

FIRAT UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
T Ü R K İ Y E



**INVESTIGATION OF HEAVY METAL CONTENTS IN THE
SEDIMENT AND WASTE WATER ALONG THE ARAB-KAND
CHANNEL (ERBIL, NORTH OF IRAQ)**

Rezhna ALI RASOOL

Master's Thesis

DEPARTMENT OF GEOLOGICAL ENGINEERING

Program of

Division of Mineral Deposits-Geochemistry

FEBRUARY 2023

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Title: Investigation Of Heavy Metal Contents İn The Sediment and Waste Water
Along The Arab-Kand Channel (Erbil, North Of Iraq)

Author: Rezhna ALI RASOOL

Submission Date: 11 January 2023

Defense Date: 06 February 2023

THESIS APPROVAL

This thesis, which was prepared according to the thesis writing rules of the Graduate School of Natural and Applied Sciences, Fırat University, was evaluated by the committee members who have signed the following signatures and was unanimously approved after the defense exam made open to the academic audience.

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..... / / 20

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DECLARATION

I hereby declare that I wrote this Master's Thesis titled “Investigation Of Heavy Metal Contents In The Sediment and Waste Water Along The Arab-Kand Channel (Erbil, North Of Iraq)” in consistent with the thesis writing guide of the Graduate School of Natural and Applied Sciences, Firat 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.

06 February 2023

Rezhna ALI RASOOL



PREFACE

In addition, this study was supported by Firat University with the project numbered MF.21.39. We thank Firat University for their support.

First of all thanks for Allah to giving us the ability to do this research, a special thanks to my parent and my husband to supporting me all the time.

We would like to express our deepest thanks and respect to my supervisor, Prof.Dr. Ahmet ŞAŞMAZ for his help supervision and guidance and support to accomplish this study and dr. Mariwan Akram Chnaray he helped me a lot, Iam very grateful to him.

Finally, I would like to express my special thanks to all who helped me to finish this research.



Rezhna ALI RASOOL
ELAZIG, 2023

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ABSTRACT

Investigation Of Heavy Metal Contents In The Sediment and Waste Water Along The Arab-Kand Channel (Erbil, North Of Iraq)

Rezhna ALI RASOOL

Master's Thesis

FIRAT UNIVERSITY
Graduate School of Natural and Applied Sciences
Department of Geological Engineering

February 2023, Page: x + 28

Erbil city wastewater flows along the Arap-Kand Channel from Turak town to Zap water for about 40 km. This work is approximately 40 km. In this study, it is aimed to examine the dimensions of heavy metal pollution in the water and sediments in the canal along the length of the canal route. For this purpose, sediment samples were taken from 5 different points and water samples from 3 different points along the canal route at different distances from Erbil to the south. These water and sediment samples were analyzed for approximately 70 elements in the Acme (Canada) analysis laboratory. At the same time, anion and cation analyzes and physicochemical parameters of the contaminated water samples were also measured.

As a result of these studies, both wastewater and sediments along the Arap-Kand Canal in the region were heavily polluted by heavy metals. In particular, metals such as Sr, Zn, Pb, Cd and Ni were significantly enriched in both water and sediments. Although these wastewaters are also highly polluted from a biological point of view, the fact that the farms in the region use both animal watering and agricultural irrigation will cause important public health problems for both the environment and the food chain in the future. These waters should never be used for irrigation and drinking purposes.

Keywords: Arap-Kand channel, wastewater, heavy metal pollution

ÖZET

Arap-Kand Kanalı Boyunca (Erbil, Kuzey Irak) Sediment ve Atık Sulardaki Ağır Metal İçeriklerinin Araştırılması

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Yüksek Lisans Tezi

FIRAT ÜNİVERSİTESİ
Fen Bilimleri Enstitüsü

Jeoloji Mühendisliği Anabilim Dalı

Şubat 2023, Sayfa: x + 28

Erbil şehri atıksuyu, Arap-Kand kanalı boyunca Turak kasabasından Zap suyuna yaklaşık 40 km boyunca akmaktadır. Bu çalışma yaklaşık 40 km. uzunluğundaki kanal güzergahı boyunca kanal içindeki su ve sedimentlerdeki ağır metal kirliliğinin boyutlarının incelenmesini amaçlanmıştır. Bu amaç için Erbil'den güneye doğru farklı mesafelerde kanal güzergahı boyunca 5 farklı noktadan sediment örneği, 3 ayrı noktadan ise su örnekleri alınmıştır. Bu su ve sediment örnekleri Acme (Kanada) analiz laboratuvarında yaklaşık 70 element için analizleri yapılmıştır. Aynı zamanda kirlenmiş su örneklerinin anyon ve katyon analizleri ile fizikokimyasal parametreleri de ölçülmüştür.

Bu çalışmaların sonucunda, yöredeki Arap-Kand kanalı boyunca hem atık sular, hem de sedimentler yoğun olarak ağır metallerce kirlenmiştir. Özellikle, Sr, Zn, Pb, Cd ve Ni gibi metaller, hem suda, hem de sedimentlerde önemli oranda zenginleşmiştir. Bu atık sular biyolojik açıdan da önemli oranda kirlenmiş olmasına rağmen, yöredeki çiftlikler hem hayvanların sulanması, hem de tarımsal sulama da kullanıyor olması, gelecekte hem çevre hem de gıda zinciri için önemli halk sağlık problemlerine yol açacaktır. Bu suların kesinlikle sulama ve içme amaçlı kesinlikle kullanılmamalıdır.

Anahtar Kelimeler: Arap-Kand kanalı, atık su, ağır metal kirliliği

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1. INTRODUCTION

Heavy metals are the most important environmental contaminants, and their toxicity is a problem of increasing significance for evolutionary, ecological, environmental and nutritional reasons. The term “heavy metals” refers to any metallic element that is toxic or poisonous even at low concentration and has a relatively high density (Marfo, 2014). “Heavy metals” are the metalloids and metals with atomic density greater than 4 g/cm³, or 5 times or more, greater than water (Gill, 2014). Heavy metals include iron (Fe), chromium (Cr), silver (Ag), cadmium (Cd), zinc (Zn), lead (Pb), nickel (Ni), arsenic (As), cobalt (Co) and iron (Fe), the platinum group elements (Tchounwou et al., 2012). Environment; is defined as the external environment in which the living beings that live on the earth continue their relationships throughout their lives and is also called "Ecosystem" for short (Costanzo et al., 2005). Furthermore, water, soil and air are considered as the main physical elements of nature. They all together have an impact on the vital activities of living organisms on earth thus when these elements are polluted, they can negatively effect on any living organisms living in the area and cause structural damage on the inanimate environment elements and disturb their qualities and this is called "Environmental Pollution". Besides the comfort that the developing technology brings to life, the size of the pollution that this development gives to the nature and the environment increases with increasing speed. These developments aimed at making life more perfect, healthier and prolonged life. However, in recent years it has damaged water, air, soil vegetation and animal, but also it ruined natural resources both in rural and urban areas. Environmental pollutions can be categorized based on sources such as: 1) Migrations and irregular urbanization. 2) Energy, water, paper, coal etc. used per person. Increase. 3) The destruction of forests, fires and erosion. 4) Overgrazing and destruction of natural vegetation cover. 5) Air pollution caused by heat in houses and workplaces. 6) Motor vehicles and marine vehicles. 7) Mineral, lime, stone and sand quarries, 8) Fertilizers and pesticides, 9) Atmospheric events and natural disasters. 10) The supply of sewage waters to the receiving environment without purification and use in the water. 11) Solid wastes and rubbish. 12) Drying of wetlands and lakes. 13) Misuse of land. 14) Illegal fishing. 15) Radiation from medical devices such as TV, computer and x-ray. 16) Industrial and urban noise (Egboka et al., 1989). Metal intake abilities of plants vary in large intervals and the plants which take up high amounts of metals are defined as “hyperaccumulator plants.” Criteria for “hyperaccumulator plants” are described as metal contents in

shoot dry matter (Cd >100 ppm, Cu >1000 ppm, Pb>1000 ppm, Zn>10000 ppm), the ability to store heavy metals in above-ground parts 10-500 times more than in usual plants, and an enrichment coefficient >1 (Kalashnikova et al., 2011). The inorganic substance intake ability of plants is also considered for the rehabilitation of contaminated environments due to industrial and mining activities. This relatively new approach is called phytoremediation, which is defined as the use of plants to remove, destroy or sequester hazardous substances from the environment. Phytoremediation has become a topical research field in the last decades as it has emerged as a cheap and effective natural way of rehabilitation of the environment. Many metal hyperaccumulators have so far been discovered as a result of scientific work on the subject (Peer et al., 2005).

Heavy metals are described as metallic elements that have an incredibly excessive density in contrast to water (Paul et al., 2012). It has been reported that metals such as cobalt (Co), copper (Cu), chromium (Cr), iron (Fe), magnesium (Mg), manganese (Mn), molybdenum (Mo), nickel (Ni), selenium (Se) and zinc (Zn) are critical vitamins that are required for a range of biochemical and physiological functions. Inadequate provision of these micro-nutrients consequences in a range of deficiency ailments or syndromes. The level of toxicity of some chosen metals for human beings follows the sequence $Co < Al < Cr < Pb < Ni < Zn < Cu < Cd < Hg$. The damaging outcomes of heavy metals in people depends on their dosage, rate of emission and length of exposure. In general, the chemical elements with the strongest metallic personality are localized in the decrease left nook of the table and those with the clearest character as non-metals are to be found in the upper proper corner. The metals decrease from left to right and from the backside to the top. Metalloids are localized around the so fashioned diagonal borderline. This capability chemical factors having a greater or less metal character. Metals can be labeled in accordance to their outer electronic sub-shell in the atom. All these uncommon earth elements are additionally metals and are consequently from time to time referred to as uncommon earth metals.

With the assumption that heaviness and toxicity are interrelated, in recent years, there has been a growing ecological and international public health subject related with environmental contamination by using these metals. Also, human exposure has risen dramatically as a end result of an exponential amplify of their use in numerous industrial, agricultural, home and technological functions. Environmental air pollution is very distinguished in factor source areas such as mining, foundries and smelters, and other metal-based industrial operations (Paul et al., 2012).

Although heavy metals are naturally going on factors that are located at some stage in the earth's crust, most environmental illness and human exposure result from anthropogenic things to do such as mining and smelting operations, industrial production and use, and home and agricultural use of metals and metal-containing compounds. Natural phenomena such as weathering and volcanic eruptions have also been mentioned to considerably make a contribution to heavy metal pollution. Industrial sources consist of steel processing in refineries, coal burning in power plants, petroleum combustion, nuclear energy stations and excessive anxiety lines, plastics, textiles, microelectronics, wooden maintenance and paper processing plant life (Paul et al., 2012).

Various kinds of heavy metals are released from unique industrial manufacturing processes, such as Cr, Cd, Ni, Cu, Zn, As, and Pb are considered most toxic among them. These metals are tremendously soluble in water and can be taken by aquatic organisms. The treatment of wastewater, therefore, must be necessary earlier than its discharge to the environment. For the treatment of wastewater, conventional approaches such as ion exchange, chemical precipitation, and electrochemical elimination can be used for the elimination of heavy metals from industrial effluent. The hazards of these tactics are that there is incomplete elimination of heavy metals, high-strength resources, and poisonous sludge is produced (Amjad et al., 2020).

Various human activities and processing of specific purposes are the primary sources of the metals contaminations into the environment. Hence, metals are now not affected by using microorganisms (non-biodegradable) and gathered in the environment and disturb the food chain. The extraction from ores and processing for more than a few applications, the mobility of heavy metals through man has led to the emission of these elements into the environment. Heavy metals are non-bio gradable and therefore accrued in the environment and ultimately contaminate the meals chain. Their pollution causes hazardous results on the environment. Carcinogen, teratogenic and endocrine disruptors effects are discovered of heavy metals and specially conduct modifications in youth (Amjad et al., 2020).

Municipal wastewater is a predominant source of pollution in aquatic environments. The remaining satisfactory of sewage sludge, which is the essential spinoff of the wastewater cure process, mostly relies upon on the chemical composition of the influent wastewater and its treatment procedures (Agoro et al., 2020). Various contaminants in the wastewater accumulate in sewage sludge, and therefore discharge of the sludge into waterbodies would expand natural load quite with a corresponding discount in dissolved oxygen degrees and nutrient enrichment (Agoro et al., 2020). In

most instances, processes generally used in the remedy of wastewater do now not warranty the quantitative removal of many contaminants, and subsequently may want to lead to another spherical of environmental pollution after discharge (Agoro et al., 2020). The contaminants in the discharged wastewater should be organic or chemical in nature. The most common chemical pollutants in wastewater include heavy metal cations, hydrocarbons, pesticides, nitrogenous compounds, pharmaceutical residues, detergents and phosphorus. Microbiological contamination could be from either animal or human fecal wastes containing different kinds of protozoa, viruses and bacteria, capable of causing diseases in humans. Similarly, the treatment of wastewater could be biological or chemical. Biological treatment employs naturally occurring microorganisms to convert the dissolved organic matter in the wastewater into dense biomass, which can be removed from the treated wastewater by sedimentation. The dissolved organic matter serves as food for the microorganisms, and so, the amount of sludge produced is far less environmentally friendly compared to the chemical method; hence, it is more commonly used. However, it is inefficient in the removal of toxic and non-biodegradable compounds. Various technologies used in this process include oxidation ponds, aeration lagoons, anaerobic lagoons, aerobic and anaerobic bioreactors, activated sludge, percolating or trickling filters, biological filters, rotating biological contractors, and biological removal of nutrients (Agoro et al., 2020).

The chemical process, on the other hand, seems to be more efficient, although the chemical additives used in most cases are very expensive and quite hazardous to the environment. Besides, a large portion of the pollutants in this category is usually not removed at the end of the process, and the cost of maintenance and regeneration is high. Disposal of the large quantity of sludge generated from this process is another cause for concern. Sludge reuse in agriculture as a soil conditioner is common in many countries because of its high organic matter and nutrient contents. However, reports have shown that this exercise often leads inadvertently to the accumulation of pollutants in soils, thus contaminating groundwater by leaching through the soil profile under certain conditions (Agoro et al., 2020). High amounts of certain metallic elements including Cd, Ni, and Zn have been found resulting from soil treatment with sewage sludge. Some of the chemical processes frequently used include chemical precipitation, ion exchange, neutralization, adsorption, disinfection (using chlorination/dechlorination, ozone, or ultraviolet radiation) and floatation, among others (Agoro et al., 2020).

A number of studies in South Africa [and other regions of the world, including Kenya, Iran, Tunisia, Poland, China, and the United States, among others have documented heavy metal contaminations in soil and aquatic environments. For instance,

Shamuyarira and Gumbo reported the occurrence of high levels of Cd, Pb, Zn and Cu, above the recommended guidelines, in sludge samples collected from five different locations in the Limpopo area of South Africa. Similarly high heavy metal concentrations for Hg, Ti, Pb Cr, Cd and Ni were recorded in soil and some wastewater samples (Agoro et al., 2020).

Soil contamination by heavy metals is of most important apprehension all through the industrialized world. Heavy steel air pollution no longer only end result in adverse effects on quite a number parameters touching on to plant first-class and yield but additionally motive adjustments in the size, composition and undertaking of the microbial community (Jiwan and Ajay, 2011). Therefore, heavy metals are considered as one of the fundamental sources of soil pollution. Heavy metal air pollution of the soil is prompted through a variety of metals especially Cu, Ni, Cd, Zn, Cr, and Pb the negative consequences of heavy metals on soil biological and biochemical homes are nicely documented. The soil properties i.e. organic matter, clay contents and pH have most important influences on the extent of the results of metals on organic and biochemical properties (Jiwan and Ajay, 2011).

Heavy metals showcase toxic role in the restoration of contaminated ecosystems cautioned that heavy metals caused a decrease in bacterial species richness and a relative make bigger in soil actinomycetes or even decreases in each the biomass and variety of the bacterial communities in contaminated soils. The order of inhibition of urease endeavor generally Diversity and exercise of soil microbes play enormous roles in recycling of plant nutrients, preservation of soil structure, cleansing of noxious chemical substances and the control of plant pests and plant boom communities are vital indices of soil quality. It is important to investigate the functioning of soil microorganisms in ecosystems exposed to long-Term infection by using heavy metals(). Chromium is typically existing in soils as Cr (III) and Cr (VI), which are characterized by using awesome chemical houses and toxicities. Cr (VI) is a study oxidizing agent and is tremendously toxic, whereas Cr (III) is a micronutrient and a non-hazardous species 10 to a hundred instances much less poisonous than Cr (VI. Have been stated to reason shifts in the composition of soil microbial populations, and known to purpose hazardous outcomes on microbial mobile in usual, an increase of metal attention adversely influences soil microbial residences e.g. respiratory rate, enzyme undertaking (Jiwan and Ajay, 2011).

The aim of this study is to assess the level of metal concentrations in surface sediments in the Arab-Kand Channel which is a major Channel draining into a Greater-

Zab River, examining the occurrence and distribution of metals and to explore the effect on heavy metals on soil and water.



2. MATERIAL AND METHODS

2.1. Study Area

As a case study, Arab-Kand village was selected for this research. It's located south west of Erbil city, about 10 km. Since the village was build long time ago without master plan, no legal registration was performed for the ownership of land parcels and houses. Both the houses and land division were made randomly without having a master plan to control the growth of the village (Ismael et al., 2019).



Figure 2.1. Arab kand location on map

The study focuses on Arab-Kand channel which lengthen from SW of Erbil City to NS of Guer town, which its length about 50 km. 24 stations are taken along the channel with about two km spacing between adjoining station (Figure 2.1 and 2.2). The soil is brown soil. This type of soil happens in areas where there is hot dry summer and cold wet winter (Mariwan et al., 2010).The thickness of floor layer is about 42-57 cm, and whole soil depth is about 42-141 cm. Soil texture ranges from silty clay to sandy clay, high clay content, and the natural remember content tiers from 0.15 to 1.26 this ratio viewed much less than the different close by areas which has less vegetate cowl (Mariwan et al., 2010).The climate of studied place is most intently strategies the Irano-

Turanian type. Characterized by using occurrences of three season, bloodless winter, slight grow length of spring and hot dry summer. The period from June to quit of September is besides rainfall; the place as wettest months are between December and May (Mariwan et al., 2010).



Figure 2.2. Location maps of the central part of the Erbil Basin (Dizayee, 2014).

The studied vicinity is placed between Latitude $36^{\circ} 03' 29''$ E to $36^{\circ}10' 45''$ E and Longitude $43^{\circ} 30' 29''$ N to $43^{\circ} 56' 11''$ N at south west of Erbil province and lengthen to north east of Guer city inside whole length area about (50 km). (Mariwan et al., 2010).

The studied area is situated in the north of Iraq (Figure 2.3) between latitude $36^{\circ}10' 45''$ E to $36^{\circ} 03' 29''$ E and longitude $43^{\circ} 56' 11''$ N to $43^{\circ} 30' 29''$ N , by using GPS

(Garmin type) .The study focuses on Arab-Kand channel which extend from SW of Erbil City to NS of Guer town, which its length about 50 km. 10 stations are taken along the channel with about 2 km spacing between adjacent station (Figure 2.2). The total elevation difference between stations 1 and 10 is about 1000 m. The sampling location is given in Figure 2.2 and 2.3.



Figure 2.3. Erbil wastewater channel at the Turaq village

2.2. Geological setting

Arab-Kand channel is a part of the unstable shelf zone that affected by Alpine orogeny in Mesozoic (Buday and Jassim, 1987) as shown in, in chamchamal-butma sub zone in foot hill zone. The main structures of studied area are Guer fold in north (Al-tamemi, 2002), Awana mountain series at middle area at SW Erbil.

Erbil Basin is the largest reservoir for groundwater in the Erbil Province (Figure 2.3). The Erbil Basin covers about area of 3,200 km² and has a depth of approximately 800 meters. This basin is one of the most important groundwater basins in the Middle East because of its nearness to the surface, not to mention the quantity and quality of its water.

Arab-Kand channel is a part of the unstable shelf zone that affected by Alpine orogeny in Mesozoic (Buday and Jassim, 1987) as shown in Figure 2.4, in chamchamal-butma sub zone in foot hill zone. The main structures of studied area are Guer fold in north Awana mountain series at middle area at SW Erbil (Al-Tamemi, 2002).

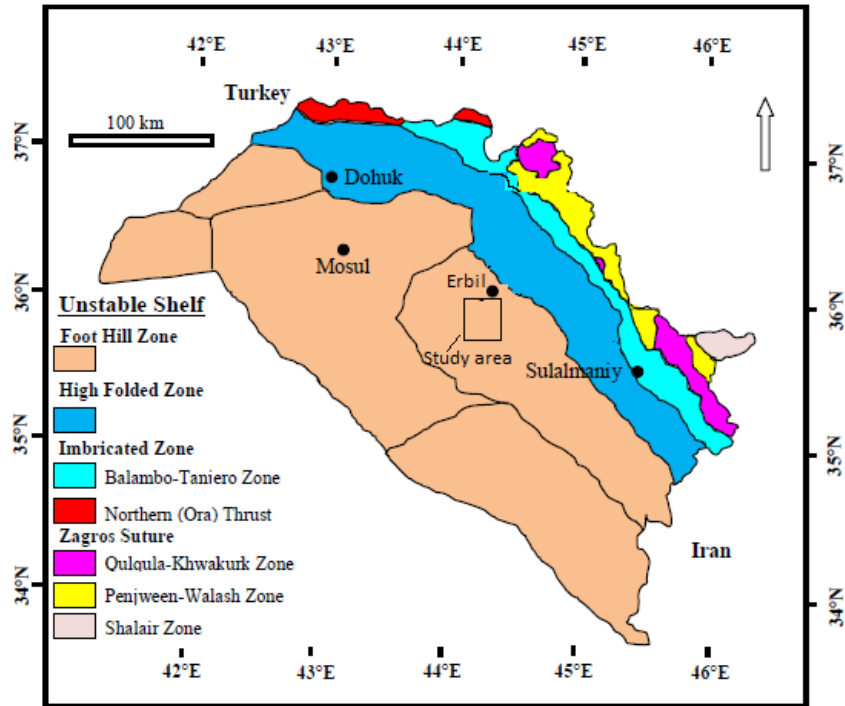


Figure 2.4. Tectonic map of the northern part of Iraq (after Jassim and Buday, 2006; modified from Tobia and Kafy, 2016)

2.3. Sample preparation

The process of taking the samples was carried out on 8/12/2021, at 8 a.m., near Arab-Kand village, known as Turaq, for collecting 10 samples of water from the area. The current study area was 1500 m long. Soil and water samples were collected at 0 meter as a starting point. Started our work with equipment such as (pens, notebooks, comforts, tubes for water, with a bake cloth to filter the water from dirt, a hafiz bag to protect the soil, gloves, shovels, glass), from destination place, and after that we covered the opening of the tube with funnel and cloth to filter, after that we labeled the tube. After that, we take the sand sample by a meter away from the aquatic part and take it into a labeled. All soil water samples were analyzed in different location such as Erbil, Turkey, and Canada.

2.4. Analysis of Sediment and Water

Triplet sediment samples were collected from the river. After the sediment samples were dried in an oven and stone pieces were removed, they were ground by using a hand mortar. For digestion of sediment samples, the mixture of HCl–HNO₃–H₂O (6 ml of mixture of 1/1/1 was used for 1.0 g) was used at 95 °C and 1h. Triplet water samples were collected from the study area and then acid was added on the samples after each pH and EC was measured in situ. In the laboratory, the samples were filtrated through 0.45m.

Five sediment samples and five water samples from the study area, the Arab-Kand village were collected from each sampling site. The sediment samples were taken from the surface of river. The dried sediment samples were ground using a hand mortar. Approximately 20–30 g samples were dried by heating in owen at 50 °C for 2 hours. The dried samples were digested in HNO₃ for 1.0h followed by the mixture of HCl–HNO₃–H₂O for 1.0 h (6ml of the mixture of 1/1/1 was used for 1.0 g of the dried sample) at 50 °C. The samples were digested using the mixture HCl/HNO₃/H₂O. 5 water samples were analyzed in ICP-MS for different metals in ACME Laboratories in Canada (Table 3.1 and 3.2). All results are given as ppm together detection limits for each elements.



3. RESULTS

3.1. Water Samples

After the Erbil wastewater treatment plant effluent from the area where the effluent discharges into the stream, water samples were taken from 3 sampling points at different distances, and trace element analyzes were carried out for 70 elements in these waters (Table 3.1). Two of the water samples were not (sample No. 2 and 4) analyzed due to the cost was so extensive. Most of the 70 elements analyzed were below the detection limit of ICP-MS and the important elements were compared with both the Turkish drinking water quality standard values and Elazig wastewater treatment plant waters in Table 3.1.

pH and electrical conductivity values of the wastewater in the study area change from 6.42-6.61 and 0.50-0.54 mS cm⁻¹, respectively. HCO₃⁻ values are lower than in Elazig region, but sulphate and nitrat values in the study area are also higher than in Elazig wastewater. This also indicates that Erbil wastewater is more polluted in terms of sulfate and nitrate than the wastewater in Elazig and conversely, the bicarbonate content is quite low. Therefore, according to Turkish dirty water quality standards (SKKY, 2008), it is highly polluted in terms of nitrate and sulfate and is included in the 4th group water quality.

Calcium, magnesium, potassium and sodium were observed in very low concentrations in Erbil wastewater. The concentration ranges for the analyzed cations were determined as 70.6-82.8 ppm for calcium, 22.3-25.9 ppm for Mg, 5.37-5.95 ppm for potassium and 44.6-49.7 ppm for sodium. These results were found to be quite low when compared to Elazig wastewater plant effluent (Sasmaz, 2021), as well as Turkish quality standard values (Table 3.1). Most of the concentrations observed here were likely influenced by lithological units, industrial, agricultural and mining operations. The increase in Na in the water may be due to the salt poured to prevent icing on the roads, especially in winter. In addition, the intense sodium excess in the waters may possibly be caused by detergent products used as cleaning materials at home, but these values are still much lower than the SKKY (2008) values and it is seen that they are included in the 1st class water quality class. (Table 3.1). The potassium content of natural waters is low. Potassium content in the majority of waters is less than 20 mg/L. Sometimes, higher concentrations of potassium can also be found in the waters. This situation may be related to the geological formations where water is present or the intensive use of potassium fertilizers in agricultural lands (Güler, 1997). Considering

these factors, the potassium values of the creeks in the study area are less than 20 mg/L and it is thought that the conditions where the geological formations create high values are not seen at the sampling points. However, the dense agricultural lands around the study area highlight the idea that these waters will be polluted due to fertilization.

Trace elements (Fe, Mn, S, P, Al, As, B, Ba, Br, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Se, Sr, U, V, Zn) is given in Table 3.1. The ICP of these elements gave values above the detection limit of the device. While some of these values were affected by the geological formations in the region, many elements were observed to be under the influence of domestic, industrial and agricultural pollution. Possibly, the probable source of metals in Erbil wastewater facilities is associated with lithological formations for Ca, agricultural and fertilization activities for P-S-K-Al-Cd, domestic detergent and packaging materials for Na-Al-B, and, industrial and mining activities for Fe-Mn-Zn-Ni-Co-Cu. Madzin et al. (2015) determined significant heavy metal pollution in waters coming from abandoned mines and industrial areas. He stated that in the concentrations of these metals in water and sediment, an ordering in the form of Fe>Mn>Zn>Pb>Cu occurred.

When the trace element values of the waters in the study area were compared with the SKKY (2008) values, phosphate and sulfur IV. class water quality, other elements are included in class I water quality (Table 3.1). Therefore, no significant pollution parameters other than P and S are observed in Erbil wastewater plant waters. However, when these waters are compared with the metal values in Elazig wastewater plant waters (Şaşmaz, 2021), it shows that they are more polluted in terms of Fe, S, Cd, Cu, Co, Ni, Sb, U and Zn. This shows that these waters in and around Erbil are probably more affected by industrial and mining/marble wastes.

Table 3.1. Trace element results from Erbil and Elazig City Wastewater Treatment Plant effluent and Turkish water quality standard values (SKKY, 2008).

Elements	Sampling points				Turkish water quality standards (SKKY, 2008)			
	Erbil -1	Erbil -3	Erbil -5	Elazig (Sasmaz, 2021)	I	II	III	IV
pH	6,61	6,42	6,50	7.6±0.2	6-9	6-9	6-9	6-9
EC mS cm ⁻¹	0,495	0,535	0,542	1.05±0.02	< 400	1000	3000	> 3000
HCO ₃ mg/L	83,1	148.7	152.9	865± 28	-	-	-	-
NO ₃ mg/L	32,1	38.47	38.04	8.66 ± 0.5	< 3	10	20	> 20
SO ₄ mg/L	86,7	105.1	109.46	12.9 ± 0.4	≤ 2	5	10	> 10
Ca mg/L	70,6	76,8	82,8	83.3± 3.4	-	-	-	-
Mg mg/L	22,3	24,8	25,9	26.9± 2.1	-	-	-	-
K mg/L	5,37	5,83	5,95	14.3± 0.8	-	-	-	-
Na mg/L	44,6	47,2	49,7	83.9± 5.6	125	125	250	> 250
Fe µg/L	17	44	58	<10	-	-	-	-
Mn µg/L	17,3	19,6	21,1	57.2± 4	100	500	3000	> 3000
S µg/L	27	33	38	33± 3	2	2	10	> 10
P µg/L	757	838	956	4274± 48	0.02	0.16	0.65	> 0.65
Al µg/L	61	61	63	104± 8	300	300	1000	> 1000
As µg/L	1,7	2,6	2,8	4.6±0.5	20	50	100	> 100
B µg/L	155	174	188	420± 32	1000	1000	1000	> 1000
Ba µg/L	64,2	64,6	67,4	47.8±5	1000	2000	2000	> 2000
Br µg/L	39	43	49	219± 12	-	-	-	-
Cd µg/L	0,08	0,16	0,22	<0.05	3	5	10	> 10
Co µg/L	0,07	0,10	1,12	0.12± 0.01	10	20	200	> 200
Cr µg/L	1,1	1,0	1,1	2.1±0.1	<5	20	50	> 50
Cu µg/L	2,6	2,7	2,9	2.2± 0.3	20	50	200	> 200
Hg µg/L	<0.1	<0.1	<0.1	<0.1	0.1	0.5	2	> 2
Ni µg/L	1,0	1,1	2,1	0.4± 0.02	20	50	200	> 200
Pb µg/L	1,0	0,3	0,4	16.9± 2	10	20	50	> 50
Sb µg/L	0,42	0,50	0,55	<0.05	-	-	-	-
Se µg/L	0,60	0,50	0,50	-	-	-	-	-
Sr µg/L	621	719	788	431± 18	-	-	-	-
U µg/L	0,59	1,00	1,22	0.72± 0.05	-	-	-	-
V µg/L	2,8	3,0	3,4	1.7± 0.1	-	-	-	-
Zn µg/L	39,6	130,3	166,2	33.6±3	200	500	2000	> 2000

3.2. Sediment Samples

Erbil city wastewater flows along the Arab-Kand canal from Turak town to Zap water for about 40 km (Figure 2.2 and 2.3). Sediment samples were taken from the creek at different distances along the Arab-Kand canal, where the effluent of the Erbil Wastewater Treatment Plant is discharged. These sediments were taken from the places where the flow is low, especially in the creek. The colors of the sediments generally change from dark brown and black to light brown, and according to the grain size analysis, they are in the group of humus, sandy, clayey and silty (35.4% silt, 18.5% clay and 46.1% sand) sediments and their organic matter content is 8.3%. It ranges from 12.6.

Variations in metal concentrations with depth in the soil cores show a significant correlation with total organic carbon content (Stephens et al, 2001). The amount of organic matter in the sediment; It originates from a variety of sources such as plant derivatives, animal detritus or fecal matter, and even artificial organic matter including groundwater systems (Hong et al, 2010). Starting from the area where the effluent of Elazig City Wastewater Treatment Plant empties into Kehli Stream, approximately 300-400 m. Sediment samples were taken from 9 different points in the flow direction of the water, Kehli Stream sediment samples were observed to have a high organic matter content. This may possibly be due to domestic and agricultural waste discharged into Kehli Creek (Şaşmaz, 2021). Similarly, the high organic matter contents observed in the sediments along the Arab-Kand channel may be due to the city of Erbil domestic and agricultural waste.

Heavy metals can be of different natural and anthropogenic sources such as industrial wastes, agricultural flows, transportation, burning of fossil fuels, geological structure, mining activities and domestic wastes. The mean metal values of the sediments in the study area vary widely (Table 3.2). In particular, when the metals in the sediments of Erbil and Elazig regions were compared, while Ca, K, Mg, Ba were higher in Erbil sediments, metals such as Fe, Al, V, Pb were observed more in Elazig sediments. Meanwhile, while there was not much difference between the metal concentrations at the sampling points in the Erbil region, it was observed that the sediment samples at point 4 (Figure 2.3 and Table 3.2) were very enriched in terms of some metals such as Pb, Zn, Ag, Au, S. This is probably due to the mining activity at this point along the canal.

Arsenic pollution in the surface sediments is 727 mg/kg on average in ore areas, 3070-11.500 mg/kg in non-ferrous metal mining areas, 2500 mg/kg in places around metal processing plants, 105-220 in areas where leather industry is located, and in coal burning processes. It reaches 800-1500 mg/kg (Kabata-Pendias, 2011). Boron concentrations were found to be between 120 and 130 mg/kg in clay soils and between 10 and 100 mg/kg in calcareous sediments. The lowest boron concentrations were observed in mafic and podzol soils (Kabata-Pendias, 2011). While B is mostly concentrated in the surface layers of soils in warm humid or arid and semi-arid regions, B in sediments usually follows the water flow and moves away from the environment in the form of oxide compounds. Craw et al. (2006) suggested that some fly ash and sewage sludge are one of the most common sources of B pollution in soils. Similarly, it has been stated that surface waters contaminated with B and water from coal mines cause various agricultural problems in the soil when used for irrigation.

Lucho-Constantino et al. (2005) found that the B level in sediments increased up to 124 mg/kg as a result of anthropogenic pollution and irrigation time. Rehabilitation and restoration of sediments with high B content is very difficult because of the high solubility (mobility) of boron in surface environments. But it is suggested that it is possible to reduce the boron content to normal values in a result of frequent washing of boron-contaminated areas with irrigation water

The distribution of Pb in mineralized sediments correlates positively with the fine granulometric fraction. Geometric mean background values for Pb in Polish sediments indicate increasing levels with increasing clay granulometric fraction content; for example (1) 12.6 in sandy sediments; (2) 16.4 in medium loamy (loamy) sediments; and (3) 20.9 mg/kg in heavy loamy sediments. During weathering, Pb sulfites are slowly oxidized and converted into carbonate forming as well as clay minerals, hydroxides and sulfates. The geochemical properties of Pb^{2+} are somewhat similar to the divalent sediment alkali metal group. Thus, Pb has the ability to replace K, Ba, Sr and even Ca in both minerals and sorption sites. The distribution of Pb in the sediment profiles is not uniform and a positive relationship has been demonstrated with hydroxides, especially Fe and Mn (Kabata-Pendias, 2011). The Sr concentrations in the surface sediments of the mine sites are between 112 and 717 mg/kg for the Keban (Elazığ) Pb-Zn mine site (Sasmaz and Sasmaz, 2009) and between 22.6 and 691.8 mg/kg for the Gümüşköy (Kütahya) mine sites. seen (Sasmaz and Sasmaz, 2017). High variations were found in the Sr content in mineral sediments of carbonatite and pyroxenite bedrock over the Stjernoy Alkaline Complex in Norway, ranging from 320 to 1300 mg/kg (Myrvang et al., 2016). Kabata-Pendias (2011) stated in their study that the main indicator showing the abundance of Sr in the sediments is related to the composition of the host rock and that the Sr content increases linearly from basic rocks (diorite) to alkali rocks (syenite). For example; Sweden (112-258 mg/kg), Japan (32-130 mg/kg), Great Britain (261 mg/kg), China (26-150 mg/kg), Russia (715-1000 mg/kg), Venezuela As in (13-39 mg/kg), Canada (210 mg/kg), USA (305 mg/kg), Sr content of sediments in different countries varies between 14.7 and 675 mg/kg (Kabata-Pendias, 2011)..

Table 3.2. Trace element results from Erbil and Elazig City of sediment Turkish sediment quality standard values

Elements	Sampling points					
	Erbil -1	Erbil -2	Erbil -3	Erbil -4	Erbil -5	Elazig (Sasmaz, 2021)
pH	7.5	7.97	7.4	6.86	7.87	7.65
EC mS cm ⁻¹	120	139	278	500	101	-
Ca %	14.9	12.96	13.4	11.76	14.46	4,40
P %	0,070	0,066	0,072	0,015	0,047	0,064
Mg %	1.28	1.56	1.40	1.38	1.37	1,35
Na %	0,022	0,043	0,022	0,026	0,024	0,05
K %	0,26	0,43	0,026	0,20	0,23	0,11
Fe %	2.03	2.41	2.11	2.19	2.02	3,58
Al %	1.75	2.27	1.76	1.48	1.78	2,40
Ga	4.6	6	4.6	3.9	4.3	5,67
Mo	0.36	0.41	0.5	1.99	0.41	1,75
Cu	22.1	22.7	27.8	95.7	18.9	63,9
Zn	44.8	49.7	76.9	467.2	44	162
Ni	80.5	99.1	85	78.5	87.6	56
Co	11.5	12.9	11.9	10.9	12.4	24,2
Mn	401	426	510	400	568	563
As	3.4	5.4	4.8	6.3	5	19,5
U	0.4	0.6	0.5	0.8	0.4	0,61
Ag (ppb)	188	39	121	1261	51	284
Au (ppb)	5.7	1.6	10.1	189	3.4	9,69
Th	2	3.2	2	0.4	2.2	1,42
Sr	194	269	230	208	227	87,1
Cd	0.19	0.26	0.23	0.57	0.2	0,49
Sb	0.18	0.15	0.17	1.36	0.13	0,46
Bi	0.13	0.13	0.13	0.68	0.09	0,16
V	45	59	46	43	44	120
La	10.3	12.5	9.6	8.1	10.5	<0.05
Cr	55.6	77.6	66.7	81.2	59.4	68,4
Ba	78.7	116	103	175	97.5	54,4
Ti	470	510	360	380	420	0,15
B	<20	<20	<20	<20	<20	<20
W	<0.1	<0.1	<0.1	0.2	<0.1	<0.1
Sc	5.1	6.8	4.9	2.8	5.1	8,92
Tl	0.08	0.14	0.09	0.11	0.08	0,08
S	300	300	700	2500	<200	0,04
Hg	58	13	48	363	26	48,3
Se	<0.1	0.2	0.1	0.4	<0.1	0,36
Te	0.03	0.04	0.03	<0.02	<0.02	0,03
Pb	11.25	9.21	12.95	43.46	8.42	71,85

3.3. Effect of pH on Metal Release from Sediments

Different studies based on combined sewer sediments have shown that heavy metals with different speciations are generally associated with sewer water (Li et al., 2013). More specifically, Zn was frequently observed in natural water and sediments. Normally, with pH decreasing in

sediment, the competition between H^+ and the dissolved metals for ligands (e.g., OH^- , Cl^- , S_2^- and phosphates) becomes more and more significant. The adsorption abilities and bio-availabilities of the metals subsequently decrease and then increase the mobility of heavy metal. Moreover, H^+ (or H_3O^+) occupies more adsorption sites at lower pH values (et al., 2013). which results in soluble and carbonate-bound heavy metals precipitated more easily than at higher pH values. Both of these processes result in faster heavy metal release rate with lower pH, and it can be found with the observed results

In the soil, heavy metals are available in the form of adsorbed particles, coiloidal, inorganic and organic complex compounds, salts and hydroxides/oxides . Ph and concentration parameters in the formation of complex compounds affect the mobility of heavy metals in the soil. At low pH, heavy metals will be released and thus the mobility will increase. The higher the concentration of natural humic substances or the formation of synthetic complex compounds, (EDTA) the fewer the compounded metal ions with complex compounds forming ligands (Li et al., 2013).

3.4. Effect of Temperature on Metal Release from Sediments

Metals of sediments have been equilibrated at temperatures ranging from 4 to 25°C in previous studies. The results concerning the effect of temperature (15–35°C) on metal release from sediments .The release rates of Zn, Cu, Pb, Cr, and Cd in the low- and high temperature experiments were observed and they were greater at high temperature than low-temperature. Normally ,With the temperature increasing, the reactions could be accelerated, and the DO concentration in the water and the dissolutions of the carbonates and hydroxides increased. Therefore, the metal release rate of the water-soluble fraction, carbonate fraction, and exchangeable fraction from the sediment into the overlying water increased (Li et al., 2013).

3.5. Electrical conductivity

Conductivity is a measure of the water's ability to conduct electricity and it is directly related to the concentration of ions in the water. Significant changes in the conductivity of water directly compromise its quality. Soil electrical (EC) is a measurement that correlates with soil properties that affect crop productivity, including soil texture, cation exchange capacity (CEC), drainage conditions, organic matter level, salinity and subsoil characteristic.

The electrical conductivity of soil varies depending on the amount of moisture held by soil particles. Sands have a low conductivity, silts have a medium conductivity and clays have a high conductivity. Soil electrical conductivity (EC) can be related to specific soil properties that affect

crop yield such as topsoil depth, Ph, salt concentrations and available water – holding capacity (Jimoh and Mahmud, 2014).



4. DISCUSSIONS

Population growth and the activities in the Erbil City area over the last 15 years have resulted in increasing in water uses, changes in distribution and timing of flow, and deterioration of water quality. The changes threaten both remaining natural ecosystem and growing human population. Wastewater is generated from human activities in Erbil Governorate. This water comes from, discharge of domestic sewage which originated from kitchens and bathrooms of dwelling public building as well as street wash water, industrial waste region from north and south industrial region, and storm water flowing in sewers during or following periods of rain fall water. Pollution is one of the major sorts of pollution in the environment; it comes about with industrial an urban growth. Along Arab-Kand valley (channel) wastewater used for irrigation by farmers in rural area. It may generate negative impact on environment and health risks for community. The farms situated in south west of the city.

Mainly those located between Toraq and till to Greater-Zab River they are depended on large scale up on the Erbil wastewater taken from sewer outfall. Municipal sewage contains human faces and contaminated with these effluents may contain pathogenic (disease- causing) organisms and, consequently, may be hazardous to human health if it used as drinking-water or in food preparation (Janan, 2009).

Erbil wastewater composes of domestic sewage, industrial wastewater and stormwater .This channel extended from southwest of Erbil city with their elongation for more than 50 Km passes through vast farmlands, orchards and several villages till its effluent discharges into Greater Zab river (Yahya et al., 2010.The channel dimension varied from place to other but generally it ranged from 2- 3.5m width and 0.5- 1.5m depth Their quantity discharge ranges from 0.85 m³/S to 1.7 m³/S measured in former part of channel, farmer families along polluted channel depend mainly on untreated wastewater for their field irrigation, especially during dry season. Vegetables are the main crops in these villages. Only in Arab- Kand village the farmers irrigate about 520 hectares of agriculture land. According to (Yahya et al., 2010), the domestic sewage consist of approximately 99.9% water, 0.02- 0.03% suspended solids, and other soluble organic and inorganic substances. Degradation of water quality due to organic and inorganic contaminants has resulted in altered aquatic biota in their quality and quantity The change in the phytoplankton community structure can be particularly useful as an assessment tool, due to their response to environmental stress (Yahya et al., 2010).

Despite the large number of researches available on the spatial and temporal variation in phytoplankton density and community structure in lakes and rivers, little information is available on the phytoplankton density variation in polluted water. Many studies have been focused on

water quality of Erbil wastewater channel for hygienic status and agricultural (Yahya et al., 2010).

4.1. Concentration of studied metals in water samples

In the present study the studied water sample was contain high amount of heavy metal this may be attributed to present near by industrial area or domestic water which dumping there waste in to the water.

Interpretation of polluted water

The concentration of HCO_3^- was ranged between (83.1-152.9) according to the FAO permissible limit our HCO_3^- exceeded the permissible standard the same result was agreed by (Islam et al., 2020). The concentration of NO_3^- was ranged between (32.1-38.04) according to (SKKY, 2008) all three water sample was higher than class 4 and the same result was observed by (Chetan and Surendra, 2018). SO_4^- was ranged between (86.7-109.46) was higher than Turkish standard of permissible limit our SO_4^- was class 4 the same result was observed by (McArthur et al., 2012) the high concentration of this ions may be attributed to industrial wastes and waste water from house hold which dumped in to the water (Islam et al., 2020). The permissible level according to guide line of (WHO,1996) was not more than 500mg/l, while according to USEPA (2004,2006) the allowable concentration must be lower than 250mg/l. Generally Iraqi Kurdistan region in land water usually contain significant amount of sulfate (Bilbas, 2004).

The high amount of (Ni) was ranged between (1.0-2.1) was observed in the water sample the same result was observed by (Hang et al., 2009), and high amount of (Pb) was ranged between (1.0-0.4) and (Zn) was ranged between (39.6-166.2) was observed in our sample the same result was observed by (Orescanin et al., 2004) also high amount of (Cd) was ranged between (0.08-0.22) was observed in our water sample the same result was observed by (Ayeni,2004). The high concentration of (Ni, Cd, Zn and Pb) caused by attributed to the contaminated water were dumping by near by industrial area . presence of (K,FeMn,S,P) in the waste water may be emissions from food, amalgam, detergents, pipes (taps included), drinking water and artist paint are included in the 'household' category or paint in the colors of yellow-red can contain some of those metals or maybe derived as contribution drainage water (Sorme and Lagerkvist, 2002). Moreover other studied metals was in the range of Turkish standard.

4.2. Concentration of studied metals in sediments samples

The concentration of metals in the sediment sample was as follow:

Calcium (Ca^{+2}) was ranged between (14.9-14.46). Increasing Ca^{+2} concentrations with distance may attribute to high Ca^{+2} % in soil content (Kahraman, 2003). Sodium (Na^{+}) was ranged between (0.022-0.024). High sodium concentration attributed to industrial waste sewage discharge. Human activity by using sodium salts in (Bathing, Kitchen) soap and detergent. Soil background of Na^{+} content is high ratio (Kahraman, 2003), irrigation in farm land, dense planet (Al- Jiburi, 1997).

Potassium (K^{+}) was ranged between (0.26-0.23). Common sources of potassium are the products formed by the weathering of orthoclase, microcline, biotite, leucite and nepheline in igneous and metamorphic rocks. Lead (Pb) was ranged between (11.25-8.42). The source of Pb in environment are comes from two source; the first one is geologic source as it is present in the structure of mineral and rocks (olivine, pyroxene, amphibole, feldspar, and chlorite). Cadmium (Cd) was ranged between (0.19-0.2). Waste water polymer-fixing (Al-Saddi, 2006) component in manufacture of solder electrical supplies ,batteries, barriers to control nuclear fission ,phosphors in the production of television ,anticorrosive coating for metals, bearing alloys, amalgam in dentistry and worm treatment for swine and poultry(Tucker, 2005). Zinc (Zn) was ranged between (44.8-44). It is widely used in industry to make dye, paint, rubber, wood preservative and ointments (Tucker et al., 2005). Copper (Cu) was ranged between (22.1-18.9) . The source of copper are chalcopyrite, chalcosite , amphibole, olivine, biotite, and plagioclase (Fostner and Wittman, 1981). Fertilizer, industrial waste, sewage water adding more copper concentration into nature (Alloway and Ayres, 1997). Nickel (Ni) was ranged between (80.5-87.6). Inters in industries of stainless steel, other corrosion – resist alloys, coins, nickel steel for armor plates, burglar proof vaults, vegetable oils, ceramics and greenish glass, Al, Ni, Co magnets and Ni– Cd batteries (Tucker et al., 2003). Iron (Fe) was ranged between(2.03-2.02).The main source of Fe are from industrial waste inside Erbil(two industrial region inside Erbil city)and recent flood in Erbil added more Fe concentrations to Arab-Kand channel by weathering and leaching of soil that comes from mountain area. Manganese (Mn) was ranged between (401-568). Source of Mn in the studied area are fertilizer, waste of industries, municipal waste, manganese is found in several food items, including grains and cereals, and is found in high amounts in other foods, such as tea. Also dust and air born particles can added more concentration into water in the studied area. Especially at west of Erbil city where the crackers exhaust fine grain particles during crushing carbonate rocks. While the concentration of (Hg) metals was ranged between (13 to 363 ppm) in sediments sample beside their toxicity due to Mercury contamination in the soil can suppress crops growth or kill plants, eventually affecting human health through bioaccumulation (Hang et al., 2006). Therefore, soil mercury is closely related to the survival of humanity and the growth of crops.

4.3. Relation between studied metals in water and sediment samples

Figure 4.1 shows metal concentration in 3 water samples along with mean value of the same metal in sediments. The chart indicates the increasing in metals content in water sample causes increase in the same metal concentration in the surrounding sediments. This means contaminated water by heavy metal has a significant positive impact on the metal concentration of soil. Furthermore, most of the metals from the studied sediments were derived from the water; Pichtel (2016) agreed with the same conclusion.

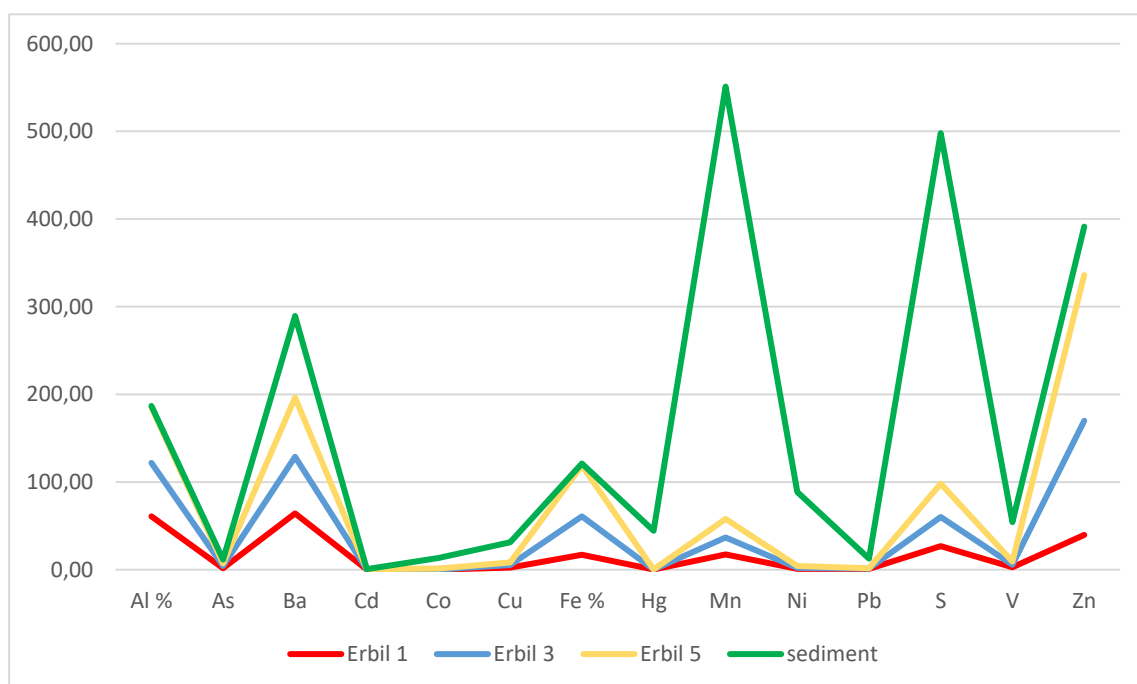


Figure 4.1. A diagram shows trace element concentration in relation between sediment and waste water samples

4.4. Waste water exploitation for Agriculture and irrigation in Arab - Kand Channel

Population growth and activity in the Erbil city limits over the past 15 years have resulted in increased water consumption, changes in the distribution and timing of flows, and deterioration of water quality. This change threatens both remaining natural ecosystems and growing human populations. In Erbil District, wastewater is generated by human activities. This water is discharged from domestic sewage coming from kitchens and bathrooms in public housing, road washing water, industrial waste areas from industrial areas in the north and south, and storm water flowing into sewers during or after rain storms. Pollution is one of the main types of pollution. It is created by industrial and urban growth. Along the Arab Kand valley (canals), sewage is used for irrigation by farmers in rural areas. It can have a negative impact on the environment and pose health risks to local communities. A farm in the southwest of the city.

mainly those between Toraq and the Greater Zab River rely heavily on Erbil's sewage drawn from sewers. Municipal sewage contains human feces, and sewage contaminated with this sewage may contain pathogenic (disease-causing) organisms and, as a result, should not be used as drinking water. or used in food preparation may pose a hazard to human health. Fecal contamination of water is routinely detected by microbiological analysis.



5. CONCLUSIONS

Based on various variables, including density and atomic weight, heavy metals can be defined in a variety of ways. In small amounts, some heavy metals like iron, cobalt, and zinc are necessary for human nutrition but are toxic in larger amounts. However, only a few metals, like lead, cadmium, and mercury are poisonous even in trace amounts. The concentration, exposure time, and exposure route all affect how toxic heavy metals are. Humans are exposed to heavy metals through dermal contact, ingestion through the skin, and inhalation of the atmosphere and drinking water.

A case of study in The Arab-Kand village was chosen for this study. It is about 10 kilometers south-west of Erbil and covers an area of 67 acres. Samples have been examined in laboratory under the supervision of supervisor who is expert in the field. Also, some samples have been sent away to Canada.

According to the WHO, mercury is a dangerous toxin that has a negative impact on aquatic life. Consuming foods contaminated with mercury can make people sick and have various physiological effects, including Minamata disease.

Because of their transportation via air, soil, and water, heavy metal toxicity and environmental impact are global issues. The possible ways of ingesting heavy metals through drinking water, air, and foods are based on various factors such as concentration and different major sources. These metals are required in trace amounts for cellular, metabolic, and hormonal functioning in humans, but if the limit is exceeded, it can lead to serious health consequences. The toxicity of these metals has a significant impact on soil by killing microorganisms that are beneficial to soil fertility and nutrition.

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