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Evaluation of Metal Concentration in Water and Soil in the Southern Region of Lake Nacogdoches

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**EVALUATION OF METAL CONCENTRATION IN WATER AND
SOIL IN THE SOUTHERN REGION OF LAKE NACOGDOCHES**

By

OLAWUNMI TAIWO, Bachelor of Science

Presented to the Faculty of the Graduate School of

Stephen F. Austin State University

In Partial Fulfillment

Of the Requirements

For the Degree of

Master of Science in Natural Sciences

STEPHEN F. AUSTIN STATE UNIVERSITY

May 2020

EVALUATION OF METAL CONCENTRATION IN WATER AND
SOIL IN THE SOUTHERN REGION OF LAKE NACOGDOCHES

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ABSTRACT

The concentrations of metals (Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sr, V, Zn) were investigated in soil and water samples collected over four different sites in the southern part of Lake Nacogdoches over one year from August 2018 through June 2019. Water samples were analyzed using the USEPA method 200.8 part 11.2 for total recoverable metals. Soil samples were analyzed using the USEPA method 3050B for total recoverable metals. Although the total concentration gives some indication of the level of contamination, it is not enough to give information on the bioavailability or mobility of the element. A modified Tessier soil sequential extraction procedure was used to determine the speciation of metals in soil samples. Thus, elements in soils are present in various physicochemical forms, which in turn influences its bioavailability. In this study, soil samples were separated into five fractions: exchangeable, adsorbed, organic bonded, carbonate, residual fraction (F1-F5). The reliability of the total metal concentration from the digestion of bulk sediment were summed and compared with

the sequential extractions of the same bulk sediment for the metal concentrations of the fractions F1–F5. High recovery rates (≥ 5 mg metal/kg soil) indicate a good reliability for majority of metals studied using the sequential extraction procedure. The metal concentrations at the ppb level were determined by using inductively coupled plasma mass spectrometry (ICP-MS). The results indicate that the water samples had Ba, Mn, and Sr at concentrations greater than 35 ppb for majority of samples. The soil samples had Ba, Co, Cr, Mn, Ni, Pb, V, and Zn at concentrations greater than 10 mg metal/kg soil for majority of samples, with Ba, Mn, and V showing the highest values (greater than 60 mg metal/ kg of soil). All metal concentration was well below the WHO and EPA drinking water standards for metals and in the typical range found in natural waters.

ACKNOWLEDGEMENTS

Foremost, I would like to express my sincere gratitude to my advisor, Dr. Michael Janusa for his hard work, patience, motivation, immense knowledge and guidance. His guidance helped me in all the time of research and writing of this thesis. I would like to express the deepest appreciation to my committee members: Drs. Onchoke, Farrish and Han for their wisdom and direction. I am particularly indebted to the entire academic staff and all workers of the Chemistry and Biochemistry Department for their special assistance towards the completion of this dissertation.

Finally, I am extremely grateful to my parents for their love, prayers, caring and sacrifices. I am very much thankful to my husband for his love, understanding, and continuing support. I will always remember the encouragement, counselling, and immeasurable contributions in making my study successful.

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CHAPTER 1

1.1 INTRODUCTION

The aim of this research is to determine the concentration of metals in samples from the southern region of Lake Nacogdoches. This chapter addresses an overview of the sources of water pollution, effects of water pollution and preventive measures. The objective of this research is then clearly defined.

1.1 Water

Life without water cannot be considered at all, it is essential for life. Water is the main constituent of the earth's surface. Water is a substance that is tasteless, odorless, and colorless; however, at red wavelengths water can absorb light slightly which makes it to have an inherent blue color. Water has one oxygen and two hydrogen atoms, connected by covalent bonds.

We often assume a waterbody is an unlimited natural resource and far too big to be polluted. This was believed to be true with a smaller population on earth. However, based on the quality of water needed to support human life, the fast

increase in our industrial civilization, and the increasing demand for water, it should be considered a limited resource.¹ Human activities further accelerates the rate of pollution leading to a significant decline in water quality and its diverse functions. ¹

Water is of extreme importance to life. All living things needs water for survival, water is essential for life to function properly. The earth's surface is covered largely by water (about 71%), while the rest is taken up by land. A significant accumulation of water is referred to as a water body, which includes oceans, sea's and lakes. Water authorities utilize these water resources as source of water for human consumption.

A lake is formed when water fills in hollows on landscape. Lakes hold 0.3 % of all the water on the Earth's surface.² Lake is a body of water that is surrounded by land. Natural disappearance of lakes can occur as result of poor hydrologic balance associated with climatic conditions such as evaporation, or by in-filling of lakes caused by sedimentation.² Once a lake is formed, it begins to age and will slowly disappear over time. The natural aging of lakes happens very slowly over the course of hundreds and thousands of years,

but with pollution activities, it may take only decades.

Bartram³ classified lakes base on several processes used in forming lakes and differentiated 11 major lake types.³

1.2 Sources of Water Pollution

The United States Environmental Protection Agency (USEPA) classifies water pollution into two types based on polluting source: point and non-point source pollution. Point source of pollution includes waste discharge outlets such as sewage pipes or smokestacks.⁴ It can be controlled by preventing the pollution, especially sedimentation rather than treating it, for example utilizing recycling processes.⁴ These types of pollution can be traced to a single identifiable source.⁴ Non-point source pollution (NPS) originates over a broad area, such as agricultural runoff, mining activities, construction sites and road erosion. This source of pollution contributes a vast amount to the total water pollution, especially sedimentation, in the United States.⁴

1.2.1 Sewage

Domestic wastewater effluents and sewage sludge are two of the major sources through which different contaminants enter aquatic systems. With the existence of humans on the

planet, disposal of sewage waste constitutes a major problem for lakes. Wastewater is produced with the use of water and its subsequent deposition in lakes, reducing the quality of water thereof. It can be said that survival and pollution are interrelated. Sewage waste can be elated hygienically and quickly a far off from their homes in advanced countries, however, sewage disposal does not end with a flush. Lakes have a natural capacity of rendering pollutants harmless through dilutions, but the intense rate of polluting activities may overcome the system.⁵

1.2.2 Chemical Waste

According to the environmental campaign organization World Wildlife Fund (WWF), *“Pollution from toxic chemicals threatens life on this planet. Every ocean and every continent, from the tropics to the once-pristine Polar Regions, are contaminated to some extent”*.⁶

Toxic heavy metals such as lead, cadmium, and mercury are constituents of toxic chemical waste. Lead was previously a primarily constitute of gasoline. It was used mainly as a fuel in our vehicles. Boats with spill tank vents releases gasoline

into reservoirs. Fumes from car exhaust rise high in the atmosphere.⁷ These toxic metals become part of atmospheric gases and are further deposited in lakes by precipitation, which is a major source of water renewal of lake water. An example of effect caused by chemical waste is spillage from failed pipes that took place at Duke Energy dump in 2014. This event sent 39,000 tons of increased levels of arsenic and selenium, that supplied drinking water to communities in both North Carolina and Virginia.

1.2.3 Thermal Pollution

Thermal pollution from factories that uses power plants increases the temperature of waterbodies.⁸ A significant factor that determines the quality of water in lakes and rivers is dissolved oxygen. Thermal pollution leads to a decrease in the level of dissolved oxygen in water with a subsequent increase the biological demand for oxygen by aquatic organisms. Many aquatic species die when the levels of dissolved oxygen become too low ⁹

1.2.4 Sediment

Sediments are fine particles of soil that erodes from of soil surfaces into water bodies.⁹ These sediments settle in

lakes and constitute a constant source of lake water pollution. Sediments act as sinks for metals that are not soluble in water and facilitate infilling of lakes. ¹⁰

1.3 Effects of Pollution

Lake water pollution has numerous effects, but two major effects are dominant. Water pollution (in terms of metals) degrades quality of water in lakes and disrupts aquatic life.

1.4 Preventive Measures

Pollution cannot be eliminated, but it can be minimized. It can be classified into three major categories:

Economics - Water pricing policies also known as polluter pay principle can be a competent tool for diminishing pollution.¹

Education -Lakes are immensely valuable, and the water they hold is one of the most cherished of our natural deposit.

However, humans exploit, misuse and pollute this vital natural resource. It is of essence that awareness is created on this issue in the public.¹ Environmental education is a key approach.

Law - Sets of guidelines and codes that are enforceable and achievable in controlling lake water pollution.

1.5 Surface Water

Surface water is the outer layer of a water body on the surface of the planet. It is liable to be influenced by heavy metal pollution either by natural occurrence or anthropogenic activities.¹⁰ Metals such as lead (Pb), chromium (Cr), arsenic (As), zinc (Zn), cadmium (Cd), copper (Cu), mercury (Hg), and nickel (Ni) are found as dissolved ions, complexes, and colloidal ions in lakes.¹¹

1.5.1 Groundwater

Ground waters are dependent on surface water. Groundwater supplies are proving inadequate as the demand for water increases. Human polluting activities have rendered most lake water unsuitable for use and have decreased the quality of water necessary for healthy life. Contaminants can penetrate from surface water and soil surfaces to groundwater through many routes (direct and downward percolation from land surfaces).¹² Groundwater naturally gets renewed through surface water (lakes, streams) and rain discharge and depends on the climatic conditions, topography of the land surface, and underlying geology.¹²

1.6 Soil

Emissions from growing industrial segment and high metal wastes constitute sources of soil contamination. Soils act as sink to these metals and constitute a constant source of water pollution. Soil erosion can cause soils to be leached into nearby Lakes and reduce the water quality. Soils near the lakes can provide rich information on the lake metal pollution. Soils contaminated with heavy metals can be detrimental to human health and the ecosystem. Plants can take up such toxic metals through its root and edible parts and circulate them within the food chain.

Heavy metals frequently observed in most contaminated soil are lead (Pb), chromium (Cr), arsenic (As), zinc (Zn), cadmium (Cd), copper (Cu), and mercury (Hg).¹⁸

1.6.1 Speciation and metal analysis methods used in Soil Analysis

The category of metals found in soil is related to the activities that occurs at the site., Several research on how to assess the speciation of metals, i.e. partitioning of metals among the various forms in which they might exist in soil has been tried . A frequently used method of metal analysis in soil

is the USEPA Methods (3050B), which reports metal concentrations as mg of metal per kg of soil.

Other types of leaching tests have been researched including sequential extraction procedure. Extraction of each fraction in sequential procedures selectively use various reagents that most efficiently extracts the metals in the fraction that it might exist.¹⁸

Riley et al.¹⁸ revealed the ranges and regulatory guidelines for soil concentration of several heavy metals (Table 1.1). The target values are used to indicate soil quality.

Table 1.2: Soil concentration ranges and regulatory guidelines for some heavy metals.¹⁸

Metal	Soil Concentration range (mg metal/kg soil)	Regulatory Limit (mg metal/kg soil)
Pb	1.0-69000	600
Cr	0.10-345	100
Cd	0.005-3950	100
Hg	>0,01-1800	270
Zn	150-5000	1500

1.7 Study Area

Bayou Loco Dam is a primary tributary of Lake Nacogdoches. It is a holomictic (mixes from top to bottom during one period of the year) reservoir in East Texas. It flows southwest for twenty-two miles to its mouth on the Angelina River, three miles west of Porella, in the north central of Nacogdoches County. It has a reservoir of 23km², surface of 8.94 km², its depository space is 49.7 million m², and has the coordinates of Latitude 31° 37N and Longitude 94° 49W .¹⁹ The primary purpose for Lake Nacogdoches is for municipal water supply to the city of Nacogdoches Texas and recreational use. At the north of the island in the lake, has upper shallow ($\leq 5\text{m}$ depth) and is rich in nutrients and minerals (eutrophic). Substrates such as gravel, slit are present at the lower part of the Lake which is deep (about 13m) and less eutrophic.¹⁹

1.8 Objectives of Research

This study aimed to evaluate the water and soil in the southern region of Lake Nacogdoches that adjoins the

Nacogdoches Surface Water Treatment Plant. The research had two main objectives:

1. Quantitative analysis of specific metals for water and soil in the southern region of Lake Nacogdoches.
2. Evaluate the lower south end of Lake Nacogdoches to establish a baseline of water quality (in terms of metals). In addition, the metal content of the soil was analyzed.

1.9 Justification of Research

Contamination risk assessment of pollutants in lakes is fundamental for its control; therefore, routinely monitoring for concentrations of pollutants is essential. Lake ecosystems are fragile and cannot manage themselves. In order to sustain their lake functions, it needs to be systematically and objectively managed.²⁰ Exposed to external effects from the atmosphere, lakes are subjected to change through time. Invariably expansion in databases and insight on lakes can provide a better understanding of the conditions and problems that develop in lakes.²⁰ The present condition of a lake is achieved through an aggregated effect derived from interactions between the characteristics of lakes itself and the surroundings (its watershed, climate). The condition of Lake

Nacogdoches will be quantitatively analyzed for specific metals (Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sr, V, Zn) in the water and soil present.

Fish is a high source of nutritional value in human diet. Toxicity of heavy metals in fish can outweigh their beneficial effects; therefore, assessing this aquatic environment will help in sustaining a conducive environment for aquatic life. For example, Trout is an example of a fish group that is highly sensitive to changes in aquatic habitat.

The primary source of drinking water in the City of Nacogdoches comes from Lake Nacogdoches and Wilcox-Carrizo aquifer. Lake water quality goals are usually aimed at either conserving the current quality or improving its quality. This can only be achieved if such qualities are evaluated. This research has created a reference for later studies that can be used to compare future data and provide the basis for lake pollution control.

CHAPTER 2

LITERATURE REVIEW

2.1 Metals

Modern civilization is highly dependent on metals for daily life activities. Many metals, particularly heavy metals are dangerous to our health, but some are essential. Their concentration (from their source) may not be high enough to cause ill health; however, with constant exposure, an accumulative toxic effect can affect health. Ability to exist in different forms of matter and its persistence and resistance to degradation (in contrast with organic pollutant) makes toxic heavy metals a lifetime pollutant.²⁰ In required concentrations, these metals play a vital role in the biological activities of plants and animal. If present in higher concentrations in plants and animals, these metals can displace other essential metals from binding sites. ²⁰

The concentration and type of metals present in a lake is directly related to the water source (tribute) and the

geochemical characteristics of the soil and/or rock type on which the lake occurs. Due to human activities, nature's slowly occurring geo chemical cycle has been accelerated with a subsequent increase in the level of available metals .²⁰

The metals selected for this research were chosen because they are the major pollutants of aquatic ecosystems.

2.1.1 Chromium

Chromium can be found naturally in the earth's crust and can be deposited anthropogenically. Industrial and agricultural practices increase the toxicity of chromium. Chromium (III) and Chromium (VI) are the most stable forms. Hexavalent state of chromium is of great concern because of its high toxicity. Chromium (III) is essential to humans and can be converted to Cr⁶⁺ (toxic form) .^{14,20} Its toxicity depends on the temperature, pH (below pH five insoluble in water), valence form, and presence of other compounds. Chromates can be tasted in water at very low concentrations. Thus, it is unusual for chromium to be ingested in large quantities due to its ease of detection.²⁰ It is usually found in lakes within the range of 0.0002 to 0.019 ppm. USEPA stipulated Chromium allowed concentration in drinking water is 0.1 mg/L (see Table 2.1).

2.1.2 Copper

Copper is one of the most used metals. Pipes commonly used in the establishment of water systems in industries and for refrigerant lines in HVAC (heating, ventilation, and air-conditioning) systems, as well as in additives designed to control algal growth are made of copper.²¹ Toxicity of copper (Cu) decreases with an increase in water hardness. Copper has its safe concentration limit in drinking water at 1.3 mg/L (see Table 2.1)

2.1.3 Nickel

Nickel carbonate is the most produced form of nickel. It may be discharged into the surroundings from the stacks of large heating system used in the production of alloys from power plants and trash incinerators. Electroplating industries and industries that use nickel as a catalyst in organic chemical manufacturing release large amounts of nickel. This accounts for 16% of US annual production.²¹ These industries release regulated wastewater that contains nickel. Nickel adheres to small fragments of dust that settle on the ground and paved

into lakes during erosion. When nickel is subjected to acidic conditions, mobility in soil is increased and might seep into groundwater. Nickel concentration in surface water is within the range of (0-12.5 µg/kg).²¹

2.1.4 Lead

United States Environmental Protection Agency has set regulations in drinking water for the check of lead and copper. This is known as the Lead and Copper Rule. Lead constitutes one of the most toxic metals and has no nutritional value even at low concentrations, unlike other metals.¹⁵ There is an amount of lead that present in pipes, plumbing fittings, fixtures, solder and flux, but prohibits a lead content level in the above 0.25%.¹⁵

Babies can ingest lead from toys and tins used in preserving foods.¹⁵ It causes retardation in the physical and mental development in children; children could show slight deficits in attention span and learning abilities and an increase in blood pressure. WHO allowed weekly intake in food for adults is 3mg, equivalent to 0.05 mg/kg body weight. (see Table 2.

Table 2.1: USEPA water quality standard for some

Metals in drinking water ²⁰

Contaminants	MGLG* (mg/L)	MCL** (mg/L)
Antimony	0.006	0.006
Arsenic	0	0.010
Barium	2	2
Beryllium	0.004	0.004
Cadmium	0.005	0.005
Chromium	0.1	0.1
Copper	1.3	1.3
Selenium	0.05	0.05
Thallium	0.0005	0.002
Manganese	0.05	0.05
Lead	0	0.015
Zinc	0	2

*Maximum Contaminant Level Goal (MCLG) – the level of a contaminant in drinking water below which there is no known or expected risk to health (EPA values). MCLGs allow for a margin of safety and are non-enforceable public health goals

**Maximum Contaminant Levels (MGL)- National Secondary Drinking Water Regulations (secondary standards) are non-enforceable guidelines regulating contaminants that may cause cosmetic effects or aesthetic effects in drinking water. USEPA recommends secondary standards to water systems but does not require systems to comply

2.1.5 Arsenic

Arsenic contamination in drinking water is one of the major sources through which arsenic toxicity is obtained in most countries.¹⁵ It is produced anthropogenically as a byproduct of smelting of non-ferrous ores. Pesticides, herbicides, insecticides and treated woods contain arsenic. Arsenic possesses a serious risk to human health and is referred to more specifically as arsenicosis. Arsenic occurs both naturally and anthropogenically.²⁰ It causes neurological problems and pulmonary diseases in humans. Arsenic has its maximum contaminant level (MCL) in drinking water as 0.010 mg/L (see Table 2.1).

2.1.6 Cadmium

The biological half-life of Cadmium in humans is 20 - 30 years, which makes it a distinctive hazard. Cadmium is present in fertilizers composed of commercial sludge and runoff from conventional phosphate fertilizers, which is one of the

most common routes through which it obtained. Cadmium is generally recovered as a byproduct from Zinc Concentrates.²¹ It causes proteinuria, a condition that affects the proximal tubule of the kidney. USEPA studies shows safe levels of Cadmium in drinking water is 0.005 mg/L (see Table 2.1).

2.1.7 Manganese

Manganese is often found naturally with iron and is the twelfth most abundant metal.²² It plays an important role in several physiologic processes as a constituent of multiple and an enzyme activator of other enzymes. Anthropogenic sources of manganese include dry cell batteries, metal alloys, micronutrient fertilizer additives, and chemical reagents. Manganese has been detected in mines and processing as ferromanganese. Average concentration of manganese in soil is between 600 and 900 mg/kg.²² The World Health Organization guidelines for drinking waters for manganese is 400 mg/L.

2.1.8 Zinc

Zinc is an essential nutrient for good health; however, excess amount can be harmful. Higher zinc concentration is

increased in drinking water when stored in metal tanks.²² Wastewater from industrial plants have been found to have zinc present in certain concentration. Zinc also inhibits decomposition of microorganism in soils. Zinc affects plant yield and growth. In humans, excessive zinc intake can lead to stomach aches and vomiting.²² Zinc maximum contaminant level in drinking water is 2 mg/L (See Table 2.1)

2.2 Water Hardness and Toxicity

Many of the world's hard water lakes are in regions where human activities are intense. Agricultural, urban growth, and eutrophication contribute largely to water hardness. Toxicity of water can be compared with hardness of water. Water with a calcium ion concentration between 0 - 75 mg/L is referred to as soft water.²² It arises from the presence of alkaline earth metals in water and other anthropogenic activities. Water hardness can be derived from the aqueous ions of calcium and magnesium. Calcium is important in an aquatic system but can be toxic at high concentration levels.²¹ Calcium and other ions present in hard water compete with other metals for available binding sites on the cell membranes of aquatic plant and animal life. Thus, heavy metals such as chromium, copper, lead, and zinc decrease as water hardness

increases. Metal toxicity can be greatly affected by the hardness of the water. In general, as hardness increases the toxicity of a metal will decrease.²² Toxic metals and potentially toxic metals are well known for their adverse effect health and have given rise to strict limiting rules on drinking water. However, the influence of essential metals is not often considered. Water hardness (calcium and magnesium ion concentrations) can be used to estimate cadmium toxicity level.²¹

2.3 Effects of Rate of Flow and Toxicity

Martin ²³ conducted a research study that evaluated the rate of flow and concentration of heavy metals. The study area lies in the Sabine National Forest located in the southern part of Sabine County, Texas. It was found that the rate of flow is inversely proportional to the concentration of metals. It was deduced from this that lakes with slow flow rate can have a higher concentration of metals. Two of the studies were on streams: stream in contact with a spring had a “flushing effect” and stream, which depended solely (no contact with flowing water) on run-off tended to pick up nutrients and metals.²³

This indicated that there is a difference in metal concentration in a stale body of water as compared to a flowing body of water.

2.4 Effects of pH on Toxicity

A key factor in determining the acidity nature of water is the pH. The lower the pH value (increase in acidity), the higher is the corrosive nature of the water. An increase in pH can be caused by a decreased rate of photosynthetic activity and the assimilation of carbon dioxide and bicarbonates. Ziegler²⁴ studied the effects of pH on heavy metals in two East Texas ponds (Needham and Lowe Ponds) located in South Central Rusk County and found that the Lake acidity increased with decreasing pH value.

2.5 Instrumentation

The impact of a pollutant depends on the toxicity of a pollutant, the amount of the pollutant, and the lifetime of the pollutant. Some metals can be toxic even when present in trace amounts of concentrations. It is therefore of importance that these metals can be detected to a very low detectable limit.

Instruments that were initially used for concentration analysis were challenged with narrowed accuracy, interferences and arduous to automate. It was necessary to develop instruments that are more effective for analysis.²⁵ ICP-MS utilizes an extremely high energy (from its plasma source) to fully ionize samples.²⁶

After a careful consideration of objectives and quality of data needed for this proposed research, ICP-MS was chosen to be used for the metal analysis of samples.

Metals can be present in an insoluble form in lakes. To effectively evaluate the water quality present in lake, sediments in lakes, which act as sinks to these metals, should also be analyzed. Metals in these sediments are usually twice as much of its amount in a soluble form. Subsequently, sediments convert and releases these metals with an increased toxicity in its soluble form. For example, mercury which adheres to sediments and has a long-life span is converted to methylmercury (which is a more toxic and soluble form).²⁷ To be effectively analyzed, methods that do not alter the sample chemical composition significantly need to be used. In addition, knowledge of the chemical composition fractions is essential to have insight into the potential physical

dispersion and transport of chemical constituents on the sediments. Previously, single extraction methods were normally used to analyze soil samples. This was efficient in offering a better contrast between anomalous and background samples; however, it lacks efficiency in the determination of the total metal concentrations. Evaluative methods for the analysis of suspended sediments for trace metals and organic compounds is extremely important.

Taking into consideration physical-chemical parameters such as pH, ionic strength of soil solution and metallic cation concentration, this research will use the Modified Tessier sequential extraction methods for extracting several soil fractions. Although it requires more time, the quality of data obtained with Tessier's method overrides the required time. Community Bureau of Reference (BCR)28 sequential extraction scheme uses 51 hours for analysis (per sample) despite a reduction in a step to Tessier's sequential method. Ultrasound accelerated small-scale single extractions have also been proposed.²⁹ The single extraction schemes are usually applied to 1 g of sample suspended in 40 mL of extractant in 22 mins per sample.³⁰

2.5.1 Inductively Coupled Plasma Mass Spectrometer (ICP-MS)

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is a technique that is used to determine the concentration of metals in different samples. The emissions caused by excitation of metals are observed and measured at different wavelength for each metal. The ICP spectrometer can be coupled with other instruments for analysis such a mass spectrometer.

Li Sun ³¹ studied the influence of metals on the quality of Lake Texoma using ICP-MS. Lake Texoma is located between Texas and Oklahoma with an inflow mainly from two rivers, the Red River (discharging downwards) and the Washita River (entering northwest). Trace elements (V, Cr, Mn, Co, Ni, Cu, Zn, As, Rb, Cd, Cs, Pb, U, Tl and Mo) were measured by ICP-MS. Overall, it was determined that elemental contaminants in Lake Texoma were at lower levels than the drinking water standards Maximum Contaminant Level Goal (MCLG^{*}) (see Table 2.1) set by the USEPA, except for Tl.

It was also observed that all the concentrations of metals in water were below the United States Environmental

Protection Agency standard with the exception of Pb, Tl and U: U, 0-0.316 $\mu\text{g/L}$ (EPA-0); Tl, 0-11.09 $\mu\text{g/L}$ (EPA-2 $\mu\text{g/L}$); Cr, 0.55-4.69 $\mu\text{g/L}$ (100 $\mu\text{g/L}$); Cd, 0-0.411 $\mu\text{g/L}$ (EPA-5 $\mu\text{g/L}$); Pb, 0-1.532 $\mu\text{g/L}$ (0 $\mu\text{g/L}$); Al, 0-0.27mg/L (2nd EPA standard** 50-200 $\mu\text{g/L}$); Cu, 0-9.53 $\mu\text{g/L}$ (EPA 1300 $\mu\text{g/L}$); Zn, 2.17-45.78 $\mu\text{g/L}$ (2nd EPA standard** 5000 $\mu\text{g/L}$); As, 0.36-6.93 $\mu\text{g/L}$ (10 $\mu\text{g/L}$); Ba, 0.065-0.14 mg/L (2 mg/L).

Its capacity for speedy multielement analysis and detection power of inductively coupled plasma mass spectrometry (ICP-MS) and were shown by the analysis of a river water reference material. Beauchemin ³² studied the concentration of trace metals; eighteen metals in the river water reference material were readily detected using (Na, Mg, Al, K, Ca, V, Cr, Mn, Ni, Cu, Zn, Br, Sr, Rb, Mo, Sb, Ba, and Ce) while eight additional metals concentrations were observed only when ICP-MS was used (Co, As, Zr, Nb, Cd, Sn, Pb, and U).

2.5.2 Atomic Absorption

Water analysis have been performed using atomic absorption spectroscopy. The levels of some heavy metals Pb, Cd, Cu, Zn, and Hg in water samples collected from an industrial zone and the Thatipudi Reservoir around Visakhapatnam, India, were analyzed by Terry.³³ The concentrations were found between 0.025 - 0.067 mg/L. The results obtained from the industrial effluents in the area studied showed that the heavy metals (Pb, Cd, Cu, Zn) apart from Hg had a larger content. Metals (Cu, Cd, Pb, Zn, Cr, Ni, Fe, and Mn) were measured in water samples and sediments at Bebar Peat swampy forest river. Metal concentrations in water (Cu, Cd, Pb, Cr, and Ni) were within the Environmental Protection Agency maximum levels for these metals (13, 2.0, 6.5, 570, 470 mg/L), respectively.

CHAPTER 3

MATERIALS AND METHODS

3.1 Sample Collection

Sample sites were selected based on accessibility in the southern region of Lake Nacogdoches. Water and soil samples were collected at four different sites, shown in Figure 3.1

3.1.1 Water Samples

Water samples were collected just below the water over four different sites in the southern part of Lake Nacogdoches over one year (Figure 3.1): East dock (Site 1), West dock (Site 2), Swimming Area (Site 3), and Nacogdoches Surface Water Treatment Plant (NSWTP) inlet (Site 4). The water parameters (turbidity, pH, dissolved O₂, conductivity, and temperature) were measured at each site. At each location, water samples were collected in triplicate using 125 mL polyethylene sample bottles and stored over ice until returned to the lab. Samples for metal analysis were preserved with 0.5 mL of concentrated nitric acid (Flinn scientific, Analytical grade reagent, 70% purity v/v) and stored in a refrigerator.

3.1.2 Soil Samples

Composite soil samples were collected on the edge of the water line (less than 0.25 m away from water, 5-8 cm deep), over 1 m x 1 m at three different sites of the southern part of Lake Nacogdoches. Soil samples were collected in triplicate at each site in a zip lock bag using a plastic shovel. Samples were placed on ice while in transit. Soil samples were oven (60 °C) dried prior to digestion and analysis.

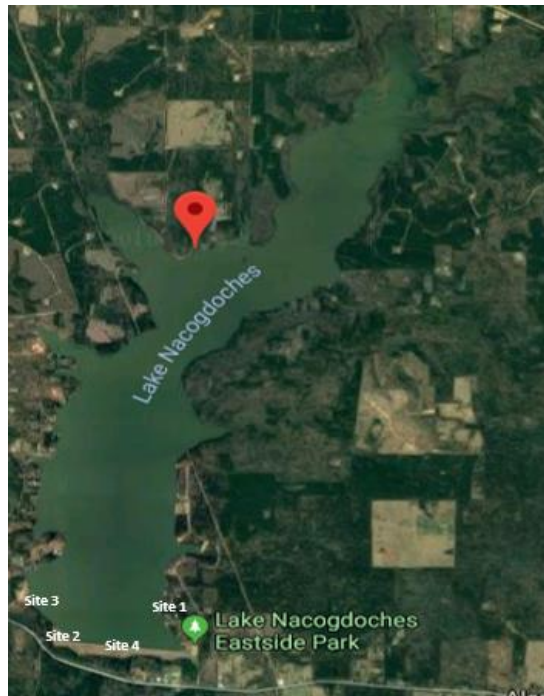


Figure 3.1: Aerial view of Lake Nacogdoches in Nacogdoches Texas (source: Google Earth Map).

3.2 Instrumentation

3.2.1 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

ICP-MS is used for accurate and precise determination of trace metals concentration. An ELAN 9000 ICP-MS (PerkinElmer SCIEX, Concord, Ontario, Canada) was used for analysis of the following metals: Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sr, V, and Zn. The ICP-MS recommended operating conditions by the manufacturer were used, sample uptake rate (1.0 mL min^{-1}), nebulizer (Cross flow), plasma gas flow rate (15 L min^{-1}), spray chamber (Ryton®, Double pass) rf power (1000 W), detector mode (Auto), auxiliary gas flow rate (1.0 L min^{-1}), carrier gas flow rate (0.9 L min^{-1}), Samples were introduced into the ICP -MS plasma torch and converted into a fine aerosol that ionizes the sample towards the end of the plasma (Figure 3.2). This is further introduced into the mass spectrometer via an interface cone allows the detection of mass-to-charge ratio. To opposite pairs of the rods, Alternating AC and DC voltages were Quadrupole mass

spectrometer is one of the most parallel conductive rods that filters off interfering ions and applied. Ion signals are amplified and detected using a detector.³⁴ Calibration was done using blanks and standards prepared at different concentrations (10, 25, and 50 ppb). Analyzes of standard reference samples were used to determine the precision of the procedure.

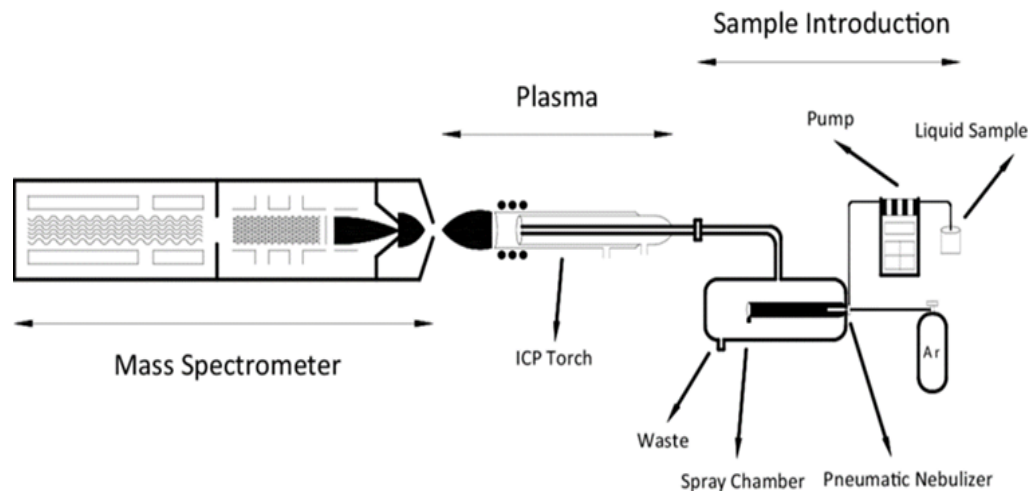


Figure 3.2: Schematic diagram of ICP-MS.³⁴

3.3 Total Digestion of Soil Samples

Soil digestion was conducted by following USEPA method 3050B. Samples were collected from the top layer of the soil surface (about 0–15 cm depth). A 250mm sieve was used to remove stones and plant fragments. Approximately

sixty grams of soil sample was weighed, and oven (120 °C) dried until a constant weight was obtained. Samples were sieved to achieve homogeneity and triplicate samples of 0.5000 g were weighed for each site. Digestion was performed by adding 5 mL of (1:1) HNO₃ to the 0.5000 g soil sample and refluxing for 10 minutes at 95°C. After the soil sample was cooled, 2.5 mL of concentrated nitric acid was added to the soil sample and refluxed for 30 minutes. This step was repeated twice to ensure complete oxidation had occurred. The soil sample was then heated for 2 hours at 95°C. The next step involved adding 1 mL of 35% H₂O₂ in several increments with a couple of minutes of reflux between additions. This process was continued until decomposition of organic matter was complete. After the H₂O₂ (Flinn scientific, Analytical grade reagent) step was complete, sample was heated at 95 °C for 2 hours. Sample was cooled for 30 minutes or was refrigerated overnight. Sample was filtered with 0.45 µm filter (Digifilter) and Digitube filter apparatus and diluted with 18.2 MΩ water and diluted back to 50 mL.

3.4 Total Digestion of Water Samples

Water samples were digested by following USEPA method 200.8 part 11.2.⁵⁸ Digestion was performed by adding 1 mL of

(1:1) nitric acid to 50 mL of water sample. All samples were covered with a ribbed watch glass and heated at 95° C for 2 hours. Samples were cooled for 30 minutes or refrigerated overnight. Samples were filtered with 0.45 µm filter (Digifilter, Scp science) and Digitube filter apparatus (Scp Science) and diluted with 18.2 MΩ water to 50 mL. Some samples were split in half and spiked for validation of results.

3.5 Soil Sequential Extraction Method

Assessment of the inherent effects of sediment contamination with the use of total metal concentration insinuates that metals present in the various soil fractions have uniform impact on the surrounding, which is not accurate. The total concentration of trace elements in soil gives no insight into element bioavailability or mobility, it gives only an indication on the level of contamination. The presence of metals in soils in various forms soils, affects its availability. The examination of the forms in which these metals are present has been analyzed using sequential extraction procedures. This gives a better understanding of processes that influence elements bioavailable.

A modified Tessier soil extraction method by Urasa and Macha³⁵ was used in partitioning the soil samples into specific fractions to effectively understand the different forms of metal. Different reagents were used to selectively extract the different species/forms in the five-step process (Figure 3.3). Five fractions in which metals are likely to be released in solution were extracted under specific conditions: exchangeables, adsorbed, organically bonded, carbonates, and sulfide/residual. The use of total metal concentration as a criterion to assess the potential effects of sediment contamination implies that all forms of metals have equal impact on the environment, which is not necessarily accurate. Although the total concentration of trace elements in soil gives some indication of the level of contamination, it provides no insight into element bioavailability or mobility. Metals in soils are present in various physicochemical forms, which in turn influences its availability. Sequential chemical extraction techniques have been widely used to examine these physicochemical forms, and thus to better understand the processes that influence element.

3.5.1 Exchangeable Fractions (F1)

For the extraction of the exchangeable fraction (F1), 25 mL of 0.5 M of KNO_3 was added to 2.000 g of sample in a beaker. The sediment-extractant suspension was shaken for 16 hours (overnight) at 2000 rpm in a reciprocating shaker (Thermo Fisher Scientific) at 25 °C and then centrifuged to separate the supernatant. A polyethylene container was used in storing the extract in a refrigerator prior to analysis.

Extraction of this fraction is achieved through the utilization of an ion displacing reagent (KNO_3), and a good cation exchanger metal. This is use to separate metals in fractions of the soil constrained via electrostatic forces to the negative sites on the soil surface through adsorption-desorption processes.^{36,37} Ion exchange processes are utilized to release weakly adsorbed metals retained on the top layer of the soil by relatively weak electrostatic interaction. Clay minerals, organics, and amorphous materials are the soil fractions associated with these exchangeable metals.

Modified Sequential Extraction process

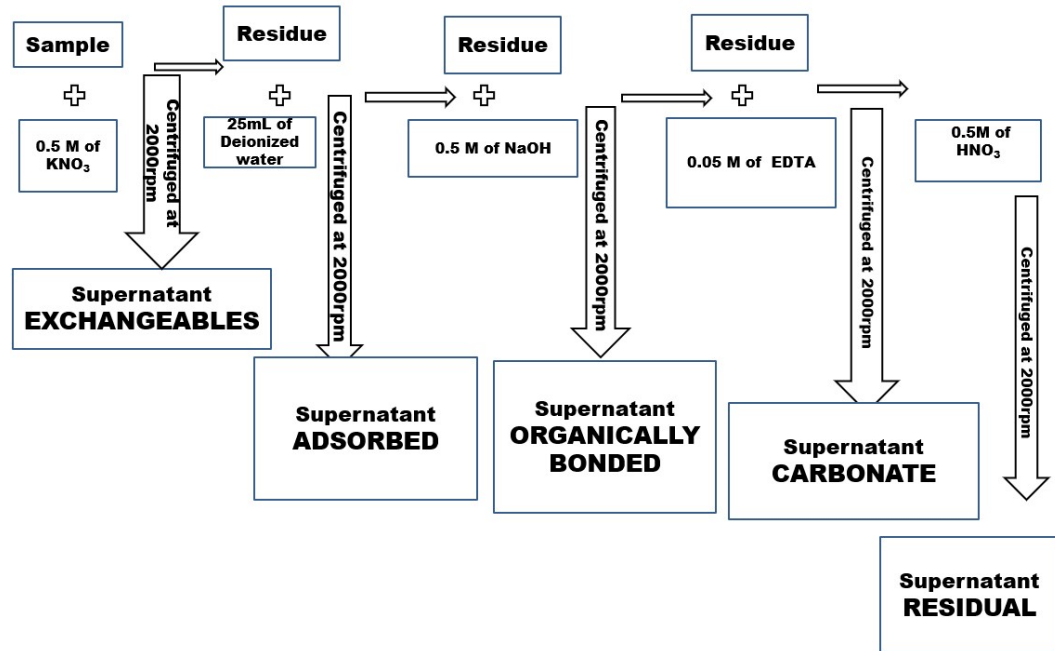


Figure 3.3: Schematic diagram of extraction process.³⁵

3.5.2 The Adsorbed Fraction (F2)

The adsorbed fraction (F2) of a soil can be negligible and extracted by H₂O. It consists of the water-soluble species which are made up of ions complexed with soluble organic matter and free ions.³⁸ This fraction is bioavailable and labile. The most available of this fraction are the potentially mobile metal and metalloid species.³⁹ For the extraction of the

adsorbed fractions (F2), 25 mL of H₂O was added to the residue in a beaker. The extractant suspension was agitated for 2 hours at 2000 rpm in a reciprocating shaker at 25 °C and then centrifuged for 30 mins in order separate the supernatant. This process was repeated three times.

3.5.3 The Organic Fraction (F3)

For the organic fraction (F3), 25 mL of 0.5 M of NaOH was added to the residue in a beaker. The sediment extractant suspension was shaken for 16 hours (overnight) at 2000 rpm in a reciprocating shaker at 25 °C and then centrifuged to separate the supernatant. The organic fraction is thought to relate to stable high molecular weight humic substances that leach small amounts of metals in a slow manner and thus considered as not mobile or available. Metals can be transported throughout the environment in organic and inorganic forms when adsorbed onto organic matter and mineral surfaces in organic and inorganic forms.

3.5.4 The Carbonate Fraction

The carbonate fraction (F4) contains the metals, which can be associated with soil carbonates. These metals can be precipitated or co-precipitated with carbonate. This fraction is

bound by covalent forces, and therefore there is no easy displacement of metal as in the previous fraction.⁴¹

For the extraction of the carbonate fraction, 25 mL of 0.05 M of EDTA was added to approximately 2.000 g of sample. EDTA enhances the metal mobilization by virtue of its strong complexing ability and displaces metals from insoluble organic or organometallic complex through the formation of stable and soluble metal–EDTA complexes.⁴²

3.5.5 Residual Fraction

In the sulfide/residual fraction (F5), it is not expected that the metals present are released under natural conditions. After the four fractions above are removed, this fraction of the soil can still hold some metals within the crystal structures. This fraction is relevant in the evaluation of long-term risk. The residual fraction is the most difficult to extract and where metals have the toughest associations with crystalline composition of primary and secondary minerals. Concentrated nitric acid, HNO_3 , was used to release the metal attached to the crystal lattice of the soil. For the extraction of this fraction, 25 mL of concentrated 0.5 M HNO_3 was added to the sample.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Physico-Chemical Properties of Lake Water

The physico-chemical characteristics of water samples collected from the four different sites are summarized in Tables 4.1-4.4.

4.1.1 pH measurements

Lake water pH is a good indication for lake transformation and factors affecting the aquatic ecosystem. The data showed that the pH in water samples over all sites during the fall (7.15-8.32) were slightly more basic than that collected during the spring (6.78- 7.66). Rainwater tends to be slightly acidic due to carbon dioxide that it collects from the atmosphere. The aquatic environment is impacted the most because over the time, the diluted acid accumulates to lower the overall pH of the water body. Acid rain deposition on soils can release aluminum and magnesium, which can further increase acid levels. The water pH was within the safe limit

(6.5–8.5) that is safe for the organs like eyes, skin and thus it is considered for outdoor bathing ⁴³. Similar trend in pH was reported by Islam⁴⁴. Biochemical processes are affected by the pH, this makes it an important yardstick of environmental standard and pollution level in water system ^{45,46}. The acidity nature of the lake water was normal for this area, which was similar to the acidity obtained at Sam Rayburn reservoir at segment at 0610, which ranges from 5.9 to 8.1.⁶² The disposal and delocalization of industrial wastes, domestic wastewater contamination, presence of chemical detergent, can increase the alkalinity in Lakes⁴⁷. The pH was within the acceptable limits in the both seasons.

4.1.2 Electrical Conductivity (EC)

The electrical conductivity (EC) over all sites were higher during the fall than the spring. Increase in salt concentration accelerates EC level in Lakes. High evaporation can also be attributed to high salinity. The EC were all below the WHO limits ($750 \mu\text{S cm}^{-1}$), reflecting low possible level of pollution⁴⁸. The EC level during both seasons at all sites were within the prescribed standards.

4.1.3 Temperatures

Water temperatures were higher during fall than the spring months at all sites. Increase in temperature accelerates the rate of evaporation, which affects the solubility of ions and causes an increase in EC.⁴⁸ The temperature was within the limit (8–35 °C), which favors aquatic life during both seasons. Lake Sam Rayburn reservoir temperature in segment 0610 averages ranged from 17 °C to 31 °C, which was similar to our data.⁶²

4.1.4 Dissolve Oxygen (DO)

The dissolved oxygen (DO) during spring sampling was higher than the fall months over all sites. A reduction in DO in water can be attributed to higher temperature in fall. Biological activities during the fall could be influenced by the depletion of oxygen and warmer temperatures. DO and temperature are inversely correlated for all sampling sites. Higher DO concentration was observed during the spring month and lower in fall months. DO holding capacity of water can decrease due to rapid saturation caused by increased temperatures.⁴⁹ There was no observed low DO (<5 ppm) values, which was also observed in lake Sam Rayburn at station 15357⁶² (< 5.33

mg/L) in both summer and spring months which showed good water quality. Kong and Ye (2014)⁵⁰, also reported a positive correlation between increased temperature and decreased DO.

4.1.5 Turbidity

The water turbidity reported in this study was generally higher during spring than the summer. A possible reason for the high turbidity could be associated with more ground water in the spring causing more runoff. The fall and spring seasons typically have similar rain patterns in the area. The highest turbidity values were reported at site 4, and it is likely due to the water flow towards the Nacogdoches Water Surface Treatment Plant inlet⁵⁰.

4.2 Total Metal Concentration in Lake Water

The total concentration of metals in water samples collected from four different sites in the southern region of Lake Nacogdoches are presented in Tables 4.5-4.8. The tables include all the water samples analyzed using USEPA method 200.8 part 11.2.⁵⁸ For each site, 12 samples were analyzed over 4 collection dates (three samples per collection date).

Results indicate that the water samples had Ba, Mn, and Sr at measurable amounts (greater than 35 ppb for majority of samples) while the rest of the metals (Cd, Co, Cr, Cu, Ni, Pb, V, Zn) studied had values well below 5 ppb. Low levels of Cd could be attributed to low industrial sources for the lake, such as metal processing and plating. Copper content can be due to domestic sewage and runoff from farmed lands 51. The results of this study were very similar to that reported on the Korotoa Lake⁵² and a study conducted by Harguinteguy et al. (2014)⁵³.

Overall, the findings reflect that the total metal concentration in water samples in Lake Nacogdoches at the different sites were very similar between sites (Figures 4.1-4.11) with very little variation between fall and spring seasons with the exception that Sr was higher in the fall than the spring and Mn was much higher (six-fold) on the collection date in October for all sites. Examining the reliability of spectrometer, recovery data indicates that Mn was having difficulty on that date. We ran three different recovery samples that day and obtained 80%, 100%, and 120% recovery on Mn for the same sample. This might explain the high Mn numbers for October as compared to the other Mn data. All metals concentration

was within the typical range found in natural waters and were below the WHO and USEPA drinking water guidelines.

The metal Ba, Mn and Sr in water comes primarily from natural sources. Barium also can enter the environment from industrial emissions and anthropogenic activities. Ba concentration was observed to be high in the exchangeable fraction of the lake soil (will be discussed later), which makes it available and mobile in the environment.

4.3 Total Metal Concentration in Lake Soil

The total concentration of metals in soil samples collected from three different sites in the southern region of Lake Nacogdoches are presented in Tables 4.9-4.19. The “Site Total Digested” column are the results of total digestion of soil samples using USEPA method 3050B.⁵⁹ For each site, 12 samples were analyzed over 4 collection dates (three samples per collection date).

The metal concentrations of the soil samples were all within the typical ranges found in soil (Table 4.9-4.19). Results indicate that Ba, Co, Cr, Mn, Ni, Pb, V, and Zn at measurable amounts (greater than 10 mg of metal/kg soil for majority of samples) while Cd and Cu, were well below 2 mg metal per kg

of soil. In comparison with Sam Rayburn reservoir for segment 0610, all records were below the calculated chronic criterion (4.4 µg/L, 37.5 µg/L) for Cu, Zn and the acute criterion for Pb (15.54 µg/L). Barium, Mn, and V all had high levels of metal concentration (as compared with metals studied) an approximately mean value for all samples of 61, 207, and 80 mg of metal per kg of soil, respectively.

Overall, all metals studied were in the typical range found in soils; however, there was a large variation in Co, Cr, Mn, Ni, Pb, V, and Zn between sites due to soil variation while soil samples tended to have similar results at a particular site (Figures 4.12-4.22). The metal with the largest variation was Mn with site 1 at approximately 455, site 2 at 134, and site 3 at 31 mg metal/kg of soil. Data was consistent throughout collections at a site and validation recovery data was within limits indicating this is a real trend between sites.

Analyzes for variations over time (Figures 4.23-4.25) show no conclusive trends observed in concentrations of metals during the sampling period. Manganese showed no clear trend during the fall and spring seasons of site 1; however, site 2 had slightly higher Mn concentrations during the spring periods than the fall, but nothing can be confirmed

without additional data. Site 3 (figures 4.25) had Mn concentrations that were very similar over the entire sampling period. Particulate earthy material carried by runoff waters from the nearby drainage basin, Precipitation, and discharge from upper waters (sorption and/or solubility reactions) can integrate Mn into the lake sediments. It was observed that vanadium concentrations were significantly higher during the spring season (Fig. 4.23-4.26) than in the fall (90.797) at sites 2 and 3, but once again, nothing can be confirmed without additional data. Even though, the reason for seasonal changes in total dissolved V concentrations are still unknown⁵⁴. High levels may result from the release of sediments and suspended particles due to increased biological activity.

4.4 Speciation of Selected Metals (Ba, Mn, Sr, Cd, Co, Cr, Cu, Ni, Pb, V, Zn) by using a Modified Tessier sequential procedure

To obtain each fraction of the soil, different reagent (as summarized in Figure 3.3) were used to extract the metals bounded in the matrix in different forms. For each site, nine samples were analyzed over three collection dates (three samples per collection date).

The metal species that had measurable amounts (approximately 5 – 30 mg metal/kg soil) extracted in the exchangeable phase were Ba, Mn, and Sr, which coincide with the metals that had higher concentrations in the water samples. Barium had by far the largest exchangeable amounts available; however, there is one set of data on June 11 at site 2 (Table 4.9) that is questionable as compared to the rest of the Ba data (site 1 – 32.13, site 2 – 109.89, site 3 – 6.22 mg Ba/kg soil). There are no validation recovery data available that indicates instrumentation issues. However, based on data comparison, it is believed that this Ba data set on June 11 is invalid. If this data is removed for Ba, the numbers are closer to the expected values. Soil samples with the exchangeable species are generally called “bio-available”, as they are readily available for plants uptake and are exchangeable relative to the surrounding.⁵¹ Results indicate that most of the species studied are not in the bio-available form.

None of the metals studied showed any significant amounts (≤ 1.11 mg metal / kg soil) being collected during the adsorbed fraction.

Within the organic bonded fraction, only V (6 - 11 mg V/kg soil) and Cu (1 – 4 mg Cu/kg soil) showed any measurable amounts indicating that most of the metal species studied did not release any soluble trace metals during the degradation of the organic matter. Fraction 4 involved the changing of pH to influence solubility of the sediment carbonates. Cobalt, Cr, Cu, Mn, Ni, Pb, Sr, V, and Zn had measurable amounts (1 – 10 mg metal/kg soil) obtained during the carbonate fraction; however, Mn had higher concentrations between 30-50 mg Mn/kg soil at sites 1 and 2.

The sulfide/residual fraction involves the primary and secondary minerals that are usually contained in their crystalline lattice structure. These metals are not expected to be released in solution over normal conditions. Barium, Co, Cr, Cu, Mn, Ni, Pb, Sr, V, and Zn produced metal concentrations during this phase between 1 to 10 mg metal/kg soil. Higher concentration of Ba (20-50 mg Ba/kg soil) and Mn (55 – 245 mg Mn/kg soil) were obtained during this extraction phases. The trend of large variation of Mn between sites found for the total digested soils was also apparent in the extraction sulfide/residual fraction (site 1 – 245.85, site 2 - 54.29, site 3- 4.89 mg Mn/kg soil). Data was consistent throughout

collections at a site and validation recovery data was within limits indicating this is a real trend between sites. A summary of all data for a site obtained for each of the eleven metals studied in this research are shown in Tables 4.9-4.19 and Figures 4.23-4.54. These tables show the metal concentrations obtained in each fraction at each site and gives the total extracted by Sequential extraction process as compared to that obtained through total digestion. Individual site and fraction data based on collection dates are in Tables 4.20-4.39.

Sequential extractions were compared with the total metal concentration from the digestion of the bulk sediment, in order to give an appropriate judgment of the reliability of the sequential extraction procedure. Similar amounts (about 85-95% similarities) were obtained between the two experiments indicating some reliability of the sequential extraction procedure for Ba (exception June 11 data as mentioned above), Cd, Co, Cu, Mn, Pb, and Sr. Poor recovery rates for Cr, Ni, V and Zn indicate that different reagents, concentrations, and/or contact times may be needed to improve the process. Both soil composition and nature of the metal played important roles in determining the success of the

extraction process based on binding sites and strengths. It should be noted that no appreciable amounts (0.01-0.07 mg metal / kg of soil) were collected for Cd in any of the phase extractions.

Table 4.1: Physio-Chemical Properties (Temperature, pH, Salinity, EC, Turbidity, Oxidation Reduction, Dissolved O₂, Total dissolved Solids) of East Dock (Site 1) Lake Water over Sampling

Date	2019/03/08	2019/02/01	2018/10/19	2018/09/07	Mean	*
Temp.[°C]	11.16	10.61	21.11	31.23	18.53	13-30
pH	7.26	6.78	7.15	7.57	7.19	6.5-9
Oxidation Reduction potential [mV]	167.49	140.15	156.92	200.68	166.31	
EC	72.09	69.62	121.37	153.00	104.02	90-3000
Abs.[µS/cm]						
Total	10.57	47.96	65.40	68.00	57.59	46-750
Dissolved Solids [ppm]						
Salinity [psu]	0.05	0.04	0.06	0.06	0.05	0.20
Dissolved O₂ [ppm]	10.57	10.48	6.46	5.04	8.14	2-10
Turbidity [FNU]	12.77	24.97	4.01	5.63	11.84	0.8-22

*Typical range for lake or stream
n=1

Table 4.2: Physio-Chemical Properties (Temperature, pH, Salinity, EC, Turbidity, Oxidation Reduction, Dissolved O₂, Total dissolved Solids) of West Dock (Site 2) Lake Water over Sampling Times

Date	2019/03/08	2019/02/01	2018/10/19	2018/09/07	mean	*
Temp.[°C]	13.31	10.83	21.82	31.05	19.25	13-30
pH	7.58	7.37	7.66	8.16	7.69	6.5-9
Oxidation Reduction potential	198.70	233.25	208.91	179.21	205.02	
EC	80.49	67.00	121.98	147.99	104.36	90-3000
Abs.[μS/c]						
Total Dissolves Solids	51.71	46.00	65.00	66.00	57.18	46-75
Salinity [psu]	0.05	0.04	0.06	0.06	57.18	0.20
Dissolved O₂ [ppm]	11.00	8.70	6.37	7.30	8.34	2-10
Turbidity [FNU]	15.88	25.56	3.84	3.98	12.31	0.8-22

*Typical range for lake or stream
n=1

Table 4.3: Physio-Chemical Properties (Temperature, pH, Salinity, EC, Turbidity, Oxidation Reduction, Dissolved O₂, Total dissolved Solids) of Swim Area (Site 3) Lake Water over Sampling Times

Date	2019/03/08	2019/02/01	2018/10/19	2018/09/07	*	mean
Temp.[°C]	11.82	10.78	21.91	30.46	13-30	18.74
pH	7.66	7.33	7.72	8.32	6.5-9	7.75
Oxidation Reduction potential [mV]	198.95	237.72	215.46	216.27		217.10
EC Abs.[µS/cm]	73.04	67.00	121.98	145.43	90-3000	101.86
Total Dissolved Solids	49.00	46.00	64.98	65.57	46-750	56.39
Salinity [psu]	0.05	0.04	0.06	0.06	0.20	0.05
Dissolved O₂ [ppm]	11.36	8.83	6.84	6.88	2-10	8.48
Turbidity [FNU]	16.33	25.26	3.71	2.20	0.8-22	11.88

*Typical range for lake or stream
n=1

Table 4.4: Physio-Chemical Properties (Temperature, pH, Salinity, EC, Turbidity, Oxidation Reduction, Dissolved O₂, Total dissolved Solids) of Inlet NSWTP (Site 4) Water over Sampling Times

Date	2019/03/08	2019/02/01	2018/10/19	2018/09/07	mean	*
Temp.[°C]	11.14	10.52	21.65	30.31	18.41	13-30
pH	7.50	7.48	7.52	7.90	7.60	6.5-9
Oxidation Reduction potential [mV]	197.20	193.56	197.12	235.31	205.80	
EC Abs.[µS/cm]	71.78	66.00	121.42	148.03	101.81	90-3000
Total Dissolved Solids [ppm]	48.75	45.34	65.00	67.02	56.52	46-750
Salinity [psu]	0.05	0.04	0.06	0.06	0.05	0.20
Dissolved O₂ [ppm]	10.96	8.96	7.18	5.75	8.21	2-10
Turbidity [FNU]	18.99	26.19	2.66	2.27	17.28	0.8-22

*Typical range for lake or stream

Table 4.5: Mean Concentrations of Total Metals in Lake Nacogdoches Water (ppb) at East Dock (Site 1)

Date	3/8/199	2/1/19	10/19/19	9/7/18	mean ± s. d	*	**	***
Ba	45.40	44.74	39.81	34.65	41.15 ± 4.61	700	2000	5-100
Cd	0.01	0.02	0.00	0.03	0.02 ± 0.02	3	5	0-1
Co	0.26	0.28	0.13	0.22	0.23 ± 0.09	400		0.2-10
Cr	0.64	0.75	0.12	0.25	0.44 ± 0.28	50	100	0-9
Cu	0.19	0.91	0.02	1.93	0.77 ± 1.38	2000	1300	0-10
Mn	58.49	45.06	176.03	42.82	80.6 ± 57.94	400		3-65
Ni	2.21	2.61	0.86	5.31	2.75 ± 1.7	70	100	0-40
Pb	0.44	0.59	0.11	0.07	0.31 ± 0.24	10	15	0-6
Sr	63.19	61.58	91.06	89.86	76.43 ± 14.81			
V	1.78	2.06	0.37	0.48	1.18 ± 0.8			0.5-10
Zn	3.07	1.13	3.08	7.07	3.59 ± 4.49	3000	2000	0-30

*WHO drinking water standard metal ppb⁵⁷
 **EPA drinking water standard metal ppb⁵⁸
 *** Typical range of natural waters metal ppb⁵⁹
 number of samples per date collected, n = 3
 s. d = standard deviation

Table 4.6: Mean Concentrations of Total Metals in Lake Nacogdoches Water (ppb) at West Dock (Site 2)

Date	mean ± s. d	3/8/19	2/1/19	0/19/19	9/7/18	***	**	*
Ba	41.06±4.07	44.16	45.46	38.50	36.11	5-100	2000	700
Cd	0.02±0.02	0.00	0.01	0.00	0.03	0-1	5	3
Co	0.27±0.19	0.27	0.47	0.19	0.14	0.2-10		400
Cr	0.49±0.3	0.69	0.81	0.14	0.28	0-9	100	50
Cu	0.79±1.53	0.57	0.54	1.84	0.19	0-10	1300	200
Mn	85.99 ±80.42	34.93	44.18	219.15	45.69	3-65		400
Ni	2.74±1.59	2.36	2.72	0.81	5.05	0-40	100	70
Pb	0.28±0.23	0.42	0.55	0.09	0.04	0-6	15	10
Sr	79.21±13.48	67.15	65.52	91.70	92.47			
V	1.25±0.81	1.81	2.19	0.35	0.63	0.5-10		
Zn	2.61±2.25	5.50	0.70	1.51	2.72	0-30	2000	300

*WHO drinking water standard metal ppb⁵⁷
 **EPA drinking water standard metal ppb⁵⁸
 *** Typical range of natural waters metal ppb ⁵⁹
 number of samples per date collected, n = 3
 s.d = standard deviation

Table 4.7: Mean Concentrations of Total Metals in Lake Nacogdoches Water (ppb) at Swim Area (Site 3)

Date	3/8/19	2/1/19	10/19/19	9/7/18	***	**	*	mean ± s. d
Ba	46.23	45.53	38.56	35.62	5-100	2000	700	41.49±4.87
Cd	0.00	0.01	0.00	0.03	0-1	5	3	0.01±0.02
Co	0.23	0.33	0.12	0.10	0.2-10		400	0.2±0.1
Cr	0.74	0.85	0.18	0.22	0-9	100	50	0.5±0.32
Cu	0.36	0.55	0.00	0.22	0-10	1300	2000	0.29±0.23
Mn	38.79	40.38	219.26	42.11	3-65		400	85.14±80.91
Ni	2.40	2.73	0.82	5.10	0-40	100	70	2.77±1.6
Pb	0.39	0.55	0.08	0.02	0-6	15	10	0.26±0.23
Sr	67.87	66.29	93.22	94.06				80.36±13.92
V	1.88	2.24	0.35	0.33	0.5-10			1.21±0.91
Zn	3.42	0.51	0.85	3.00	0-30	2000	3000	1.95±1.97

*WHO drinking water standard metal ppb⁵⁷
 **EPA drinking water standard metal ppb⁵⁸
 *** Typical range of natural waters metal ppb ⁵⁹
 number of samples per date collected, n = 3
 s. d = standard deviation

Table 4.8: Mean Concentrations of Total Metals in Lake Nacogdoches Water (ppb) at Inlet NSWTP (Site 4)

Date	mean ± s. d	3/8/19	2/1/19	10/19/19	9/7/18	***	**	*
Ba	44.43±6.74	45.68	45.59	52.07	34.37	5-100	2000	700
Cd	0.02±0.02	0.00	0.02	0.00	0.03	0-1	5	3
Co	0.2±0.09	0.23	0.31	0.14	0.09	0.2-10		400
Cr	0.54±0.34	0.76	0.94	0.22	0.21	0-9	100	50
Cu	0.43±0.31	0.43	0.82	0.21	0.25	0-10	1300	2000
Mn	85.75±85.8	35.10	42.74	227.88	37.26	3-65		400
Ni	2.88±1.61	2.44	2.87	0.96	5.24	0-40	100	70
Pb	0.27±0.26	0.38	0.62	0.07	0.00	0-6	15	10
Sr	81.78±14.4	68.80	67.27	95.39	95.64			
V	1.27±0.97	1.91	2.43	0.38	0.33	0.5-10		
Zn	2.11±2.24	3.61	0.69	3.85	0.29	0-30	2000	3000

*WHO drinking water standard metal ppb⁵⁷
**EPA drinking water standard metal ppb⁵⁸
*** Typical range of natural waters metal ppb⁵⁹
number of samples per date collected, n = 3
s.d = standard deviation

Table 4.9: Mean Concentrations of Extractions for Barium in Lake Nacogdoches Soil (mg metal/kg soil)

	Ba site 1	Ba Site 2	Ba Site 3
Exchangeable	32.13 ± 18	109.89 ± 228.21	6.22 ± 6.05
Adsorbed	0.65 ± 0.44	0.46 ± 0.68	1.18 ± 0.45
Organic Bonded	0.01 ± 0.01	0.01 ± 0.01	0.01 ± 0.02
Carbonate	3.58 ± 4.12	1.65 ± 1.68	2.53 ± 2.21
Sulfide Residual	41.32 ± 21.48	22.44 ± 13.32	52.88 ± 34.32
Total Extracted (mg/kg) n=9	77.69 ± 18.52	134.45 ± 228.24	62.51 ± 7.77
Site total digested (mg/kg) n=12	60.34 ± 18.25	58.2 ± 18.33	63.09 ± 41.20
¥	70-3000		

¥ Typical range for soils mg/kg ⁶⁰

Table 4.10: Mean Concentrations of Extractions for Cadmium in Lake Nacogdoches Soil (mg metal/kg)

	Cd site 1	Cd Site 2	Cd Site 3
Exchangeable	0.01±0.01	0.01±0.01	0.02±0.02
Adsorbed	0.03±0.01	0.03±0.01	0.01±0.01
Organic Bonded	0.01±0.01	0.01±0.01	0.01±0.01
Carbonate		0.01±0.01	0.01±0.01
Sulfide / Residual	0.02±0.01	0.01±0.02	0.01±0.01
Total Extracted (mg/kg) n=9	0.08±0.02	0.07±0.03	0.08±0.03
Site total digested (mg/kg) n=12	0.03±0.01	0.03±0.01	0.03±0.05
¥	0.01-0.7		

¥ Typical range for soils mg/kg ⁶⁰

Table 4.11: Mean Concentrations of Extractions for Cobalt
in Lake Nacogdoches Soil (mg metal/kg soil)

	Co Site3	Co Site 2	Co site 1
Exchangeable	0.06 ± 0.04	0.03±0.03	0.03 ± 0.02
Adsorbed	0.03 ± 0.02	0.08 ± 0.05	0.03 ± 0.02
Organic Bonded	0.03 ± 0.02	0.04 ± 0.03	0.08 ± 0.08
Carbonate	0.14 ± 0.1	0.84 ± 0.35	2.22 ± 1.49
Sulfide / Residual	0.55± 0.36	3.22 ± 1.54	13.20 ± 5.04
Total Extracted (mg/kg) n=9	0.67 ± 0.38	5.41 ± 1.58	15.56 ± 5.26
Site total digested (mg/kg) n=12	1.41 ± 0.27	7.44 ± 2.42	12.89 ± 3.82
¥	3-50 (10)		

¥ Typical range for soils mg/kg (mean)⁶⁰

Table 4.12: Mean Concentrations of Extractions for

Chromium in Lake Nacogdoches Soil (mg metal/kg soil)

	Cr site 1	Cr Site 2	Cr Site 3
Exchangeable	0.00±0.00	0.00±0.00	0.00±0.00
Adsorbed	0.03±0.02	0.34±0.24	0.08±0.08
Organic Bonded	0.05±0.03	0.08±0.05	0.22± 0.09
Carbonate	3.36±0.06	0.38±0.35	1.13± 0.73
Sulfide / Residual	1.03±0.64	4.71±2.33	4.52± 1.58
Total Extracted (mg/kg) n=9	4.47±0.64	5.51±2.37	3.48± 1.74
Site total digested (mg/kg) n=12	17.89±6.30	36.80±15.31	15.0±36.68
¥	7-1500 (50)		

¥ Typical range for soils mg/kg (mean)⁶⁰

Table 4.13: Mean Concentrations of Extractions for Copper in Lake Nacogdoches Soil (mg metal/kg soil)

	Cu site 1	Cu Site 2	Cu Site 3
Exchangeable	0.05±0.06	0.02±0.03	0.07±0.07
Adsorbed	0.09±0.07	0.13±0.07	0.14±0.2
Organic Bonded	3.38±3.27	1.08±1.00	2.59±2.51
Carbonate	1.16±0.27	0.95±0.49	9.07±24.64
Sulfide / Residual	1.91±2.06	0.62±0.59	1.31±0.37
Total Extracted (mg/kg) n=9	6.59±3.87	2.80±0.59	13.18±24.7 7
Site total digested (mg/kg) n=12	2.68±1.11	1.20±0.30	1.00±0.20
¥	3-300 (26)		

¥ Typical range for soils mg/kg (mean)⁶⁰

Table 4.14: Mean Concentrations of Extractions for Manganese in Lake Nacogdoches Soil (mg metal/kg soil)

	Mn site 1	Mn Site 2	Mn Site 3
Exchangeable	7.56± 5.57	11.05± 4.9	6.60± 4.94
Adsorbed	0.09± 0.43	0.74± 0.41	0.47± 0.35
Organic Bonded	0.03± 0.03	0.02± 0.02	0.01± 0.03
Carbonate	48.90± 27.33	33.39± 24.35	0.95± 0.83
Sulfide / Residual	245.85± 153.77	54.29± 24.34	4.89± 2.89
Total Extracted (mg/kg)	302.43± 156.27	99.49± 34.76	12.93± 5.79
Site total digested (mg/kg) n=12	455.50± 117.10	133.85±47.10	31.22± 4.90
¥	20-3000 (490)		

¥ Typical range for so(mean)⁶⁰

Table 4.15: Mean Concentrations of Extractions for Nickel in Lake Nacogdoches Soil (mg metal /kg soil)

	Ni site 1	Ni Site 2	Ni Sie 3
Exchangeable	0.03±0.03	0.04±0.03	0.31±0.55
Adsorbed	0.03±0.02	0.25±0.19	0.72±1.14
Organic Bonded	0.08±0.05	0.07±0.04	0.32±0.59
Carbonate	4.59±4.22	2.59±2.03	4.20±7.17
Sulfide / Residual	4.29±1.61	5.28±3.33	1.67±1.01
Total Extracted (mg/kg) n=9	9.02±4.52	8.24±3.90	7.22±7.37
Site total digested (mg/kg) n=12	18.05±7.22	20.30±6.37	3.07± 0.52
¥	<5-150 (18)		

¥ Typical range for soils mg/kg (mean)⁶⁰

Table 4.16: Mean Concentrations of Extractions for Lead in Lake Nacogdoches Soil (mg metal/kg soil)

	Pb site 1	Pb Site 2	Pb Site 3
Exchangeable	0.01±0.01	0.00±0.00	0.01±0.01
Adsorbed	0.03±0.02	0.08±0.07	0.03±0.02
Organic Bonded	0.01±0.01	0.00±0.00	0.00±0.00
Carbonate	4.46±3.57	2.88±1.74	3.30±6.13
Sulfide / Residual	9.47±4.04	4.12±1.32	3.34±1.69
Total Extracted (mg/kg) n=9	13.98±5.39	7.08± 2.19	6.68±6.34
Site total digested (mg/kg) n=12	12.42±3.07	9.84±4.76	4.16±1.35
¥	<10-70 (26)		

¥ Typical range for soils mg/kg (mean)⁶⁰

Table 4.17: Mean Concentrations of Extractions for Strontium in Lake Nacogdoches Soil (mg metal/kg soil)

	Sr site 1	Sr Site 2	Sr Site 3
Exchangeable	6.98±3.84	8.16±2.09	16.10±29.3
Adsorbed	0.26±0.19	0.10±0.09	0.35±0.30
Organic Bonded	0.01±0.01	0.01±0.01	0.02±0.02
Carbonate	0.69±0.58	0.81±0.51	4.48±8.53
Sulfide / Residual	1.26±0.46	0.89±0.97	7.72±5.06
Total Extracted (mg/kg) n=9	9.20±3.92	9.97±2.36	28.67±31.7
Site total digested (mg/kg) n=12	8.36±3.16	8.69±3.16	10.23±5.08
¥	7-(1000)	(200)	

¥ Typical range for soils mg/kg (mean)⁶⁰

Table 4.18: Mean Concentrations of Extractions for

Vanadium in Lake Nacogdoches Soil (mg metal/kg soil)

	V site 1	V Site 2	V Site3
Exchangeable	0.01±0.01	0.01±0.01	0. 0.01
Adsorbed	0.03±0.03	0.68±0.47	0.30± 0.24
Organic Bonded	6.31±5.65	11.31±7.37	9.67± 4.84
Carbonate	4.77±6.99	1.78±1.22	9.68± 19.62
Sulfide / Residual	6.40±1.63	9.36±2.31	8.12± 1.74
Total Extracted (mg/kg) n=9	17.52±9.13	23.14±7.83	27.78± 20.28
Site total digested (mg/kg) n=12	78.92±31.71	108.70±44.83	53.55± 26.21
¥	7-1200 (200)		

¥ Typical range for soils mg/kg (mean)⁶⁰

Table 4.19: Mean Concentrations of Extractions for Zinc in Lake Nacogdoches Soil (mg metal/kg soil)

	Zn Site 1	Zn Site 2	Zn Site 3
Exchangeable	0.01±0.01	0.00±0.00	
Adsorbed	0.11±0.09	0.40±0.33	0.16±0.22
Organic Bonded	0.01±0.02	0.00±0.00	0.00±0.00
Carbonate	3.79±1.87	2.92±4.41	2.34±4.26
Sulfide / Residual	2.51±2.29	5.50±4.95	5.07±3.57
Total Extracted (mg/kg)n=9	6.43±2.96	8.82±6.63	7.75±5.56
Site total digested (mg/kg) n=12	18.65±7.30	40.41±23.13	22.88±12.98
¥	13-300	(75)	

¥ Typical range for soils mg/kg (mean)⁶⁰

Table 4.20: Mean Concentrations of Exchangeable Fraction
in Lake Nacogdoches Soil (mg metal/kg soil) at East Dock

Date	6/11/19	3/8/19	2/1/19	mean ± s. d
Ba	53.75	27.76	14.85	32.13± 18
Cd	0.01	0.01	0.01	0.01± 0.01
Co	0.04	0.02	0.00	0.03± 0.02
Cr	0.00	0.00	0.00	0± 0.00
Cu	0.11	0.02	0.00	0.05± 0.06
Mn	13.28	8.69	0.69	7.56± 5.60
Ni	0.05	0.02	0.01	0.03± 0.03
Pb	0.00	0.00	0.00	0.01± 0.01
Sr	7.50	8.41	5.02	6.98±3.84
V	0.00	0.00	0.00	0.01±0.01
Zn	0.00	0.02	0.00	0.01±0.01

n= 3 for each sample date
s. d= standard deviation

Table 4.21: Mean Concentrations of Absorbed 1 Fraction in Lake Nacogdoches Soil (mg metal/kg soil) at East Dock

Date	6/11/19	3/8/19	2/1/19	mean ± s. d
Ba	0.64	0.94	0.00	0.74±0.6
Cd	0.00	0.00	0.00	0.01±0.01
Co	0.01	0.01	0.00	0.01±0.01
Cr	0.00	0.00	0.00	0.01±0.01
Cu	0.00	0.05	0.01	0.03±0.04
Mn	0.90	0.60	0.02	0.51±0.4
Ni	0.01	0.01	0.00	0.01±0.01
Pb	0.00	0.00	0.00	0.01±0.01
Sr	0.15	0.38	0.00	0.18±0.18
V	0.01	0.00	0.01	0.01±0.01
Zn	0.00	0.07	0.01	0.03±0.04

n= 3 for each sample date
s. d= standard deviation

Table 4.22: Mean Concentrations of Absorbed 2 Fraction in

Lake Nacogdoches Soil (mg metal/kg soil) at East Dock

Date	6/11/19	3/8/19	2/1/19	mean ± s. d
Ba	0.00	0.17	0.00	0.06±0.09
Cd	0.00	0.00	0.00	0.01±0.01
Co	0.00	0.00	0.00	0.01±0.01
Cr	0.00	0.00	0.00	0.01±0.01
Cu	0.01	0.06	0.00	0.03±0.04
Mn	0.07	0.25	0.00	0.11±0.12
Ni	0.00	0.01	0.00	0.01±0.01
Pb	0.00	0.00	0.00	0.01±0.01
Sr	0.00	0.09	0.00	0.04±0.05
V	0.02	0.00	0.00	0.01±0.02
Zn	0.00	0.10	0.00	0.04±0.06

n = 3 for each sample date
s. d = standard deviation

Table 4.23: Mean Concentrations of Absorbed 3 Fraction in

Lake Nacogdoches Soil (mg metal/kg soil) at East Dock

Date	6/11/19	3/8/19	2/1/19	mean ± s. d
Ba	0.00	0.17	0.00	0.06±0.09
Cd	0.00	0.00	0.00	0.01±0.01
Co	0.00	0.00	0.00	0.01±0.01
Cr	0.00	0.00	0.00	0.01±0.01
Cu	0.01	0.06	0.00	0.03±0.04
Mn	0.07	0.25	0.01	0.12±0.12
Ni	0.00	0.01	0.00	0.01±0.01
Pb	0.00	0.00	0.00	0.01±0.01
Sr	0.00	0.09	0.00	0.04±0.05
V	0.02	0.00	0.01	0.01±0.02
Zn	0.00	0.10	0.00	0.04±0.06

n= 3 for each sample date
s. d= standard deviation

Table 4.24: Mean Concentrations of Organic Bonded

Fraction in Lake Nacogdoches Soil (mg metal/kg soil) at

Date	6/11/19	3/8/19	2/1/19	mean ± s. d
Ba	0.00	0.01	0.00	0.01±0.01
Cd	0.00	0.00	0.00	0.01±0.01
Co	0.17	0.02	0.05	0.08±0.08
Cr	0.08	0.02	0.03	0.05±0.03
Cu	3.63	3.34	3.15	3.380.27
Min	0.04	0.01	0.01	0.03±0.03
Ni	0.12	0.03	0.08	0.08±0.05
Pb	0.00	0.00	0.00	0.01±0.01
Sr	0.00	0.01	0.00	0.01±0.01
V	0.00	6.26	12.65	6.31±5.65
Zn	0.00	0.03	0.00	0.01±0.02

n= 3 for each sample date
s. d= standard deviation

Table 4.25: Mean Concentrations of Carbonate Fraction in Lake Nacogdoches Soil (mg metal/kg soil) at East Dock

Date	6/11/19	3/8/19	2/1/19	mean ± s. d
Ba	8.48	0.65	1.60	3.58± 4.12
Cd	0.00	0.01	0.00	0.01± 0.01
Co	0.00	2.02	3.76	2.22± 1.49
Cr	0.08	0.02	0.03	3.36± 6.06
Cu	3.63	3.34	3.15	3.38± 3.27
Mn	0.04	0.01	0.01	0.03± 0.03
Ni	0.12	0.03	0.08	0.08± 0.05
Pb	0.00	0.00	0.00	0.01± 0.01
Sr	0.00	0.01	0.00	0.01± 0.01
V	0.00	6.26	12.65	6.31± 5.65
Zn	0.00	0.03	0.00	0.01± 0.02

n= 3 for each sample date
s. d= standard deviation

Table 4.26: Mean Concentrations of Sulfide/Residual Fraction in Lake Nacogdoches Soil (mg metal/kg soil) at East Dock (Site 1)

Date	6/11/19	3/8/19	2/1/19	mean ± s. d
Ba	26.70	68.21	29.05	41.32± 21.48
Cd	0.01	0.02	0.01	0.02± 0.01
Co	16.99	15.52	7.08	13.2± 5.04
Cr	1.48	0.81	0.80	1.03± 0.64
Cu	0.58	4.49	0.67	1.91± 2.06
Mn	191.52	311.49	234.52	245.85± 153.77
Ni	5.15	5.43	2.28	4.29± 1.61
Pb	13.07	10.96	4.37	9.47± 4.04
Sr	1.05	1.77	0.95	1.26± 0.46
V	8.36	5.43	5.39	6.4± 1.63
Zn	0.00	5.25	2.26	2.51± 2.29

n= 3 for each sample date
s. d= standard deviation

Table 4.27: Mean Concentrations of Exchangeable Fraction
in Lake Nacogdoches Soil (mg metal/kg soil) at West Dock

Date	6/11/19	3/8/19	2/1/19	mean ± s. d
Ba	279.25	31.38	19.02	109± 228
Cd	0.00	0.01	0.02	0.01± 0.01
Co	0.06	0.02	0.01	0.03± 0.03
Cr	0.00	0.00	0.00	0.00
Cu	0.03	0.00	0.00	0.02±0.03
Mn	16.23	10.42	6.48	11.05±4.79
Ni	0.06	0.02	0.01	0.04±0.03
Pb	0.00	0.00	0.00	0.00±0.00
Sr	10.28	6.88	7.31	8.16±2.09
V	0.00	0.00	0.00	0.01±0.01
Zn	0.00	0.00	0.00	0.00±0

n= 3 for each sample date
s. d= standard deviation

Table 4.28: Mean Concentrations of Absorbed 1 Fraction in Lake Nacogdoches Soil (mg metal/kg soil) at West Dock

Date	6/11/19	3/8/19	2/1/19	mean ± s. d
Ba	0.39	1.28	0.02	0.57±0.67
Cd	0.00	0.00	0.00	0.01±0.01
Co	0.01	0.00	0.00	0.01±0.01
Cr	0.00	0.00	0.02	0.01±0.02
Cu	0.00	0.01	0.03	0.02±0.02
Mn	0.26	0.30	0.03	0.2±0.14
Ni	0.01	0.00	0.01	0.01±0.01
Pb	0	0	0	0±0
Sr	0.08	0.19	0.01	0.1±0.09
V	0.02	0.01	0.04	0.03±0.03
Zn	0.00	0.00	0.01	0.01±0.02

n= 3 for each sample date
s. d= standard deviation

Table 4.29: Mean Concentrations of Absorbed 2 Fraction in Lake Nacogdoches Soil (mg metal/kg soil) at West Dock

Date	6/11/19	3/8/19	2/1/19	mean ± s. d
Ba	0.21	0.11	0.12	0.15± 0.1
Cd	0.00	0.00	0.00	0.01± 0.01
Co	0.07	0.00	0.02	0.03± 0.04
Cr	0.33	0.01	0.11	0.16± 0.17
Cu	0.04	0.04	0.05	0.05± 0.05
Mn	0.39	0.05	0.28	0.25± 0.27
Ni	0.27	0.01	0.07	0.12± 0.14
Pb	0.08	0.00	0.01	0.04± 0.05
Sr	0.04	0.05	0.03	0.04± 0.02
V	0.52	0.06	0.33	0.31± 0.34
Zn	0.42	0.00	0.13	0.19± 0.24

n= 3 for each sample date
s. d= standard deviation

Table 4.30: Mean Concentrations of Absorbed 3 Fraction in Lake Nacogdoches Soil (mg metal/kg soil) at West Dock (Site 2)

Date	6/11/2019	3/8/19	2/1/19	mean ± s. d
Ba	0.21	0.11	0.15	0.16± 0.09
Cd	0.00	0.00	0.00	0.01± 0.01
Co	0.07	0.00	0.02	0.04± 0.04
Cr	0.33	0.01	0.13	0.17± 0.17
Cu	0.04	0.04	0.06	0.06± 0.05
Mn	0.39	0.05	0.40	0.29± 0.27
Ni	0.27	0.01	0.08	0.13± 0.13
Pb	0.08	0.00	0.01	0.04± 0.05
Sr	0.04	0.05	0.04	0.05± 0.02
V	0.52	0.06	0.42	0.34± 0.33
Zn	0.42	0.00	0.17	0.2± 0.23

n= 3 for each sample date
s. d= standard deviation

Table 4.31: Mean Concentrations of Organic Bonded Fraction in Lake Nacogdoches Soil (mg metal/kg soil) at West Dock (Site 2)

Date	6/11/2019	3/8/19	2/1/19	mean ± s. d
Ba	0.00	0.00	0.00	0.01±0.01
Cd	0.00	0.00	0.00	0.01±0.01
Co	0.07	0.01	0.03	0.04±0.03
Cr	0.12	0.02	0.07	0.08±0.05
Cu	1.81	0.25	1.17	1.08±1
Mn	0.03	0.00	0.01	0.02±0.02
Ni	0.09	0.03	0.07	0.07±0.04
Pb	0.00	0.00	0.00	0±0
Sr	0.00	0.01	0.00	0.01±0.01
V	14.02	2.38	17.51	11.31±7.37
Zn	0.00	0.00	0.00	0±0

n= 3 for each sample date
s. d= standard deviation

**Table 4.32: Mean Concentrations of Carbonate Fraction in
Lake Nacogdoches Soil (mg metal/kg soil) at West Dock**

Date	6/11/2019	3/8/19	2/1/19	mean ± s. d
Ba	0.38	0.82	3.72	1.65± 1.68
Cd	0.00	0.00	0.02	0.01± 0.01
Co	0.93	0.42	1.15	0.84± 0.44
Cr	0.67	0.10	0.35	0.38± 0.35
Cu	0.71	0.56	1.56	0.95± 0.49
Mn	35.75	8.20	56.21	33.39± 24.35
Ni	3.56	2.78	1.41	2.59± 2.03
Pb	2.95	1.05	4.64	2.88± 1.74
Sr	0.84	0.34	1.23	0.81± 0.51
V	2.33	0.60	2.41	1.78± 1.22
Zn	0.00	0.00	8.74	2.92± 4.41

n= 3 for each sample date
s. d= standard deviation

Table 4.33: Mean Concentrations of Sulfide/Residual Fraction
in Lake Nacogdoches Soil (mg metal/kg soil) at West Dock

Date	6/11/2019	3/8/19	2/1/19	mean ± s. d
Ba	9.11	21.63	36.58	22.44± 13.32
Cd	0.01	0.00	0.01	0.01± 0.02
Co	4.00	2.30	3.35	3.22± 1.54
Cr	6.43	2.44	5.23	4.71± 2.33
Cu	0.71	0.00	1.13	0.62± 0.59
Mn	70.42	34.10	58.33	54.29± 24.34
Ni	7.71	3.23	4.90	5.28± 3.33
Pb	4.09	3.71	4.56	4.12± 1.32
Sr	0.64	0.00	2.01	0.89± 0.97
V	10.28	7.40	10.38	9.36± 2.31
Zn	8.81	0.00	7.68	5.5± 4.95

n= 3 for each sample date
s. d= standard deviation

Table 4.34: Mean Concentrations of Exchangeable Fraction
in Lake Nacogdoches Soil (mg metal/kg soil) at Swim Area

Date	6/11/2019	3/8/19	2/1/19	mean ± s. d
Ba	12.50	1.77	4.35	6.22±6.05
Cd	0.01	0.01	0.04	0.02±0.02
Co	0.04	0.09	0.05	0.06±0.04
Cr	0.	0.	0.	0±0
Cu	0.12	0.08	0.00	0.07±0.07
Mn	6.55	1.21	12.01	6.6±4.94
Ni	0.12	0.12	0.69	0.31±0.55
Pb	0.00	0.00	0.00	0.01±0.01
Sr	7.85	34.81	5.62	16.1±29.73
V	0.00	0.00	0.00	0.01±0.01
Zn	0.12	0.21	0.19	0.18±0.11

n= 3 for each sample date
s. d= standard deviation

Table 4.35: Mean Concentrations of Absorbed 1 Fraction in Lake Nacogdoches Soil (mg metal/kg soil) at Swim Area

Date	6/11/19	3/8/19	2/1/19	mean ± s. d
Ba	0.70	0.98	0.08	0.59±0.43
Cd	0.00	0.00	0.00	0.01±0.01
Co	0.00	0.01	0.00	0.01±0.01
Cr	00	0.	0.	0±0
Cu	0.00	0.05	0.00	0.02±0.04
Mn	0.11	0.64	0.01	0.26±0.32
Ni	0.00	0.03	0.66	0.24±0.66
Pb	0.00	0.00	0.00	0.01±0.01
Sr	0.12	0.47	0.03	0.21±0.29
V	0.00	0.00	0.02	0.01±0.02
Zn	0.00	0.11	0.00	0.04±0.08

n= 3 for each sample date
s. d= standard deviation

Table 4.36: Mean Concentrations of Absorbed 2 Fraction in
Lake Nacogdoches Soil (mg metal/kg soil) at Swim Area

Date	6/11/19	3/8/19	2/1/19	mean ± s. d
Ba	0.11	0.24	0.06	0.14±0.11
Cd	0.00	0.00	0.00	0.01±0.01
Co	0.01	0.00	0.00	0.01±0.01
Cr	0.11	0.00	0.00	0.04±0.06
Cu	0.00	0.17	0.00	0.06±0.14
Mn	0.10	0.08	0.12	0.1±0.1
Ni	0.03	0.00	0.67	0.24±0.66
Pb	0.02	0.00	0.00	0.01±0.01
Sr	0.04	0.13	0.04	0.07±0.06
V	0.35	0.00	0.06	0.14±0.17
Zn	0.08	0.07	0.00	0.06±0.07

n= 3 for each sample date
s. d= standard deviation

Table 4.37: Mean Concentrations of Absorbed 3 Fraction in Lake Nacogdoches Soil (mg metal/kg soil) at Swim Area

Date	6/11/19	3/8/19	2/1/19	mean ± s. d
Ba	0.11	0.24	0.06	0.14± 0.11
Cd	0.00	0.00	0.00	0.01± 0.01
Co	0.01	0.00	0.00	0.01± 0.01
Cr	0.11	0.00	0.00	0.04± 0.06
Cu	0.00	0.17	0.00	0.06± 0.14
Mn	0.10	0.08	0.12	0.11± 0.1
Ni	0.03	0.00	0.67	0.24± 0 .65
Pb	0.02	0.00	0.00	0.01± 0 .01
Sr	0.04	0.13	0.03	0.07± 0 .06
V	0.35	0.00	0.07	0.15± 0 .17
Zn	0.08	0.07	0.00	0.06± 0 .07

n= 3 for each sample date
s. d= standard deviation

Table 4.38: Mean Concentrations of Organic Bonded Fraction in Lake Nacogdoches Soil (mg metal/kg soil) at

Date	6/11/2019	3/8/19	2/1/19	mean ± s. d
Ba	0.01	0.00	0.01	0.01±0.02
Cd	0.00	0.00	0.00	0.01±0.01
Co	0.02	0.03	0.01	0.03±0.02
Cr	0.22	0.29	0.13	0.22±0.09
Cu	1.11	5.17	1.48	2.59±2.51
Mn	0.04	0.00	0.00	0.02±0.03
Ni	0.07	0.18	0.69	0.32±0.59
Pb	0.00	0.00	0.00	0±0
Sr	0.02	0.01	0.03	0.02±0.02
V	9.75	10.47	8.77	9.67±4.84
Zn	0.00	0.00	0.00	0±0

n= 3 for each sample date
s. d= standard deviation

Table 4.39: Mean Concentrations of Carbonate Fraction in Lake Nacogdoches Soil (mg metal/kg soil) at Swim Area

Date	6/11/19	3/8/19	2/1/19	mean ± s. d
Ba	3.91	0.00	3.67	2.53±2.21
Cd	0.01	0.00	0.01	0.01±0.01
Co	0.22	0.08	0.11	0.14±0.1
Cr	1.77	0.65	0.97	1.13±0.73
Cu	0.70	24.91	1.58	9.07±24.64
Mn	1.76	0.15	0.92	0.95±0.83
Ni	8.88	2.45	1.27	4.2±7.17
Pb	7.47	0.28	2.12	3.3±6.13
Sr	10.70	0.79	1.93	4.48±8.53
V	24.40	1.75	2.88	9.68±19.62
Zn	0.00	0.00	7.00	2.34±4.26

n= 3 for each sample date
s. d= standard deviation

Table 4.40: Mean Concentrations of Sulfide/Residual Fraction in Lake Nacogdoches Soil (mg metal/kg soil) at Swim Area (Site 3)

Date	6/11/2019	3/8/2019	2/1/2019	mean ± s. d
Ba	16.44	91.48	50.72	52.88± 34.32
Cd	0.01	0.00	0.01	0.01± 0.01
Co	0.74	0.71	0.55	0.67± 0.36
Cr	4.01	2.99	3.44	3.48± 1.58
Cu	1.17	1.64	1.09	1.31± 0.37
Mn	5.87	5.44	3.33	4.89± 2.89
Ni	2.27	2.01	0.71	1.67± 1.01
Pb	2.33	5.37	2.29	3.34± 1.69
Sr	4.95	13.01	5.19	7.72± 5.06
V	9.36	8.57	6.40	8.12± 1.74
Zn	3.48	3.33	8.37	5.07± 3.57

n= 3 for each sample date
s. d= standard deviation

Figure

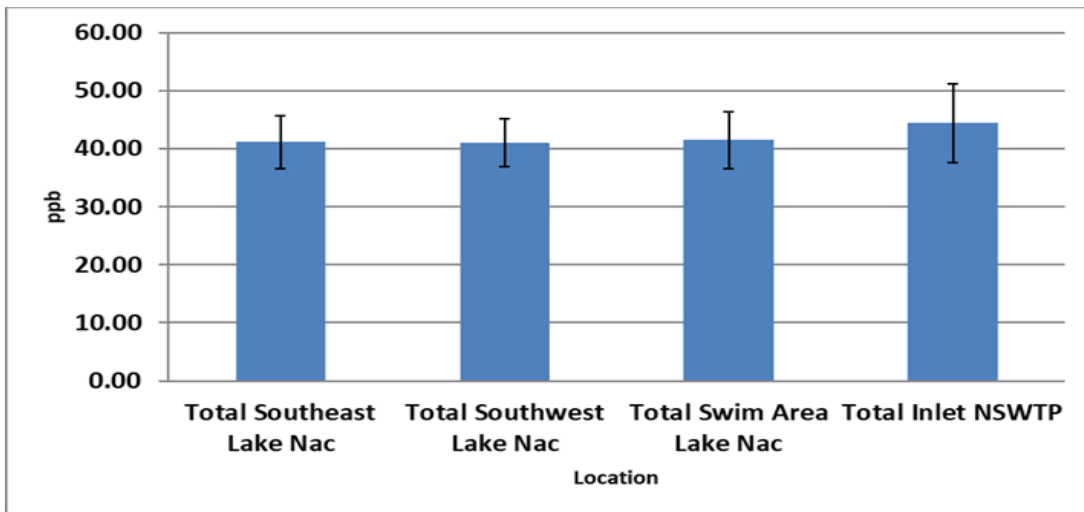


Figure 4.1: Mean Concentration of Total Ba for All Water Sites in South Lake Nacogdoches

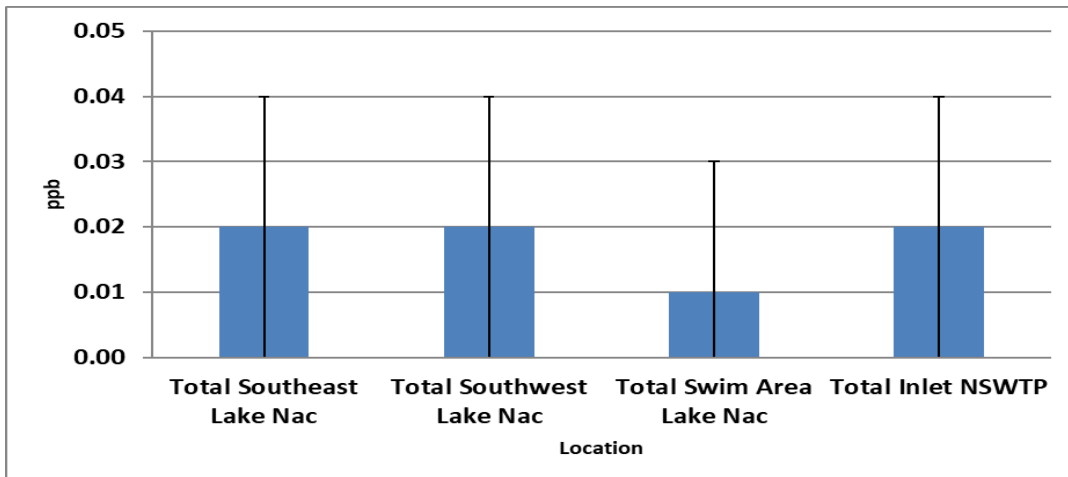


Figure 4.2: Mean Concentration of Total Cd for All Water Sites for South Lake Nacogdoches

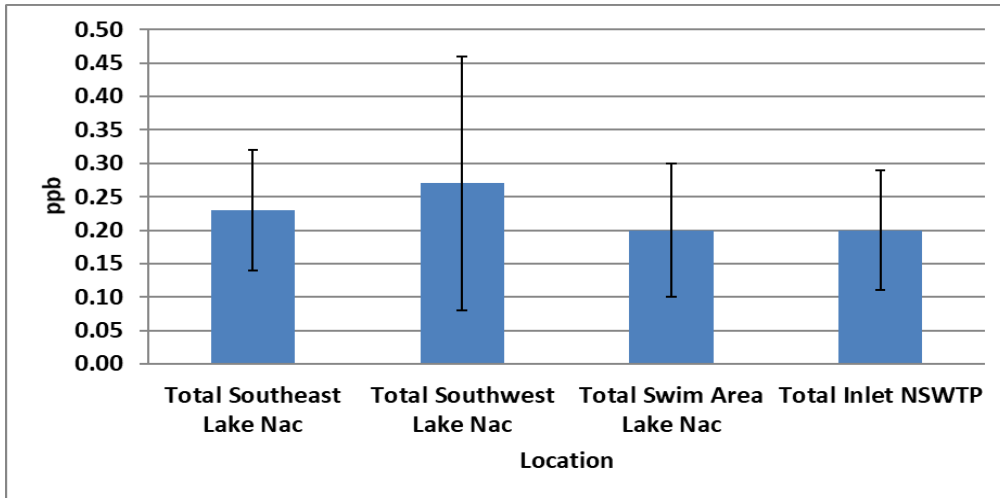


Figure 4.3: Mean Concentration of Total Co for All Water Sites for South Lake Nacogdoches

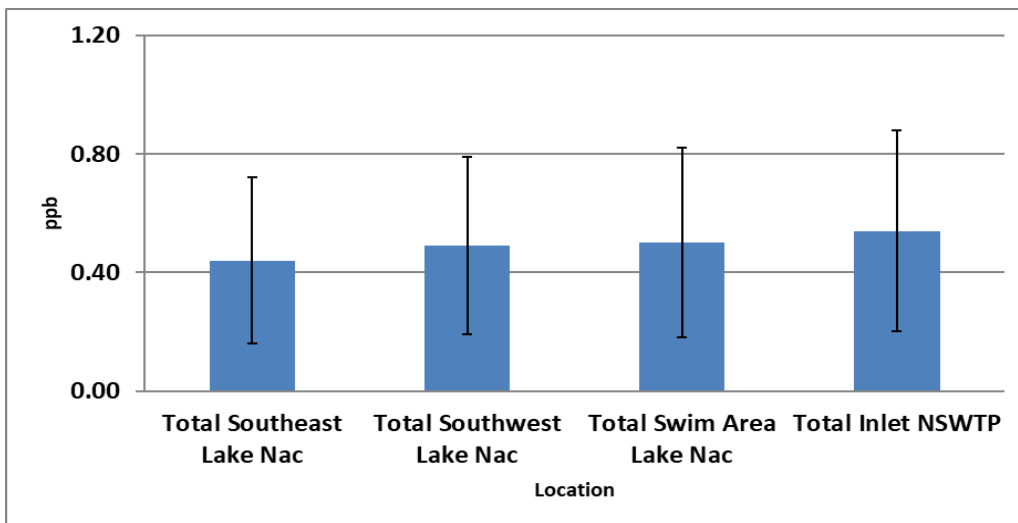


Figure 4.4: Mean Concentration of Total Cr for All Water Sites for South Lake Nacogdoches

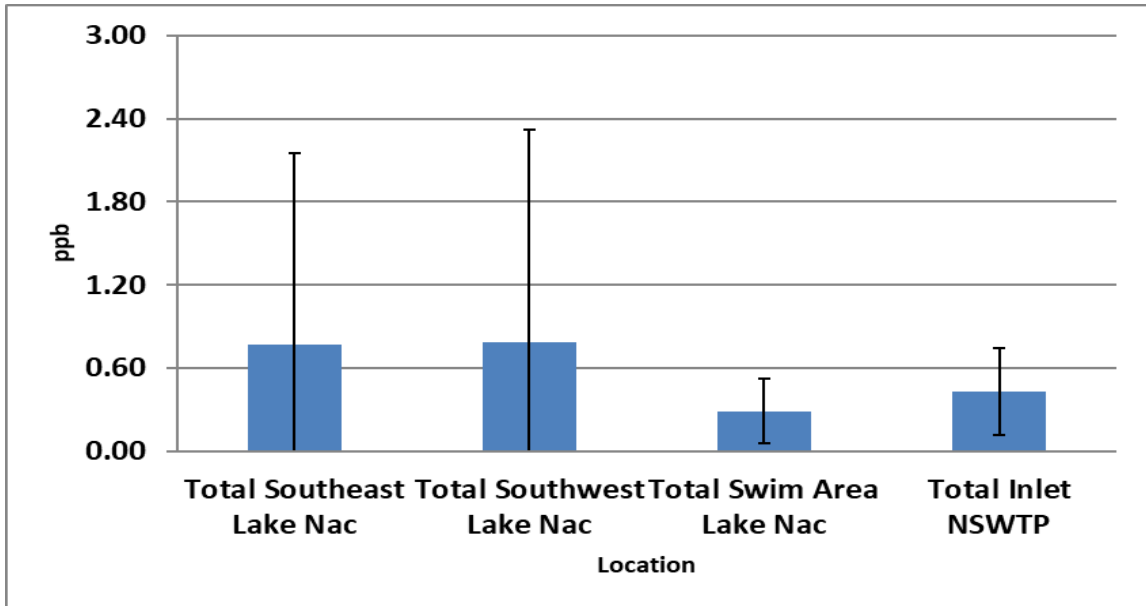


Figure 4.5: Mean Concentration of Total Cu for All Water Sites for South Lake Nacogdoches

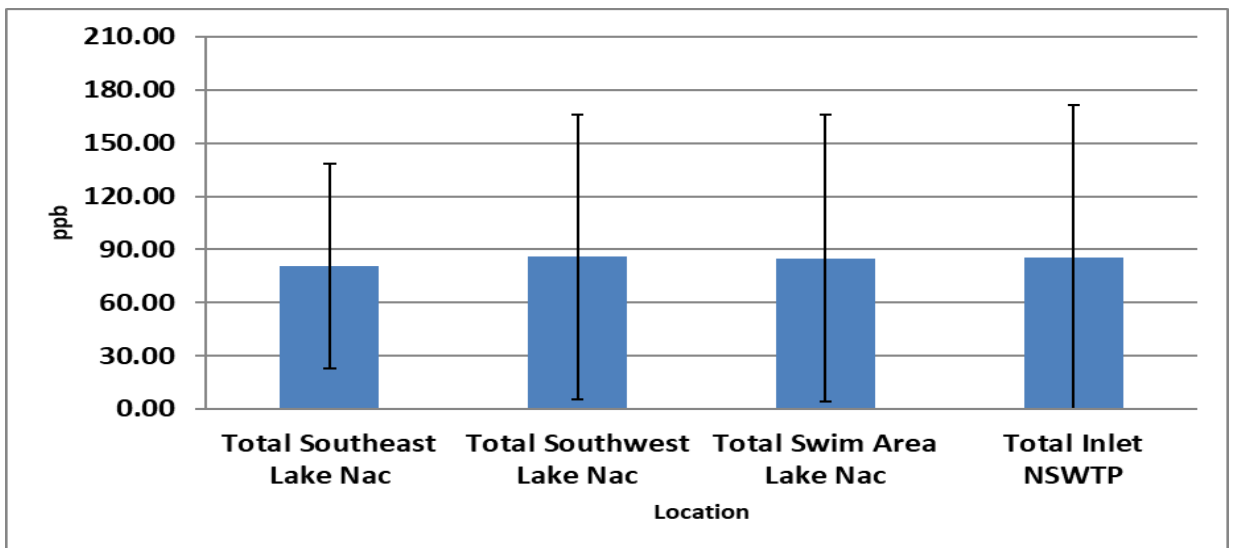


Figure 4.6: Mean Concentration of Total Mn for All Water Sites for South Lake Nacogdoches

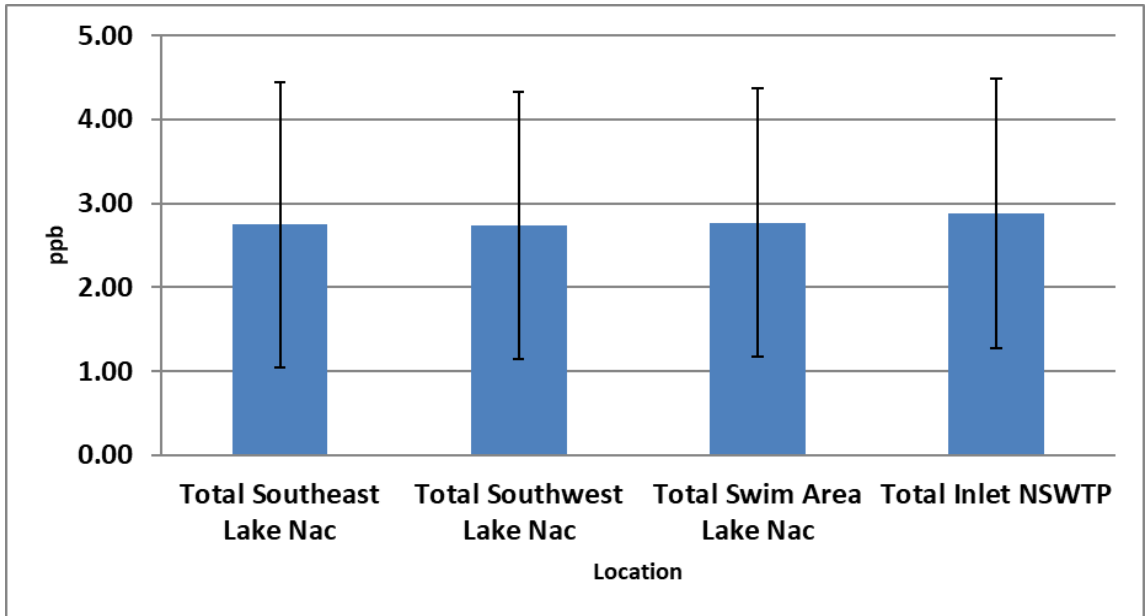


Figure 4.7: Mean Concentration of Total Ni for All Water Sites for South Lake Nacogdoches

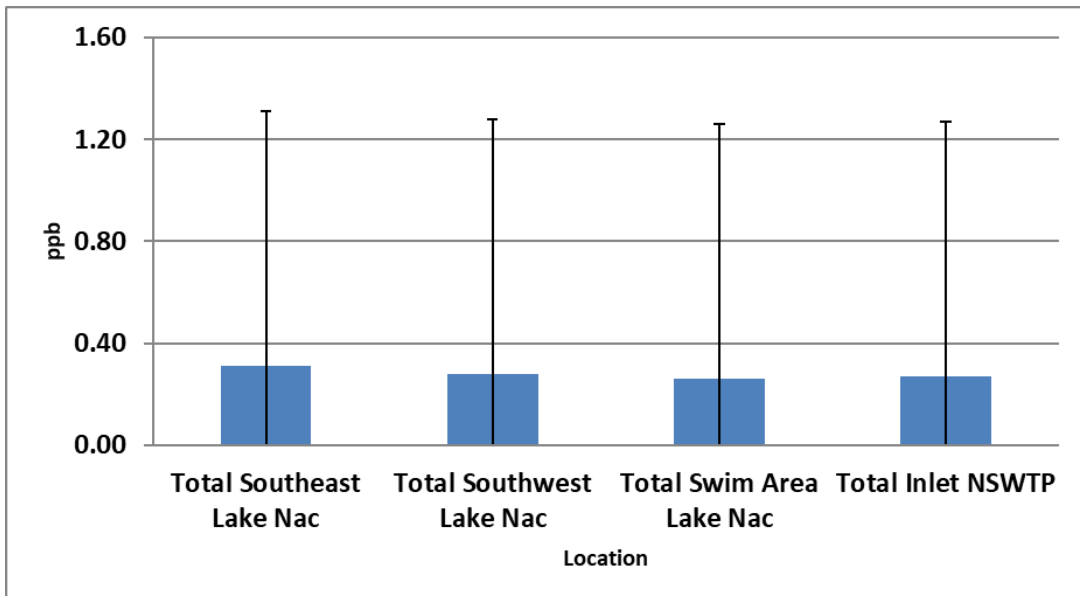


Figure 4.8: Mean Concentration of Total Pb for All Water Sites for South Lake Nacogdoches

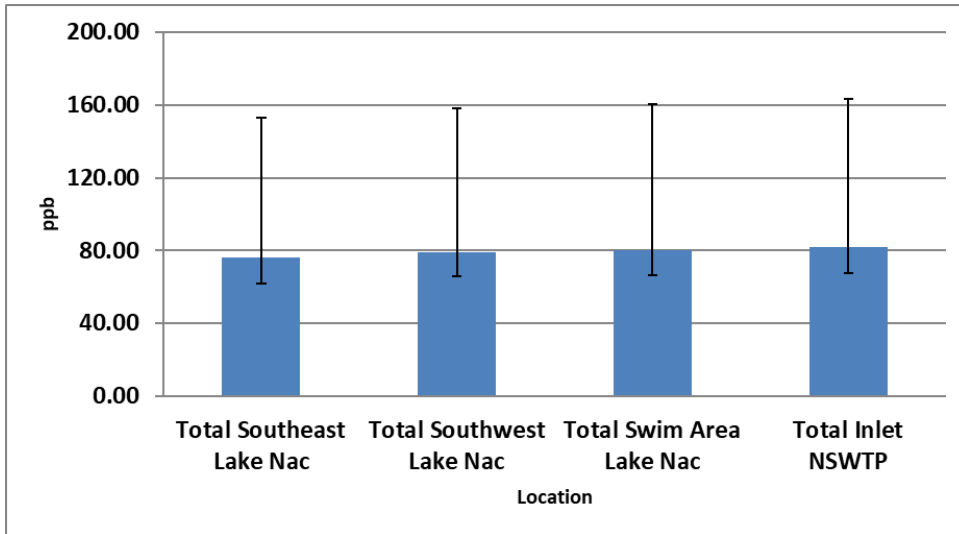


Figure 4.9: Mean Concentration of Total Sr for All Water Sites for South Lake Nacogdoches

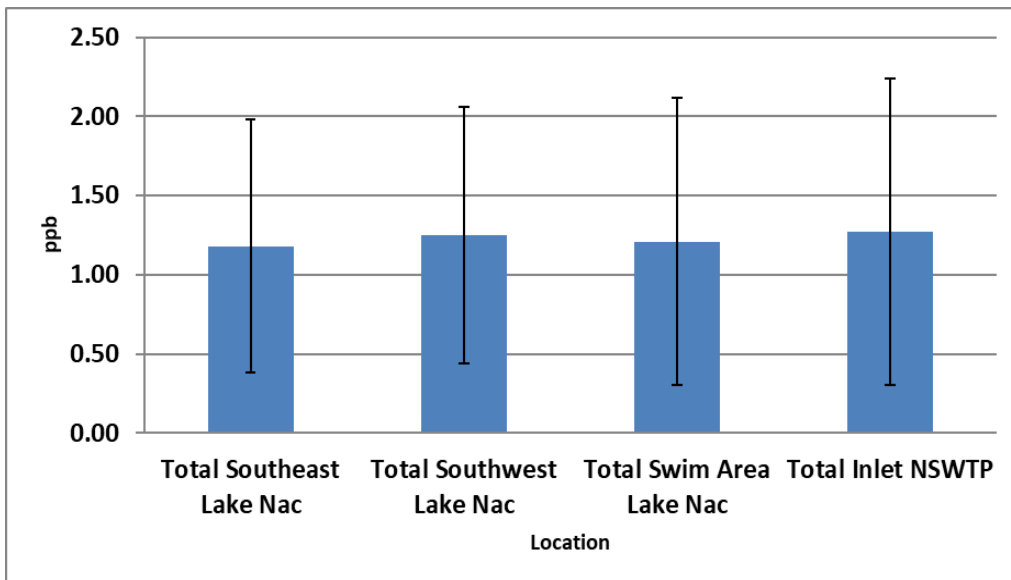


Figure 4.10: Mean Concentration of Total V for All Water Sites for South Lake Nacogdoches

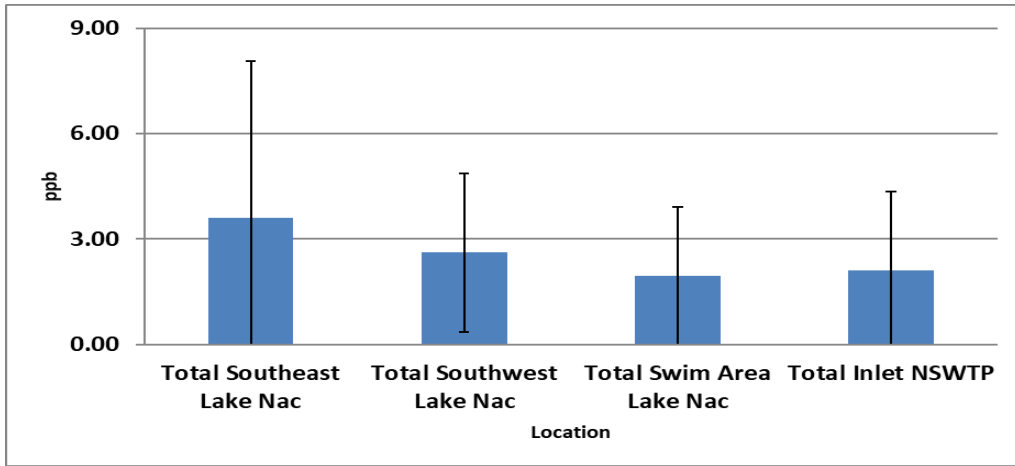


Figure 4.11: Mean Concentration of Total Zn for All Water Sites for South Lake Nacogdoches

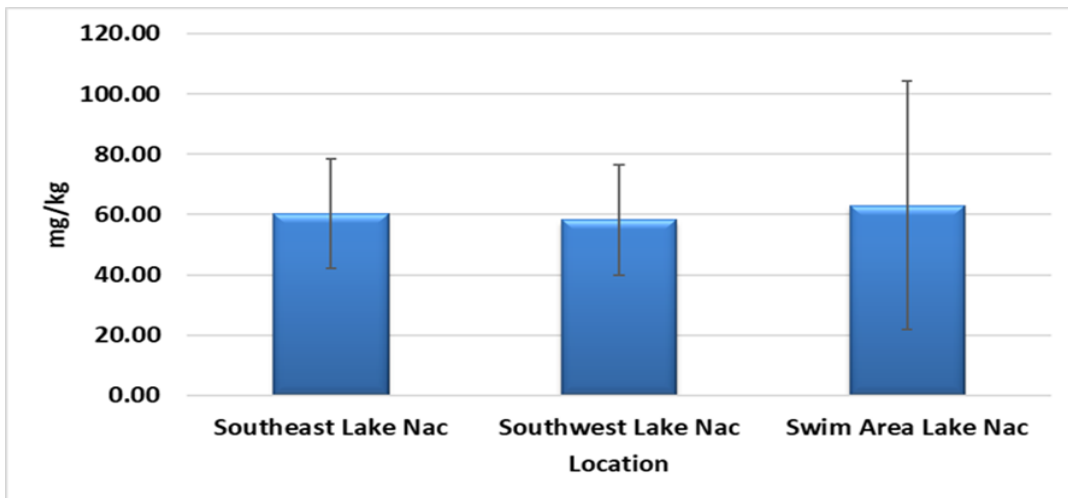


Figure 4.12: Mean concentration of Total Ba for All Soil Sites for South Lake Nacogdoches

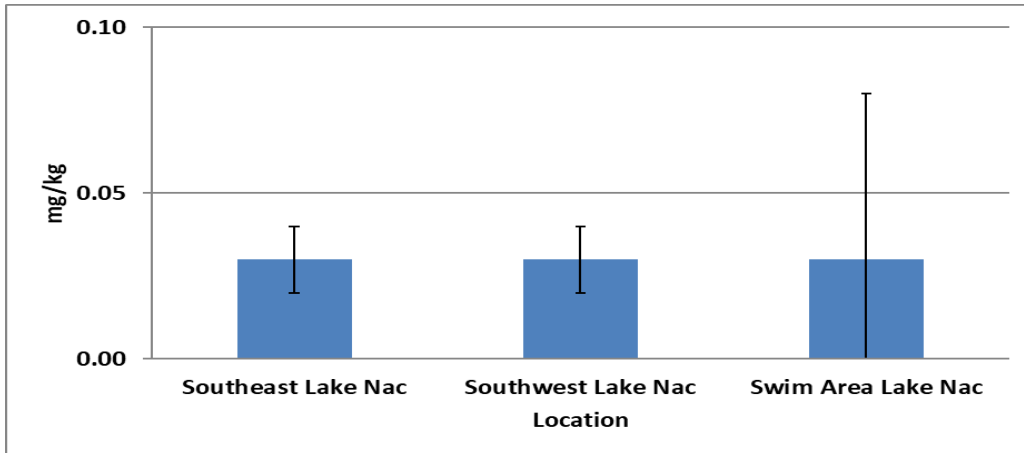


Figure 4.13: Mean Concentration of Total Cd for All Soil Sites for South Lake Nacogdoches

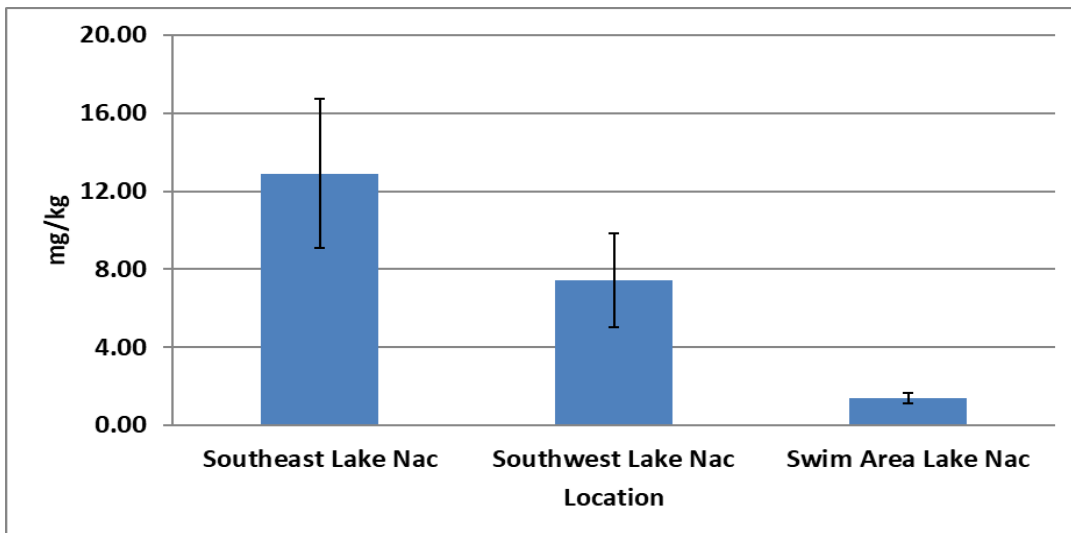


Figure 4.14: Mean Concentration of Total Co for All Soil Sites for South Lake Nacogdoches

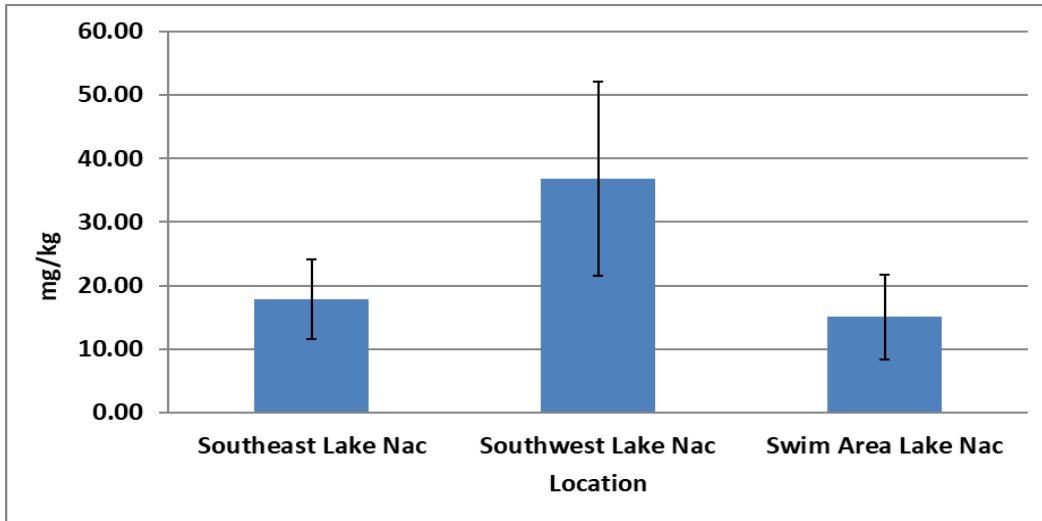


Figure 4.15: Mean Concentration of Total Cr for All Soil Sites for South Lake Nacogdoches

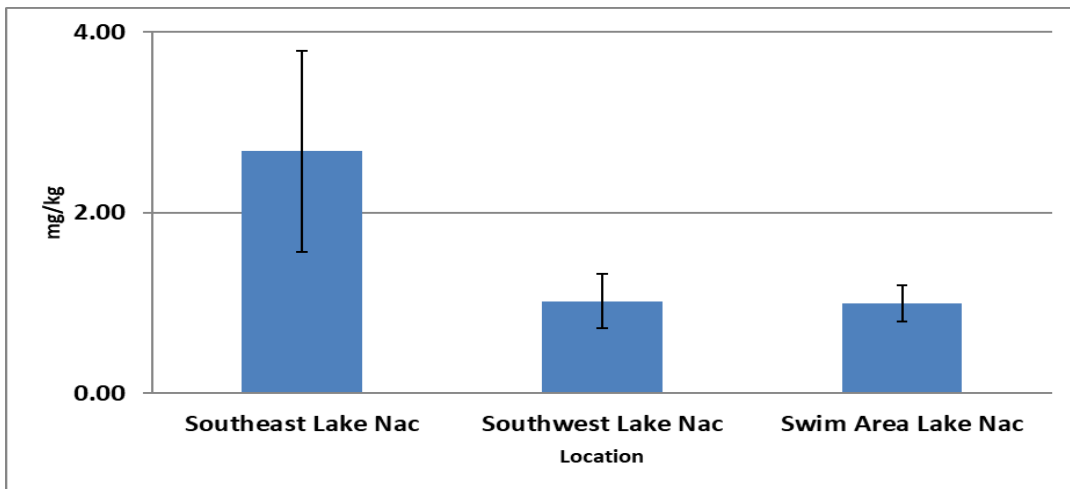


Figure 4.16: Mean Concentration of Total Cu for All Soil Sites for South Lake Nacogdoches

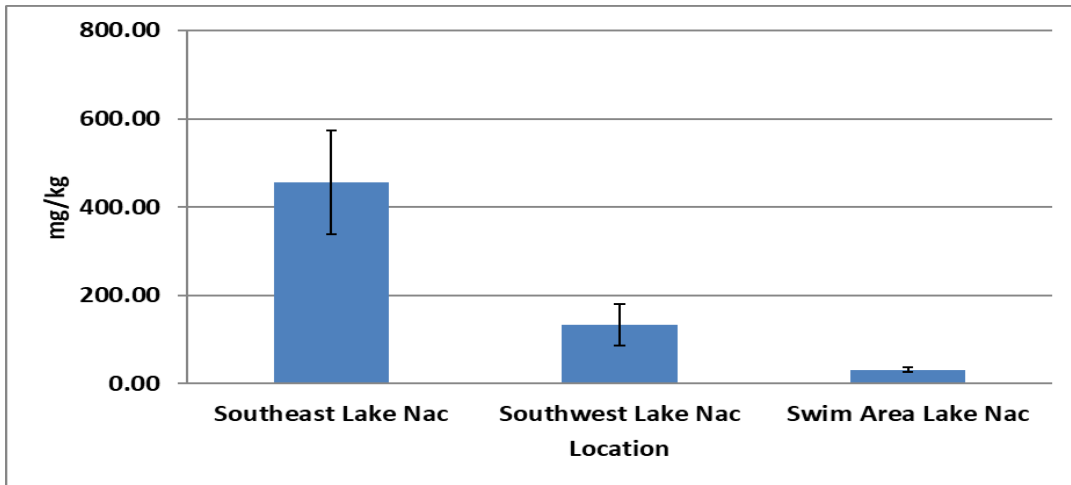


Figure 4.17: Mean Concentration of Total Mn for All Soil Sites for South Lake Nacogdoches

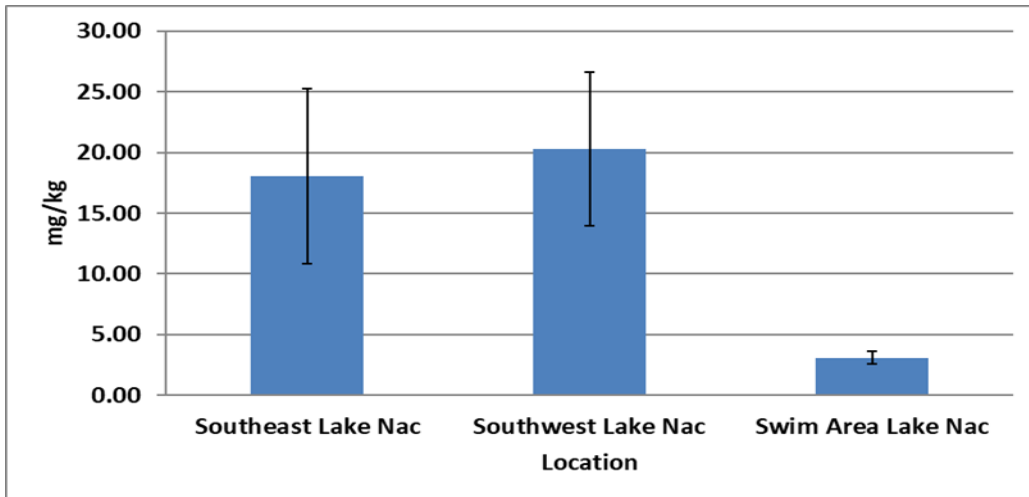


Figure 4.18: Mean Concentration of Total Ni for All Soil Sites for South Lake Nacogdoches

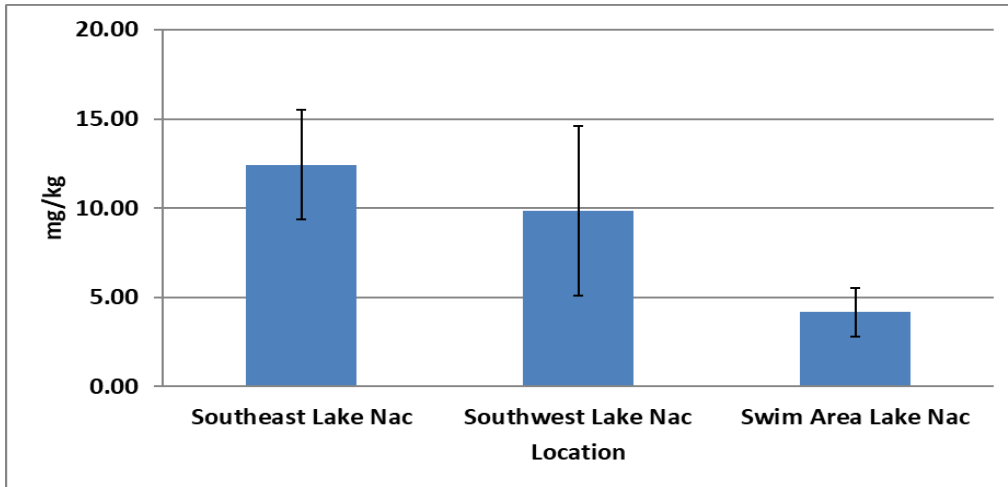


Figure 4.19: Mean Concentration of Total Pb for All Soil Sites for South Lake Nacogdoches

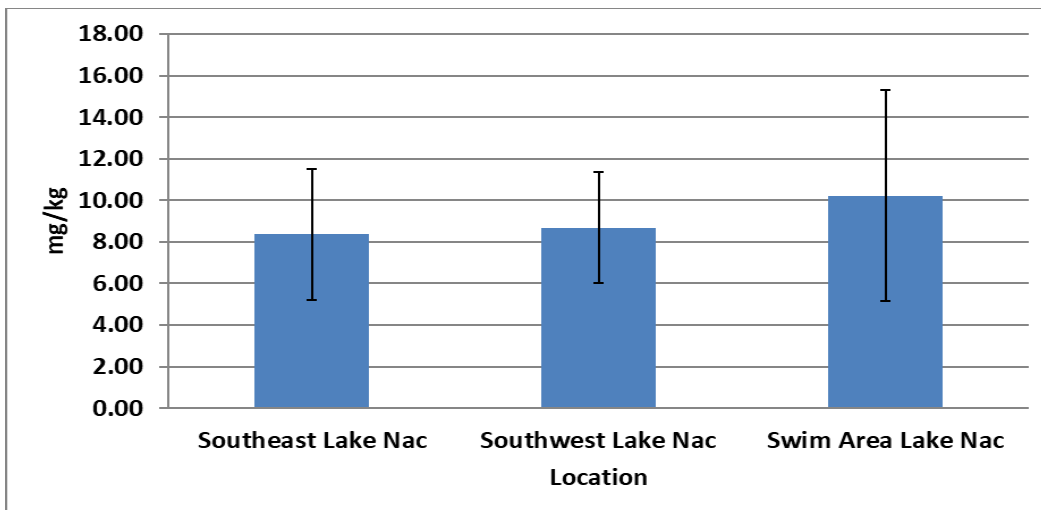


Figure 4.20: Mean Concentration of Total Sr for All Soil Sites for South Lake Nacogdoches

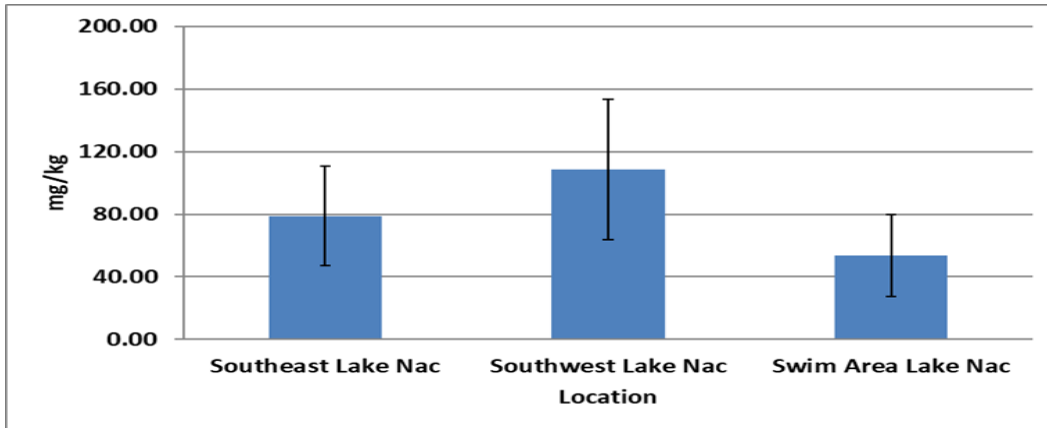


Figure 4.21: Mean Concentration of Total V for All Soil Sites for South Lake Nacogdoches

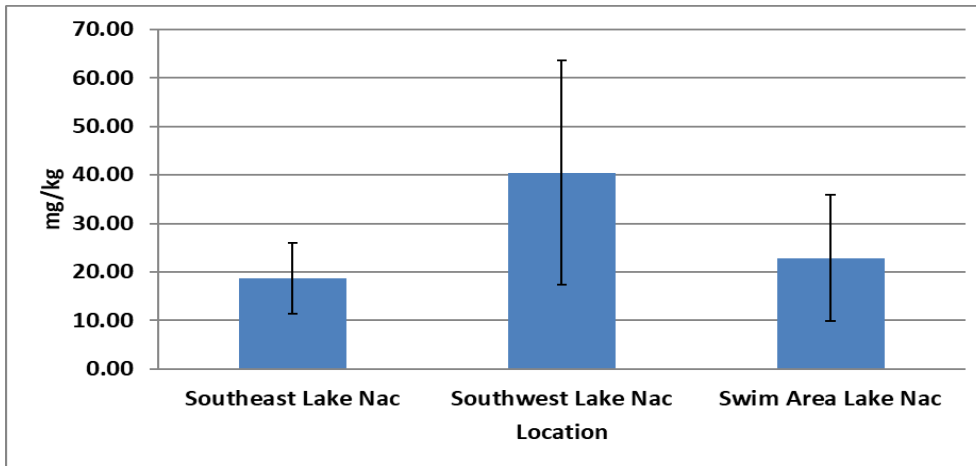


Figure 4.22: Mean Concentration of Total Zn for All Soil Sites for South Lake Nacogdoches

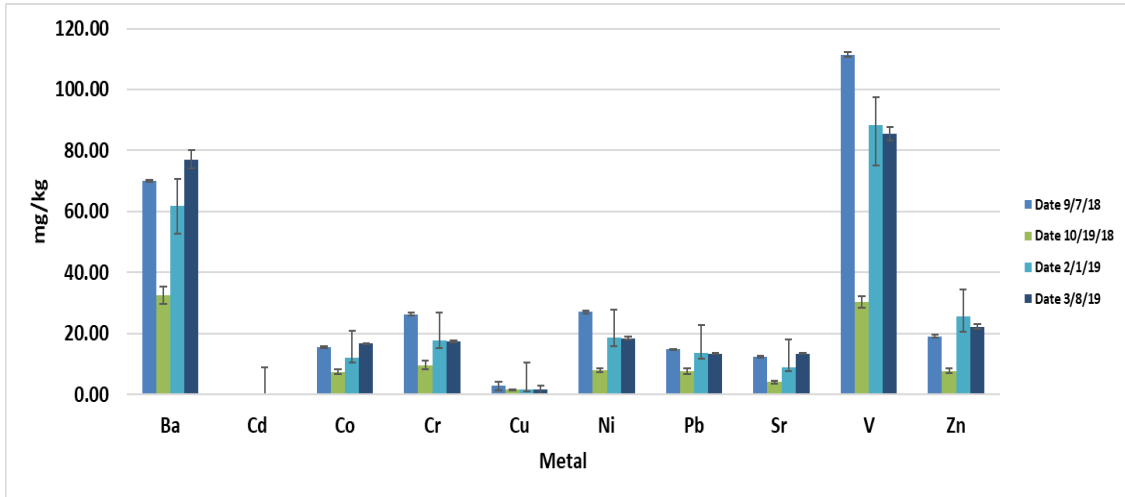


Figure 4.23: Mean Concentration of Mn (mg metal /kg soil) for East Dock (Site 1) in Lake Nacogdoches over Sampling Time

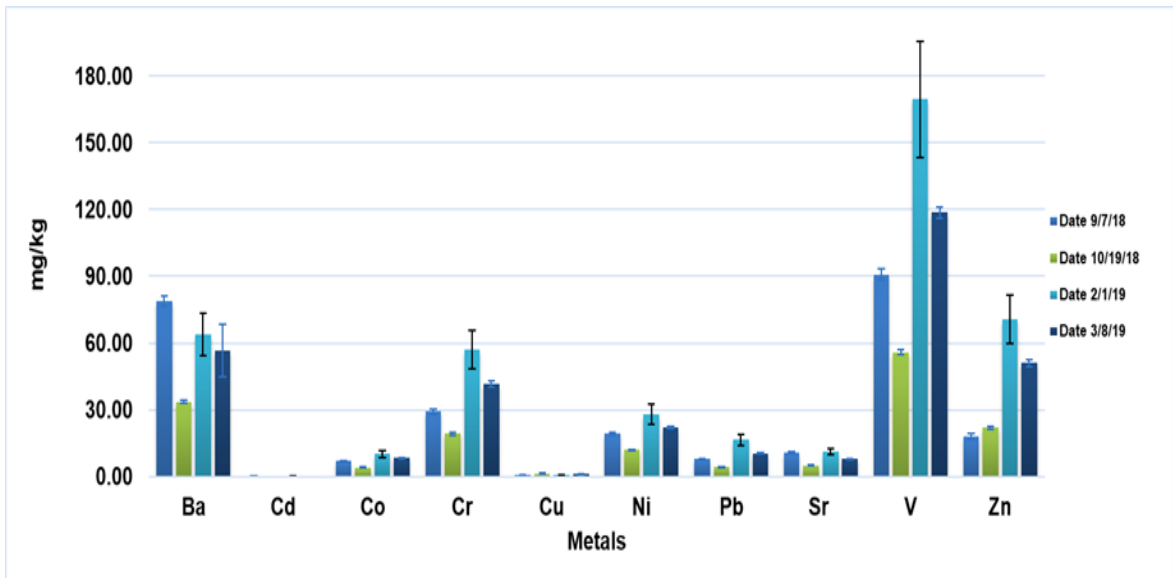


Figure 4.24: Mean Concentration of Mn (mg metal /kg soil) for South west (Site 2) in Lake Nacogdoches over Sampling Time

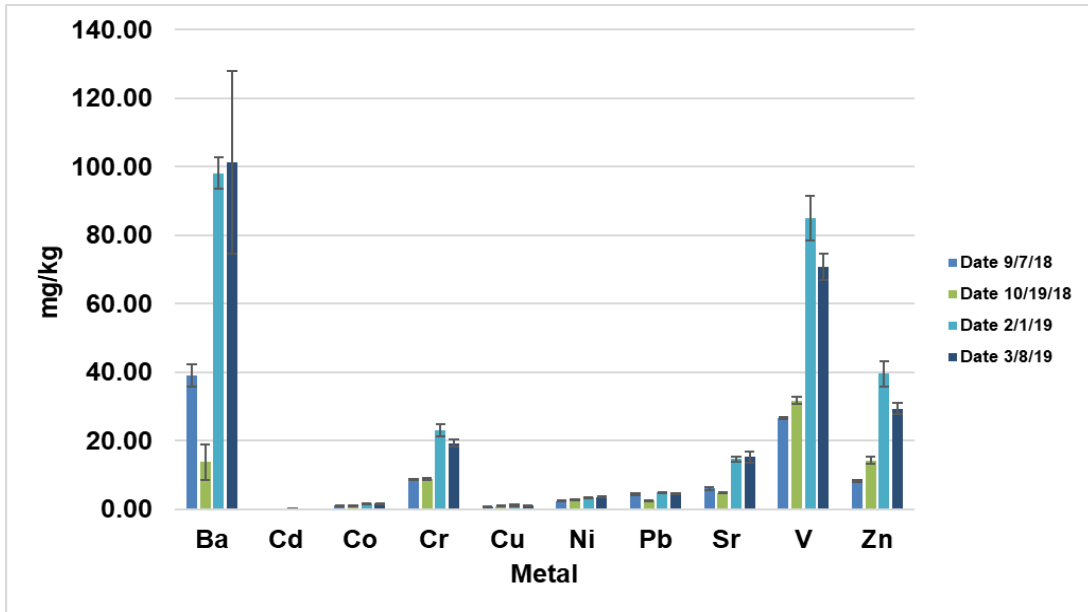


Figure 4.25: Mean Concentration of Mn (mg metal /kg soil) for Swim area (Site 3) Lake Nacogdoches over Sampling Time

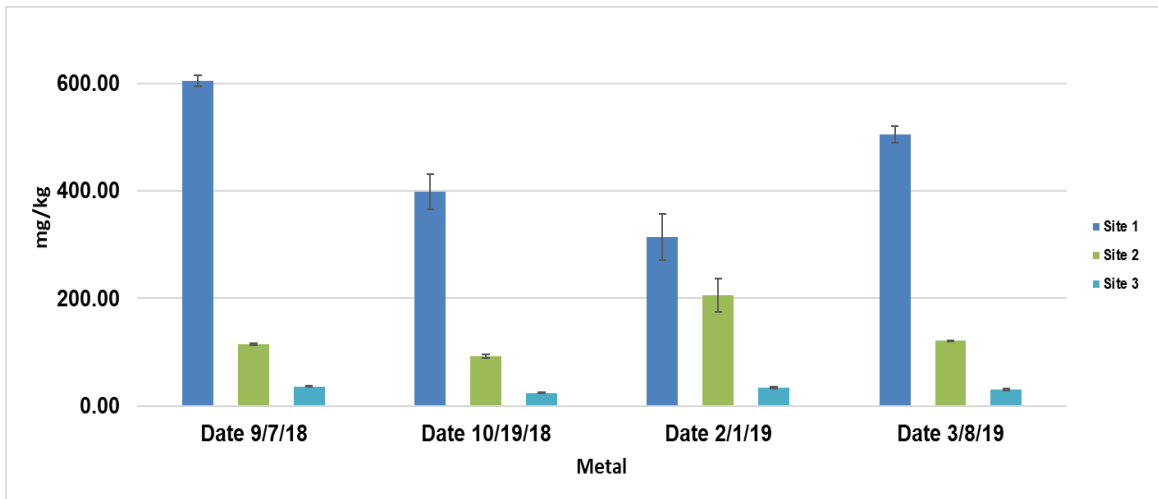


Figure 4.26: Mean Concentration of Total Mn for All Soil Sites for South Lake Nacogdoches over Sampling Times

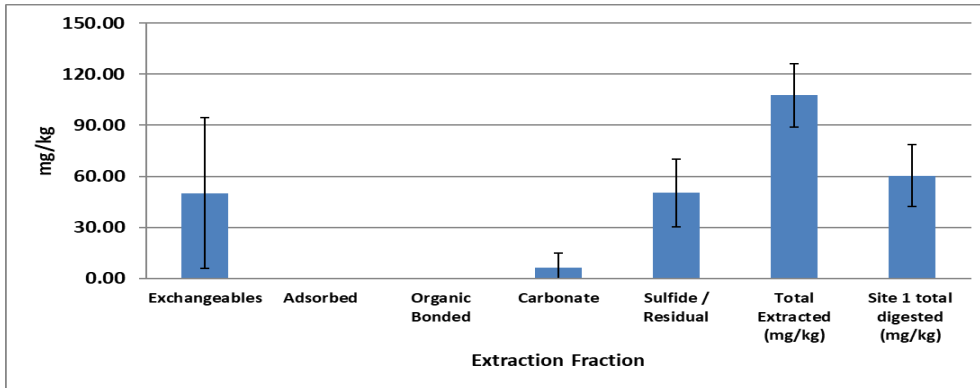


Figure 4.27: Mean Concentration of Extraction Fractions of Ba (mg metal /kg soil) for East Dock (Site 1) in Lake Nacogdoches

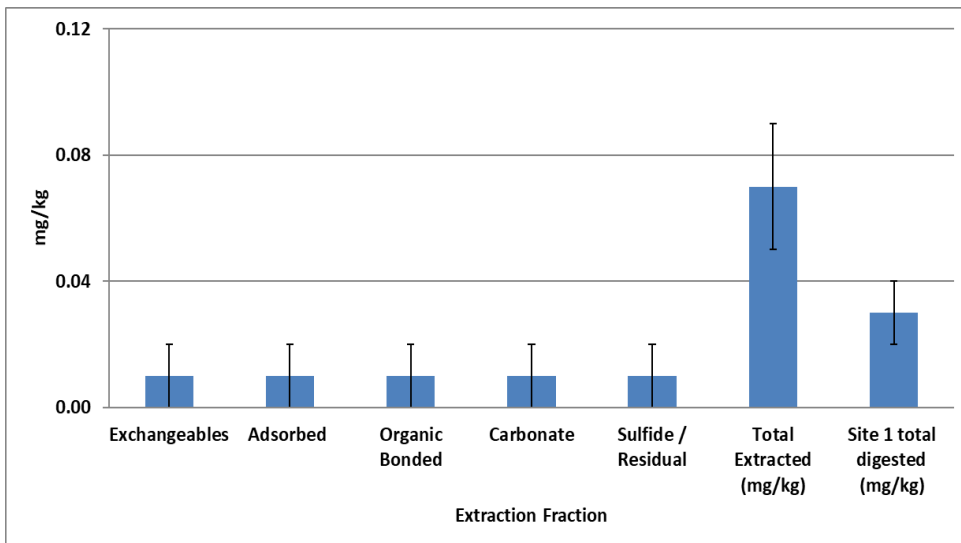


Figure 4.28: Mean Concentration of Extraction Fractions of Cd (mg metal /kg soil) for East Dock (Site 1) in Lake Nacogdoches

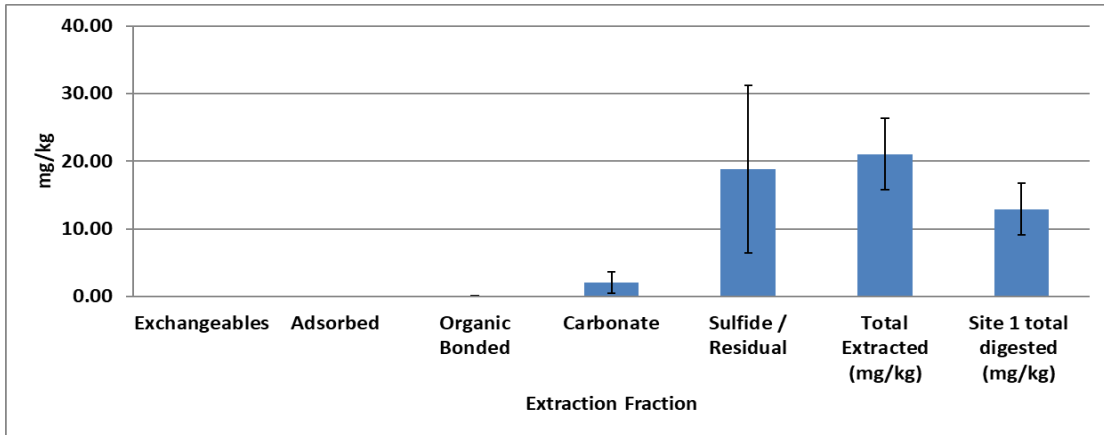


Figure 4.29: Mean Concentration of Extraction Fractions of Co (mg metal /kg soil) for East Dock (Site 1) in Lake Nacogdoches

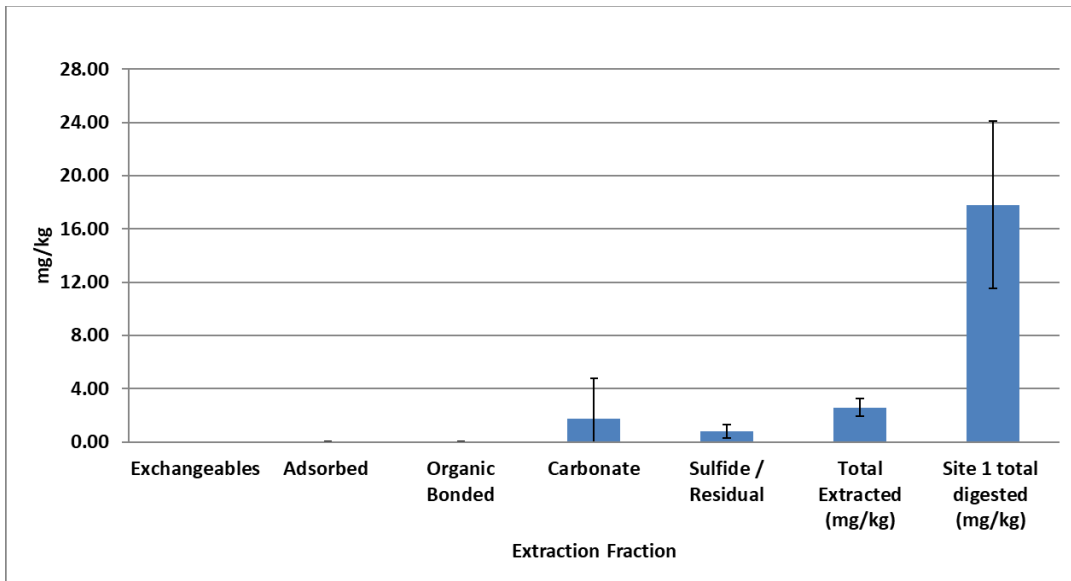


Figure 4.30: Mean Concentration of Extraction Fractions of Cr (mg metal /kg soil) for East Dock (Site 1) in Lake Nacogdoches

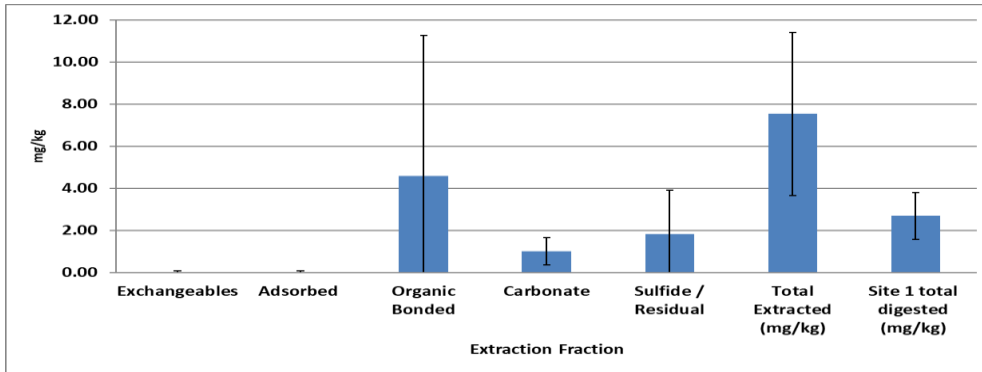


Figure 4.31: Mean Concentration of Extraction Fractions of Cu (mg metal /kg soil) for East Dock (Site 1) in Lake Nacogdoches

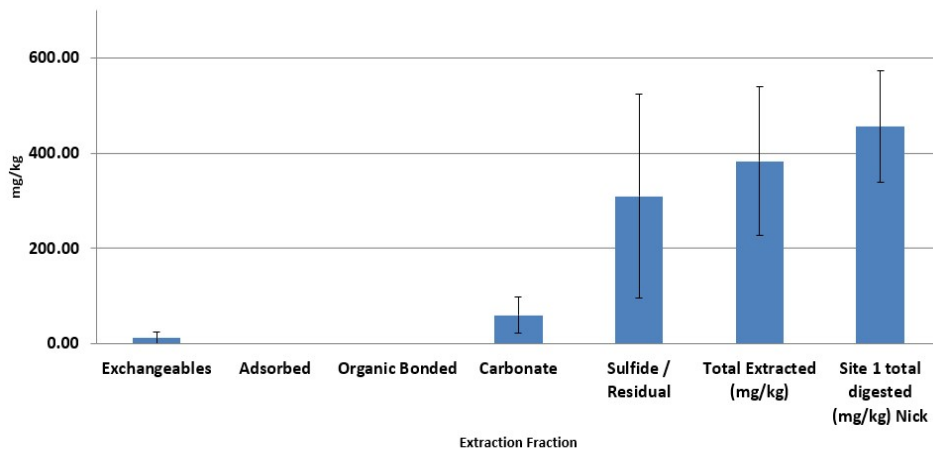


Figure 4.32: Mean Concentration of Extraction Fractions of Mn (mg metal /kg soil) for East Dock (Site 1) in Lake Nacogdoches

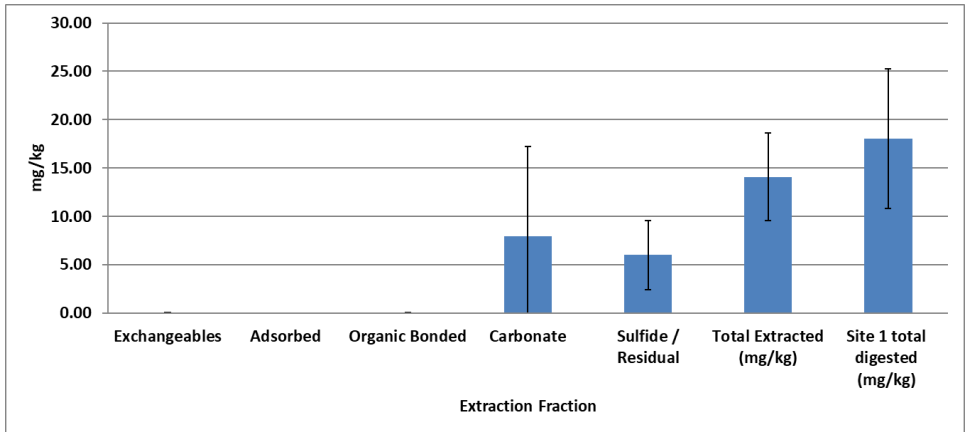


Figure 4.33: Mean Concentration of Extraction Fractions of Ni (mg metal /kg soil) for East Dock (Site 1) in Lake Nacogdoches

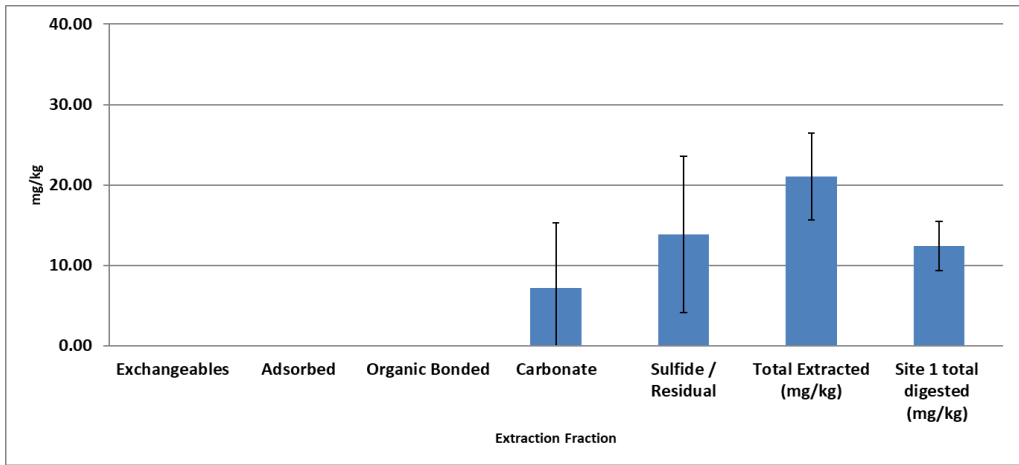


Figure 4.34: Mean Concentration of Extraction Fractions of Pb (mg metal /kg soil) for East Dock (Site 1) in Lake Nacogdoches

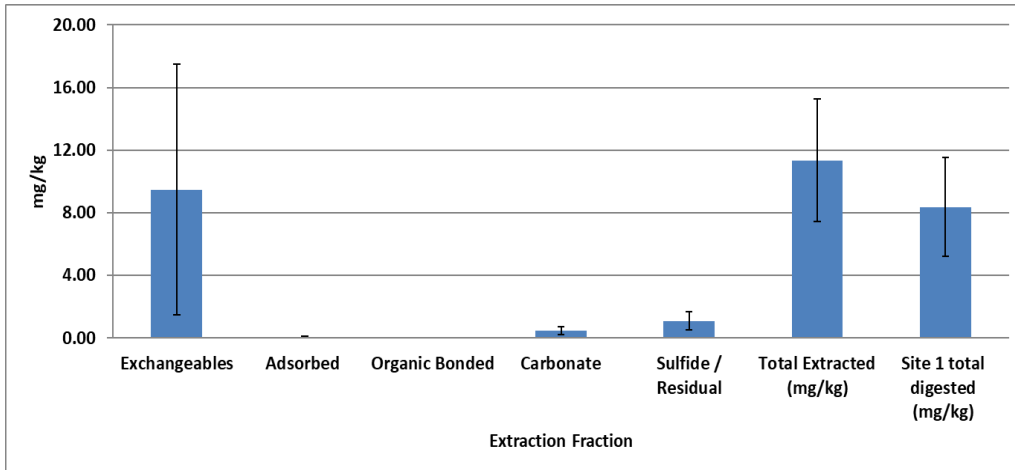


Figure 4.35: Mean Concentration of Extraction Fractions of Sr (mg metal /kg soil) for East Dock (Site 1) in Lake Nacogdoches

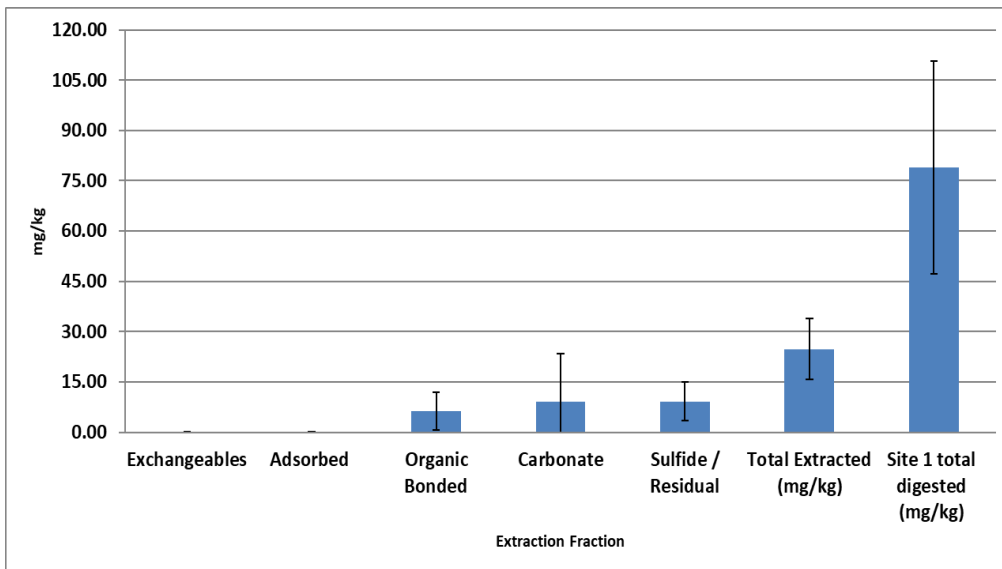


Figure 4.36: Mean Concentration of Extraction Fractions of V (mg metal /kg soil) for East Dock (Site 1) in Lake Nacogdoches

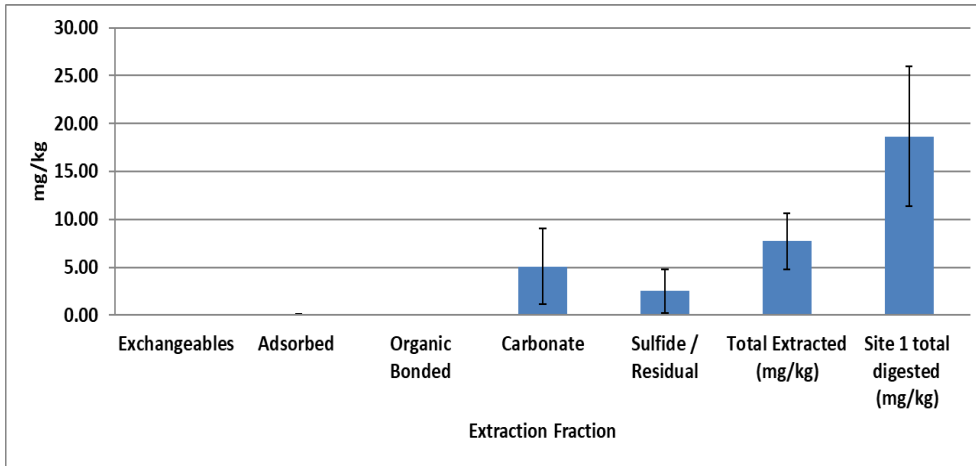


Figure 4.37: Mean Concentration of Extraction Fractions of Zn (mg metal /kg soil) for East Dock (Site 1) in Lake Nacogdoches

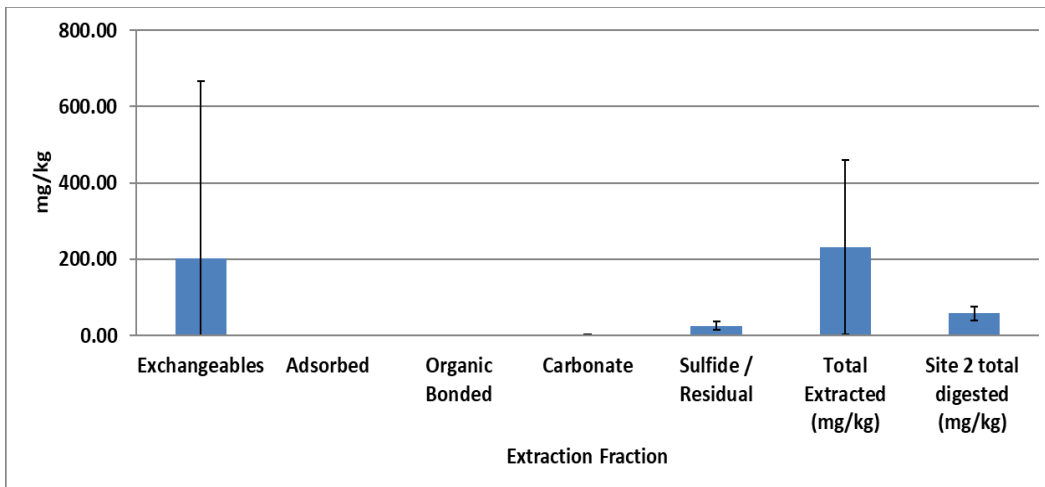


Figure 4.38: Mean Concentration of Extraction Fractions of Ba (mg metal /kg soil) for West Dock (Site 2) in Lake Nacogdoches

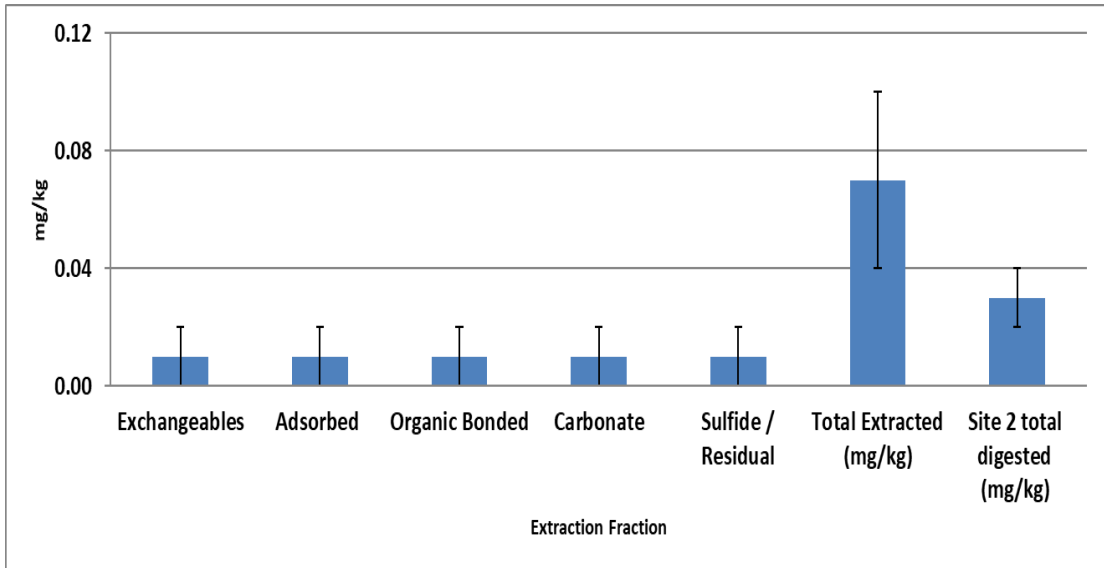


Figure 4.39: Mean Concentration of Extraction Fractions of Cd (mg metal /kg soil) for West Dock (Site 2) in Lake Nacogdoches

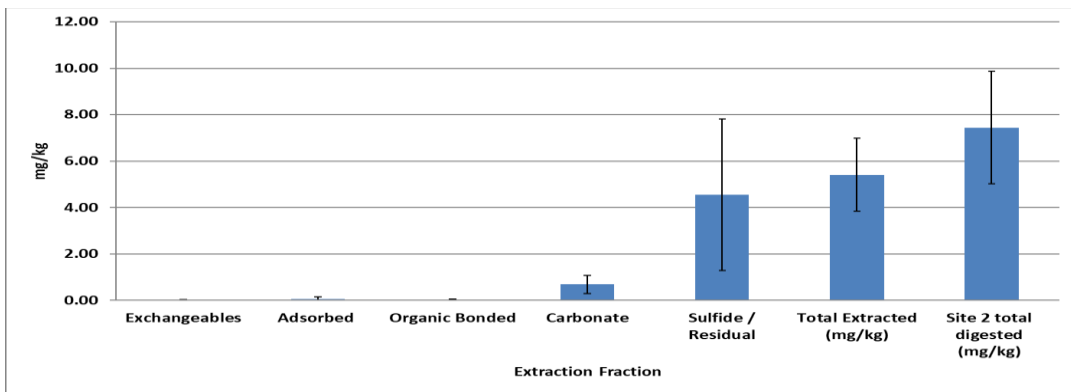


Figure 4.40: Mean Concentration of Extraction Fractions of Co (mg metal /kg soil) for West Dock (Site 2) in Lake Nacogdoches

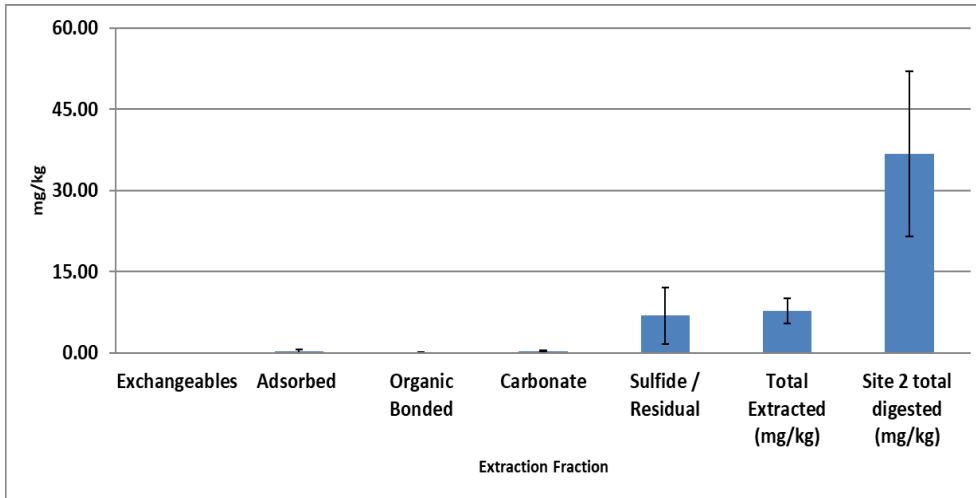


Figure 4.41: Mean Concentration of Extraction Fractions of Cr (mg metal /kg soil) for West Dock (Site 2) in Lake Nacogdoches

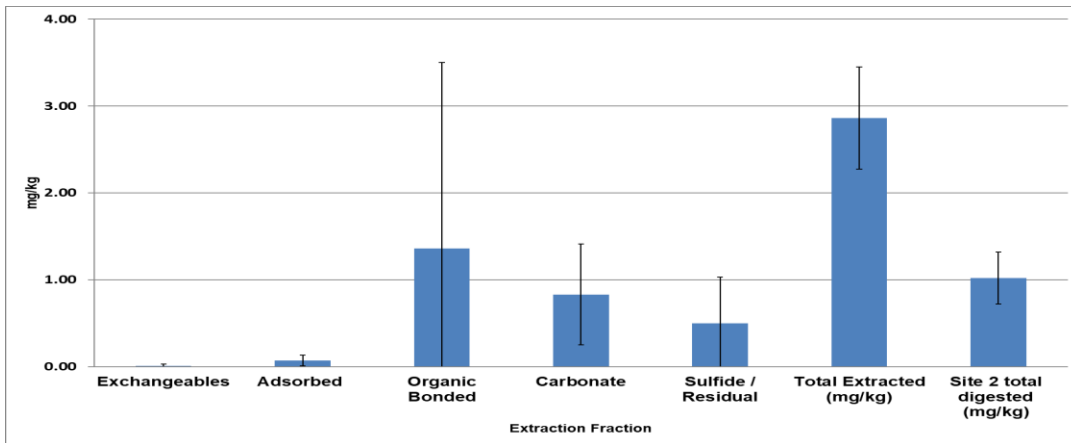


Figure 4.42: Mean Concentration of Extraction Fractions of Cu (mg metal /kg soil) for West Dock (Site 2) in Lake Nacogdoches

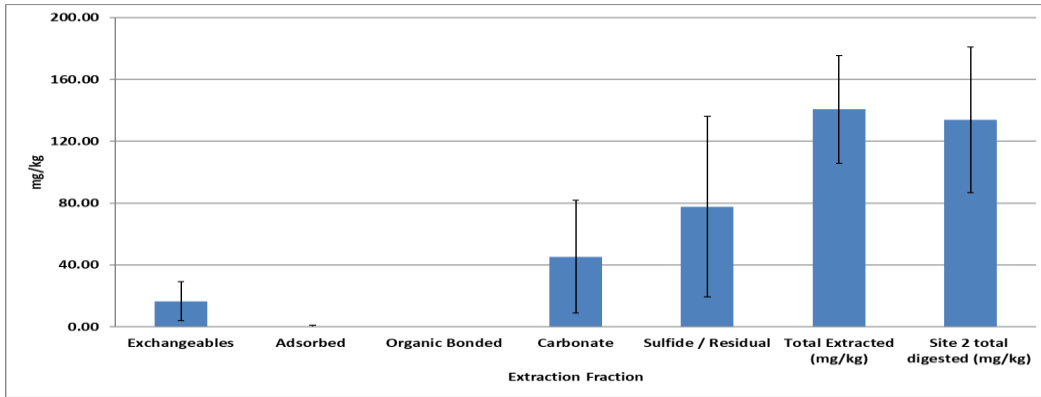


Figure 4.43: Mean Concentration of Extraction Fractions of Mn (mg metal /kg soil) for West Dock (Site 2) in Lake Nacogdoches

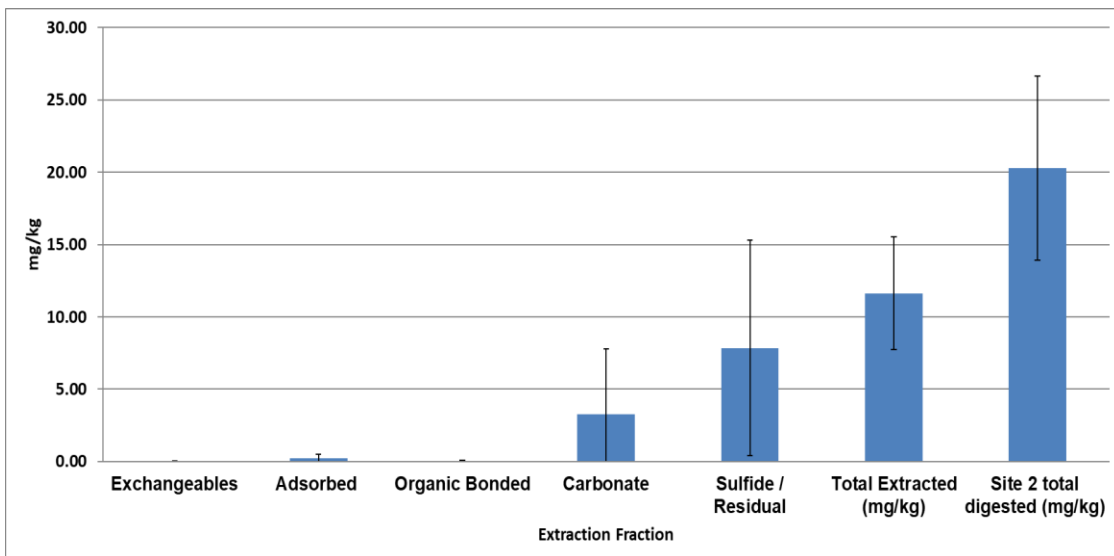


Figure 4.44: Mean Concentration of Extraction Fractions of Ni (mg metal /kg soil) for West Dock (Site 2) in Lake Nacogdoches

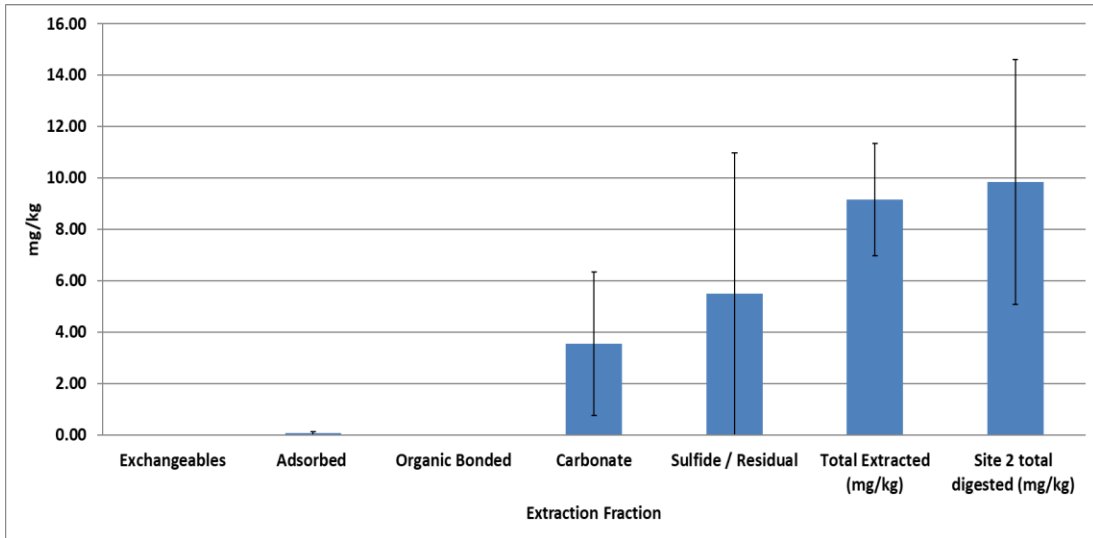


Figure 4.45: Mean Concentration of Extraction Fractions of Pb (mg metal /kg soil) for West Dock (Site 2) in Lake Nacogdoches

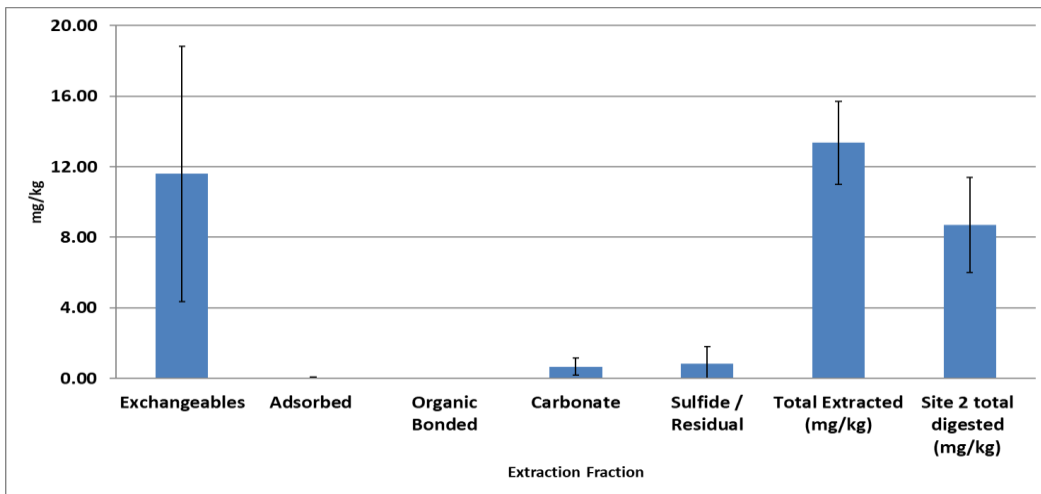


Figure 4.46: Mean Concentration of Extraction Fractions of Sr (mg metal /kg soil) for West Dock (Site 2) in Lake Nacogdoches

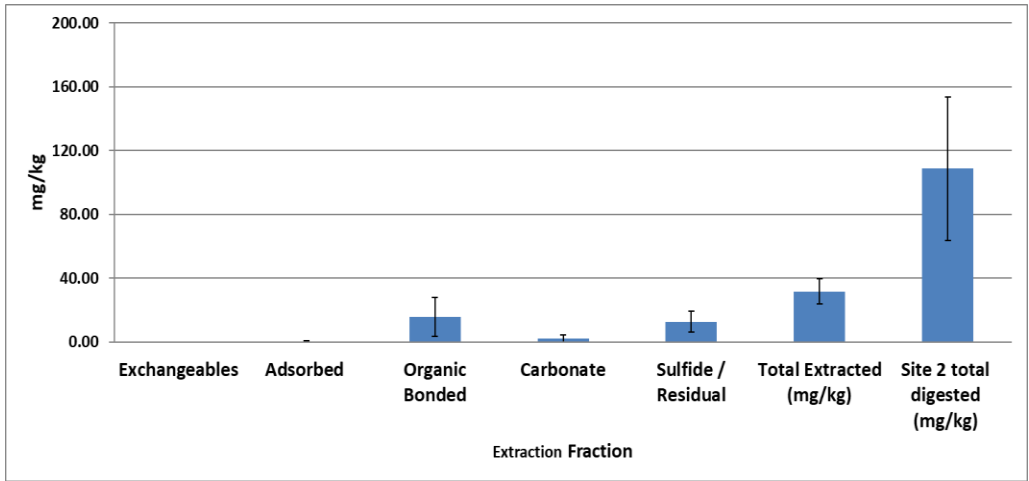


Figure 4.47: Mean Concentration of Extraction Fractions of V (mg metal /kg soil) for West Dock (Site 2) in Lake Nacogdoches

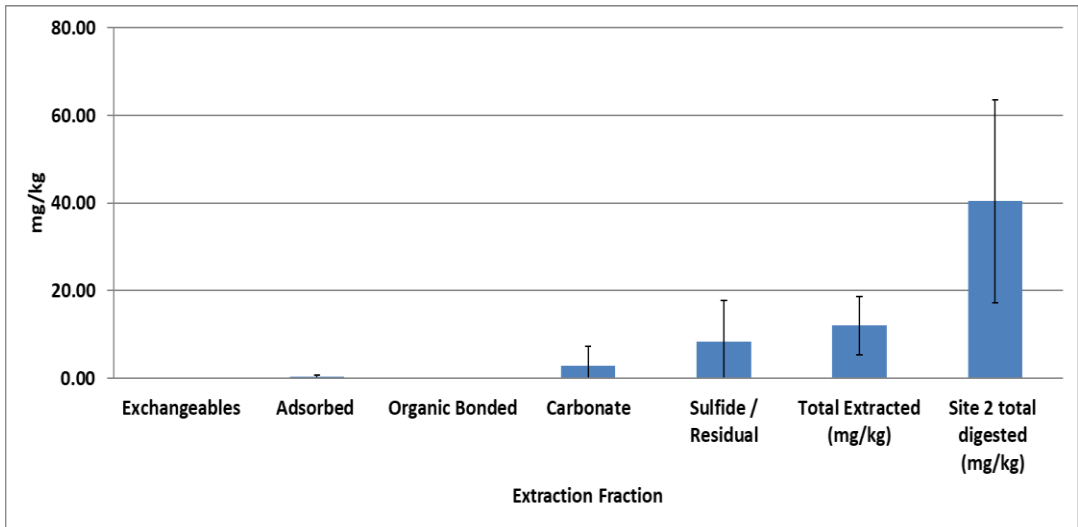


Figure 4.48: Mean Concentration of Extraction Fractions of Zn (mg metal /kg soil) for West Dock (Site 2) in Lake Nacogdoches

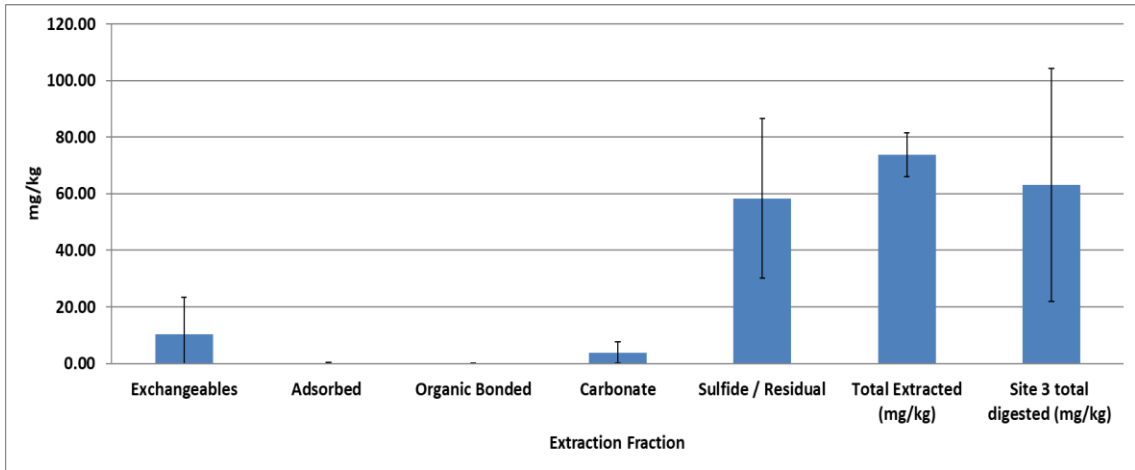


Figure 4.49: Mean Concentration of Extraction Fractions of Ba (mg metal /kg soil) for Swim Area (Site 3) in Lake Nacogdoches

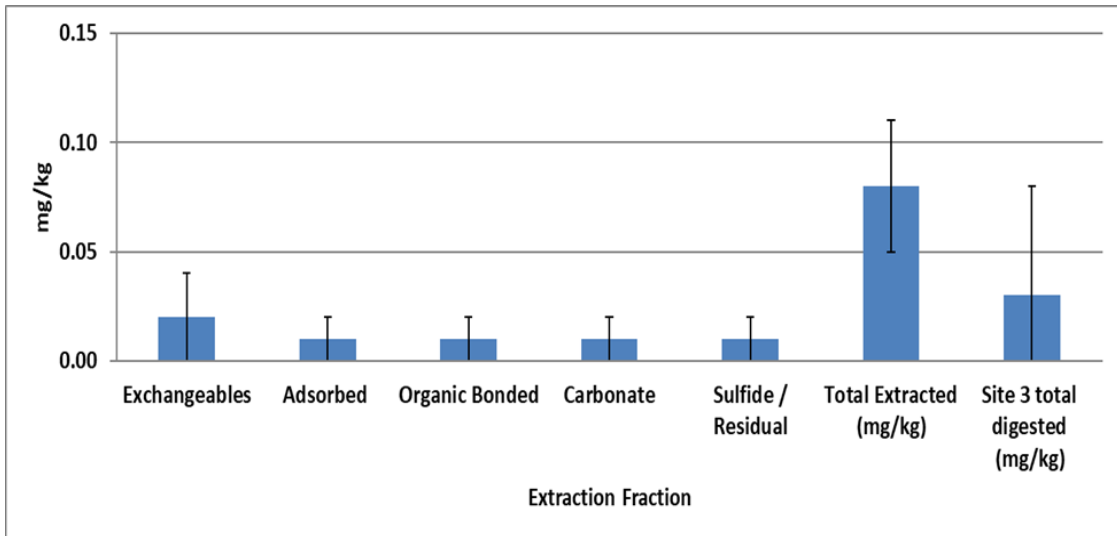


Figure 4.50: Mean Concentration of Extraction Fractions of Cd (mg metal /kg soil) for Swim Area (Site 3) in Lake Nacogdoches

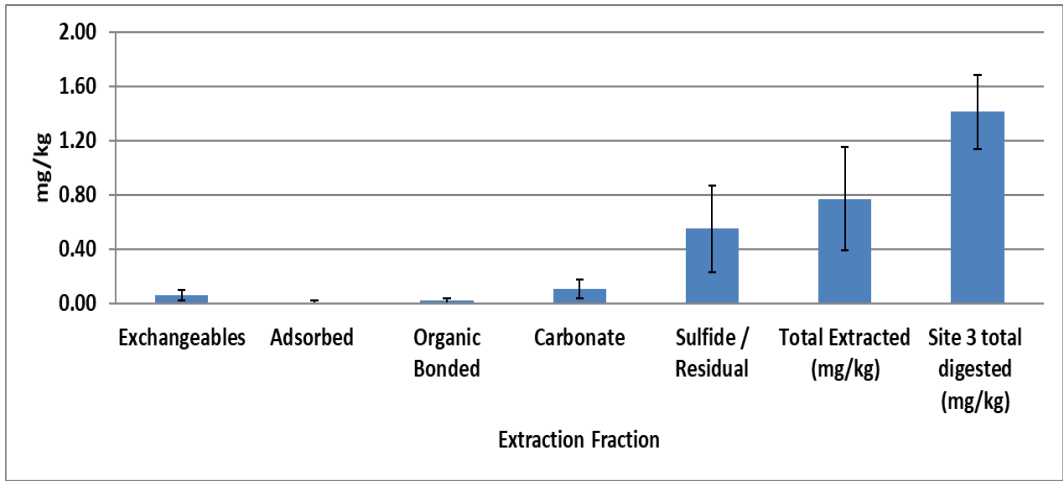


Figure 4.51: Mean Concentration of Extraction Fractions of C0 (mg metal /kg soil) for Swim Area (Site 3) in Lake Nacogdoches

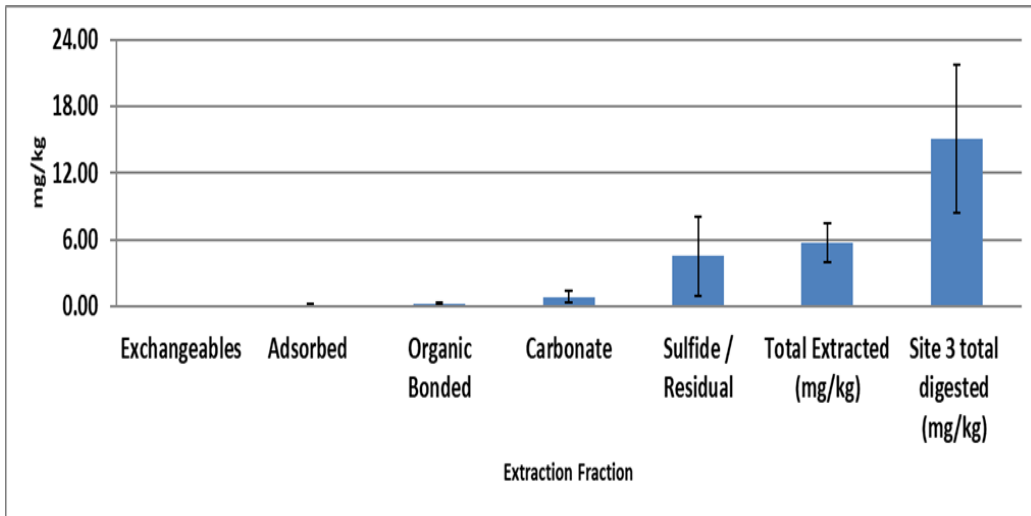


Figure 4.52: Mean Concentration of Extraction Fractions of Cr (mg metal /kg soil) for Swim Area (Site 3) in Lake Nacogdoches

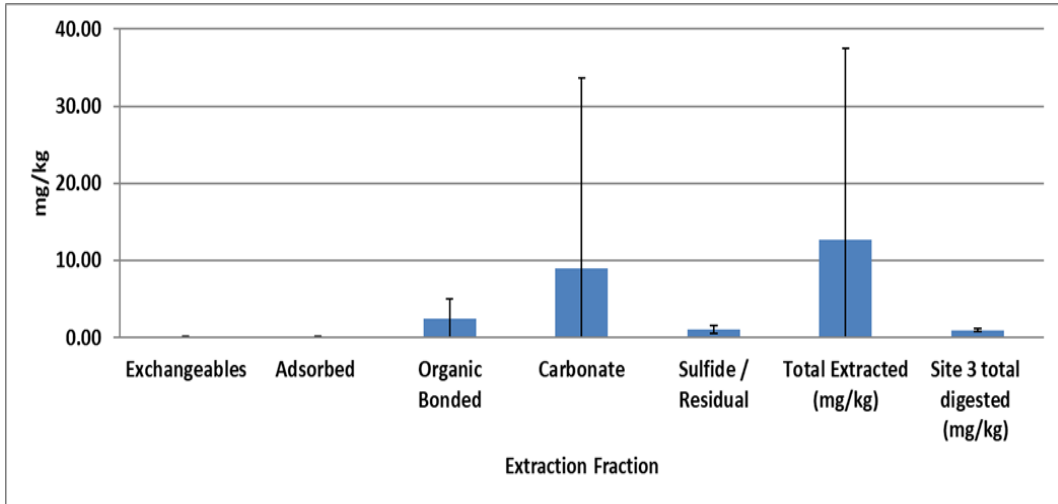


Figure 4.53: Mean Concentration of Extraction Fractions of Cu (mg metal /kg soil) for Swim Area (Site 3) in Lake Nacogdoches

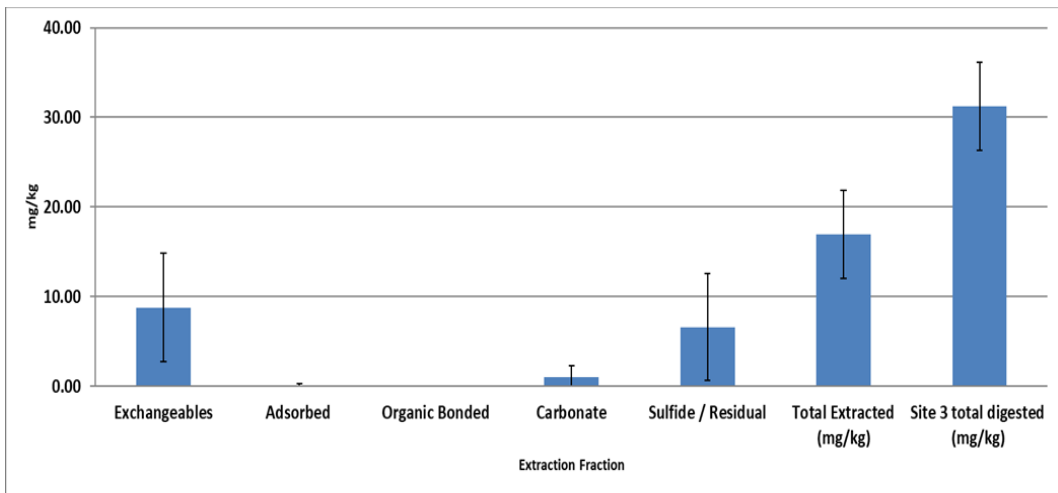


Figure 4.54: Mean Concentration of Extraction Fractions of Mn (mg metal /kg soil) for Swim Area (Site 3) in Lake Nacogdoches

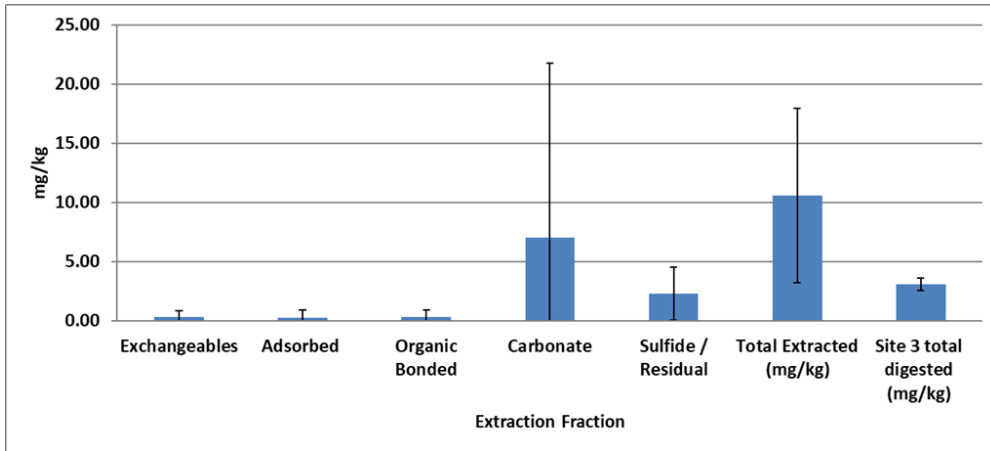


Figure 4.55: Mean Concentration of Extraction Fractions of Ni (mg metal /kg soil) for Swim Area (Site 3) in Lake Nacogdoches

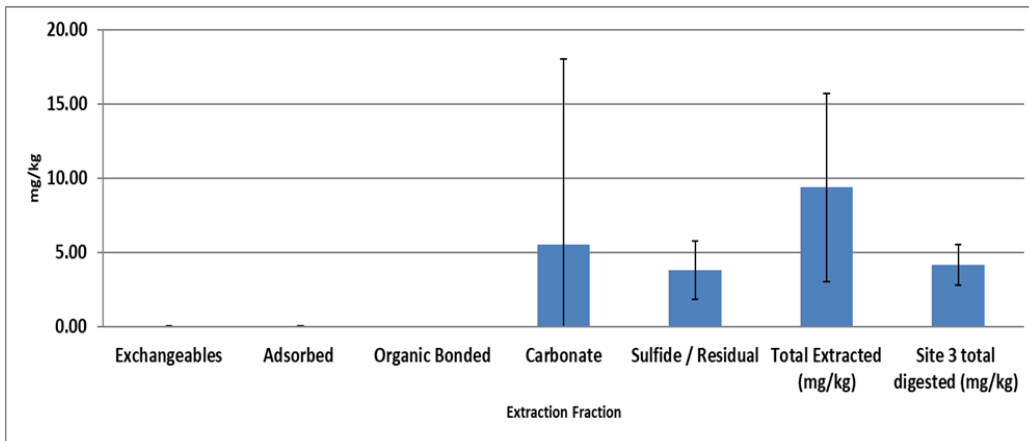


Figure 4.56: Mean Concentration of Extraction Fractions of Pb (mg metal /kg soil) for Swim Area (Site 3) in Lake Nacogdoches

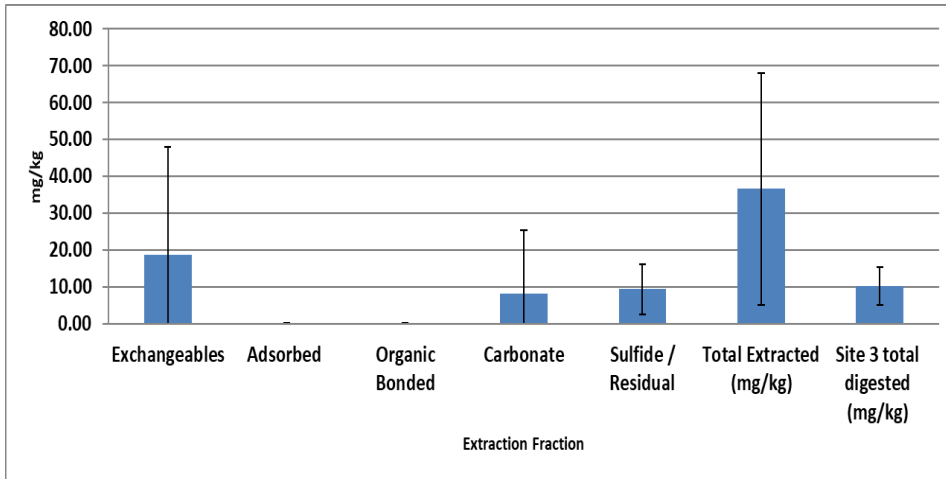


Figure 4.57: Mean Concentration of Extraction Fractions of Sr (mg metal /kg soil) for Swim Area (Site 3) in Lake Nacogdoches

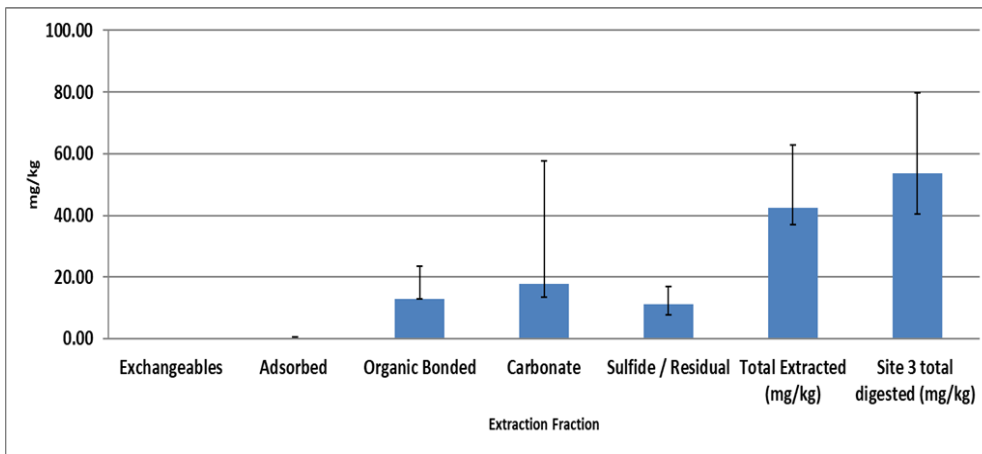


Figure 4.58: Mean Concentration of Extraction Fractions of v (mg metal /kg soil) for Swim Area (Site 3) in Lake Nacogdoches

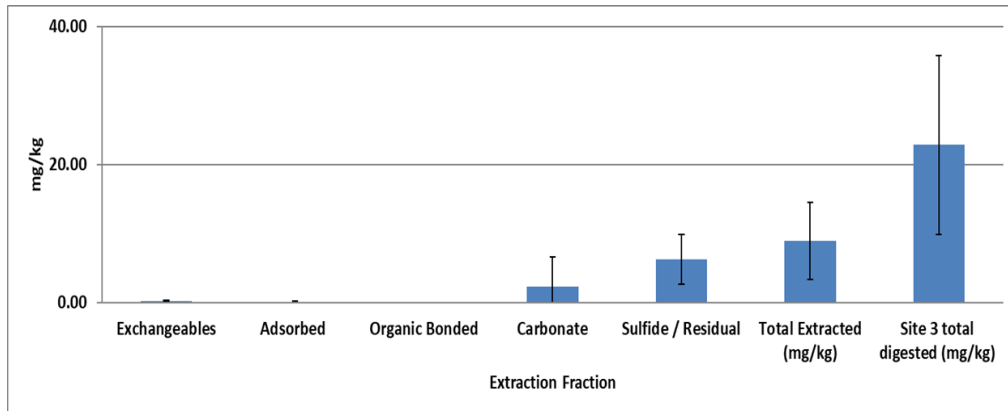


Figure 4.59: Mean Concentration of Extraction Fractions of Zn (mg metal /kg soil) for Swim Area (Site 3) in Lake Nacogdoches

CHAPTER 5

CONCLUSIONS

5.1 Conclusions

The experiment consisted of obtaining samples from four different sampling sites twice each semester along the southern area of Lake Nacogdoches and over a one-year period and testing for selected metal concentrations in the lake water and soil samples. Samples were analyzed using the EPA protocols 200.8 and 3050B. Sequential extraction procedures on the soils were also performed.

This research measured several physico-chemical properties with the most notable finding being with the water turbidity. The water turbidity reported in this study was generally higher during spring than the summer. The highest turbidity values were reported at site 4, and it's likely due to the water flow towards the Nacogdoches Water Surface Treatment Plant inlet. Water temperature was higher during fall than the spring months. The dissolved oxygen (DO) during spring sampling was higher than the

fall months. It is believed that the higher temperature in fall contributes to the reduction of DO in the water. DO and temperature are inversely correlated for all sampling sites.

Results indicate that the water samples had Ba, Mn, and Sr at measurable amounts (greater than 35 ppb for majority of samples) while the rest of the metals studied had values well below 5 ppb. All metals studied were well below the WHO and EPA drinking water standards for metals and in the typical range found in natural waters. The total metal concentration in water samples in Lake Nacogdoches at the different sites were very similar between sites with very little variation between fall and spring seasons with the exception that Sr was higher in the fall than the spring.

Results indicate that the soil samples had Ba, Co, Cr, Mn, Ni, Pb, V, and Zn at measurable amounts (greater than 10 mg of metal/kg soil for majority of samples) while Cd, Cu, and Sr were well below 10 mg of metal per kg of soil. All metals studied were in the typical range found in soils; however, there was a large variation in Co, Cr, Mn, Ni, Pb, V, and Zn between sites due to soil variation while soil samples tended to have similar results at a particular site. The metal with the largest variation was Mn.

The metal species that had measurable amounts (approximately 5 – 30 mg metal/kg soil) extracted in the exchangeable phase were Ba, Mn, and Sr, which coincide with the metals that had higher concentrations in the water samples. Barium had by far the largest exchangeable amounts available. Results indicate that most of the species studied are not in the bio-available form. None of the metals studied showed any appreciable amounts being collected during the adsorbed fraction. Within the organic bonded fraction, only V and Cu showed any measurable amounts indicating that most of the metal species studied did not release any soluble trace metals during the degradation of the organic matter. Cobalt, Cr, Cu, Mn, Ni, Pb, Sr, V, and Zn all had measurable amounts (1 – 10 mg metal/kg soil) obtained during the carbonate fraction. Mn had by far the largest carbonate amounts available. Barium, Co, Cr, Cu, Mn, Ni, Pb, Sr, V, and Zn produced metal concentrations during the sulfide/residual phase. The highest concentrations obtained were from Ba and Mn during this extraction phase. The trend of large variation of Mn between sites found in the total digested soils was also apparent in the extraction sulfide/residual fraction.

Sequential extraction procedure (SEP), Similar amounts were obtained between the two sites indicating some reliability of the sequential extraction procedure for Ba, Cd, Co, Cu, Mn, Pb, and Sr. Poor recovery rates for Cr, Ni, V and Zn indicate that different reagents, concentrations, and/or contact times may be needed to improve the process. Both soil composition and nature of the metal played important roles in determining the success of the extraction process based on binding sites and strengths.

5.2 Recommendations

I recommend that more experiments should be performed to validate the instrument used; there were some metals (Cr, Ni, V and Zn) that we question the reliability of the results which may have contributed to the poor correlation between the total extracted vs total digestion results for the questionable metals. The extraction conditions could be varied to improve the optimization for the characteristics of the target metal and extraction fraction.

Based on the variation of the metals between sites and the different types of soils, I recommend XRD analysis to find out more characteristics of the soil.

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Style manual designation: American Chemical Society (ACS)
Style Guide

This thesis was typed by Olawunmi