

**Republic of Iraq**  
**Ministry of Higher Education**  
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**College of Science**  
**Department of Biology**



**Determination of some Heavy Metals Bioaccumulation in  
Water, Sediments, and *Phragmites australis* and  
*Ceratophyllum demersum* Plant in Euphrates  
River in Al-Samawa City/ Iraq**

A Thesis Submitted in Partial Fulfillment of the Requirements for the  
Master's Degree of Science in Biology

By

**Wassan Shaker Razzak**

B. Sc. Biology/ 2008

Supervisors

**Assist. Professor Dr. Ibtehal Aqeel Al-Tae**

**Assist. Professor Dr. Ali Abdulhamza Al-Fanharawi**

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بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

﴿فَتَعَلَى اللَّهِ الْمَلِكُ الْحَقُّ وَلَا تَعْجَلْ بِالْقُرْآنِ مِنْ قَبْلِ

أَنْ يُقْضَىٰ إِلَيْكَ وَحْيُهُ وَقُلْ رَبِّ زِدْنِي عِلْمًا﴾

صدق الله العلي العظيم

سورة طه: الآية "١١٤"

***Dedication***

*I dedicate all my efforts*

*To whom I worship for his merciful*

***Allah***

*To The leaders of my Life Prophet .....*

***Mohammed and his Family***

*To my life love who gave me life*

***My parents***

*To The candle that I honor my husband who supported me*

***Osama***

*To the stars that shining my life .....My children*

***Ali, Fatima Al-Zahra and Mohammed***

*To lovers who encouraged me to pass hardness*

***My brothers & sisters***

*To everyone helped and supported me to do this work.....*

*I introduce my work with love & respects*

*Wassan Sh. Razzak*

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*Wassan*

### Abstract

The current study was conducted the levels of five heavy metals in water of Euphrates river, sediments, and two type of aquatic plants (*Phragmites australis* and *Ceratophyllum demersum*) from November 2019 to October 2020, three sites were selected, samples collected in the morning monthly for measuring physical and chemical parameters which included (air and water temperature, pH, turbidity (Tur), electrical conductivity (EC), total dissolved solids (TDS), dissolved oxygen (DO), biological oxygen demand (BOD<sub>5</sub>), total hardness (TH), Calcium hardness, Magnesium hardness, total organic Carbon (TOC), and soil texture; and seasonally for examining rates of five heavy metals (Copper, Zinc, Cadmium, Chromium, Lead) in water as dissolved and particulate, in sediment as exchangeable and residual phase, in *Phragmites australis* and *Ceratophyllum demersum*.

The rates of physicochemical parameters for the study sites were as follows: air temperature ranged between (11-43 C°), water temperature (9-31 C°), pH (7.5-8.5), Tur (18.49- 53.27 NTU), EC (950-1920 µs/cm<sup>2</sup>), TDS (820-1450 mg/l), DO (5.2-10.3mg/l), BOD (2-15 mg/l), TH (620-1260 mg.CaCO<sub>3</sub>/l), Ca hardness (120-208 mg.CaCO<sub>3</sub>/l), Mg hardness (68.14-189.6 mg.CaCO<sub>3</sub>/l), TOC (0.055-2.87%), soil texture analysis showed percentage (silt 90% - 5% for each sand and clay).

Annual mean value of (Cu, Zn, Cd, Cr, Pb) in water was (1.75, 0.81, 1.23, 1.71, 0.81) µg/l respectively in dissolved phase, and (3.56, 39.81, 2.64, 6.99, 7.14) µg/g dry weight respectively in particulate phase, in sediment (1.3, 1.25, 0.27, 0.23, 8.64) µg/g dry weight respectively in exchangeable phase, (2.11, 4.78, 0.2, 2.93, 0.61) µg/g dry weight respectively in residual phase, (3.18, 8.78, 0.14, 0.64, 1.83) µg/g dry weight respectively in *P. australis*, and (7.63, 16.01, 1.76, 2.19, 3.97) µg/g dry weight respectively in *C. demersum*.

*C. demersum* recorded highest concentrations of heavy metals than dissolved phase and *P. australis* in all studied elements, so this plant can use as efficient bio remover for those elements.

Heavy metals in water were exceeded permissible limits of Iraqi water and WHO standards, while in sediment elements were within limits.

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### *List of Abbreviations*

Abbreviations	Terms
WT	Water temperature
TUR	Turbidity
EC	Electrical conductivity
TDS	Total dissolved solids
DO	Dissolved Oxygen
BOD <sub>5</sub>	Biological Oxygen Demand
TOC	Total organic carbon
TH	Total hardness
Ca	Calcium
Mg	Magnesium
HMs	Heavy metals
Cu	Copper
Zn	Zinc
Cd	Cadmium
Cr	Chromium
Pb	Lead
SPSS	Statistical package for the social science
LSD	Less significant difference



## Introduction

Pollution means any change in quality and quantity of environmental components, any change causes a defect in ecosystem balancing and losing ability to get rid of it in natural processes (Okoro *et al.*, 2013).

Pollution with heavy metals is the most dangerous type of contamination (Brodny and Tutak, 2019). Main feature of non-biodegradable, toxicity, and ability of bioaccumulation of heavy metals over time made it impact on existence, diversity and abundance of species in aquatic ecosystem (Mao *et al.*, 2017), often called trace elements due to existence in low concentration in ecosystem (Pouls & Payne, 2005).

Heavy metals contamination in water system is aggravated continuously over time due to increasing in population growth and industrial development (Martin *et al.*, 2015).

Since mining, industrial revolution and evolution of agriculture during 30 years ago, heavy metals pollution become a series threat to the nature specially human life because of consumption fish lived in polluted water, elements like lead (Pb), chrome (Cr), copper (Cu) and cadmium (Cd) have been arranged under bio amplified through food chain in aquatic ecosystem (Saha *et al.*, 2018).

Heavy metals exist as a dissolved and particulate state in fresh water , most of it such as (Zn, Pb, Cd, Cu) had been proved that they are highly toxic and carcinogenic (Qu *et al.*, 2018).

In previous years phytoremediation was revealed, which known as employment plants to decrease contamination in ecosystem (Pilon-Smits, 2005), and this deemed as perfectly suitable way for elimination heavy metals in water as well as soil, good features of phytoremediation is relatively effective, low cost and ecofriendly (Bonanno and Vymazal, 2017).

Ability of some plants for phytoremediation and ruling accumulation parameters related with physicochemical properties of water (Ranjbar *et al.*, 2017).

Aqueous plants which are responsible of phytoremediation called macrophytes which are worldwide spreading in coastal region of river and sea water (Galletti *et al.*, 2010). Macrophytes are efficient in reducing heavy metals (HMs) concentrations, about 400 species of plant have the capacity to uptake HMs, submerged and floating plants widespread such as *Phragmites australis* and *Ceratophyllum demersum* (Tomasevic *et al.*, 2013).

*Ceratophyllum demersum* is natively submerged aquatic plant considered as intensive sweeper for HMs from polluted water, while *Phragmites australis* another abundance type has active aqueous stems and extra tolerance for different sorts of wastes including HMs (Duman & Koca, 2014). *P. australis* (common reed) is a submerged vascular plant grows as a grass can live in excessive environmental circumstances, even in extra-concentrations of toxic pollutant like heavy metals (Batty & younger, 2004).

Amounts of HMs rates fluctuate during seasons of year although segregation continuous above ground biomass in vegetative system that means growing of plants optimizing the ability of accumulation, seasonally fluctuation in HMs rates among elements led to no constant pattern rates resort to it (Okweye, 2013).

Tigris and Euphrates are main important sources of water for daily life activities like drinking and irrigation in Iraq, with continuous increasing in population growth, industrial development and livestock grazing caused pollution to environment especially to the water, so the need raised to reveal the levels and type of contamination and investigate how healthy is water then deal with pollution factors and find solutions to eliminate the risks on living organism (Gatea, 2018).

Recently water sources affected from lack of rains, dam construction in neighboring countries and climate change caused drop levels of water, throwing waste, sewage and private generators of people all these factors contributed in rising water pollution (Abbasi, 2014).

All pollutants dropped to the water lead to series problems nowadays and near future due to high toxicity of some metals, HMs pollution influence on diversity in water ecosystem (Sun *et al.*, 2019), major effects caused on human health according to continuous consumption of polluted water (Liu *et al.*, 2018).

Due to uncontrolled contamination source, no future plans for limiting it and lack of studies on the first important source of water in Muthanna governorate so we paid attention to do this study

### **Aims of The study**

- 1- Studying some physical and chemical parameters for water of the river and monitor locational and seasonal changes occur on it.
- 2- Measuring the concentrations of some heavy metals such as Copper (Cu), Zinc (Zn), Cadmium (Cd), Chromium (Cr), and Lead (Pb) in:
  - a- Water as a dissolved and particulate phase.
  - b- Sediment as a residual and exchangeable phase.
  - c- Two type of aquatic plants (*Phragmites australis* and *Ceratophyllum demersum*).
- 3- Study correlation between heavy metals in water, sediment and plants with physicochemical parameters.

## 2. Literatures Review

### 2.1. Heavy Metals

Heavy metals refers to the elements which have atomic number more than 20, and intensity more than  $5\text{g/cm}^3$ , another term of heavy metals is trace elements due to its existence in concentration of organism mass smaller than 0.01 % (Morillo *et al.*, 2004). American Protection Agency used that term to refer to the elements that lies between second and sixth in periodic table clique (EPA, 2001). Heavy metals considered under pollutants that have lethal and sub-lethal effects on living organism, which lately were paid more attention to study the effects on environment , human health, communities existing in aquatic environment and on ecosystem (Boyd, 2010).

Heavy metals were put under two fundamental categories: essential and non-essential element, essential refers to the elements which are indispensable for vital events in organisms involving human as example forming pigments and enzymes such as Mn, Fe, Cr, Cu, Co, Zn and Se (Ametepey *et al.*, 2018). Even essential elements are indispensable, but it could be toxic for ecosystem when exist in high concentrations Non-essential elements which have unknown vital function but those elements are competing on active enzyme and membrane protein sites such as sliver (Hg), lead (Pb), and cadmium (Cd), or known as metalloid(Kobielska *et al.*, 2018).

Most dangerous pollutant types is pollution with heavy metals (HMs) which contain large group, about 38 elements, some of them are necessary for biological activities in a specific proportions and some are toxic for tissues like Ni, Cd and Pb (Rajeshkumar *et al.*, 2018). Contaminated water with heavy metals is universal problem (Ali and Khan 2018).



Rivers and coastal region are exposure to heavy metals inputs and cause great harm for ecosystem, due to complicated attitude and making interactions in water and wetlands made more difficulties to get rid of those pollutants (Galletti *et al.*, 2010).

Contamination with organic pollutants are easily ended by natural processes put contamination with heavy metals are on the contrary, accumulated and amplified during time, heavy metals elements reach to aquatic system specially fresh water as a main environmental medium by different ways due to development of rural and civic life next to the rivers either natural sources or human resources, existence of heavy metals in water indicates that there are sources for those pollutants, distribution and rates of heavy metals were from anthropogenic input (He *et al.*, 2019).

### **2.1.1 Source of Heavy Metals**

Heavy metals release to aquatic system naturally during geological processes such as erosion so elements reach to the water from natural source, which are usually rocks or sediments, and released metals are either in a dissolved or particulate state in drained rain water on earth surface, or particulates in air reach to the water by winds from other places (Deng *et al.*, 2020).

Volcanic activities are also considered a natural source contribute in pollution of aquatic system by acid rain loaded with heavy elements, acid rain have the ability to melt the soil and release heavy elements to the water, and weathering rocks, by physical and chemical weathering, severe dehydration and water shortage, soil washing, forest fire and all processes that man has not entered with its occurrence (Kabata and Pendias, 2001).

Organism death and water currents which returns sediments of depths for water column that providing aquatic water with more heavy elements (AlKam &Abdullah, 2013).

Dissolution of soluble salts and atmospheric deposition from mining waste with neighboring ecosystem, also hydrological operations on successive transport and precipitation on heavy elements in natural ecosystem (Papagiannis *et al.*, 2004). Heavy metals in atmosphere from dust and storms which could be transported for hundreds or thousands of kilometers causing intensive environmental pollution (Fomba *et al.*, 2013).

Agricultural activities and surface flow agricultural arranged as anthropogenic resources, using chemical fertilizers, pesticides, nitrogen fertilizer and adding little nutrients such as Zn, Fe and Cu and pollutants from animal waste, drainage of agricultural waste specially in dry season during Summer (AKinjokun *et al.*, 2018). Utilization copper sulfate as a pesticide in agricultural fields, controlled and uncontrolled industrial waste discharge to the water is dangerous like metallic paint industry which contains high concentration of toxic metals like Cd, Ni, and Cr, paper and food industry, leather tanning also pharmaceutical industry all of those materials produce toxic waste, which classified to solid, liquid and clay, Plastic and rubber industry, household items and tires included (Al-Hejuje *et al.*, 2017).

Paints are widely used in industrial application including textile, food processing, painting and makeup, waste of those industrial are source of concern because many paints are not biodegradable due to nature of its chemical and its molecular weight (Chileshe *et al.*, 2019).

Factories of iron, steel, copper, aluminum, the glass, gas and benzene station are another main source of heavy metals in the environment (Karim *et al.*, 2015).

Rubbish burning which its fly ash contains a lot of toxic elements including pb, Zn, cd, and Co. Ash could precipitate and cause pollution of soil and water , besides pollution from thermal and electrical power stations (Demirak *et al.*, 2006).

Coastal wet lands considered a purifying filter for HMs , however filtration happening depends on pH, oxygen concentration, rates of carbon, and other physicochemical parameters which rules exchange of HMs through water and sediments (Bonanno & Orlando-Bonaca, 2018).

### **2.1.2 Pollution with Heavy Metals**

Pollution could be defined as any change in environmental constituents which cause a bad influence on ecosystem or existence of pollutants in great concentrations more than allowed levels that effect on human health or kill other living organism (Bonanno & Vymazal, 2017).

Water pollution refers to the addition any material or energy to the water environment leads to change physical, chemical and biological formation of this environment causing water quality defect so it becomes harmful when used (Jordan *et al.*, 2014). Many reasons for water and sediments pollution one of them is a result of human by industrial processes such as petrochemical plat and oil refinery and other oil related activities (He *et al.*, 2019).

Availability of water in good quality and abundant amounts is necessary in present time because water exposed to critical consumption by agriculture , industry and daily using , industrial wastes and sewage which lead to growing algae; so studying levels of contaminations for evaluation abundance water if it safe to utilize by human or not (jia *et al.*, 2016).

There are permitted environmental parameters for heavy metals concentrations if they are exceeded cause diverse effects for living organism so many researchers

studied heavy elements and emphasized the ability of accumulation and negative effects on aquatic organism.

Prusty *et al.*, (1994) referred that zinc is considered as a secondary nutrient, and plays important role in enzymatic activities, in case of decrease leads to low growth rate, but it should stay in acceptable levels and care should be taken when its presence in concentrations that exceed permissible limits, zinc like other heavy metals is harmful to the living organism.

Kabala *et al.*, (2001) mentioned that even Copper is one of essential nutrients and living organism need it in small proportions to complete biological processes, but when its rate is above specified limits leads to cause damages, if its rate exceeds 20 mg/kg from dry weight copper will be poisonous.

Duruibe *et al.*, (2007) mentioned that human body needs zinc but excessive rates leads to occur symptoms like growth deficiency, and in high concentration cause diarrhea and vomiting.

Storelli *et al.*, (2007) referred that despite of being one of the primary minerals copper causes inflammation and cirrhosis of the liver when excessively consumed in foods.

Lead is not essential for living organism and can prove toxic, Pb is somewhat immobile in sediments and accumulates in plant tissues specially in roots so it minimizes translocation to other organs (Renner *et al.*, 2004).

Benoff *et al.*, (2000) indicated that exposure to lead can cause many health problems such as convulsions, coma and kidney failure. Cadmium is non-essential element, plants need it in very small amount quantities in some physiological and biochemical processes in plant tissues.

Popoola *et al.*, (2015) mentioned that increasing in Pb consumed amount leads to accumulate in blood, bones and soft tissue because it is not excreted easily from the body, it affects the kidneys, nervous system, touch disorder and growth deficiency in children, embryos are the most sensitive for Pb.

Its accumulation in different tissues causes damages for food chain component organisms (Luo *et al.*, 2018).

Latest statistics indicate that water consumption ratio multiplied several time, more than population growth rates in twentieth century, in 2025 a third of world people will face great water crises due to population increasing, the development of industrial and agricultural processes (Al-Zubaidi *et al.*, 2016).

Land leveling, aquacultures, tourism, extraction of natural resources from the ground such as oil and gas production (mining) all those causatives influenced on diversity, food chain and water purity (Bonanno and Orlando, 2018). The use of agricultural fertilizers like phosphate fertilizers and continuous emissions from coal combustion (Dong *et al.*, 2012).

Al-khafaji (2011) illustrated in his study effect of industrial water on water quality of Al-Garaf River in Al-Nassiriya City and the role of waste water in increasing levels of heavy metals.

Barauh and Sarma (2011) referred that household waste, bathrooms, dish washing water, kitchen waste and chemical detergent which are daily generated in densely populated cities, those sources are finally washed off by sanitation systems nearby rivers that providing large amounts of pollutants.

Al- Hassen *et al.*, (2012) showed that increasing of some heavy metals in aquatic environment of Basra city came from throwing sewage and household waste directly to the river.

Hamdan (2015) clarified that pollution of soil with heavy metals in Basra result from population and urban growth and industrial activity including paper factory, electrical power stations, transportation, hospital waste.

Khairallah *et al.*, (2017) mentioned in a study on the level of some heavy metals in Euphrates River at the Souq Al-Shuyukh district that income of heavy metals to the water causing series threatening leading water to become unsafe for using to drink, irrigation and to aquatic organism.

Khazaal (2019) demonstrated that cars repair workshops, gas stations, laundry stations, washing textiles contribute increasing in rates of HMs in water and sediments.

## 2.2 Heavy Metals in Water

According to APHA (2003), there are three forms of heavy metals in aquatic environment :

- 1- Dissolved heavy metals: it is the elements in aqueous phase that pass through filter paper with diameter (0.45  $\mu\text{m}$ ) when the water is filtered.
- 2- Particulate heavy metals: it includes the elements inside water components with suspended matter that does not pass through filter paper with diameter (0.45  $\mu\text{m}$ ) when the sample is filtered.
- 3- Benthic sediments' heavy metals: which include two branched :
  - A- Exchangeable metals which involve items that are not included in the silica structure, but they are lined on the surface of the bottom sediment particles.
  - B- Residual metals: which involve items that are included in the silica structure.

When those elements reached to the water contents either by soil erosion or by dust, or from sewage and industrial waste or from agricultural and municipal activities, being either dissolved in water or associated with phytoplankton and fauna

or associated with benthic sediments (Hamdan, 2015), the environmental and health hazards when those elements reach to the food chain in the water to the wanderings, swimming, and bottoms organisms in addition to the aqueous plant, further more reaching to the different layers of the water by the effect of water movement current, or by the influence of the movement of aquatic organism especially relatively large fish, or with bodily waste and organic crumbs when the end of life cycle then accumulate again and reach to human the final recipient of aquatic products (Al-Hejuje *et al.*, 2017).

They are distributed between dissolved and particulate phase in water, and it could be adsorbed on surface of suspended matter and benthic sediments, these conditions are affected by physical, chemical and biomass characteristics (Khair Allah, 2017). Heavy elements are not soluble for a long time in water as they appear as suspended colloids or are stabilized by organic or metallic plankton (Al-Hejuje, 2014).

Physical and chemical properties play important rule in distribution, determination of concentrations and moving between water layers, pH, dissolved oxygen and organic carbon are main parameters which influence in concentration of elements in suspended matter and organism availability in benthic sediments, increasing pH in water is blocking decay particulate bounds of HMs and supporting adsorption of dissolved HMs ions to granulate, as a result granulate will relatively precipitate to the bottom or filtered to the soil during water moving (Almukhtar *et al.*, 2018).

Weiner (2000) mentioned that many soluble of heavy elements can link with other components when pH is high, and returns to soluble state again when its value becomes very low.

Huang & Lin, (2003) studied some HMs rates in Keelung river in Taiwan and they found high concentrations in (Pb, Cd, Cu and Zn) due to throwing industrial waste in it.

Vazquez *et al.*, (2004) studied some element concentrations in Nysa river in Germany and they found that Cd concentration ranged between (0.39-0.04) and Zn concentration ranged between (55.1-3.33)  $\mu\text{m/l}$  and they attributed those rates to smelting and mining activities.

Diagomanolin *et al.*, (2004) they studied concentrations of elements in karoon river in Iran and they found that rates of Ni, Cu and Cr in winter were (69.3-110.7, 70.3-5.5, 1.7-118.3)  $\mu\text{m/l}$  respectively and in spring rates were ( 60.7- 41.1, 28.7-0.5, 19.8-0.7)  $\mu\text{m/l}$ , they attributed results to many factories of paints, papers and solids which dropped waste to the river.

Puyate, *et al.*, (2007) emphasized in his study on Oogoo River in Nigeria that increasing pH value and organic matter contribute in cadmium fixation.

Papafilippaki *et al.*, (2007) studied dissolved heavy metals in Keritis river in Greece, they found rates concentrations of Zn, Cu, Pb, Cd and Cr in drought season were (39, 6.62, 2.59, 0.019, 3.25)  $\mu\text{m/l}$  while rates in humid season were (4, 0.88, 0.28, 0.005, 3.25)  $\mu\text{m/l}$  respectively.

Kar *et al.*, (2008) determined concentration of Mn, Ni, Pb, Cu, Cd, Cr, Zn and Fe in Ganga river in India ranged between (0.025- 2.72, 0.012- 0.375, 0.25- 0.001, 0.003- 0.32, 0.001-0.003, 0.001- 0.044, 0.012-0.37, .025- 5.49)  $\mu\text{m/l}$  respectively positive correlation was showed between conductivity and (Cr, Cd) of water but Mn showed a negative correlation with conductivity.



Nair *et al.*, (2010) studied pollution with heavy metals of Meenachil river in India and found that water of this river not drinkable because of high concentration of Pb, Fe and Cd, he attributed those results to drainage house hold water, agricultural residues, addition to the rocky nature of the river basin because this region is free from industrial activities.

Olatunji & Osibanjo (2012) determined in their study the concentration of some heavy elements in Niger river of Nigeria and they found that concentration of Ni, Zn, Pb, Cu, Cr, and Cd It had reached to (2.27, 0.78, 0.03, 0.05, 2.08, 3.85)  $\mu\text{m/l}$  respectively the results showed significant positive correlation between HMs rates with organic carbon.

Skorbiłowicz *et al.*, (2016) studied heavy metals distribution on Bug river in Poland, they measured the concentration of (Pb, Zn, Cu, Cr, Cd, Fe and Mn), they found that its concentrations exceeded international specification values due to agricultural activities and mining processes.

Krika & Krika. (2017) evaluated pollution with heavy metals in water and sediment along Nil River in Algeria, they found that rates of Pb and Cd in water were greatly higher than rates of Cu and Zn, studied area considered strongly contaminated by domestic waste water agricultural activities. Yan *et al.*, (2017) mentioned that lower levels of pH influence on releasing and precipitation of heavy metals.

Islam *et al.*, (2018) studied physicochemical parameters to determine its influence on heavy metals concentration in water of Rupsha river in Bangladesh, they found that concentration of (Pb, Mn, Cr, Fe, Ni, and Ag) was higher than limited rates of "World Health Organization" WHO, significant negative and positive relation

between the rates of HMs and physicochemical parameters were found and the river was considered highly polluted.

Wang *et al.*, (2019) studied correlation between dissolved heavy metals and physicochemical parameters in Laoshan Bay, China, the results showed significant between Cr and Hg levels with physicochemical parameters except chemical oxygen demand (COD) but Pb and Cu were not correlated with physicochemical parameters.

Jin *et al.*, (2019) studied some elements in Yangtze river and sediment in China, they found high concentrations of HMs which significantly influenced with turbidity of water and pH of sediments.

Many researchers made a native studies to measure rates of pollution with heavy metals in aquatic environmental in Iraq.

Al-Lami & Al-Jaberi, (2002) determined rates of some heavy elements in area above the center of Tigers river and they found that rates of Pb, Zn, Cd, Ni and Cu were exceeded the permissible limits.

Al-Fatlawi (2005) studied Euphrates river in area between Al-Hindiya dam and Al-kafel district in the middle of Iraq, he found that the concentration of Zn, Cu, pb and Fe had reached to (2.2, 4.4, 0.7 and 1.2) mg/l.

Fahad (2006) studied Al-Gharaf river, he found that rates of heavy elements were declining in winter and rising in the other seasons except Ni because of throwing household sewage without treatment it.

Al-Imarah *et al.*, (2007) studied levels of heavy metals in water and sediments of the southern parts of Shatt Al-Arab, they found that the rates of Cu, Cd and Pb were high as a result of industrial and human activities.

Al-Khafji *et al.*, (2011) noticed in Euphrates river in Nasiriya that the rates of Mn, Cd, Pb and Cu were high as a result of industrial activities in vicinity.

Salman & Hussein (2012) clarified in their study on Euphrates between Al-Hindia dam and region 74 in Kufa that rates of Co, Cu, Mn, Pb, Ni, Zn, Ni, Fe and Cr in dissolved phase were (1.16, 2.48, 6.12, 0.1, 0.07, 10.50, 105.69, 0.075, 2.14)  $\mu\text{g/l}$  respectively, while annual rates in particulate phase were (8.09, 13.65, 33.71, 0.50, 0.193, 59.98, 660, 0.245, 10.22)  $\mu\text{g/l}$  respectively.

Abdullah, (2013) evaluated the quality of Shatt Al-Arab water with heavy elements (Zn, Pb, Ni, Cu and Fe) were taken and the researcher found that water of Shatt Al-Arab were not highly polluted with those elements and the rates of HMs were from anthropogenic source.

Hassan *et al.*, (2014) made a study on Euphrates river to measure (Pb, Mn, Cu, Co, Zn, Ni, Fe, Cr and Cd) and he found that rate of concentrations in particulate phase higher than in dissolved phase and arrangement of concentration in particulate phase were (Ni<Cr<Pb<Co<Cd<Cu<Mn<Zn<Fe).

Al-Enazi, (2014) in his study on aquatic environment in Basra and after many samples of different region was taken he found that water was polluted with Cu, Co, Pb and Fe and that pollution affecting the health of population in case of drinking without treatment ensure decreasing rates of pollutants.

Nasir & Al-Najar (2015) explained in their study to determine rates of (Co, Pb, Fe) in Shatt Al-Arab water, they found that rate of concentrations exceeded permissible limits in water.

Al-Mayah *et al.*, (2017) studied physicochemical parameters and rates of heavy metals in Al-Gharraf river in Al-Haay City in south of Iraq, they found most of physicochemical parameters exceeded permissible limits of Iraqi standard specifications and WHO standard for drinking, the rates of Lead and Cadmium were

031- 0.21 ppm and 0.002-0.089 ppm in water in dissolved phase and the rates also exceeded permissible limits.

Al-Hejuje *et al.*, (2017) studied pollution with (Cd, Cu, Fe, Mn, Ni, Pb and Zn) in five station of Shatt Al-Arab river, they found that rates of studied elements were higher in particulate phase than in dissolved phase and the concentrations exceeded permissible values.

Al-Zurfi *et al.*, (2019) studied some heavy metals and physicochemical parameters in water of Bahr Al-Najaf they found that rates of (Pb, Zn, Cd, Fe, and Mn) were exceeded the permissible limits and water hardness was high, BOD<sub>5</sub> recorded in some months higher than permissible limits.

Fadhil *et al.*, (2019) studied levels of toxic elements of (Ni, Pb, Hg, Cr, As, and Cd) in Shatt Al-Arab river, they found that sediment was highly polluted while the rates in water was not exceeded the permissible limits, they mentioned that physicochemical parameters greatly influence on distribution and accumulation of heavy metals.

Al-Taher *et al.*, (2020) evaluated the rates of heavy metals in water and sediment on Euphrates river in Al-Nassireyah city, the results showed that order of elements was Mn > Pb > Zn > Cu > Fe > Cd, and in sediments it was Fe > Mn > Zn > Cu > Pb > Cd, they found local and seasonal variation in the rates of elements and the river was highly polluted.

### **2.3 Heavy Metals in Sediment**

Existence of heavy elements in surface sediments or aquatic plants considered as a sign of water pollution, sediments are potential source of pollution in the environment, either as a carrier or a store for those pollutants, heavy elements forming dissolved ketones as combination of heavy metals are easy to attract and

catch by clay or organic compounds iron and manganese hydroxides therefore it accumulate on surface sediments or is absorbed by aquatic plants (Bonanno and Vymazal, 2017).

Many studies about pollution of sediments with heavy metals round the world and in Iraq.

Hornberger *et al.*, (2000) studied concentrations of Zn, Mn, Ni, V, Al, Cu, Cr and Fe in sediments of San Francisco Bay, California and the rates within standard ranges.

Demirak *et al.*, (2006) studied heavy elements in sediments and water of stream in the south western in Turkey and he found the rates of Cu, Zn, Cd, Pb, and Cr in sediments were (13.00, 37.00, 0.80, 83.60, 19.70) µg/g from dry weight respectively.

Kruopiene, (2007) studied distribution of heavy elements in sediments of Nemunas river in Lithuania, where Cu, Cr, cd, Fe, Zn, Pb, Ni and Mn rates were affected by the waste generated by cities, but it didn't pass local and international standers.

Varol (2020) studied content of some trace elements in sediment of Keban Dam Reservoir in Turkey, he found that higher concentration of studied elements were in samples of sites which received domestic waste charge and industrial waste, Cr and Ni concentrations were exceeded permissible limits and rates of (Cu, Zn, Pb , Fe, and Mn) were not exceeded limited values.

Sharma *et al.*, (2020) studied impact of heavy metals in sediment and water of Yamuna River, India, they found that levels of rates higher than safe limits, total organic carbon significantly influence on accumulation of HMs rates.

Youssef *et al.*, (2020) studied pollution with heavy metals in Hurghada in Egypt, they estimated the rates of (Zn, Cu, Fe, Mn, Pb, and Cd ) the order of those elements

was  $Mn > Zn > Pb > Cu > Cd$ , according to the results studied area was unpolluted and tiny proportion attributed to anthropogenic source.

In Iraq many researchers studied about sediments pollution.

Al-Juboury *et al.*, (2009) studied heavy metals in modern sediments of Tigris river and its tributaries in the north of Iraq, he attributed relative and qualitative differences between two rivers to many factors such as the rocky nature of the river sources and river morphology as well as the specific weight and size of these minerals.

Salah *et al.*, (2012) estimated heavy metals in sediment and water of Euphrates River in Anbar Province, they found that mean rates of Ni, Fe, Cd, Cu, and Mn in sediment exceeded permissible limits, sediment were highly polluted with Cd and Cr and moderate with Zn.

Issa and Qanbar (2016) studied sediments contamination with (Cd, Cu, Cr, Pb, Co, Mn and As ) of Euphrates river, Shatt Al-Hindiya they found that sediment moderately contaminated with (Cr, Cu and Co) and was not polluted with (As, Cd and Mn).

Al-Jaberi *et al.*, (2016) studied concentration of heavy metals in sediment and water of Shatt Al-Arab river, they found that rates were in order  $Cr > Mo > Ni > Zn > Cu > Pb$  in sediment, the soil of studied sites considered moderately polluted but not high polluted with Pb.

Al-Jawad *et al.*, (2020) studied pollution of the sediments of northern part of Shatt Al-Arab with Cu, Pb, Cd, Ni and Zn, he found that study area very polluted with Pb, Cd and Ni and acceptable pollution with Zn and Cu.

## 2.4 Heavy Metals in Plants

### 2.4.1 *Phragmites Australis*

*Phragmites australis* (common reed) widespread species, arise and partially submerged macrophytes, belongs to Poaceae family, grows in wetland even water was distinguished as shoal and putrefactive, *p. australis* is a large slender with stem reached up to 6-8 m in height (Mirza *et al.*, 2010). Roots grow from rhizomes and other submerged parts of shoots, seeds are rare in many populations and extremely variable (Mal & Narine, 2004). *P. australis* classification by national plant data center of USA (USDA, 2002) as following:

Kingdom Plantae – Plants

Subkingdom Tracheobionta – Vascular plants

Superdivision Spermatophyta – Seed plants

Division Magnoliophyta – Flowering plants

Class Liliopsida – Monocotyledons

Subclass Commelinidae

Order Cyperales

Family Poaceae – Grass family

Genus *Phragmites* Adans . – L. reed **P**

Species *Phragmites australis* – L. common reed

*P. australis* can grow in extreme circumstanced as example its growing in pH ranged between 2.5- 9.5, this plant can accumulate (Cd, Cu, Pb, Ni, and Zn) in it leaves more than *Typha australis* plant (Batty & Younger, 2004). *P. australis* considered as macrophytes, this plant has the ability to accumulate heavy elements and used widely in water treatment to remove those pollutants (Bonanno and Pavone, 2015).

Bragato *et al.*, (2009) Studied concentration of Zn, Cu, Ni and Cr in *Phragmitus australis* in a constructed wetland of North Italy, they revealed that rates of taken elements were high in rhizomes and stems than leaves, *P. australis* showed significant efficiency in utilizing studied elements, *P. australis* could be used in biological treatment.

Goher & Ali, (2009) studied aquatic plant (*P. australis* and *Cyperus rotundus*) as a sign for pollution in Ismailia channel in Egypt and he found that those plants had high capacity to accumulate Pb and it could be used as a biosensors to lead contamination.

Sagehashi *et al.*, (2011) in his laboratory study in Shanghai/ China confirmed that *p. australis* is the main accumulator for Pb, Cr, and Ni by moving elements from the stem to leaves where it store.

Eid *et al.*, (2020) studied uptake of six heavy metals in Lake Burullus in Egypt by *P. australis* tissues, stems, leaves and belowground, monthly during growing season, they found good ability for accumulating (Cd, Cu, Fe, Ni, Pb and Zn) but no significant difference in values between three tissues.

Salman & Hussein (2012) made a study in Euphrates river on *Ceratophyllum demersum*, *Phragmitus australis*, *Typha domingensis* and *Potamogeton pectinatus* plants and he found that those plants had the ability to accumulate heavy metals due to rates of concentrations which were higher in studied plants more than sediments and water, this susceptibility varies with the variability of the source of contamination and different plant type.

Fadhil & Al-Baldawi (2019) evaluated the ability for up taking heavy metals of *P. australis* from Tigris River in Baghdad city by exposure the plants to waste water from Al-Daura refinery weekly for 42 days, they noticed significant increasing in



biomass about 60% in wet weight in the period of experiment, and the plant uptake 62.3% from pollutants, that proved high efficient in removing pollutants and good tolerance to extreme contamination.

### **2.5 *Ceratophyllum Demersum***

*C. demersum* is a widespread submersed plant, distinguished with ability to grow in muddy and shallow areas even with low light, many studied showed its capacity to accumulate Zn, Pb and Cu (Keskinan *et al.*, 2004).

*C. demersum* is a rootless plant, belong to ceratophyllaceae family grow as a dense net and can adaptive with high salinity environment (Arnolds *et al.*, 2018). *C. demersum* classification by national plant data center of USA (USDA, 2002) as following:

Kingdom Plantae – Plants

Subkingdom Tracheobionta – Vascular plants

Superdivision Spermatophyta – Seed plants

Division Magnoliophyta – Flowering plants

Class Magnoliopsida – Dicotyledons

Subclass Magnoliidae

Order Nymphaeales

Family Ceratophyllaceae – Hornwort family

Genus *Ceratophyllum* L. – hornwort **p**

Species *Ceratophyllum demersum* L. – coon's tail

Keskinan *et al.*, (2004) clarified that *C. demersum* main accumulator for Cu, Fe and Zn according to easily and rapid absorption to high level of concentration of those elements.

Borisova *et al.* (2014) made a laboratory study in China to investigate capacity of accumulation of *C. demersum* for some heavy metals and they found that *C.*

*demersum* had a positive mechanism to adaptive with heavy metals exposure, and they found that *C. demersum* was capable of remove more than 70% of lead concentration from the site of study in 15 days.

Duman and Koca (2014) proved the of ability of *C. demersum* in accumulation both of chromium and lead in 7 days after exposure to those elements and results exhibited synergistic effect with EC.

Chen *et al.*, (2015) investigated the ability of accumulation high levels lead by *C. demersum* by exposing the plant to different concentration of lead, (5–80  $\mu\text{M}$ ) for 7, 14 or 21 days, the results showed increasing of accumulation with increasing concentration of lead, according to the results *C. demersum* has efficiency in removing lead.

Deák *et al.*, (2019) studied concentrations of heavy metals in Dambovita River in Romania, they found the higher rates were in water due to a lot of pollutant sources, macrophytes showed ability to decline and accumulation heavy metals specially in *Ceratophyllum demersum*.

Hanaf, (2009) studied cumulative ability in three aquatic plants in water of Shatt Al-Arab, he mentioned that concentrations of Cu and Pb in *C. demersum* in most result were the higher compared with other studied plants.

Mahmoud *et al.*, (2018) mentioned that *C. demersum* grow widely in coastal region of Euphrates river and it is an efficient accumulator for trace elements and could be used for water treatment.

Al-Edani *et al.*, (2019) studied the ability of three plants to accumulate (Fe, Cd, Cu, and Pb) in two sites of Shatt Al-Arab river, they found that rates of elements were high *C. demersum* that reflected good efficiency in removing element pollutants followed by *P. australis* and finally in *Cyperus rotundus*.

## 2.6 Phytoremediation

During the past two decades there has been increasing interest in processes that convert toxic elements in the environment to less harmful ones, the natural processes that occur naturally, including biological treatment which uses living organism such as plants, animals, algae and microorganism by using different ways to remove or break pollutants and restore the polluted to relatively normal position (Venkatesharaju *et al.*, 2010).

Biological treatment has a great importance in preserving environment and thus preserving human life from increasing concentrations of pollutants, it also decompose or remove substances that take a long time in decomposition and convert pollutants to safe or inactive compounds in different ways (Nakanishi *et al.*, 2004).

Some aquatic organism have the ability to aggregate and accumulate heavy metals into concentrations that exceed many times of environment, the definition of bioaccumulation is the ability to concentrate pollutants in the bodies of living organism, including heavy metal, pesticides and hydrocarbons (Xu *et al.*, 2017).

Aqueous plants have different mechanism to deal with heavy metals such as transforming absorbed elements to aerial parts, phytostabilization by preventing movement of heavy elements in polluted soil, phytovolatilization which means ejection volatile metals in excretion from leaves, this process occur during bulky amounts up taking that eliminate contamination water from spreading (Bonanno and Vymazal, 2017).

There many environmental factors temperature, salinity, acidity, nutrients and the amount of oxygen, all those factors affected the accumulation by affecting the interference between ions of elements and cell walls (Nageb, 2015).

Many types of aquatic plants used as biological indicator for pollution and to remove pollutants because its tolerance for pollution and live in different environments with simple requirements, there are many types of plants have the ability to extract and accumulate heavy metals from polluted area, rapid growth, dense and deep roots, ease of harvesting and extraction, accumulation of high levels and wide range of elements make the plant ideal for phytoremediation (Maresca *et al.*, 2020).

Pajevic *et al.*, (2008) studied pollution with heavy metals in Danube river in Yugoslavia, they mentioned that aquatic plants have the ability to accumulate chemical elements can remove heavy metals in quantities ranging from several tenths to thousand times higher than in water.

Fawzy *et al.*, (2012) determined concentration of heavy metals in water, sediment and Aquatic plants of Nile river, they found that *C. demersum* showed high cumulative capacity compared with *P. australis* and other studied plants.

El-Khatib *et al.*, (2014) proved in his study the efficiency of *C. demersum* in accumulation high amounts of Pb in 7 days.

Nafea & Zyada (2015) studied heavy metals pollution aquatic plants, sediment and water of Lake Burrullas, Northern Delta, Egypt, they proved that *P. australis* and *C. demersum* are good biological filters for element pollutants, the results showed that *C. demersum* was cumulative high rates of copper and iron and could accumulate more rates of HMs than *P. australis*.

Ahmad *et al.*, (2016) determined rates of (Cd, Pb and Co) accumulation inside cells of *ceratophyllum demersum* and *Potamogeton natans* in Kashmir Himalayan Ramsar site, *ceratophyllum demersum* plant showed high efficiency in accumulating

heavy elements compared to *Potamogeton natans* and the efficiency was increased by increasing the concentration of the elements and increasing the exposure period.

Valchev *et al.*, (2017) evaluated concentrations of HMs in wetlands of Danube river in Bulgaria, they found concentrations of (Pb, Zn, Cd, and Cu ) in water were lower than in macrophytes of three studied sites and *c. demersum* was richest in Zn followed Cu, pb and Cd.

Chitimus *et al.*, (2019) studied absorption capacity from the soil to heavy elements by *P. australis* Bistrița and Cracau River in Romania, they recorded very high ability to accumulate elements, the highest absorption was to Cadmium elements.

Al-Afify and Abdel-Satar (2020) studied risk of pollution with heavy metals in water and sediment and aquatic plant in Nile river in Egypt, they found that rates were sediment>plants>water and *c. demersum* exhibit clear capacity in accumulation of (Mn, Fe, and Cu) compared with other studied plant (*Eichlornia crassipes*).

Yi *et al.*, (2020) studied Baiyangdian lake in China, they noticed that the accumulation of (Mn, Zn, Fe and Fe ) in roots and leaves of *Phragmites australis* more than rates in sediments so that would help to use it as a biological indicator for pollution and as an environmental cleaner.

Many Iraqi researchers studied bioaccumulation ability of aquatic plant:

Majid *et al.*, (2014) studied bioaccumulation ability of *Typha angustifolia* and *Phragmites australis* in stream bank of Qalyasan in Sulaimania city, they found the rates of heavy elements in *P. australis* were Mn> Cu > Cr > Pb and the two studied plants have potential efficiency in phytostabilization and phytoextraction for elements pollutants.

Farhood (2017) studied bioaccumulation of heavy metal in *P. australis* and *C. demersum* in two station on Euphrates in Thi-Qar province, he found that (Cu, Cd, and Pb) were higher in *C. demersum* more than *P. australis* and the concentrations in two studied plants were higher than rates of water in dissolved phase.

Al-Atbee *et al.*, (2019) studied accumulation of ( Cr, Cd, Ni and Pb) in *P. australis* and *C. demersum* in Al-Chibayish Marshes, South of Iraq, they found that highest rates were in sediment then in two studied plants, the lowest rates were in dissolved phase of water.

### 3. Materials and Methods

#### 3.1. Description of Study Area

Euphrates is one of the biggest rivers in southwest Asia, river streams from mountainous region in turkey, then flows to southeast passing Syrian lands after many tributaries flow into the river, then enters Iraq lands in Al-Qaim city in Anbar governorate, meets with Tigris river forming Shaat al-Arab which flows in Arabian Gulf, length of the river from the source to the downstream is about 2940 (KM) , 1176 (KM) in Turkey and 610 (KM) in Syria and 1160(KM) in Iraq (Ministry of Water Resources 2005)

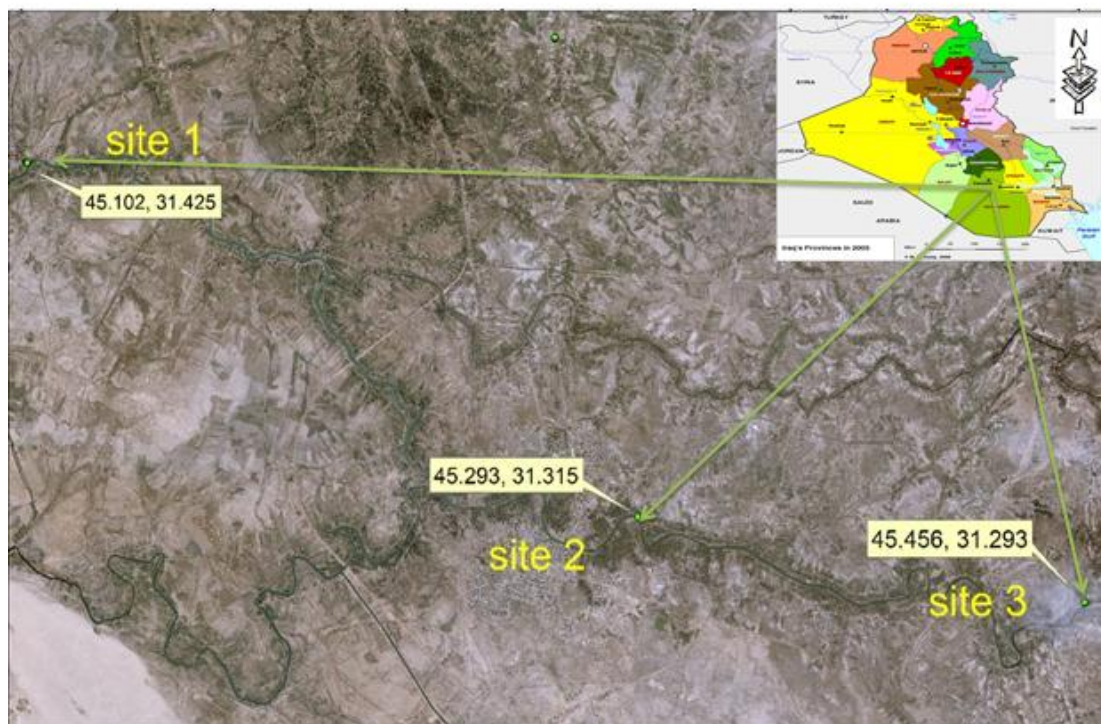
When the river enters Iraq lands it passing throw many cities then enters Muthanna governorate at Tal al-Khart area at north of Hilal District and ends from Muthanna city in two areas (left side in Darraji and right Al- Hushli) then enters Dhi-qar province. Length of the river in Muthanna governorate is about 110 (KM) and width is change between 100-120 M in the center and in some narrow areas reach to 70M.

The main provider for drinking water and watering transplanted is Euphrates river and on extension of each side of it grows heavily of natural plant *Phragmites australis* in addition some other type like *Ceratophyllum demersum* which grow during four seasons of the year, three station were taken for the study:

**First Site:** It lies on longitude (45.1023638) and latitude (31.4254749), at the entrance of the river to Sammawa city in Hilal region which considered as rural area where livestock grazing abundantly like a buffalo and cows and there are drainage and sewers throwing waste directly to the water (Figure: 3-1, image: 3-1).

**Second Site:** It lies on longitude (45.4562525) and latitude (31.2936821), at a distance about 20 kilometers from the first point second site lies in the center of Samawa city where exist many restaurants throw waste to the river too, and sewage waste thrown to the river without any treatment (Figure: 3-1, image: 3-2).

**Third site:** It lies on longitude (45.2931319) and latitude (31.3154022), at last situation of the river in Samawa city in Al-Abas distant which is far from Samawa city about 18 kilometers where sewage tube drops waste to the water and also rich of livestock grazing (Figure: 3-1, image: 3-3).



**Fig (3-1): The sites of study in Euphrates river**





**Image (3-1): First site**



**Image (3-2): Second site**



**Image (3-3): Third site**

### **3.2. Samples collection**

Samples were collected monthly to examine the physical and chemical properties of the water and seasonally to measure the concentrations of some heavy metals in water and sediment and two types of plants from November 2019 to October 2020 as following:

- Water samples were collected from the middle of the river at depth 30 cm and put in polyethylene bottles with capacity 5 liters which washed with Nitric acid then rinsed by distilled water .
- Sediments samples were collected by using Van veen Grab sampler and kept in labeled plastic bags.
- Full parts of two plants *Phragmites australis* and *Ceratophyllum demersum* were taken and washed with river water to remove clay then transferred to the laboratory.

**Table (3-1): List of Instruments used in study**

Instruments	Company	Original
Geographic position system (GPS)	Garmin Ltd	Taiwan
Sensitive balance	Kem and Shhn, ABS120-4j	Germany
Centrifuge	Universal	China
Water distillatory	LabTech	Korea
Turbidity meter	WTW-Turb-550	Europe
Thermometer	HANNA	USA
Multimeter	HANNA	USA
BOD <sub>5</sub> Incubator	Memmert	Germany
Hot plate	staurt	Germany
Flame Atomic Absorption	SHMADZU	Japan
Electrical oven	Memmert	Germany
Shaker	LabTech	Korea

**Table (3-2): List of chemical materials used in study**

NO.	Material	Chemical formula	company
1	Sodium azide	NaN <sub>3</sub>	BHD
2	Sulfuric acid	H <sub>2</sub> SO <sub>4</sub>	BHD
3	Sodium thiosulphate	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> .5H <sub>2</sub> O	BHD
4	Starch	(C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ) <sub>n</sub>	India
5	Sodium hydroxide	NaOH	Flauka
6	EDTA.Na <sub>2</sub>	C <sub>10</sub> H <sub>16</sub> N <sub>2</sub> O <sub>8</sub> Na <sub>2</sub>	BHD
7	Erochrome Black T (EBT)	C <sub>20</sub> H <sub>12</sub> N <sub>3</sub> O <sub>7</sub> Na	BHD
8	Nitric acid	HNO <sub>3</sub>	BHD
9	Perchloric acid	HClO <sub>4</sub>	BHD
10	Hydrochloric acid	HCl	BHD

11	Hydrofluric acid	HF	BHD
12	Muroxide	C <sub>8</sub> H <sub>8</sub> N <sub>6</sub> O <sub>6</sub>	BHD
13	Sodium chloride	NaCl	BHD
14	Manganese (II) Sulphate Monohydrate	MnSO <sub>4</sub> .H <sub>2</sub> O	BHD
15	Potassium iodide	KI	GCC
16	Potassium hydroxide	KOH	BHD

### 3.3 Methods for Examining Physical and Chemical Parameters

**3.3.1 Air and water Temperature:** was measured by using mercury thermometer amphitheater from (0 – 100) C°.

#### 3.3.2 pH, Total Dissolved Solids (TDS) and Electrical Conductivity

**(EC):** were measured by using portable multimeter device, after being calibrated with standard solution, unit of TDS is mg/l where unit of EC was microSiemens (μs/cm<sup>2</sup>) .

**3.3.3 Turbidity:** was measured by using turbidity meter, unit of turbidity is Nephelometric (NTU).

#### 3.3.4 Dissolved Oxygen

Azide modification way was used, samples were collected and kept in Winkler bottles and treated with concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) for oxygen fixation and alkaline azid reagent in the field of work, then titrated with sodium thiosulphate and used starch as an indicator in laboratory (APHA, 2007 ) unit is mg/l .

**3.3.5 Biological Oxygen Demand (BOD<sub>5</sub>):** Samples were put in BOD<sub>5</sub> incubator for five days in temperature 20C° after each samples were provided with nitrogen inhibitor and sodium hydroxide (APHA, 2003)

**3.3.6 Total Hardness:** According to Lind (1979) total and Calcium hardness were estimated by titration with EDTANa<sub>2</sub> (0.01N), Magnesium (Mg<sup>+2</sup>) was calculated according to the following equation:

$$\text{mg Mg}^{+2} \text{ per liter} = 12.16 \times [\text{mEq hardness per liter} - \text{mEq Ca}^{+2} \text{ per liter}].$$

$$\text{mEq hardness per liter} = \text{mg hardness per liter} \times 0.01998 .$$

$$\text{mEq Ca}^{+2} \text{ per liter} = \text{mg Ca}^{+2} \text{ per liter} \times 0.0499.$$

### 3.4 Measurement of Heavy Metals

#### 3.4.1 Measurement of Heavy Metals in Water

##### 3.4.1.1 Dissolved Heavy Metals

Tow liters of water sample from each stations was filtered with Millipore filter paper (0.45)  $\mu\text{m}$  after washed with HNO<sub>3</sub> (0. 5N) then with ion free water and dried in 60 C° for 12h, 1.5 ml of HNO<sub>3</sub> was added to each litter to keep elements in ionic state, then 100 ml was put in 70C° and added 1ml of concentrated HNO<sub>3</sub>, finally size was completed to 25ml of free ionic free water and ready samples were kept in labeled polyethylene until measurement in Flame Atomic Absorption (APHA , 2003), unit was  $\mu\text{g/l}$  .

### 3.4.1.2 Particulate Heavy Metals

Filter papers which used to filter water was dried in 70 C° for 48h. and weighed to know weight of deposit then extracted, 0.5g from deposit in Teflon containers treated with 6ml of mixture concentrated HCL and HNO<sub>3</sub> (1:1) and evaporated approximately to dry in 80 C°, then 4ml of mixture of precloric acid HCLO<sub>4</sub> and hydrofluoric HF (1:1) was added then solution was evaporated approximately to dry, precipitation was melted in HCL (0.5N), left for 10 min. then centrifuged (3000 r/min) for 20 min., solution was taken and put in 25 ml size bottle after separation of precipitation and size was completed to 25 ml. (USEPA, 1999), samples was labeled and kept until examined with Flame Atomic Absorption , unit is µg/g dry weight.

### 3.4.2 Extraction of Heavy Metals From Sediments

Samples of sediments was taken, solids and strange parts were removed, each samples of three stations was dried in 70C° for 48h. , then samples grinded with ceramic mortar and passed through sieve with pores diameter 65µm and kept in special labeled polyethylene bottles, after that elements were extracted as exchangeable and residual fraction as following :

#### 3.4.2.1 Extraction of Exchangeable Heavy Metals

1g was weighed from dried sample and put in coated Teflon bottle, size 50 ml , 20 ml of HCL (0.5 N) was added and centrifuged (3000 r/min) for 20 min., solution was transported to special plastic bottles and kept until measuring with Flame Atomic Absorption (Hlavay *et al.*, 2004), unit is µg/g dry weight.



### 3.4.2.2 Extraction of Residual Heavy Metals

After exchangeable had been extracted, residual precipitation was taken and digested for taking remaining ions in precipitation by adding 4 ml of free ionic water to get rid of used acid and remaining exchangeable elements, then centrifuged (3000r/min) for 30 min to remove washing water then precipitation was transported to Teflon Becker, 6ml of mixture of HCL and HNO<sub>3</sub> (1:1) was added and evaporated approximately to dry in 80 C° then 4 ml of mixture of HF and HCLO<sub>4</sub> (1:1) was added and evaporated one more time nearly to dry. Precipitation was melted in 20 ml of HCL (0.5N), then left for 10 min, after that centrifuged (3000r/min) for 20 min., solution completed to 25 ml with free ionic water and kept in Precipitation was melted in 20ml of HCL (0.5N), then left for 10 min, after that centrifuged (3000r/min) for 20min., then solution completed to 25ml with free ionic water and kept in plastic labeled bottles to measure by Flame Atomic Absorption (Yi *et al.*, 2007), unit is µg/g dry weight.

### 3.5 Extraction of Heavy Metals From Plants

By drying samples of plants in 50C° for 3 days and grinded with ceramic mortar, 1g from powder was weighed and put in flask size of its 25 ml, (1:3) HNO<sub>3</sub> and HCLO<sub>4</sub> was added, samples was well shacked and left for 24h., then put in water bath for 1h to speed up digestion of tissue, 2-3 ml of distal water was added then flask put on a hot plate in (70 C°) until size was reached about 2 ml then centrifuged (3600r/min) to get precipitation and size was completed to 50 ml with distal water and kept for measuring with Flame Atomic Absorption (APHA , 2005). unit was µg/g dry weight.

### **3.6 Total Organic Carbon ( TOC ) In Sediments**

Wet oxidation method was used to determine total organic carbon according to El Wakeel and Riley (1957).

**3.7 Soil Texture** Adopted method described by (ASTM, 1985). For Particle-size analysis by different size sieve for sediment.

### **3.8 Statistical Analysis**

Statistical package for the social science (SPSS) version 25 was used to measure mean value and standard deviation for the parameters included in the study, for statistical comparison Least Significant Difference test (LSD) was used to compare mean values.

The value of correlation between physicochemical parameters and heavy metals was calculated, and the significant differences were determined at significant level  $p < 0.05$  (Schiefer, 1980).

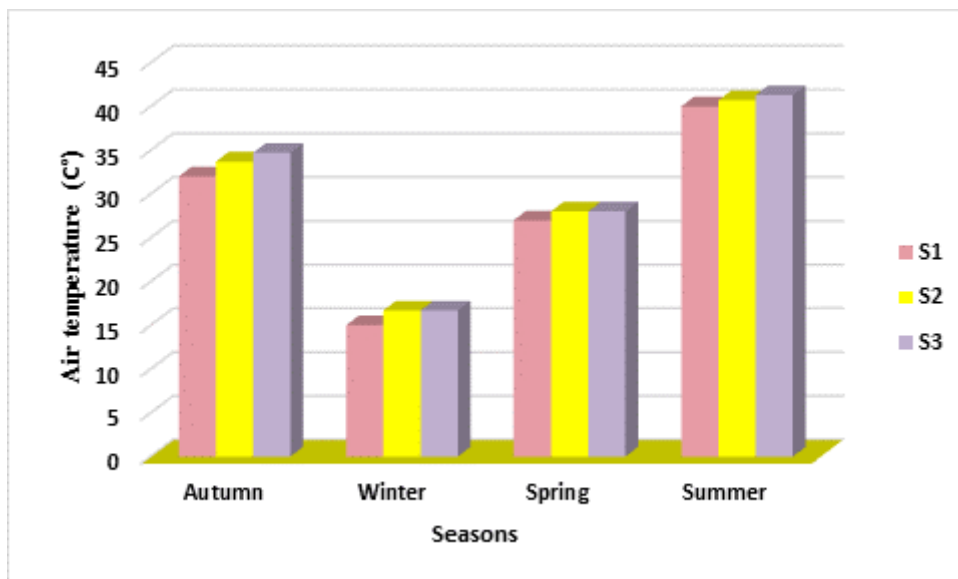


## 4. Results and Discussion

### 4.1 Physical & Chemical Parameters

#### 4.1.1 Air Temperature

The most important factor that influences on aquatic environment is temperature because changing in their properties depended on it such as dissolved oxygen levels, electrical conductivity, and levels of organic decomposition, and it influences on growing and reproduction of aquatic organism (Duruibe *et al.*, 2007). Air temperature in study sites ranged between highest mean value (41.33 °C) in third site during Summer, and lowest mean value (15 °C) in first site during Winter (Appendix:1, figure: 4-1)



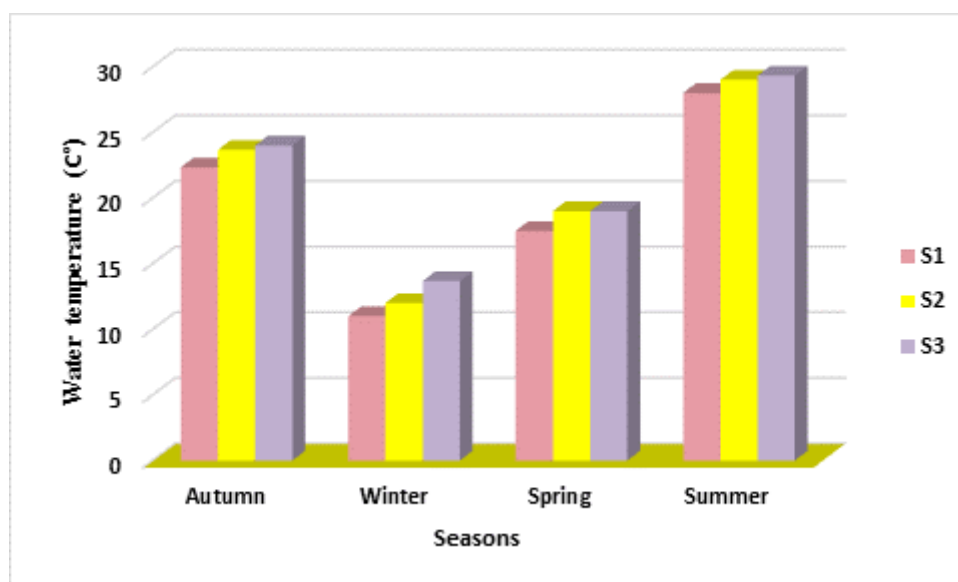
**Fig(4-1): Seasonal variations for air temperature mean value in study sites**

#### 4.1.2 Water Temperature

Temperature of water plays important role in diversity and density of aquatic organism and effects on cellular metabolism processes (Ranjbar *et al.*, 2017). Water

temperature ranged between highest mean value (29.33°C) in third site during Summer, and lowest mean value (11°C) in first site during Winter (Appendix:1, figure:4-2).

Results showed significant difference in temperature between Summer and Winter due to the nature of seasons in Iraq, length and shortness of the day between seasons (Al-Hejuje, 2014). Difference between stations may be resulted from the difference in the time of samples taking, or variation in the depth of water in each station or turbidity in water column (Hassan *et al.*, 2010).

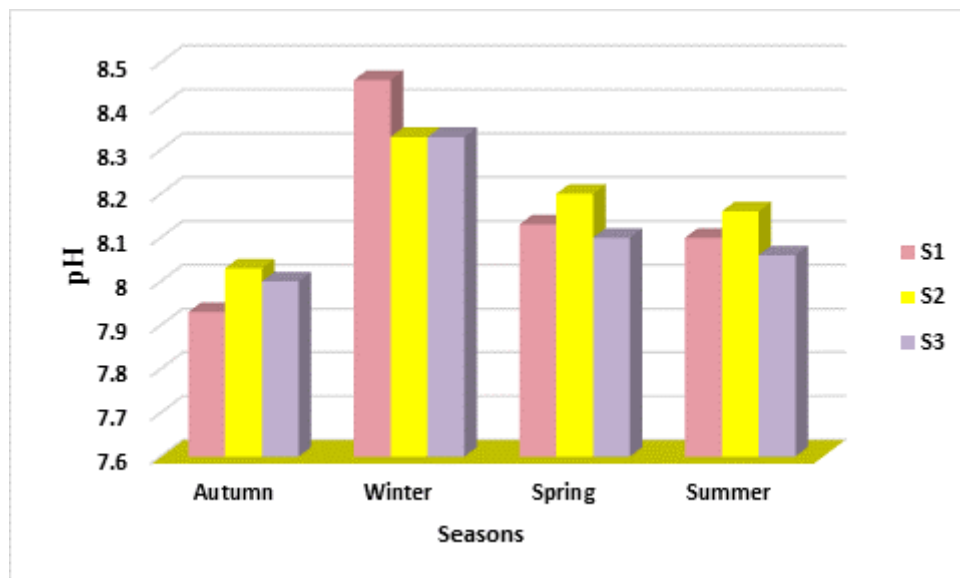


**Fig(4-2): Seasonal variations for water temperature mean value in study sites**

#### 4.1.3 pH

It is an important factor which affects aquatic organisms, as most metabolic activities depend on it (Wang *et al.*, 2015). Also pH is an important in ruling availability and accumulation of heavy metals in aquatic system (Elia *et al.*, 2018). PH ranged between highest mean value (8.47) in first site during Winter, and lowest mean value (7.93) in first site too during Autumn, (Appendix:1,figure:4-3).

The best range of pH for most of aquatic organisms is (6.5-8), out of this range organisms are vulnerable to destruction, low pH leads to release toxic compounds that subsequently affect aquatic animals and plants (Joda *et al.*, 2019). The Results showed that water of Euphrates mean values tends to light basal conformed to specifications of Iraqi water and within limits permitted by (WHO 2006). PH value was decreased in summer and a little increased in winter, that could be attributed to decrease mean value of decomposition due to lower bacterial number in winter compared to summer (Venkatesharaju *et al.*, 2010). And that's consistent with study of ( Al-Maliki, 2020; Sabri *et al.*, 2020).

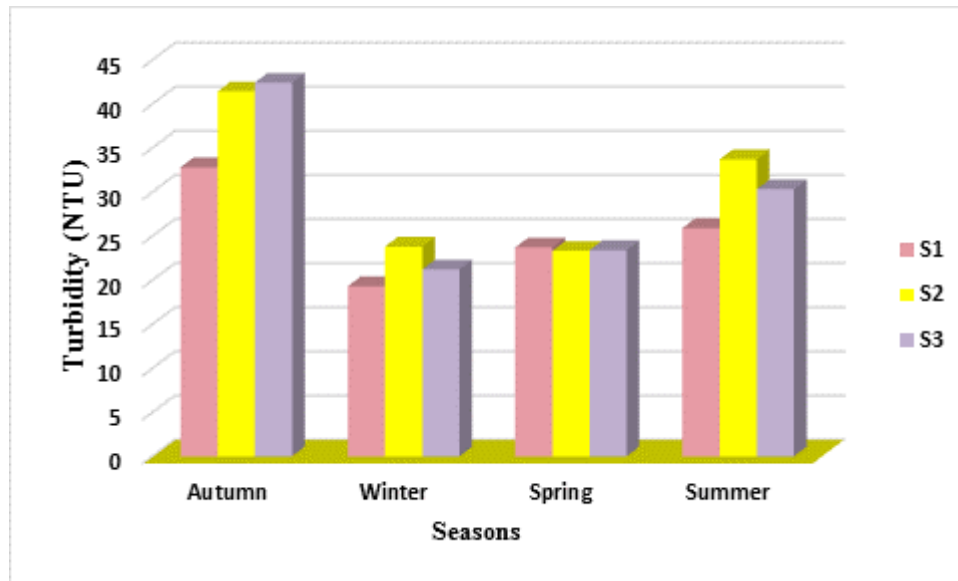


**Fig(4-3): Seasonal variations of pH mean value in study sites**

#### 4.1.4 Turbidity

It is resulting from existence of particles suspended in water such as silt, sand and clay which it consists of organic, inorganic minerals, phytoplankton and microorganism (Venkatesharaju *et al.*, 2010). Turbidity ranged between highest mean value (42.4 NTU) in third site during Autumn, and lowest mean value (19.34

NTU) in first site during Winter (Appendix:1 figure: 4-4). Turbidity exceeded allowed limits during October may be attributed to drainage which causing soil washing and flow speed (Appendix:5) (Mushtaq *et al.*, 2013), or could be attributed to banks of the river which containing big quantities of contaminated materials, sand, soil particles, and microorganism (Mustafa, 2006).



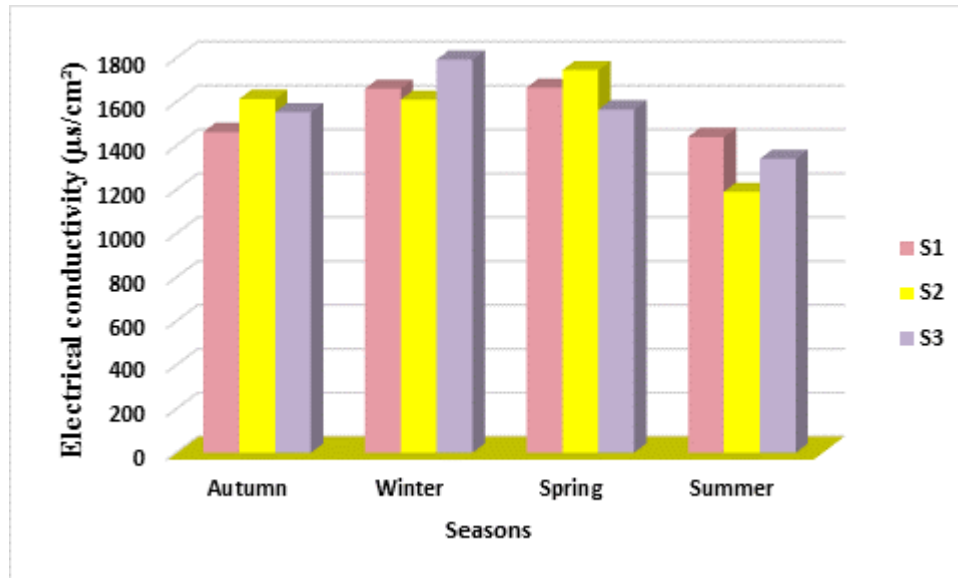
**Fig(4-4): Seasonal variations of turbidity mean value in study sites**

#### 4.1.5 Electrical conductivity

It is one of the main important factors in environmental studies to determine water quality, electrical conductivity means the ability of transfer electrical current which is affected by temperature, total dissolved solids and organic materials of water (Jayalakshmi *et al.*, 2011).

Electrical conductivity ranged between highest mean value ( $1793.33 \mu\text{s}/\text{cm}^2$ ) in third site during Winter, and lowest mean value ( $1190 \mu\text{s}/\text{cm}^2$ ) in second site during Summer, (Appendix:2, figure:(4-5)).

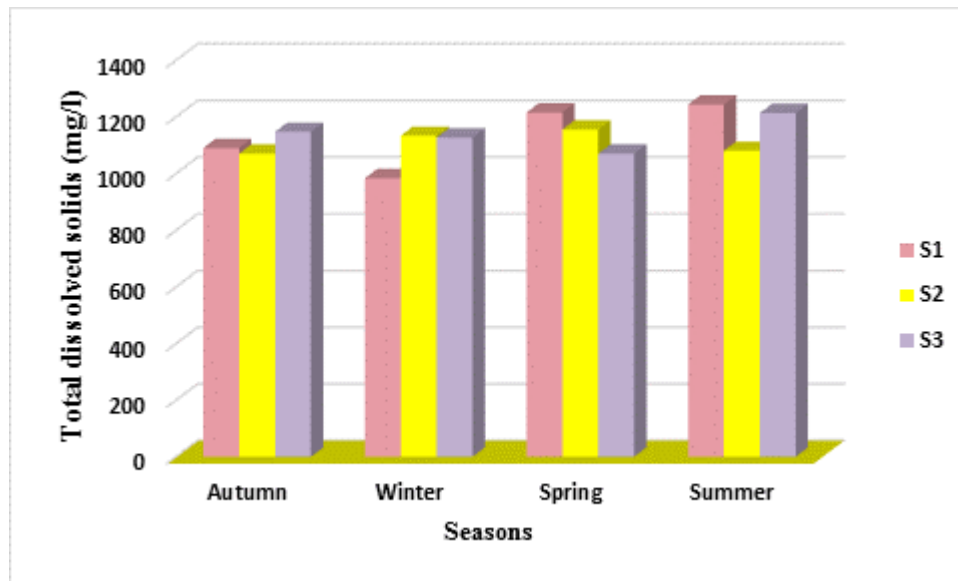
Increasing could be due to lack of rains during Winter season that led to increase in concentrations of salts, which cause increase in EC values and this agrees with studies of (Al-Seedi & Al-Auboody, 2011; Al-Sharifi, 2014).



**Fig(4-5): Seasonal variation of electrical conductivity mean value in study sites**

#### 4.1.6 Total dissolved solids

Total dissolved solids mostly consist of inorganic materials like (calcium, magnesium, sodium, potassium, chlorides, carbonate, bicarbonate and sulfate) in addition to dissolved organic matter (Mitsch *et al.*, 2015). TDS ranged between highest mean value (1243.33 mg/l) in first site during Summer, and lowest mean value (983.33 mg/l) in first site too during Winter (Appendix:1, figure:4-6). Increasing of TDS during Summer may be attributed to remnants of water purifications and desalination stations, or could attributed to increased evaporation levels caused by high temperature, decomposition products and suspended organic materials that cause environmental and physiological stress impacts (UNEP, 2006).



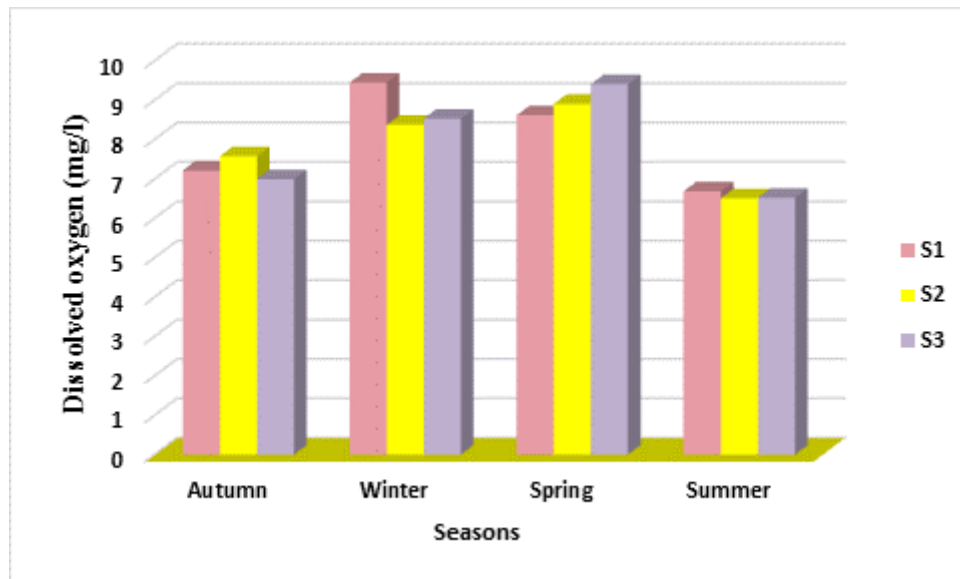
**Fig(4-6): Seasonal variations of total dissolved solids mean value in study sites**

#### **4.1.7 Dissolved Oxygen**

An important feature of water is dissolved oxygen, when the mean value of dissolved oxygen is less than 5 mg/l it will effect on the function of living organism, while dropping it less than 2 mg/l cause destruction of aquatic organism including death to most of fish (UNISCO/WHO/UNEP, 1996).

Dissolved oxygen ranged between highest mean value (9.44 mg\l) in first site during Winter, and lowest mean value (6.5 mg\l) in second site during Summer, (Appendix:1, figure:4-7). Water of Euphrates mean values in province is relatively good aeration due to levels of DO which was within permissible limits (more than 5mg/l), dissolved oxygen mean values declined during Summer may be due to solubility of gasses which decreased with increasing of temperature, where it affects significantly on solubility of oxygen and carbon dioxide (Al-Ghanmi, and Al-Shawat 2015), or could attributed to increasing in chemical and biological processes that

occur in aquatic system and related with increasing in temperature, that's agree with (Al-Hejuje, 2014).

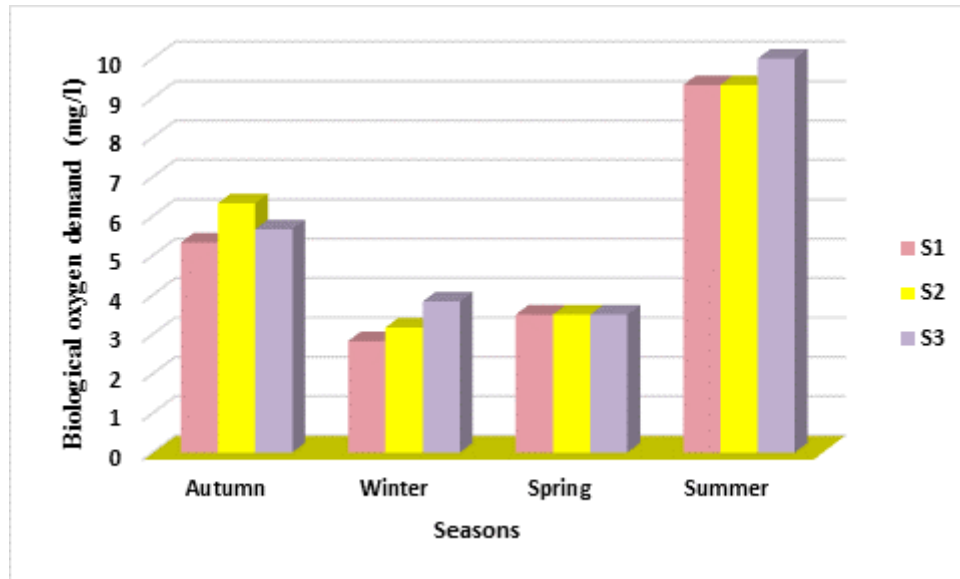


**Fig(4-7): Seasonal variations of dissolved oxygen mean value in study sites**

#### 4.1.8 Biological oxygen demand

Biological oxygen demand in water is a measure of organic pollution in water (Okweye, 2013). It refers to the amount of oxygen consumed by microorganism in oxidation operations of organic matter (Hassan *et al.*, 2010). BOD<sub>5</sub> ranged between highest mean value (10 mg/l) in third site during Summer, and lowest mean value (2.83 mg/l) in first site during Winter (Appendix:1, figure:4-8).

Results showed increasing of BOD<sub>5</sub> levels exceeded permissible limits in Summer may be due to agricultural activities include using fertilizers that provide nutrients which increase growing rates (Appendix:5) (Al-Mayah *et al.*, 2017), or could be attributed to organic matters decomposition from human activities accompanying with oxidation processes that consume oxygen (Essien-Ibok and Umoh, 2013).



**Fig(4-8): Seasonal variations of biological oxygen demand mean value in study sites**

#### 4.1.9 Total hardness

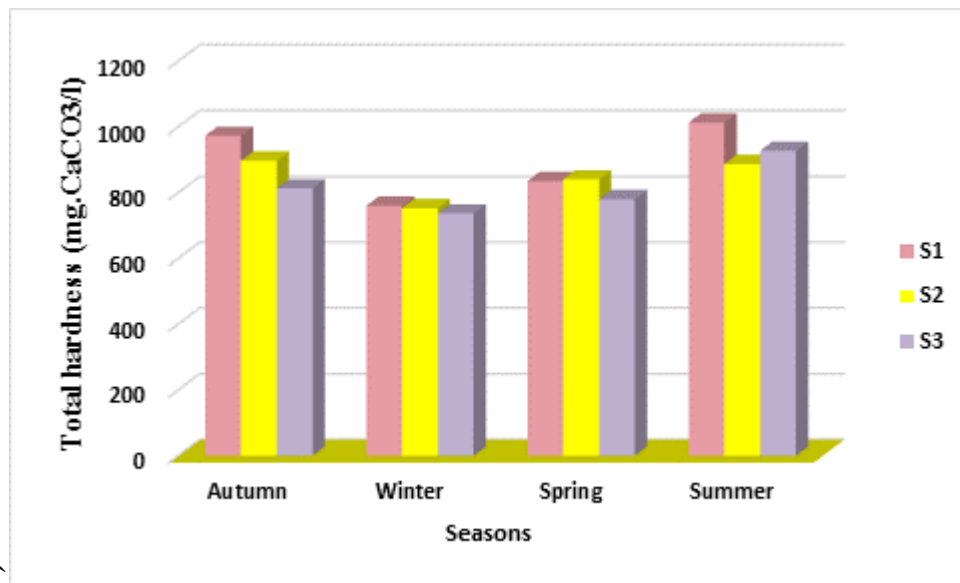
Total hardness indicates the water content of magnesium and calcium ions as well as alkaline salts like Barium and strontium, hardness either temporary caused by calcium and magnesium bicarbonate which is converted to carbonate and some of it precipitate, or permanent hardness from presence of dissolved calcium and magnesium sulfate and chlorides, and inorganic acids (Hassan *et al.*, 2014). Toxicity of heavy metals increased when water is less hard, hardness salt exists as carbonate, bicarbonate, chloride, and sulfate ( Kiyani *et al.*, 2013)

Total hardness ranged between highest mean value (1013.33 mg.CaCO<sub>3</sub>/l) in first site during Summer, and lowest mean value (736.67 mg.CaCO<sub>3</sub>/l) in third site during Winter (Appendix:1, figure:4-9).

Most studies indicate that increasing in water hardness made it not suitable for home and industrial use (Vazquez *et al.*, 2004). Total hardness is an important



parameter to determine water quality and its validity to daily use for domestic, agricultural and industrial purposes (Al-Seedi & Al-Aubody, 2011). High hardness during Summer that exceeded permissible limits may be attributed to increasing of evaporation, low water level, and high salt concentration or sedimentation large amounts of soil rich in carbonate and calcium (Appendix:5) that's agree with (Almuktar *et al.*,2018).

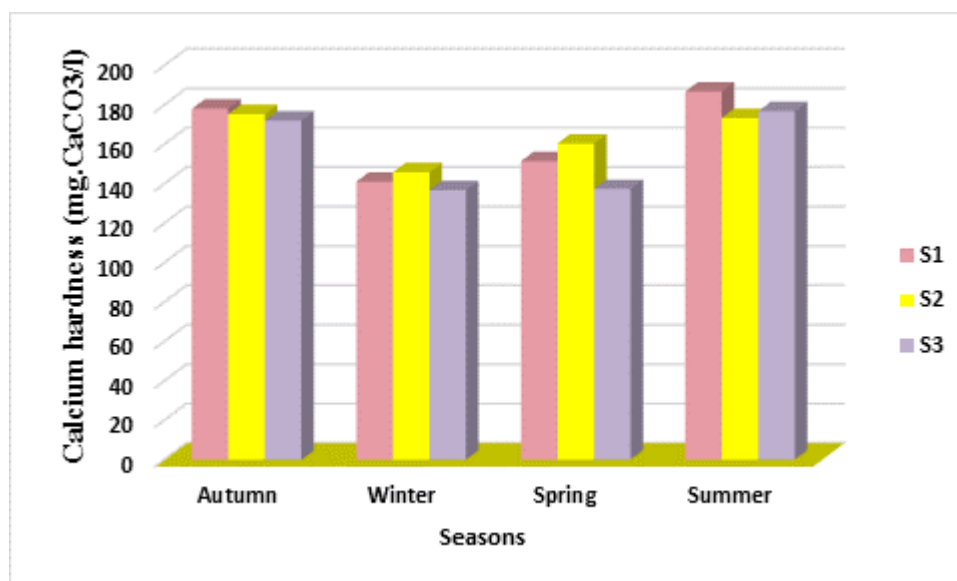


**Fig(4-9): Seasonal variations of total hardness mean value in study sites**

#### **4.1.10 Calcium hardness**

It ranged between highest mean value (186.67 mg.CaCO<sub>3</sub>/l) in first site during Summer, and lowest mean value was (136.67 mg.CaCO<sub>3</sub>/l) in third site during Winter (Appendix:1, figure:4-10).

Levels of Ca ion during period of study were higher than levels of Mg ion because Ca ion tends to conjugate with carbon dioxide more than Mg, as a result fate of large amount of Ca transformed to dissolved bicarbonate (Al-Mayah *et al.*, 2015) .



**Fig(4-10): Seasonal variations of calcium hardness mean value in study sites**

#### 4.1.11 Calcium hardness

It ranged between highest mean value (132.91 mg.CaCO<sub>3</sub>/l) in first site during Summer, and lowest mean value (93.18 mg.CaCO<sub>3</sub>/l) in third site during Autumn, while highest value (189.6 mg.CaCO<sub>3</sub>/l) in first site in August, and lowest value (68.14mg.CaCO<sub>3</sub>/l) in third site in September (Appendix:1, figure:4-11).

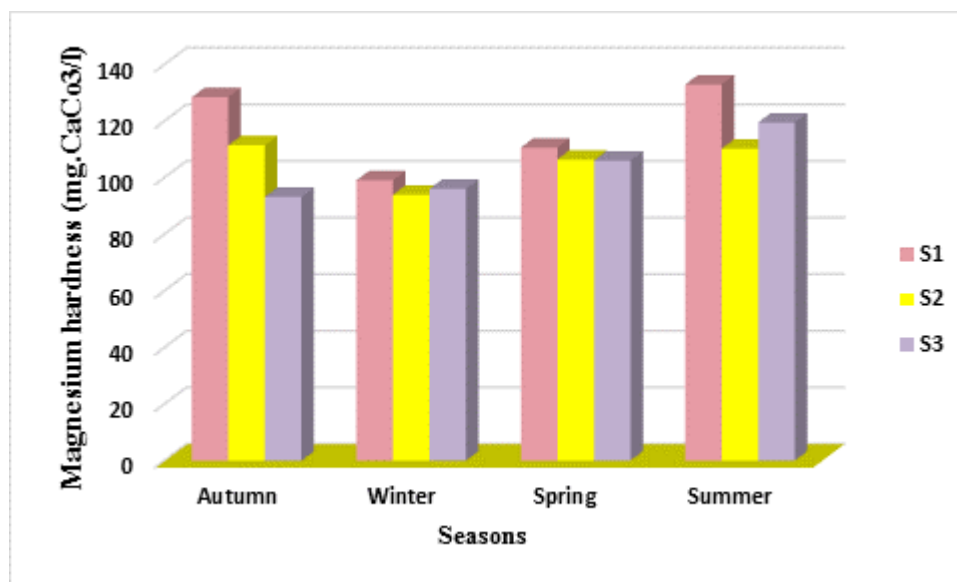
High rates of Mg hardness could be attributed to intensity of phytoplankton (Hassan *et al.*, 2014). Or attributed to chlorophyll degradation of algae and aquatic plants providing water with extra amount of Mg (Alkam *et al.*, 2013).

#### 4.1.12 Total organic carbon

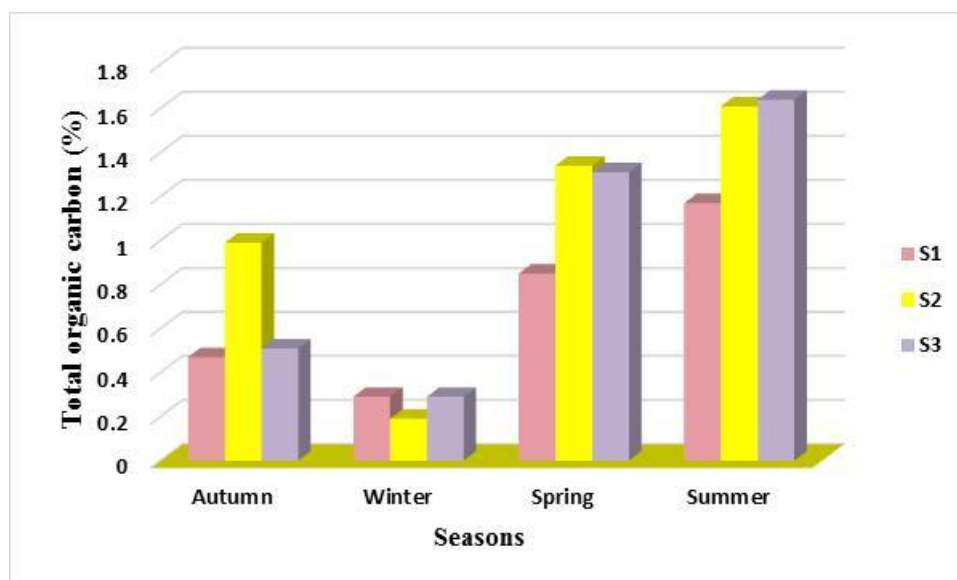
It ranged between highest mean value (1.64%) in third site during Summer, and lowest mean value (0.19%) in second site during Winter (Appendix:1, figure:4-12).

According to results highest levels of TOC observed during Summer specially in July may be return to movement of benthic sediment, and due to nature movement of

air currents and soil particles, increasing mean values of evaporation as well as breakdown of chemical compounds because of increasing in temperature degrees, these levels of TOC consistent with study of ( Al-Sharifi, 2014).



**Fig(4-11): Seasonal variations of magnesium hardness values in study sites**



**Fig(4-12): Seasonal variations of total organic carbon mean value in study sites**

Statistical analysis for physical and chemical parameters showed significant differences between seasons ( $p \leq 0.05$ ).

Significant positive correlation between water temperature and air temperature ( $r=0.992$ ); between pH and dissolved oxygen ( $r=0.603$ ), but negative correlation with air temperature, water temperature, total hardness, and Ca hardness ( $r=-0.773$ ,  $r=-0.737$ ,  $r=-0.686$ ,  $r=-0.710$ ) respectively; and showed positive correlation between turbidity with (air temperature, water temperature BOD5, and Ca hardness) ( $r=0.632$ ,  $r=0.635$ ,  $r=0.482$ ,  $r=0.684$ ) respectively but negative correlation with dissolved oxygen and pH ( $r=-0.679$ ,  $r=-0.725$ ) respectively.

Electrical conductivity showed positive correlation with BOD5, and dissolved oxygen ( $r=0.832$ ,  $r=0.772$ ) respectively but negative correlation with (air temperature, water temperature, total and Ca hardness) ( $r=-0.770$ ,  $r=-0.790$ ,  $r=0.612$ ,  $r=0.641$ ); and negative correlation between DO and air temperature  $r=-0.824$ ; total hardness showed positive correlation with (air temperature, water temperature, and BOD5) ( $r=0.809$ ,  $r=0.802$ ,  $r=0.753$ ) respectively, but negative correlation with dissolved oxygen  $r=-0.738$ ; Ca hardness showed positive correlation with BOD5  $r=0.809$ ; and positive correlation between Mg hardness with (air temperature, water temperature, BOD5, and Ca hardness) ( $r=0.654$ ,  $r=0.643$ ,  $r=0.613$ ,  $r=0.701$ ) respectively.

Results of soil texture showed that silt was forming most of soil components, while clay and sand were much less (table:4-1). Quality of sediments depends on its component, it's also effects on physical and chemical characteristics and ability to store ions, organic matter and salts (Al-Saadi,2006).

Silt refers to granular material its size bigger than clay and smaller than sand, silt formed generally from aluminum silicates sized between 0.002 to 0.1 millimeters (Abdulwahhab *et al.*, 2012).

**Table (4-1): Percentage of soil components**

study sites	silt %	clay %	sand%	soil type
S1	90	5	5	Silt
S2	90	5	5	Silt
S3	90	5	5	Silt

## 4.2 Heavy Metals

### 4.2.1 Heavy Metals in Water

Water quality and physicochemical properties play an important role in the concentration of heavy elements between dissolved and particulate phase, the rise and fall in temperatures which cause evaporation, increasing salinity, rise and fall in water depth and conductivity all these factors affect the concentration of heavy elements (Al-Taher *et al.*, 2020).

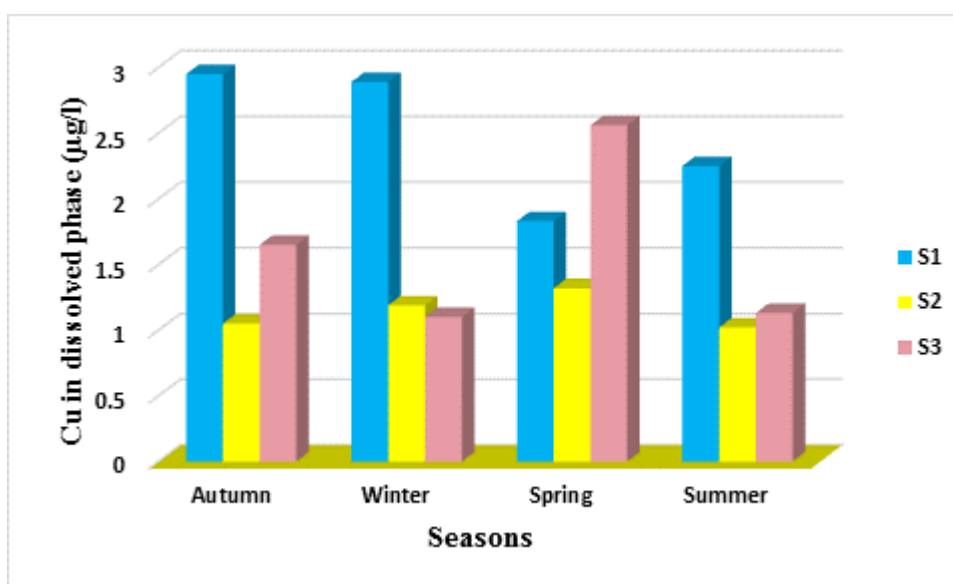
Heavy metals existed in many forms in aquatic environment such as dissolved, particulate and on benthic sediments these forms can circulate and move between layers of water and reach to all levels of food chain of environmental products and accumulate in them then transfer of its danger to all consumables, including humans (Kobielska *et al.*, 2018).

Heavy metals which enter aquatic environment, it tends to combine with other components or accumulate in aquatic plants and other organism (Wang *et al.*, 2019).

There are many factors which facilitate combining with sediment and plankton such as turbidity, total dissolved solids, and pH which its reduction affect and causing transforming between dissolved and particulate phase, in case of increase in organic matter, it is oxidized and produced CO<sub>2</sub> which dissolved in water forming carbonate reducing pH that increase solubility and release of heavy elements (Fawzy *et al.*, 2012).

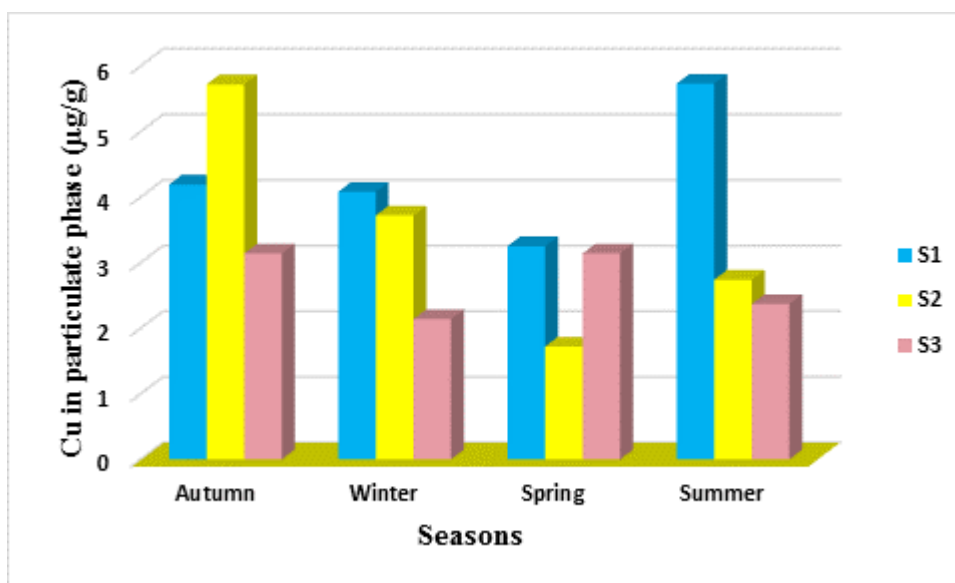
#### 4.2.1.1 Copper

Seasonal variations of Cu in dissolved phase showed that the highest mean value (2.95 µg/l) was recorded in first site during Summer, while the lowest mean value (1.02 µg/l) in second site during Summer too (Appendix:2, figure:4-13), annual mean value was (1.75 µg/l).



**Fig 4-13: seasonal variations of Cu concentrations in dissolved phase**

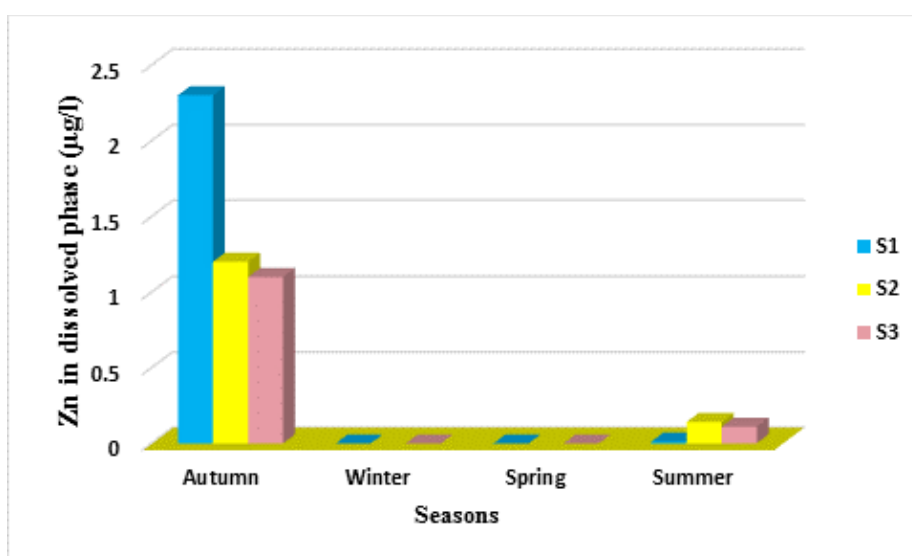
In particulate phase highest mean value 5.73 (µg/g dry weight) in first site during Summer, while lowest mean value 1.72 (µg/g dry weight) in second site during Spring (Appendix:2, figure:4-14), annual mean value was 3.56 (µg/g dry weight).



**Fig (4-14): seasonal variations of Cu concentrations in particulate phase**

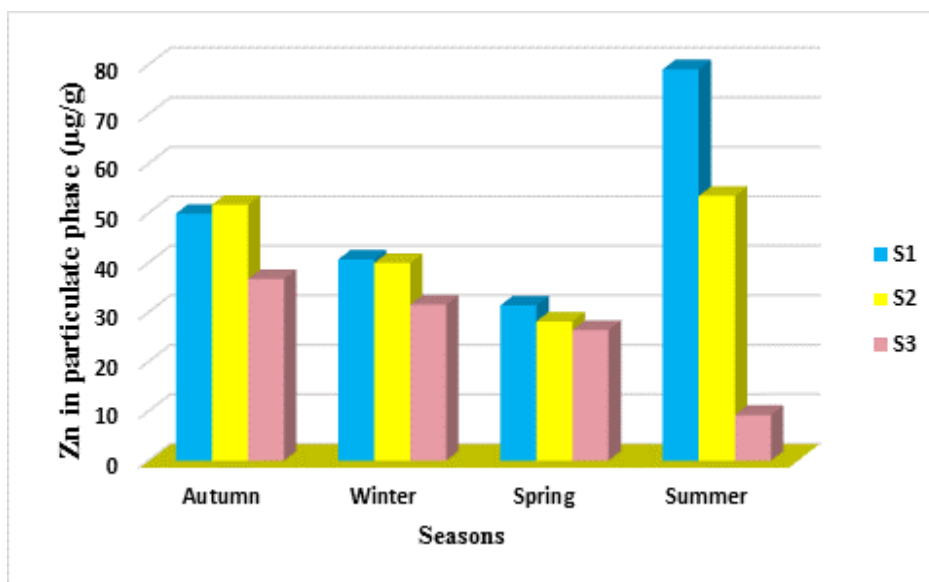
#### 4.2.1.2 Zinc

Seasonal variations of Zn in dissolved phase showed that the highest mean value (2.3 µg/l) was recorded in first site during Autumn, and the lowest mean value was not detected (ND) in three sites of study during Winter and Spring (Appendix:2, figure:4-15), annual mean value was (0.81 µg/l).



**Fig(4-15): seasonal variations of Zn concentrations in dissolved phase**

In particulate phase highest mean value (79.04  $\mu\text{g/g}$  dry weight) in first site during Summer, while lowest mean value (9.22  $\mu\text{g/g}$  dry weight) in third site during Summer (Appendix:2 figure:4-16), annual mean value was (39.81  $\mu\text{g/g}$  dry weight).



**Fig (4-16): seasonal variations of Zn concentrations in particulate phase**

#### 4.2.1.3 Cadmium

Seasonal variations of Cd in dissolved phase showed that the highest mean value (3.65  $\mu\text{g/l}$ ) in third site during Autumn while the lowest mean value of (0.15  $\mu\text{g/l}$ ) in both second and third sites of study during Winter (Appendix:2 figure:4-17), annual mean value was (1.23  $\mu\text{g/l}$ ).

In particulate phase highest mean value (11.14  $\mu\text{g/g}$  dry weight) in third site during Autumn while lowest mean value (0.11  $\mu\text{g/g}$  dry weight) in first site during Winter (Appendix:2 figure:4-18), annual mean value was (2.64  $\mu\text{g/g}$  dry weight).



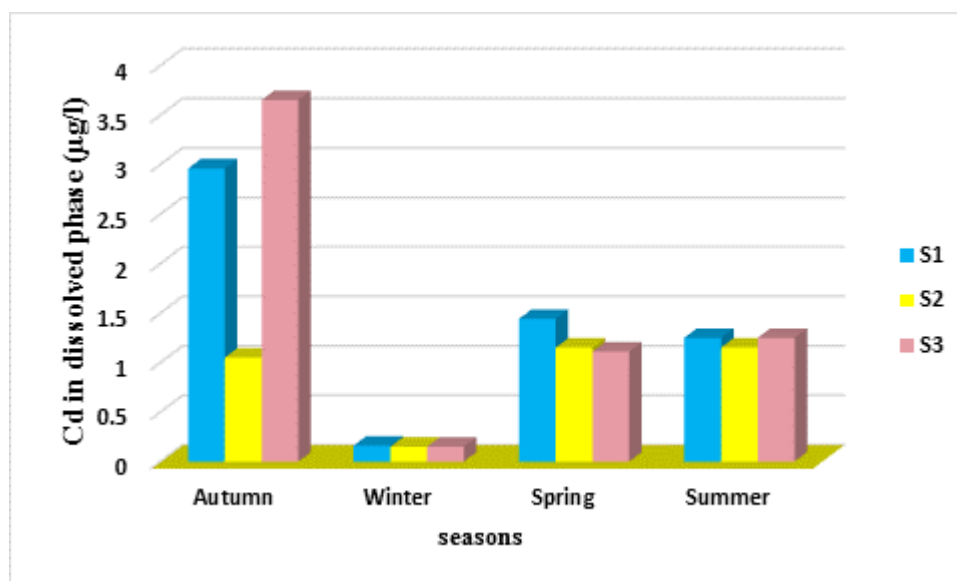


Fig (4-17): seasonal variations of Cd concentrations in dissolved phase

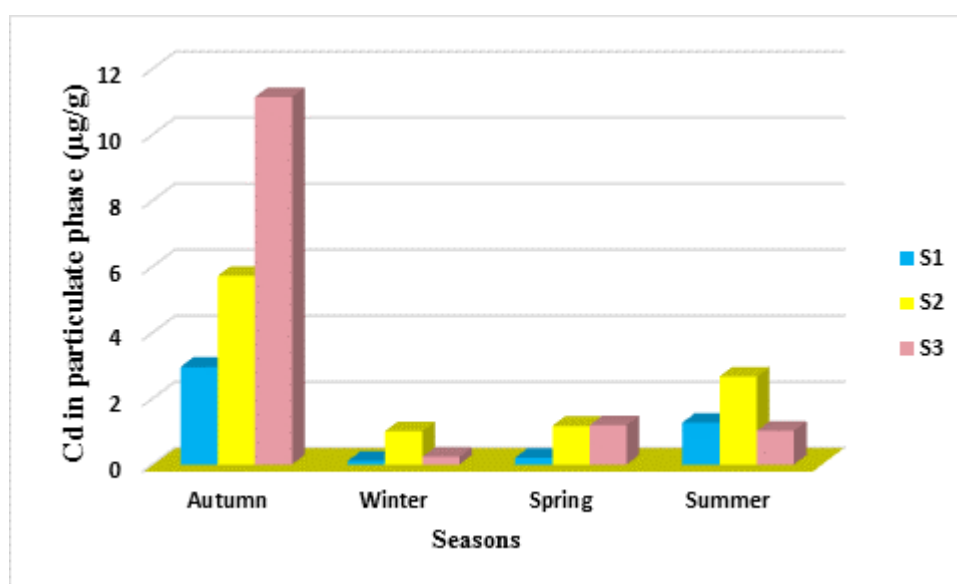
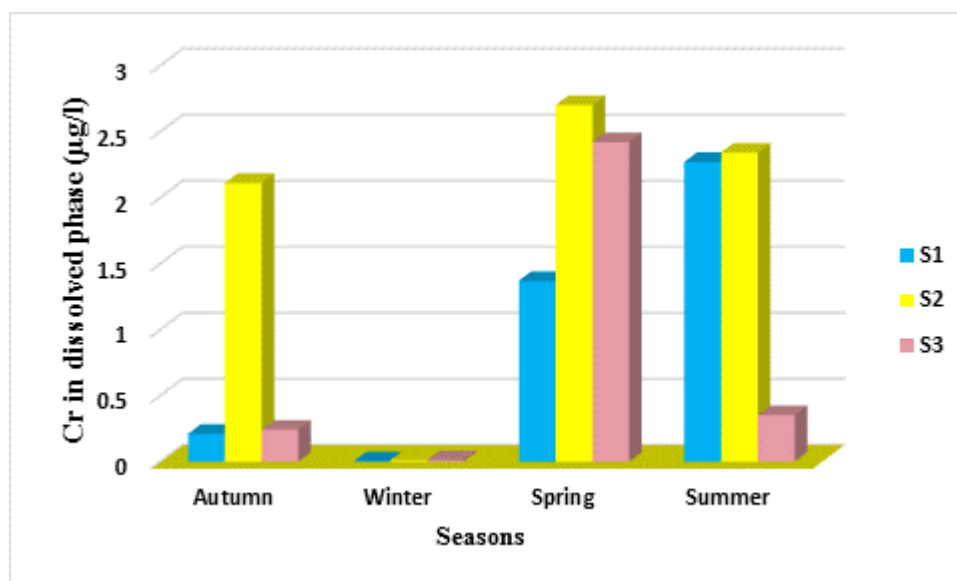


Fig (4-18): seasonal variations of Cd concentrations in particulate phase

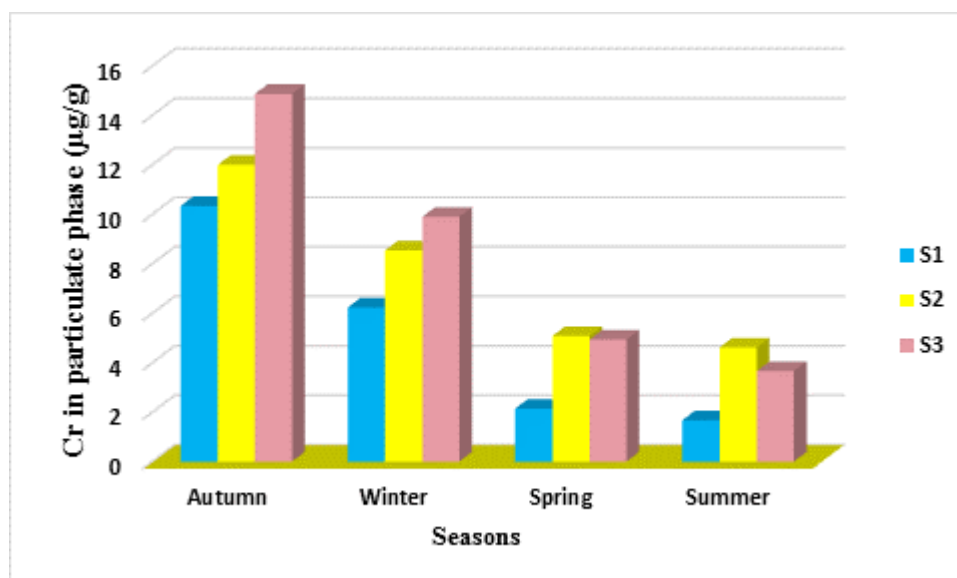
#### 4.2.1.4 Chromium

Seasonal variation of Cr in dissolved phase showed that the highest mean value (2.7 µg/l) in second site during Spring, while the lowest mean value 0.001 (µg/l) in first site during Winter (Appendix:2 figure:4-19), annual mean value was 1.17(µg/l).



**Fig (4-19): seasonal variations of Cr concentrations in dissolved phase**

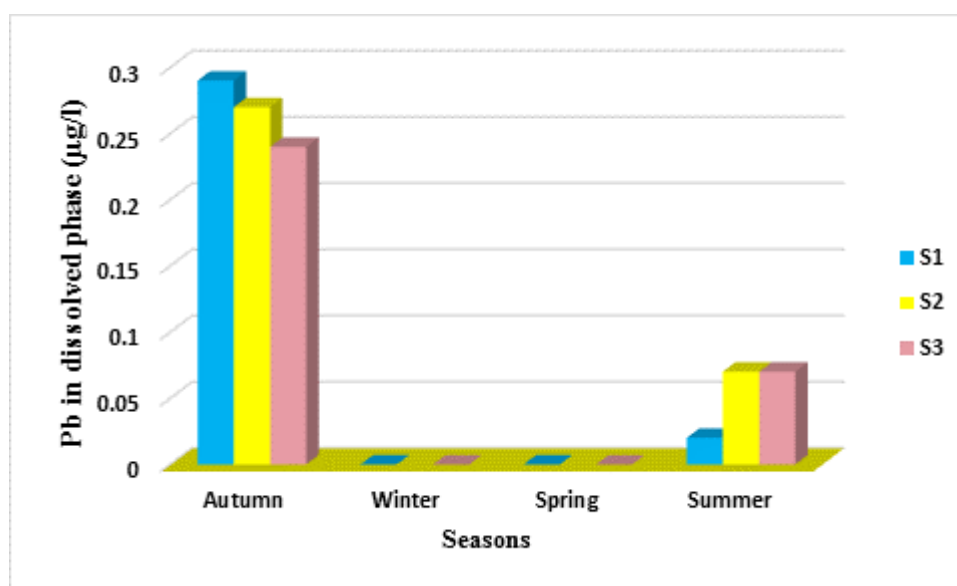
In particulate phase the highest mean value (14.86 µg/g dry weight) in third site during Autumn, while the lowest mean value (1.67 µg/g dry weight) in first site during Summer (Appendix:2 figure:4-20), annual mean value was (6.99 µg/g dry weight).



**Fig (4-20): seasonal variations of Cr concentrations in particulate phase**

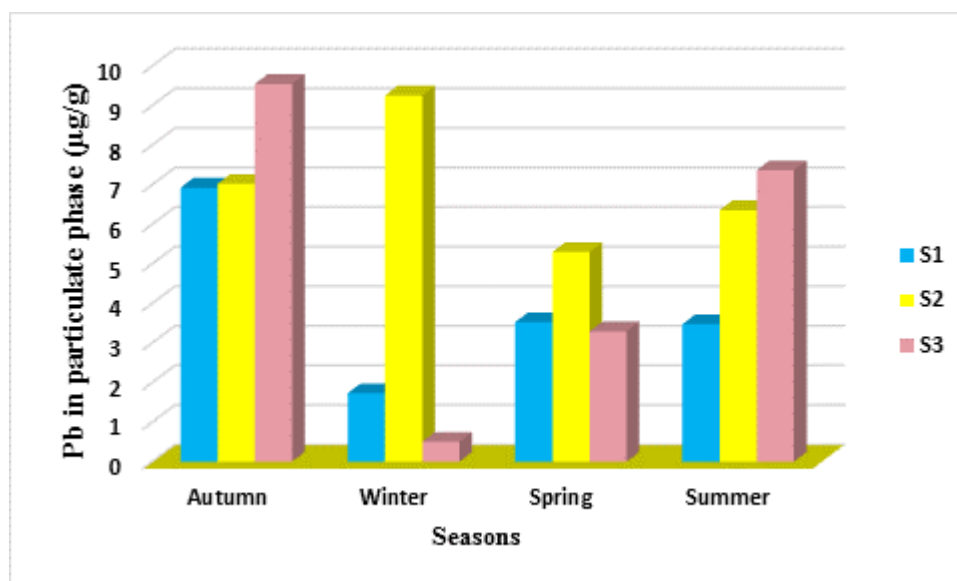
#### 4.2.1.5 Lead

Seasonal variation of Pb in dissolved phase showed that highest the mean value (0.29  $\mu\text{g/l}$ ) in first site during Autumn while the lowest mean value was ND (not detected) in three sites of study during Winter and Spring (Appendix:2 figure:4-21), annual mean value was (0.18  $\mu\text{g/l}$ ).



**Fig (4-21): seasonal variations of Pb concentrations in dissolved phase**

In particulate phase the highest mean value (9.54  $\mu\text{g/g}$  dry weight) was recorded in third site during Autumn while the lowest mean value (0.5  $\mu\text{g/g}$  dry weight) was recorded in third site during Winter (Appendix:2 figure:4-22), annual mean value was (7.14  $\mu\text{g/g}$  dry weight).



**Fig (4-22): seasonal variations of Pb concentrations in particulate phase**

Statistical analysis showed significant differences between seasons and sites for (dissolved and particulate) phase. And showed significant negative correlation between particulate Zn and TOC ( $r=-0.630$ ), dissolved Cd value with pH and TOC ( $r=-0.779$ ,  $r=-0.583$ ), dissolved Pb value with AT, WT, BOD<sub>5</sub>, pH ( $r=-0.965$ ,  $r=-0.953$ ,  $r=-0.957$ ,  $r=-0.830$ ) respectively.

Significant positive correlation between dissolved and particulate Cd value with turbidity ( $r=0.703$ ,  $r=0.879$ ) respectively, dissolved Pb with DO and particulate Pb with turbidity ( $r=0.700$ ,  $r=0.875$ ) respectively.

Results showed mean value Cu, Zn, Cd, Cr, and Pb in water exceeded permissible limits of Iraq water 1967 NO. (25) and limits of WHO (2006) (Appendix:6), there were noticeable raise in Pb, rates of Cd were raised during autumn in first site, this may be attributed to burning waste and tires near the river (Al- Hassen *et al.*, 2012), elements aren't stay in dissolved phase for long time because adsorb with sediment or combine with organic compounds (Nafea & Zyada,

2015). Decreasing of it may be attributed to tendency of elements to accumulate in aquatic plants or to adsorption with sediments or forming complexes with organic matter (Al-Jaberi *et al.*, 2016). The arrangement of studied elements in dissolved phase were Cu>Cr>Cd>Zn>Pb. The arrangement of studied elements in particulate phase were Zn>Pb>Cr>Cu>Cd, there is significant increase in element concentrations specially in Autumn and that may be attributed to soil washing by drainage (Kar *et al.*, 2008).

The results showed that the concentrations of studied elements in particulate phase higher than in dissolved phase may be attributed to presence of high concentration of particles or turbidity resulting from mixing operations or water containment of quantities of plankton that have ability to concentrate heavy metals that reinforces the link between turbidity and particulate matter and this agree with (Sabri *et al.*, 2020).

The presence of variation in concentrations of heavy elements between seasons of the year may be attributed to the variation in water properties and its contents of organic and inorganic compounds, pollutants, life activities, the difference in the duration and intensity of lighting, activity of microorganism, algae, aquatic plants, crustaceans, mollusks and different organism that withdraw quantities of minerals to activate their metabolic activities and enzymes or to build the outer shell and body envelopes according to organism type (Salman *et al.*, 2015).

Increasing of Cu concentration during Summer may be attributed to corrosion of water and sewage pipes (Arnolds, 2018).

High rates of Zn during Summer may be attributed to agricultural activities and adding fertilizers contain this element, lower rates of Zn in water could attributed to

solubility of its compound in moderately acidic and its concentrations increase with increasing in acidity and the study area is light basic (Galletti *et al.*, 2010).

Cd showed high concentrations in dissolved phase during period of study and in particulate phase in third site during Autumn could attributed to pollution with electroplating and metallic paint or from discarded batteries that are thrown into open areas and decompose under weather conditions, some of which find a way to the water (Al-Edani,*et al.*, 2019).

Increasing in Cr rates during Autumn may attributed to cement dust, electro plating, or wearing down asbestos or from agricultural waste fertilizers and pesticides (Abbasi, 2014).

High rates of Pb in particulate phase during period of study specially in second site could attributed to population density and car congestion that used  $Pb(C_4H_3)_4$  and  $Pb(CH_3)_4$  which added with fuel cause pollution with Pb, and polluted particles fall directly to the river, lower concentrations of Pb may be attributed to its ability to absorb high and fast to form organic compound (El-Khatib *et al.*, 2014).

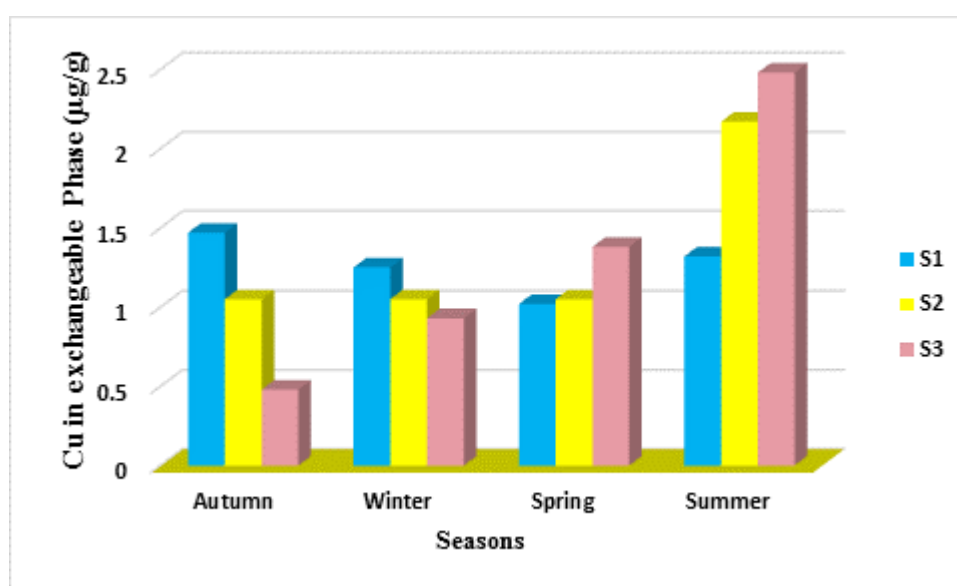
#### 4.2.2 Heavy Metals in Sediment

Sediment consider as a potential source of pollution and transcriber for heavy metals and when analyzed the top layer of sediment we will get a good quantity of pollutants which can pollute aquatic environment, heavy metals don't remain in dissolved phase for a long time but it convert to suspended colloids or installed by organic plankton and forming dissolved ketones of heavy metals which are easily absorbed and held by clay minerals or organic compounds then accumulate on sediment (Okoro *et al.*, 2013). Sediments play important role in returning heavy

metals to water systems under appropriate conditions or biological activity, elements released back into the water and then into the aquatic food chains (Salman *et al.*, 2015). Sediments provide data on the extent and quality of pollution resulting from human activity where the sediments and their components is an indication of the quality and quantity of pollution and the nature of its source by the gradual accumulation of these pollutants in the sediments by time (Goher & Ali 2009).

#### 4.2.2.1 Copper

Seasonal variations of Cu in exchangeable phase showed that the highest mean value 2.48 ( $\mu\text{g/g}$  dry weight) in third site during Summer, while the lowest mean value 0.48 ( $\mu\text{g/g}$  dry weight) in third site during Autumn (Appendix:3 figure:4-23), annual mean value was 1.3 ( $\mu\text{g/g}$  dry weight).



**Fig (4-23): seasonal variations of Cu concentrations in exchangeable**

In residual phase the highest mean value 9.54 ( $\mu\text{g/g}$  dry weight) in first site during Autumn, while the lowest mean value 1.13 ( $\mu\text{g/g}$  dry weight) in first site during Summer (Appendix:3 figure:4-24), annual mean value was 2.11 ( $\mu\text{g/g}$  dry weight).

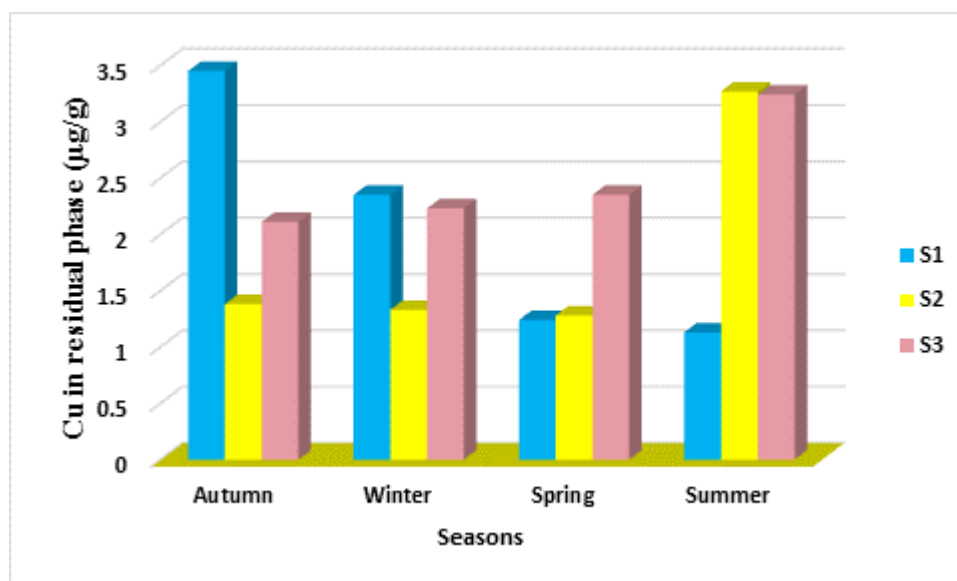


Fig (4-24): seasonal variations of Cu concentrations in residual phase

#### 4.2.2.2 Zinc

Seasonal variation of Zn in exchangeable phase showed that the highest mean value 2.01 ( $\mu\text{g/g}$  dry weight) in second site during Summer, while the lowest mean value 0.85 ( $\mu\text{g/g}$  dry weight) in third site during Spring (Appendix:3 figure:4-25), annual mean value was 1.25 ( $\mu\text{g/g}$  dry weight).

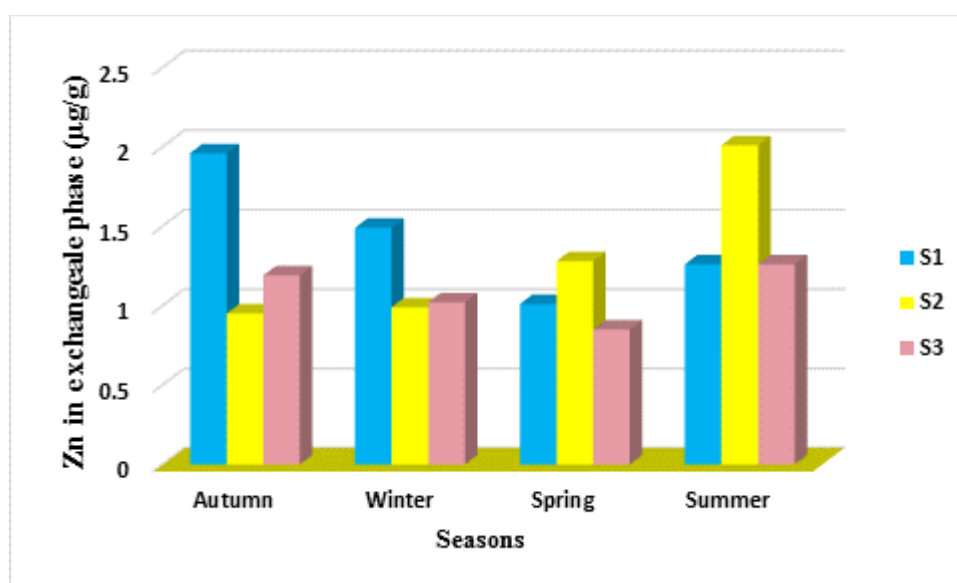
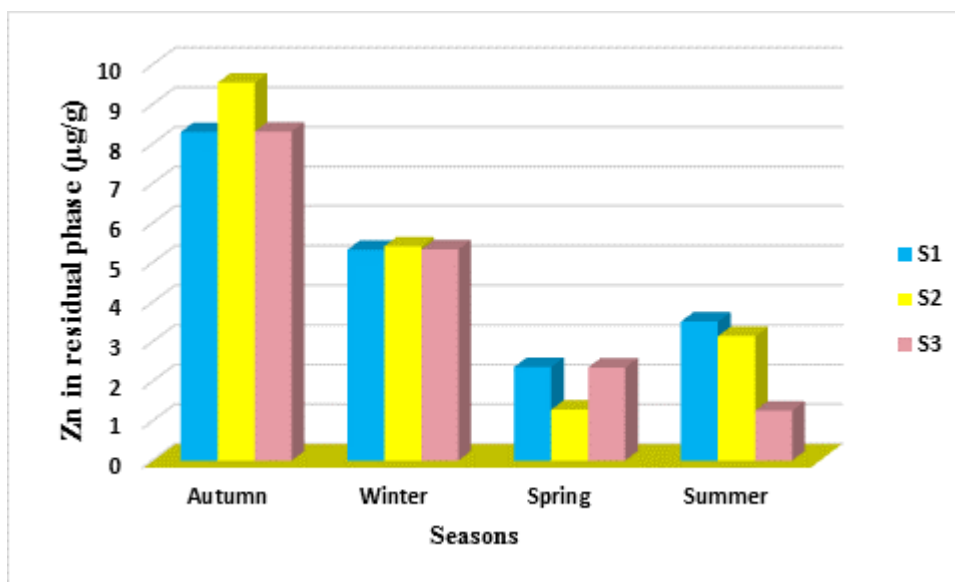


Fig (4-25): seasonal variations of Zn concentrations in exchangeable phase



In residual phase highest mean value 3.45 ( $\mu\text{g/g}$  dry weight) in second site during Autumn, while lowest mean value 1.26 ( $\mu\text{g/g}$  dry weight) in third site in Summer (Appendix:3 figure:4-26), annual mean value was 4.78 ( $\mu\text{g/g}$  dry weight).



**Fig (4-26): seasonal variations of Zn concentrations in residual phase**

#### 4.2.2.3 Cadmium

Seasonal variations of Cd in exchangeable phase showed that the highest mean value 0.69 ( $\mu\text{g/g}$  dry weight) in third site during Summer, while the lowest mean value was (ND) in first site during Winter (Appendix:3 figure:4-27), annual mean value was 0.27 ( $\mu\text{g/g}$  dry weight).

In residual phase Cd highest mean value 1.02 ( $\mu\text{g/g}$  dry weight) in second site during Summer, while lowest mean value 0.004 ( $\mu\text{g/g}$  dry weight) in third site during Winter (Appendix:3 figure:4-28), annual mean value was 0.2 ( $\mu\text{g/g}$  dry weight).

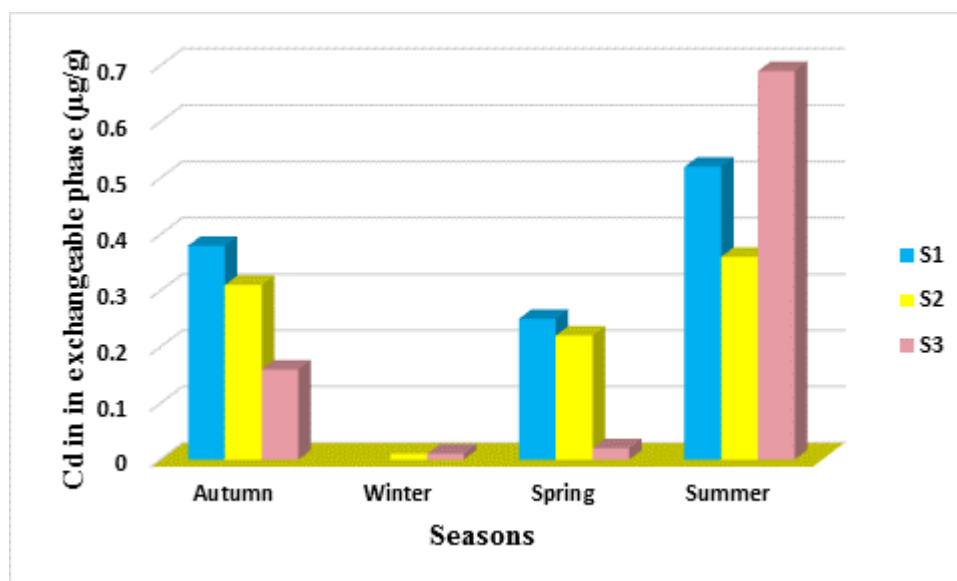


Fig (4-27): seasonal variations of Cd concentrations in exchangeable phase

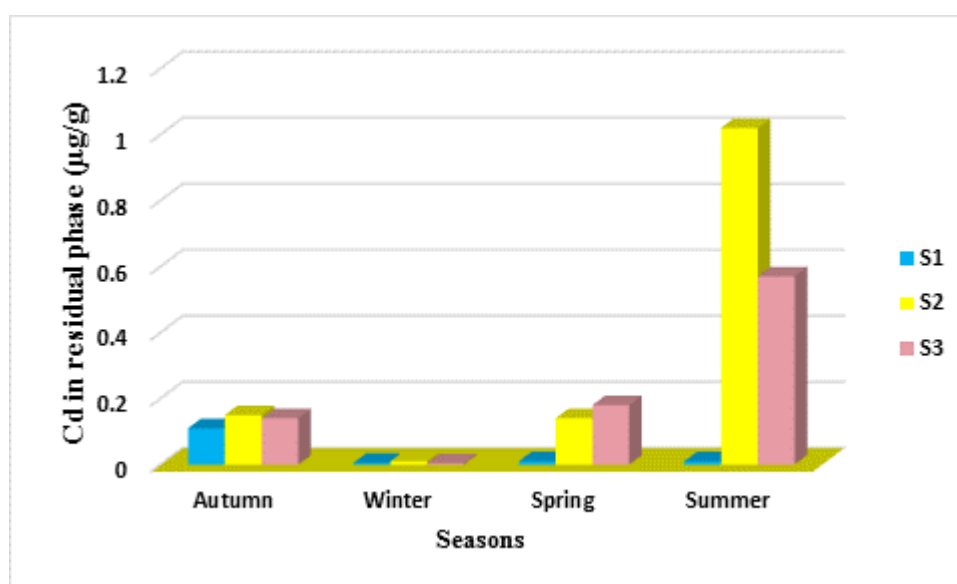
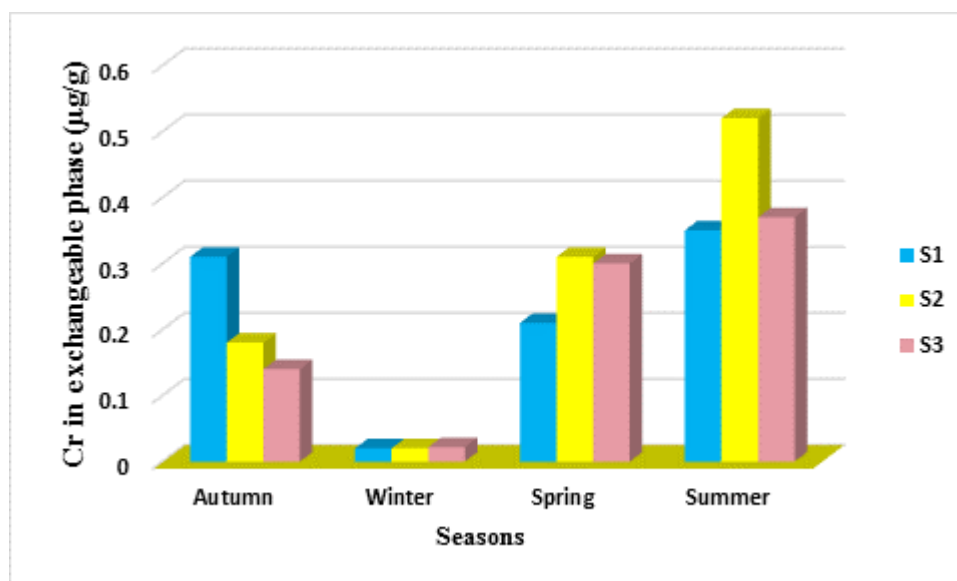


Fig (4-28): seasonal variations of Cd concentrations in residual phase

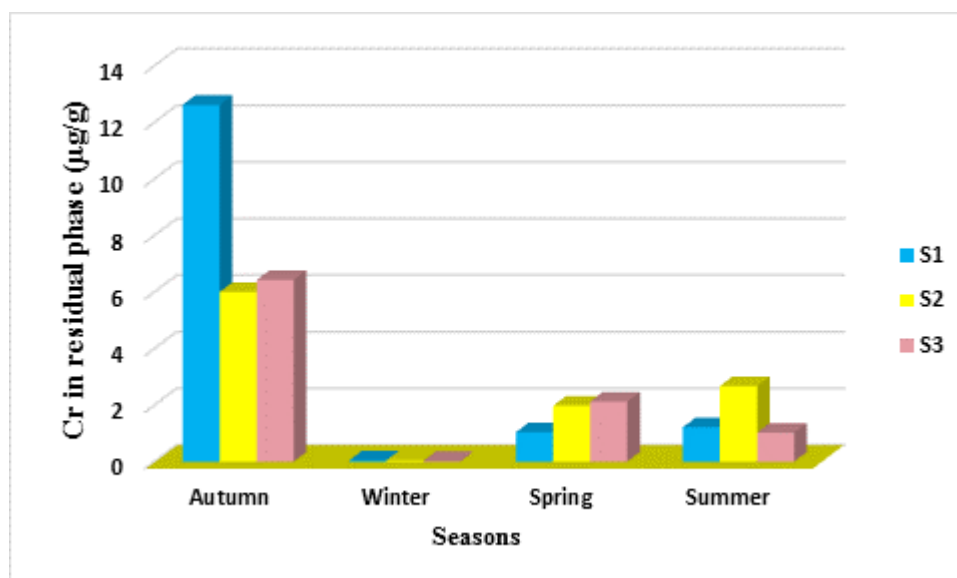
#### 4.2.2.4 Chromium

Seasonal variation of Cr in exchangeable phase showed that the highest mean value 0.52 ( $\mu\text{g/g}$  dry weight) in second site during Summer while the lowest mean value 0.02 ( $\mu\text{g/g}$  dry weight) in second site during Winter (Appendix:3 figure:4-29), annual mean value was 0.23 ( $\mu\text{g/g}$  dry weight).



**Fig (4-29): seasonal variations of Cr concentrations in exchangeable**

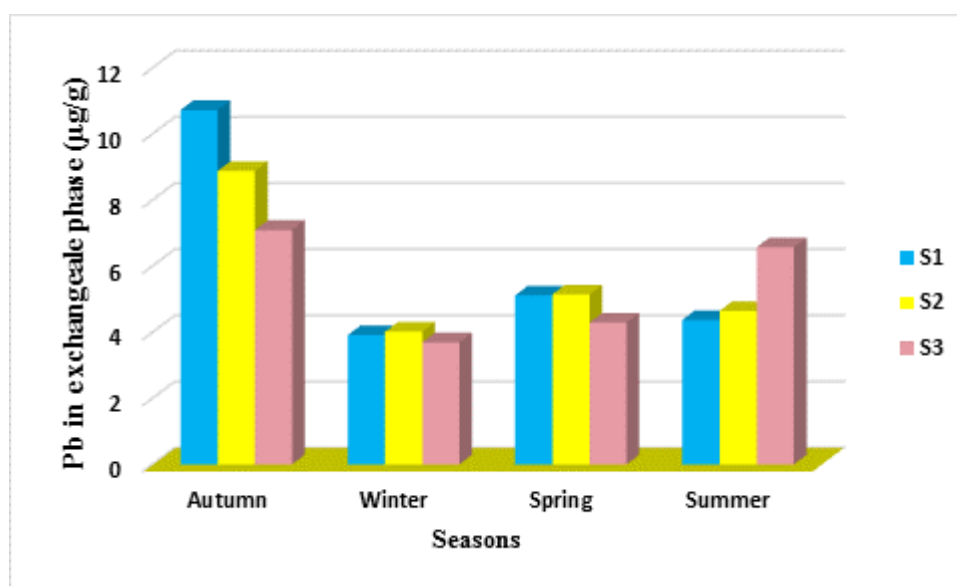
In residual phase the highest mean value 12.61 ( $\mu\text{g/g}$  dry weight) in first site during Autumn, while the lowest mean value 0.02 ( $\mu\text{g/g}$  dry weight) in third site during Winter (Appendix:3 figure:4-30), annual mean value was 2.93 ( $\mu\text{g/g}$  dry weight).



**Fig (4-30): seasonal variations of Cr concentrations in residual phase**

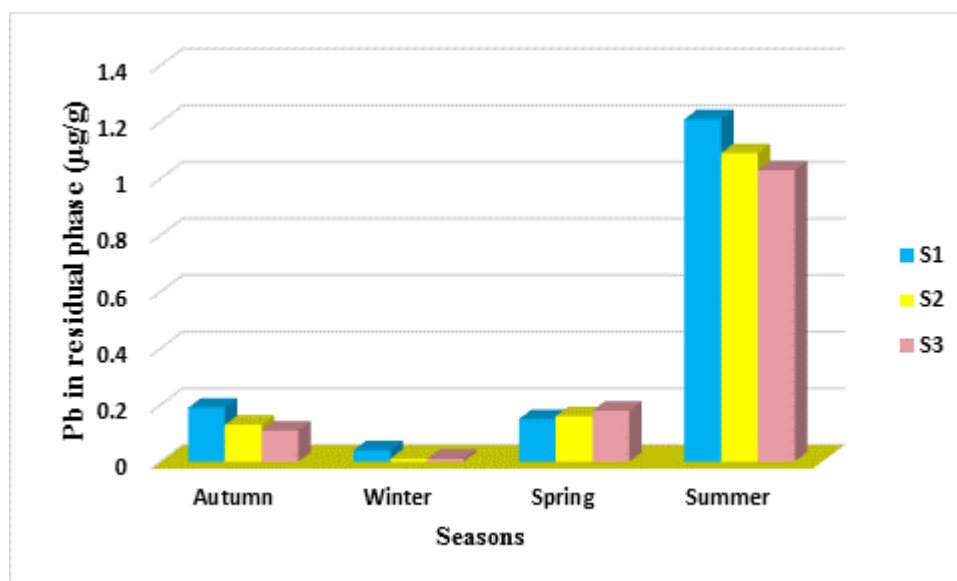
#### 4.2.2.5 Lead

Seasonal variation of Pb in exchangeable phase showed that the highest mean value 10.72 ( $\mu\text{g/g}$  dry weight) in first site during Autumn, while the lowest mean value 3.69 ( $\mu\text{g/g}$  dry weight) in third site during Winter (Appendix:3 figure:4-31), annual mean value was 8.645 ( $\mu\text{g/g}$  dry weight).



**Fig (4-31): seasonal variations of Pb concentrations in exchangeable**

In residual phase the highest mean value 1.21 ( $\mu\text{g/g}$  dry weight) in first site during Summer, while the lowest mean value 0.01 ( $\mu\text{g/g}$  dry weight) in second site during Winter (Appendix:3 figure:4-32), annual mean value was 0.61 ( $\mu\text{g/g}$  dry weight).



**Fig (4-32): seasonal variations of Pb concentrations in residual phase**

Statistical analysis showed significant differences between seasons and sites, and showed significant positive correlation between exchangeable Cu, Cd, Cr and residual Cd with BOD<sub>5</sub>; exchangeable Cd, Cr and residual Cd with air temperature, water temperature; exchangeable Cd, Cr with total hardness, Ca and Mg hardness; and exchangeable Cr with TOC; residual Cr with pH and turbidity ( $r=0.664$ ,  $r=0.878$ ,  $r=0.703$ ,  $r=0.662$ ,  $r=0.816$ ,  $r=0.844$ ,  $r=0.662$ ,  $r=0.823$ ,  $r=0.828$ ,  $r=0.160$ ,  $r=0.835$ ,  $r=0.698$ ,  $r=0.804$ ,  $r=0.619$ ,  $r=0.716$ ,  $r=0.668$ ,  $r=0.740$ ,  $r=0.663$ ) respectively.

Significant negative correlation between exchangeable Cu, Zn, Cr, and residual Cu, Cd, Pb with EC; and residual Zn with TOC, exchangeable Cd and residual Pb with DO, and TOC, exchangeable and residual Pb with pH ( $r=-0.766$ ,  $r=-0.807$ ,  $r=-0.815$ ,  $r=-0.764$ ,  $r=-0.593$ ,  $r=-0.664$ ,  $r=-0.558$ ,  $r=-0.727$ ,  $r=-0.762$ ,  $r=-0.765$ ,  $r=-0.825$ ,  $r=-0.727$ ,  $r=-0.769$ ,  $r=-0.276$ ) respectively.

The results showed noticeable rise in concentrations of studied elements in sediment more than in water but the concentrations were within universal permitted

limits in sediment according to (CBSQG, 2003) (Appendix:7), arrangement of elements in exchangeable phase were Pb>Cu>Zn>Cd>Cr while in residual phase were Zn>Cr>Cu>Pb>Cd.

Presence of heavy metals in high levels more than dissolved and particulate phase this could attributed to continuous accumulation to pollutants from human activity (Aprile & Bouvy, 2010). The results showed varying concentrations in studied minerals in sediments between seasons of the year and the concentrations in residual phase more than in exchangeable phase except Cd in Autumn season and Pb in four seasons were higher in residual phase and this could be attributed to throwing high pollutants contain these elements resulting from human sources and oxides that are caused by transport media or throw waste water containing organic substances that form complexities of these elements so increasing the rates of these two elements (Bhuyan & Bakar, 2017), or resulting from cement dust and dust storms containing high concentrations of these elements (Salman *et al.*, 2015)

Cu values raised during Summer in exchangeable and residual phase may be attributed to human activities such as changing car oil in waterways, metal plating, dyes, glues, or car and trucks washing, and washing pesticide containers (Al-Afify, & Abdel-Satar, 2020).

Zn high rates during Autumn may be attributed to agricultural activities using liquid manure, and pesticides (Bragato *et al.*, 2009), or attributed to abrasion of vehicles and brakes, also vehicle emissions and Cylinder head gaskets (Hassan *et al.*, 2010).

Cd showed high rates during Summer may be attributed to agricultural activities and using phosphate fertilizer that contain Cd elements (Al-Jaberi *et al.*, 2016).

Cr high rates in exchangeable phase during Summer may be attributed to throwing solid waste, and waste water irrigation (Salman *et al.*, 2015). High rates in residual phase during Autumn may be due to adsorption of the element by the clay minerals (Al-khafaji *et al.*, 2011).

Pb rates were high in soil during Autumn and Summer in exchangeable phase and during Summer in residual phase may be due to fuel burning that contain Pb, heavy traffic and vehicles emission, throwing damaged and rusty batteries on bank of the river (Rabee *et al.*, 2009).

### **4.2.3 Heavy Metals in Plants**

Many families of plants used as indicators for pollution of the aquatic environment due to their ability to remove heavy toxic elements from the water and collect them in their tissues and store it in non-sensitive special sites or kept in vacuoles or transformed to non-toxic forms (Memon, 2001).

#### **4.2.3.1 Heavy Metals in *Phragmites australis***

##### **4.2.3.1.1. Copper**

Seasonal variations of Cu in *P. australis* showed that the highest mean value 5.14 ( $\mu\text{g/g}$  dry weight) in first site during Summer, while the lowest mean value 1.61 ( $\mu\text{g/g}$  dry weight) in third site during Autumn (Appendix:4 figure:4-33), annual mean value was 3.18 ( $\mu\text{g/g}$  dry weight).

##### **4.2.3.1.2. Zinc**

Seasonal variations of Zn in *P. australis* showed that the highest mean value 5.14 ( $\mu\text{g/g}$  dry weight) in second site during Summer, while the lowest mean value 1.18

( $\mu\text{g/g}$  dry weight) in third site during Spring (Appendix:4, figure:4-34), annual mean value was 8.78 ( $\mu\text{g/g}$  dry weight).

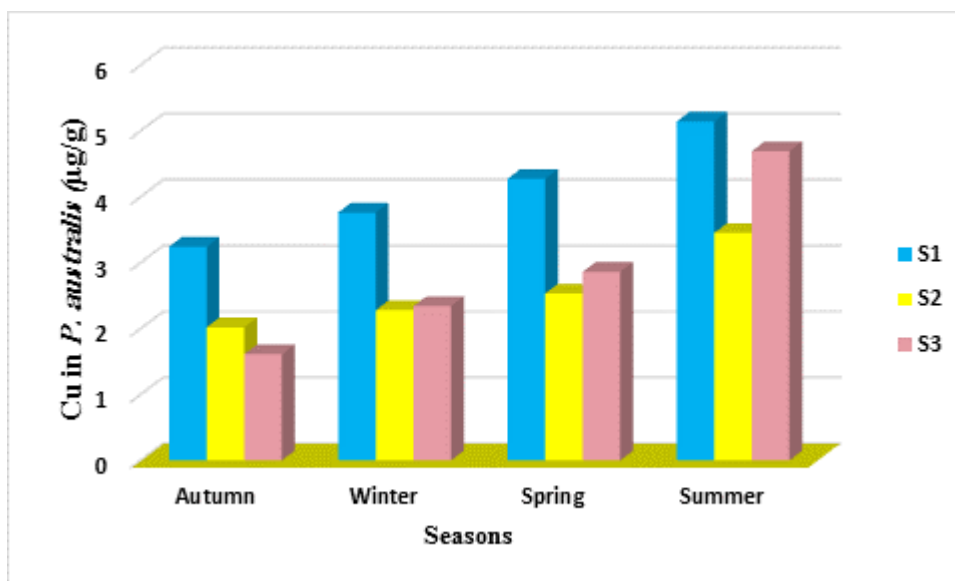


Fig (4-33): seasonal variations of Cu concentrations in *P. australis*

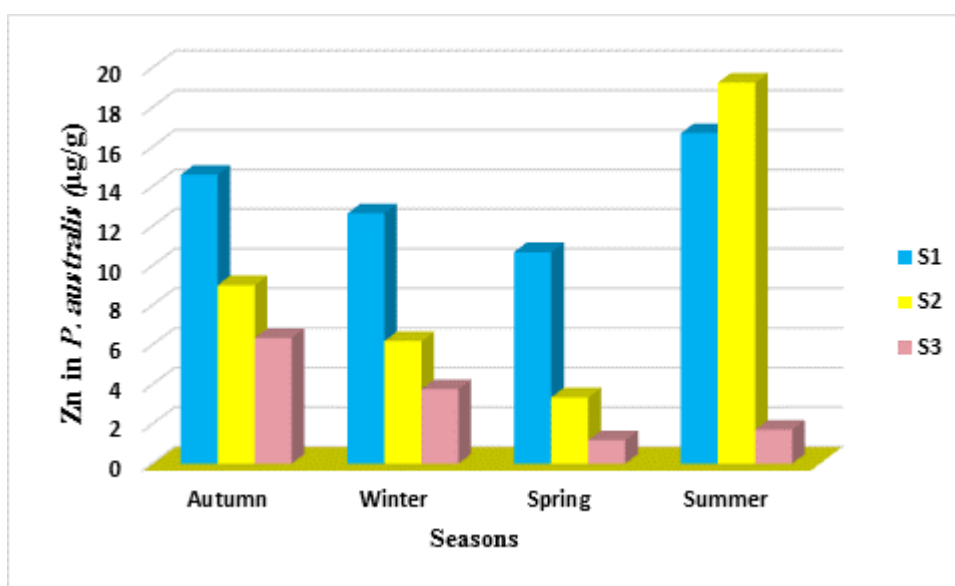


Fig (4-34): seasonal variations of Zn concentrations in *P. australis*



#### 4.2.3.1.3. Cadmium

Seasonal variations of Cd in *P. australis* showed that the highest mean value 1.28 ( $\mu\text{g/g}$  dry weight) in first site during Summer, while the lowest mean value 0.002 ( $\mu\text{g/g}$  dry weight) in third site during Winter (Appendix:4, figure:4-35), annual mean value was 0.41 ( $\mu\text{g/g}$  dry weight).

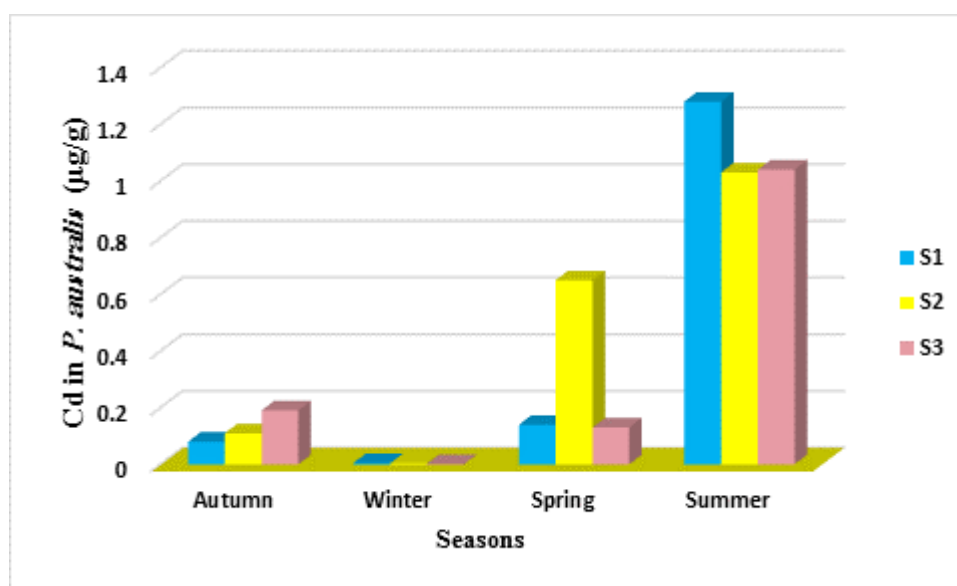


Fig (4-35): seasonal variations of Cd concentrations in *P. australis*

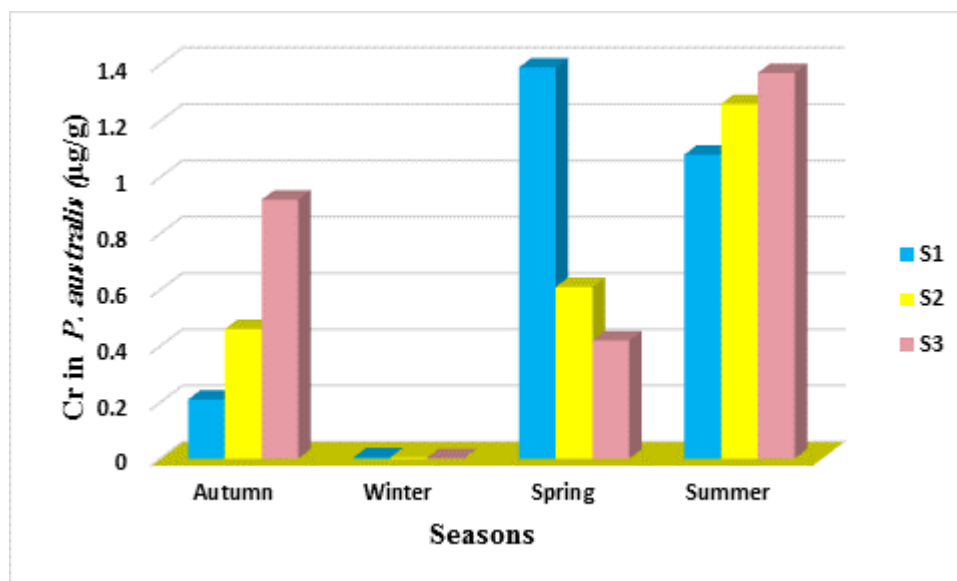
#### 4.2.3.1.4. Chromium

Seasonal variations of Cr in *P. australis* showed that the highest mean value 1.39 ( $\mu\text{g/g}$  dry weight) in first site during Spring, while the lowest mean value 0.002 ( $\mu\text{g/g}$  dry weight) in third site during Winter (Appendix:4, figure:4-36), annual mean value was 0.64 ( $\mu\text{g/g}$  dry weight).

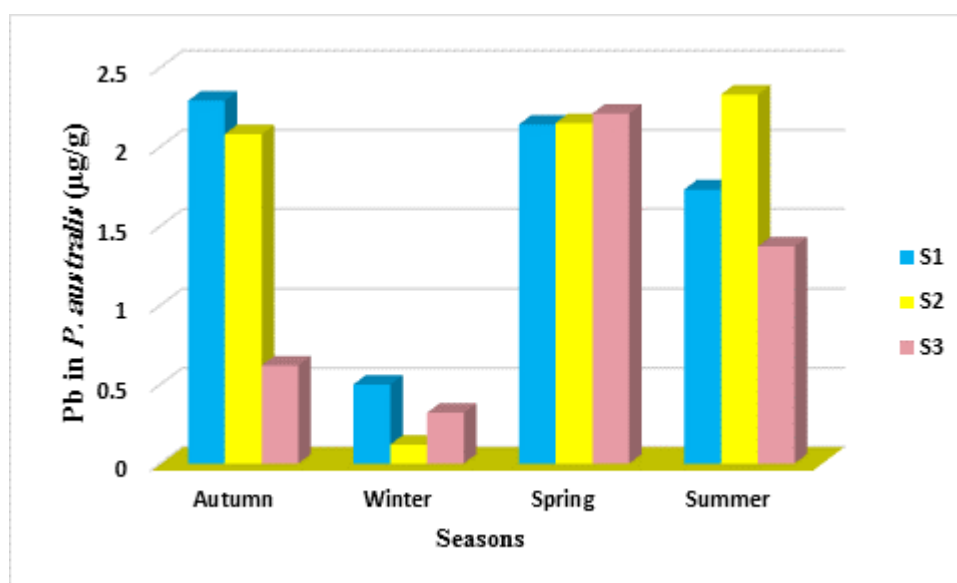
#### 4.2.3.1.5. Lead

Seasonal variations of Pb in *P. australis* showed that the highest mean value 2.33 ( $\mu\text{g/g}$  dry weight) in second site during Summer, while the lowest mean value of 0.12 ( $\mu\text{g/g}$  dry weight) in third site during Winter.

( $\mu\text{g/g}$  dry weight) in second site during Winter (Appendix:4, figure:4-37), annual mean value was 1.83 ( $\mu\text{g/g}$  dry weight).



**Fig (4-36):** seasonal variations of Cr concentrations in *P. australis*



**Fig (4-37):** seasonal variations of Pb concentrations in *P. australis*

Statistical analysis showed significant differences between seasons and sites, Significant positive correlation showed between Cu values and Mg hardness; Zn values with air temperature, water temperature, BOD<sub>5</sub>, DO, Ca hardness, and

turbidity; Cd values with air temperature, water temperature, BOD5, total and Ca hardness; Cr values with air temperature, water temperature, BOD5, and TDS; and Pb values with air temperature, total hardness and Mg hardness ( $r=0.694$ ,  $r=0.569$ ,  $r=0.602$ ,  $r=0.612$ ,  $0.583$ ,  $0.580$ ,  $r=0.732$ ,  $r=0.744$ ,  $r=0.787$ ,  $r=0.641$ ,  $r=0.629$ ,  $r=0.781$ ,  $r=0.745$ ,  $r=0.666$ ,  $r=0.637$ ,  $r=0.603$ ,  $r=0.599$ ,  $r=0.649$ ) respectively.

Significant negative correlations between Cu and EC, TOC; Zn values with TOC; Cr with DO and TOC; Pb with pH ( $r=-0.607$ ,  $r=-0.620$ ,  $r=-0.579$ ,  $r=-0.578$ ,  $r=-0.738$ ,  $r=-0.609$ ) respectively.

The results showed that the concentration of studied elements in *P. australis* were higher than in dissolved phase except Cd and that consider as good indication of the plants ability to accumulate heavy elements, the arrangement of studied elements in *P. australis* were  $Zn > Cu > Pb > Cr > Cd$ , high rates of heavy metals in *P. australis* may be attributed to passing of the river throw agricultural lands and presence of drainage caused increasing in rates of pollutants in the river therefore caused increasing in absorption and accumulation by the plant and this was emphasized by (Hanaf, 2016), or the reason of increasing in rates in Summer and Spring to low water levels and high temperature and evaporation during study period and increase in the discharge of sewage, or may be attributed to adequate proportion of the nutrient causing increase in hydrophyte growth and absorption of heavy metals and this emphasized by Majid *et al.*, (2014), increasing in Pb and Cd rates in Summer agree with (Sabri *et al.*, 2020) this could be attributed to frequent flow of pollutants of those elements from sewage opened directly into the river, *P. australis* is a biological indicator and good environmental remedy for trace elements (Hanaf 2016). The rates of studied heavy metals in *P. australis* showed differences between seasons and sites may be

due to environmental circumstances, availability of elements in water or sediments, depth of water column, and growing rates of plant (Batty & Younger, *et al.*, 2004)

### 4.2.3.2 Heavy Metals in *Ceratophyllum demersum*

#### 4.2.3.2.1. Copper

Seasonal variations of Cu in *C. demersum* showed that the highest mean value 8.89 ( $\mu\text{g/g}$  dry weight) in second site during Autumn, while the lowest mean value 5.52 ( $\mu\text{g/g}$  dry weight) in second site during Spring (Appendix:4, figure:4-38), annual mean value was 7.63 ( $\mu\text{g/g}$  dry weight).

#### 4.2.3.2.2. Zinc

Seasonal variations of Zn in *C. demersum* showed that the highest mean value 23.42 ( $\mu\text{g/g}$  dry weight) in third site during Summer, while the lowest mean value 6.26 ( $\mu\text{g/g}$  dry weight) in second site during Winter (Appendix:4, figure:4-39), annual mean value was 16.01 ( $\mu\text{g/g}$  dry weight).

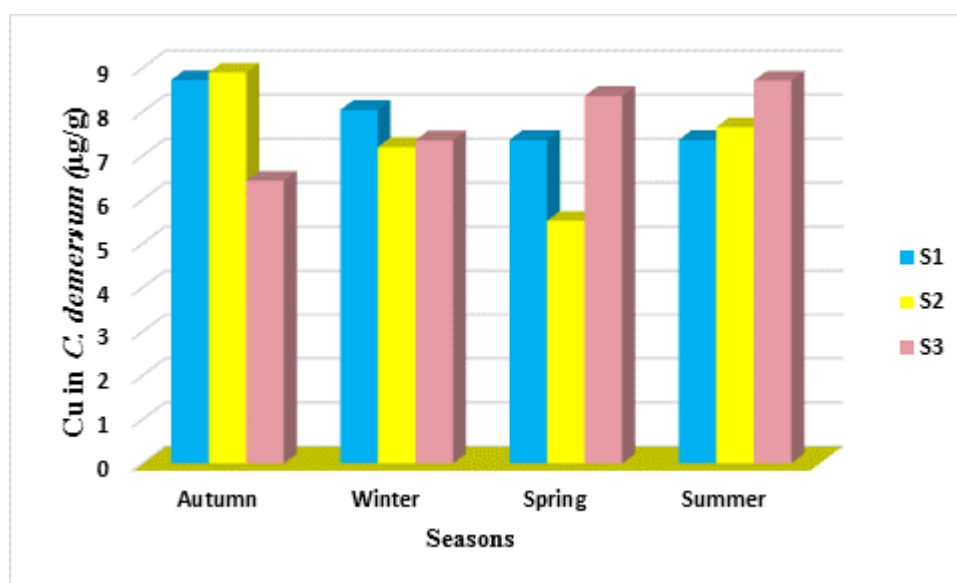


Fig (4-38): seasonal variations of Cu concentrations in *C. demersum*

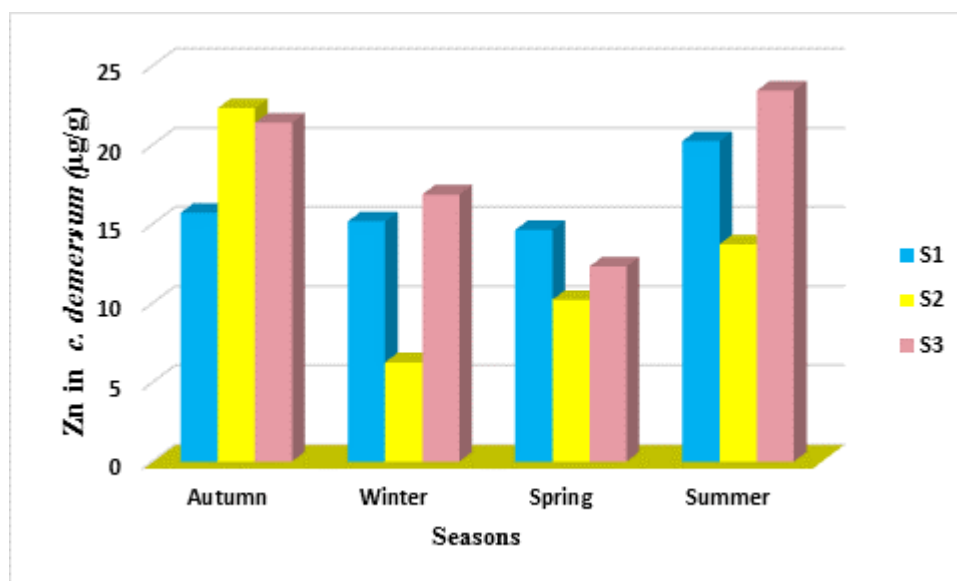


Fig (4-39): seasonal variations of Zn concentrations in *C. demersum*

#### 4.2.3.2.3. Cadmium

Seasonal variations of Cd in *C. demersum* showed that the highest mean value 4.97 (µg/g dry weight) in second site during Summer, while the lowest mean value 0.068 (µg/g dry weight) in second site during Winter (Appendix:4, figure:4-40), annual mean value was 1.76 (µg/g dry weight).

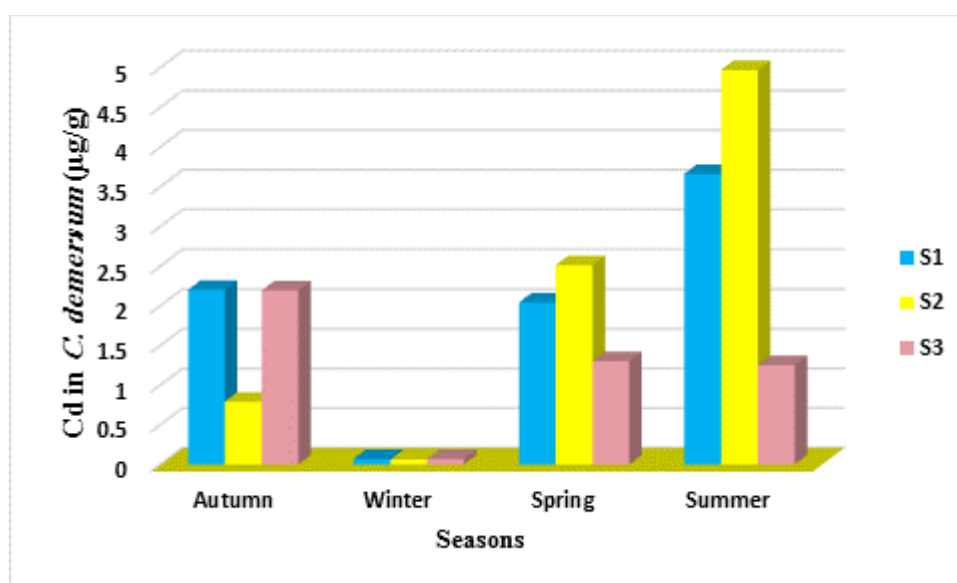


Fig (4-40): seasonal variations of Cd concentrations in *C. demersum*

#### 4.2.3.2.4. Chromium

Seasonal variations of Cr in *C. demersum* showed that the highest mean value 3.83 ( $\mu\text{g/g}$  dry weight) in first site during Autumn, while the lowest mean value 0.029 ( $\mu\text{g/g}$  dry weight) in second site during Winter (Appendix:4, figure:4-41), annual mean value was 2.19 ( $\mu\text{g/g}$  dry weight).

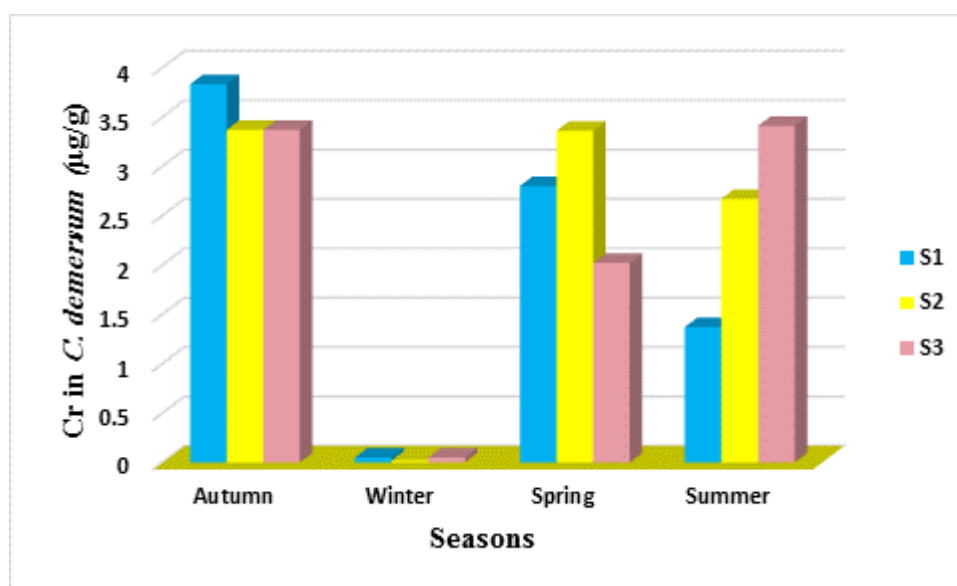
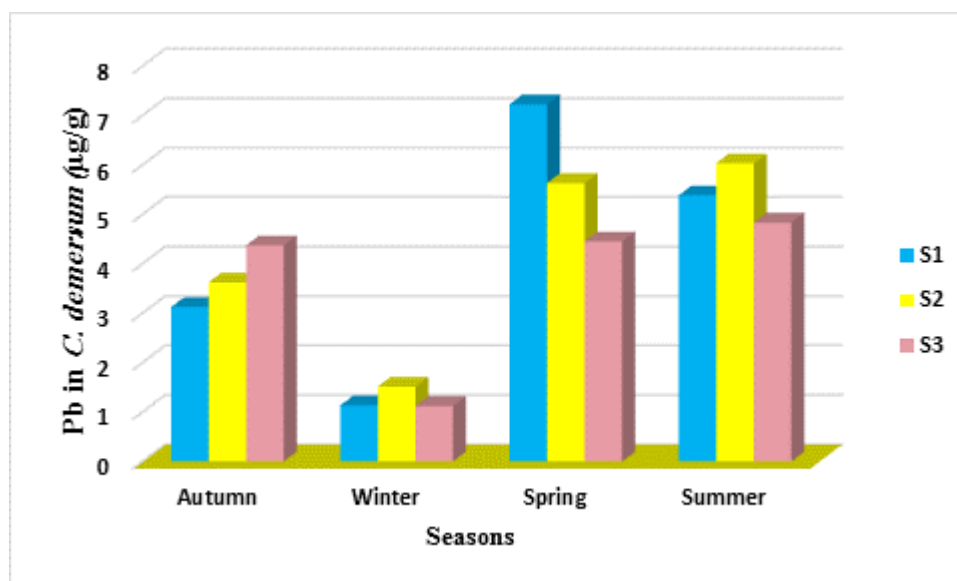


Fig (4-41): seasonal variations of Cr concentrations in *C. demersum*

#### 4.2.3.2.5. Lead

Seasonal variations of Pb in *C. demersum* showed that the highest mean value 7.22 ( $\mu\text{g/g}$  dry weight) in first site during Spring, while the lowest mean value 1.12 ( $\mu\text{g/g}$  dry weight) in third site in Winter (Appendix:4, figure:4-42), annual mean value was 3.975 ( $\mu\text{g/g}$  dry weight).



**Fig (4-42): seasonal variations of Pb concentrations in *C. demersum***

Statistical analysis showed significant differences between seasons and sites for all studied elements, Significant positive correlation showed between Cd with air temperature, water temperature, BOD5, total and Ca hardness; Cr values with air temperature, water temperature, total hardness, Ca hardness, and turbidity; Pb values with air and water temperature ( $r=0.743$ ,  $r=0.723$ ,  $r=0.605$ ,  $r=0.614$ ,  $r=0.629$ ,  $r=0.724$ ,  $r=0.674$ ,  $0.575$ ,  $r=0.647$ ,  $r=0.670$ ,  $r=0.699$ ,  $r=0.628$ ) respectively, and significant negative correlation between Zn with air temperature, water temperature, BOD5, and PH; Cd values with DO, EC, TOC; Cr with PH, TOC ( $r=-0.949$ ,  $r=-0.937$ ,  $r=-0.915$ ,  $r=-0.897$ ,  $r=-0.582$ ,  $r=-0.663$ ,  $r=-0.725$ ,  $r=-0.857$ ,  $r=-0.579$ ) respectively.

The results of *C. demersum* showed high concentrations more than *P. australis* in all studied elements that could be attributed to plant nature which is known as an immersion plant so all parts of it were exposure to heavy elements presented in water and released from sediments, and this was emphasized by Salman *et al.*, (2015) and Farhood, (2017).

Studied elements showed high rates in *C. demersum* reflecting good ability to absorption and accumulation in different mechanism (Memon,2001), the presence of significant differences among seasons and the increasing in concentrations may be attributed to the interest in agricultural activity, especially in summer and its consequences from pollutants such as fertilizers, salts and compost (Mahmoud *et al.*, 2018), the reason of the increase may be attributed to presence of an adequate ratio of nutrients led to increase in growth and capacity of absorption, consequently, an increase in accumulation (Borisova *et al.*, 2014), the reason for the rise may be due to increase in temperatures, low water levels during Summer and Autumn, and evaporation caused increase in rates of elements in water and sediments during seasons of the year. (Salman *et al.*, 2015). Mean values of studied elements were higher in *C. demersum* than *P. australis* in all elements and that's agree with the study of ( Sabri, 2020).



## Conclusions

- 1- Physical and chemical parameters results showed that they were with permissible limits except BOD<sub>5</sub>, total hardness and turbidity.
- 2- Existence of significant differences in heavy metals between seasons and sites in water, sediment, and two of aquatic studied plants refers to continuous supplement of metals pollutants.
- 3- Levels of studied heavy metals in water exceeded permissible limits of Iraqi determinants 1967 and limits of WHO.
- 4- Heavy metals concentrations in sediment were within permissible limits.
- 5- The results showed high rates of Cu and Cr in dissolved phase that indicate constantly input of anthropogenic pollutants to the river.
- 6- High concentrations of elements in exchangeable and residual phase of sediment indicate to accumulation of pollutants in the bank of the river.
- 7- The ability to use aquatic plants as indicator for pollution with heavy metals and good accumulator for it.
- 8- High rates of heavy metals in *C. demersum* were more than in dissolved phase; and *P. australis* shows good affinity of accumulation and phytoremediation.

## Recommendations

- 1- Studying accumulation of heavy metals by invertebrates, fish and aquatic plants.
- 2- Carrying out comparative study between another aquatic plants ability for accumulation heavy metals.

3- Customizing places for sanitary landfill and Emphasis using it instead of throwing on the banks of the river and prevent waste burning.

4- Monitoring and analyze water to determine causative of pollution and put solutions to reduce it and prevent deforestation.

5- Treating waste water and drainage before throwing to the river and limit using pesticides.

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Appendixes

**Appendix 1: Physical & chemical parameters in study sites (2019 –2020)** First line is ranges, second line is (average  $\pm$  standard deviation)

Study sites Parameters	S1	S2	S3
Air temperature (C°)	15-40 27.63 $\pm$ 10.78	16.67-40.67 29.06 $\pm$ 10.4	16.67-41.33 29.59 $\pm$ 10.73
Water temperature (C°)	11-28 19.71 $\pm$ 7.22	12-29 20.92 $\pm$ 7.21	13.67-29.33 21.5 $\pm$ 6.71
PH	7.93-8.47 8.16 $\pm$ 0.22	8.03-8.33 8.18 $\pm$ 0.12	8-8.33 8.12 $\pm$ 0.14
Turbidity (NTU)	19.34-32.83 25.45 $\pm$ 5.62	23.3-41.35 30.55 $\pm$ 8.65	21.19-42.4 29.33 $\pm$ 9.53
Electrical conductivity ( $\mu$ s\cm <sup>2</sup> )	1440-1665 1557.08 $\pm$ 122.11	1190-1745 1539.58 $\pm$ 241.38	1340-1793.33 1562.92 $\pm$ 185.18
Total dissolved solids (mg/l)	983.33-1243.33 1132.92 $\pm$ 119.92	1070-1155 1109.58 $\pm$ 41.1	1070-1213.33 1139.17 $\pm$ 59.15
Dissolved Oxygen mg/l	6.5-8.9 7.84 $\pm$ 1.04	6.25-9.4 7.86 $\pm$ 1.33	6.68-9.44 7.99 $\pm$ 1.26
Biological oxygen demand (mg/l)	2.83-9.33 5.25 $\pm$ 2.91	3.17-9.33 5.58 $\pm$ 2.87	2.98-10 5.75 $\pm$ 2.98
Total hardness (mg.CaCO <sub>3</sub> /l)	760-1013.33 895.42 $\pm$ 118.26	753.33-896.67 844.17 $\pm$ 65.4	736.67-926.67 814.17 $\pm$ 81.3
Calcium hardness (mg.CaCO <sub>3</sub> /l)	141-186.67 164.25 $\pm$ 21.59	145.67-175.33 163.67 $\pm$ 13.71	136.67-176.67 155.67 $\pm$ 21.64
Magnesium hardness (mg.CaCO <sub>3</sub> /l)	99.03-132.91 117.75 $\pm$ 15.76	93.9-111.43 105.48 $\pm$ 8	93.18-119.53 103.68 $\pm$ 11.91
Total organic Carbon (%)	0.29-1.17 0.7 $\pm$ 0.39	0.19-1.61 1.03 $\pm$ 0.61	0.29-1.64 0.94 $\pm$ 0.64s

**Appendix 2: Heavy metals concentration in Euphrates River study sites (2019-2020)** First line is ranges, second line is (average  $\pm$  standard deviation)

Elements		Autumn	Winter	Spring	Summer
Cu	Dissolved phase ( $\mu\text{g/l}$ )	1.05-2.95 1.88 $\pm$ 0.97	1.1-2.89 1.73 $\pm$ 1.03	1.32-2.56 1.9 $\pm$ 0.62	1.02-2.25 1.47 $\pm$ 0.68
	Particulate phase ( $\mu\text{g/g dry Wt}$ )	3.14-5.72 4.59 $\pm$ 1.32	2.14-4.08 3.31 $\pm$ 1.03	1.72 $\pm$ 3.25 2.7 $\pm$ 0.85	2.37-5.73 3.61 $\pm$ 1.84
Zn	Dissolved phase ( $\mu\text{g/l}$ )	1.1-2.3 1.53 $\pm$ 0.67	ND 0 $\pm$ 0	ND 0 $\pm$ 0	0.01-0.14 0.09 $\pm$ 0.07
	Particulate phase ( $\mu\text{g/g dry Wt}$ )	36.65-51.66 46.06 $\pm$ 8.2	31.25-40.6 37.34 $\pm$ 5.05	26.39-31.33 28.62 $\pm$ 2.51	9.22-79.04 47.24 $\pm$ 35.32
Cd	Dissolved phase ( $\mu\text{g/l}$ )	1.05-3.65 2.31 $\pm$ 1.30	0.15-0.16 0.15 $\pm$ 0.01	1.11-1.44 1.23 $\pm$ 0.18	1.15-1.25 1.22 $\pm$ 0.06
	Particulate phase ( $\mu\text{g/g dry Wt}$ )	5.72-11.14 7.61-3.06	0.11-1.01 0.45 $\pm$ 0.49	0.21-1.19 0.86 $\pm$ 0.56	1.02-2.67 1.65 $\pm$ 0.89
Cr	Dissolved phase ( $\mu\text{g/l}$ )	0.21-2.11 0.85 $\pm$ 1.09	0.001-0.01 0.006 $\pm$ 0.004	1.37-2.7 2.16 $\pm$ 0.70	0.35-2.34 1.65 $\pm$ 1.12
	Particulate phase ( $\mu\text{g/g dry Wt}$ )	10.33-14.86 12.39 $\pm$ 2.29	6.24-9.9 8.22 $\pm$ 185	2.14-5.07 4.05 $\pm$ 1.65	1.67-4.61 3.31 $\pm$ 1.5
Pb	Dissolved phase ( $\mu\text{g/l}$ )	0.24-0.29 0.27 $\pm$ 0.03	ND 0 $\pm$ 0	ND 0 $\pm$ 0	0.02-0.07 0.07 $\pm$ 0.05
	Particulate phase ( $\mu\text{g/g dry Wt}$ )	6.92-9.54 7.83 $\pm$ 1.48	0.5-9.25 3.82 $\pm$ 4.73	3.29-5.29 4.03 $\pm$ 1.09	3.47-7.36 5.73 $\pm$ 2.02

**Appendix 3: Heavy metals concentrations in sediment of Euphrates River (2019- 2020).** First line is ranges, second line is (average  $\pm$  standard deviation)

Elements		Autumn	Winter	Spring	Summer
Cu	Exchangeable phase	0.48-1.47 1 $\pm$ 0.5	0.93-1.25 1.08 $\pm$ 0.16	1.02-1.38 1.15 $\pm$ 0.2	1.32-2.48 1.99 $\pm$ 0.60
	Residual phase	1.38-3.45 2.31 $\pm$ 1.05	1.33-2.35 1.97 $\pm$ 0.56	1.24-2.35 1.62 $\pm$ 0.62	1.13-3.27 2.55 $\pm$ 1.22
Zn	Exchangeable phase	0.95-1.96 1.37 $\pm$ 0.53	0.99-1.49 1.17 $\pm$ 0.28	0.85-1.03 0.96 $\pm$ 0.09	1.26-2.01 1.51 $\pm$ 0.43
	Residual phase	8.29-9.54 8.71 $\pm$ 0.72	5.32-5.41 5.35 $\pm$ 0.05	1.28-2.36 1.2 $\pm$ 0.62	1.26-3.51 2.63 $\pm$ 1.21
Cd	Exchangeable phase	0.16-0.38 0.28 $\pm$ 0.11	ND-0.01 0.01 $\pm$ 0.01	0.02-0.25 0.16 $\pm$ 0.13	0.36-0.69 0.52 $\pm$ 0.17
	Residual phase	0.11-0.15 0.13 $\pm$ 0.02	0.004-0.01 0.01 $\pm$ 0	0.01-0.18 0.11 $\pm$ 0.09	0.01-1.02 0.53 $\pm$ 0.51
Cr	Exchangeable phase	0.14-0.31 0.21 $\pm$ 0.09	0.02-0.022 0.02 $\pm$ 0.001	0.21-0.31 0.27 $\pm$ 0.06	0.35-0.52 0.41 $\pm$ 0.09
	Residual phase	5.99-12.61 8.34 $\pm$ 3.7	0.02-0.04 0.03 $\pm$ 0.011	1.04-2.12 1.71 $\pm$ 0.59	1.02-2.67 1.63 $\pm$ 0.9
Pb	Exchangeable phase	7.09-10.72 8.9 $\pm$ 1.8	3.69-4.01 3.87 $\pm$ 4.73	4.29-5.14 4.84 $\pm$ 0.48	4.37-6.57 5.19 $\pm$ 1.2
	Residual phase	0.11-0.19 0.14 $\pm$ 0.04	0.01-0.04 0.02 $\pm$ 0.016	0.15-0.18 0.16 $\pm$ 0.01	1.03-1.21 1.11 $\pm$ 0.09



**Appendix 4: Heavy metals in *Ceratophyllum demersum* and *Phragmites australis***  
( $\mu\text{g/g}$  dry weight) (2019- 2020) First line is ranges, second line is (average  $\pm$  standard deviation)

Elements		Autumn	Winter	Spring	Summer
Cu	<i>P. australis</i>	1.61-3.24	2.28-3.76	2.53-4.27	3.46-5.14
		2.29 $\pm$ 0.85	2.79 $\pm$ 0.84	3.22 $\pm$ 0.92	4.43 $\pm$ 0.87
	<i>C. demersum</i>	6.43-8.89	7.2-8.4	5.52-8.36	7.36-8.71
		8.01 $\pm$ 1.37	7.53 $\pm$ 0.45	7.08 $\pm$ 1.44	7.91 $\pm$ 0.71
Zn	<i>P. australis</i>	6.34-14.58	3.76-12.63	1.18-10.68	1.7-19.24
		9.98 $\pm$ 4.20	7.52 $\pm$ 4.59	5.07 $\pm$ 4.98	12.54 $\pm$ 9.47
	<i>C. demersum</i>	15.7-22.31	6.26-16.86	10.21-14.62	13.72-23.42
		19.8 $\pm$ 3.58	12.76 $\pm$ 5.7	12.38 $\pm$ 2.21	19.13 $\pm$ 4.94
Cd	<i>P. australis</i>	0.08-0.19	0.002-0.005	0.13-0.85	1.03-1.28
		0.13 $\pm$ 0.07	0.004 $\pm$ 0.002	0.37 $\pm$ 0.41	1.12 $\pm$ 0.14
	<i>C. demersum</i>	0.79-2.2	0.068-0.073	1.3-2.51	1.25-4.97
		1.73 $\pm$ 0.81	0.07 $\pm$ 0.002	1.95 $\pm$ 0.61	3.29 $\pm$ 1.89
Cr	<i>P. australis</i>	0.21-0.92	0.001-0.004	0.42-1.39	1.08-1.37
		0.53 $\pm$ 0.36	0.003 $\pm$ 0.001	0.81 $\pm$ 0.51	1.24 $\pm$ 0.15
	<i>C. demersum</i>	3.37-3.83	0.029-0.05	2.02-3.36	1.37-3.41
		3.52 $\pm$ 0.27	0.04 $\pm$ 0.012	2.73 $\pm$ 0.67	2.41 $\pm$ 2.48
Pb	<i>P. australis</i>	0.62-2.29	0.12-0.5	2.14-2.21	1.37-2.33
		1.67 $\pm$ 0.91	1.83 $\pm$ 0.86	2.17 $\pm$ 0.03	1.81 $\pm$ 0.48
	<i>C. demersum</i>	3.12-4.37	1.12-1.51	4.45-7.22	4.83-6.03
		3.7 $\pm$ 0.63	1.25 $\pm$ 0.22	5.77 $\pm$ 1.39	5.41 $\pm$ 0.06

**Appendix5: Water Iraqi (1967) and WHO standards (2004) for physical & chemical parameter**

parameters	Iraqi standards	WHO standards
<b>PH</b>	6.5-8.6	6.5-8.5
<b>Tur (NTU)</b>	----	50
<b>TDS (mg/l)</b>	----	1500
<b>DO (mg/l)</b>	More than 5	----
<b>BOD<sub>5</sub> (mg/l)</b>	Less than 5	----
<b>TH (mg.CaCO<sub>3</sub>/l)</b>	500	500

**Appendix6: Water Iraqi (1967) and WHO standards (2006) for concentration of heavy metals (µg/l)**

Element	Iraqi standards	WHO standards
<b>Cu</b>	<b>0.05</b>	<b>1</b>
<b>Zn</b>	<b>0.5</b>	<b>5</b>
<b>Cd</b>	<b>0.05</b>	<b>0.005</b>
<b>Cr</b>	<b>0.05</b>	<b>0.05</b>
<b>Pb</b>	<b>0.05</b>	<b>0.05</b>

**Appendix7: World permissible limits for concentrations of heavy metals in sediment according to (CBSQG, 2003) mg/g dry weight**

Element	Permissible limits
Cu	32
Zn	120
Cd	0.99
Cr	43
Pb	36

## الخلاصة

الدراسة الحالية قدرت مستويات خمسة من العناصر الثقيلة في مياه نهر الفرات، والرواسب ونوعين من النباتات المائية (القصب والشمبلان) من تشرين الثاني (2019) إلى تشرين الأول (2020) وأختيرت ثلاث مواقع، جُمعت العينات في الصباح شهرياً لقياس الصفات الفيزيائية والكيميائية التي تضمنت (درجة حرارة الهواء والماء، الأس الهيدروجيني (pH)، العكارة (Tur)، التوصيلية (EC)، الاملاح الذائبة الكلية (TDS)، الأوكسجين الذائب (DO)، المتطلب الحيوي للأوكسجين ( $BOD_5$ )، العسرة الكلية (TH)، عسرة الكالسيوم والمغنيسيوم، ومستوى الكربون العضوي (TOC) وتحليل نسيج التربة، كما تم فصلياً قياس مستوى العناصر الثقيلة (النحاس، الخارصين، الكاديوم، الكروم والرصاص) في الماء بحالتي الذائب والدقائق وفي الرواسب بحالتي المتبادل والمتقي وفي القصب والشمبلان.

معدلات الصفات الفيزيائية والكيميائية في مواقع الدراسة كالتالي: درجة حرارة الهواء تراوحت بين (11-43 م°)، ودرجة حرارة الماء (9-31 م°)، الأس الهيدروجيني (7.5-8.5)، والعكارة تراوحت بين (18.49-53.27 NTU)، التوصيلية الكهربائية (950-1920 مايكروسيمنز/سم<sup>2</sup>)، الأملاح الذائبة الكلية (820-1450 ملغم/لتر)، الأوكسجين الذائب (5.2-10.3 ملغم/لتر)، المتطلب الحيوي للأوكسجين (2-15 ملغم/لتر)، أما قيم العسرة الكلية (620-1260 ملغم. كربونات الكالسيوم. لتر<sup>-1</sup>)، عسرة الكالسيوم (120-208 ملغم. كربونات الكالسيوم. لتر<sup>-1</sup>)، عسرة المغنيسيوم تراوحت بين (68.14-189.6 ملغم. كربونات الكالسيوم. لتر<sup>-1</sup>)، محتوى الكربون العضوي (0.055-2.87%)، أظهر تحليل مكونات التربة نسبة (90% من الغرين، 5% لكل من الرمل والطين).

المعدل السنوي للعناصر الثقيلة في المياه (Cu, Zn, Cd, Cr, Pb) تراوح بين (1.71، 1.23، 0.81، 1.75)، (0.81 مايكروغرام/لتر على التوالي في الحالة الذائبة، (3.56، 39.81، 2.64، 6.99، 7.14) مايكروغرام/غرام وزناً جاف على التوالي في الحالة الدقائقية، وفي الرواسب (1.3، 1.25، 0.27، 0.23، 8.64) مايكروغرام/غرام وزناً جاف على التوالي في الحالة المتبادلة و(2.11، 4.78، 0.2، 2.93، 0.16) مايكروغرام/غرام وزناً جاف على التوالي في الحالة المتبقية، و (3.18، 8.78، 0.14، 0.64، 1.83) مايكروغرام/غرام وزناً جاف على التوالي في القصب، و (7.63، 16.01، 3.97، 2.19، 1.76) مايكروغرام/غرام وزناً جاف على التوالي في الشمبلان.

الشمبلان سجل أعلى تركيز للعناصر الثقيلة المدروسة من الحالة الذائبة للماء والقصب، لذلك يمكن أن يستخدم هذا النبات كمزيل بيئي كفوء لهذه العناصر.

العناصر الثقيلة في المياه تجاوزت الحدود المسموحة حسب المواصفات القياسية العالمية والعراقية بينما لم تتجاوز الحدود المسموحة في الرواسب.



جمهورية العراق  
وزارة التعليم العالي والبحث العلمي  
جامعة المثنى / كلية العلوم  
قسم علوم الحياة

## تقدير التراكم الحيوي لبعض العناصر الثقيلة في مياه، رواسب، ونباتي القصب والشمبلان نهر الفرات السماوة/ العراق

الرسالة مقدمة كجزء من متطلبات نيل درجة الماجستير في  
علوم الحياة

من قبل

وسن شاكر رزاق

بكالوريوس علوم حياة / 2008

بإشراف

أ.م.د. إبتهاال عقيل الطائي

أ.م.د. علي عبد الحمزة الفنهر اوي