006	0.216
12-Feb	ND	0.427	ND	0.210	0.128	0.215
16-Apr	ND	0.180	ND	0.217	0.013	0.328
30-Jun	ND	0.366	ND	0.186	ND	0.379
29-Sep	ND	0.266	ND	0.238	0.155	0.151
Mean (standard deviation)	0.073 (0.152)	0.262 (0.146)	ND	0.215 (0.033)	0.061 (0.079)	0.258 (0.105)

Table 6: Two way ANOVA Table for Ni

Tests of Between-Subjects Effects

Dependent Variable: Metal concentration

Source	Type III Sum of Squares	Degree of freedom	Mean Square	F	Significance
Corrected Model	1.711 ^a	29	.059	24.810	.000
Intercept	1.889	1	1.889	794.745	.000
Location	.972	5	.194	81.763	.000
Date	.019	4	.005	1.966	.111
Location * Date	.720	20	.036	15.141	.000
Error	.143	60	.002		
Total	3.743	90			
Corrected Total	1.853	89			

R Squared = .923 (Adjusted R Squared = .886)

Post Hoc test reveals mean concentration of Ni in site A is significantly higher than site C but lower than sites B, D, and F ($p < 0.05$). Mean concentration in site B is significantly higher than sites A, C, and E ($p < 0.05$). Mean concentration in site D is significantly higher than sites A,

C, and E. Mean concentration in site E is significantly lower than sites B, D, and F but higher than in site C ($p < 0.05$). The mean concentrations of Ni are significantly highest in site B and lowest in site C.

The high concentration of Ni in site B relative to other sites may be attributed to increased discharge of Ni containing particulates mainly from roadways and automobiles. Site B is near a major highway and a busy parking lot. Vehicle traffic contributes a significant amount of Ni to the environment. However, Ni was below detectable limit in site C which is characterized by a constant high water flow throughout the sampling period. This anomaly observed at this site, despite its proximity to a flooring company and a high traffic volume, may be attributed to some other factors. Biological processes, ionic strength, pH, activities of organic and inorganic chelators, and scavenging processes have been found to influence the concentration of metal ions in water [26]. The local conditions within the stream having some of these factors may have favored the conversion of Ni in this site into an immobile form. Concas et al. [27] suggested that heavy metals may be transferred from stream water to stream sediments through precipitation as the pH of stream increases and through adsorption. Another possibility for this observation may be due to dilution effect augmented by increased flow of the stream, particularly after a rain event. Perhaps, Ni may have been transported further downstream.

Further analysis of Ni in this site C reveals a higher concentration of Ni in samples collected upstream (0.523 mg/L) and lower concentration downstream (0.052 mg/L). This variation may be due to physical reasons, as contributions of pollutants to the environment

vary daily. Another possible reason for this observation may be due to the proximity of the upstream region to higher and more constant traffic density than the downstream region. Concentration of Ni in both the upstream (0.523 mg/L) and midstream (0.500 mg/L) regions were observed to be almost the same. Both sites are located along the State of Franklin Road while the downstream region is completely off this road. It is located further towards downtown (an area characterized by residential buildings and very low traffic).

Because there is no significant difference in the concentration of Ni with the dates samples were collected, the type and volume of human activities at sampling sites played a major role irrespective of the weather condition as seen in Table 5.

Copper

A significant variation was observed in the distribution of Cu in site A relative to other sites examined. Results for the concentration of Cu in the different sites at different sampling dates are shown in Table 7. These values are averages obtained from the triplicate measurements made for each sample. Mean concentrations of Cu varied from, 0.083 mg/L (0.140), 0.130 mg/L (0.032), 0.040 mg/L (0.046), 0.098 mg/L (0.040), 0.076 mg/L (0.055), and 0.098 mg/L (0.040), in sites A, B, C, D, E, and F, respectively.

Table 7: Mean concentrations of Cu (standard deviations) in mg/L determined in samples collected from different sites at different periods of the year

Concentration of Cu in the Different Sites (mg/L)						
Date	Site A	Site B	Site C	Site D	Site E	Site F
13-Jan	0.349	0.178	0.0214	0.306	0.150	0.107
12-Feb	0.014	0.121	0.121	0.093	0.121	0.150
16-Apr	ND	0.107	ND	0.107	0.050	0.036
30-Jun	0.043	0.121	0.021	ND	0.021	0.107
29-Sep	0.007	0.121	0.036	0.014	0.036	0.093
Mean (Standard deviation)	0.083 (0.140)	0.130 (0.032)	0.040 (0.046)	0.098 (0.040)	0.076 (0.055)	0.098 (0.040)

Analysis of variance showed that the concentrations of Cu among the different sites, and with respect to dates of sample collection are significantly different ($p < 0.05$) as shown in Table 8.

Table 8: Two way ANOVA Table for Cu

Tests of Between-Subjects Effects

Dependent Variable: Metal concentration

Source	Type III Sum of Squares	Degree of freedom	Mean Square	F	Significance
Corrected Model	.612 ^a	29	.021	61.205	.000
Intercept	.702	1	.702	2035.059	.000
Location	.069	5	.014	39.953	.000
Date	.248	4	.062	179.728	.000
Location * Date	.295	20	.015	42.813	.000
Error	.021	60	.000		
Total	1.335	90			
Corrected Total	.633	89			

a. R Squared = .967 (Adjusted R Squared = .951)

Post Hoc test reveals that mean concentration of Cu in site A is significantly higher than site C but lower than sites B and D ($p < 0.05$). Mean concentration in site B is significantly higher than sites A, C, D, E, and F ($p < 0.05$). Mean concentration in Site C is significantly lower than sites A, B, D, E, and F ($p < 0.05$). Site D is significantly higher than sites A, C, and E but lower than site B. Mean concentration in site E is significantly lower than sites B, D, and F but higher than site C. And site F is lower than site B but higher than site C.

The concentrations of Cu were significantly higher in site B and lower in site C. High concentration of Cu observed in site B relative to other sites may be due to its proximity to a large parking lot, the mechanic workshop, and a road with constant traffic. Cu is also another heavy metal released from anthropogenic sources especially from roadways and automobiles. A significant amount of Cu may have been retained in the water surface due to moderate flow within the stream. Another possibility may be that the local condition within the creek favors the mobilization of Cu into the soluble phase. The lower concentration observed in site C may be attributed to dilution effects within the creek due to constant flow throughout the sampling period. Cu may have been transported further downstream or perhaps had been converted into a non-bio-available form.

With respect to the dates samples were collected, mean concentration of Cu is significantly higher in samples collected in the month of January than in any other month ($p < 0.05$), and samples collected in February is significantly higher than concentrations in samples collected in the months of April, June, and September.

Mean concentrations of Cu in all the sites examined with respect to period of sample collection, as shown in Table 4, varied from 0.050 - 0.185mg/L. This high concentration of Cu observed in the month of January relative to other months may be due to reduced water flow in most of the creeks at this time of the year. Snow and ice in the creeks associated with this period may have trapped and prevented the transportation of Cu particulates released from automobiles and domestic wastes discharge away from sampling sites. Higher concentrations have been observed in samples collected from low and moderate water flow relative to higher flow. Kar et al. [82] also observed the highest concentration of Cu during the winter. They suggested that this may be due to sudden rainfall followed by discharge from upstream environment.

Zinc

A wide variation was also observed in the distribution of Zn in the sites examined. Results for the concentrations of Zn in the different sites at different sampling dates are shown in Table 9. These values are averages obtained from the triplicate measurements made for each sample. Mean concentrations of Zn varied from, 6.96 mg/L (13.09), 13.78 mg/L (23.73), 1.33 mg/L (2.30), 1.87 mg/L (2.65), 3.31 mg/L (3.92), and 4.93 mg/L (8.62) in sites A, B, C, D, E, and F, respectively.

Table 9: Mean concentrations of Zn (standard deviations) in mg/L determined in samples collected from different sites at different periods of the year

Concentration of Zn in the different Sites (mg/L)						
Date	Site A	Site B	Site C	Site D	Site E	Site F
13-Jan	32.2	46.4	0.662	1.70	0.592	21.5
12-Feb	0.124	2.42	0.137	6.87	6.75	2.68
16-Apr	ND	0.627	0.089	0.678	0.178	0.487
30-Jun	ND	ND	0.029	0.108	0.100	ND
29-Sep	2.51	19.45	5.75	0.013	8.94	ND
Mean (Standard deviation)	6.96 (13.09)	13.78 (23.73)	1.33 (2.30)	1.87 (2.65)	3.31 (3.92)	4.93 (8.62)

Analysis of variance showed that concentrations of Zn among the different sites and with respect to dates of sample collection are significantly different ($p < 0.05$) as shown in Table 10. The Post Hoc test reveals that mean concentration of Zn is significantly higher in site B than in sites A, C, D, E and F ($p < 0.05$). There is no significant difference in the mean concentrations of Zn between site A and sites B, C, D, E, and F. Also, mean concentrations in sites C, D, E, and F, are individually significantly different from site B.

Table 10: Two way ANOVA Table for Zn

Tests of Between-Subjects Effects

Dependent Variable: Metal concentration

Source	Type III Sum of Squares	Degree of freedom	Mean Square	F	Significance
Corrected Model	10176.987 ^a	29	350.931	6.728	.000
Intercept	2588.987	1	2588.987	49.635	.000
Location	1592.262	5	318.452	6.105	.000
Date	3566.847	4	891.712	17.096	.000
Location * Date	5017.879	20	250.894	4.810	.000
Error	3129.608	60	52.160		
Total	15895.583	90			
Corrected Total	13306.595	89			

a. R Squared = .765 (Adjusted R Squared = .651)

High concentration of Zn observed in site B relative to other sites, suggests that it may be due to atmospheric depositions of Zn from automobiles. Automobiles are significant contributors of Zn to the environment. Another of possible source of Zn may be from domestic wastewater as suggested by Meng et al. [3]. They suggested that possible contamination of surface water by Zn may be from terrestrial sewage discharge. Besides, the release of Zn from anthropogenic sources, the high concentration of Zn observed in site B may be due to the local conditions within the creek, which may have favored its mobility into the soluble phase. Another possible reason may be due to the moderate water flow within this creek. Higher concentrations of metals have been observed in samples collected at low and moderate flow [93]. The moderate flow observed in this creek may have reduced the rate of transportation of Zn further downstream.

The mean concentrations of Zn not been significantly different in sites A, C, D, E, and F may be due to the large standard deviation observed. Probably, Zn may have been released naturally from the sediments and beds into the water. Variation in the concentrations of Zn within the same site suggests that the release of the metal into surface water varied daily depending on the volume of discharge from anthropogenic sources and the geology of the catchment. Of all the metals analyzed, concentration Zn was very high in almost all the sites. This suggests that besides roadways and automobiles, Zn may also have been discharged from other sources, which may be either from wastewater or natural sources. Another possible reason may be due to its high solubility. Concas et al. [27] suggested that the high concentration of Zn observed in surface water may be as a result of Zn may be loosely bond to the solid phase. This makes it easy for Zn to enter into the soluble phase.

With respect to the dates of sample collection, mean concentration of Zn is significantly higher in samples collected in the month of January than in samples collected at any other month during the sampling period ($p < 0.05$). There is no significant difference between the mean concentrations of Zn in samples collected in the months of February, April, June and September ($p > 0.05$), respectively. Probably, Zn released from automobiles and roadways may have settled on the surface of stagnant creeks blocked by snow. As rainfall intensity increased, water volume increased and washed Zn further downstream with time. This observation may also be attributed to change in condition of the stream overtime. Although storm events following a long dry period are characterized by increased influx of pollutants from catchment surfaces into water bodies during the earlier part of rainfall, infiltration through the bed can inhibit the release of pollutants into water surface [7]. Another possibility may be that Zn is released randomly from domestic wastewater and nature, so its concentration varied daily irrespective of time.

Iron

A wide variation was observed in the distribution of Fe in the sites examined. Results for the concentration of Fe in the different sites at different sampling dates are shown in Table 11. These values are averages obtained from the triplicate measurements made for each sample. Mean concentrations of Fe varied from 1.05 mg/L (1.30), 0.601 mg/L (0.240), 0.727 mg/L (0.364), 1.33 mg/L (0.701), 3.01 mg/L (3.29), 1.06 mg/L (0.701), in sites A, B, C, D, E, and F, respectively.

Table 11: Mean concentrations of Fe (standard deviations) in mg/L determined in samples collected from different sites at different periods of the year

Concentration of Fe in the different Sites (mg/L)						
Date	Site A	Site B	Site C	Site D	Site E	Site F
13-Jan	3.55	1.03	1.15	2.56	4.42	0.593
12-Feb	0.369	0.516	0.393	0.593	8.66	0.784
16-Apr	0.325	0.478	1.15	1.73	0.727	2.36
30-Jun	0.620	0.519	0.462	1.02	0.601	0.795
29-Sep	0.399	0.462	0.478	0.760	0.625	0.754
Mean (standard deviation)	1.05 (1.30)	0.601 (0.240)	0.727 (0.364)	1.33 (0.701)	3.01 (3.29)	1.06 (0.701)

Analysis of variance showed that the concentration of Fe among the different sites and with respect to the dates of sample collection are significantly different ($p < 0.05$) as shown in Table 12.

Table 12: Two way ANOVA Table for Fe
Tests of Between-Subjects Effects
Dependent Variable: Metal concentration

Source	Type III Sum of Squares	Degree of freedom	Mean Square	F	Significance
Corrected Model	250.155 ^a	29	8.626	707.599	.000
Intercept	151.142	1	151.142	12398.312	.000
Location	57.851	5	11.570	949.104	.000
Date	38.295	4	9.574	785.340	.000
Location * Date	154.009	20	7.700	631.674	.000
Error	.731	60	.012		
Total	402.029	90			
Corrected Total	250.886	89			

a. R Squared = .997 (Adjusted R Squared = .996)

The Post Hoc test reveals that mean concentration of Fe in site E is significantly higher than mean concentrations in sites A, B, C, D, and F ($p < 0.05$). Mean concentrations of Fe in site D is significantly higher than in sites A, B, C, and F ($p < 0.05$) but lower in site E. Mean concentration in site F is significantly higher than mean concentrations in sites B and C but lower than sites D and E. Mean concentration of Fe in site C is significantly higher than site B but lower than mean concentrations in sites A, D, E, and F ($p < 0.05$).

The highest concentration of Fe observed in site E relative to other sites suggests that activities within the brick making company contribute a significant amount of Fe to the surface water in addition to possible sources from automobiles. Probably activities within the area favor the mobilization of Fe into the soluble phase. This excess load of Fe may also be attributed to geology of the catchment area as Fe is significantly abundant in nature. Physical and chemical weathering releases these heavy metals into the environment. Lowest concentration of Fe in site B may be due to negative correlation between Fe and Cu, Zn, and Ni, as highest concentration of Ni, Zn, and Cu were observed in this site. Another possibility may be that local condition in site B does not favor the mobilization of Fe into the soluble phase. Very low concentration was also observed in site C. Further analysis of Fe in site C showed a higher concentration of Fe in samples collected midstream (0.144 mg/L) and lower upstream (0.016 mg/L). This high concentration observed midstream may be attributed to its proximity to a building construction site and flow condition of the stream. Moderate flow was observed midstream. Mean concentrations of Fe in samples collected in the month of January are significantly higher than the mean concentrations of Fe collected at any other month. There is a significant decrease in mean concentrations of Fe from January to September. The mean

concentrations of Fe in all the sites at the different months of sample collection varied from 0.582-2.22 mg/L. A gradual decrease in Fe was observed from January to September.

According to Joo-Hyon et al. [7], even though discharge load of most dissolved metals increased as rainfall depth or antecedent dry period (ADP) increased, dissolved Fe is relatively abundant from natural background sources and so effects of ADP or rainfall depth could not be observed.

Other probable factors that may have impeded the visible effects of rain depth and ADP is the spatial and temporary variations of rainfall intensity and local drain conditions.

Lead

Pb was below detectable limits in all the sites except in sites A and E with concentrations of 0.795 mg/L and 0.040 mg/L respectively. Analysis of variance showed that there is no significant difference in the concentration of Pb among the different sites and with respect to dates of sample collection ($p > 0.05$) as shown in Table 13.

Table 13: Two way ANOVA Table for Pb

Tests of Between-Subjects Effects

Dependent Variable: Metal concentration

Source	Type III Sum of Squares	Degree of freedom	Mean Square	F	Significance
Corrected Model	32.963 ^a	29	1.137	1.370	.151
Intercept	1.745	1	1.745	2.104	.152
Location	7.772	5	1.554	1.874	.112
Date	4.142	4	1.035	1.248	.300
Location * Date	21.049	20	1.052	1.269	.236
Error	49.772	60	.830		
Total	84.480	90			
Corrected Total	82.735	89			

a. R Squared = .398 (Adjusted R Squared = .108)

Pb detected in two out of the six sites examined suggests that Pb pollution by atmospheric deposition is minimal. This may be due to the ban in the use of Pb in gasoline for automobiles and in construction. Pb detected in sites A and E strongly suggests that it may have been discharged randomly from an external source. Perhaps, Pb may have been released from domestic waste discharge because the highest concentration was observed in site A, located in an area characterized by low traffic density and surrounded by buildings used as offices, recreation facility, study center, and homes. Though Pb is not currently used in constructing houses, homes made with lead containing materials are still in existence. Before Pb was banned, it was used in pipes, drains, and soldering materials for home construction, in making cable coverings, as paint pigments, and in PVC plastics. Pb is released gradually from weathering, flaking, chalking, and dust. Chronic exposure has been known to cause serious health defects especially in fetuses and infants.

High concentration of Pb (3.36 mg/L) observed in site A in the month of June suggests that it may be from a random source and high temperature favors its weathering and release of from the surface into the creek. Karamanis et al. [70] observed a positive correlation between metal concentrations and temperature, with maximum values at maximum water temperature.

Cadmium

Cd was below detectable limits in sites A, C, and F but was detected in sites B, D, and E with its concentrations observed to be, 0.010 mg/L, 0.002 mg/L, and 0.001 mg/L, respectively. Analysis of variance showed that the concentrations of Cd among the different sites and with respect to date of sample collection are significantly different as shown in Table 14.

Table 14: Two way ANOVA Table for Cd

Tests of Between-Subjects Effects

Dependent Variable: Metal concentration

Source	Type III Sum of Squares	Degree of freedom	Mean Square	F	Significance
Corrected Model	.005 ^a	29	.000	7.687	.000
Intercept	.000	1	.000	16.569	.000
Location	.001	5	.000	9.203	.000
Date	.001	4	.000	8.595	.000
Location * Date	.003	20	.000	7.126	.000
Error	.001	60	2.426E-5		
Total	.007	90			
Corrected Total	.007	89			

a. R Squared = .788 (Adjusted R Squared = .685)

Post Hoc test reveals that mean concentration in site B is significantly higher than mean concentrations in sites A, C, D, E, and F. With respect to dates of sample collection, the mean concentration of Cd is significantly higher in samples collected in the month of June than in any other month samples were collected ($p < 0.05$).

Cd being detected in sites B, D, and E may be due to the proximity of these sites to a mechanic workshop, a vicinity where machine parts are been coupled, and a transportation company respectively. Cd is often released from batteries, motor oils, or car exhaust. Cd being below detectable limits in sites A, C, and F strongly suggests that its pollution by atmospheric deposition is minimal. This may be due to the ban in the use of Cd in nickel-cadmium batteries, PVC plastics, paint pigments, cigarettes, and motor oil.

With respect to dates of sample collection, the mean concentration of Cd is significantly higher in samples collected in the month of June than in any other month ($p < 0.05$). The high concentration of Cd (0.008 mg/L) observed in the month of June suggests that increased rainfall depth, intensity, and duration during this time of the year may have scoured and mobilize Cd from catchment surfaces into the creek. Another possibility for this observation may be due to increased temperature. Throughout the sampling period, the highest temperature was recorded in the month of June. Perhaps high temperature favors the weathering and release of Cd from surfaces into the creek.

Correlation of Heavy Metals in Different Sites

Correlation between metals in the different sites examined was determined using Pearson's correlation coefficient. In site A, a strong positive correlation exists between Ni and Cu, Ni and Zn, and Ni and Fe as shown in Table I of Appendix B. On the other hand, a weak negative correlation was found between Pb and Zn, Pb and Fe, and Pb and Cu. No association was found between concentration of Cd and concentrations of Ni, Cu, Fe, and Pb, respectively. Metals with strong positive correlations are related linearly, an increase in concentration of one metal leads to increase in concentration of the other and vice versa. Metals with negative correlations show an inverse relationship. Increase in concentration of one leads to decrease in concentration of the other and vice versa.

For site B, a strong positive correlation exists between Cu and Zn and Cu and Fe. A negative correlation exists between Ni and Cu, Ni and Zn, and Ni and Fe, as shown in Table 2 of Appendix B. No correlation was found between concentration of Pb and concentrations of Zn,

Fe, Ni, and Cd, respectively. The strong negative association between Fe and Ni may be responsible for the low concentration of Fe observed in this site, which had a relatively high concentration of Ni compared to other sites examined.

In site C, a strong negative correlation was found between Fe and Cu ($r=-0.627$). No association between concentrations Ni, Pb, Cd, and Zn with each other in this site was found. In site D, a strong positive correlation exists between Cu and Fe, and a weak negative correlation exists between Zn and Ni, and Zn and Fe as shown in Table 3 of Appendix B.

In site E, a strong positive relationship exists between Ni and Zn and Cu and Fe. Concentrations of other metals showed a weak relationship with each other as shown in Table 4 of Appendix B. In site F, a weak positive correlation exists between Ni and Fe, and a weak negative relationship exists between Ni and Cu and Ni and Zn. Other metals did not show any correlation with each other.

With respect to the dates samples were collected, a positive association was observed between Pb concentrations and temperature with an r value of 0.670 as shown in Table 5 of Appendix B. A weak negative correlation was observed between temperature and concentrations of Ni and Cd, with r values of -0.330, and -0.173 respectively. And a strong negative association was observed between temperature and concentrations Zn, Cu, and Fe, with r values of -0.795, -0.896, and -0.969 respectively.

Correlation between mean concentrations of the metals determined in all the sites throughout the sampling period, as shown in Table 4, showed a strong positive correlation between Ni and Cu, Ni and Zn, and Ni and Cd, respectively. And a weak positive correlation was

observed between Pb and Zn. On the other hand, a negative correlation was observed between Fe and Ni, Fe and Cu, Fe and Pb, Fe and Zn, and Fe and Cd, respectively. This result helps in understanding the behavior and distribution of these metals with each other in the medium analyzed.

CHAPTER 6

CONCLUSION

Concentrations of Ni, Cu, Zn, Cd, Pb, and Fe in the sites examined were observed to be higher than the maximum values recommended by the USEPA to which any aquatic community should be exposed. Because heavy metals are non-degradable and tend to bio-accumulate, their levels may increase over time resulting in elevated concentrations in the organisms that live in these creeks. Metals may eventually get to humans through the food chain. From the statistical test, there is a significant difference in the concentrations of Ni, Cu, Zn, Fe, and Cd in the water samples among the different sites except for the concentrations of Pb that showed no significant difference. Concentrations of Zn, Fe, Cu, and Cd showed a significant difference in their distribution with respect to dates samples were collected except for concentrations of Ni and Pb that showed no significant difference. High concentrations of Ni, Zn, Cu, and Cd were observed in site B, and Fe in site E relative to other sites. Low concentrations of the metals analyzed were observed in site C except for concentration of Fe which was observed to be lower in site B relative to other sites. Pb was only detected in sites A and E. Cd was detected in sites B, D, and E. High concentrations of Ni, Cu, and Zn observed in site B, Fe in site D, Pb in site A, and Cd in site B indicate that human activities play a significant part in determining the source and volume of heavy metal pollution in an area. High traffic contributes a significant amount of Ni, Zn, and Cu to the environment. Activities that involve the use of motor oils and batteries contribute a significant amount of Cd to the environment. Domestic wastewater

contributes a significant amount of Zn, Cu, and Pb. And activities around the brick making company contribute a significant amount of Fe in addition to sources from nature.

A strong positive correlation was found between Ni and Cu, Ni and Zn, and Ni and Fe. A weak negative correlation was found between Pb and Zn, Pb and Fe, and Pb and Cu in site A. No correlation was found between Cd and Ni, Cu, Fe, and Pb in site A. In site B, a strong positive correlation was found between Cu and Zn and a weak negative correlation exists between Ni and Cu, Ni and Zn, and Ni, and Fe. No correlation was found between Pb and Zn, Pb and Fe, Pb and Ni, and Pb and Cu in site B. In site C a strong negative correlation was found between Fe and Cu. No correlation was found between the other metals. In site D, a strong positive correlation was found between Cu and Fe. In site E, a strong positive correlation was found between Ni and Cu, and Ni and Fe. In site F, a weak positive correlation exists between Ni and Fe and a weak negative correlation was found between Ni and Cu, and Ni and Zn. Mean concentrations of Pb obtained during the sampling period correlated positively with temperature.

Pb being below detectable limit in most of the sites examined shows its use in gasoline for automobiles and in home construction and the residual amounts since its ban is minimal. The anomaly observed in site C despite its proximity to high traffic volume and the flooring company indicates that activities within the company have an influence on the concentration of the metal species in surface water. Local conditions within creeks determined by pH, biological processes, and activities of chelators are equally important. Lower concentration recorded at higher flow relative to moderate and lower flow indicates that dilution effect governed by

specific flow condition, climate, and geochemistry of the catchment also influence the concentration of metals species in water.

Individual anomaly observed within a site indicates that concentration of metals vary daily depending on contributions from human activities and hydrology of the catchment. High concentrations were observed in samples collected after storm runoff following a long dry period and lower concentration in samples collected after storm runoff following a long wet period. Human error in sample collection and storage may also be responsible.

High concentrations of the metals were observed in samples collected the month of January except for Cd. A high concentration of Cd was recorded June. This shows that time and weather influence the concentrations of metals in water. Order of relative abundance of the metals are Zn > Fe > Ni > Pb > Cu > Cd.

Future Direction

In this work, concentrations of heavy metals were determined in samples collected from water surfaces only. An anomaly was observed in site C despite its proximity to an area with high human activity. For future work, water samples and sediments should be collected concurrently to evaluate if there will be any significant difference in the distribution of the metals between them. Parameters like pH and rainfall intensity and duration should be measured and correlated with metal concentrations.

Sample collection was done within a certain window period on each date to ensure uniformity in sample treatment and handling. However, this window period was somehow

extended due to delay in arrival time at the sites as a result of delay in traffic. Also, samples were collected in large polythene bottles and difficulty was encountered in their transportation and storage prior to the analysis. Other un-anticipated problems like blockage of the aspirator of the atomic absorption spectrophotometer, and gas running out during the analysis were encountered. As a result of the difficulties encountered while using the instrument, samples were analyzed on different days. In the future, sample collection should be distributed among a group so that all samples are collected at exactly the same time. On site measurements with simpler and less bulky instruments should be explored to overcome problems associated with transportation and storage.

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APPENDICES

APPENDIX A

CALIBRATION CURVES FOR DIFFERENT METALS

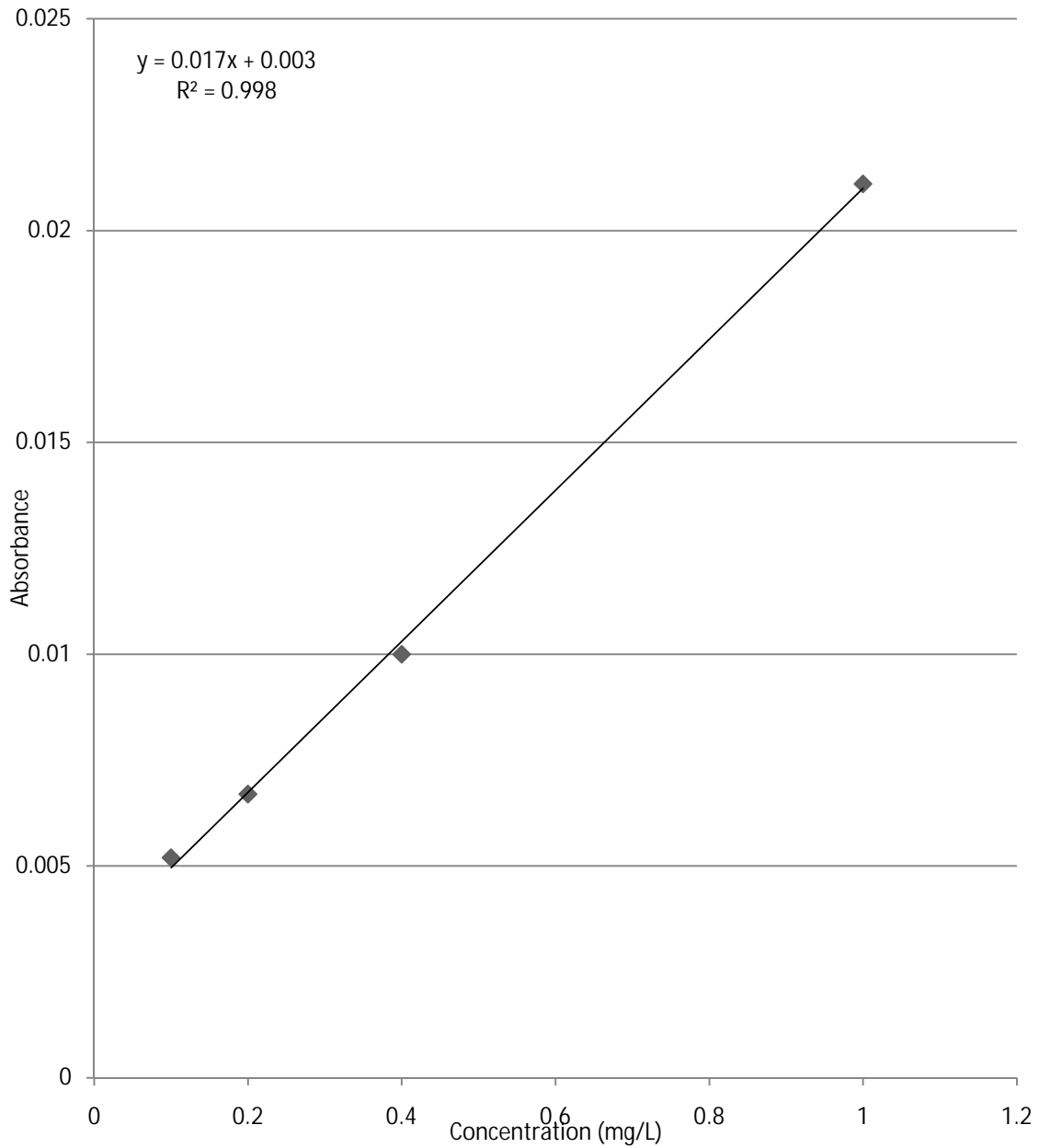


Figure 2: Calibration Curve for Ni used to determine concentration of Ni in samples collected from different creeks

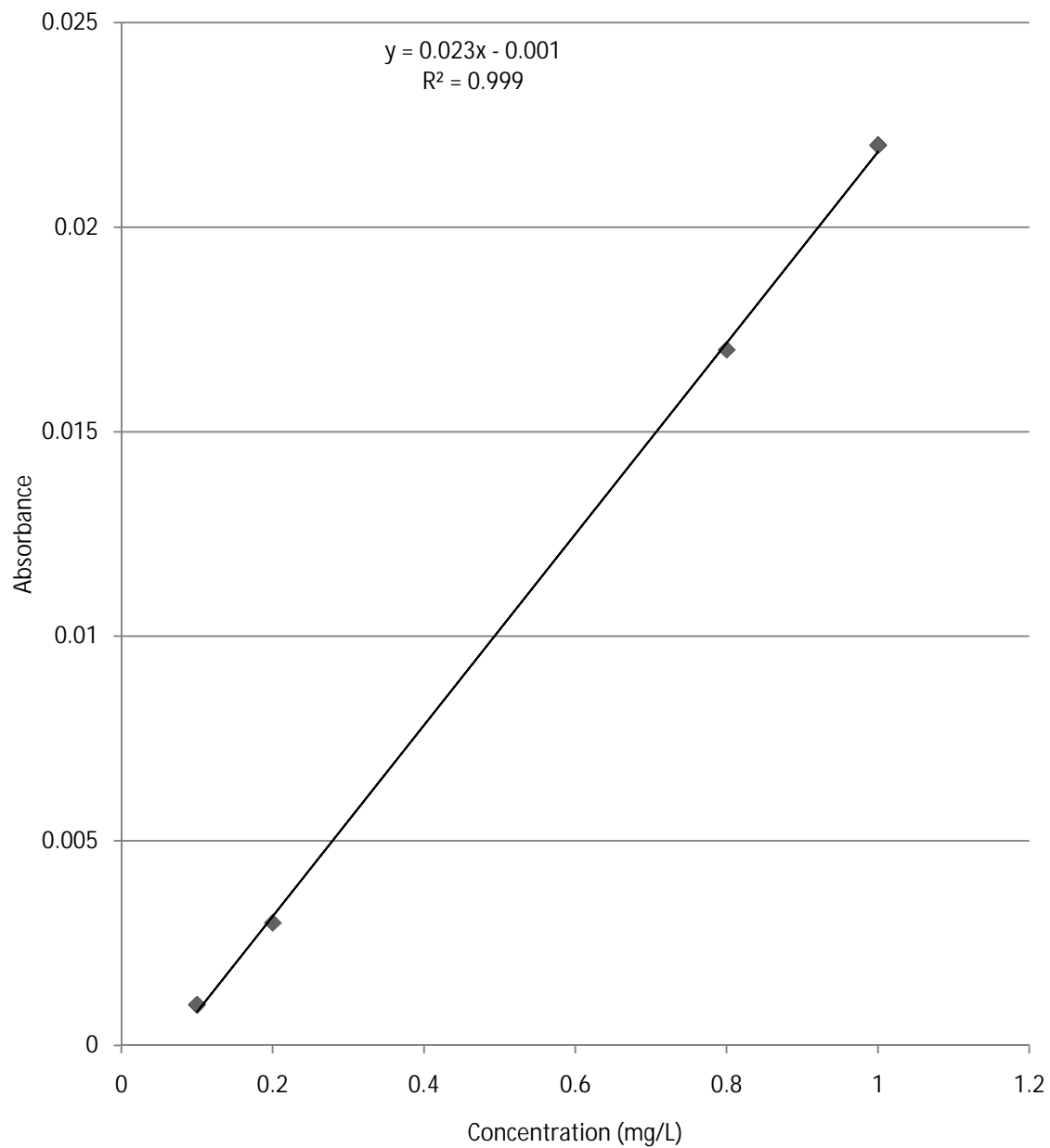


Figure 3: Calibration Curve for Cu used to determine concentration of Cu in samples collected from different creeks

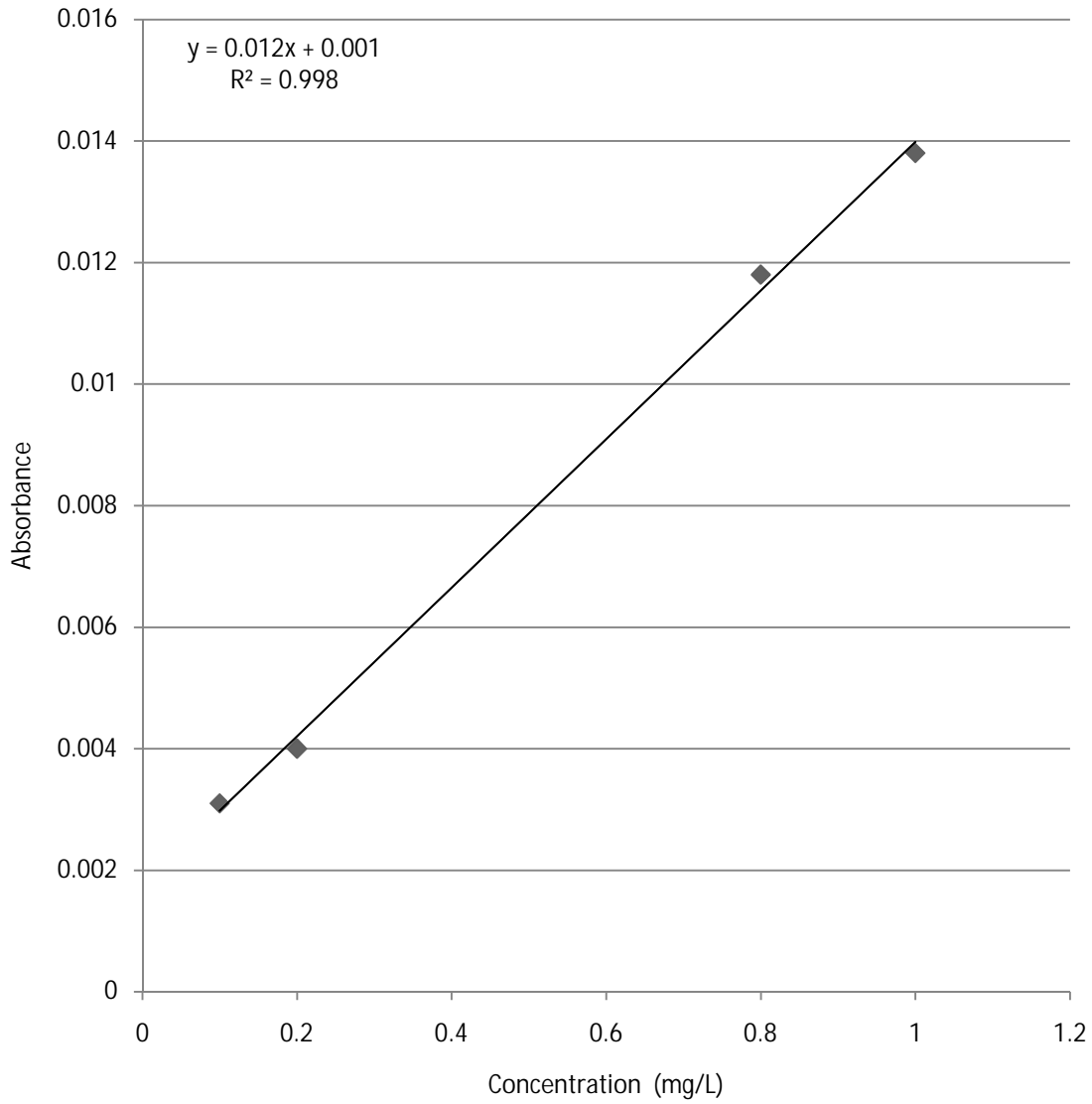


Figure 4: Calibration Curve for Fe used to determine concentration of Fe in samples collected from different creeks

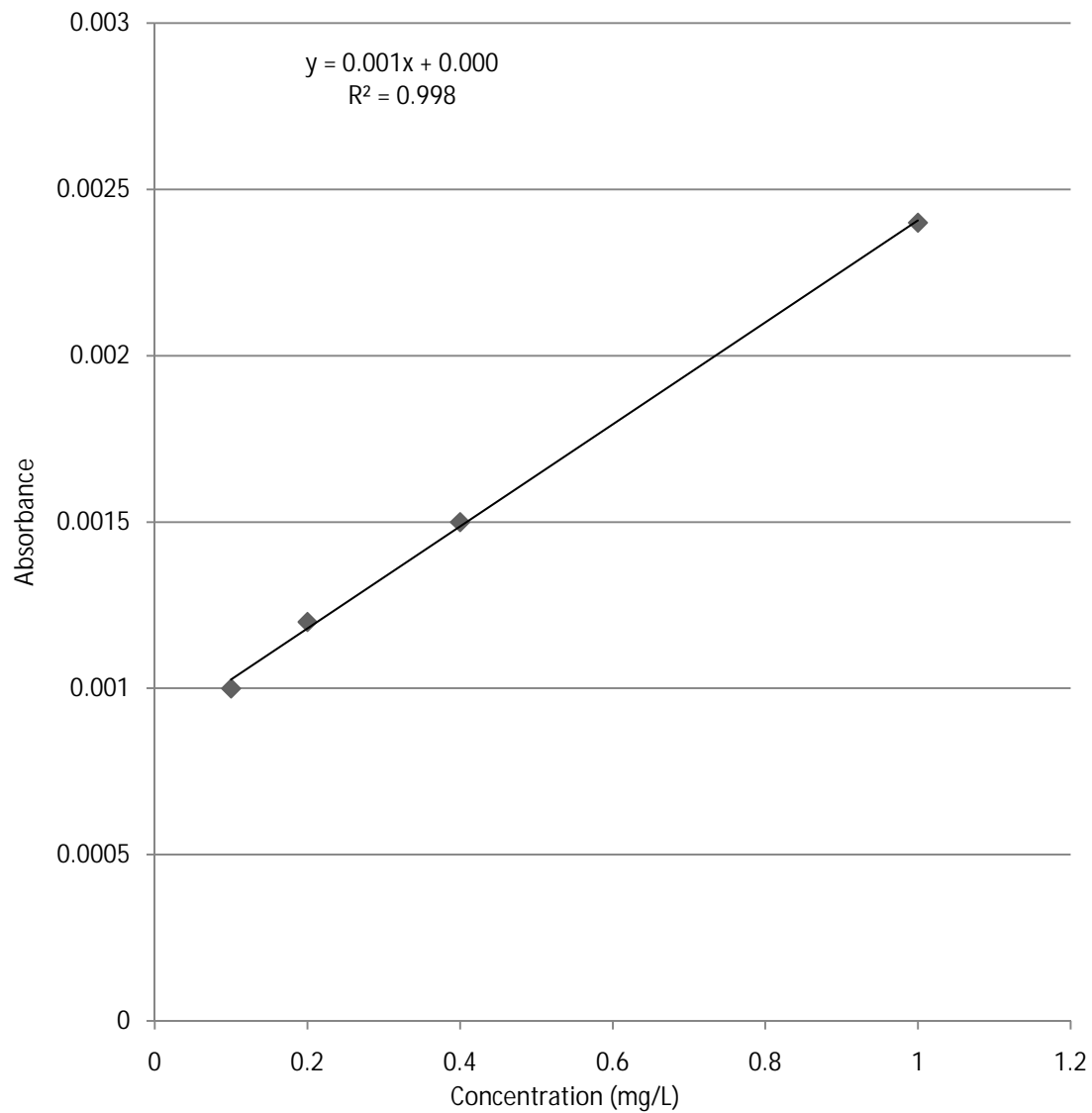


Figure 5: Calibration Curve for Pb used to determine concentration of Pb in samples collected from different creeks

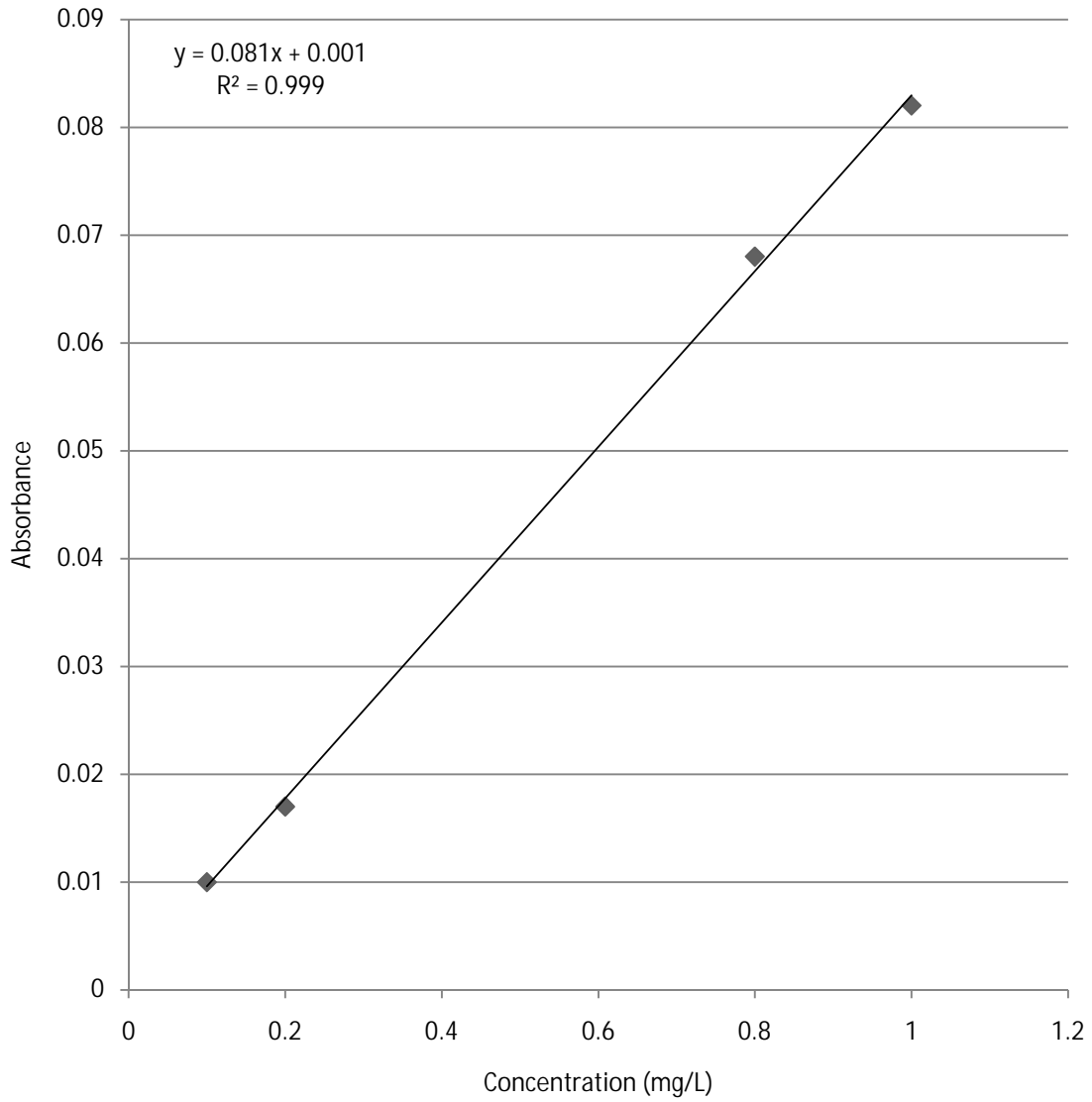


Figure 6: Calibration Curve for Cd used to determine concentration of Cd in samples collected from different creeks

APPENDIX B

CORRELATION COEFFICIENT TABLES FOR DIFFERENT METALS

Table 1: Pearson correlation Table between metals in site A

	Ni	Cu	Pb	Zn	Fe	Cd
Ni	1					
Cu	0.994	1				
Pb	0.271	-0.176	1			
Zn	0.997	0.989	-0.301	1		
Fe	0.997	0.999	-0.197	0.993	1	
Cd	-	-	-	-	-	1

Table 2: Pearson correlation Table between metals in site B

	Ni	Cu	Pb	Zn	Fe	Cd
Ni	1					
Cu	-0.57	1				
Pb	-	-	1			
Zn	-0.694	0.975	-	1		
Fe	-0.65	0.978	-	0.995	1	
Cd	0.859	-0.28	-	-0.394	-0.313	1

Table 3: Pearson correlation Table between metals in site D

	Ni	Cu	Pb	Zn	Fe	Cd
Ni	1					
Cu	0.331	1				
Pb	-	-	1			
Zn	-0.213	0.233	-	1		
Fe	0.283	0.834	-	-0.297	1	
Cd	-	1	-	-	-	1

Table 4: Pearson correlation Table between metals in site E

	Ni	Cu	Pb	Zn	Fe	Cd
Ni	1					
Cu	-0.015	1				
Pb	-	-	1			
Zn	0.996	-0.016	-	1		
Fe	0.314	0.804	-	0.286	1	
Cd	-	-	-	-	-	1

Table 5: Pearson correlation coefficient between temperature and mean metal concentration and among mean concentration of metals collected during the sampling period

	Temperature	Ni	Cu	Pb	Zn	Fe	Cd
Temperature	1						
Ni	-0.330	1					
Cu	-0.896	0.903	1				
Pb	0.670	-0.309	-0.090	1			
Zn	-0.795	0.483	0.692	0.333	1		
Fe	-0.905	-0.389	-0.305	-0.77	-0.472	1	
Cd	-0.173	0.518	0.671	-0.200	0.780	-0.570	1

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