

**TÜRKİYE**  
**FIRAT UNIVERSITY**  
**GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES**



**COMPARISON OF ELEMENT CONCENTRATIONS IN WATER  
AND FISH SAMPLES FROM MOSUL DAM LAKE IN IRAQ AND  
KRALKIZI-DICLE LAKES IN TURKEY**

**Shaida HADI**

Master's Thesis

DEPARTMENT OF CHEMISTRY

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**TÜRKİYE**  
**FIRAT UNIVERSITY**  
**GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES**

Department of Chemistry

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KRALKIZI-DICLE LAKES IN TURKEY**

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ELAZIG

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## DECLARATION

I hereby declare that I wrote this Master's Thesis titled “Comparison of Element Concentrations in Water and Fish Samples from Mosul Dam Lake in Iraq and Kralkızı-Dicle Lakes in Turkey” in consistent with the thesis writing guide of the Graduate School of Natural and Applied Sciences, Fırat University. I also declare that all information in it is correct, that I acted according to scientific ethics in producing and presenting the findings, cited all the references I used, express all institutions or organizations or persons who supported the thesis financially. I have never used the data and information I provide here in order to get a degree in any way.

21 January 2021

**Shaida HADI**



## PREFACE

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**Shaida HADI**  
ELAZIG, 2021

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## ABSTRACT

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### Comparison of Element Concentrations in Water and Fish Samples from Mosul Dam Lake in Iraq and Kralkızı-Dicle Lakes in Turkey

**Shaida HADI**

Master's Thesis

FIRAT UNIVERSITY  
Graduate School of Natural and Applied Sciences  
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In this study, it is aimed to compare the element concentrations in water and fish samples taken from Mosul dam and Kralkızı-Dicle dam lakes. For digestion of fish samples, microwave (MW) oven was used. The measurements were carried out by using inductively coupled plasma-mass spectrometry (ICP-MS).

From the results obtained, it was found that all trace elements in water are lower than the maximum acceptable concentrations (MAC), for both from Iraq and Turkey. Related with studied elements in fish samples, Cd, Cr and Cu levels in all fish samples were found lower than the MACs (100, 1000 and 20 000 ppb, respectively) while Pb (427 ppb) in one sample and Ni (750 and 895 ppb) in two samples are higher than the MAC value (500 ppb Ni).

Related with the validation, standard reference material (SPS-SW2 surface water-trace elements) were analyzed for the studied elements. The obtained results showed that the results are reliable.

It was concluded that toxic trace elements should be determined periodically.

**Keywords:** toxic trace elements; ICPMS, fish, water, digestion

## ÖZET

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### Irak- Musul ve Türkiye Kralkızı-Dicle baraj sularında balıklarındaki element konsantrasyonlarının karşılaştırılması

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Bu çalışmada Musul barajı ve Kralkızı-Dicle baraj göllerinden alınan su ve balık örneklerindeki element konsantrasyonlarının karşılaştırılması amaçlanmıştır. Balık örneklerinin sindirimi için mikrodalga (MW) fırın kullanıldı. Ölçümler, endüktif olarak bağlanmış plazma-kütle spektrometresi (ICP-MS) kullanılarak gerçekleştirildi.

Elde edilen sonuçlardan, sudaki tüm eser elementlerin hem Irak hem de Türkiye için kabul edilebilir maksimum konsantrasyonlardan (MAC) daha düşük olduğu bulunmuştur. Balık örneklerinde incelenen elementlerle ilgili olarak, tüm balık örneklerinde Cd, Cr ve Cu seviyeleri MAC'lardan (sırasıyla 100, 1000 ve 20.000 ppb) düşük bulunurken, bir örnekte Pb (427 ppb) ve Ni (750 ve 895 ppb) iki örnekte MAC değerinden (500 ppb Ni) daha yüksektir.

Doğrulama ile ilgili olarak, incelenen elemanlar için standart referans malzeme (SPS-SW2 yüzey suyu iz elementleri) analiz edilmiştir. Elde edilen sonuçlar, sonuçların güvenilir olduğunu gösterdi.

Toksik eser elementlerin periyodik olarak belirlenmesi gerektiği sonucuna varıldı.

**Anahtar Kelimeler:** Toksik eser elementler, ICP-MS, balık, Su, sindirim

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## SYMBOLS AND ABBREVIATIONS

### Symbols

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|       |                              |
|-------|------------------------------|
| $R^2$ | : Coefficient of correlation |
| ppb   | : Part per billion           |
| SD    | : Standard deviation.        |

### Abbreviations

---

|         |                                                            |
|---------|------------------------------------------------------------|
| AEMs    | : Anion exchange membranes.                                |
| AFS     | : Atomic fluorescence Spectrometry                         |
| CDOM    | : Chromophoric dissolved organic matter                    |
| CEMs    | : Cation exchange membranes                                |
| CNTs    | : Carbon nanotubes                                         |
| ETAAS   | : Electrothermal Atomic absorption spectroscopy            |
| FAAS    | : Flame atomic absorption                                  |
| GFAAS   | : Graphite furnace atomic absorption spectrometry          |
| HM      | : Heavy metal                                              |
| IARC    | : International Agency for Research on Cancer              |
| ICP-AES | : Inductively coupled plasma atomic emission spectrometry  |
| ICP-MS  | : Inductively Coupled plasma-mass spectrometry             |
| ICP-OES | : Inductively coupled plasma optical emission spectrometer |
| IE      | : Ion Exchange                                             |
| LOD     | : Limit of detection                                       |
| LOQ     | : Limit of quantification                                  |
| LWC     | : Liquid water content                                     |
| MAC     | : Maximum acceptable concentrations                        |
| MF      | : Microfiltration                                          |
| MW      | : Microwave                                                |
| NF      | : Nanofiltration                                           |
| ROS     | : Reactive oxygen species                                  |
| RSD     | : Relative standard deviation                              |
| SPS     | : Standard reference material                              |
| SQGs    | : Sediment quality guidelines                              |
| SRM     | : Standard reference materials                             |
| SW2     | : Surface water                                            |
| TIMS    | : Thermal ionisation of Mass spectrometry                  |
| UF      | : Ultrafiltration                                          |
| WHO     | : word organization health                                 |

# 1. INTRODUCTION

## 1.1. Background

The organization of heavy metals in an aqueous environment depends on its association with other elements and its toxicity. Natural weathering of rocks and volcanic eruptions, and human activities attract heavy metals to him in an unhealthy food way that he eats and polluted water that pollutes the aquatic environment. Water pollution could be described as a chemical, physical, or biological element that causes an aesthetic adverse effect on aquatic life and water users. Nonetheless, the bulk of water contaminants are substances that stay dissolved or stored in water that have an sometimes unacceptable environmental solution [1, 2]. Heavy metals in water increase its concentration and quantity due to industry, human activities, agriculture, or from the natural source. The collection of heavy metals in water has a lot of harm to human health[3]. Safe drinking water is the fundamental human safety need. Contamination Drinking water poses a significant danger to public safety. Full Earth Water comprises 3 percent of freshwater. Just a tiny amount of this fresh water (0.01 per cent) is available for individual consumption [4]. Only this tiny amount of fresh water is under tremendous strain from exponential population growth, Environmental shift, urbanization Human use requiring money and food [5, 6]. Using a lot of fishes as it is a basic food to obtain proteins, amino acids. Fish an easy and main source for gathering proteins, and fish can therefore be eaten two to three days a week owing to the medicinal benefits of omega 3 polyunsaturated fatty acids found in fish oil [7], it is very rich in the presence of omega-3 fatty acids inside fishes EPA and DHA are two important fats in omega-3 which are useful for brain growth and strengthening of bones and pregnant women, studies confirm that peoples who eat fishes continuously reduce on them life heart disease, hypertension and cancers the long chain contains polyunsaturated fatty acid and lips soluble vitamins, also is useful for getting rid of some diseases such as heart attack and Paralysis....etc [8, 9]. However, it collects proteins as well, as they are a source of collection of heavy and toxic minerals within them. Through eating them, these heavy and toxic minerals are transmitted to humans and cause many diseases because people use them from all over the world as a protein meal. A major cause of water pollution is heavy and toxic minerals, fishes are able to obtain minerals through their respiration and a large amount of gill [9, 10]. Water pollution is a very important topic because water is the source of life, if water polluted it will affect the life of a human, animals, and plants in general, the presence of some heavy metals with a few basic concentrations are essential such as manganese (Mn), iron (Fe), copper (Cu), zinc (Zn), but some heavy metals are not essential and very harmful even if they are at a concentration of few like mercury (Hg), cadmium (Cd), lead (Pb) enter the human body through fish and causes many diseases [11]. The presence of

heavy metals in fish varies from place to place depends on some of the causes some of them seasons, the chemical and physical properties of those waters in which the fish live. Aqueous parameters in which both of them are able to recognize the presence of heavy metals in the water are PH and salinity a strong relationship is between them whenever the PH of water increased presence of heavy metals increase [12]. Sewage carrying a large number of contaminants in carrion of water. In ecotoxicology, heavy metal contamination is important as it is extremely permanent, bio accumulates and biomagnifies in every current food chain and therefore is lethal to species at higher trophic rates in the chain[10]. We used ICP-MS to identify heavy metals in water and fish, determination of trace elements in fish should be done with a multi-element device such as ICP-MS because it can identify many elements at the same time, but it should be used with caution, Before using minerals, they must be extracted from the fish by digestion using the acid to break apart there are most way for digestion one of them is microwave digestion [13].

## **1.2. Heavy Metals Pollution**

Heavy metals have detrimental impacts on the receiver environment's biological equilibrium and the diversity of marine species, the accumulation of heavy metals can cause morphological changes in fish tissues [14]. Metals in freshwater bodies are formed in particulate matter or in soluble materials, like labile and non-labile fractions. Labile metal materials are the most harmful for animals. They contain numerous ionic types of specific fish quality [15]. We took some samples from the Tigris River because this river has been very polluted in the last twenty years, The pollution of the Tigris River is due to dozens of pipes with sewage and agricultural wastewater, and those coming from hospitals and power stations, all of which flow into the Tigris even the government of Iraq an alarm rang, especially in the past years in which there was very little water. Experts add that one liter of polluted water pollutes four liters of pure water. Also because of industrial, agricultural and anthropogenic activity on these rivers many heavy metals and some other pollutant will find there but the pollution of heavy metals is much more than other pollutants because heavy metals are non-degradable, deposition of them occurred by two process precipitation and hydrolization [16, 17]. The Tigris River is one of the most important rivers that cross between Iraq and Turkey, and this river has a very important role for people and eating their fish They may be harmful to the environment and human health, increase of toxic metals in the human body causes diseases, including (nervous disorders, bone, immune system disorders, cancer, kidney disease, heart disease.... etc.). Metals like Arsenic (As), cadmium (Cd), chromium (Cr), lead (Pb), and copper (Cu), even if they are with very little concentration, their toxicity harms the human cells when it enters the human body by eating and drinking. Such chemicals often build up in certain fish organs which may contribute to lethal effects and a range of sub-lethal results because they are poisons, persistent and difficult to

biodegrade [7]. When freshwater are contaminated with heavy metals, the fishes depended on environmental factors such as (temperature, salinity, and PH) or biological factors such as (size, age, type, and diet) [8, 18]. When contaminates the freshwater fish which is a meal famous for proteins over all the world, they automatically start taking heavy metals inside it is body through the gills Since the gills consist of three to four gill arches containing several capillaries which, in effect, charge oxygen from the water to the rest of the fish, when the fish opens its mouth, enables water to flow through the gills, the vessels and capillaries remove the oxygen from the water and send it to the rest of the body of the fish and then the water goes out on the other side of the gills, In the other side, fish gills are important organs for respiration, osmoregulation, and excretion. The Gills serve as a very well water quality indicator. They are prone to any adjustments in water components as gill filaments and lamellae have a very wide surface area for direct and sustained interaction with water pollutants, by these way Metals spread throughout its body, muscles, liver, bones, teeth ... etc., The fishes liver is a crucial organ associated with essential metabolism and is the primary organ for the deposition, biotransformation and excretion of toxins in fish [14]. The presence of some toxic metals such as Zinc(Zn), Copper(Cu), and Cadmium(Cd) with a high concentration in water increases the risk of entering it into a living system directly or indirectly, its long-term survival in water causes many diseases, including physiological problems to produce blood and is affected on the liver [16]. Heavy metal poisoning depends on the strength of the ability to enter the enzyme process to the breakdown of the cells form. The main metals that cause anxiety are Lead (Pb), Arsenic (As) and Cadmium (Cd), especially when we eat seafood that enters the human body [8]. Heavy metals in water are very harmful to health because it turns into the human body and harms human growth, reduces hemoglobin, causes cancer and harms all members of the body and the digestive system also kills all living organisms because the density of heavy metals is four or five times more than the density of water [17] determining non-essential elements ratio in fish is very important because fish is a main meal because of the large number of proteins in it. The presence of heavy metals depends on their quality, and the chemistry of water is directly affected by the presence of minerals in fish Metals in fish can keep their effects in the water and the health of the human body because they are very dangerous to the kidneys, heart, liver and intestines. And at this time there are many international program to confirm the presence of metals in fish if they are useful for eating or not and with this program, they can monitor all things in the water [19]. In fact, the higher concentration of metals in the setting, the greater can be fished and collected [20]. Bioaccumulation heavy metals in the food chain and have a negative impact Organisms, which in extreme cases even lead to death [21].

### **1.3. Water Treatment Techniques and Removal of Heavy Metal from Water**

There's many different methods used to eliminate toxins that any system has its advantages and disadvantages. With the accelerated industrialization of human civilization, numerous chemicals are introduced into wastewater, including heavy metal ions, organics, fungi, viruses, and so on, which are extremely hazardous to human safety [22].

#### **1.3.1. Technique of coagulation/Separation**

Different separation methods have been done, like centrifugation, sedimentation, and filtration[23]. Coagulation is the classical water treatment technology widely used in treating drinking water, in the coagulation/flocculation method, the chemical, namely, either coagulants or flocculants, are added within the water to play a significant role in the removal of heavy metals. Metal salts, like ferric sulfate, alum, and ferric chloride, aluminum chloride are traditional coagulants. The application of these metal salts to the aqueous solution will cause a sequence of complicated chemical reactions such as dissolution, polymerization, and hydrolysis. Coagulation performance of extracting heavy metals from water solution has been tested in various ways, ranging from batch tests to field trials. The rate of elimination of heavy metals depends more on the hydrolyzed organisms of these inorganic coagulants in fresh water [24]. The problem of the coagulation method is that it produces a large volume of sludge owing to the solvent use of the separating method [4, 25].

#### **1.3.2. Ion Exchange Strategy for Separation**

The Ion Exchange (IE) method is focused on interactions among charged moieties. An efficient material for ion exchange must be of high ability and Aim ion selectivity. Separation of the ion exchange in which one ion removes another ion found in wastewater. There is less sludge forming in ion exchange due to coagulation phase [25, 26]. Ion exchange membranes are typically constituted of hydrophobic substrates, immobilized ion functionalized groups, and mobile counter-ions focused on the type of ionic groups, Ion exchange membranes are commonly classified into (CEMs) cation exchange membranes and (AEMs) anion exchange membranes. Generally, the ion-functionalized groups connected to the IEMs will separate after the penetration of enough water molecules, released cations, or anions for the transport of identical ions. The most common functional moieties in cation exchange membranes CEMs include sulfonic acid, carboxylic acid groups, and phosphoric acid [27].

### 1.3.3. Flotation Technique

The application of flotation has proven to be outstanding potential because of the strong performance and production for the latest appliances usable today [28]. Flotation Technique is a separating method in which rigid particle-like metal splits into the water, tiny droplets join wastewater in this process, and heavy metal prevents foam adsorption. The flotation cycle parameter is the frequency of bubble forming, the number of bubbles and the velocity of the bubble [25]. Air flotation is often used to boost and increase equilibrium, taking oil to the top in liquid-water mixtures [29]. Increasing flotation period and height of the column raises the amount of oil separation [30].

### 1.3.4. Filtration Technique

Filtration to execute different functions, such as monitoring the cellular climate and excreting waste materials [31]. Membrane filtration is one of the strongest filtration since we can extract heavy metal and kill certain dangerous microorganisms with the aid of the device. There are several factors that impact on filtration of membranes, particle size, concentration of the pH solution and pressure applied [25]. Processes of membrane filtration involving microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF) in drinking water output have increased rapidly. Microfiltration and ultrafiltration are used to extract inorganic particles, organic colloids (i.e. microorganisms), and dissolved biological matter from micro particles and macromolecules [32]. It was noticed that they could filter huge amounts of water without problems [33].

### 1.3.5. Chemical Precipitation Technique

The method of chemical precipitation is one of the major common processes used in many sectors since it is the comparably cheap cost [25]. This method is used extensively in heavy metals area and industrial effluent recovery (mining, metallurgy) [34]. Chemical precipitation is found widely in heavy metals. Stay rid of inorganic effluent upon pH change to the necessary requirements (pH 11), the dissolved metal ions are transferred to the insoluble solid state by means of a chemical process with a precipitant like lime. Generally, the metal precipitated from its solution usually takes the form of (OH) hydroxide, given their differing initial concentrations; a close total elimination of industrial wastewater was achieved at pH 11 for all metals, the mathematical method of chemically precipitated heavy metal removal is discussed in Eq.

$M^{2+} + 2OH^{-} \leftrightarrow M(OH)_2$  [35]. The disadvantages of current chemical treatment are the high expense of chemical reagents, inadequate sulfate removal and the development of heavy sludge to be disposed of [36].

### **1.3.6. Electrochemical technique**

Removal of heavy metal through electrochemical therapy, metals pass into their respective electrodes. Electrochemical processing ability depends on some factors like mass transport, electrode material, cell parameter, current density, and water composition, if we equate the electrochemical process with other procedures such as the process of coagulation, chemical treatment is much safer as it does not generate any side effects, the downside of electrochemical therapy is that it needs a significant amount of energy which often involves high maintenance and is often restricted because of the short service life of the electrode content [25]. There are some types of electrochemical technique electrodialysis, electrodialysis is a membrane isolation in which ionized organisms migrate across an ion-exchange membrane in the solution by adding an electrical potential, Membrane electrolysis technique, a chemical cycle powered by an Electrolytic ability can also be used to extract metallic impurities from wastewater for metal finishing. Electrochemical precipitation methods have ability to treat inorganic effluent with a metal concentration greater than 2000 mg/L, the electrochemical method can operate at each acidic and in basic conditions [35]. The method of electrocoagulation, the existence of polyelectrolytes such as sodium silicate, calcium carbonate and polyacrylamide have no major impact on the handling of wastewater from the pulp and paper mill industries and can thus be removed reducing operating and environmental costs [36, 37].

### **1.3.7. Adsorption**

The process of adsorption was deemed an effective strategy for extracting heavy metal ions from water owing to the potential to eliminate toxins only at very low concentrations, low energy usage, and availability of raw materials to produce various adsorbent forms. There are various types of adsorbent have been used for the heavy metals removal from water including fly ash, modified chitosan, extracellular polymeric substances, manganese oxides, peanut hulls, granular biomass, peat, sewage sludge ash, landfill clay, and activated carbon. The nanotechnology movement provides ample space for modern adsorption processes. Due in particular to its extraordinary chemical and physical properties, carbon nanotubes (CNTs) have emerged as outstanding adsorbent, CNTs are a stationary material. They are almost poor adsorbents in themselves, but increasing an extra functional group to their surface will significantly improve their selectivity and sensitivity to heavy metals and their strength to adsorb the latter, CNT surfaces must be activated and functionalized with extra content to render them more sensitive to various forms of contaminants [38]. The most advanced media for this technique are triggered alumina, bone char, and clay adsorption [39].

## **1.4. Traces Toxic Element and Health Hazards**

### **1.4.1. Lead (Pb)**

Inorganic lead has been one of the oldest exercising toxins is a naturally occurring material and an industrially manufactured product that is very poisonous to humans, particularly children. Kids are the most susceptible to lead as they have less successful renal excretion and higher ingestion of the gastrointestinal tract. The fetal brain is more susceptible to the adverse effects of lead relative to the adult brain [40, 41]. So harmful effects of lead cause anemia, proximal renal tubular injury, hypertension, immune system suppression of cardiac failure (antibody inhibitors) and neurological damage [15]. In another hand lead is neurotoxic and, because of its ability to enter erythrocytes, it may be widely spread to organs of the human body where it accumulates and causes damage. Lead toxicity stems from its tendency to substitute itself with certain divalent cation, both zinc and calcium, affecting their role in the cell, especially in cellular organs such as mitochondrion, where their accumulation affects the energetic metabolism and promotes free radicals. One of the propose why lead will take the position of different cations in the cell is its capacity to shape stable associations with sulfur and oxygen, specific components in places where proteins touch the metal, and in fact, because of its broader ionic spectrum and higher electronegativity lead are more related to such proteins than another cations such as zinc and calcium; Nevertheless, the divide of the lead charge is unusual due to the existence of two inert electrons in its electron cloud, which change the composition and work of the protein joined to impede its functionality [42].

### **1.4.2. Copper (Cu)**

Cu is acutely poisons (lethal) to freshwater fish in soft water at less of concentrations ranging between 10 – 20 part per billion (ppb) [43]. In another way deficient metabolism of Cu may cause two genetic diseases, Mense disease and Wilson disease. Cu Aggregation can be prone to Mense disease that is a deadly illness Condition Wilson disease may even arise when Cu aggregates in the brain and eyes in the shape of a chain. Heavy ingestion of Cu may even cause renal failure and even death [41]. Cu can be published to catalyze the creation of extremely reactive hydroxyl radicals, and become free [44]. Approximately 15 million tons of Cu are used annually worldwide for construction, electricity, agriculture, manufacturing or other uses; one third of this Cu is also from reusing and the rest was also from mining because Cu is a non - biodegradable potentially toxic contaminant that builds up continuous releases in the environment. Copper is both important and harmful to life, copper is an integral trace metal required for all living things to evolve and metabolize; People require between (1-2.5 mg) in one day in vertebrates, such as fish, Cu are part of many enzymes and glycoprotein, are essential for

the role of the nervous system, and are required for production of hemoglobin. In another hand Cu is toxic Cu is one of the most harmful components to marine life, it can accumulate and inflict permanent damage to certain organisms at rates only above that required for development and reproduction. Cu is highly toxic to water fish at concentrations varying from 10 to 20 ppb via its gills in soft water, Cu under acidic environments becomes more hazardous ( $\text{pH} < 6$ ) [43].

#### **1.4.3. Chromium (Cr)**

Is an important trace element in many organisms and humans. Cr can reduce body lipids and also increase lean body weight [41]. However, in water bodies, the most soluble sources of chromium are, based on the physicochemical properties. The oxidation states are Cr (III) or ( $\text{Cr}^{3+}$ ) and Cr (VI) or ( $\text{Cr}^{6+}$ ) respectively. Hexavalent chromium ( $\text{Cr}^{6+}$ ) is known to be poisonous (i.e. carcinogenic) owing to its strong oxidative capacity and ability to cross cell membranes [45], their results are low compared with those of well-balanced food and exercise. But that may have an undesired lethal impact in excess of the amount. Lack of Cr may influence the growth and disruption of glucose, lipid and protein metabolism [41]. Chromium is a human carcinogen in workplace environments mainly by inhalation use [46]. Severe chromium compound toxicity induces unnecessary mucosal excretion, harm to the gill of the respiratory epithelium, and the fish can die by symptoms of strangulation. The harmful consequences of Cr in fish contained hematological, histological and morphological changes, growing of inhibition/reduction, the formation of reactive oxygen species (ROS) and compromised resistant function [45]. Cr (VI)-induced health issues are [47].

- The Immune System Faded
- Skin ailments
- Affect ulcer and stomach upset
- Issue with respiratory track
- Switch the genetic content
- Pulmonary cancer
- Damage to kidneys and liver
- Risk of death

#### **1.4.4. Cadmium (Cd)**

The delivery and toxicity of Cd can be influenced by a number of substances. It can be seen in rainbow trout which fish fed ascorbic acid-deficient diet has raised hepatic Cd levels. This effect is also being observed for ascorbic acid-deficient mice. Once Cd has been processed by the skin, it is transferred firstly to the liver and kidneys. The first time Cd reaches the blood, it is found in the plasma pool, but is slowly passed to the erythrocytes while the equilibrium is achieved among the erythrocyte pool and the plasma pool [48]. Since Cd has been biomarker for

direct detection of cancer are of an essential to republic health [49]. The Cd in outside water can be both dissolved and insoluble. Among the substances that have been removed, some that could be harmful to animals, include simple and versatile inorganic and organic complexes of ions. The severe toxic action disruption to the central nervous system and the strong tissues, with very low doses of Cd, may cause different symptoms over a long exposure time. Acute harmful Cd concentrations for various types of fish vary between 2-20 mg / L. Cd is accumulated in the body's weak tissues among a 50-70 per cent concentration of both the kidneys organ and the liver organ. Cd is bound to the red blood cell of the entire body. Cd-induced renal harmful in humans is characterized by proteinuria, renal tubular cell injury, reduced proximal tubular absorption, and elevated creatinin rates [15]. Cd, which may induce elevated blood pressure in an extreme concentration, renal, Insufficiency, which can kill testicular tissues which erythrocytes Cd also induces bone demineralization, lung function loss, and Lung cancer risk [9]. Another related health problems of cadmium are as follows [47].

- Diarrhea:
- Vomiting
- Issues with stomach
- Cracks of the body
- Injury to the DNA
- Loser of reproduction and fecundity
- Causes damage to the nervous system
- injury to the immune system
- The origin of cancer

#### **1.4.5. Nickel (Ni)**

Is a common trace metal that exists in rock, water, food, and the biosphere. It is published in the atmosphere of both natural sources and human-made sources. Nickel is further released from oil-fired power stations, coal-fired power stations and waste incinerators. Nickel may make breathing diseases and is carcinogenic [45]. Nickel indirectly induces oxidative stress [50]. So nickel could be a trace metal necessary, but its function within the body is totally unknown. Possibly a limited value of Ni is required by the personal body to generate erythrocytes. The illness in the case of it is excess long-term exposure may contribute to reduced body weight, cardiac and liver injury, and inflammation of the skin. High dietary Ni level can be linked with an elevated risk of thyroid disorders, obesity, and heart illness [51].

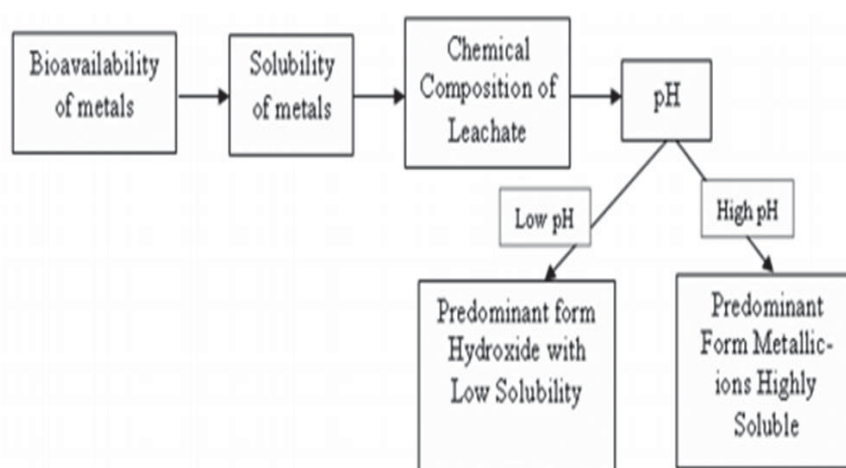
### **1.5. Mechanism of Heavy Metal Absorption and Collecting by Fish**

Throughout addition, metals that are ingested through the gills or the intestinal wall are spread to various tissues of the body through the bloodstream, used to carry proteins. Metals can engage in the vital functions of life inside the tissues, but may also perform harmful acts or be detoxified by attaching to the material, metallothionin (MT), Transporters (which passed metals through the plasma membrane), as well as metallothionin (MT) and some other metal-binding proteins control the intracellular amounts of metallic metal. Metal itself could not be metabolized and it can just be expelled from the body through excretion [48]. One question that is sometimes left unsolved understands the mechanisms by which metals are introduced into the fish. Many scholars have shown that gills play a major, maybe even dominant, function in metal taking. This could be valid especially to metal fractions of water-solubility. The explanation for this is that it is impossible in most situations to differentiate between food tract input and gill input [52]. For gills, the skin may not play a major function in the absorption of heavy metals: they are not only the primary organs of exchange of gases because, as an extremely advanced and transparent portion of the skin surface, but they are often a significant location for the ingestion of vital and non-essential metal ions from the water. Of starters, when fish have been exposed to soluble zinc and cadmium, certain metals are present during their gills. It has been seen that cadmium is ingested by perfused rainbow trout gills, a large absorption occurring directly when exposure the ingested metals are spread across the whole body and deposited throughout different organs. The taking of toxic metals from diet is dependent on different influences. Several studies say that only where the metal content of the diet reaches a certain threshold amount does a substantial ingestion of the metal by fish occur. In addition, feeding frequencies and consumption rates and relations with water-borne metals can alter the collection of food-related metals in fish [53]. Metals exist in particulate or soluble form in the natural waters. Fixable Species have percentages which are labile and non-labile. The composites with labile content they are the most harmful for fishing. They have various ionic types Fish sustainability. Most details show the concentrations of metals in the labile Fraction and proportion of specific metal ions largely depend on environmental conditions [20]. The metals with greater concern in natural waters are mercury Hg, lead Pb, cadmium Cd, cooper Cu, zinc Zn, aluminum Al, manganese Mn and Cr (around to decrease toxicity). Chondrion-rich chloride cells that account for around 10 percent of the gill volume Cells, perform an significant role in the transmission of ions; their apical presence and rate of transport of ions are strongly associated. The mucous cells are less abundant than the chloride cells, which were able to generate large amounts of mucus when stressed on animals [54]. the temperature of water can trigger differences in deposition process in different bodies. Higher temperatures help cadmium build-up particularly in the most heavily damaged organs: kidneys and liver. Increased collection of metals by fish at rise in temp is likely the result of increasing metabolic rates including higher metal absorption rates and binding [20].

## 1.6. Bioavailability of Heavy Metal

Bioavailability is the term used to describe heavy metals in water-soluble type that the populations of plants and animals will carry on and assimilate readily [11]. Bioavailability called a calculation of the degree and magnitude of which a product enters the site of operation in water toxicology. Its measurement is one of the important characteristics of ecotoxicology when measuring intake or dosages obtained from water or some other route of presentation. The level of bioavailability is always a restricting factor in responding to an organism. Bioavailability distance is generally a restricting factor in the reaction of an organism. Bioavailability limits are usually due to solubility constraints, sorption of different solids or humic matters, or partitioning into difficult environmental stages, including the minerals many variables influencing metals bioavailability, may incorporate the pH of the application medium. The existence of chemicals vying for binding sites (like calcium, sodium, and magnesium), and ultimately, different species such as the amount and form of binding sites at the site of action. Over decades, these factors have contributed to substantial improvements in the measurement of metal toxicity in freshwater bodies. In this study, we track the background of the creation of measures enabling bioavailability tests in natural waters [55]. Bioavailability is defined in relation to approaches designed to minimize environmental impacts caused by wastewater [56], so bioavailability is primary problem in biota risk evaluation of heavy metals. Free-ion-activity model offers a stronger foundation for estimating the distribution and toxicity of metals according to the overall metal concentration [57]. Better pollutant bioavailability models have been assumed to boost our capacity to assess toxic effects of polluted sediments [58]. The possibility that certain parameters of the product other than metal interaction influence supply including pH and calcium (Ca) concentrations [57]. Unlike freshwater, the bioavailability of pollutants present in ocean waters seawater is unlikely to be influenced by the comparatively small PH spectrum of this medium, based on freshwater pollutant toxicity studies, suggests that hardness water could impact the bioavailability of pollutants more as a feature of a shift in PH than those in hardness itself (Figure 1.1). Through extrapolation, this finding may suggest that a small increase in salinity in ocean seawater not followed by a major shift in PH will have negligible effect on the bioavailability in pollutants. However, a wide depression of seawater pH induced by freshwater dilution in estuaries will excess the bioavailability for heavy metals [59]. For example, here we have Cr, Chromium's bioavailability was already observed less than other toxic metals, and is confused by its speciation and redox behavior. Chromium (VI) is more easily passing the cellular membranes than Chromium (III). Most Cr was contained in natural sediments Linked to the proportion of silicate lattice and not usable biologically. Cr (III)s very poor assimilability has contributed to its usage as that of an inert tracer from ingested particulate material to test carbon absorption in aquatic invertebrate organisms, efficiencies in absorption vary from 10% for phytoplankton to

much more as 90% of bacteria. The lower levels of soluble chromium (III) in mussels than chromium (VI) is associated with studies indicating that the cellular absorption of chromium (III) from equilibrium solutions is at minimum 10 times greater than the chromium (VI), and then both consumed food and dissolved process Chromium (III) passes biological membranes even less readily than Chromium (VI) [21]. A free ionic form becomes typically more acidic than the non-dissociated type. Therefore, metals are usually more hazardous in acid than that of the alkaline PH. In a new study of bioavailability and poisoning in fish in reduced-alkalinity lakes (PH<6.0 to 6.5) in spring and winter, fish also have higher body or tissue levels in Al, Cd, Pb and Hg than fish at high level of PH in similar lakes. This was due to improved bioavailability for metals at low PH and higher aqueous calcium concentrations, which enhanced the biological sheath permeability of these metals [59].



**Figure 1.1.** Correspondence among metal bioavailability, solubility of metals, pH, and metal shape[21]

### 1.7. Objective of this Research

To determine the concentration of Nickel Ni , Cadmium Cd , Chromium Cr , Lead Pb , and Copper Cu in water and fishes in Tigris River from turkey in Diyarbakir kiralkzi-dicle dam lakes and from Iraq in Mosul dam lake by ICP-MS. And determining them toxicity to human health and dinking water.

### 1.8. Research Question

- 1- Effect of heavy metal (HM)s in water ?
- 2- Could heavy metals be removed of the water ?
- 3- How is water contaminated with heavy metals ?
- 4- What impact do heavy metals have on fish ?
- 5- Which metals are poisonous to fish ?

6- What are the benefits of fish ?



## 2. LITERATURE REVIEW

### 2.1. Heavy Metal

Large amounts of heavy metals are dumped into waste water in drains. Such metals may be deposited intensely and biomagnified in soil, sand and Aquatic food chains contributing to sublethal consequences or mortality of local fish supplies [60].

The degree of intensification was correlated with numerous human activities, such as heavy manufacturing, forestry, livestock and aquaculture, owing to the steady upward growth of the world population produced elevated emission rates in different habitats water contamination has also been one of the many important study subjects within the populations. The toxic effects of heavy metals on fish can influence individual growth rates; Functions in biology, longevity, and reproduction. High metals fall into the heads of animals Three paths: gills, digestive system, and the surface of the body (Simonov, Ira-Adeline, et al 2016) [12].

Also, essential metals can be harmful to high concentration organisms biological activities, fish are typically capable of collecting high rates of pollutants from their environments. Discharge of contaminants such as heavy metals threatens the diversity of marine organisms as well as habitats by toxic effects, decreased growth rate and fecundity Although less focus was paid to the impact of metal accumulation on the wellbeing of fish and the impact of fish safety on metal accumulation trends in specific tissues. The study revealed no major variations between males and females in metal concentrations, Increasing age and length increased levels of metals in the liver. (Monsefrad, F., J. et al., 2012) [61].

Phytoremediation is an efficient and cost-effective technical method for separating or replacing inert metals and chemical contaminants from polluted soil and water. This system is socially sustainable and will be cost-effective.

Varol, et al (2011) worked on the (i) determine the place and temporal dissemination of heavy metals (HM) in surface deposits from the Tigris River, in Turkey. (ii) and defined the natural and anthropogenic sources of metals using multivariate statistical methods. (iii) To explore the ratio of heavy metal pollution in the Tigris River using contamination indices, (iv) also assess environmental dangers of certain metals in the study area by comparison with sediment quality guidelines (SQGs). To determine heavy metals 0.25 g sediment subsamples were digested in 12 ml HNO<sub>3</sub> (65

per cent) Teflon vessels: HCl (37 per cent) (3:1) mixture in a microwave oven (MARSS press, CEM). The residue extracts were analyzed for cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), and zinc (Zn) by a (FAAS) flame atomic absorption spectrometry equipped with deuterium background correction. As Cd and Pb in extracts was measured by using a (GFAAS) graphite furnace atomic absorption spectrometry. At (Madden), the highest concentrations of heavy metals were observed owing to metallic wastewater discharges from a copper mining plant in Maden Township At (Hasankeyf) the lowest mean values of As, Ni and Zn were found while the lowest mean values of Cd, Co, Cr, Cu, Fe, Mn and Pb were estimated at (Batman) [62].

According to the Fu, et al. (2014) study, the levels of heavy metals in deposits is not an independent factor but interacts with environmental factors around them work into the interactions between heavy metals and different environmental variables allows to better analyze the impacts of heavy metals on the atmosphere and to understand the emission features of the natural community. The Jialu River is a significant tributary of the Huaihe River and has been extensively contaminated by a number of pollutants such as industrial and domestic wastewater, agricultural waste and untreated or poorly handled waste The aims of his work were: (i) to establish the degree of concentration and distribution trends of various heavy metals in the Jialu River surface sediments(ii) evaluate the potential ecological threats of heavy metals, (iii) describe the effect of metal emissions on natural processes and (iv) define important environmental variables impacting contamination of heavy metals. The (AFS) atomic fluorescence spectrometer used to test As, Cd and Hg. Where sediments were digested using aqua regia. As estimation, thiourea – HCl mixture decreased the digestion solution before calculation Cr, Cu, Ni, Pb, Zn as well as other elements (Al, Ba, Ca, Co, Fe, K, Mg, Mn, Na, Sr, Ti, and V) were analyzed using an (ICP-OES) inductively coupled plasma optical emission spectrometer with inductive couplings. The sediment was digested with a combination of HCl – HNO<sub>3</sub>–HF – HClO<sub>4</sub>. Details of the analytical methods were given elsewhere the amount of arsenic As in the Huaihe River Basin is 3.3 times higher than in the Jialu River, while the levels of Cd and Zn in the Jialu River are 3.7 and 1.5 times higher than in the Huaihe River Basin, respectively. but the amounts of other heavy metals in the Jialu Riverand the Huaihe Basin are similar [63].

## 2.2. Inductively Coupled Plasma – Mass Spectrometry

Inductively coupled plasma – mass spectrometry (ICP-MS) may be considered one of the leading strategies in the area of metal research, based on evaluating metal and metalloid ultra-trace rates in a broad range of sample forms, benefits of ICP-MS are (e.g., high sensitivity, a pronounced multi-element character, a wide linear dynamic range and the possibility to obtain isotopic information) By means of ICP-SFMS the majority of interferences produced through the spectral overlap of the signal of a specific analyte ion with such of a polyatomic ion with the same nominal mass can be determined (Balcaen, Lieve, et al. 2015) [64].

And if quadrupole mass analysers are the best Percentage of all inductively coupled plasma mass spectrometers installed worldwide, weight resolution limitations Have contributed to the creation of mass spectrometers with high resolution. These devices, known as ICP-MS High Resolution The magnetic field (HR-ICP-MS), sector field ICP-MS or double focus ICPMS (DF-ICP-MS), The ICP-MS multi-collector is based on a rather recent technique To measure high precision compositions of the isotopes and Accuracy, typically only obtained with the mass spectrometry of thermal ionisation (TIMS). Specific simultaneous isotope detection reduces conventional causes of variability in quadruple-based measurements of the ICP-MS isotope ratio owing to serial scanning mode and plasma flicker noise.(Moldovan, Mariella, et al. 2004) [65].

In the study of Bajc et. al (2016), The connection between the concentrations of fish weight or length and metal was examined [13]. An study of the Pearson association in the rudd's meat and liver The detrimental relation related to size (length, weight) was reported for Zn and Mn. However, with the scale of rudd the amounts of Fe in the kidney and Cd in liver and kidney increased. A Varian SpectrAA 220 atomic absorption spectrophotometer was used to assess the concentration of Pb, Cd, Zn, Cu, Mn and Fe in fish tissues. Varies in the degree of fish metabolism With age. The portion of the surface area to The amount, diet and concentration of fish of certain bio-important compounds Interested in the production accumulation process with a fish age [13].

In another study by Mortuza et. al (2015), samples of 1 litre of water is obtained bottles of polyethylene washed beforehand cleaned with non-ionic detergent, rinsed with distilled water and then immersed in 10% HNO<sub>3</sub> for 24 hour and then rinsed with deionized water before using. Bottles is rinsed with during sampling water was tested three times and loaded to brim to a maximum of one meter under the surface of the water In all of the three specified points of sampling inductively coupled plasma(ICP MS) was

used for Digested water tests, including heavy metals. 4 ml of nitric acid( $\text{HNO}_3$ ) and 2.5 ml of sulfuric acid ( $\text{H}_2\text{SO}_4$ ) used for digestion 0.5g of powdered dried fish by the way of Hanson The average HMs concentration in *C. gariepinus* and *O. spilurus* followed the order  $\text{Fe} > \text{Zn} > \text{Pb} > \text{Cr} > \text{Ni} > \text{Co} > \text{Cd}$ , and  $\text{Zn} > \text{Fe} > \text{Pb} > \text{Cr} > \text{Co} > \text{Ni} > \text{Cd}$  respectively [60].

In the study of Yi and Zhang (2012), the connection between the size of the animal and concentrations of essential and non-essential metals were examined. The aim of their research is to define heavy metal (Cd, Cr, Cu, Hg, Pb, Zn) levels in the muscle tissue of 7 fishes species largest amounts of mercury have been reported in catfish. The concentrations of chromium differed among the species, with the highest amounts shown by the common carp. Results indicate that in most situations there are strong associations between fish sizes and metal rates With negative associations found mainly in catfish and yellow head catfish classes of mercury and chromium [66].

### 2.3. Wet Digestion/Acid Oxidation

Wet digestion is used more frequently because of reduced analyte loss at low-temperature and speed. Wet digestion allows use of certain mineral acids, such as HCl,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$  for the decomposition of the organic sample matrix which can be carried out in an open or closed environment through traditional heating or digestion through microwave digestion (MW). MW technique is more effective than traditional heating requires as it is reduces the period and the chance of digester pollution. Digestion of the heavy metals in the tissues of fish includes chemicals such as perchloric acid, nitric acid, sulfuric acid and hydrochloric acid accompanied by MW absorption. The defining step is the digestive cycle about the administrative period and the efficacy of the real metal found in the sample. (Idera, Fabunmi, et al. 2015) [67].

Many wet oxidation procedures are suggested but they all fell into four groups differing mainly in the combination used in digestion:

- o Sulfuric acid and peroxide to hydrogen
- o Nitrogen and sulfuric acid
- o Perchloric acid and nitric acid or sulfuric acid
- o Nitric acid.

According to Ayanda et al. (2019 ), the frozen fish samples were permitted to defrost, dissect and, for metal examination, the livers, muscles and gills of these fish species were collected. 1 g of each of these body parts were washed, processed into powder and Digested in ratio of concentrated nitric acid( $\text{HNO}_3$ ) and hydrochloric acid(HCl) 3:1 At 70 C for 30 minutes, while the mixture remained on Warm bath before you detect a shift in color. The solution that

result is time to cool was allowed and then filtered into a 50 mL flask with distilled water to make up to mark was added [9].

## **2.4. PH**

Human actions such as agricultural processes and dumping of hazardous waste have an impact on the pH of water bodies. A increase in water pH may have implications for marine species that are highly vulnerable to water temperature and composition shifts. Measuring pH is extremely difficult, so indirect methods are mostly used to reflect acidity of the particles. An ion balance is the most common: the charge balance of observable cations and anions The pH depends on the liquid water content of particles (LWC), since pH is the aqueous concentration of  $H^+$ . (LWC), the liquid water content will differ significantly over the course of a day and between seasons, greatly affecting pH. (H. Guo et al 2015).[68]

A water source 's pH-value is a function of acidity or alkalinity. It is an indicator of hydrogen atom behavior since the hydrogen concentration is a strong reflection of water acidity or alkalinity. The WHO recommendations placed the pH within the range of 6.5-8.5 for drinking water,. (Li, Yali, et al. 2008) [69].

Natural rainwater is never a pH inferior to 5.6 (Raven and Johnson 1992). It is attributed to air emissions (oxides of nitrogen and sulphur) from cars and thermal power plants that contribute to acid rain. Sewage and chemical effluents though may still affect the pH composition of river and lake waters. The pH is a very important factor in oxidation and trace element reduction Studies of laboratory oxidation done with mine effluent samples have confirmed a maximum oxidation rate at temperature levels from 27 to 350C. Scavenging the toxins in the environment impacts the chemical components and pH of rainwater raised rainfall would have much dilution effect on all fluorescent parts and that rainwater pH changes would contribute importantly to the change in the composition of chromophoric dissolved organic matter CDOM fluorescence [70, 71]

## **2.5. Effect of Heavy Metals on Water**

Drinking water hardness has a significant impact on public safety and repeated exposure to polluted water was acting known to raise the incidence of cancer and renal, liver and reproductive disorders etc. The impact of industrial pollution on people in drinking water is cumulative rather than severe. Considering water safety on public health is also important, as waterborne illnesses tend to be a significant cause of death in many areas of the world. As such, synergistic effects of trace heavy metals and specific anions found in water may be a significant factor in public safety,

and work into the association between trace elements and anions, and their impact on humans is of prime importance. (Wasana, Hewa MS, et al. 2017) [72].

Although some heavy metals become essential for human safety, an excess concentration of these metals can become negative effects by natural cycles and anthropogenic behaviors, the heavy metals are introduced into the world. Material processes contribute to Waste mostly released into the atmosphere Heavy metals also can enter the environment via a bio-geo system heavy metals in drinking water, including their types and quantities, factors affecting metal concentrations, sources, human exposure, risk, and removal. Despite significant progress, research is needed to ensure safe drinking water. Thirty-five metals pose a hazard to human safety due to industrial and/or residential use, of which 23 are heavy metals. Inorganic As and Cd are listed as human carcinogens according to the International Agency for Research on Cancer (IARC) ( Chowdhury, Shakhawat, et al. 2016) [73].

The permitted value of Cd according to WHO is 0.003 mg per L. according to WHO Chromium value in water is 0.05mg/L. WHO permitted value for Nickel is 0.02mg/L, and for the lead, The permissible value according to WHO in drinking water is 0.01mg/L (Jamshaid, Muhammad, et al 2018) [4].

Arsenic is caused cancer disease risk and skin illness, whereas Cd is linked to kidney illness and cancer. Another effects such as heart problems and blood cholesterol from Sb, anemia from Pb, kidney and liver illness from Hg, and gastrointestinal disease from Cu were also published. water consumption of 1 L / day with As of 50 µg / L could lead to liver , lung, kidney cancer during one's lifetime; In 13 /1000 individuals, or bladder. Another research showed a spike Incidence of skin lesions 0.0012 mg / kg / day as a dosage by beverage drink Subchronic effects, like the risk of stillbirths, were developed by six-fold in women who consumed drinking water with As  $\geq 200$  µg/L during pregnancy (Chowdhury, Shakhawat, et al. 2016) [73].

## **2.6. Effect of Heavy Metals on Fishes**

Heavy metals may pass to aquatic organisms from water and sediments and biomagnify from low trophic level to higher as the top of the food chain of the aquatic world, fish may produce large quantities of heavy metals by gill, surface skin and oral food and drink ingestion Consumption of seafood is known as one of the key routes for human access to heavy metal contaminants. Classified as, Cd Cadmium, and Pb Lead toxic elements which do not have a determined role in any biological process. As, Cd and Pb are grouped as toxic substances that have no documented function in any biological cycle Pb induces renal insufficiency; Harm to the heart, coma, psychiatric retardation and even death and cause liver disease. Cd Cadmium has a kidney injury and is responsible for acute hypocalcemia and a reduction in growth Even though Cu, Fe, Mn, and Zn are essential metabolism problems, they will present major danger for safety

if concentrations add up to those holding limits. Relatively high Cu and Zn rates induce nephritis; Anuria, and severe renal lesions Heavy metal toxicity of fish muscles has been documented due to fish muscle is the main component of human feeding. However, the fish muscle is not enough to show heavy metal contamination in the entire fish body due to its weak accumulation. Analysis of other tissues like the gill and liver would be equally important. The gill may collect water-dissolved heavy metals through the ion exchange method relationship all types of fish With various methods of eating, the carnivorous was observed. The fish is more polluted with heavy metals than with herbivores. and ubiquitous species(Jia, Yuyu, et al. 2017) [74].

The accumulation of bioaccumulated heavy metals in the fish tissue depends on certain environmental factors, including pH, temperature, environmental alkalinity, pollutant content, sampling site and the ecological and physiological features of the species such as feeding preferences, age, sex, life cycle, habitat and location through the aquatic food chain. Nevertheless, the bioaccumulation of heavy metals in fish may contribute to possible health hazards for humans by fish consumption (Miri, Mohammad, et al. 2017) [75].

Metals may usually be classified as essential biologically and non-essential. Non-essential metals (e.g. aluminium, Cadmium, mercury, tin and lead may not have any Established biological feature (also known as xenobiotics or alien elements) and their toxicity increases with increasing concentration ,essential metals such as copper, zinc, chromium, nickel, Cobalt, molybdenum and iron on the other Hand, have a recognized biological function, and therefore them toxicity occurs at high concentrations. The lack of essential elements can also have a detrimental health impact, although its high content can also result in harmful consequences that are equal to or greater than those produced by non-essential metals [76].

## **2.7. Techniques used to Identify Trace Elements**

Determination of trace elements in contaminated samples such as water, soil and food. And samples need complete preparation before using the devices, and there are many methods for identifying trace elements. (FAAS) flame atomic absorption spectrometry is one of the common traditional methods for the measurement of trace element ions Despite the relative flexibility and cost-effectiveness of the hardware also Electrothermal Atomic absorption spectroscopy (ETAAS). Inductively coupled plasma atomic emission spectrometry ( ICP-AES), also indicated to as (ICP-OES) inductively coupled plasma optical emission spectrometry. (ICP-MS) Inductively coupled plasma mass spectrometry is generally utilized in cycle multi-elemental determination at the ultra-trace and trace level in liquid samples with various model combinations. The ability to measure accurate isotope ratios by (ICP-MS) is used in the measurement of metal concentrations by the(ID) isotope-dilution method, which is regarded as a

primary technique of measurements. (ID ICPMS) isotope dilution inductively coupled plasma gives the chance of absolute quantification for metals with two or higher isotopes in each sample material. (LA ICPMS) Laser ablation inductively coupled plasma is not fully taken for quantitative studies mainly because of the fractionation effects and the constant lack of enough reference elements for the wide difference of samples. The trace elements measurement is generally taken with atomic spectrometry, potentiometry, voltammetry, nuclear methods, and X-ray.



### 3. MATERIAL AND METHODS

#### 3.1. Study Area

First, confirm that the Mosul Dam Lake is an artificial reservoir situated between latitude (36°36'N - 36°50'N) and longitude (42°27'E - 42°58'E) on the Tigris River about 60 km north of Mosul City and 80 km from Syria and Turkey 's borders (Figure 3.1.). The lake area is approximately 385 km<sup>2</sup>; the length is approximately 45 km and the width ranges from 2 to 14 km at maximum operating level (330 meters above sea level) with a maximum storage capacity of 11.11×10<sup>9</sup> m<sup>3</sup> and a maximum water depth of 80 m. Within Iraq, its drainage basin occupies 4200 km<sup>2</sup>. Much water that inters into the lake comes from Turkey. The Tigris River's mean annual discharge ranged from 270 to 1371 m<sup>3</sup>/s at Mosul station for the period 1931-1997. The biggest monthly discharge typically takes place during April and May and minimal discharge occurs during October and September [77].

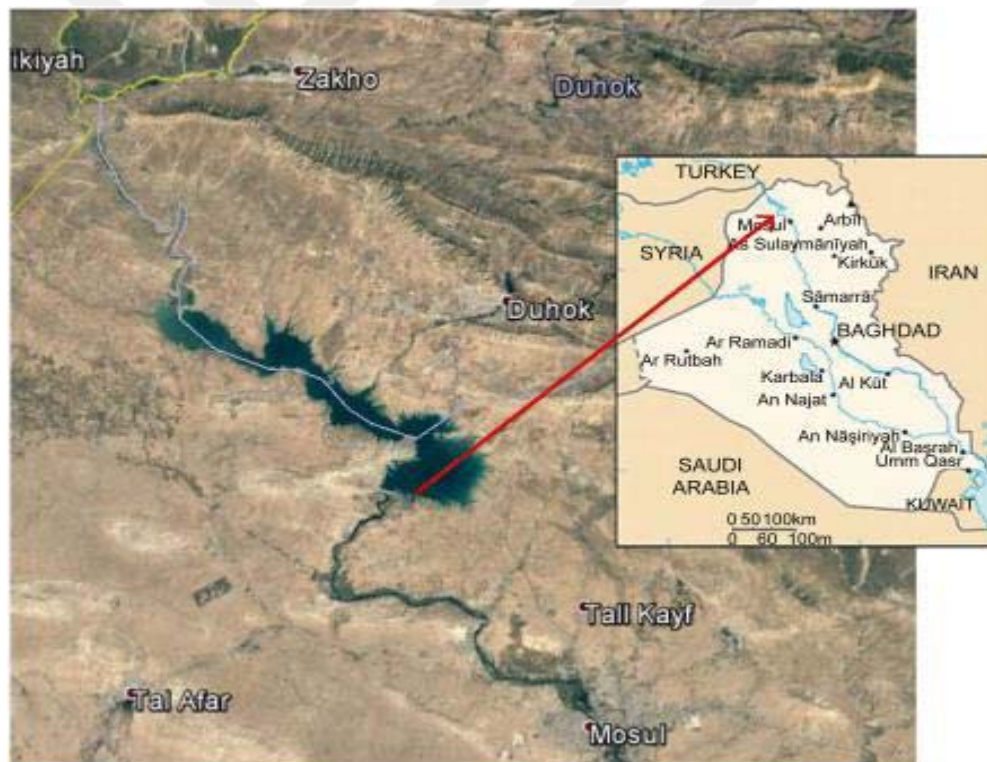


Figure 3.1. Location Map of Study Area[78].

Kralkızı and Dicle dams are integrated project. Such facilities are situated within the Diyarbakır provincial boundaries and are 50 km from downtown Diyarbakır (Figure 3.2). On the Maden River, and 22 km downstream of the Kralkızı Dam, are the Dicle Dam and the hydroelectric power station. The dam was completed in 1997. In the end, Dicle Dam is built to irrigate 128,080 ha. It has provided the city of Diyarbakir with around 85 percent of drinking

water since 2001. The dam has 110 MW of installed hydroelectric capacity. The Kralkızı dam was built in 1985-1997. The Kralkızı Dam acts as a Dicle Dam storage facility. The hydropower plant has a gross installed capacity of 94 MW. The site's latitude is 38,6684530N and its longitude is 40,2012430E. Kralkızı Dam is situated on Maden River, one of the Tigris River 's main tributaries, 81 km from Diyarbakır, and 6 km from Dicle Township. The site's latitude is 38,3697530N and its longitude is 39,9795970E.



**Figure 3.2.** Location map of study area [33]

### 3.2. Water Sample

Seven water samples (Figure 3.3) from Mosul dam and kiralkizi-dicle dam in different locations were selected for the analysis detailed description of water samples and their sample ID is given in Table 3.1



**Figure 3.3.** Water samples

**Table 3.1.** Water samples and their sample ID

| No. | Sample         | Sample ID |
|-----|----------------|-----------|
| 1   | Mosul Water 1  | R36       |
| 2   | Mosul Water 2  | R37       |
| 3   | Mosul Water 3  | R38       |
| 4   | Mosul Water 4  | R39       |
| 5   | Mosul Water 5  | R40       |
| 6   | Dicle Water    | R41       |
| 7   | Kralkızı Water | R42       |

### 3.3. Fish Sample

Five *Cyprinus carpio* fish samples (Figure 3.4) from Mosul dam and dicle dam in different locations were selected for the analysis detailed description of fish samples and their sample ID is given in Table 3.2.



**Figure 3.4.** Fish samples

**Table 3.2.** Fish sample and their sample ID

| No. | Sample     | Sample ID |
|-----|------------|-----------|
| 1   | Mosul Fish | R31       |
| 2   | Mosul Fish | R32       |
| 3   | Mosul Fish | R33       |
| 4   | Dicle Fish | R34       |
| 5   | Dicle Fish | R35       |

### 3.4. Operating Conditions For ICP-MS Instrument

ICP-MS (PerkinElmer ELAN 9000 ICP-MS) the technique has been used for investigation in this research project. The conditions of the operation of the ICP-MS technique for analysis of elements in sample studies are described (Table 3.3) and a picture of the instrument is shown (Figure 3.5).

**Table 3.3.** ICP-MS Operating Conditions and Analytical parameters

| Parameters              | Description                  |
|-------------------------|------------------------------|
| ICP-MS                  | PerkinElmer ELAN 9000 ICP-MS |
| Nebulizer               | Crossflow                    |
| Spray chamber           | Ryton, double-pass           |
| RF power                | 1000 W                       |
| Plasma gas flow rate    | 15 L min <sup>-1</sup>       |
| Auxiliary gas flow rate | 1.0 L min <sup>-1</sup>      |
| Carrier gas flow rate   | 0.9 L min <sup>-1</sup>      |
| Sample uptake rate      | 1.0 mL min <sup>-1</sup>     |
| Detector mode           | Auto                         |
| Integration time        | Element-dependent            |
| Internal standard       | Ir                           |



**Figure 3.5.** Photographic picture of ICP-MS

### 3.5. Sample Preparation:

#### 3.5.1. Sample Preparation for Fish

Fish samples were stored in plastic bags after taking their length were between (38-56 cm ) they were carried to the analytical laboratory belong Chemistry Department at Science Faculty at Firat University, and washed them then prepared small pieces of fish muscle by a stainless steel knife. samples were extracted with ( $\text{HNO}_3$ ) acid, fish samples were collected in different positions in tow dams.

#### 3.5.2. Digestion of Fish Samples (Wet Digestion)

By taking (0.56 –1.54)g of each fish muscles into vessels and (5-8)ml according to weight of species when it was 0.5g, and less added 5ml of nitric acid  $\text{HNO}_3$  but when it was greater than 0.5g we added 8ml of acid, then we put it into the microwave (microwave Mars Xpress) (Figure 3.6) at  $180^\circ\text{C}$  in 20 min for heating and 5 min for cooling by (Balik program) after that took the samples out of a microwave and left it to cool. Then added 15.0 ml of distilled water on each of them some of their solutions are clear not filtrated, and some of their solutions are not clear filtrated to remove any not dissolved particle, then diluted to (18-30) ml with distilled water.



**Figure 3.6.** Photographic picture of Microwave Mars Xpress

### 3.5.3. Sample Preparation for Water

As soon as water samples were taken, nitric acid was added and so, their pH was adjusted to 2.

### 3.5.4. Calibration Graphs

To determine the concentrations of elements in the samples, calibration graphs were obtained as similar in Figures 3.7.

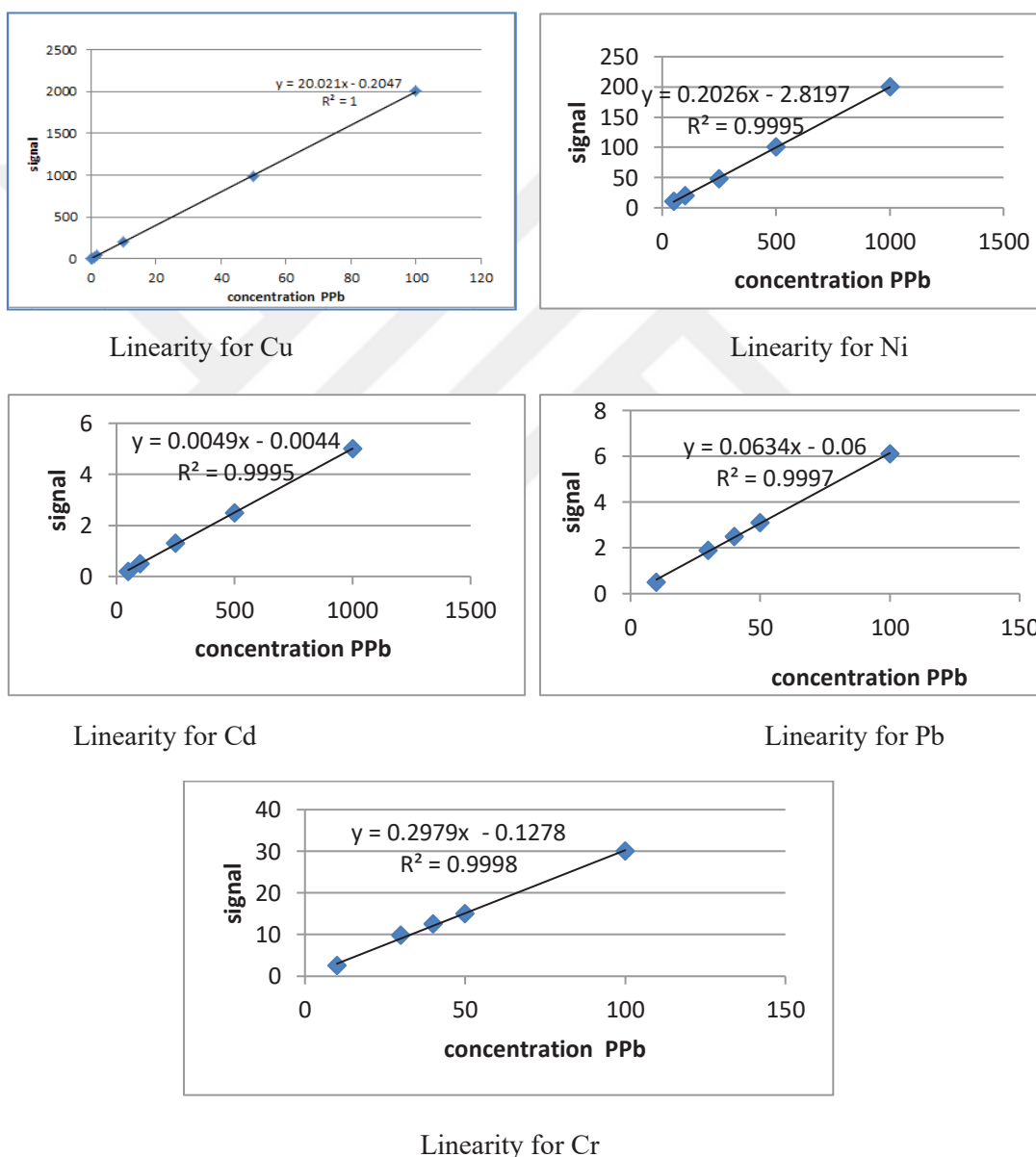


Figure 3.7. Calibration Graphs.

## 4. RESULTS

### 4.1. Concentration of elements in analysed fish and water samples:

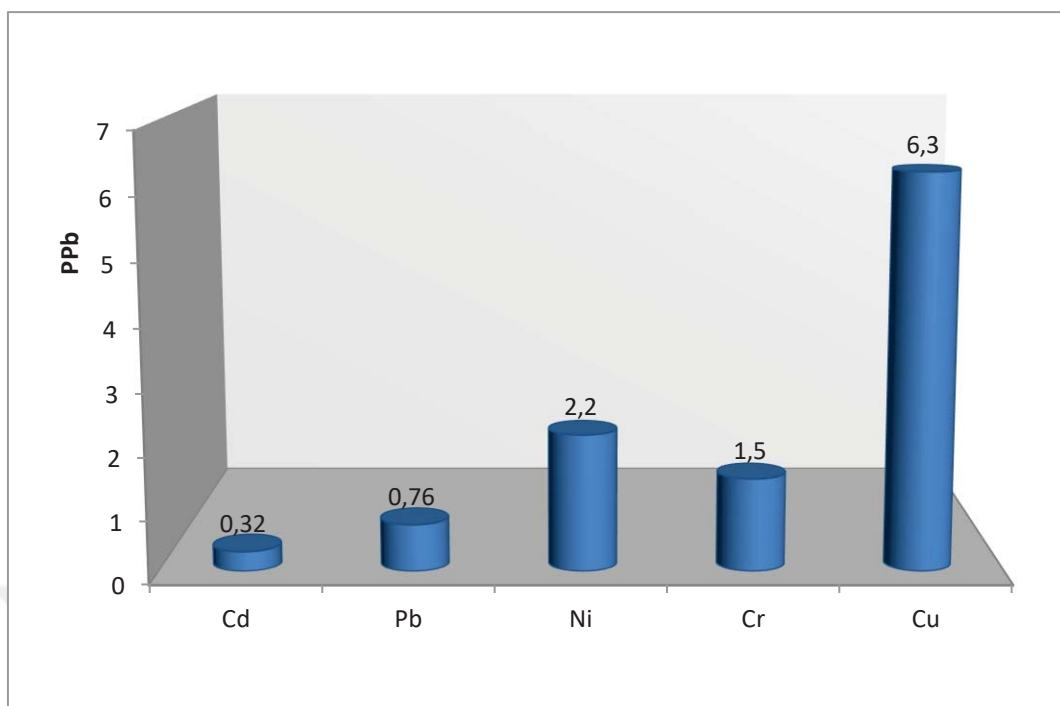
Inductively coupled plasma mass spectroscopy ICP-MS are used to determine the concentration of 5 elements (Cd, Pb, Ni, Cr, Cu) in fish and water samples from Tigris River in Turkey and Iraq in different dam lake.

#### 4.1.1. Elements in Water Samples

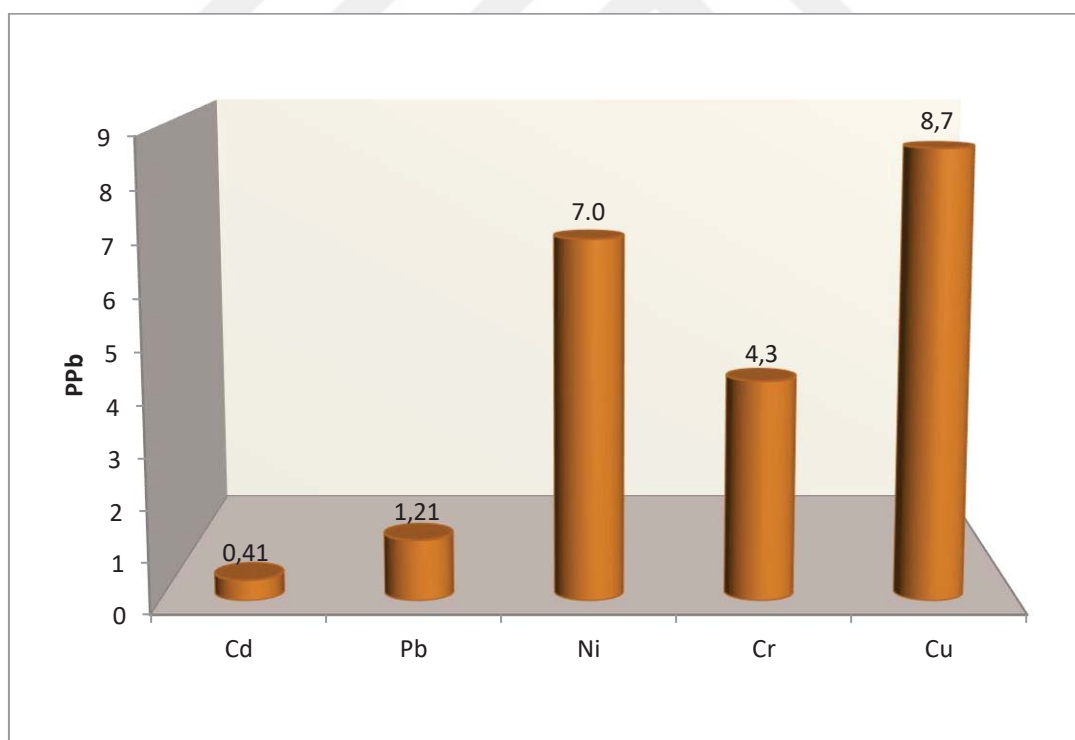
Seven samples of water from different places: 5 of them are from Mosul dam and 2 from kiralkizi-Dicle dam. Table 4.1 show concentration of five elements (Cd, Pb, Ni, Cr, Cu) in all samples with location of those samples (Figures 4.1-4.8).

**Table 4.1.** Element Level for All Water samples, n=3.

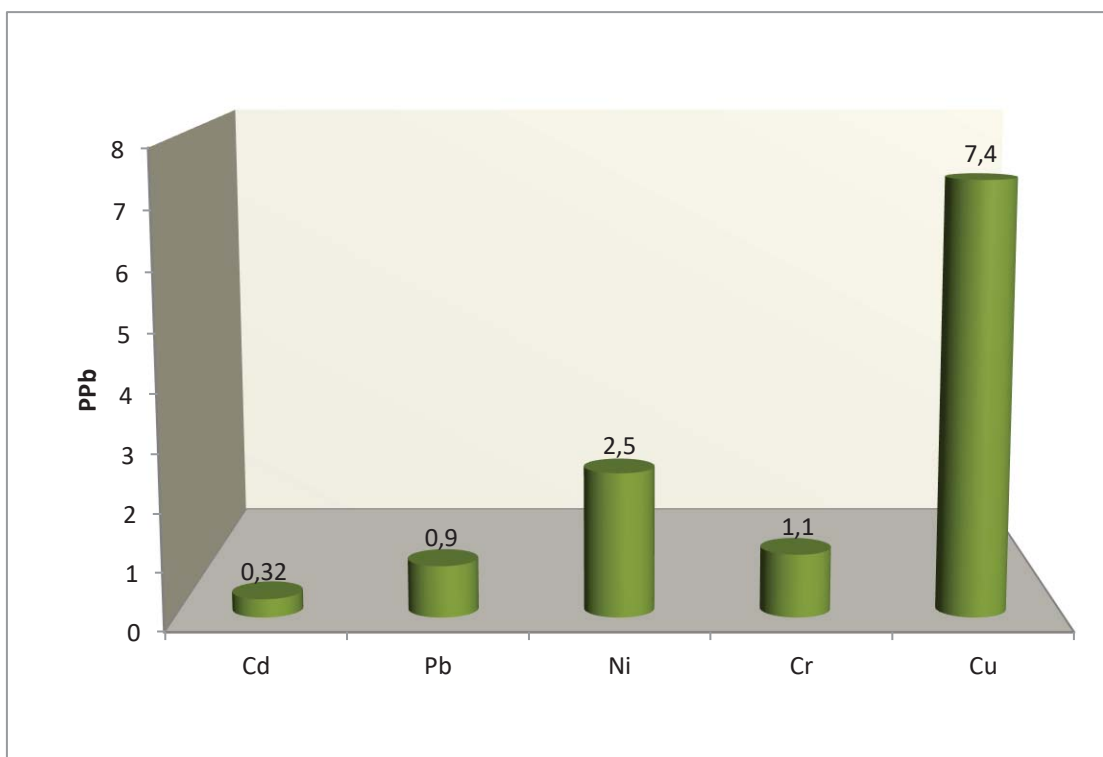
| Location        | Elements  |           |           |           |            |
|-----------------|-----------|-----------|-----------|-----------|------------|
|                 | Cd (µg/L) | Pb (µg/L) | Ni (µg/L) | Cr (µg/L) | Cu ( µg/L) |
| Mosul water 1   | 0.32      | 0.76      | 2.2       | 1.5       | 6.3        |
| Mosul water 2   | 0.41      | 1.21      | 7.0       | 4.3       | 8.7        |
| Mosul water 3   | 0.32      | 0.90      | 2.5       | 1.1       | 7.4        |
| Mosul water 4   | 0.37      | 0.82      | 1.9       | 1.3       | 7.0        |
| Mosul water 5   | 0.34      | 0.63      | 2.0       | 1.6       | 6.0        |
| Dicle water     | 0.35      | 0.54      | 1.5       | 1.3       | 5.6        |
| Kiralkizi water | 0.32      | 0.50      | 1.7       | 1.9       | 6.0        |
| Allowable level | 3         | 10        | 50        | 50        | 1500       |



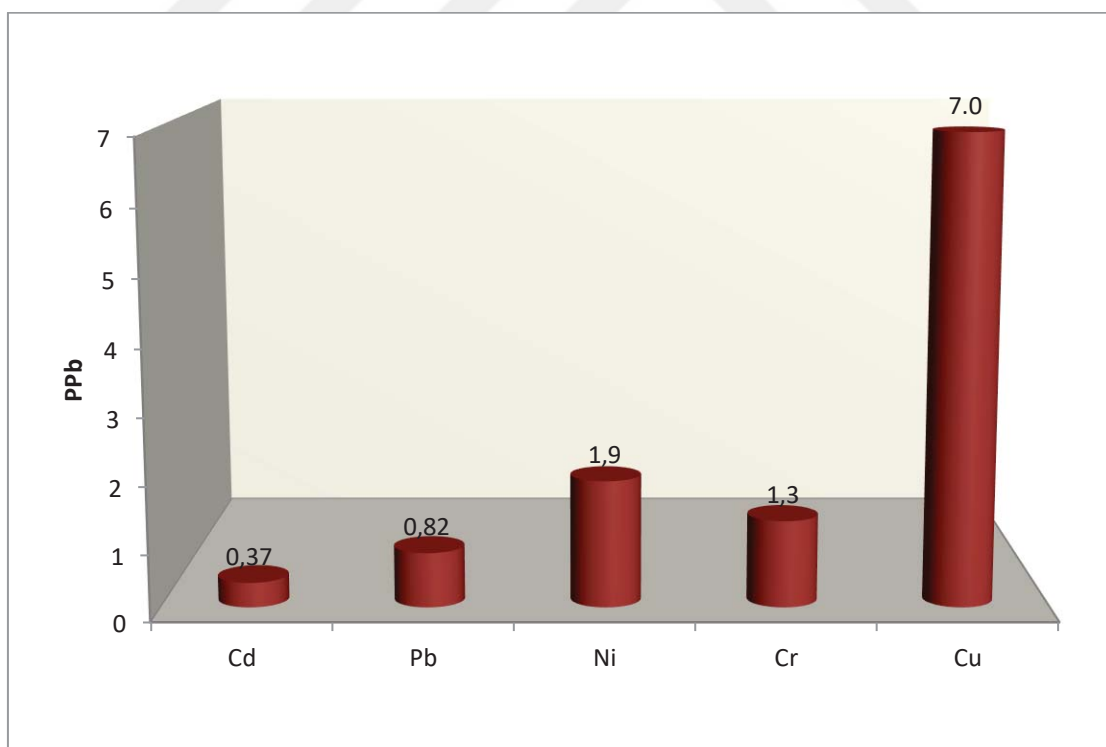
**Figure 4.1.** Element in Mosul water 1



**Figure 4.2.** Element in Mosul water 2



**Figure 4.3.** Element in Mosul Water 3



**Figure 4.4.** Element in Mosul Water 4

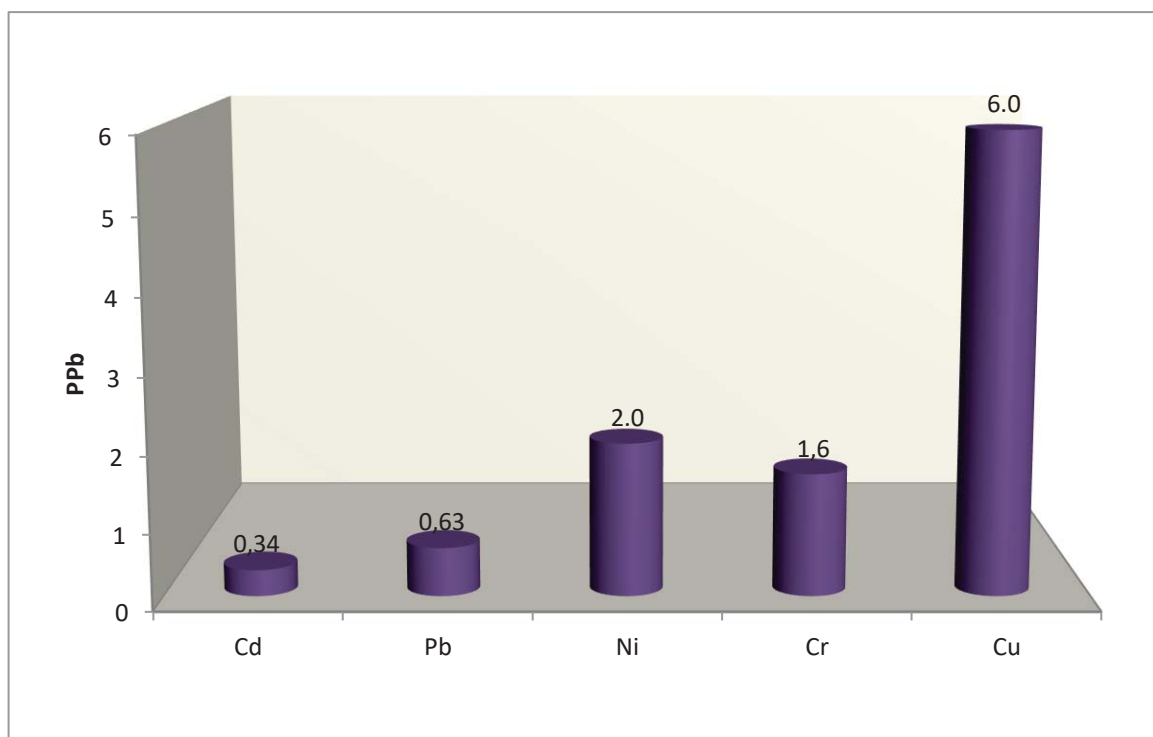


Figure 4.5. Element in Mosul water 5

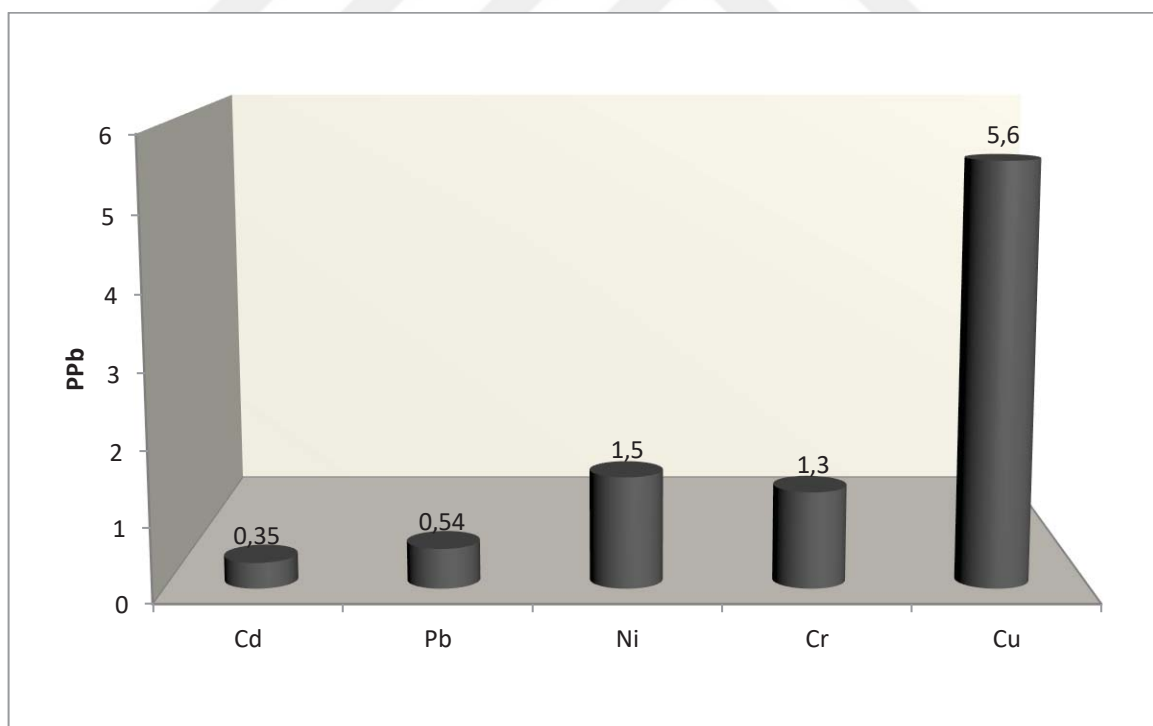
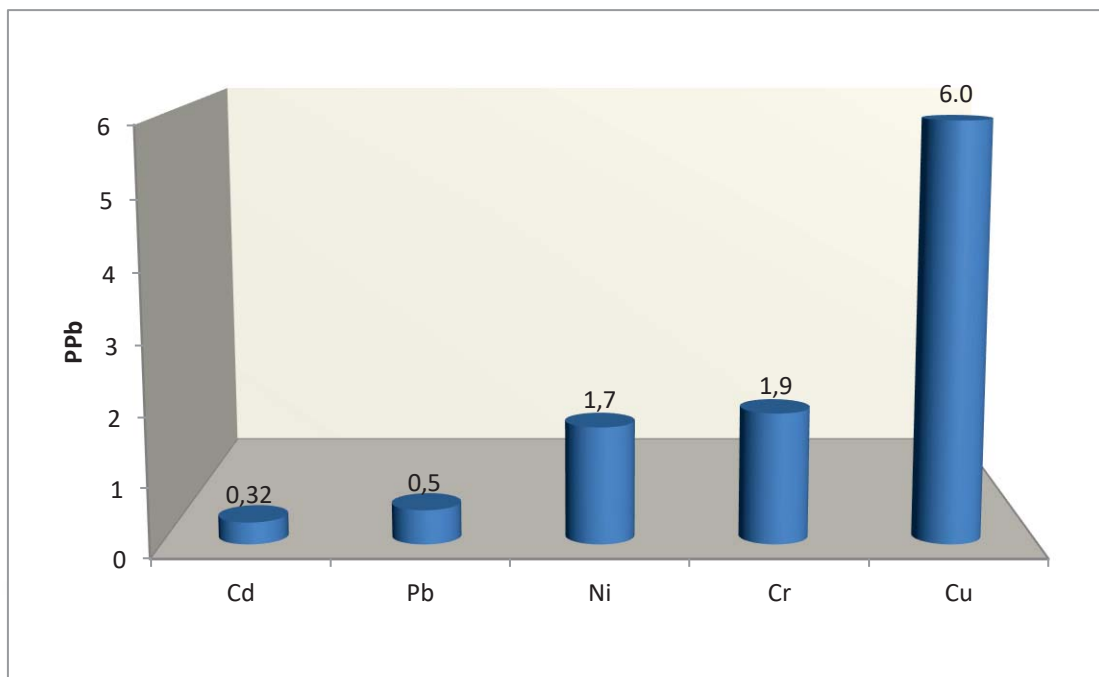
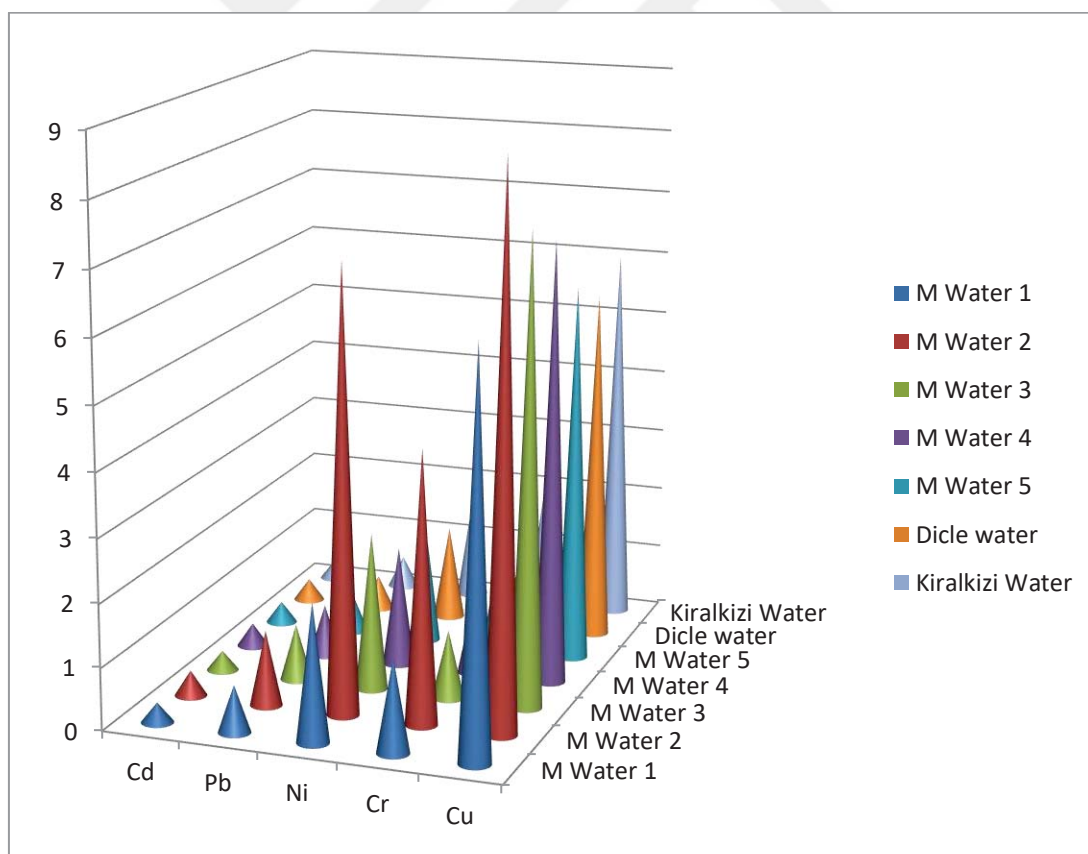


Figure 4.6. Element in Dicle water



**Figure 4.7.** Element in kiralkizi water



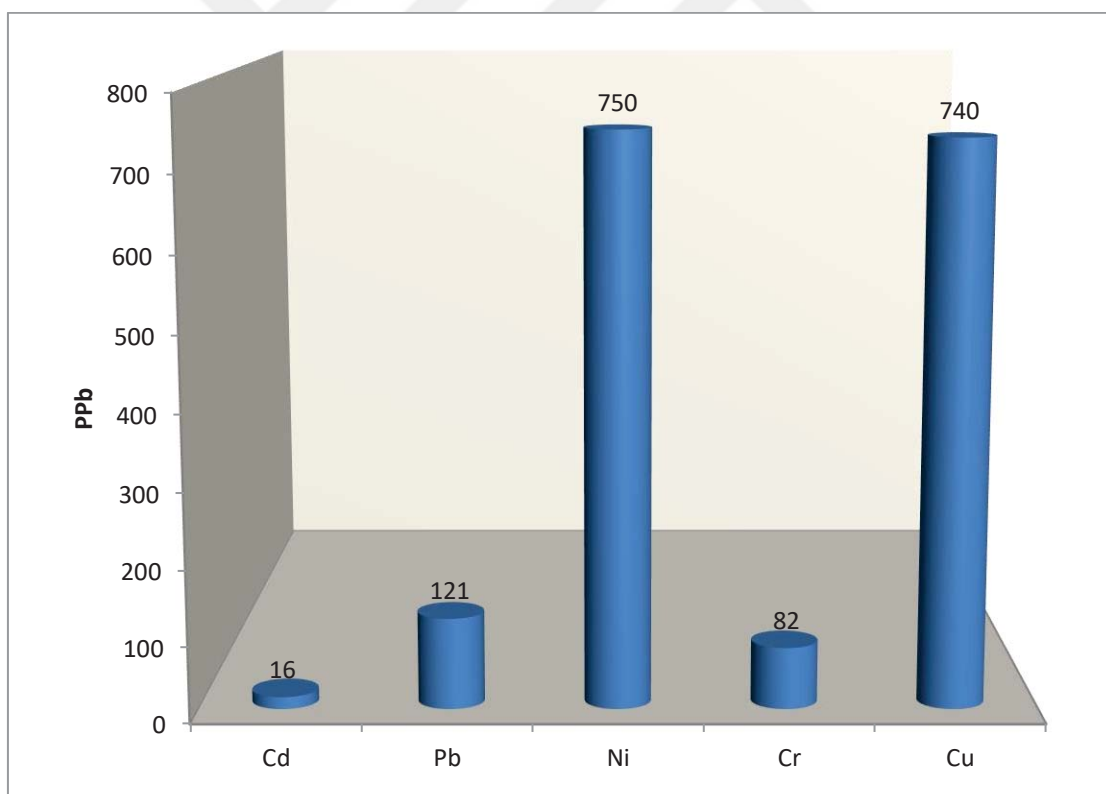
**Figure 4.8.** Elements Level for All Water Samples

#### 4.1.2. Elements in Fish Samples

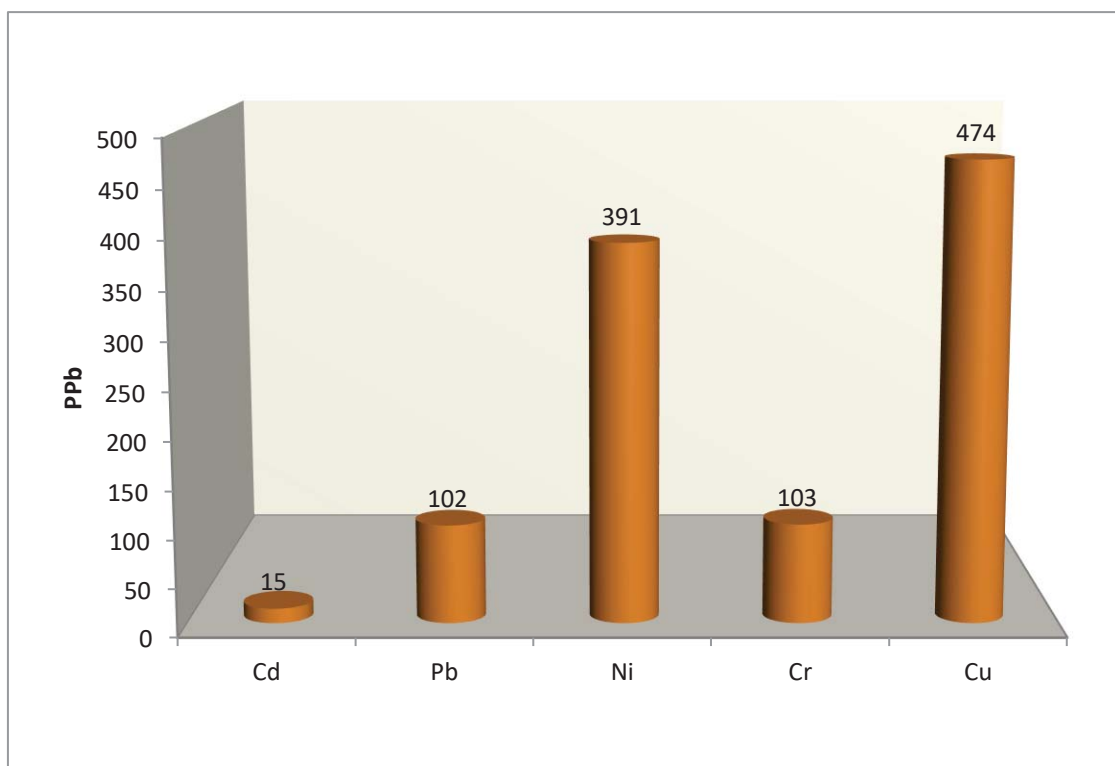
According to fish samples fish samples were collected from different location around Mosul, Dicle dams by the long of Tigris river in Turkey and Iraq 5 samples are collected 3 of them from Mosul, 1 from dicle, and 1 from kiralkizi dams, that shown in Table 4.2 with concentration of five elements (Cd, Pb, Ni, Cr, Cu) in all samples (Figures 4.9-4.14).

**Table 4.2.** Element Concentrations in fish samples, ( $\mu\text{g/kg}$ )

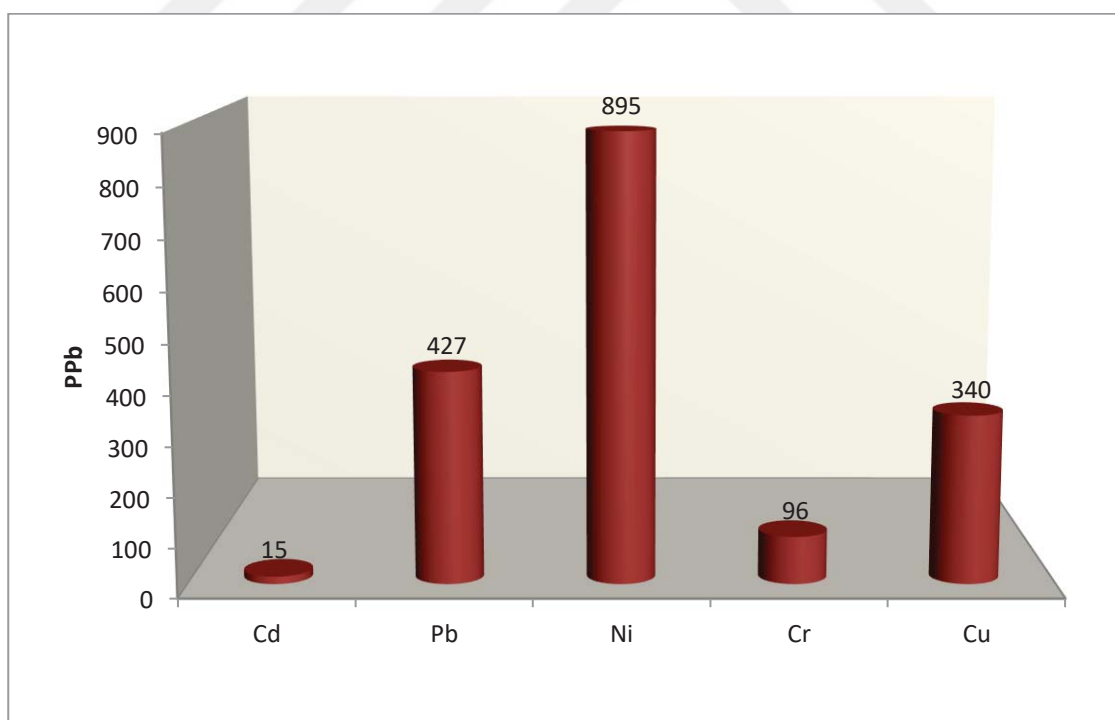
| Samples          | Cd  | Pb  | Ni  | Cr   | Cu    |
|------------------|-----|-----|-----|------|-------|
| Mosul Fish 1     | 16  | 121 | 750 | 82   | 740   |
| Mosul Fish 2     | 15  | 102 | 391 | 103  | 474   |
| Mosul fish 3     | 15  | 427 | 895 | 96   | 340   |
| Dicle fish       | 13  | 131 | 213 | 53   | 968   |
| Dicle fish       | 12  | 139 | 109 | 124  | 164   |
| Allowable levels | 100 | 300 | 500 | 1000 | 20000 |



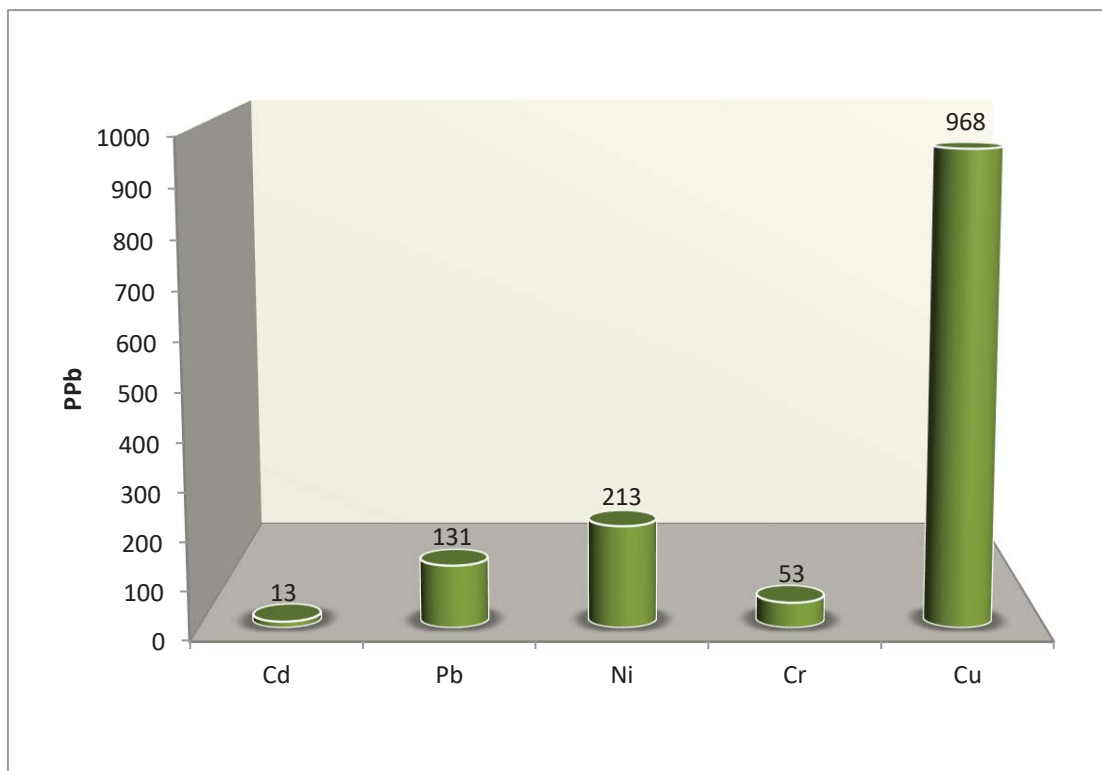
**Figure 4.9.** Elements in Mosul fish 1



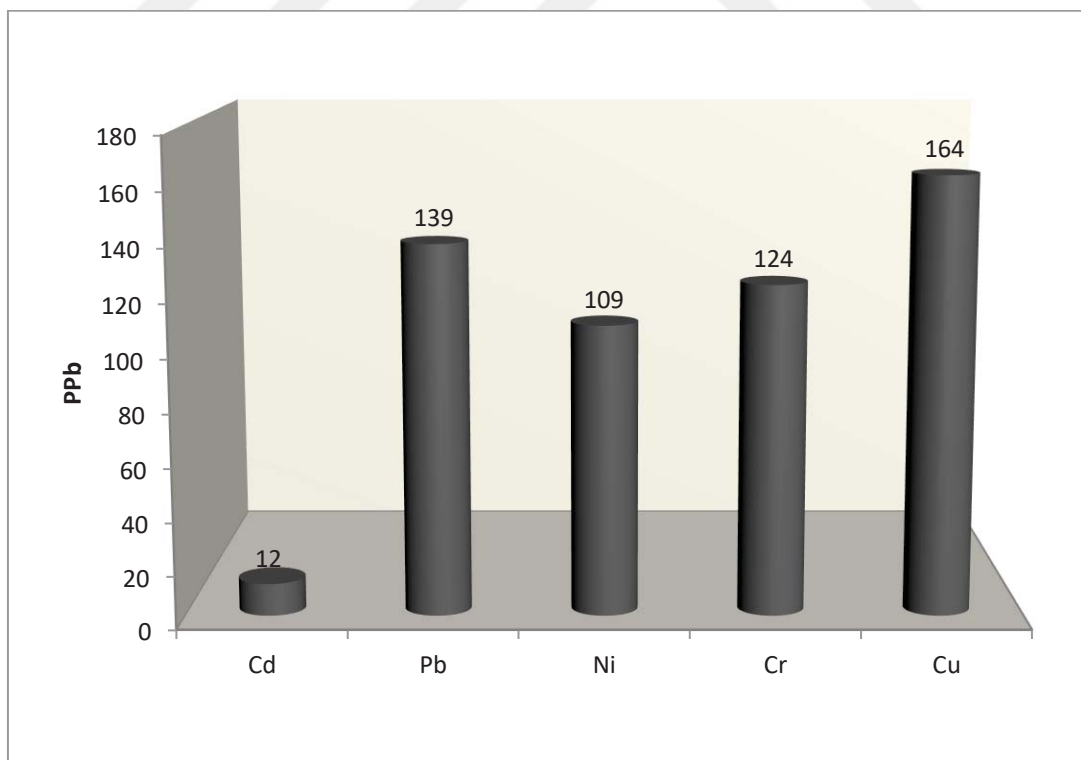
**Figure 4.10.** Elements in Mosul Fish 2



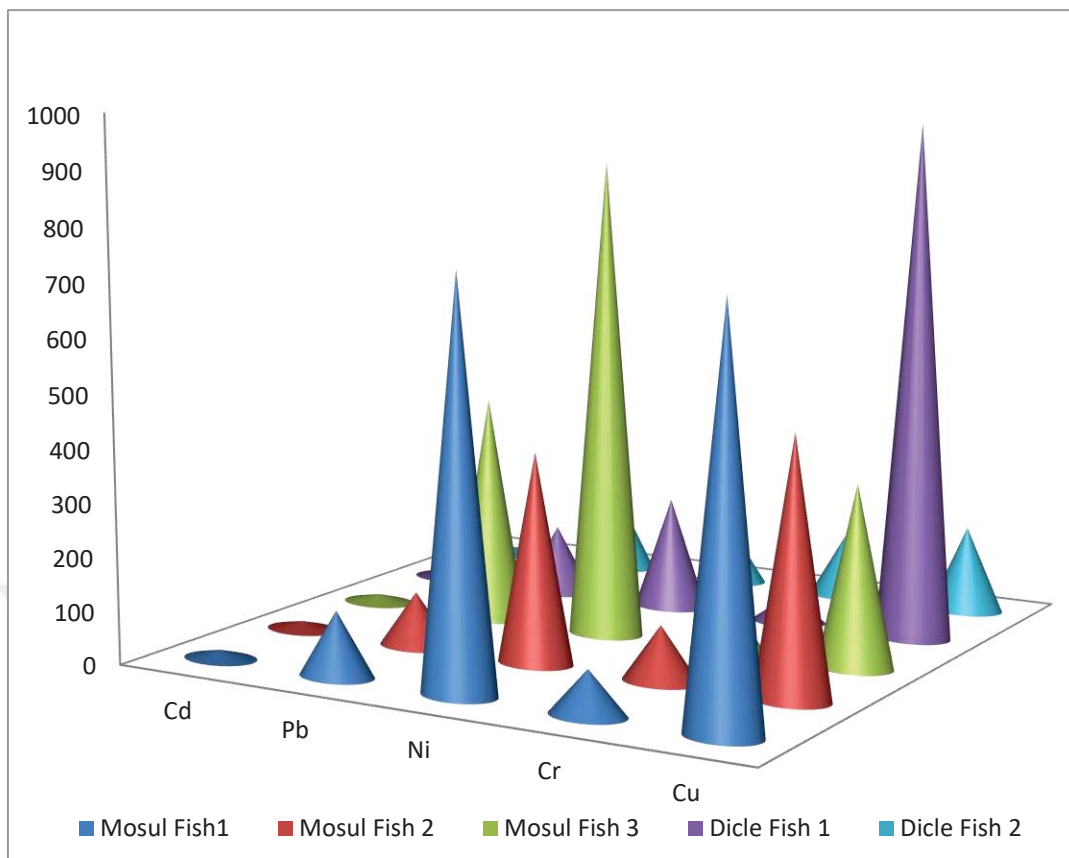
**Figure 4.11.** Element in Mosul water 3



**Figure 4.12.** Element in dicle fish 1



**Figure 4.13.** Element in dicle fish 2



**Figure 4.14.** Elements Level for all Fish Samples

## 4.2. Validation Parameteres

Due to the value of the validation method during the field of chemical analysis, the numerous international organizations and conference released a variety of guidance documents in that subject. Validation method are mean, standard deviation (SD), accuracy, precision, limit of quantification (LOQ), and the limit of detection (LOD).

### 4.2.1. Mean

Mean is the sum of all point then dividing by the number we added.

### 4.2.2. Standard Deviation (SD) and Variance

The SD can be calculated by this equation

$$SD = \sqrt{\frac{\sum_i (x_i - \bar{x})^2}{n-1}} \dots\dots\dots 1$$

The variance is signified by  $S^2$  and standard deviation is the square root of the variance, signified by S are the distribution metrics most widely used. We realize that variance is a

representation of the way a data set is spaced out. This is measured as the average square deviation of each number from a data set mean by this equation[79].

$$\text{Variance} = SD^2 \dots\dots\dots 2$$

#### 4.2.3. Accuracy

The Accuracy is defined as the closeness in between analyte's actual value in the study and the values calculated via the analytical process. Also, we can get the accuracy parameter from relative error[80, 81].

#### 4.2.4. Precision

The Precision is described as relative standard deviation (RSD) which is measured as a percentage of standard deviation divided by the mean of repeated samples[82].

$$RSD = SD / \bar{X} \dots\dots\dots 3$$

Where  $\bar{X}$  is the mean

RSD is multiplying by 100% to obtain percentage relative standard deviation.

#### 4.2.5. Limit of detection (LOD)

LOD is described as the Lowest analyte concentration in a sample that may be detectable but not generally quantitated under the experimental conditions specified [83, 84].

$$LOD = 3.3 \times SD_b / a \dots\dots\dots 4$$

Where  $SD_b$  is standard deviation of blank , and ( $a$ ) is slope in calibration curve line.

#### 4.2.6. Limit of quantification (LOQ)

LOQ is described as an analyte's lowest concentration in a sample which can be measured with reasonable precision and accuracy under the method's specified operating conditions[84, 85].

$$LOQ = 10 \times SD_b / a \dots\dots\dots 5$$

Where  $SD$  is standard deviation of blank , and ( $a$ ) is slope in calibration curve line.

#### 4.2.7. Linearity

Linearity is the variety that can be obtained directly or by a mathematical transition of the results of the analysis, proportional to the analyte concentration over the stipulated range. The calibration curve equation that relates to the variables dependent ( $y$ ) and independent ( $x$ ) are  $y = ax + b$ . The mathematical method based on linear regression was also used to estimate, from

one set of experimental measurements, the coefficients of the calibration curve. For the coefficient of correlation ( $R^2$ ), the value of 0.99 was used as the limit to set the coefficients of the curve[80].

### 4.3. Analytical Performance

It was found that the relative standard deviation (rsd) obtained in this study are between 4%-15%. Related with the accuracy, the results obtained for standard reference materials (SRM) were given in Table 4.3.

**Table 4.3.** Certified and observed results for SRM, ppb.n=3

| SRM                         | Cd    |      | Pb    |      | Cr    |      | Ni    |      | Cu    |      |
|-----------------------------|-------|------|-------|------|-------|------|-------|------|-------|------|
|                             | Cert. | find | Cert. | find | Cert. | Find | Cert. | find | Cert. | find |
| Sps-Sw2<br>surface<br>water | 2.5   | 2.4  | 25    | 24   | 10.0  | 9.5  | 50    | 48   | 100   | 96   |

Cert. is certified.

From those results it can be established that relative error are in ranges of 3%-7%. The LOD and LOQ values were found to be 0.2 and 0.6 ppb for Cd, 0.3 and 0.9 for Pb, 0.3 and 1.0 for Cr, 0.3 and 1.0 for Ni, and 0.4 and 1.1 for Cu, respectively.

## 5. DISCUSSION

In this work, analytes were performed by the inductively coupled plasma mass spectrometry (ICP-MS) that is multiple element analysis, ~1 to 0.001 ppb analytical working range. To determine trace and ultra-trace analyte concentrations, microwave oven MasXpress model was used in the digestion of samples of fishes and water from Iraq and Turkey dam lakes. Using ICP-MS as measurement method, it can be established that relative error are in ranges of 4%-7%. The LOD and LOQ values were found to be 0.2 and 0.6 ppb for Cd, 0.3 and 0.9 for Pb, 0.3 and 1.0 for Cr, 0.3 and 1.0 for Ni, and 0.4 and 1.1 for Cu, respectively. Related with the precision, the relative standard deviation (rsd) were found between 4%-15%. For Turkey's water limit of detection was between 0.046- 13.46 and for Iraq was between 0.174 - 35.51, and the limit of quantification for Turkey was in the range of 0.14 - 40.81 and for Iraq 0.53 - 107.63. Hence Turkey's fishes limit of detection was between 29.61-1349.5 and for Iraq was between 33.55-9494, and the limit of quantification for Turkey was in the range of 89.7-4089.54 and for Iraq 101.68-28769.7, the highest concentration for Iraq water samples was 8.7 µg/L for Cu in location 1, and in Turkey was 6 µg/L also for Cu in Kiralkizi but for fishes, Iraq sample 3 had the highest concentration in Ni 895 µg/L, and Turkey fish samples Dicle 1 had the highest concentration 968 µg/L for Cu. So this was our purpose from this study to detect the concentration of heavy metals between Iraq and Turkey from water and fish samples.

## 6. CONCLUSION

The purpose of this study is to compare the concentration of heavy metals in the water and fish samples taken from Dicle river in Iraq and Turkey. The results showed that the concentrations of the elements studied from Iraq are generally higher than from Turkey. This can be attributed to chemical wars and weapon many years ago and many other sources of pollution. For this study, ICP-MS was used to identify metals concentration that is multiple element analysis, ~1 to 0.001 ppb analytical working range.

It is predicted that conducting similar studies should be periodically worked. So, some elements may be found as differently regarding the toxic Cd, Pb, Ni and Cr.



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# CURRICULUM VITAE



## PERSONAL INFORMATIONS

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### Researcher Information

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### EDUCATION

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**Master Degree** : “Comparison of Element Concentrations in Water and Fish Samples from Mosul Dam Lake in Iraq and Kralkızı-Dicle Lakes in Turkey”

Firat University, GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES, Department of Chemistry, 2021

Supervisor: Prof. Dr. Mehmet YAMAN

**Bachelor** : Zakho University, Faculty of Science, Department of Chemistry, 2017

**High School** : Veen, Zakho City, 2013

### RESEARCH EXPERIENCES

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✓ Laboratory Instruments you use, Microwave Oven, ICP-MS.....

### WORK EXPERIENCE

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**2014 – 2015: I worked with (people in need) organization**

**2015 – 2016: I worked in the General Hospital in Zakho**

**2018 - 2020: Teaching in High School**