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Assessment Of Some Heavy Elements and Hydrocarbons in the Water, Sediments and Dominant Aquatic Plants at Al-Chibayish marshes

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بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

وَمَا أَوْتِيْتُمْ مِنَ الْعِلْمِ

إِلَّا قَلِيْلًا

سورة الاسراء ، الآية 85

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Rehab ,2018

Dedication

**I would like to dedicate this simple work To
My parents, may God have mercy on them
Whom I will not forget her favor, as long as I live
My sisterShaffa
Who supported me and stood next to me
My husband....Aqeel
My dear children
Redha and Zainab**

Rehab

Summary

Samples of water , sediments and dominant species of aquatic plants (submerged (*Ceratophyllum demersum*) and emergent (*Phragmites australis* , *Typha domingensis* and *Schoenoplectus litoralis*)) from four stations which selected at Al- Chibayish marsh in Thi-Qar province, southern Iraq, the first station (Ab usubat), the second station (Al-Baghdadiya 1), the third station (Al-Baghdadiya 2), and the fourth station (Al-Hammara), were collected seasonally from Augst, 2017 to April ,2018 ,to determine the concentration of some heavy elements Cadmium(Cd),Chromium(Cr),Nickel(Ni) and Lead(Pb) in dissolved and particulate phases of water, and in the sediments(exchangeable and residual phase). Heavy elements pollution index (HPI) , Geoaccumulation index (Igeo) indices and Bioaccumulation factor (BAF) were calculated as indicators for heavy elements pollution in water, sediments and aquatic plants respectively . Also, the present study included determine the concentration and origin of hydrocarbons in water, sediments and aquatic plants in Al-Chibayish marsh.

As well as measures of some ecological parameters (air and water temperatures, potential of hydrogen (pH), salinity (sal.), electrical conductivity (EC), turbidity, total suspended solid (TSS), dissolved oxygen (DO) ,and biological oxygen demand (BOD₅) ,in addition to that the grain size and Total organic carbon TOC% were measured in the sediments samples.

Results showed that the ranged of measurable values were : Air temperatures (14-47)°C, water temperatures (10.5-33) °C, pH (7.24-8.15) ,Salinity(2.5-3.4) PSU(Practical Salinity Unit), EC(4.53-6.15) mS/cm (Millisemince/centimeter), turbidity(1.3-50.55)NTU (Nephelometric Turbidity Unit), TSS(1.68-97.22) mg/l, DO (0.7-7.75) mg/l and BOD₅ (0.75-3.5) mg/l , while in sediments grain size analysis show that the range of sand (1-24)% ,silt (59-86)% ,clay (7-25)% . Total Organic Carbon(TOC) were also determined the range values were 9.93% to 13.49%.

The mean concentrations of the studied elements(Cd, Cr, Ni and Pb) in dissolved phase were (0.06 , 2.03 ,0.56 , 2.97)µg/l, respectively , whereas in the exchangeable phase of particulate were(14.47 , 53.97 , 90.91 ,332.78)µg/g dry weight respectively , and in the residual phase of particulate were (12.21 , 225.60 ,243.66 ,242.25) µg/g dry weight respectively . HPI values were ranged

from 4.39 to 12.51 referred to unpolluted water according to the permissible values of dissolved elements.

In sediments , the mean concentrations of the elements in the exchangeable phase were (0.41 , 19.70 , 46.37, 25.20) $\mu\text{g/g}$ -dry weight, respectively ,while in the residual phase were (0.27, 82.95 ,75.32, 14.41) $\mu\text{g/g}$ -dry weight, respectively. According to Igeo values, the sediments of Al- Chibayish marsh can be classified as unpolluted with Cd and Pb , while unpolluted to moderately polluted with Cr , and moderate to strongly polluted with Ni .

In aquatic plants , the mean heavy elements concentrations in the *Phragmites australis* were (0.20, 5.27,4.21,6.19) $\mu\text{g/g}$. In *Typha demingensis* were (0.20 ,3.96 ,3.05 ,5.60) $\mu\text{g/g}$. *Schoenoplectus litoralis* were(0.20 ,4.58 ,3.49 ,4.31) $\mu\text{g/g}$. While *Ceratophyllum demersum* were(0.51 ,9.73 ,51.44 ,9.99) $\mu\text{g/g}$, for Cd ,Cr ,Ni and Pb, respectively. According to BAF values the *Ceratophyllum demersum* species was greater than other species for all the studied elements.

Total Petroleum Hydrocarbons (TPHs) were determined in water ,sediments and aquatic plants samples using spectrofluorometry. Aliphatic (n-alkanes) and polynucleic Aromatic Hydrocarbons(PAHs) compounds have been identified using capillary Gas Chromatography (GC) and High performance liquid chromatography instruments (HPLC) respectively .

Results showed that the range of TPHs concentrations in water was (1.91 – 6.79) $\mu\text{g/l}$, in the sediments was (2.98-17.98) $\mu\text{g/g}$ dry weight, while in aquatic plants was (6.00-34.91) , (5.25-30.68) , (7.78-30.74) , (9.01-34.29) $\mu\text{g/g}$ dry weight, for *Phragmites australis*, *Typha demingensis* , *Schoenoplectus litoralis* and *Ceratophyllum demersum*, respectively.

N-alkanes concentrations in water ranged (0.32-2.98) $\mu\text{g/l}$, while in sediments were (0.62-29.75) $\mu\text{g/g}$ dry weight . The carbon chain length of n-alkanes in water and sediments samples were recorded from C16-C38 . While the total aliphatic (n-alkanes) concentrations in aquatic plants was (4.69-31.52),(10.73-54.25),(17.09-64.36),(5.23-40.85) $\mu\text{g/g}$ dry weight, for *Phragmites australis*, *Typha demingensis*, *Schoenoplectus litoralis* and *Ceratophyllum demersum*, respectively.

The range of PAHs compounds in water was (2.44-37.78) ng/l ,dominated by Acenaphthylene and Acenaphthene (as light PAHs) and Benzo(K)fluranthene and Indeno(1,2,3,c,d)Pyrene (as heavy PAHs). Whereas in sediments the PAHs

ranged from (6.56-52.36) ng/g dry weight dominated by anthracene and Acenaphthene (as light PAHs) and Benzo[g,h,i]perylene , Indeno(1,2,3,c,d)Pyrene (as heavy PAHs). While The range of PAHs compounds in aquatic plants was (54.42-86.66),(37.02- 80.54),(6.31-137.15),(11.74-151.90) ng/g dry weight, for *Phragmites australis*, *Typha demingensis* , *Schoenoplectus litoralis* and *Ceratophyllum demersum*, respectively.

The CPI index and Pristine/Phytane values indicated that the source of n-alkanes hydrocarbons in the water ,sediments and aquatic plants of Chibayish marsh was biogenic and anthropogenic .Whereas the LMW/HMW, BaA/(BaA +Chr) (Benzo(a)anthracene/(Benzo(a)anthracene +Chrysene), Phenanthrene/Anthracene ratios, indicated that the source of PAHs compounds in the water , sediments and aquatic plants were pyrogenic and petrogenic .

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List of abbreviations

Name	Acronym
American Public Health Association	APHA
Biological Oxygen Demand	BOD ₅
Carbon Preference Index	CPI
Consensus-Based Sediment Quality Guidelines of Wisconsin	CBSQG
Dissolved Oxygen	DO
Electrical Conductivity	EC
Flame Atomic Absorption Spectrophotometer	FAAS
Geo-accumulation Index	I-geo
Heavy Metal Pollution Index	HPI
Microgram / liter	µg/l
Milligram / liter	mg/l
Millisemince /centimeter	ms/cm
Nephelometric Turbidity Unit	NTU
Practical Salinity Unit	PSU
Total Organic Carbon	TOC
Total Suspended Solid	TSS
World Health Organization	WHO

Chapter One

Introduction & Review of Literatures

1.1 - Introduction

Many countries of the world are known for their natural features, ancient monuments, great rivers or great forests, and Iraq is famous for the existence of the marshes. (Hussain, 2014).

Marshes are frequently or consistently overflowed wetlands characterized by emergent herbaceous vegetation adjusted to immersed soil condition, changing water streams, and mineral soil (USEPA, 2008). The Iraqi marshlands are made by the Euphrates and Tigris rivers system in the lower part of the Mesopotamian basin. They cover an area of about 15000-20000 km² (Bedair *et al*, 2006).

Southern marshes of Iraq form large triangular region restricted by three southern provinces: Thi-Qar to the west, Maysan to the northeast and Basrah to the south. They are vast open zone that includes both permanent and seasonal marshes (Al-Ansari and Knutsson, 2011).

Three major areas Al-Hawizeh marsh, Al- Hammar marsh and the Central marshes form the gist of the marshes land of southern Iraq. Al-Hawizeh marshes in the east of the Tigris River, are partitioned into the Iraqi-Iranian border. In this region, the main source of water the Tigris River and partially the river karon inside Iran (Alwan, 2006). While Al-Hammar marsh, is located southern the Euphrates River, it extends from Nasiriyah city in the west to the outskirts of the Basrah city in the east. This area ranges from 2800 km² to 4500 km² during the flood seasons. The Euphrates river provides AI-Hammar marsh with water, which is the main source, as well as small amounts of water come from the Tigris river (UNEP, 2006; Ajmi, 2013). The central marshes constitute the heart of Iraq's southern marshes and are located at the top of the concourse of the Tigris and Euphrates rivers. They receive water from Euphrates river, which feeds the region through a some of tributaries. The Central marshes cover an area of 3,000 km² and can expand to 4,000 km² during the flood season (UNEP, 2006).

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Such specific wetlands of the southern part of Iraq play an important role in the conserving diversity of species in the Middle East, because of their large size, the abundance of their aquatic flora and their separation from the other systems (Bedair *et al.*, 2006).

Marshes are consider as biological filters of the Earth, and are often called as “Earth’s kidney”. They are consider as intermediate region between aquatic and terrestrial system which playing a significant role in purifying the polluted water for centuries. The majority of marshes have been exploited for their natural cleansing capacity for assimilating different contaminants (Joyce, 2012).

In natural system, marshes sediment accumulate types of chemicals that enter the water bodies through natural and anthropogenic activities (Li *et al.*, 2006; Adekola and Eletta, 2007; Lu *et al.*, 2011). Marshes system can act as a sink of various compounds either through sedimentation or bio-accumulation. The Mesopotamian marshlands are known as sink for different compounds (Mitsch and Gosselink, 2007).

There are several materials or energy that are introduced directly or indirectly to the aquatic environment as a result of various human activities and that leads to harmful effects on human health and aquatic organisms and also leads to the disruptive kinds of water activities. Otherwise a change in the properties of water will make it lose its validity for use in different purposes (GESAMP, 1993). Therefore, studying the pollution of the southern marshes is one of the important studies in determining the origin of pollution and its percentage in this region.

The most important and harmful pollutants of the aquatic environment are petroleum hydrocarbons and heavy elements that affect water in its dissolved phase, particulate, organisms and sediments (Al-Saad *et al.*, 2009).

1.1.1. Heavy Elements

Heavy elements which have specific gravity more than 5g/cm^3 and have negative effects on the environment when over-utilizes and also influence the health of humans, animals and plants. These compounds are often called trace elements because they are present in low concentrations in the earth's crust up to 0.1% (Minkoff and Baker, 2001).

Heavy elements are present in the aquatic environment at very little concentrations when these water bodies are away from origin of pollution, but concentrations may increase as a result of fast growth of populations and different human activities (Osma *et al*, 2013).

Heavy elements is one of the most important and dangerous types of pollution which threatens the aquatic environment with its living and non-living components, and therefore affects the living organisms (Al-Ani *et al*, 2014).

Pollution of water with heavy elements is a serious concern in today's world (Miretzky *et al*. 2004). Consequently, pollution of heavy elements has become a main environmental problem because of its toxicity, non-degradable and constant nature. This leads to their accumulation in plants, microorganisms, and various aquatic organisms, which, in turn are, transferred to humans through the food chain and therefore lead to multiple human health problems (Varol and Şen, 2012).

In natural aquatic environment, elements are ordinarily at the concentrations differing from nanogram to microgram in a liter. Recently, heavy elements' exceeding the carrying limit of waters have caused some problems with respects to aquatic ecosystem balance (Ndimele and Jimoh 2011). The elements concentrations may increase above natural levels due to the release of industrial, agricultural, household and other wastes (Reza and Singh 2010). There are various sources that supply the aquatic environment

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with heavy elements and different concentrations, and can be partitioned into two main sources: natural resources and anthropogenic resources (Kamon *et al.*, 2000).

Natural resources include the soil washing, weathering of natural mineral rocks, agricultural lands and natural events, which carried by rainwater, flood water to the aquatic environment. Also, heavy elements enter the aquatic environment because of organisms hydrolysis after death (Klavins *et al.*, 2000; Yu *et al.*, 2001). While the other source of heavy elements is anthropogenic sources, they represent all sources of human activity like fertilizers, industrial waste, agricultural pesticides, textiles, traffic emissions, weathering of buildings, dyes, the utilization of oil refinery products and atmospheric deposition (Wei and Yang, 2010). Household wastes play an important role in adding heavy elements to the aquatic environment.

These elements are essential and necessary to sustain the life of living organisms such as copper, zinc, and iron which play main roles in the functioning of enzyme systems. On the other hand at higher concentrations become toxic. The other group of biological elements is constrained or non-essential and contains elements that pollute the aquatic and harmful to their biota even at trace levels to exposure. For example, lead, cadmium and chromium the exposure to them causes serious health effects, including reduced growth and development, organ damage, cancer disease, nervous system damage, and in dangerous cases, death. (Al-Ani *et al.*, 2014; Al-Hejuje, 2014).

These elements exist in the aquatic environment in a variety of forms including:

Dissolved heavy elements, which consist the ions of elements and the organic or inorganic chemical compounds existent in the water column and which have a diameter lower than 0.45 μm . One of the most important factors affecting the release of elements and their solubility is the value of pH which

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affecting the solubility of the element. The height of one unit towards alkaline leads to reduced solubility of copper, cadmium, iron, and manganese by one hundred times. The conflict occurs when the pH value of one unit is lower than it was. Therefore, pH changes affect the deposition and release of elements in the aquatic environment (Lindsay, 1979; Yan *et al.*, 2018).

The particulate heavy elements are the elements in the suspended matter that have a diameter higher than 0.45 μm . and have been divided into two kinds: biotic, which includes elements found in microorganisms (phytoplankton, zooplankton, bacteria, and fungi) and some vital activity products and abiotic which consists of the heavy elements that are present in the organic and inorganic chemical compounds like clay particles, silts, quartz, siliceous silica compounds and residues of dead organisms (Zoumis *et al.* 2001).

Heavy elements in sediments: In sediments, there are six different geochemical types of elements associated with sediments. In the first one, these elements are connected with the sediment in the most labile obtained mode and are known as exchangeable elements. The second form extracts are jointed mainly with carbonates and are highly sensitive to pH variations. The third type, the elements attached to manganese oxide and partly amorphous ferrous oxide while in the fourth type, to amorphous and poorly crystalline ferrous oxide. Fifth, the elements compounds with the organic matter and sulfides are released. Finally, the residual portion, a fraction of elements are strongly united to the lithogenic minerals of the sediments (Hassan ,2007 ; Al-Haidarey, 2009; Al-Hejuje,2014).

Sediments have a high ability to accumulation and retention the elements and pollutants. However the sediments may become a source of water contamination when their surface are saturated with heavy elements, particularly when the concentrations of elements in freshwater are reduced.

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This effect is most distinct at high temperatures, velocity of water and fine sediment particles (Hassan *et al.*, 2010). Measuring the concentration of heavy elements in sediments gives a clear perception of the level of contamination in the aquatic environment. These elements are bound to particulate materials, which finally settle down and become united into sediments. Sediment-bound contaminants can be taken up by rooted aquatic plants and other aquatic organisms, (Laluraj and Nair, 2006).

Some of the chemical and physical factors including pH ,water temperature (WT), salinity (Sal.) , organic matter (O.M) and dissolved oxygen (DO) have important roles in solubility and remobilizing of heavy elements and their absorb by plants (Kabat-Pendias and Pendias,2001; Canli and Atli,2003). The increasing water temperature and decreasing dissolved oxygen in the ecosystem improve the copper toxicity (Odum,2000), whereas decrease of pH value (< 7.0) causes reduction of the copper mobilization, particularly in low concentration of dissolved organic matter (Mueller,*et al*,1989) .On the other hand, high pH value ($\text{pH} > 8.0$) leads to formation the toxic copper hydroxide (Odum,2000). Elements toxicity is control by alkalinity according to creating the insoluble carbonates (Akbulut and Tuncer,2011). Conversely , increasing salinity causes decreasing the cadmium toxicity (Odum,2000).

Heavy elements are present in the aquatic environments as portion of the food chain; their presence is normally in an acceptable amount unless they are part of pollution(Alagarsamy and Zhang,2010). Heavy elements like copper, iron, zinc, manganese, cobalt and nickel are necessary for normal body functions, whereas cadmium , lead and mercury are not essential(Singh *et al.*,2017) . In the Mesopotamian marshlands, heavy elements are introduced either in particulate phase or in soluble through different sources including urban runoff and agricultural discharge (Husain,1994). Heavy elements can be double-edged sword; they possibly will have beneficial and dangerous

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effects on animal, plant and human life depending on their concentrations, toxicity, and ability to accumulate in aquatic environment (Mueller *et al.*, 1989 and Al-Maarofi *et al.*, 2013). Heavy elements can also reduce the growth rates of aquatic organisms and damage their reproduction. (Belzile *et al.*, 2004).

1.1.2. Hydrocarbons

The word Petroleum means in Greek language : Petra and oleum, that actually means "rock oil" and mentions to hydrocarbons that happened usually in the sedimentary rocks of the Earth's crust in the shape of liquids, gases, semisolids, or solids (Dobian , 2016).

Hydrocarbon pollutants in the ecosystem is a very serious problem whether it originates from petrol, pesticides or other poisonous organic material. Environmental pollution produced by petroleum is of huge concern due to the fact that petroleum hydrocarbons are harmful to all kinds of life. (Bishop, 1997; Abha and Singh, 2012; Al-Ali *et al.*, 2016). Crude oil and oil derivatives are the main origins of hydrocarbons in the aquatic system. Other sources are the ones which are referred to as natural or biogenic hydrocarbons (Al- Saad, 1995; Karem, 2017) .

Pollution by petroleum hydrocarbons in the environment is widespread in recent time because modern society utilized so many petroleum-based products for example, fuel oil, kerosene, gasoline and asphalt (Medeiros *et al.*, 2005; Frena *et al.*, 2017). Petroleum is a complex of various organic compounds that were made during different ages of geology under conditions which were created with physical and chemical properties (Stogiannidis and Laan ,2015).

According to Boyd *et al* (2001) the crude oil components are divided into three main groups:

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1- lightweight molecular components which contain 1 to 10 carbon atoms, and have boiling points of more than 150 oC Examples: Benzene, Toluene, Ethyl-benzene, Xylene and Alkanes.

2- Medium molecular weight components which consist of Hydrocarbons with carbon atoms ranging from 11 to 22 and boiling grades from 150 to 400o C that include two-ring aromatic hydrocarbons.

3-Heavy molecular weight components which include more than 22 carbon atoms. Most of their components are wax, asphalt, polycarbonate compounds and polycyclic aromatic hydrocarbons (PAHs) such as anthracene and phenanthrene .

Depending on the difference in solubility in organic solvents, Crude oil composition compounds can be divided into four main groups(Zhu *et al*, 2001):

1-Saturated hydrocarbon: including normal and branched alkanes in aliphatic formula (C_nH_{2n+2}), and cyclic alkane in the alicyclic formula (C_nH_{2n}) .The saturated hydrocarbons constitute the largest proportion of crude oil. N-Alkane is a type of saturated hydrocarbons which includes odd and even carbon numbers which are up to 64 carbons with no alkyl branch. The " Odd "carbon numbers are generated basically from the natural origin , whereas "Even" carbon numbers come from the Anthropogenic origin (Fagbote and Olanipekun , 2013;Al-Hejuje,2014).

Great variety of hydrocarbon compounds are created by organisms . A Planktonic algal alkanes are dominated by odd n-alkanes in the low molecular weight (n-C15 and n-C17) (Gelpi *et al.*, 1970; Blumer *et al.*, 1971). Higher terrestrial plant waxes have longer chains (C23-C33) of n-alkanes with robust odd/even carbon preference (Eglinton and Hamilton, 1963). Microorganisms like bacteria contain n-alkanes ranging from C15 - C31 with slight odd/even carbon preference (Han and Calvin, 1969).

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N-Alkanes are usually utilized to characterize organic matter from different environments because of their origin specificity. Long chain n-alkanes with an odd numbers of carbons (C₂₇-C₃₅) are the main components of epicuticular waxes of advanced plants, whereas aquatic algae are dominated by shorter chain n-alkanes with an odd number of carbons (predominantly C₁₅, C₁₇ and C₁₉)(Al-Bedhani,2014).

2 -Aromatic Hydrocarbon are extensive pollutants that are present in the aquatic ecosystem and they also have been utilized to evaluate oil or pyrogenic pollution in sediments. (Abreu-Mota *et al.*, 2014).They consist of monocyclic Aromatic compounds such as benzene, tulene, Xylene and polycyclic aromatic hydrocarbons(PAHs),and are also known as POM (Polycyclic Organig Matter), such as naphthalene, anthracene, benzo(a)peyren and phenanthrene, which have two or more fused aromatic rings (ATSDR,2012) . These compounds have specific environmental attention because they are potentially carcinogenic compounds or may convert carcinogens by microbial metabolism (Al-Saad , 1995). Therefore, they have been listed in the United States Environmental Protection Agency (US -EPA) priority contaminants list.(Readman *et al.*,2002).

Polycyclic aromatic hydrocarbons(PAHs)have two or more fused aromatic rings with two carbon atoms joint between rings in their molecules. PAHs having two or three fused rings are often known as ‘light’ PAHs, while those having four or more fused rings are called ‘heavy’ PAHs(Yang *et al.*,2014;Ahmed *et al.*,2015).

Generally, PAHs arrive the environment through numerous ways and are usually found as a mixture containing two or more of these compounds, e.g. soot . Some PAHs are synthetic in the industry (CCME,2010). The persistence of PAH in the ecosystem is mainly because of their low water solubility (Freeman and Cattell, 1990). Their solubility

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decreases and their hydrophobicity increases with increase in the number of fused benzene rings (Chaillan *et al.*, 2004).

Sixteen PAHs compounds were put in the list of precedence environmental pollutants by the United States Environmental Protection Agency (US-EPA). They were: Naphthalene (C₁₀H₈), Phenanthrene (C₁₄H₁₀), Anthracene (C₁₄H₁₀), Fluoranthene (C₁₆H₁₀), Pyrene (C₁₆H₁₀), Chrysene (C₁₈H₁₂), Benzo (a)anthracene (C₁₈H₁₂), Benzo (b)fluoranthene (C₂₀H₁₂), Benzo (k)fluoranthene (C₂₀H₁₂), Benzo (e)pyrene (C₂₀H₁₂), Benzo (a)pyrene (C₂₀H₁₂), Perylene (C₂₀H₁₂), Benzo (ghi)perylene (C₂₂H₁₂), Dibenzo (ah) anthracene (C₂₂H₁₄), Indeno (cd)pyrene (C₂₂H₁₂) and Coronene (C₂₄H₁₂) (Anatoly, 2008).

3-Resins (polar compounds) which are known are NSO compounds because they have nitrogen, sulfur and oxygen (e.g., pyridines and thiophenes).

4-Asphaltenes. These consist of compounds with high molecular weights that are complex and have weak hydrocarbon properties which have heavy elements like Ni, Co, V, Fe and NSO compounds.

Sources of Hydrocarbons pollution

Industrial activities, navigation traffic, the spillages, accidents and the transport of oil and its derivatives, export ports, washing of loading docks and pumping of water in the budget play important role in the pollution of the aquatic ecosystem with oil compounds (N.R.C, 2003; Anisuddin *et al.*, 2005).

Other source of pollution of hydrocarbons are household, agricultural and industrial waste discharges and uncontrolled releases from power plants, (Ajibola *et al.*, 2005; Frena *et al.*, 2017). Air emissions also add significant amounts of hydrocarbons due to fuel combustion, vehicle exhaust emissions, factory stoves, , cooking coves, and utilization of asphalt in road paving (Aceves and Grimalt, 1993; Gogou *et al.*, 1994; Dhale *et al.*, 2003).

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The other source of hydrocarbons is biogenic during the decomposition process of organisms having biogenic hydrocarbons or natural seepage (Al-Saad, 1995) .

Petroleum Hydrocarbons compounds are commonly conveyed into the aquatic environment in the form of solutions either as tempest waters, domestic wastes ,urban runoffs, or industrial discharges, but only a little portion of the load ultimately remains in solution. Instead, they are scavenged from the water column to the bottom sediments through flocculation and sedimentation, giving increase to concentrations in the sediment greater in amount than in the water column(Olver,2008). In aquatic ecosystem, hydrocarbons tend to connect with particulate organic matter because of their hydrophobic nature, then they are deposited in the underlying sediments,(Qiu *et al.*,2009) which are known as excellent sinks for such pollutants.(Commendatore *et al.*,2012). Therefore the sediment act as an important sink for the oil hydrocarbon compounds and other organic contaminants, and its pollution could signify a very great health hazard for several aquatic biota that exist in the aquatic ecosystems (Ali *et al.*, 2015).

PAHs may reach aquatic ecosystem from industrial effluents, domestic sewage and exhaust of fuel and diesel burning motors, surface run off from land, deposition of particulates airborne, and especially from oil products and spillage of oil into water bodies (Al-Hejuje,2014 and Al-Bedhani,2014).

The different components of oil vary in their toxicity to organisms. The most hazardous and toxic compounds are aromatic compounds with low molecular weights like benzene, toluene and zeolins because of their solubility in water (Boelsterli, 2000), PAHs are toxic and dangerous in the long term and a large proportion of them are carcinogenic (Zhu *et al.*, 2001) such as Benzo (a) Pyrene, Anthracene, Florenthene, Benzo (a) Anthracene, Chrycene, Benzo (bck) Flouranthene, Dibenzo (ah) anthracene), followed by

cycloalkane compounds in terms of toxicity, olefins and then normal alkanes (Landis, 2003).

To determine the concentrations of contaminants in a region, the study should rather identify concentrations in water, sediments and chose organisms as bioindicator. Therefore such a study could give a complete picture of the environmental situation(Singh *et al.*,2017).

1.1.3 Aquatic Plants

Aquatic plants are one of the characteristics of the marshes which have been known by their multiple functions. They are of direct importance as food for different organisms like humans, animals and fish. Also they play role in industry, economy and tourism,(Brix,1997; Patel and Kanugo,2010). They also play an important role in cleaning the environment and protecting the health of water through utilizing plants in environmental sound technologies by their great vegetation cover and high productivity. Thus many countries have resorted to using these low-cost plants to address many environmental problems by establishing artificial wetlands and cultivating them with different kinds of aquatic plants that are good in improving the ecosystem (UNEP,2001).

Types of Macrophytes in marshes

Aquatic plants of wetlands can be divided according to habitat and vegetative sites from the water surface into three major types(Al-Mayah *et al.*,2016) :

1-Emergent Plants

The green parts of this type are appear above the water's surface ,whereas the roots are submerged in the substrate (Haberl *et al.*, 2003). with the ability to support themselves without substrate except in the early stages of growth like *Typha domingensis* (common cattail) and *Phragmites australis* (common reed).

2-Floating Plants

Its vegetative members have the ability to float as a thin layer on the upper surface of water in the wetland, and there are two kinds: floating as fixed such as *Namphaea alba* and *Nymphoides spp*, or floating as free like *Salvinia natans* and *Lemna minor*.

3- Submergent plants

These plants have the ability to grow below the surface of the water in the photic zone, and have two types: either fixed in the bottom by the roots like *Vallisneria spiralis*, or are not anchored in the bottom because they do not have roots like *Ceratophyllum demersum* and *Najas spp*.

The distribution and behavior of aquatic plants in marshes are influenced by some environmental factors such as pH, temperature, and water level depend on the profusion of oxygen seasonally floods and restoration, which are the main factors for primary productivity and phytoplankton growth that represents the base of the pyramid in the food chain. (Wetzel, 2001 and Ajmi *et al*., 2017).

According to the diversity of aquatic plants, its wide spread and good tolerance to the fluctuating in the environmental conditions, various kinds of plant families have been utilized as bioindicator to study water contamination (Benabid, *et al.*, 2008).

Aquatic plants have been often used to evaluate wetland pollution all over the world and well documented to be indicator of contamination [Zayed *et al.*, 1998; Zhu *et al.*, 1999; Kamal *et al.*, 2004; Souza *et al.*, 2013].

Aquatic plants that use as biological response to assess the variations in the environment are called Biomonitoring. Generally, biomonitoring programs can be divided into qualitative, quantitative and semi-quantitative (Chaphekar, 1995). Biomonitoring of contaminants using certain of plants to accumulate large amount of various pollutants without apparent dangerous effects. Biomonitoring can be achieved into two ways based on kinds

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samples, organism widespread native and passive-active biomonitoring (Lewis,1995) . It has a significant role in the functioning of ecosystems (Hellawell,1986). Nevertheless, any change in economic and ecological effects would threaten this ecosystem (Davidson *et al*,2006; Ajmi *et al* .,2017) .

Aquatic plants may accumulate considerable amounts of contaminants in their tissues. They absorb most of these chemicals through root and shoot structures due to their fast growth and great biomass (Bonanno and Lo Giudice, 2010; Matache *et al.*, 2013). Consequently, aquatic plants are so proposed as pollution-monitoring organisms (Shine *et al.*,1998).

Plants that have ability to take up pollutants that exceed the established background concentrations and greater than other species from the same soils or water bodies are known as hyperaccumulators. (McGeer *et al.*,2003). There are many populations found in soils or water that rich in pollutants, this either due to geochemical factors or because of pollution (Prasad , 1997; Brooks and Herman, 1998; Benabid, 2008).

Plants can be divided as accumulators, indicators or excluders depending on absorption and translocation of the contaminants by the plants above-ground level. Accumulators can continue to be accumulate concentration of pollutants in their tissues. Indicator plants are described as plants which have mechanisms to control translocation of contaminants from roots to shoots ,while excluders plant can control the pass of pollutants into plants root. (Baker, 1981 ; Chaudhry *et al.*, 1998; Malik *et al*,2017).

In general, suitable bioindicators have the ability to:

- 1-Accumulate certain or selected elements.
- 2-Toxic-tolerance with no sensitivity to the accumulating pollutants/material.
- 3-Existent in large amounts in the ecosystem under study.
- 4-Wide distribution in various environments, and wide geological condition.

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5-Easy to recognize and sample.

6-No seasonal changes in availability and applicability.

7-Presence of a relationship between accumulation and input to the ecosystem.

Plants utilize various adaptive mechanisms to accumulate or exclude pollutants and in this manner keep up their growth. Accumulation and tolerance of pollutants by the plants is an intricate phenomenon (Murtaza, 2010). The movement of pollutants across the root layer, loading and translocation of these compounds through xylem and sequestration and detoxification of them at the cellular and whole plant levels are vital mechanisms adopted by accumulator plants (Lombi *et al.*, 2002).

Understanding the mechanisms involved in phytoremediation is essential to effectively utilize this technique on environments. Plants have the normal ability to deal with pollutants by means of processes for example bioaccumulation and translocation. A technique which uses plants for the uptake of pollutants from sediments and water or absorb the pollutants is mentioned as phytoremediation (Greipsson, 2011).

Phytoremediation that uses the momentous ability of plants to concentrate elements and other compounds from the environment and to metabolize different molecules in their tissues appears very promising for the elimination of pollutants from the environment (Gurbisu and Alkorta, 2003).

Diverse methods have been presented to exploit the capability of aquatic plants for the elimination of dangerous compounds from polluted aquatic environments. Schwitzkebel (2000) clarified variety of technological subsets of phytoremediation.

1-Phytoextraction: also called a phytoabsorption or phytoaccumulation, the pollutants are being up absorb by the plant roots from the polluted water and sediments and then they are being accumulated in the biomass above the ground as in shoots (Rafati *et al.*, 2011). While, the transmission of

pollutants into the shoots is not easy method, it is chiefly required for the effective phytoextraction, due to compounds store in roots then it will be an unfeasible process to deal with the biomass, (Tangahu *et al.*, 2011).

2-Phytostabilization: the pollutants, in this type of technique are immobilized in the soil by utilizing distinctive plants that having capability to steady the contaminants (Singh, 2012). In this process, the mobility of the pollutants will be reduced which lead to the decrease of bioavailability of these pollutants. This help in reducing the movement of pollutants into the groundwater and prevent their ability to arrive into the food web (Erakhrumen, 2007). In this technique, the elements are immobilized by their sorption into the roots, reducing their valence number and afterward making them complex and immobilize in rhizosphere (Ghosh , 2010).

3- Phytotransformation: the process in which the complex organic molecules are altered into the simpler one by degrading them and the simpler one would be united in the tissues of plants (Schwitzquebel , 2000) .

4-Phytovolatilization: in this method plants absorb the contaminants from the sediments, changed into the volatile form and then extract to the atmosphere. Phytovolatilization can be utilized for organic pollutants and other heavy elements such as Se and Hg. But as explained earlier, it transmits the contaminants into the atmosphere, from one medium to another, and does not remove the pollutants forever (Schwitzquebel ,2000) .

5- Phytodegradation: In this mechanism , the enzymes utilized for degrade the dangerous organic contaminants . And this technique can occur inside or outside the plants as the plants can also release the enzymes outside.

6-Rhizo/Phytofiltration: Phytofiltration is utilized to prevent mixing the organic contaminants in surface waste water with the water streams or groundwater by using aquatic plants for filtration purpose as they can adsorb or absorb the contaminants (Khan *et al.*, 2007).

7- Phytostimulation: Which consist of the stimulus of enzymes existent in the rhizosphere which can lead to the bioremediation processes using different microorganisms degradation by secreting exudates.

Certain aquatic plants have the potential to eliminate or reduce pollution levels through metabolic processes carried out by the plant and lead to the removal or analysis of different contaminates(Al- Sanjari , 2011).

1.1.4 Heavy elements in aquatic plants.

Several studies have developed on the risk of water pollution and the use of bio-indicator of pollution as more environment friendly and less expensive. The focus on different plant species, especially aquatic plants for their role in the accumulation of pollutants or degraded and converted to a less toxic or non-toxic (Vymazal *et al.*, 2007). Plants were classified into three categories according to their ability to absorb, accumulate and tolerant heavy elements in their tissues (Chosh and Singh, 2004) :

1-Hyperaccumulators:

Plants that tolerant the maximum level of heavy elements.

2-Indicators: Plants that regulate the absorption of heavy elements so that the internal concentration reflects the external level.

3-Excluders: plants that maintain a constant and low concentration of heavy elements in their tissues

The use of macrophyte as biological indicator in monitoring the heavy elements has some advantages as they tolerate high concentrations of the heavy elements in surrounding environment, their samplings are easy, and individuals are big (Zhou *et al.* 2008).

The plants provide good evidence of water pollution with heavy elements because of their ability to accumulate in their tissues more than in the surrounding environment (Coleman *et al.*, 2001), their rapid growth ,adaptation to live in different environments and simple requirements (Dirilgen, 2001).

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Aquatic plants uptake heavy elements from both water and sediment in the case of deep submersible plants and this will in some way reflect the contamination of water and sediment. Marseille *et al.* (2000) notice that plants growing in a polluted environment contain a greater concentration than those growing in a clean environment.

Aquatic plants can accumulate elements through their roots, stems, and leaves. Various species show different abilities for metal uptake, and the utilization of these species for bioremediation has numerous economic and ecological benefits, including low cost, high efficiency, energy savings, and prevention of secondary pollution (Vaiopoulou and Gikas, 2012). Plants that can uptake and store heavy elements can be used to eliminate or remove those pollutants from an aquatic environment.

The mechanisms of plant tolerance to the higher levels of the elements may be related to the peptides containing the thiol group SH- these are called Phytochelatins (Cobbett, 2000) or through Metallothioneins, which are proteins in the plant cell that play an important role in the removal of toxicity by binding to the elements in cell (Rausser, 1999).

1.1.5- Hydrocarbons in aquatic plants :

When hydrocarbons enter the plant bodies, they transfer from the roots through the intercellular spaces by the vascular system. The presence of hydrocarbons in plant tissue destroys the cell membrane, destroys vascular or green plastids. This process depends on the amount of hydrocarbons, physical conditions and plant species. Al-Saad (1994) confirmed that plants are capable of removing hydrocarbons from the aquatic environment. The environment of the southern marshes is expected to be uncontaminated environment because of the susceptibility of plant species to the removal of these pollutants from the environment. The accumulation of hydrocarbons within plant bodies depends on several physical factors, including

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temperature, dissolved oxygen levels, nutrient concentrations, pH, salinity. The concentrations of hydrocarbons within the bodies of plants depend on the amount of fat as there is a correlation between the amount of fat and the concentration of hydrocarbons in plant tissues (Nasir, 2007).

Many organisms are capable of assembling hydrocarbons in their bodies at high concentrations (Ackman *et al.*, 1996). Aquatic plants play an important role in the treatment of environmental pollution with hydrocarbons through its ability to accumulate these compounds.

Most aquatic organisms produce their own hydrocarbon compounds or get them during feeding and accumulate these compounds in their tissues during bioaccumulation process. The amount of these compounds from the natural or biogenic source is low in the aquatic environment and its production is within narrow limits (Cajneravelli *et al.*, 1995). The existence of high-chain carbon compounds (C₂₅-C₃₀) indicates the presence of plants in order to concentrate these compounds in the wax layer which covering the leaves of plants (Eglinton and Hamilton, 1963; AL-Saad, 1994).

plants can uptake PAHs compounds from sediment through their roots and translocate them to other parts of plant. Uptake rates are generally governed by concentration, water solubility, physicochemical state and soil type. Some plants contain substances which was used to protect plants against PAHs compounds effects. Other plants can synthesize PAHs that act as growth hormones (Yin Zhong *et al.*, 2011).

The technique can be used plants for the removal of environmental pollutants such as organic pollutants that includes polychlorinated biphenyls (PCBs), poly aromatic hydrocarbons (PAHs) and pesticides is refer to as phytoremediation (Greipsson, 2011), which method is novel, cost effective and ecofriendly (Vithanage *et al.*, 2012).

1.1.6- Aims of the present study:

The aims of the current study is to :

1. Detect the temporal and spatial variations of some environmental parameters (chemical and physical) of water and sediments at Al-Chibayish marshes .
2. Determine the concentrations , sources and speciation distribution of both heavy elements and hydrocarbons in water and sediments of Al-Chibayish marshes.
3. Apply some water pollution indices to assess the water pollution status at Al-Chibayish marshes.
4. Detect if there is biogenic or anthropogenic sources that cause the deterioration of the quality of water and the environmental factors .
5. Determine the ability of some aquatic plant to accumulate heavy elements and hydrocarbons compounds in their tissues and the possibility of using them as bio-indicators .

1.2- Literatures Review :

Many studies were conducted to estimate the pollutants concentration such as heavy elements and petroleum hydrocarbons in waters, sediments and aquatic plant as bio-indicators in Shatt Al-Arab , Tigris and The Euphrates rivers, but few studies were conducted with the Iraqi marshes .These studies including:

1.2.1- Literatures concern with hydrocarbons :

Al-Saad, (1994) detected the distribution and level of hydrocarbons in some of aquatic plants collected from Hor Al-Hammar and the result of these study showed the concentrations of total hydrocarbons ranged between 0.06 µg/g in *Potamogeton pterifolius* to 0.59 µg/g dry weight in *Namphoides indica*.

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Al-Saad and Al-Timari(1994) referred the nature of n-alkanes in the sediments of the marshes which are from anthropogenic and biogenic resources.

Al-Saad *et al.*(1996) stated that the sources of normal paraffin in aquatic plants of Hor Al-Hammar and mentioned that these plants contained n-alkanes ranging from C14 to C23 ,in addition to isoprenoid and high Carbon Preference index (CPI) values which indicate biogenic sources of these compounds.

Al-Timari *et al.*(1997) explained that the source of the n- alkanes in the sediments core from two stations in the Hor Al-Hammar marshes is a common source of Biogenic(phytoplankton, Diatoms, plants) and as well as Anthropogenic source.

Al-Khatib , (1998), mentioned the distribution of total hydrocarbons and n- alkanes compounds and their sources in sediment cores from Shatt Al-Arab Estuary and North-West Arabian Gulf and the mainly sources of hydrocarbons compounds in Shatt Al-Arab river are biogenic and anthropogenic sources.

A study of Al-Saad and Al-Adhub(2005) dealt with the environmental pollution of heavy elements, total hydrocarbons and source of hydrocarbons and fatty acids in Al-Hammar marsh indicating the relationship between hydrocarbons and the percentage of fat, and the presence of two kinds of biological and oil pollution.

Rushdi *et al.* .(2006)reported the sources and composition of extractable organic matter in mesopotamian marshland surface sediments, and found that n-alkane values ranged from 4.1 to 31.1 µg/g d.w , and their sources were anthropogenic and biogenic.

Al-Imarah *et al.* (2006a) studied the seasonal variations of the total hydrocarbons content in the water and sediments of the southern Iraq marshes after rehabilitation. Water samples and sediments were collected from several

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stations along the southern marshes, Stations were selected from Hor al-Hawayzah, central marshes and Al-Hammar marsh.

Al- Khafaji ,(2007) estimated the concentration and distribution of petroleum hydrocarbons (TPHs) in water ,sediment and two emerged aquatic plants (*Phragmites australis*) and (*Typha domengensis*)in three selected stations in the Euphrates river near Al-Nassiriya city .And found *p. australis* recorded higher concentration of TPHs than *T. domingensis*.

Al-Khatib(2008) study the concentrations, origin, distribution and type of hydrocarbons in water ,sediments and some aquatic biota of Hor Al-Hawaiza, southern Iraq. The result showed the concentration of hydrocarbon compounds which recorded in this study for water, sediment, and biota are within the range for unpolluted area in the world.

Talal (2008) study the seasonal and regional variations of hydrocarbon levels and n-alkanes in water, sediments and three species of aquatic plants (as bioindicators) in Hor Al-Hammar ,and also mentioned that the origins of n-alkanes in water ,sediments and aquatic plants were biogenic according to CPI and UCM values.

Al-Saad *et al*(2009) study the levels of petroleum hydrocarbons and trace elements in the water and sediment samples from different locations in the marshland of southern Iraq, showed the concentrations of these pollutants could be due to natural and anthropogenic sources. These concentrations are within the range values reported for other comparable regions.

Talal *et al* (2010) explained the seasonal and regional variation of hydrocarbon concentrations and origin of the normal alkanes samples from southern Iraq marsh sediments, founds a regional and seasonal variations in the values of TPHs ,whereas Carbon Preference Index (CPI) values and Pristan to Phytan indicate the biogenic sources of n-alkanes in sediments.

Al-Taie (2013) study the concentrations and origin of hydrocarbons and determine the values and the coefficients of Heavy elements to the sediments

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of casement in Hor AL-Azim reality within Hwaiza Marshes in two area Azim1 and Azim 2. The results of this study showed the origin of n-alkanes was biogenic and anthropogenic, also origin of the aromatic compounds were pyrogenic and petrogenic. Also identified coefficient assembly geochemical heavy elements, and found the sediments in this region were unpolluted environments to few polluted with heavy elements (lead, copper, Chrome), except nickel, which showed in some depth ratios of pollution beyond critical limits. The results also showed grain size analysis of sediments of the region as silty clay with small amounts of sand.

Al-Hejuje, (2014) explained that the source of n-alkanes hydrocarbons in the water and sediments of Shatt Al-Arab river is mainly pyrogenic, biogenic and at least petrogenic. Whereas, the PAHs compounds source in the water of Shatt Al-Arab river is mainly petrogenic and pyrogenic, while it is pyrogenic only in the sediment.

Al-Ali *et al*, (2016) determination the Total Petroleum Hydrocarbons (TPH) concentration in soil, water and tomato plant *Lycopersicon esculentum* L. at (root, stem, and leaf) in four stations Safwan, Shuaiba, Abu Al-kasibe and Garma Ali at Basra city. The result of this study show that higher concentrations of (TPH) in the soil and water of Safwan than other stations and also show the higher concentration was found in tomato root of Safwan station compare to other stations and this level was highest than other parts of plant in the same station and other stations.

Hassan *et al*, (2016) study the concentrations of PAHs compounds in some aquatic macrophytes in Hilla river. The results of this study illustrate that the PAHs concentration in macrophytes different among their species.

1.2.2- Literatures concern with heavy elements:

Abaychi (1995) determined the concentrations of some heavy elements in sediment sample of Al-Hamar marshes.

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Al-Tae (1999) referred that the aquatic plant have ability to accumulate the trace element ,and founded the concentration of these compounds in the plants tissue was higher than in the water and sediment of shatt Al-Hilla River .

Al-Saffi, (2005) found that the relationship between seasonal changes of several heavy elements with the seasonal changes of the discharge of the Shatt Al-Arab River water and the quality and quantity of Phytoplankton.

Azize *et al* (2006) studied the contamination of water, sediments, and tow spices of plants (*Typha domingensis* and *Phragmites australis*)in Shatt al-Basrah Canal, and found the concentration of heavy elements was higher in sediments than in water, and the area was contaminated with different levels of copper, lead and zinc.

Awad and Abdulsahib (2007) studied the level of mercury in the sediments and waters of the Shatt al-Basra and found it is higher than the concentrations in the sediments and water of the Al-Amarah and Al-Basrah marshes and are less in concentrations of many aquatic plants studied in the same area.

Jassim (2008) explain the efficiency of some aquatic plants to improve water quality in some localities of Basrah city and three selected southern marshes. Trial of aquatic plants of free surfaces system was also conducted, and used some species of aquatics plants in experiment, and measured several ecological factors to detect role of aquatic plant.

Mahmood(2008) study some chemical and physical properties, as well as nutrients (nitrogen and phosphorus), total organic carbon and trace elements in waters and sediments from 8 sites in southern Iraq. Five of which covered an area from Al-Qurnah to Ras Al-Beesha with 3 sites in Al-Huwayzah, Central marsh and Al-Hammar marsh.

Awad *et al* (2008) study concentrations of trace elements in aquatic plants and sediments of the southern marshes of Iraq (Al-Hawizah and Al-Hammar),the results showed higher concentration of trace elements in sediment than in plants. Generally , the levels of the studied elements in

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plants and sediments were lower than the other as with compared areas of the world.

Al-Kenzawi and Al-Rawi(2009) determine the role of emergent aquatic plants in changing the water quality at Al-Shafi marsh, southern Iraq, selected three dominant emergent aquatic macrophytes which were *Phragmites australis*, *Typha domengensis* and *Schoinoplectus litoralis* , measured water environmental variables in(pre the marsh, in the marsh(distributed emergent macrophytes), and post the marsh] . This study concluded that emergent aquatic plants play important role in changing some of water characteristics.

Al-Yaseri (2011) determination the concentrations of trace elements (Cd , Pb , Mn ,Zn ,Cu , Ni and Fe) in sediment of the southern part of Al- Hammar marsh, and found that the sediment polluted with heavy elements due to different sources such as urban wastes , industrial effluents , land washout and boats activities .

Mashkhool (2012) estimated the concentration of heavy metal Zn ,Cu ,Pb, Ni and Cd in the water (dissolved and particulate phase) ,sediments and two species of plant (*Phragmites austrialis* and *Typha demersum*) from two stations within Al-Chibayish marsh during the summer and winter seasons .This study concluded the accumulation pattern of heavy metal was greatest in the particulate phase followed by the sediments then plant and the lowest as dissolved phase .

Al-Maarofi *et al.*,(2013) study desiccation versus re-flooding, heavy elements distribution and seasonal variation in marshes of the Mesopotamia, southern Iraq. The result shows significant differences between the re-flooded marshes versus the reference marsh, which indicates that desiccation caused changes in environmental variables ,. In addition, the special distribution of heavy elements shows that Al-Hammar and Al-Hawizeh marshlands were efficient for elements concentration reduction,

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especially for Ni, while the Central marshland has the major contribution as source to elements.

Al-Awady *et al.*, (2015) measured the concentration of some trace elements in water (dissolved and particulate) phase, sediment and accumulation in two species of aquatic plants *Phragmites australis* and *Ceratophyllum demersum* in Euphrates river near the center of Al-Nassiriyah city, and observed particulate phase of water concentrated trace elements more than their concentration as dissolved phase, while higher concentration of elements were sediment more than their concentrations in water and plants. And the accumulation of trace elements in plants, and showed that their concentration in *Ceratophyllum demersum* was more than their concentration in *Phragmites australis*.

Al-Khafaji (2015) estimated the concentrations of heavy elements Zinc, Lead, Copper, Cadmium and Nickel in water (dissolved and particulate phases), sediments and in two species of plants (*Typha domingensis* and *Vallisneria spirallis*) from two stations in Al-Chibayish marsh in Thi-Qar province, southern Iraq. The results indicated that the mean concentration of heavy elements was greatest in the particulate phase followed by the sediment and plants respectively. Higher concentration of the studied heavy elements were observed in *Typha domingensis* more than their concentration in *Vallisneria spirallis*.

Habeeb *et al.*, (2015) detected the physical and chemical properties in eastern the Euphrates drainage from the Abo-Garak, Babylon province, also study some heavy metal (Fe, Cd, Pb) in water, sediments and two species of aquatic plants *Ceratophyllum demersum* and *Hydrilla verticillata*. Higher concentration of the studied heavy elements were observed in *Ceratophyllum demersum* more than their concentration in *Hydrilla verticillata*.

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Ewaid (2016) evaluated the water quality of Al-Gharraf river, the largest branch of Tigris river south of Iraq by the heavy metal pollution index (HPI) depending on 13 chemical, physical, and biological parameters of water quality measured monthly and showed the HPI value was 98.6 slightly below the critical value for drinking water of 100, and the water quality in the upstream stations is better than downstream due to increase the accumulation of pollutants along the river.

Al-Sabah and Aldhahi, (2017) used some mathematical models for assessment water and sediment quality of Auda marsh, southern Iraq ,and found the values of Geoaccumulation index (I-geo) for metals (Fe,Pb,Zn and Cu) varied from -3.42 to -1.44,these indicated that all stations are unpolluted with heavy elements situation (Igeo <0).

Al-Maliky (2018) use the constructed wetland systems for treating wastewater. These systems were planted with *Phragmites australis*, *Typha domingensis* and *Ceratophyllum demersum* respectively. And were measured some chemical, physical and biological parameters to assess the ability of aquatic plants to treat wastewater the results indicated that the system was highly effective in the removing of target pollutant.

Chapter Two

Materials & Methods

2.1- Description of the study area:

Central marshes (Al- Chibayish) are bordered to the north by the Amara road, Tigris river to the east, the Gharaf river to the west and the Chibayish road adjacent to the Euphrates river in the south. Hor al- Chibayish is located north of the Euphrates and in the middle of the central marshes. Before the drying, it was supplied with water from Tigris river but after the rehabilitation in 2003, it became supplied from the Euphrates River (IMOS,2006; UNEP,2002,; Hussain,2014).

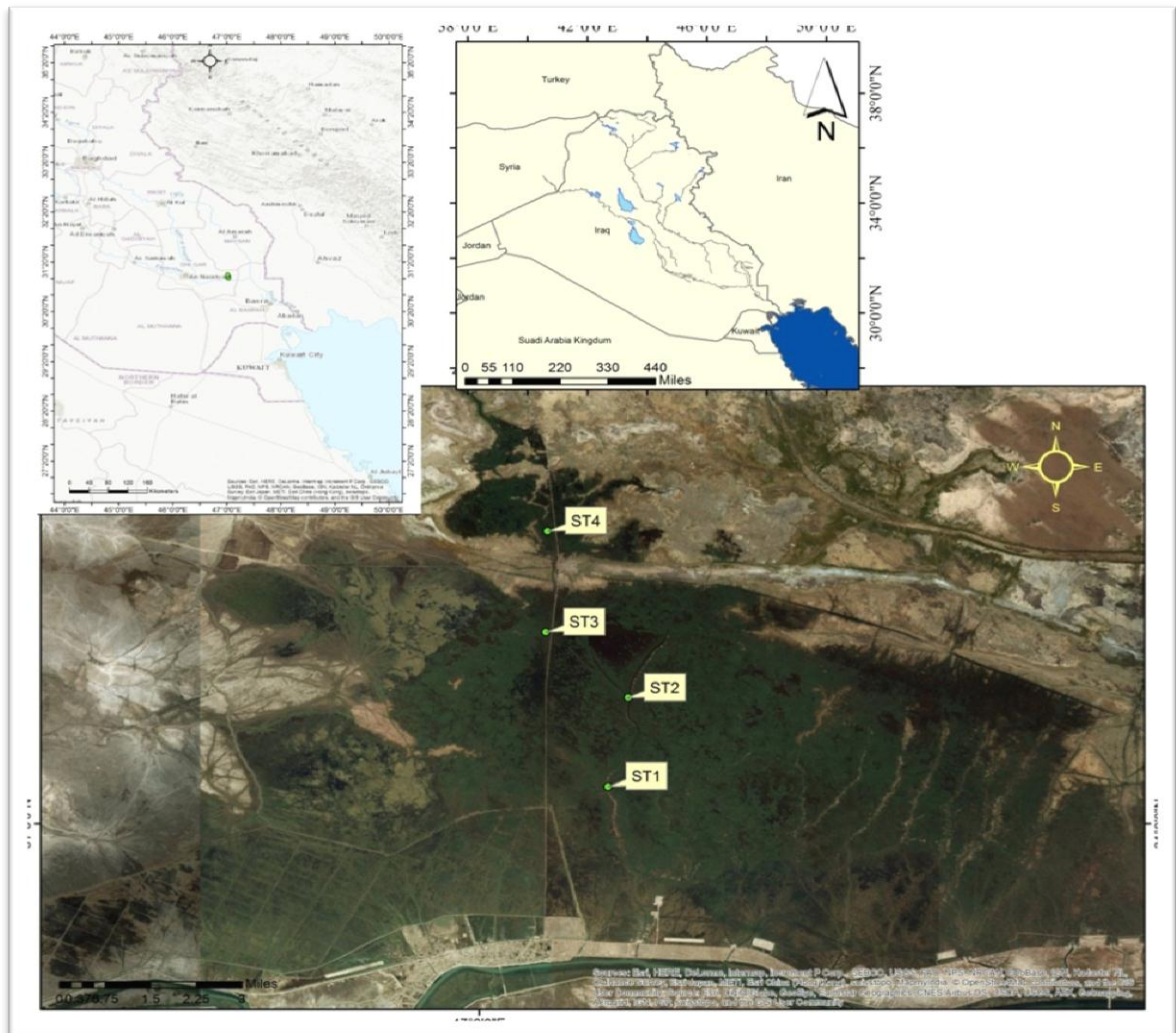


Fig (1) map of the study stations

2.1.1 Sampling sites

The samples were collected from four stations as follows:

Abu Subat (station 1) (N:31° 00' 34.7" E: 47° 01' 50.3")

This station is located at the beginning of the study area and is characterized by the presence of aquatic plant *Typha domingensis*, *Phragmites australis*, *Ceratophyllum demersum* and a little of the *Schoenoplectus litoralis*. The area is also characterized by the presence of birds, especially the Pied King fisher species(*Ceryle rudis*) and a few numbers of the White egret birds (*Egretta garzetta*). This station is uninhabited by human.



Picture(1): station one at Al- Chibayish marsh (Al-Atbee,2018)

Baghdadiya 1 (Station 2) N:31° 01' 57.5", E: 47° 02' 7.7"

It is the station that follows the Abu Subat station .The distance between first station and this station about 2.850 Km has a lot of aquatic plants Table (1) likes *Typha domingensis* and *Phragmites australis* and the plant species *Najas* spp is very dense and it is one of the free submerged plants therefore this area was characterized that its water was very low turbidity. It is uninhabited by human.



Picture(2): station two at Al- Chibayish marsh (Al-Atbee,2018)

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Baghdadiya 2 (Station 3) N:31° 02' 58.4" E: 47° 00' 57"

This area is populated and has many human activities such as fishing and there was a density of aquatic plants (Table 1), ducks and birds and there are many buffaloes, and this area is a way to pass boats. This station is about 2.725km from the second station.



Picture(3): station three at Al- Chibayish marsh (Al-Atbee,2018)

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AL-Hamara (station 4) N:31° 04' 32.4" E: 47° 00' 58.5"

The distance between the third station and this station is about 3.32Km . This station has a large number of inhabited houses and characterized by the presence of birds and practice the breeding of buffaloes and abundant aquatic plants of all kinds and also characterized by the shallow water in it .



Picture(4): station four at Al- Chibayish marsh (Atbee,2018)

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Table(1) :Appearance of plants species that found in study stations

Species	Stations	Summer	Autumn	Winter	Spring
<i>Phragmites australis</i>	St.1	+++	+++	++	+++
	St.2	+ ++	+++	++	+++
	St.3	++	+++	++	+++
	St.4	++	+++	++	+++
<i>Typha domingensis</i>	St.1	+++	+++	+++	+++
	St.2	+++	+++	+++	+++
	St.3	+++	+++	+++	+++
	St.4	+++	+++	+++	+++
<i>Schoenoplectuslitoralis</i>	St.1	+++	+++	+++	+
	St.2	-	-	-	-
	St.3	+++	+++	+++	++
	St.4	+++	+++	+++	++
<i>Ceratophyllum demersum</i>	St.1	+++	+++	++	++
	St.2	-	-	-	-
	St.3	++	+++	++	-
	St.4	+++	+++	+	+++
<i>Potamogeton pectinatus</i>	St.1	-	-	-	-
	St.2	-	-	-	-
	St.3	++	-	-	-
	St.4	-	-	-	-
<i>Potamogeton perfoliatus</i>	St.1	+ +	++	-	+ +
	St.2	-	-	-	-
	St.3	-	-	-	+ +
	St.4	-	-	-	+ +
<i>Najas spp</i>	St.1	-	-	-	-
	St.2	+++	+++	+++	+++
	St.3	++	++	++	-
	St.4	--	-	-	-
<i>Potamogeton crispus</i>	St.1	-	-	-	+ +
	St.2	-	-	-	
	St.3	-	-	-	
	St.4	-	-	-	

+++ : dominant ; ++ : moderate ; - : not found

2.2- Field work and measurements:

Field work and measurements were done seasonally from Augst, 2017 to April, 2018, at four stations at Central marshes of Iraq (Al- Ghibayish marsh).

2.2.1- Air temperature (AT:°C): was measured using graduated(0-100°C) simple thermometer.

2.2.2- Water temperature (WT:°C), salinity (Sal: PSU), Potential of hydrogen ions (pH) and Electrical Conductivity (EC: ms/cm):

were measured in situ using Multimeter type (Multi 350 i SET 5).

2.2.3-Water turbidity (Turb.:NTU) :was measured in the field using turbidity meter type (TURB 355 IR WTW).

2.2.4-Dissolved Oxygen (DO) and Biological Oxygen Demand (BOD₅) :

Winkler bottles (transparence) 300 ml were filled with the water to detect the dissolved oxygen level ,the oxygen level was fixed at each bottle in the field by adding 2 ml manganese sulfate solution, 2 ml alkaline iodide azid solution ,and 2 ml concentrated sulfuric acid. Another Winkler bottles (dark) were filled with the water sample to detect the BOD₅ values, which were left without fixation and stored in ice box until reaching the laboratory.

2.2.5- water samples:

Water samples were collected from the each stations at least 20 -30 cm under the water surface ,at the middle of the station. At each station about 5 liters were collected directly by dark glass bottles (for petroleum hydrocarbon determination), which preserved in situ with 20 ml (chlorofom), and about 10 liters of water were collected by polyethylene containers (for heavy metals determination).

2.2.6- Sediments samples:

Sediments samples were taken seasonally from each station using a Van veen grab sampler, the water was allowed to drain off, using polyethylene bags for the samples preserved and other sediments samples were stored in aluminum foil, then the samples were placed in an ice box until reaching the lab.

2.2.7- Plant samples:

Plant samples were collected by hand and washed several time with marsh water to remove the adherence particulate as possible , then samples were divided in to two groups, one of them wrapped in aluminum foil for hydrocarbon analysis while the other group was kept in polyethylene pag for determined the trace elements, and stored inside ice-packed until reached the lab.

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Table(2): the chemical materials names which used in the study .

Chemical material name	Company name
Anhydrous sodium sulphate (Na_2SO_4)	Merck
Alumina (Al_2O_3)	Supleco
Silica gel (SiO_2)	Fluka
n-hexane	Merck
Methanol	Merck
benzene	Merck
Chloroform (CHCl_3)	Merck
Glass wool	Supleco
Potassium hydroxide (KOH)	Merck
Manganese sulphate (MnSO_4)	Merck
Potassium iodide (KI)	Merck
Sodium hydroxide (NaOH)	Merck
Sulphuric acid (H_2SO_4)	Merck
Sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$)	Merck
Starch	Merck
Distal water	
PAHs Standards of hydrocarbon compound kit	Ultra Scientific
Standards of aliphatic (n-alkanes) compounds	Supelico and Chrompak
Nitric acid HNO_3	B.D.H
Hydrochloric acid HCl	B.D.H
Hydrofluoric acid HF	Fluka
Perchloric acid HClO_4	B.D.H

Table (3): A list of instruments that were used in field and laboratory works.

Instruments	Model	Manufacturer
Oven	2712	Kottermann/Germany
Oven	ED 53	Binder/ Germany
Soxhlet	RE 6-50D	Heraeus/ Germany
Shaker	KS 500	Janke & Kunkel IKAWERK/ Germany
Sediment Blender	02102	Fritsch Pulaerisette/ Germany
Balance	170 2001	Sartorius/ Germany
Centrifuge	Mark IV Auto Bench Centrifuge	Baird & Tatlock / England
Furnas	GIM 11/7	Carbolite / England
Flame Atomic Absorption Spectrophotometer (FAAS)	A A- 7000	Shimadzu / Germany
Gas- Liquid chromatography	7890A	Agilent /USA
HPLChromatography	DG4-20A5R	Shimadzu Lc-solution Analysis Report/Japan
Filtration apparatus	labglass	Germany
Hot Plate	H22	Gerhardt Bonn /Germany
Spectrofluorometer	RF-540	Shimadzu / Japan
Water Mixer	Heidolph	Jencons(Scientific)Ltd / UK
Multimeter	350 I SET 5	Germany
Turbidity meter	355IR WTW	Germany

2.3 - Laboratory work and analysis:

2.3.1- Water samples:

2.3.1.1- Total Suspended Solids (TSS):

According to the method described in APHA (2005), the total suspended solids were measured, by filtration process through a pre-weighted mile pore filters paper (0.45 μ m), then dried in oven at 105⁰C overnight to remove all water, then calculate the net weight of TSS by using the following equation.

$$\text{TSS (mg/l)} = \frac{A-B*1000}{V}$$

Where

A=weight of filter +dried residue ,mg .

B= weight of filter ,mg

V=Volume of sample (ml).

2.3.1.2-Dissolved Oxygen (DO) and Biological Oxygen Demand (BOD₅)

Azid modification method was used to determine the level of dissolved oxygen in water samples, in which (100 ml) of a fixed sample was titrated against solution of sodium thiosulfate Na₂S₂O₃.5H₂O (0.0125N) and using 1 ml of starch solution as indicator .while the dark bottles (for BOD₅ determination) were incubated in the dark at 20⁰C for five days. After the period of incubation, the dissolved oxygen was fixed and determined according to azide modification Winkler method (Lind, 1979) BOD₅ was calculated as:

$$\text{BOD}_5 \text{ (mg/l)} = \text{DO(mg/l) before incubation} - (\text{DO(mg/l) after incubation})$$

2.3.2- Sediments samples:

2.3.2.1- Loss-on-ignition (Total Organic Carbon (TOC %))

Amount of Total Organic Carbon in sediments were measured according to burning method (Sparks *et al.*,1996) taking 2 gm of dried and sieved sediments(63 μ m) were placed in pre-weighted crucible and burned at 550⁰C ,then placed in desiccators and weighted more than one to reach constant weight, The difference in mass of crucible and sediments sample before and after burning was calculated as TOC%.

2.3.2.2- Grain size analysis (%)

Mean grain size analysis was carried out (in the sedimentary lab/ sediments department/Marines sciences center/ Basrah University)using the pipette method(Folk, 1974) for silt and clay grains and standard sieves (63 μ m pore size) for sand grains then the triangle texture had been applied to describe the sediments texture.

2.3.3-Heavy Elements:

2.3.3.1- Heavy elements extraction and analysis:

High-purity deionized water was used for the preparation of standards and reagents ,and used only polyethylene and plastic containers ,because the use of glass material was avoided heavy metals adsorption on the glass. Also used high-quality concentrated (69% w/v) nitric acid, hydrofluoric acid (48%), perchloric acid (70%), hydrochloric acid (35.4%), and ammonium (32%). The standard solutions were prepared from a stock solution of 1000 mg/l.

2.3.3.2 - Dissolved Phase:

Water samples (5L) was collected at each station, were filtered as soon as possible through pre-washed (0.5N HCl) and pre-weighted millipore filters paper (0.45 μ m pore size). the retained matter on the surface of filters were considered as particulate phase while the filtrate water was considered as dissolved phase. Then , the filtrate was pre-concentrated according to Riley

and Taylor (1968) method, using chelating ion exchange resin (Purolite-C-100 resin in hydrogen form), about 5 L of filtrate was pass through 1.5 cm diameter ion exchange column which was filled with the resin to approximately depth 12 cm.

The resin was packed freshly and reactive before use by passing 30 ml of (2N) HNO_3 , then add 100 ml of deionized water, and 30 ml of (3N) NH_4OH , and then 100 ml of deionized water. The filtrate water allowed to pass through the column with a flow rate of about 8 ml/min, the bounded heavy metals were eluted using 50 ml of 2N HNO_3 . Then column was washed with 100 ml of deionized water, the elutes were collected in 100 ml clean teflon beaker, put it on hot plate at 70° C until the sample volume became less than 25 ml, then the sample was completed to 25 ml with deionized water and placed in tightly stopper polyethylene vials to be ready for analysis of the metals using Flame Atomic Absorption Spectrophotometer (FAAS).

The concentration of elements as dissolved ($\mu\text{g/L}$) was calculated according to the following equation:

$$\text{Concentration } (\mu\text{g/L}) = A * B * 1000 / V$$

Where :

A: Element concentration that calculated from standard curve (mg/L)

B: Final volume of extracted sample (mL)

V: Initial volume of sample (mL)

2.3.3.3- Particulate Phase:

Exchangeable elements:

After filtration, the filters were dried in oven at 60°C until dry and then weighted, to extracted the exchangeable heavy metals used 30 ml HCl (0.5N) for overnight in an orbital shaker with 300 rpm, then the solution was

centrifuged at 5000 rpm for 20 minute, the supernatant was filtered using filter paper (Watman No. 1). The filtrate was stored in tightly stopper polyethylene vials to be ready for analysis (Chester and Voutsinou, 1981).

Residual elements:

The residue from the above mentioned steps was washed by 40 ml deionized water, then centrifuge for 20 minutes to remove the residual of the exchangeable phase. Then samples were digested with 5 ml concentrated HNO_3 acid in teflon beaker at 70°C on hot plate near dryness state. The digestion was further proceeded with 5ml of 1:1 mixture concentrated HClO_4 and HF acids, then digested near dryness state. The residue was dissolved in 30 ml of 0.5 HCl , put on hot plate at 70°C and then made up to 30 ml with deionized water, filtered by filter paper (Watman No. 1). The samples were stored in tightly stopper polyethylene vials to be ready for analysis (Sturgen, *et al.* 1982).

The concentration of elements as Particulate Phase ($\mu\text{g/g d.w.}$) was calculated according to the following equation :

$$\text{Concentration } (\mu\text{g/g d.w.}) = A*B/W$$

Where:

A: Element concentration that calculated from standard curve(mg/L)

B: Final volume of extracted sample (ml)

W: weight of sample (g).

2.3.3.4- Sediments:

The sediment samples were dried in an oven at 50°C for approximately 3 days, grind finely using an electrical mortar and sieved through a $63 \mu\text{m}$ mesh sieve, and stored in polyethylene bags until analysis.

Exchangeable elements in Sediments:

From the fraction of the grinded and sieved sediments, taken (1 g) and put in 50 ml polyethylene tube. The exchangeable heavy metals were extracted

according to the method of Chester and Voutsinou (1981) mentioned above in section (2.3.3.3). Samples were stored in tight stopper polyethylene vials to be ready for analysis.

Residual elements in Sediments:

The residual heavy metals were extracted according to Sturgen *et al.* (1982) procedure mentioned before in section (2.3.3.3). Samples were stored in tight stopper polyethylene vials to be ready for analysis.

The concentration of elements in sediments ($\mu\text{g/g d.w.}$) was calculated according to the equation mentioned above in section (2.3.3.3).

To check for contamination of the digestion procedure and sample manipulation, a blank solution was prepared and carried through each set of the analyses. Then, all the samples were analyzed using flame atomic absorption spectrophotometer (FAAS) at the department of Marine Environmental Chemistry/ Marines sciences center/University of Basrah.

2.3.3.5- Plant sample

Plant samples after rinsed thoroughly with distilled water, then dried, grounded and sieved using a $63\mu\text{m}$ and put (1g) into teflon beaker with 5 ml nitric acid then 2 ml perchloric acid, heated at 70°C until all the materials were dissolved. After digestion, add 10 ml of (0.5 N HCl) and the samples were diluted with deionized water to a volume of 25 ml and filtered. Samples were stored in tight stopper polyethylene vials to be ready for analysis, using FAAS (Estefan *et al.*, 2013).

2.3.4- Hydrocarbons:

2.3.4.1- water samples:

The hydrocarbons in water sample (about 4L) were extracted according to UNEP (1989) by mixing with (40 ml) chloroform for 30 min. using electrical shaker, the liquid fraction was drained, and the residual (about 1L) was transferred into separator funnel and left for 5 minutes until stability. The organic (lower) phase was carefully poured into a glass column provided

with glass wool at the bottom, then (5g) of anhydrous sodium sulfate (Na_2SO_4) to remove the excess water, then the chloroform extracts collected and dried by air. Then the residual was dissolved with n-hexane (25 ml), and passed through glass column (packed with glass wool at the bottom, about 10 gm deactivated silica gel (100-200 mesh), 10 gm deactivated alumina (100-200 mesh), and 5gm anhydrous sodium sulfate (Na_2SO_4) at the top to eluted aliphatic fractions from the column with n-hexane (25 ml), while the aromatics were eluted with benzene (25 ml). The samples were air dried and stored until detection with spectrofluorometer for (total petroleum hydrocarbons (TPHs) or Gas-liquid chromatography instruments for (aliphatic (n-alkanes) and High performance liquid chromatography instruments HPLC for (polynucleic aromatic hydrocarbons (PAHs)).

2.3.4.2- Sediment and plant samples:

The samples were dried in an air, grinded finely in an electrical stainless steel mortar and sieved through a 63 μm mesh sieve, stored in glasses containers until analysis. 20 grams of sieved sediments (for sediments sample) and 5 grams of sieved plants (for plant samples) were placed in cellulose thimble and soxhlet extracted using soxhlet intermittent extraction (Goutex and Saliot, 1980) with mixed solvents (120 ml) methanol : benzene (1:1 v/v) for 24-36 hrs. at temperature doesn't exceed 40°C. At the end of this period, the combined extracts were saponification for 2 hrs. by adding (15ml) 4M MeOH (KOH) at the same temperature, then cooled to room temperature, using separator funnel to extracted the unsaponification matter with (40 ml) n-hexane. The upper unsaponification matter with hexane (hydrocarbons) was taking and passed through chromatographic column provided with glass wool at the bottom then layer from silica gel and layer of alumina, in the top placed layer from anhydrous sodium sulfate to

collected the aliphatic fraction, then add 40 ml of benzene to collected the aromatic fraction.

2.3.4.3- Calibration:

Total petroleum hydrocarbons (TPHs) :

Basrah Regular Crude oil was used as a reference sample for the preparation of standard solutions by dissolving (0.003g) of crude oil in a known volume of pure n- hexane (10 ml).

Spectrofluorometer was used to quantify the total petroleum hydrocarbons in the extracted water, sediments and plants samples, at 360nm emission intensity, 310 nm excitation, and monochromatic slits of 10 nm.

Aliphatic (n-alkanes) Hydrocarbons compounds:

Standards of aliphatic compounds were used to inject in gas chromatography to determine qualities and quantities of aliphatic compounds in water, sediments and plants samples. Column (model Agilent 125-103KHP-5 .Siloxan with dimensions (30 m.*320 μ m*0.25 μ m) was used for aliphatic separation, helium was used as carrier gas in Gas Chromatography with linear velocity of 3 ml./min. with flam ionization detector (FID). The operating temperatures were 280⁰C and 300⁰C, respectively for detector and injector. The temperature of column was held at 35⁰C for 10 minute as initial temperature, then 5⁰C/minute to 300⁰C for 17 minute.

Polynucleic Aromatic Hydrocarbons compounds (PAH_s):

HPLC type (Shimadzu LC) inject by Standard polynucleic aromatic compounds were used to determine the qualities and quantities of PAHs compounds in water, sediments and plants. The condition operation for HPLC were: the column was C18 (250mm,25cm,4.6mm) the mobile phase was acetonitrile /water (90:10 v/v) flow rate was 0.5ml/min,the injection volume was 20 μ l, the wavelength of UV/visible was 254 nm .

2.4-Hydrocarbons pollution indices:

To explain the source of hydrocarbons (anthropogenic or biogenic) in aquatic environments, used a number of relationships between different hydrocarbons. These are as follows:

2.4.1-Carbon Preference Index (CPI):

CPI represents the ratio of normal alkanes which have odd to even carbon number. If the CPI value is greater than (1), the source of the hydrocarbon compounds is biogenic. While n-alkanes from anthropogenic source have a CPI value less than or close to (1) (Tolosa *et al.*, 1996; Al-Hejuje,2014).

$$CPI = \frac{\sum \text{Odd}}{\sum \text{Even}}$$

2.4.2-Ratio of Pristine (pri) to Phytane (Phy), Pri / Phy:

If the proportion of the Pristine to the Phytane is greater than one, the origin is biogenic, and if one or less is the human anthropogenic origin. Pristine and Phytane are widespread in the aquatic environment, they were often considered as good indicators of hydrocarbons pollution (NRC, 2003).

2.4.3-Ratio of low molecular weights to high molecular weights of PAHs

If the ratio of low molecular weights to high molecular weights is above one, the source of PAHs is Petrogenic from petroleum compounds and their derivatives, but if the value is below one the source is Pyrogenic of (Vrana *et al.*, 2001; Al-Khatib, 2008; Al-Hejuje, 2014).

2.4.4-Ratio of Phenanthrene compound to Anthracene compound:

The source of the PAHs is Petrogenic, if the value of the ratio is greater than the number (10). When the value of the ratio is smaller than the number (10), the source of the PAHs is Pyrogenic (Doong and Lin, 2004; Al-Khion, 2012 and Al-Hejuje, 2014).

2.4.5-Ratio of fluoranthene to Pyrene(FI/Py)

If the value of (FI/Py) is less than one, the source of the PAHs is Petrogenic, while if the value of (FI/Py) is greater than the number 1, the source of PAHs is Pyrogenic. (Qiu *et al.*, 2009; Kafilzadeh *et al.*, 2011).

2.4.6- Anthracene/(Anthracene+ phenanthrene)

Which indicates that the origin of the aromatic compounds petrogenic if the value of less than 0.1, and if they are greater than 0.1 they indicate the origin of pyrogenic (Yunker *et al.*, 2002).

2.4.7-Ratio of Benzo (a) Anthracene/(Benzo (a) Anthracene+ Chrysene), (BaA/(BaA+Chr)).

If the value of BaA/(BaA + Chr) is less than (0.2), it indicates that the source of PAHs is Petrogenic. If its value is between 0.2-0.35, this indicates that the source of PAHs either Petrogenic or Pyrogenic, but if its value is greater than 0.35 the source of PAHs is Pyrogenic (Yunker *et al.*, 2002; Tolosa *et al.*, 2004; Gao *et al.*, 2007).

2.4.8- Indeno (1,2,3)Pyrene/(Indeno(1,2,3)+ Benzo(g,h,i) Perylene

If value of this ratio is less than(0.2), the source of PAHs is Petrogenic, if the value of the PAHs is 0.2-0.5, this indicates either Petrogenic or Pyrogenic origins . If the value is higher than 0.5, the source of the PAHs is Pyrogenic (Yunker *et al.*, 2002; Tolosa *et al.* 2004; Gao *et al.*, 2007).

2.5-Heavy Metals Pollution Indices:

2.5.1- Geoaccumulation Index (I_{geo}):

The geo accumulation index I_{geo} , as introduced by Müller (1969) to assessment the pollution in sediments, as follows:

$$I_{geo} = \log_2(C_n / 1.5 B_n)$$

Where :

C_n : is the concentration of the metal (n) which measured in the sediments.

B_n : is the background concentration to the metal (n).

1.5: is the factor used because of possible variation in background values due to lithological variability.

The geo accumulation index to classification sediments pollution as in (Table 4) below:

I-geo	Pollution Sediments Case
≤ 0	unpolluted
$0 \leq I_{geo} < 1$	unpolluted to moderately
$1 \leq I_{geo} < 2$	moderately polluted
$2 \leq I_{geo} < 3$	moderately polluted to polluted
$3 \leq I_{geo} < 4$	strongly polluted
$4 \leq I_{geo} < 5$	strongly to extremely polluted
$geo \geq 5$	extremely polluted

2.5.2-Heavy Metal Pollution Index (HPI):

The heavy metal pollution index (HPI) is a method of rating that shows the composite influence of all heavy metal on the overall quality of water and contamination (Reza and Singh, 2010). HPI in water was developed by assigning weight or rating (W_i) for each selected element. The weighing factors was between zero and one, reflecting the relative importance of individual quality considerations.

$$W_i = K / S_i \quad (1)$$

Where :

W_i : is the unit of weightage, k : is the constant of proportionality ($k=1$), and S_i : is the recommended standard for i th parameter.

The sub index (Q_i) of the i th parameter was calculated according to Reza and Singh (2010):

$$Q_i = \frac{[M_i - I_i]}{S_i - I_i} * 100 \quad (2)$$

where:

M_i : is the monitored value of heavy metal of i th parameter in $\mu\text{g/l}$

I_i : is the ideal value

S_i : refers to the standard value of the i th metal.

The HPI model (Mohan *et al.*, 1996) was calculated as:

$$\text{HPI} = \sum_{i=1}^n W_i Q_i / \sum_{i=1}^n W_i \quad (3)$$

The higher HPI value causes the greater damage to health. critical pollution index value is 100 (Reza and Singh, 2010).

2.5.3 -Metal Bioaccumulation Factor (BAF):

Bioaccumulation Factor of different elements from terrestrial plants to soil, rooted aquatic plants to sediment, and aquatic plants to water(dissolved phase) was calculated using the equation given by Wilson and Pyatt (2007).

$$\text{BAF}(\%) = \frac{C_{\text{plant tissue}}}{C_{\text{(sediment or water)}}} \times 100$$

Where:

$C_{\text{plant tissue}}$ the concentration of elements in plant tissue.

$C_{\text{(sediment/ water)}}$ the concentration of elements in sediment or water.

2.6- Statistical Analysis:

Analysis Of Variance (One –Way ANOVA) was applied by Minitab ver. 16.1 software to identify the existence of spatial and temporal significant differences. The relationship between the parameters and indices was calculated using the Pearson, s Correlation Coefficients.

Chapter Three

Results

3.1- Physicals and Chemicals variables:

3.1.1-Temperature:

During the studied period air temperature was changed seasonally with lowest value recorded in winter (14 °C) at station 2, while the highest value recorded in summer (47°C) at station 1 (Fig. 6-A) .Water temperature follows the change in the air temperature with lowest value recorded in winter (10.5°C) at station 2 and highest value in summer (33°C) at station 1(Fig.6-B). Analysis of Variance test (ANOVA) showed non-significant differences in water temperature among stations. In contrast, there were significant differences ($p \leq 0.05$,) were found among seasons, the highest mean value (31.50°C) in summer and lowest mean value (11.30°C) in winter.

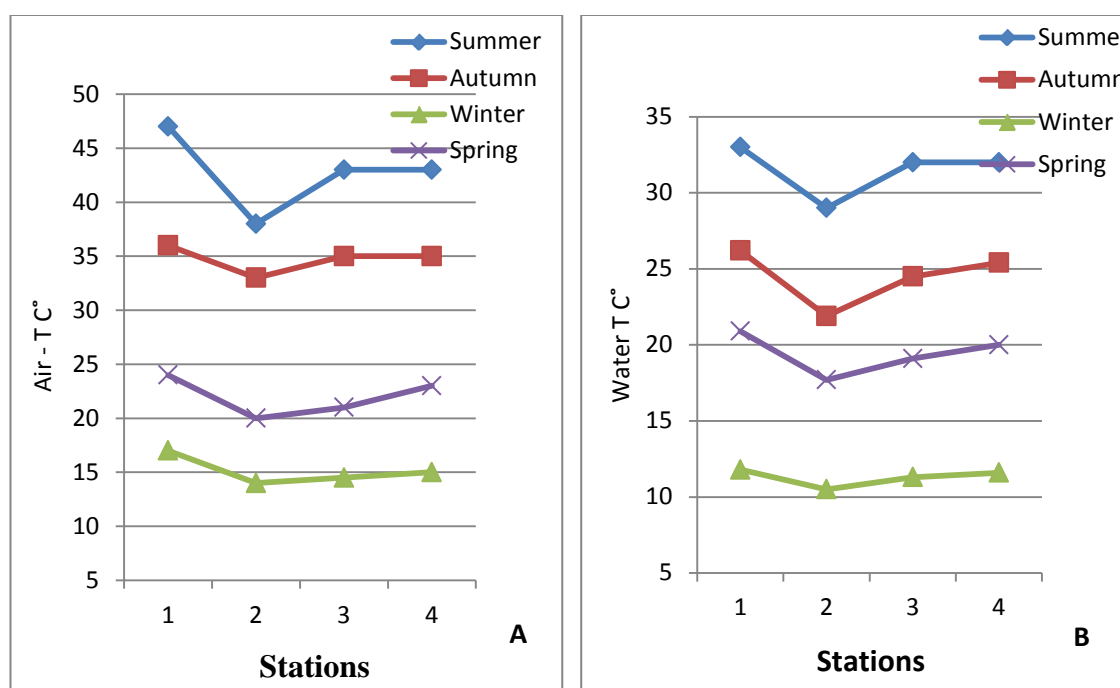


Fig.(2): A : Air and B: Water temperatures (°C) at the studied stations.

3.1.2-Potential of hydrogen ions (pH):

pH values were on the alkaline side at all the studied stations and at all the studied periods. The highest value was recorded in summer (8.15) at station 4 while the lowest value (7.24) was recorded in spring at station 2 (Fig.7). Significant differences ($P \leq 0.05$) were found among stations, the highest mean

value (7.9) at station 4 and lowest mean value (7.47) at station 2. While non-significant differences were found among seasons,

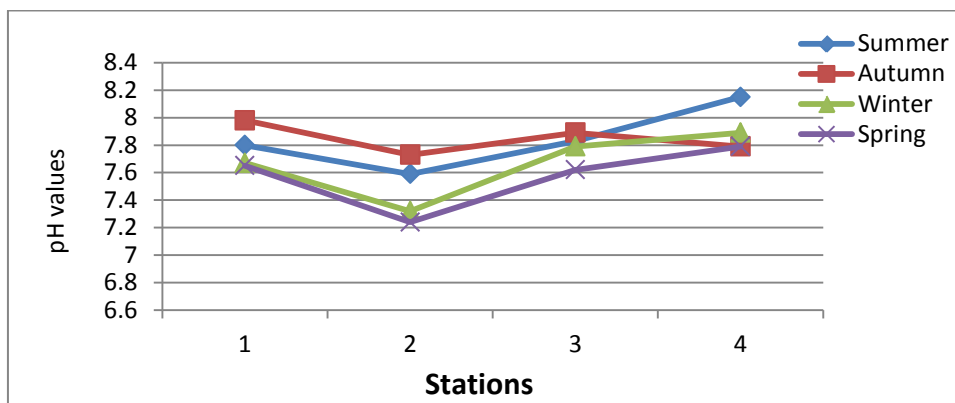


Fig. (3): Seasonal variation of (pH) at the studied stations

3.1.3-Salinity (Sal.):

The highest value of salinity was recorded in summer (3.4PSU) at station 4, while the lowest value (2.5 PSU) was recorded in winter at station 3 (Fig.8). Non-Significant differences were found among seasons, the highest mean value (2.98PSU) in summer and lowest mean value (2.60PSU) in winter, significant differences ($P \leq 0.05$) were found among stations the highest mean value (3.28PSU) at station 4 and lowest mean value (2.65PSU) at station 1.

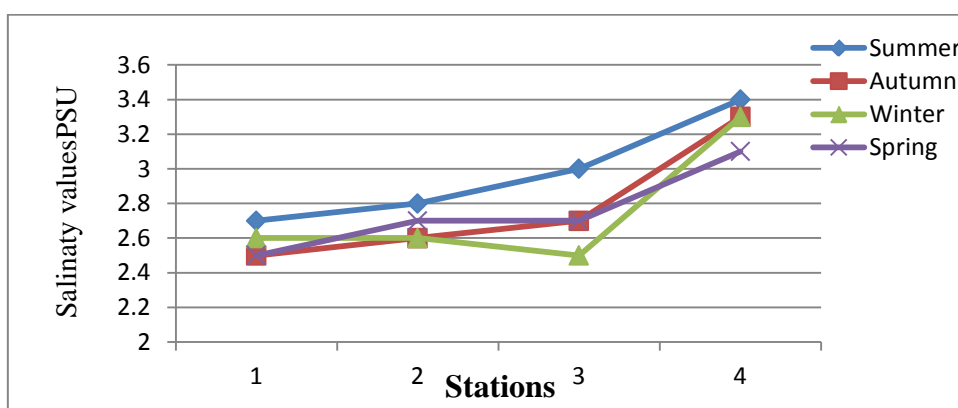


Fig.(4) : Seasonal variation of salinity (PSU) at the studied stations

3.1.4-Electrical Conductivity (EC):

The highest value of EC (6.15 ms/cm) was recorded in summer at station 4 ,while the lowest value recorded was (4.53 ms/cm) in winter at station 1(Fig.9). Significant differences ($P \leq 0.05$) were found among stations. the

highest mean value (6.01 ms/cm) at station 4 and lowest mean value (4.72 ms/cm) at station 1. Non-significant differences were found among seasons, the highest mean value (5.44 ms/cm) in summer and lowest mean value (5.02 ms/cm) in winter.

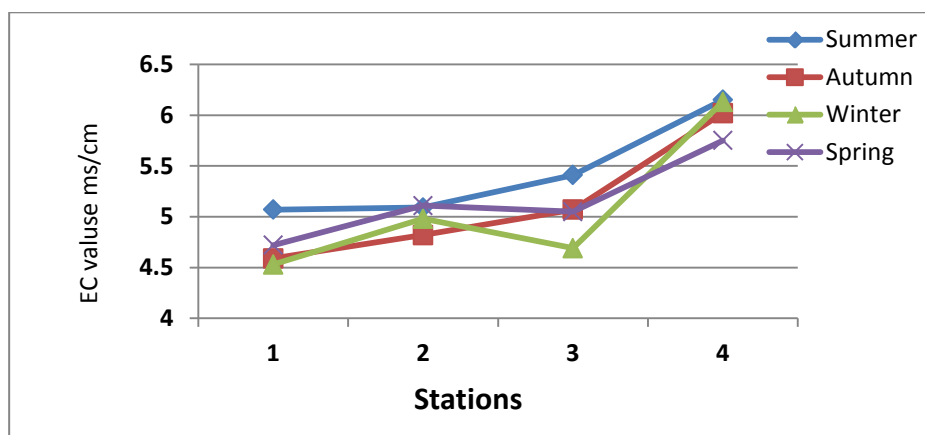


Fig (5)Electrical Conductivity(EC ms/cm) at the studied stations

3.1.5-Turbidity:

The highest value of turbidity was recorded in winter (50.55 NTU) at station 4, while the lowest value (1.3 NTU) was recorded in summer at station 2 (Fig.10). Non-Significant differences were found among seasons, the highest mean value (27.14 NTU) was recorded in winter, while the lowest mean value (15.98 NTU) was recorded in autumn. But, significant differences ($P \leq 0.05$) were found among stations, the highest mean value (45.59NTU) was recorded at station 4, whereas the lowest mean value (3.08NTU) was recorded at station 2.

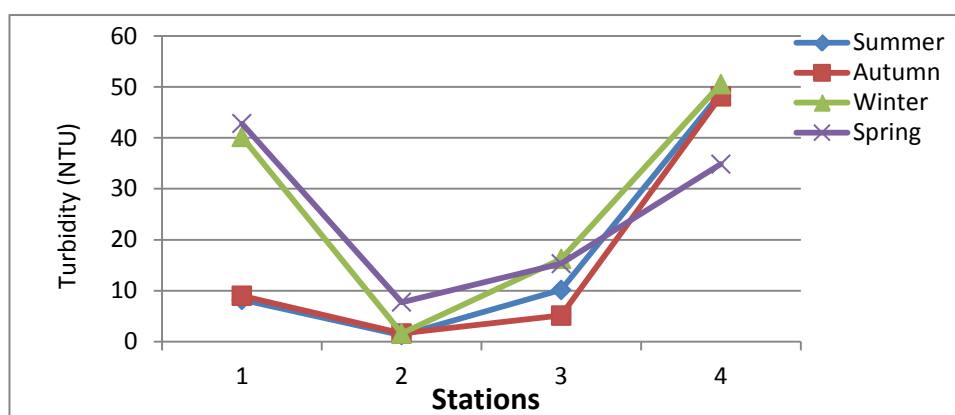


Fig.(6) : Turbidity as NTU at the studied stations

3.1.6-Total Suspended Solids (TSS):

Total suspended solid showed highest value (97.22 mg/l) in spring at station 1, while lowest value (1.68 mg/l) in summer at station 2 (Fig.11). Non-Significant differences were found among stations, the highest mean value (39.17mg/l) was recorded at station 4, while the lowest mean value (2.99 mg/l) was recorded at station 2. Also no-significant differences were found among seasons, the highest mean value (40.69 mg/l) was recorded in spring, while the lowest mean value (11.96 mg/l) was recorded in autumn.

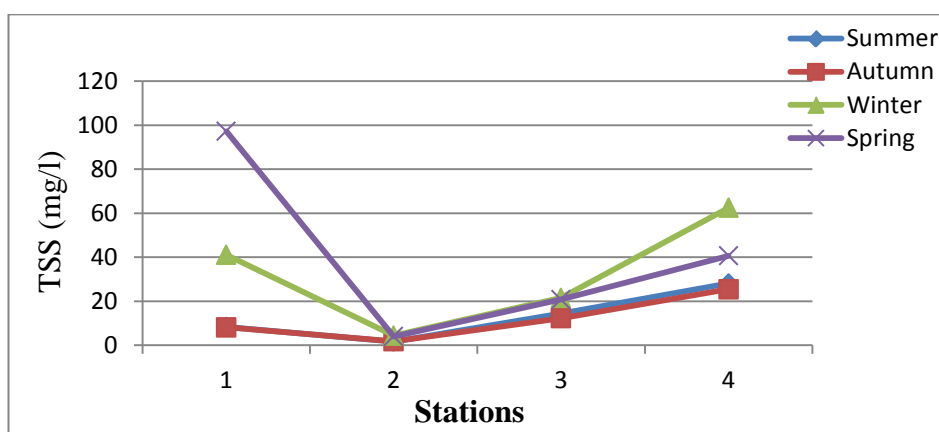


Fig.(7): Total Suspended Solids (TSS) as (mg/l) at the studied stations.

3.1.7-Dissolved Oxygen(DO)and Biological Oxygen Demand(BOD₅):

Highest value of dissolved oxygen (7.75 mg/l) was recorded in winter at station 3, while lowest value (0.7 mg/l)was recorded in summer at station 2(Fig.12-A). Non-Significant differences were found among stations. Whereas significant differences ($P \leq 0.05$) were found among seasons, the highest mean value (7.03 mg/l) was recorded in winter, while the lowest (0.87 mg/l) was recorded in summer.

BOD₅ highest value (3.5 mg/l) was recorded in spring at station 4, while the lowest value (0.75mg/l) at station 2 in winter (Fig.12-B). Non-significant differences were found among stations. But significant differences ($P \leq 0.05$)

were found among seasons , the highest mean value (2.11mg/l) was recorded in spring, while the lowest mean value (1.08) was recorded in winter.

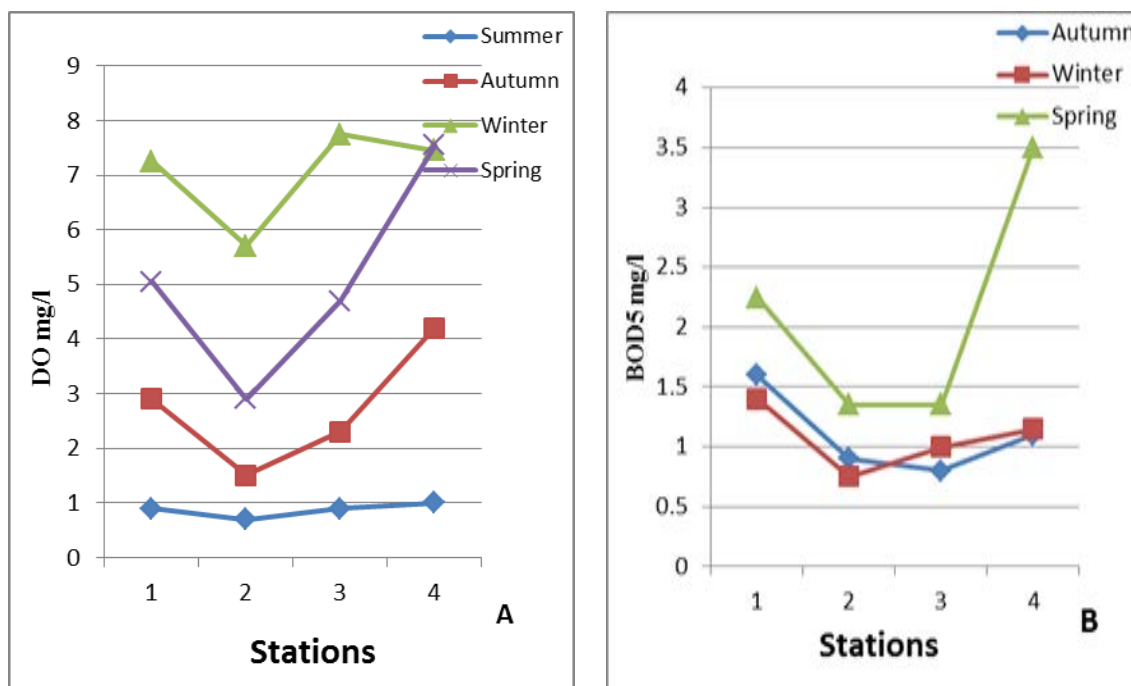


Fig.(8): A: Dissolved Oxygen (DO) and B:Biological Oxygen Demand (BOD₅) concentrations (mg/l) at the studied stations

3.1.8-Grain size:

Sand % : The highest percentage of sand (24%) was recorded at station 4 in autumn while the lowest percentage (1%) was recorded at station 1 in summer, (Fig.13-A). Significant differences ($P \leq 0.05$) were found among stations, the highest mean percentage (19.50%)was found at station 4, but the lowest mean percentage (2%) was found at station 1. Whereas non-significant differences were found among seasons.

Silt % : The highest percentage of silt (86%) was found at station 1 in spring, but the lowest percentage (59%) was found at station 3 in winter and at station 4 in autumn (Fig.13-B). Among seasons, found non-significant differences. Whereas among stations significant differences ($P \leq 0.05$) were found ,the highest mean percentage (80.25%) was found at station 1 , and the lowest mean percentage (66.25%) was found at station 4.

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Clay %: The highest percentage of clay (25%) was detected at station 1 in autumn, while lowest percentage (7%) was detected at station 2 in autumn and station 3 in summer (Fig.13-C). Non-Significant differences were found among seasons or among stations .

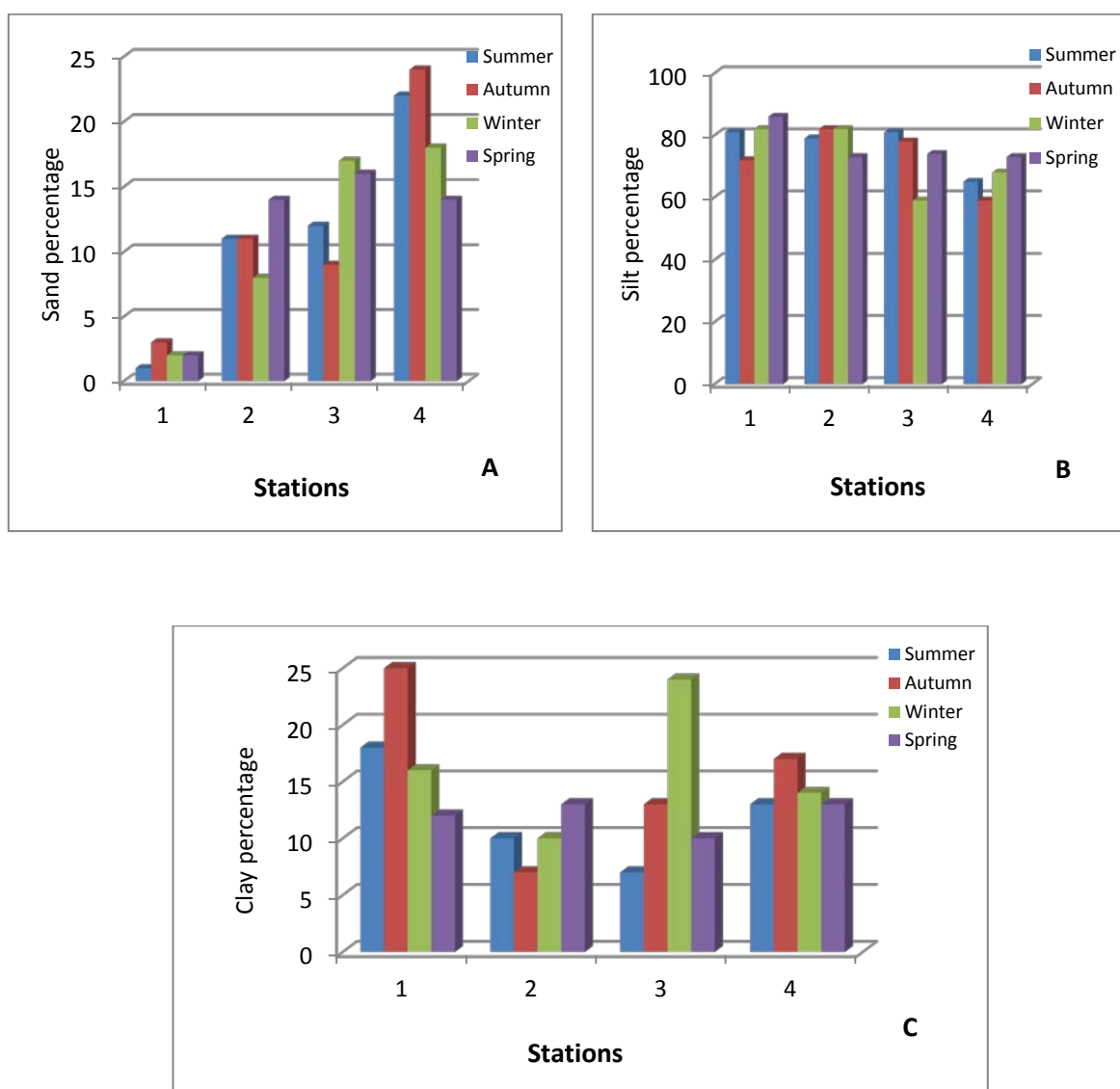


Fig (9) Grain size (%)in the sediments of the studied area

3.1.9-TOC%: The highest percentage of TOC (13.49%) was recorded at station 4 in winter while the lowest percentage (9.93%) was recorded at station 2 in summer (Table 5). Non-significant differences were found among stations or among seasons .

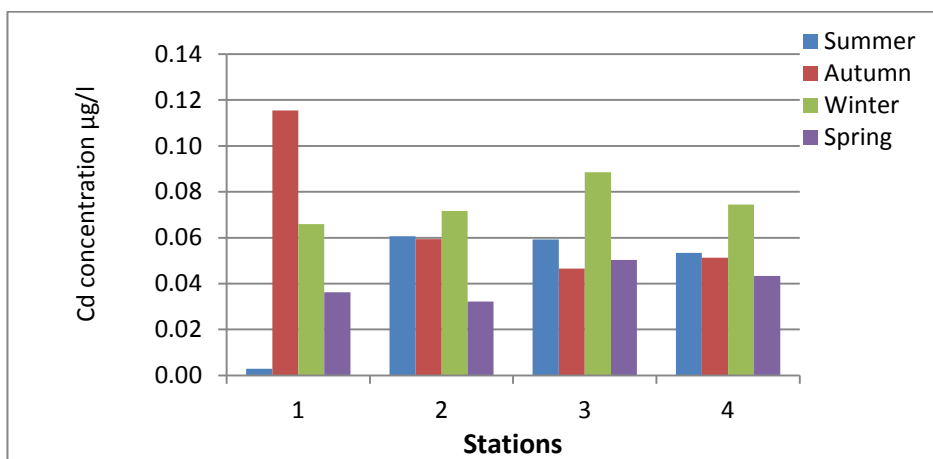
Table (5) Total Organic Carbon (TOC %) during the studied period in the sediment of studied area .

Stations	Season	TOC % (Mean \pm SD)
Station 1	Summer	10.58 \pm 0.23
	Autumn	11.84 \pm 0.47
	Winter	12.68 \pm 1.21
	Spring	12.26 \pm 0.16
Station 2	Summer	9.93 \pm 1.43
	Autumn	10.32 \pm 0.20
	Winter	12.62 \pm 0.12
	Spring	11.61 \pm 0.17
Station 3	Summer	10.26 \pm 0.64
	Autumn	10.06 \pm 0.32
	Winter	11.14 \pm 1.39
	Spring	11.43 \pm 1.51
Station 4	Summer	11.49 \pm 4.99
	Autumn	11.65 \pm 0.22
	Winter	13.49 \pm 0.16
	Spring	13.18 \pm 1.37

3.2- Heavy Elements:

Cadmium (Cd):

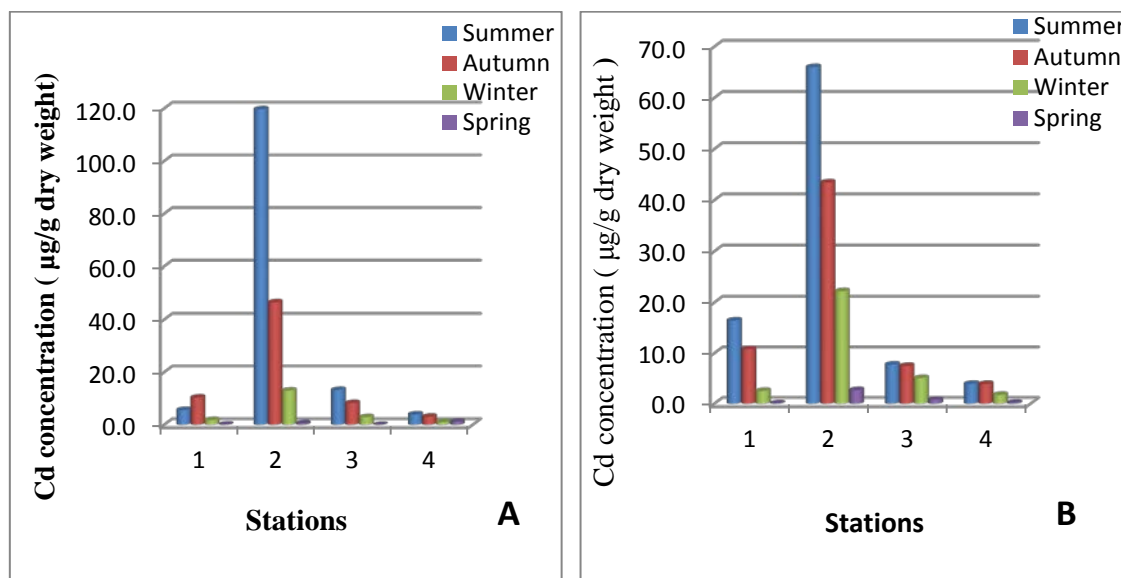
The concentrations of cadmium in dissolved phase ranged from (0.003 μ g/l) at station 1 in summer to (0.116 μ g/l) at station 1 in autumn (Fig.14). Non-significant differences were found among stations or among seasons.



(Fig.10) The concentrations of Cadmium in water as dissolved phase (µg/l)

In particulate phase, the highest concentrations of the exchangeable phase was (119.67µg/g dry weight) at station 2 in summer, while the lowest concentrations (ND) at station 3 in spring. Non-significant differences were found among stations or among seasons (Fig.15-A).

In residual phase of particulate, the concentrations of cadmium ranged from (0.11µg/g dry weight) at station 1 in spring to (66.02 µg/g dry weight) at station 2 in summer. Non-significant differences were found among seasons, whereas significant differences ($P \leq 0.05$) were found among stations, the highest mean value (33.60µg/g dry weight) was recorded at station 2 and the lowest mean value (2.47µg/g dry weight) was recorded at station 4 (Fig.15-B).



(Fig.11) The concentrations of Cadmium in particulate phases : A (exchangeable) and B (residual).

The concentrations of cadmium in sediments of the exchangeable phase ranged from (0.08µg/g dry weight) at station 3 in spring to (0.58µg/g dry weight) at station 1 in winter. Significant differences ($P \leq 0.05$) were found among seasons, the highest mean value (0.50 µg/g dry weight) in autumn, while the lowest mean value (0.24 µg/g dry weight) in spring, non-significant differences were found among stations.

In the residual phase of sediments, the cadmium concentrations ranged from undetectable value (ND) at station 1,2,3 in Spring season to (0.49µg/g dry weight) at station 4 in winter (Table 6). Significant differences ($P \leq 0.05$) were found among seasons, the highest mean value (0.43 µg/g dry weight) in summer, and the lowest mean value (0.006 µg/g dry weight) in spring. Non-significant differences were found among stations.

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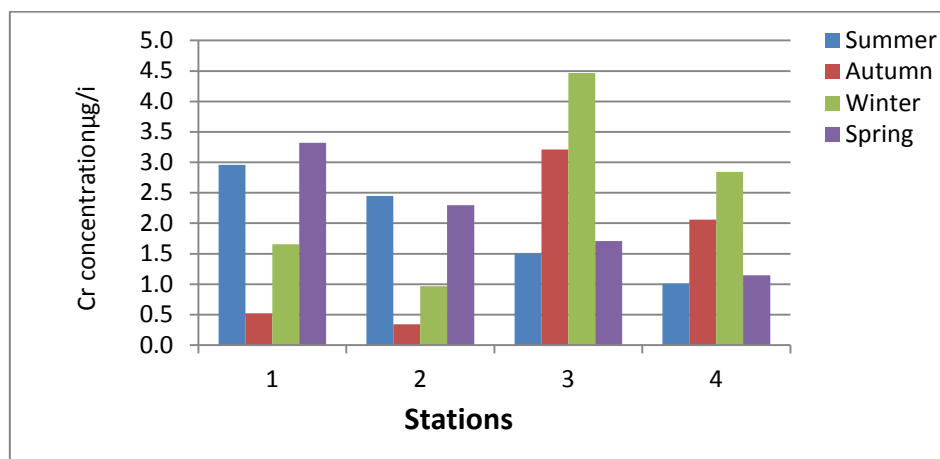
Table(6) :The concentrations of cadmium in sediments at the studied stations during the studied periods (mean \pm Standard deviation (SD)).

Stations	Seasons	Exchangeablephase	Residual phase	Total
Station 1	Summer	0.32 \pm 0.11	0.39 \pm 0.03	0.72
	Autumn	0.45 \pm 0.08	0.33 \pm 0.04	0.87
	Winter	0.58 \pm 0.02	0.21 \pm 0.06	0.80
	Spring	0.36 \pm 0.09\	ND	0.36
Station 2	Summer	0.21 \pm 0.02	0.47 \pm 0.03	0.69
	Autumn	0.49 \pm 0.08	0.29 \pm 0.05	0.78
	Winter	0.43 \pm 0.02	0.26 \pm 0.02	0.70
	Spring	0.20 \pm 20	ND	0.20
Station 3	Summer	0.39 \pm 0.02	0.41 \pm 0.01	0.81
	Autumn	0.52 \pm 0.08	0.22 \pm 0.06	0.75
	Winter	0.48 \pm 0.02	0.24 \pm 0.02	0.73
	Spring	0.08 \pm 0.01	ND	0.08
Station 4	Summer	0.43 \pm 0.02	0.43 \pm 0.07	0.87
	Autumn	0.45 \pm 0.04	0.18 \pm 0.03	0.64
	Winter	0.47 \pm 0.05	0.49 \pm 0.07	0.97
	Spring	0.32 \pm 0.008	0.02 \pm 0.03	0.35
Mean		0.41	0.27	0.69

ND : not detected

Chromium (Cr) :

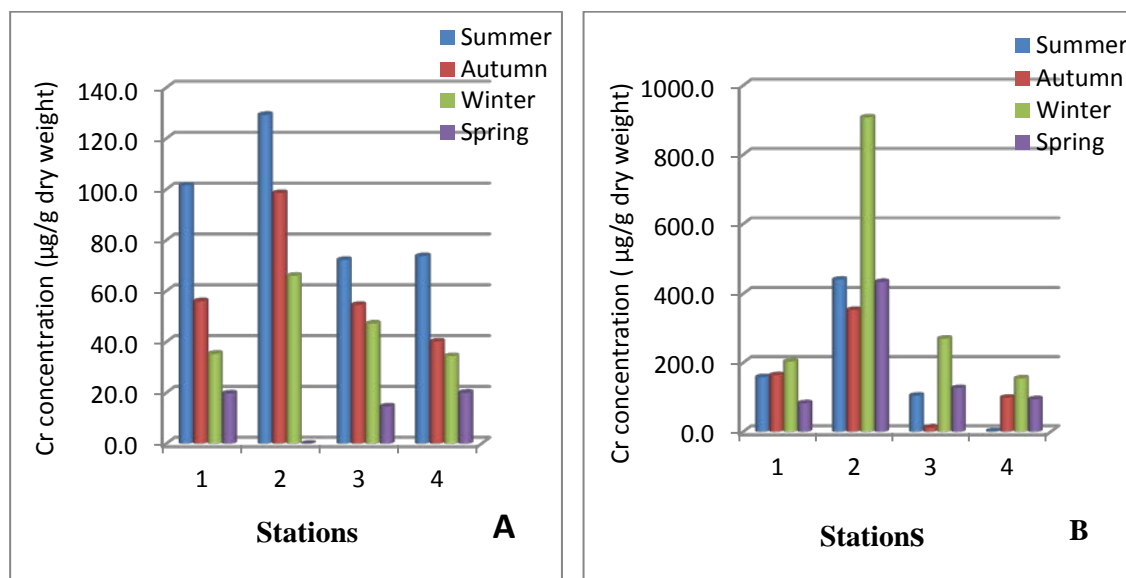
The concentrations of chromium in dissolved phase ranged from (0.344 μ g/l) at station2 in autumn to (4.465 μ g/l) at station 3 in winter (Fig.16). Non-significant differences were found among stations and seasons.



(Fig.12) The concentrations of chromium in water as dissolved phase (µg/l)

In particulate phase, the concentrations of the exchangeable phase ranged from (ND) at station 2 in spring to (129.28 µg/g dry weight) at station 2 in summer. Non-significant differences were found among stations. But significant differences ($P \leq 0.05$) were found among seasons, the highest mean value (94.22 µg/g dry weight) was recorded in summer and the lowest mean value (13.61 µg/g dry weight) was recorded in spring (Fig.17-A).

The chromium concentrations in the residual phase of particulate ranged from (2.53 µg/g dry weight) at station 4 in summer to (907.55 µg/g dry weight) at station 2 in winter. Non-significant differences were found among seasons, but significant differences ($P \leq 0.05$) were found among stations, the highest mean value (534 µg/g dry weight) was recorded at station 2 and the lowest mean value (87.6 µg/g dry weight) was recorded at station 4 (Fig.17-B).



(Fig.13) The concentrations of chromium in particulate phases:A(exchangeable) and B(residual).

In sediments ,the concentrations of chromium in the exchangeable phase ranged from (3.16µg/g dry weight) at station 2 in spring to (42.86µg/g dry weight) at station 3 in summer . Significant differences ($P \leq 0.05$) were found among seasons, the highest mean value (27.90 µg/g dry weight) was recorded in summer , and the lowest mean value (9.75 µg/g dry weight) was recorded in spring, also significant differences ($P \leq 0.05$) were found among stations ,the highest mean value (30.40 µg/g dry weight) was recorded at station 3, while the lowest mean value (11.55 µg/g dry weight) was recorded at station2.

The concentrations of chromium in the residual phase of sediments ranged from (44.43 µg/g dry weight) at station 2 in spring to (132.89 µg/g dry weight) at station 1 in winter. Significant differences ($P \leq 0.05$) were found among stations ,the highest mean value (97.67 µg/g dry weight) was recorded at station 1 and the lowest mean value (67.76 µg/g dry weight) was recorded at station 2. Also significant differences ($P \leq 0.05$) were found among seasons, the highest mean value (117.02 µg/g dry weight) was recorded in winter and the lowest mean value (56.54 µg/g dry weight) was recorded in spring (Table 7).

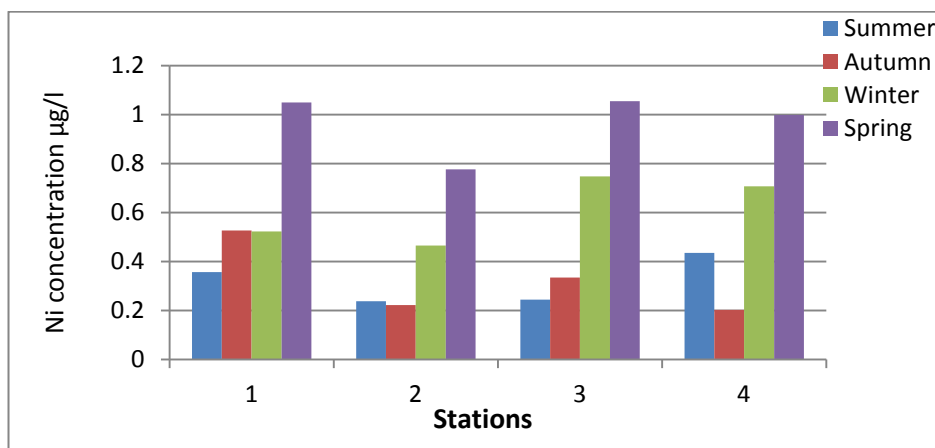
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Table(7): The concentrations of chromium in sediments at the studied stations during the studied periods (mean \pm Standard deviation (SD)).

Stations	Seasons	Exchangeablephase	Residual phase	Total
Station 1	Summer	18.29 \pm 18.18	89.39 \pm 5.24	107.68
	Autumn	22.58 \pm 0.55	94.03 \pm 6.48	116.61
	Winter	22.70 \pm 1.8	132.89 \pm 8.21	155.59
	Spring	12.20 \pm 1.18	62.72 \pm 5.83	74.93
Station 2	Summer	19.10 \pm 0.44	61.24 \pm 0.54	80.34
	Autumn	11.33 \pm 1.24	61 \pm 1.22	72.33
	Winter	9.82 \pm 1.45	96.59 \pm 1.47	106.41
	Spring	3.16 \pm 1.64	44.43 \pm 2.83	47.59
Station 3	Summer	42.86 \pm 1.00	85.83 \pm 0.48	128.70
	Autumn	31.21 \pm 0.63	82.03 \pm 1.41	113.25
	Winter	30.37 \pm 0.54	127.61 \pm 5.42	157.99
	Spring	10.52 \pm 0.17	57.59 \pm 1.53	68.12
Station 4	Summer	31.36 \pm 1.5	75.34 \pm 3.82	106.70
	Autumn	6.79 \pm 0.99	48.91 \pm 1.70	55.71
	Winter	16.45 \pm 0.87	110.99 \pm 0.43	127.44
	Spring	13.12 \pm 0.11	61.44 \pm 1.08	74.57
Mean		19.70	82.95	102.65

Nickel (Ni):

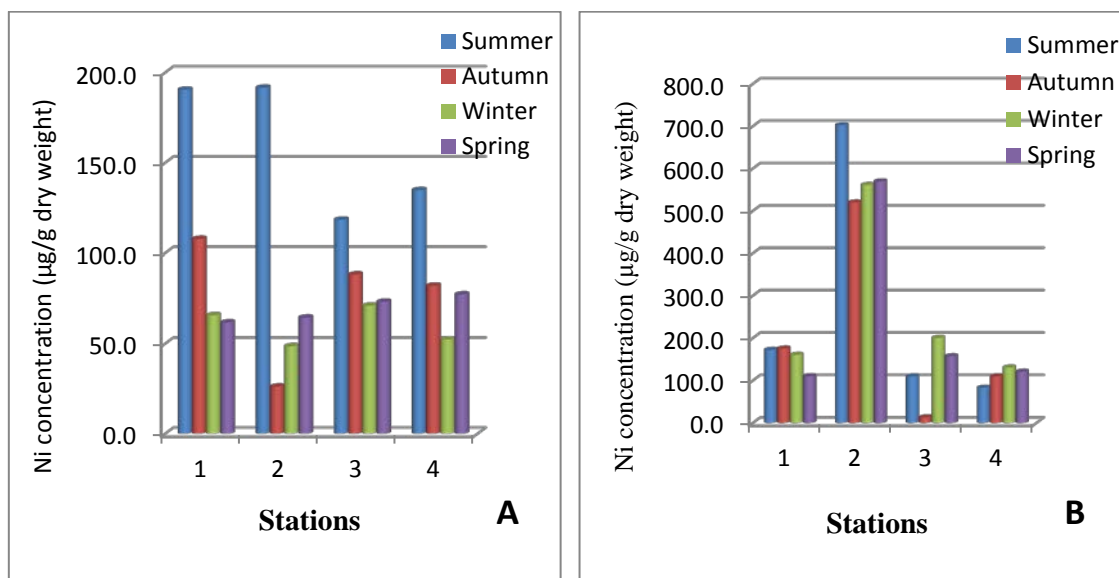
The nickel concentrations in the dissolved phase ranged from (0.20 $\mu\text{g/l}$) at station 4 in autumn to (1.05 $\mu\text{g/l}$) at station 3 in spring (Fig.18). Significant differences ($P \leq 0.05$) were found among seasons, the highest mean value (0.97 $\mu\text{g/l}$) during spring and the lowest mean value (0.32 $\mu\text{g/l}$) during summer. Whereas non-significant differences were found among stations.



(Fig.14) The concentrations of nickel in water as dissolved phase(µg/l)

In particulate phase , the concentrations in the exchangeable phase ranged from (26.16 µg/g dry weight) at station 2 in autumn to (191.60 µg/g dry weight) at station 2 in summer. Significant differences ($P \leq 0.05$) were found among seasons, the highest mean value (158.83 µg/g dry weight) was recorded in summer and the lowest mean value (59.45 µg/g dry weight) was recorded in winter, but non-significant differences were found among stations (Fig.19A).

The concentrations of nickel in the residual phase of particulate ranged from (13.33 µg/g dry weight) at station 3 in autumn season to (702.54 µg/g dry weight) at station 2 in summer . Non-significant differences were found among seasons, but significant differences ($P \leq 0.05$) were found among stations, the highest mean value (588.39 µg/g dry weight) was founded at station 2 and the lowest mean value (111.19 µg/g dry weight) was founded at station 4(Fig.19-B).



(Fig.15) The concentrations of Nickel in particulate phases: A(exchangeable) and B(residual).

In sediments, the concentrations of nickel in the exchangeable phase ranged from (14.76µg/g dry weight) at station 2 in spring to (88.07µg/g dry weight) at station 1 in summer. Significant differences ($P \leq 0.05$) were found among seasons, the highest mean value (69.71 µg/g dry weight) was recorded in summer and the lowest mean value (37.16 µg/g dry weight) was recorded in winter, also significant differences ($P \leq 0.05$) were found among stations, the highest mean value (61.96 µg/g dry weight) was recorded at station 1, while the lowest mean value (26.42 µg/g dry weight) was recorded at station 2.

Nickel concentrations in the sediments residual phase was ranged from (50.56 µg/g dry weight) at station 2 in summer to (112.56 µg/g dry weight) at station 1 in winter. Significant differences ($P \leq 0.05$) were found among stations, the highest mean value (85.97 µg/g dry weight) was recorded at station 1, and the lowest mean value (65.80 µg/g dry weight) was recorded at station 2. Also significant differences ($P \leq 0.05$) were found among seasons, the highest mean value (99.56 µg/g dry weight) was recorded in winter and the lowest mean value (60.55 µg/g dry weight) was recorded in summer (Table 8).

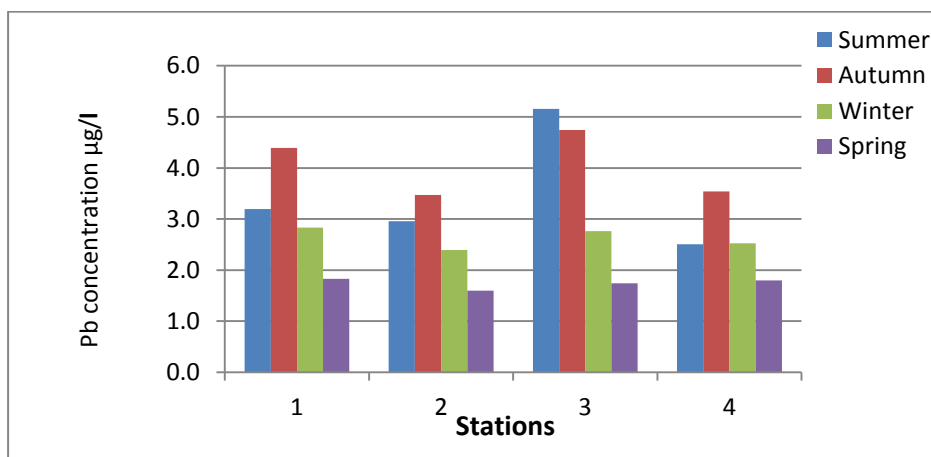
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Table(8):The concentrations of nickel in sediments at the studied stations during the studied periods (mean \pm Standard deviation (SD)).

Stations	Seasons	Exchangeablephase	Residual phase	Total
Station 1	Summer	88.07 \pm 4.43	67.51 \pm 1.10	155.59
	Autumn	55.49 \pm 2.01	83.08 \pm 4.03	138.57
	Winter	47.72 \pm 2.32	112.65 \pm 8.51	160.37
	Spring	53.82 \pm 4.75	77.96 \pm 6.24	131.79
Station 2	Summer	43.99 \pm 0.34	50.56 \pm 1.42	94.55
	Autumn	24.10 \pm 1.07	61.22 \pm 2.84	85.32
	Winter	18.94 \pm 1.29	87.06 \pm 1.52	106.00
	Spring	14.76 \pm 5.30	63.64 \pm 5.54	78.41
Station 3	Summer	81.51 \pm 0.69	66.81 \pm 1.20	148.32
	Autumn	56.38 \pm 1.15	71.56 \pm 1.12	127.95
	Winter	50.97 \pm 0.73	103.80 \pm 4.23	154.78
	Spring	37.06 \pm 1.04	75.17 \pm 1.68	112.82
Station 4	Summer	65.26 \pm 3.00	57.33 \pm 2.01	122.59
	Autumn	14.95 \pm 2.30	53.99 \pm 2.84	68.94
	Winter	31.00 \pm 1.06	94.74 \pm 0.88	125.75
	Spring	46.89 \pm 0.72	74.92 \pm 0.59	121.82
Mean		46.37	75.32	121.70

Lead (Pb):

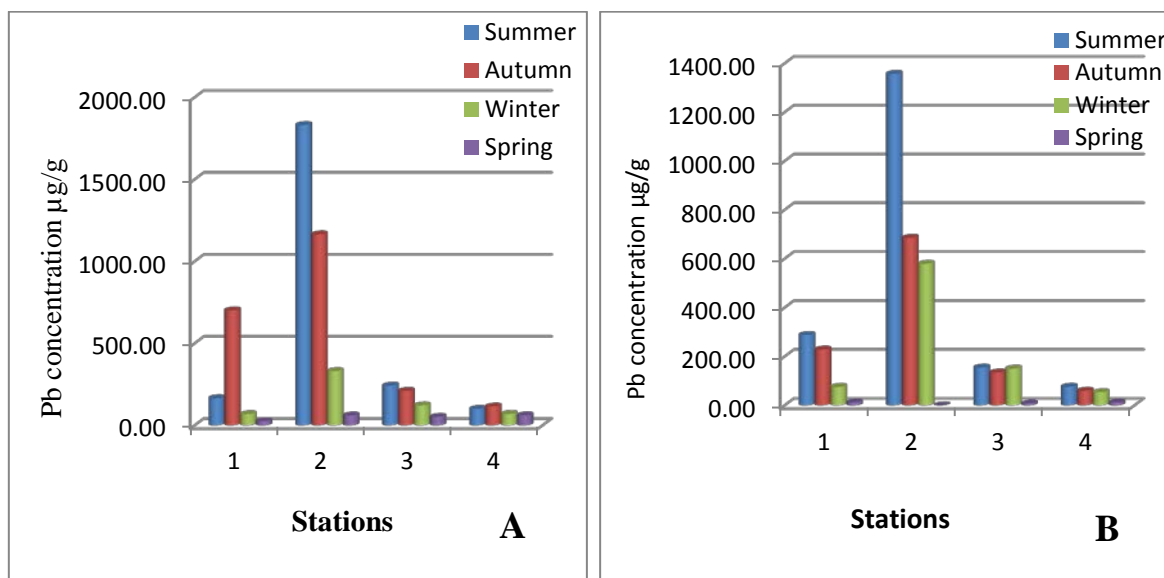
The lead concentrations in dissolved phase , was ranged from (1.59 μ g/l) at station 2 in spring to (5.15 μ g/l) at station 3 in summer (Fig.20) . Non-significant differences were found among stations. Whereas significant differences($P \leq 0.05$) were found among seasons, the highest mean value (4.04 μ g/l) during autumn and the lowest mean value (1.74 μ g/l) during spring.



(Fig.16) The concentrations of Lead in water as dissolved phase(µg/l).

In particulate phase , the concentrations in the exchangeable phase ranged from (26.14 µg/g dry weight) at station 1 in spring to (1831.24 µg/g dry weight) at station 2 in summer. ANOVA test show non-significant differences were found among stations and seasons (Fig.21-A).

The concentrations of lead in the residual phase of particulate ranged from (ND) at station 2 in spring season to (1357.27 µg/g dry weight) at station 2 in summer. Significant differences ($P \leq 0.05$) were found among stations, the highest mean value (655.5 µg/g dry weight) was recorded at station 2 and the lowest mean value (50.5µg/g dry weight) was recorded at station 4. While non- significant differences were found among seasons (Fig.21-B).



(Fig.17):The concentrations of lead (µg/g dry weight)in particulate phases: A(exchangeable) and B(residual).

In sediments, the concentrations of lead in the exchangeable phase ranged from (18.53µg/g dry weight) at station 3 in spring to (30.45.18 µg/g dry weight) at station 1 in autumn. Non- significant differences were found among stations, while significant differences ($P \leq 0.05$) were found among seasons, the highest mean value (28.86 µg/g dry weight) was recorded in autumn, while the lowest mean value (21.69 µg/g dry weight) was recorded in spring.

In the residual phase of sediments the concentrations of lead ranged from (6.44 µg/g dry weight) at station 2 in spring to (19.61 µg/g dry weight) at station 4 in winter . Significant differences ($P \leq 0.05$) were found among seasons, the highest mean value (17.88 µg/g dry weight) was recorded in winter and the lowest mean value (7.24 µg/g dry weight) was recorded in spring .While among stations non- significant differences (Table 9) .

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Table(9):The concentrations of lead in sediments at the studied stations during the studied periods (mean \pm Standard deviation (SD)).

Stations	Seasons	Exchangeablephase	Residual phase	Total
Station 1	Summer	23.04 \pm 1.10	15.74 \pm 0.72	38.79
	Autumn	30.45 \pm 1.24	16.64 \pm 0.95	47.10
	Winter	27.91 \pm 1.01	16.65 \pm 0.50	44.56
	Spring	23.41 \pm 1.84	7.74 \pm 0.61	31.16
Station 2	Summer	20.32 \pm 0.58	13.09 \pm 1.50	33.42
	Autumn	28.54 \pm 0.88	14.66 \pm 1.27	43.21
	Winter	26.15 \pm 0.99	17.59 \pm 1.21	43.75
	Spring	19.49 \pm 5.41	6.44 \pm 0.49	25.94
Station 3	Summer	24.19 \pm 0.73	16.28 \pm 0.54	40.48
	Autumn	29.18 \pm 0.88	17.21 \pm 0.42	46.39
	Winter	24.74 \pm 0.50	17.66 \pm 0.93	42.41
	Spring	18.53 \pm 0.36	7.22 \pm 0.61	25.76
Station 4	Summer	24.31 \pm 0.68	14.96 \pm 0.89	39.27
	Autumn	27.26 \pm 1.60	11.89 \pm 0.56	39.17
	Winter	25.68 \pm 0.72	19.61 \pm 1.85	45.31
	Spring	25.32 \pm 0.61	7.57 \pm 0.36	32.90
Mean		25.20	14.41	39.62

Heavy metals in plants :

Phragmites australis

The concentrations of cadmium in *P. australis* was ranged from (0.03 $\mu\text{g/g}$ dry weight) at station 3,4 in spring to (0.29 $\mu\text{g/g}$ dry weight) at station 3 in winter (Fig.22-A) Non-significant differences were found among stations .But significant differences ($P \leq 0.05$) were found among seasons, the highest mean value (0.259 $\mu\text{g/g}$ dry weight) was recorded in winter and the lowest mean value (0.04 $\mu\text{g/g}$ dry weight) was recorded in spring.

The concentrations of chromium in *P. australis* was ranged from (1.06 $\mu\text{g/g}$ dry weight) at station 2 in summer to (12.52 $\mu\text{g/g}$ dry weight) at station

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2 in winter (Fig.22-B) Non-significant differences were found among stations .Whereas significant differences ($P \leq 0.05$) were found among seasons, the highest mean value ($11.19 \mu\text{g/g}$ dry weight) was recorded in winter and the lowest mean value ($1.95 \mu\text{g/g}$ dry weight) was recorded in summer.

The concentrations of nickel in *P. australis* was ranged from ($0.83 \mu\text{g/g}$ dry weight) at station 2 in summer to ($8.80 \mu\text{g/g}$ dry weight) at station 4 in winter (Fig.22-C) Non-significant differences were found among stations. Whereas significant differences ($P \leq 0.05$) were found among seasons, the highest mean value ($7.65 \mu\text{g/g}$ dry weight) was founded in winter and the lowest mean value ($2.01 \mu\text{g/g}$ dry weight) was founded in summer.

The concentrations of lead in *P. australis* was ranged from (1.02g dry weight) at station 2 in spring to ($37.19 \mu\text{g/g}$ dry weight) at station 3 in autumn (Fig.22-D) Non-significant differences were found among stations or among seasons.

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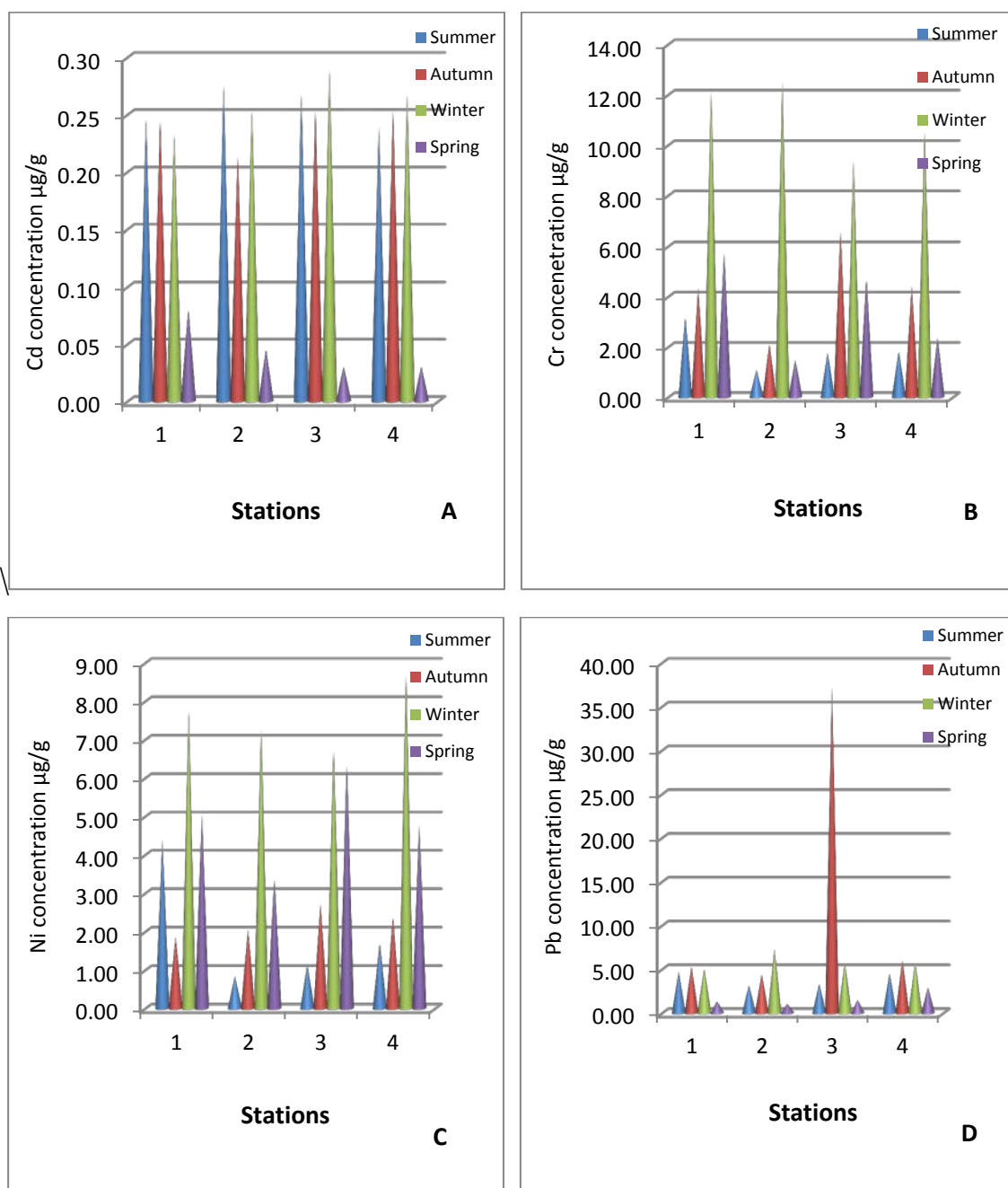


Fig.(18) Concentrations of heavy elements A(Cd),B(Cr),C(Ni),D(Pb ($\mu\text{g/g}$ dry weight) in *Phragmites australis*.

Typha domingensis :

The lowest concentration of Cd in *T. domingensis* was (ND) in spring at station 2, while the highest concentration was (0.39 µg/g dry weight) in winter at station 3 (Fig 23-A). ANOVA test show non-significant differences were found among stations ,but significant differences ($P \leq 0.05$) were found among seasons, the highest mean value (0.30 µg/g dry weight) was recorded in winter and the lowest mean value (0.03 µg/g dry weight) was recorded in spring .

The concentration of Cr in *T. domingensis* was ranged from (ND) in spring at station 4, to (12.28 µg/g dry weight) in winter at station 3 (Fig.23-B). Non-significant differences were found among stations ,while significant differences ($P \leq 0.05$) were found among seasons, the highest mean value (11.08 µg/g dry weight) was recorded in winter and the lowest mean value (0.73 µg/g dry weight) was recorded in autumn.

The concentration of Ni in *T. domingensis* was ranged from (0.35 µg/g) in autumn at station 2 and station 3, to (7.30 µg/g dry weight) in winter at station 3 (Fig.23-C). Non-significant differences were found among stations ,while significant differences ($P \leq 0.05$) were found among seasons, the highest mean value (6.52 µg/g dry weight) was founded in winter and the lowest mean value (0.62 µg/g dry weight) was recorded in autumn.

The concentration of Pb in *T. domingensis* was ranged from (2.32 µg/g dry weight) in spring at station 4 to (11.29 µg/g dry weight) in winter at station 2 (Fig.23-D). Non-significant differences were found among stations ,while significant differences ($P \leq 0.05$) were found among seasons, the highest mean value (8.30 µg/g dry weight) was founded in winter and the lowest mean value (2.52 µg/g dry weight) was recorded in spring.

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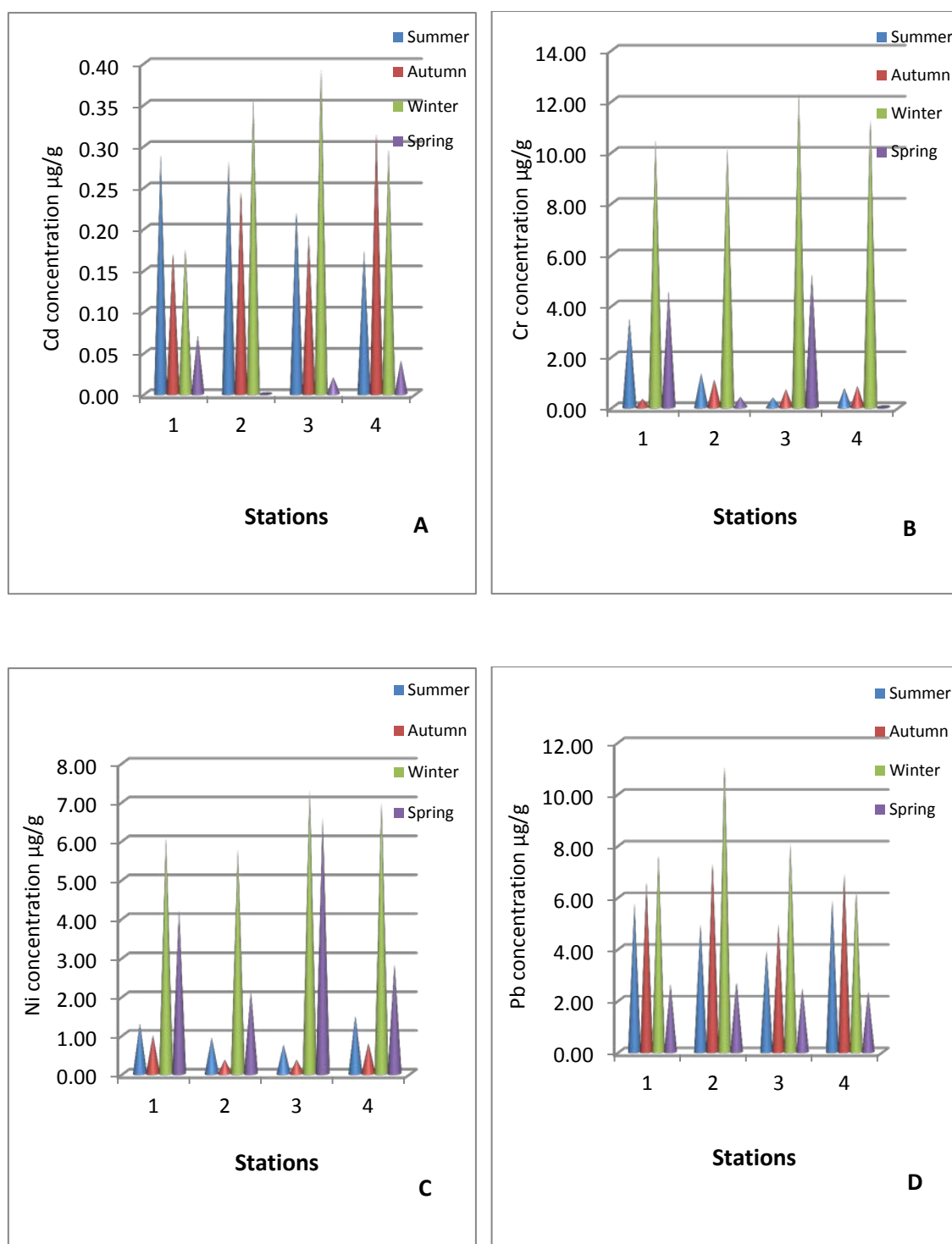


Fig.(19) Concentrations of heavy elements A(Cd),B(Cr),C(Ni),D(Pb) ($\mu\text{g/g}$ dry weight) in *Typha domingensis*

Schoenoplectus litoralis:

Note: *S. litoralis* wasn't found at station 2.

The concentration of Cd in *S. litoralis* was ranged from (0.04 µg/g dry weight) in spring at station 3, to (0.33 µg/g) in summer at station 3 (Fig.24-A). Non-significant differences were found among stations, while significant differences ($P \leq 0.05$) were found among seasons, the highest mean value (0.26 µg/g dry weight) was recorded in summer and the lowest mean value (0.06 µg/g dry weight) was recorded in spring.

The concentration of Cr in *S. litoralis* was ranged from (0.60 µg/g dry weight) in spring at station 4, to (12.28 µg/g dry weight) in winter at station 3 (Fig.24-B). Non-significant differences were found among stations, while significant differences ($P \leq 0.05$) were found among seasons, the highest mean value (11.39 µg/g dry weight) was recorded in winter and the lowest mean value (1.78 µg/g dry weight) was recorded in autumn .

The concentration of Ni in *S. litoralis* was ranged from (0.69 µg/g dry weight) in summer at station 3, to (7.67 µg/g dry weight) in winter at station 4 (Fig.24-C). Non-significant differences were found among stations or among seasons.

The concentration of Pb in *S. litoralis* was ranged from (1.16 µg/g dry weight) in spring at station 3, to (6.57 µg/g dry weight) in winter at station 1 (Fig.24-D). Non-significant differences were found among stations ,but significant differences ($P \leq 0.05$) were found among seasons, the highest mean value (5.72 µg/g dry weight) was recorded in autumn and the lowest mean value (2.12 µg/g dry weight) was recorded in spring.

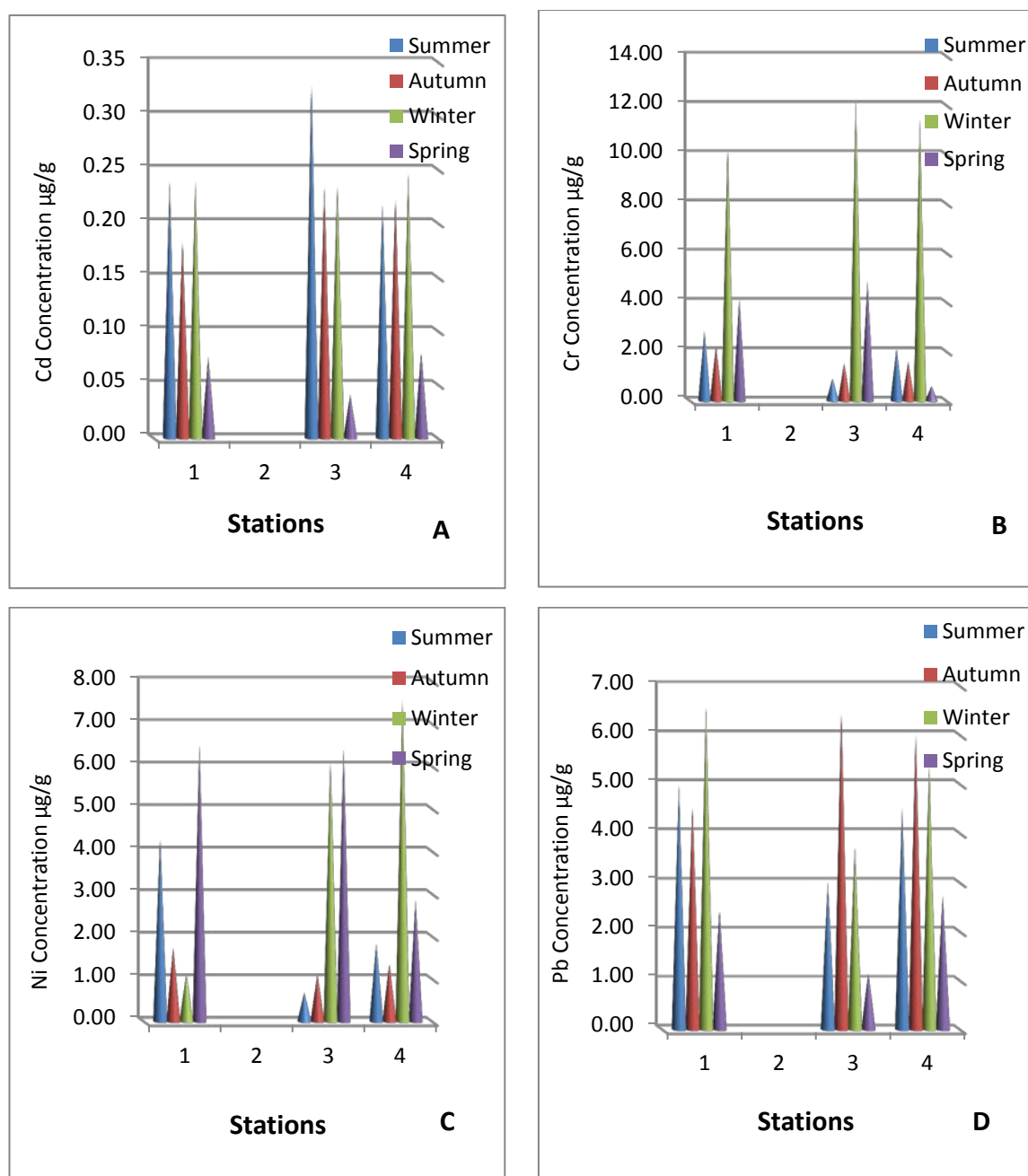


Fig.(20) Concentrations of heavy elements A(Cd),B(Cr),C(Ni),D(Pb) ($\mu\text{g/g}$ dry weight) in *Schoenoplectus litoralis*

***Ceratophyllum demersum*:**

Note : *C. demersum* wasn,t found at station 2.

The concentration of Cd in *C. demersum* was ranged from (0.34 µg/g dry weight) in spring at station 4, to (0.87 µg/g) in summer at station 4(Fig.25-A). Non-significant differences were found among stations or among seasons.

The concentration of Cr in *C. demersum* was ranged from (2.18 µg/g) in summer at station 1, to (23.35 µg/g) in winter at station 4(Fig.25-B). Non-significant differences were found among stations, while significant differences ($P \leq 0.05$) were found among seasons, the highest mean value (18.21µg/g dry weight) was recorded in winter and the lowest mean value (4.29 µg/g dry weight) was recorded in summer.

The concentration of Ni in *C. demersum* was ranged from (35.14 µg/g) in autumn at station 3,to (74.20 µg/g) in spring at station 1(Fig.25-C). Non-significant differences were found among stations or among seasons.

The concentration of Pb in *C. demersum* was ranged from (5.56 µg/g) in winter at station 3, to (13.99 µg/g) in autumn at station 1(Fig.25-D). Non-significant differences were found among stations or among seasons.

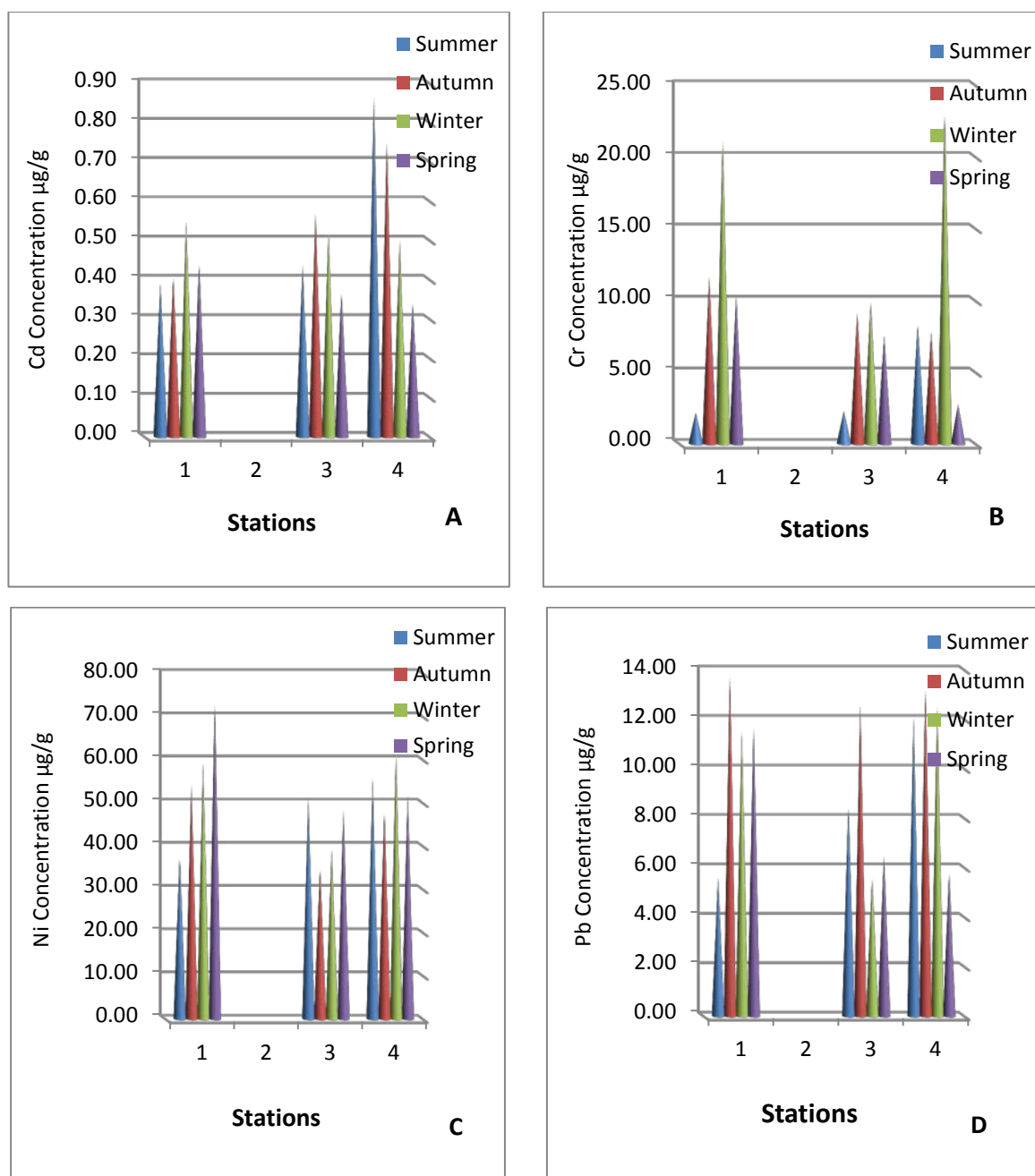
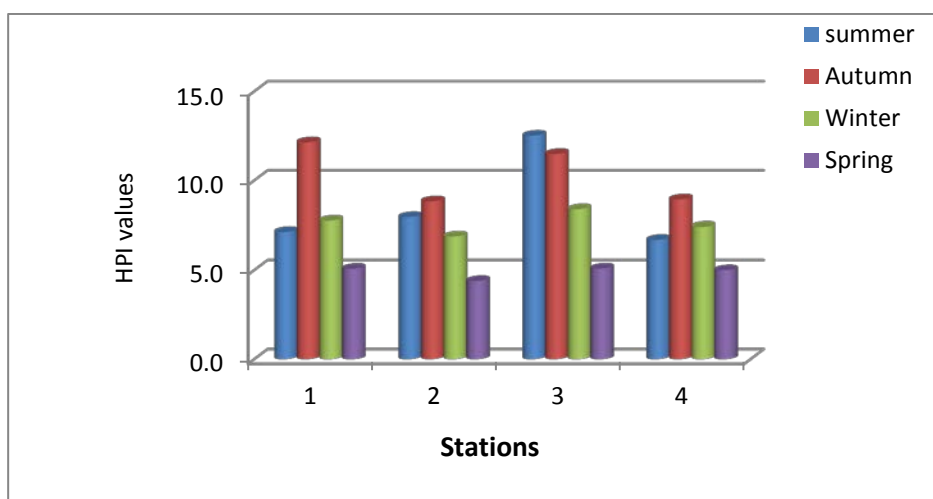


Fig.(21)Concentrations of heavy elements A(Cd),B(Cr),C(Ni),D(Pb)($\mu\text{g/g}$ dry weight)in *Ceratophyllum demersum* .

3.2.1-Heavy metal Pollution Indices:

3.2.1.1-The Heavy Metals Pollution Index(HPI):

The highest value of HPI (12.512) was found at station 3 in summer , while the lowest value (4.385) was found at station 2 in spring (Fig.26). ANOVA test showed non-significant differences were found among stations ,but significant differences ($P \leq 0.05$) were found among seasons. The highest mean value(10.346) was recorded in autumn and the lowest mean value (4.736) was recorded in spring. Generally, the water was unpolluted with heavy metals along the studied period at all the studied stations.



Fig(22)The HPI values at the studied stations during the studied periods

3.2.1.2- The Geo-accumulation Index (I_{geo}):

The values of I_{geo} in sediments for cadmium ranged from (-4.09, unpolluted) at station 3 in spring to(-0.61 , unpolluted) at station 4 in winter (Table 10). Non- significant differences were found among stations. While significant differences ($P \leq 0.05$) were found among seasons, the lowest mean value (-2.87 unpolluted) was found in spring , but the highest mean value (-0.90unpolluted) was found in winter.

The values of I_{geo} in sediments for chromium ranged from (-0.44 , unpolluted) at station 2 in spring to (1.29 , moderately polluted) at station 3 in

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winter (Table 10). Significant differences ($P \leq 0.05$) were found among seasons, the lowest mean value (0.02 unpolluted to moderately) was found in spring, but the highest mean value (1.07 moderately polluted) was found in winter. Also significant differences ($P \leq 0.05$) were found among stations, the lowest mean value (0.25 unpolluted to moderately) was found at station 2, but the highest mean value (0.86 moderately polluted) was found at station 3.

The values of I_{geo} in sediments for nickel ranged from (1.00, moderately polluted) at station 4 in autumn to (2.22, moderate to strongly polluted) at station 1 in winter (Table 10). Significant differences ($P \leq 0.05$) were found among seasons, the lowest mean value (1.55 moderately polluted) was found in autumn, but the highest mean value (1.97 moderately polluted) was found in winter. Also significant differences ($P \leq 0.05$) were found among stations, the lowest mean value (1.41 moderately polluted) was found at station 2, but the highest mean value (2.1 moderate to strongly polluted) was found at station 1.

The values of I_{geo} in sediments for lead ranged from (-1.07, unpolluted) at station 2 in spring to (-0.20, unpolluted) at station 1 in autumn (Table 10). Significant differences ($P \leq 0.05$) were found among seasons, the lowest mean value (-0.91 unpolluted) was found in spring, but the highest mean value (-0.29 unpolluted) was found in winter. Non-significant differences were found among stations.

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Table(10):The I-geo values and descriptions the status of sediments pollution at the studied stations during periods of the study.

Stations	Season	I-geo Cd value	Description	I-geo Cr value	Descriptions	I-geo Ni value	Descriptions	I-geo Pb value	Descriptns
Station 1	Summer	-1.06	unpolluted	0.72	U-MPolluted	2.17	M –S polluted	-0.48	unpolluted
	Autumn	-0.77	unpolluted	0.85	U-MPolluted	2.00	M –S polluted	-0.20	unpolluted
	Winter	-0.89	unpolluted	1.27	Moderately	2.22	M –S polluted	-0.28	unpolluted
	Spring	-2.06	unpolluted	0.21	U-MPolluted	1.93	Moderately	-0.79	unpolluted
Station 2	Summer	-1.09	unpolluted	0.32	U-MPolluted	1.45	Moderately	-0.69	unpolluted
	Autumn	-0.92	unpolluted	0.17	U-MPolluted	1.31	Moderately	-0.32	unpolluted
	Winter	-1.08	unpolluted	0.72	U-MPolluted	1.62	Moderately	-0.30	unpolluted
	Spring	-3.28	unpolluted	-0.44	Unpolluted	1.18	Moderately	-1.07	unpolluted
Station 3	Summer	-0.86	unpolluted	1.00	Moderately	2.10	M –S polluted	-0.42	unpolluted
	Autumn	-0.99	unpolluted	0.81	U-MPolluted	1.89	Moderately	-0.22	unpolluted
	Winter	-1.02	unpolluted	1.29	Moderately	2.17	M –S polluted	-0.35	unpolluted
	Spring	-4.09	unpolluted	0.08	U-MPolluted	1.70	Moderately	-1.06	unpolluted
Station 4	Summer	-0.77	unpolluted	0.73	U-MPolluted	1.82	Moderately	-0.46	unpolluted
	Autumn	-1.21	unpolluted	-0.21	Unpolluted	1.00	Moderately	-0.46	unpolluted
	Winter	-0.61	unpolluted	0.98	U-MPolluted	1.87	Moderately	-0.25	unpolluted
	Spring	-2.09	unpolluted	0.21	U-MPolluted	1.82	Moderately	-0.71	unpolluted

3.2.1.3- Bioaccumulation Factor (BAF) in aquatic plant:

Bioaccumulation Factor (BAF) in emergent species was calculated according to the concentration of heavy elements in plants tissue to sediments, while in submergent species was calculated according to the concentration of heavy elements in plants tissues to water (Table 11).

Result showed that the mean value of BAF of different elements in aquatic plants species followed an order as mentioned below.

Cd: *C. demersum* > *T.domingensis* > *P. australis* > *S. litoralis*.

Cr: *C. demersum* > *P. australis* > *S. litoralis* > *T.domingensis*.

Ni: *C. demersum* > *P. australis* > *S. litoralis* > *T.domingensis*.

Pb: *C. demersum* > *P. australis* > *T.domingensis* > *S. litoralis*

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Table (11): Bioaccumulation Factor (BAF) of heavy elements in aquatic plants

Plant species	Metals	Metal concentration in plant	Metal concentration Water and sediment	BAF
<i>P. australis</i>	Cd	0.20	0.65 (S)	31.01
	Cr	5.27	99.62 (S)	5.29
	Ni	4.20	120.81 (S)	3.48
	Pb	6.19	38.7 (S)	15.99
<i>T.domingensis</i>	Cd	0.20	0.65 (S)	31.15
	Cr	3.96	99.62 (S)	3.97
	Ni	3.05	120.81 (S)	2.52
	Pb	5.61	38.73 (S)	14.47
<i>S. litoralis</i>	Cd	0.20	0.65 (S)	30
	Cr	4.58	99.62 (S)	4.60
	Ni	3.49	120.81 (S)	2.89
	Pb	4.31	38.73 (S)	11.13
<i>C. demersum:</i>	Cd	0.51	0.06 (W)	895050
	Cr	9.73	2.03 (W)	479900
	Ni	51.44	0.56 (W)	9259230
	Pb	9.99	2.97 (W)	336850

S: metal concentration in sediments ($\mu\text{g/g}$ dry weight ppm)

W: metal concentration in water ($\mu\text{g/l}$ ppb)

3.3-The Hydrocarbons:

3.3.1-Total Petroleum Hydrocarbons (TPHs):

3.3.1.1- TPHs in water :

The concentrations of TPHs in water samples ranged from ($1.91\mu\text{g/l}$) at station 1 in summer to ($6.79 \mu\text{g/l}$) at station 4 in inter. Non-significant differences were found among stations, the highest mean value ($3.79 \mu\text{g/l}$) was recorded at station 3 and the lowest mean value ($2.14 \mu\text{g/l}$) was recorded at station 1 (Fig.27). Also non-significant differences were found among

seasons, the highest mean value ($4.38 \mu\text{g/l}$) was recorded in winter and the lowest mean value ($1.34 \mu\text{g/l}$) was recorded in summer (Fig.28).

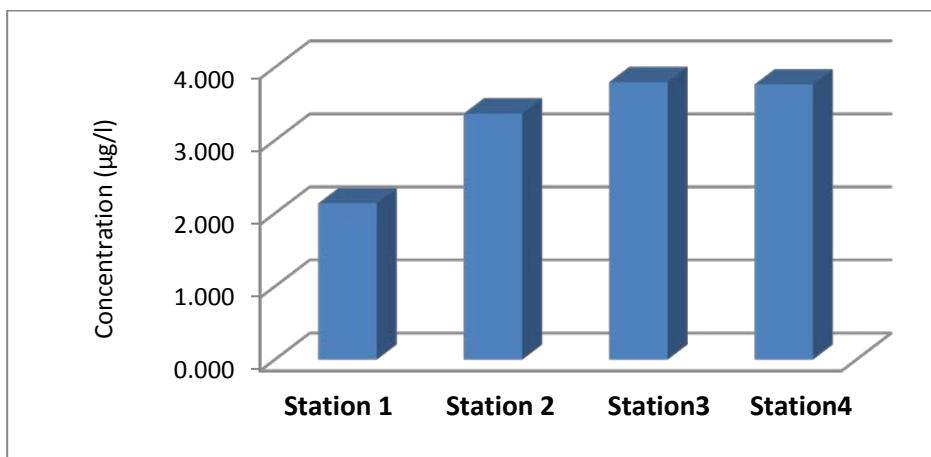


Fig.(23) : Regional variations of TPHs ($\mu\text{g/l}$) in water samples during the studied periods.

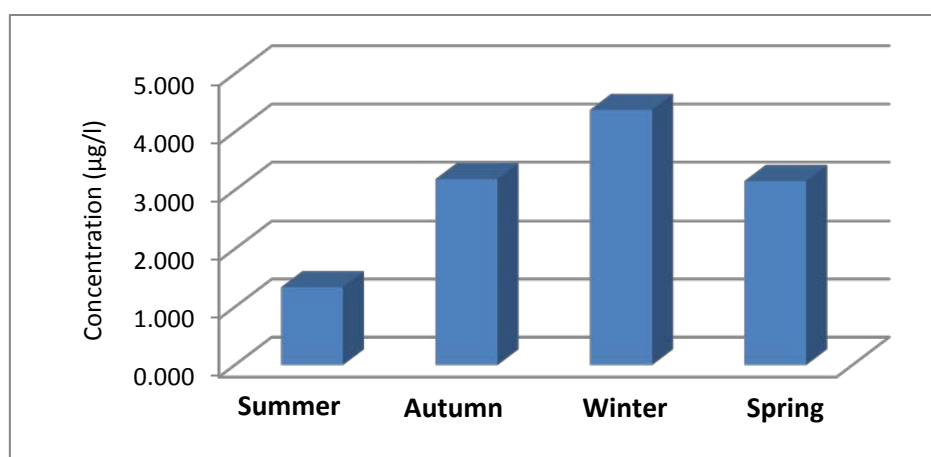


Fig.(24) : Seasonal variations of TPHs ($\mu\text{g/l}$) in water samples at the studied stations.

3.3.1.2-TPHs in sediments:

The concentrations of TPHs in sediments samples were greater than those in water samples and ranged from ($2.98 \mu\text{g/g}$) at station 2 in summer to ($17.98 \mu\text{g/g}$) at station 4 in winter. Non-Significant differences were found among stations, the highest mean value ($15.14 \mu\text{g/g}$) was founded at station 4, while the lowest mean value ($5.59 \mu\text{g/g}$) was founded at station 3 (Fig.29). Significant differences at ($P \leq 0.05$) were found among seasons, the highest

mean value ($13.23 \mu\text{g/g}$) was founded in winter, while the lowest mean value ($5.29 \mu\text{g/g}$) was founded in summer (Fig.30).

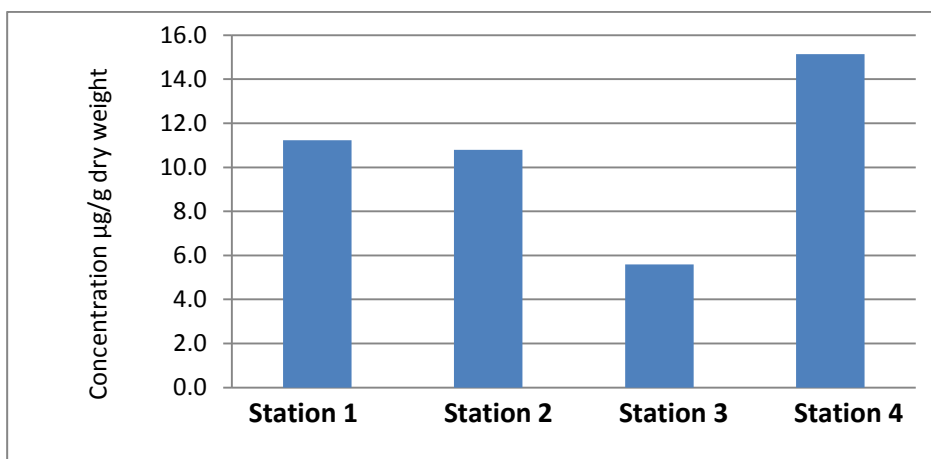


Fig.(25): Regional variations of TPHs ($\mu\text{g/g dry weight}$) in sediments samples during the studied periods.

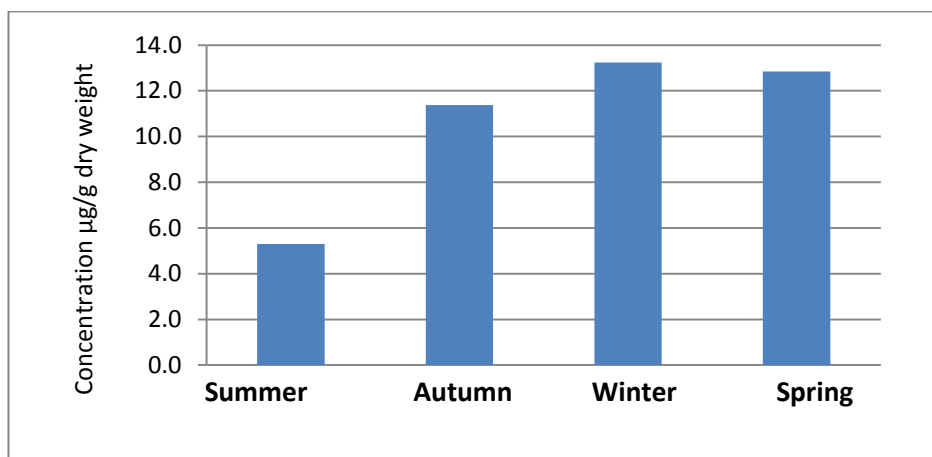


Fig.(26) : Seasonal variations of TPHs ($\mu\text{g/g dry weight}$) in sediments samples at the studied stations.

3.3.1.3-TPHs in aquatic plants:

TPHs in *Phragmites australis* :

The concentrations of TPHs in *P. australis* species during the four seasons ranged from ($6.00 \mu\text{g/g dry weight}$) at station 1 in winter to ($34.910 \mu\text{g/g dry weight}$) at station 4 in summer. Non-significant differences were found among stations, the highest mean value ($18.56 \mu\text{g/g dry weight}$) was recorded at station 4 and the lowest mean value ($9.58 \mu\text{g/g dry weight}$) was

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recorded at station 1. Significant differences ($P \leq 0.05$) were found among seasons, the highest mean value ($20.67 \mu\text{g/g}$ dry weight) was recorded in summer and the lowest mean value ($8.25 \mu\text{g/g}$ dry weight) was recorded in winter. (Fig.31)

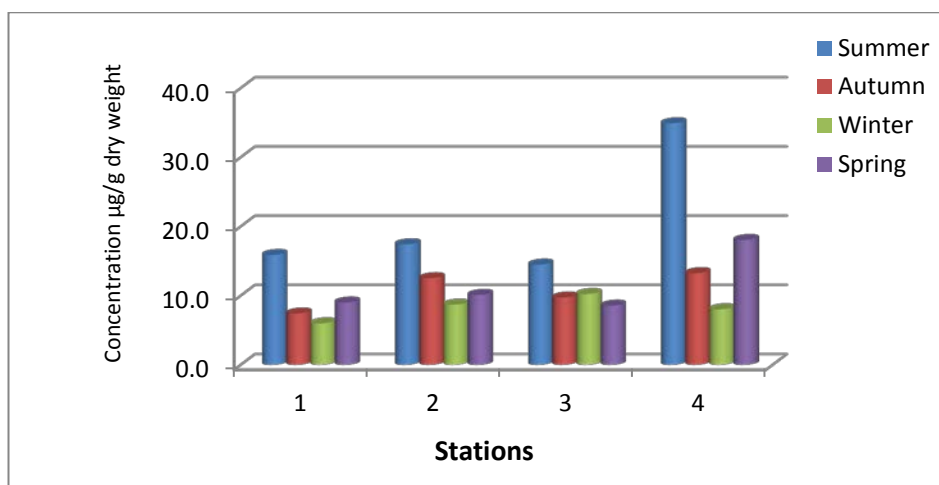
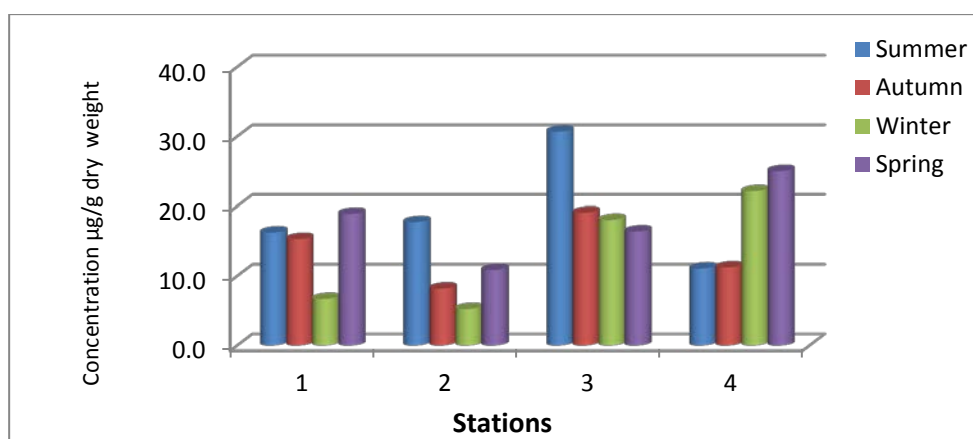


Fig (27): Seasonal variations of TPHs ($\mu\text{g/gd.w}$) *P. australis* from different sampling stations.

TPHs in *Typha domingensis*

The concentrations of TPHs in *T. domingensis* speices during the four seasons ranged from ($5.25 \mu\text{g/g}$ dry weight) at station 2 in winter to ($30.68 \mu\text{g/g}$ dry weight) at station 3 in summer. Non-significant differences were found among stations or among seasons. (Fig.32)



Fig(28): Seasonal variations of TPHs ($\mu\text{g/gd.w}$) *T. domingensis* from different sampling stations.

TPHs in *Schoenoplectus litoralis*:

The concentrations of TPHs in *S. litoralis* speices during the study period ranged from (7.78 $\mu\text{g/g}$ dry weight) at station 3in winter to (30.74 $\mu\text{g/g}$ dry weight) at station 1 in summer. Non–significant differences were found among stations or among seasons. (Fig.33).

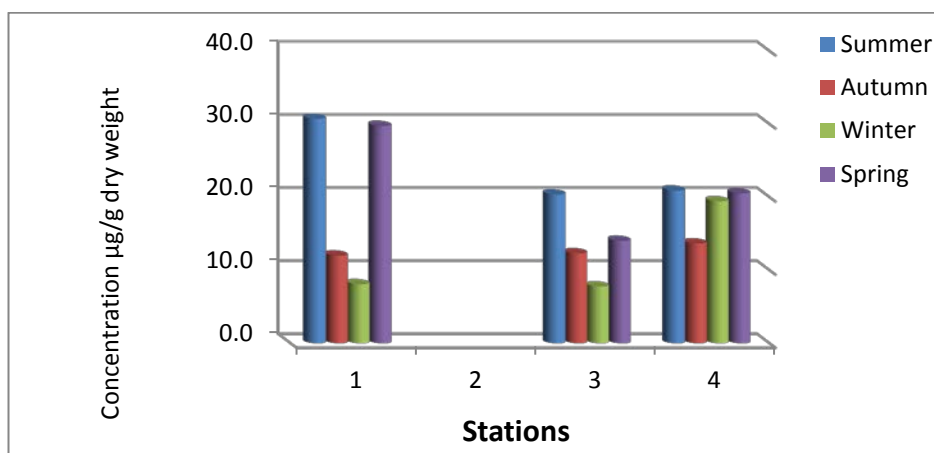


Fig (29):Seasonal variations of TPHs ($\mu\text{g/gd.w}$) *S. litoralis* from different sampling stations.

TPHs in *Ceratophyllum demersum*:

The concentrations of TPHs in *C. demersum* species during the study period ranged from (9.01 $\mu\text{g/g}$ dry weight) at station 1in winter to (34.29 $\mu\text{g/g}$ dry weight) at station 3 in summer. significant differences ($P \leq 0.05$) were found among seasons the highest mean value (25.73 $\mu\text{g/g}$) was founded in Summer, while the lowest mean value (10.00 $\mu\text{g/g}$) was founded in winter, non–significant differences were found among stations.(Fig.34).

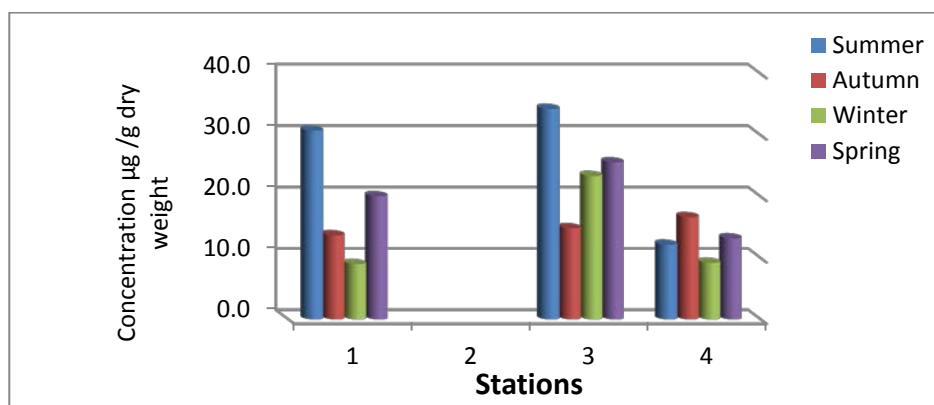


Fig (30):Seasonal variations of TPHs ($\mu\text{g/gd.w}$) *C. demersum* from different sampling stations

3.3.2-The Normal Alkanes (N-alkanes):

3.3.2.1-N-alkanes in water :

The carbon chains length of n-alkanes in water samples were recorded from C16-C36, the dominant of odd carbon were C23,C25,C27,C29,while the dominant of even carbon were C20,C22,C24,C26,C30. Fig(35) explain the percentage of n-alkane compound in water. The other of hydrocarbons compounds numbers present in the aliphatic fraction , including pristane and phytane. The seasonal values of n-alkanes in water at the studied stations were illustrated in tables (12-15).

The highest concentrations of n-alkanes in water (2.98 μ g/l) was recorded at station 2 in winter , while the lowest concentrations (0.32 μ g/l) was recorded at station 4 in summer, significant differences($P \leq 0.05$) were found among seasons. The highest mean value (1.91 μ g/l) was recorded in winter , while the lowest mean value (0.61 μ g/l) was recorded in summer (Fig.36). While non-significant differences were found among stations (Fig.37).

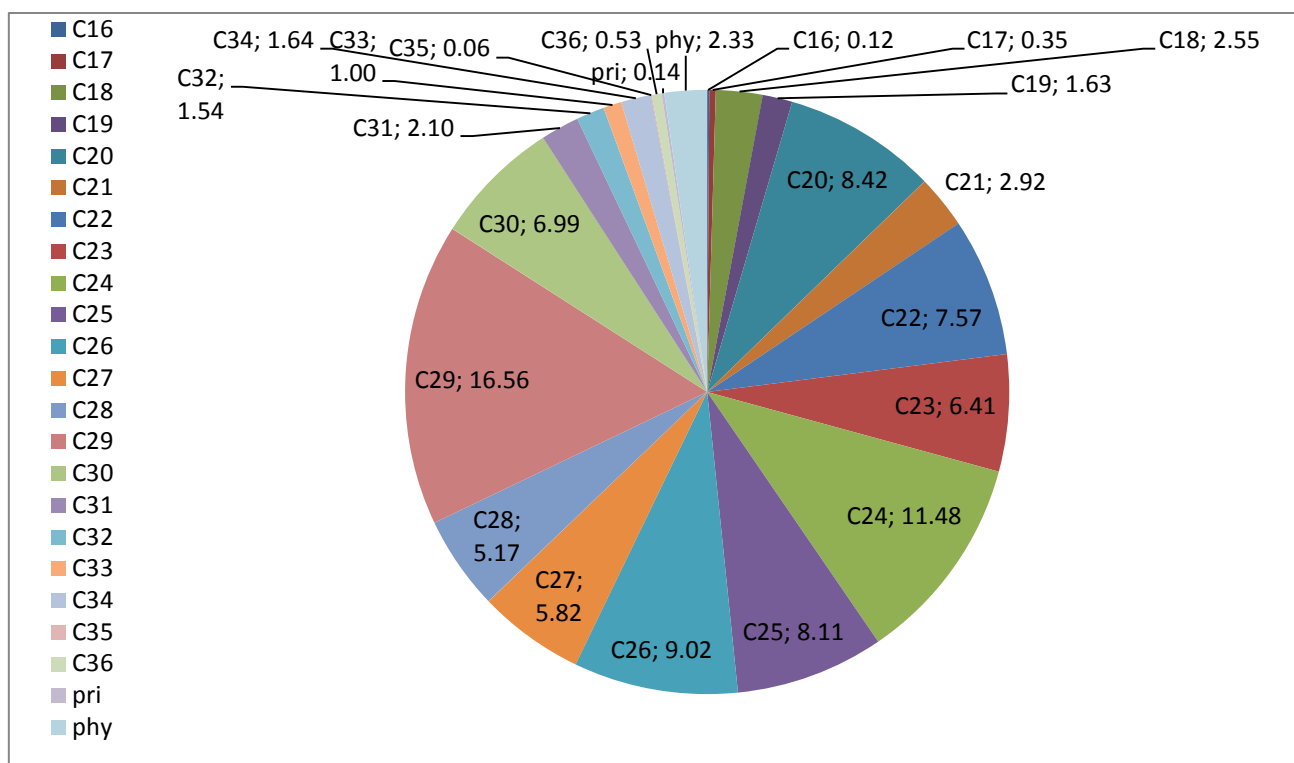


Fig.(31): The percentage of n-alkanes hydrocarbons in water samples during studied periods .

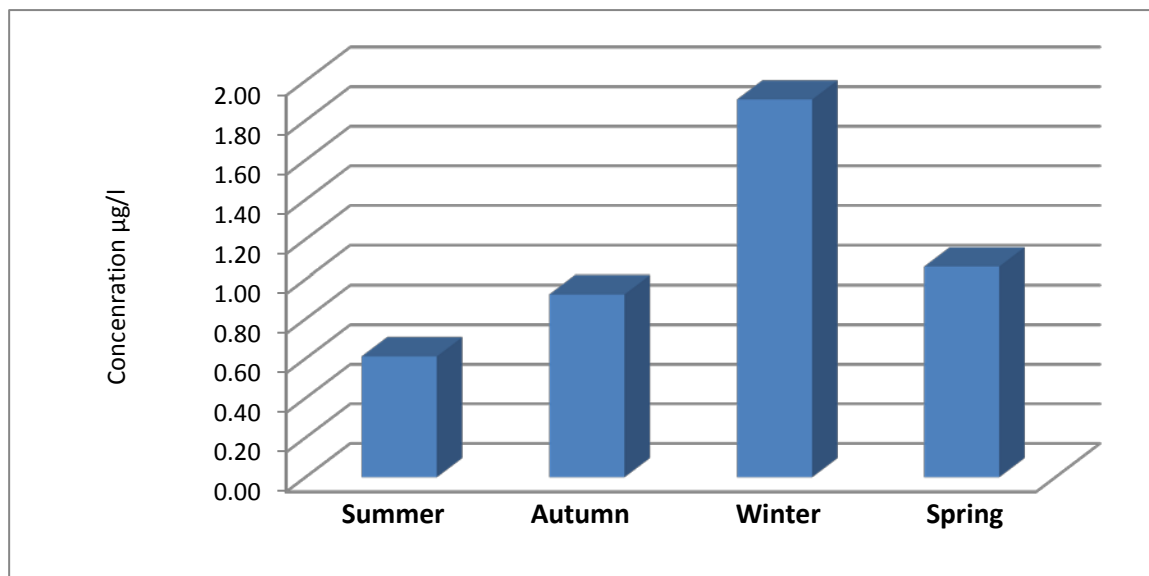


Fig.(32): Seasonal variations in total n-alkanes hydrocarbons ($\mu\text{g/l}$) in water samples during the studied periods.

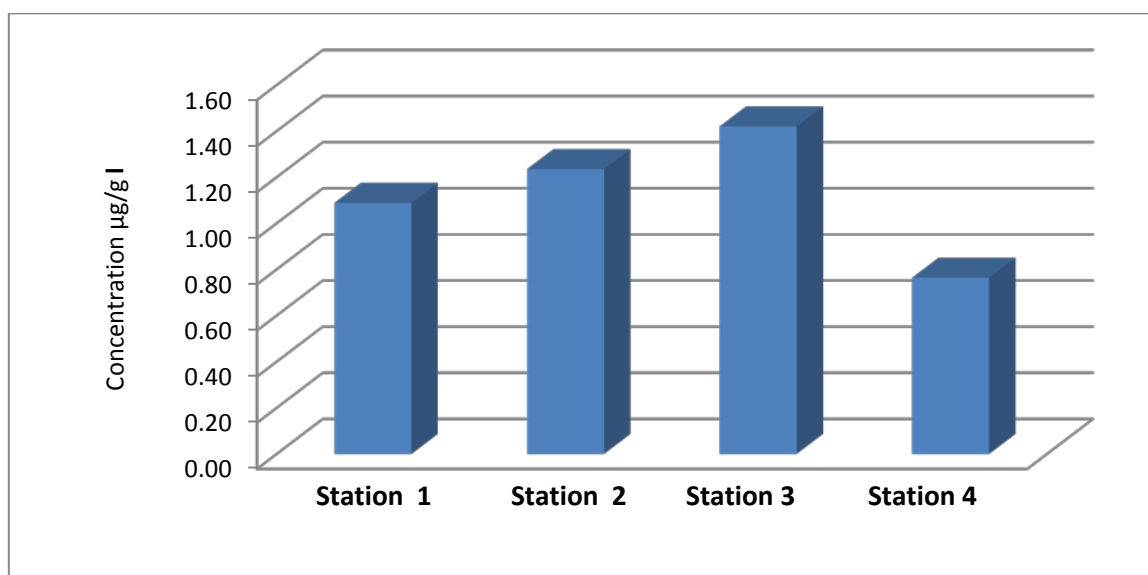


Fig.(33): Regional variations in total n-alkanes hydrocarbons ($\mu\text{g/l}$) in water samples during the studied periods.

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Table(12): N-alkanes hydrocarbons concentrations in water (µg/l) at the studied stations during summer season.

Carbon number	Stations			
	St(1)	St(2)	St(3)	St(4)
C16	ND	ND	ND	0.021
C17	0.007	0.004	0.006	0.013
C18	0.033	0.009	0.029	0.037
C19	0.017	0.006	0.013	0.010
C20	0.036	0.009	0.028	0.005
C21	0.009	0.009	0.027	0.011
C22	0.040	0.015	0.044	0.026
C23	0.026	0.019	0.052	0.021
C24	0.032	0.029	0.060	0.031
C25	0.030	0.035	0.122	0.017
C26	0.034	0.030	0.069	0.021
C27	0.034	0.045	0.100	0.020
C28	0.026	0.047	0.051	0.013
C29	0.048	0.145	0.102	0.010
C30	0.017	0.128	0.045	0.005
C31	0.027	0.073	0.050	ND
C32	0.005	0.023	0.018	ND
C33	0.011	0.027	0.034	ND
C34	0.021	0.055	0.011	0.061
C35	ND	ND	0.011	ND
C36	0.074	ND	0.022	ND
Total	0.529	0.706	0.892	0.320
odd	0.209	0.362	0.515	0.102
even	0.319	0.345	0.377	0.219
Pristane	ND	ND	0.011	ND
Phytane	0.033	0.012	0.038	0.025
Pri/Phy	ND	ND	0.296	ND
CPI	0.656	1.050	1.368	0.465

ND: not detect

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Table(13): N-alkanes hydrocarbons concentrations in water (µg/l) at the studied stations during autumn season.

Carbon number	Stations			
	St(1)	St(2)	St(3)	St(4)
C16	ND	ND	ND	ND
C17	ND	ND	ND	0.004
C18	ND	ND	0.044	0.009
C19	0.016	ND	0.024	0.007
C20	0.040	0.035	0.037	0.010
C21	0.041	0.037	0.029	0.022
C22	0.088	0.080	0.068	0.026
C23	0.119	0.112	0.090	0.029
C24	0.170	0.148	0.147	0.035
C25	0.136	0.124	0.115	0.060
C26	0.125	0.126	0.108	0.026
C27	0.097	0.076	0.077	0.050
C28	0.067	0.046	0.060	0.028
C29	0.066	0.030	0.047	0.040
C30	0.091	0.032	0.067	0.023
C31	0.058	0.034	0.031	0.010
C32	0.058	0.022	0.038	0.009
C33	0.058	ND	0.039	0.011
C34	0.047	ND	0.035	0.065
C35	ND	ND	ND	ND
C36	ND	ND	ND	ND
Total	1.277	0.902	1.056	0.464
odd	0.591	0.413	0.452	0.232
even	0.686	0.489	0.604	0.232
Pristane	ND	ND	ND	ND
Phytane	ND	ND	0.056	0.011
Pri/Phy	ND	ND	ND	ND
CPI	0.860	0.846	0.749	1

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Table(14): N-alkanes hydrocarbons concentrations in water (µg/l) at the studied stations during winter season.

Carbon number	Station s			
	St(1)	St(2)	St(3)	St(4)
C16	ND	ND	ND	ND
C17	ND	ND	ND	ND
C18	0.0324	0.020	0.032	0.029
C19	0.0427	0.034	0.036	0.041
C20	0.0514	0.033	0.053	0.046
C21	0.1285	0.083	0.058	0.109
C22	0.1497	0.095	0.139	0.161
C23	0.1920	0.120	0.182	0.200
C24	0.1978	0.124	0.226	0.210
C25	0.1723	0.106	0.227	0.181
C26	0.1209	0.078	0.197	0.131
C27	0.0842	0.050	0.140	0.078
C28	0.0609	0.044	0.089	0.075
C29	0.0392	2.196	0.057	0.034
C30	0.5820	ND	0.036	ND
C31	ND	ND	0.023	ND
C32	ND	ND	ND	ND
C33	ND	ND	ND	ND
C34	ND	ND	ND	ND
C35	ND	ND	ND	ND
C36	ND	ND	ND	ND
Total	1.854	2.982	1.495	1.294
odd	0.659	2.589	0.724	0.652
even	1.195	0.394	0.771	0.642
Pristane	ND	ND	ND	ND
Phytane	ND	ND	ND	ND
Pri/phy	ND	ND	ND	ND
CPI	0.551	6.571	0.939	1.015

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Table(15): N-alkanes hydrocarbons concentrations in water (µg/l) at the studied stations during spring season.

Carbon number	Stations			
	St(1)	St(2)	St(3)	St(4)
C16	ND	ND	ND	ND
C17	0.011	0.019	ND	ND
C18	0.054	0.029	0.102	0.030
C19	0.024	ND	0.034	ND
C20	0.063	0.086	0.707	0.285
C21	0.026	ND	ND	ND
C22	0.064	0.033	0.278	0.112
C23	0.034	ND	ND	ND
C24	0.048	0.065	0.372	0.184
C25	0.068	ND	0.039	ND
C26	0.079	0.055	0.251	0.124
C27	0.074	ND	0.043	0.030
C28	0.045	0.038	0.156	0.084
C29	0.018	0.024	0.051	0.037
C30	0.034	ND	0.106	0.061
C31	0.037	ND	0.036	ND
C32	0.014	ND	0.062	0.029
C33	ND	ND	ND	ND
C34	ND	ND	ND	ND
C35	ND	ND	ND	ND
C36	ND	ND	ND	ND
Total	0.693	0.349	2.236	0.975
odd	0.292	0.043	0.203	0.067
even	0.400	0.306	2.034	0.908
Pristane	0.015	ND	ND	ND
Phytane	0.064	ND	0.137	0.044
Pri/phy	0.234	ND	ND	ND
CPI	0.730	0.142	0.100	0.073

3.3.2.2-N-alkanes in sediments:

The carbon chains length of n-alkanes in sediment samples were recorded from C16- C38. the dominant of odd carbon chains were C25, C27,C29 and C33, while the dominant of even carbon chains were C20, C22,C24,C26, C28,30,32. The other of hydrocarbons compounds numbers present in the aliphatic fraction, including pristine and phytane. Fig.(38) explain the percentage of n-alkanes in sediments. The seasonal values of n-alkanes in sediment at the studied stations were illustrated in tables (16-19).

In sediment the highest concentrations of total n-alkanes ($29.75\mu\text{g/g}$ dry weight) was recorded at station 1 in winter, while the lowest concentrations ($0.62\mu\text{g/g}$ dry weight) was recorded at station 4 in summer. Significant differences ($P \leq 0.05$) were found among seasons (Fig.39), the highest mean value ($14.64 \mu\text{g/g d.w}$) was recorded in winter, while the lowest mean value ($1.45 \mu\text{g/g d.w}$) was recorded in summer. Non-significant differences were found among stations (Fig.40) .

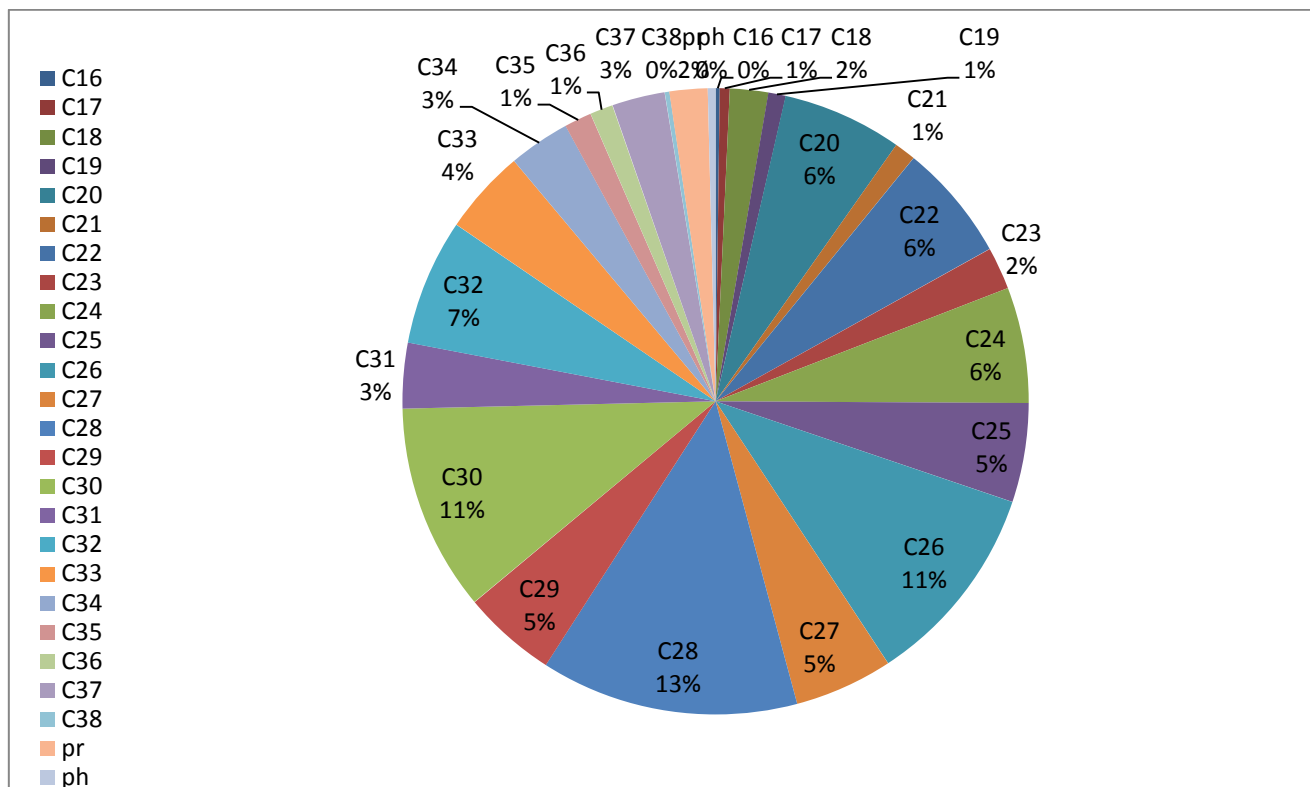


Fig.(34):The percentage of n-alkanes in sediments during the studied periods.

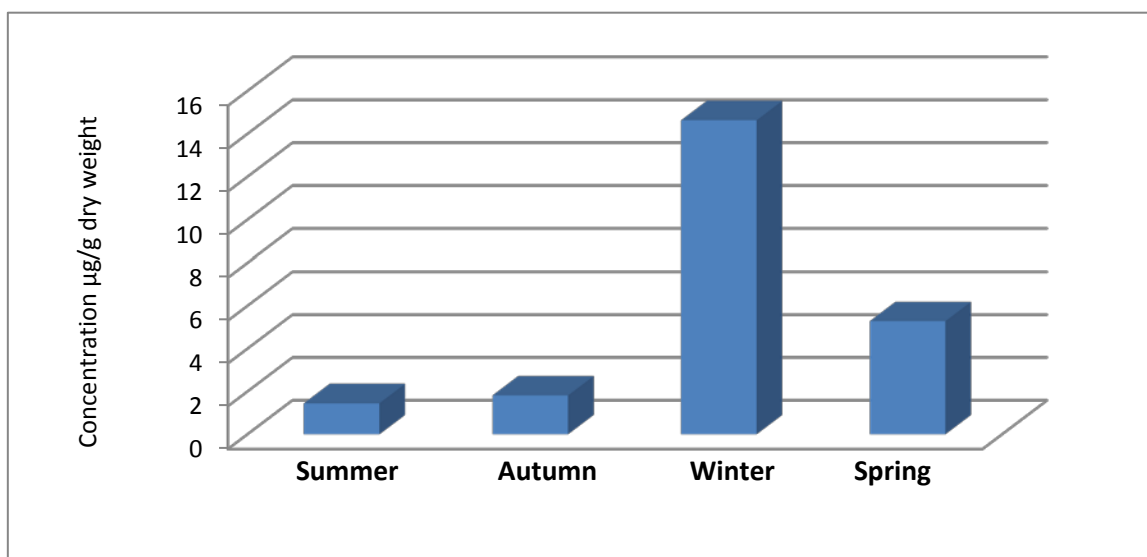


Fig.(35): Seasonal variations of total n-alkanes hydrocarbons (µg/g dry weight) in sediment samples during the studied periods

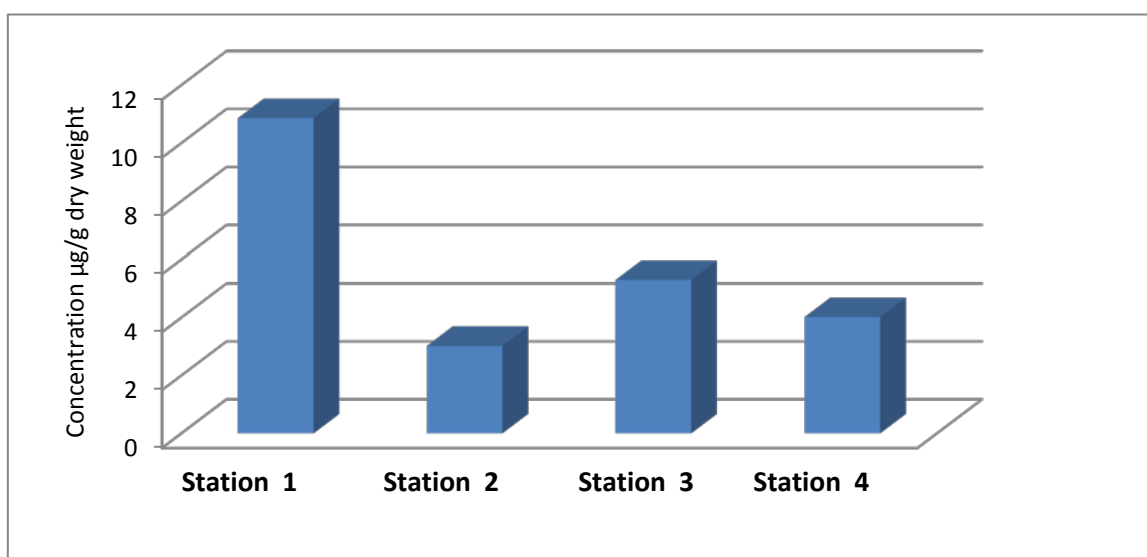


Fig.(36): Regional variations of total n-alkanes hydrocarbons (µg/g dry weight) in sediment samples during the studied periods.

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Table(16): N-alkanes hydrocarbons concentrations in sediments (µg/g dry weight) at the studied stations during summer season.

Carbon number	Stations			
	St(1)	St(2)	St(3)	St(4)
C16	0.004	ND	ND	ND
C17	0.014	0.013	0.012	0.004
C18	0.039	0.042	0.059	0.006
C19	0.031	0.054	0.091	0.019
C20	0.029	0.070	0.189	0.016
C21	0.040	0.038	0.133	0.031
C22	0.058	0.044	0.125	0.037
C23	0.046	0.035	0.135	0.062
C24	0.079	0.046	0.122	0.097
C25	0.099	0.098	0.155	0.048
C26	0.077	0.053	0.107	0.051
C27	0.153	0.121	0.200	0.028
C28	0.086	0.077	0.172	0.053
C29	0.162	0.129	0.222	0.024
C30	0.114	0.175	0.224	0.024
C31	0.044	0.060	0.085	0.005
C32	0.023	0.101	0.064	0.082
C33	0.112	0.119	0.118	0.006
C34	0.046	0.071	0.025	ND
C35	0.090	0.070	0.085	0.031
C36	0.020	0.021	0.064	ND
Total	1.367	1.438	2.385	0.624
odd	0.792	0.738	1.235	0.258
even	0.575	0.700	1.150	0.366
Pristane	0.011	0.009	0.009	ND
Phytane	0.052	0.056	0.078	0.005
Pri/phy	0.216	0.169	0.115	ND
CPI	1.376	1.055	1.074	0.703

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Table(17): N-alkanes hydrocarbons concentrations in sediments ($\mu\text{g/g}$ dry weight) at the studied stations during autumn season

Carbon number	Stations			
	St(1)	St(2)	St(3)	St(4)
C16	ND	0.007	ND	ND
C17	0.004	0.019	0.008	ND
C18	0.019	0.056	0.009	0.011
C19	0.014	0.038	0.011	0.040
C20	0.040	0.056	0.047	0.035
C21	0.073	0.096	0.060	0.024
C22	0.058	0.109	0.056	0.050
C23	0.095	0.086	0.062	0.040
C24	0.106	0.134	0.150	0.039
C25	0.155	0.188	0.202	0.041
C26	0.089	0.118	0.138	0.074
C27	0.132	0.229	0.243	0.040
C28	0.068	0.144	0.163	0.106
C29	0.108	0.162	0.230	0.048
C30	0.062	0.191	0.247	0.110
C31	0.150	0.161	0.305	0.091
C32	0.039	0.066	0.086	0.032
C33	0.091	0.501	0.152	0.017
C34	0.042	0.107	0.046	0.018
C35	0.019	0.110	0.070	0.016
C36	0.058	0.106	0.049	ND
Total	1.422	2.682	2.334	0.832
odd	0.840	1.588	1.343	0.357
even	0.582	1.094	0.991	0.475
Pristane	ND	0.008	ND	0.009
Phytane	0.009	0.034	0.008	0.052
Pri/phy	ND	0.240	ND	0.172
CPI	1.443	1.452	1.355	0.750

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Table(18): N-alkanes hydrocarbons concentrations in sediments (µg/g dry weight) at the studied stations during winter season.

Carbon number	Stations			
	St(1)	St(2)	St(3)	St(4)
C16	0.033	ND	ND	ND
C17	0.144	0.030	0.042	0.041
C18	0.893	ND	0.108	0.049
C19	0.311	ND	0.041	0.033
C20	1.384	0.021	2.357	0.241
C21	0.316	ND	0.057	0.056
C22	1.078	0.108	2.400	0.389
C23	0.738	0.058	0.164	0.168
C24	1.347	0.175	1.927	0.456
C25	2.096	0.191	0.292	0.527
C26	4.065	0.520	1.399	1.143
C27	ND	0.412	0.380	1.226
C28	6.372	0.510	0.964	1.584
C29	ND	0.355	0.405	1.056
C30	4.863	0.392	0.671	1.208
C31	ND	0.237	0.247	0.714
C32	3.097	0.230	0.425	0.679
C33	1.591	0.104	0.131	0.287
C34	1.026	0.098	0.275	0.293
C35	0.395	ND	ND	ND
C36	ND	ND	0.190	0.138
C37	ND	ND	ND	2.589
Total	29.75	3.441	12.475	12.876
odd	5.591	1.386	1.760	6.697
even	24.159	2.055	10.715	6.179
Pristane	0.147	0.56	ND	ND
Phytane	1.187	0.189	0.141	0.063
Pr/ph	0.124	0.296	ND	ND
CPI	0.231	0.675	0.164	1.084

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Table(19): N-alkanes hydrocarbons concentrations in sediments (µg/g dry weight) at the studied stations during spring season.

Carbon number	Stations			
	St(1)	St(2)	St(3)	St(4)
C16	ND	ND	0.140	ND
C17	ND	ND	0.112	0.005
C18	0.033	0.018	0.422	0.070
C19	0.021	0.039	0.079	0.014
C20	0.188	0.060	1.104	0.023
C21	0.042	0.054	ND	0.044
C22	0.360	0.076	0.762	0.070
C23	0.149	0.047	ND	0.156
C24	0.446	0.054	0.408	0.064
C25	0.532	0.079	0.033	0.054
C26	1.660	0.092	0.247	0.106
C27	1.280	0.157	0.044	0.088
C28	1.634	0.172	0.159	0.113
C29	1.109	0.242	0.059	0.100
C30	1.181	0.452	0.098	0.040
C31	0.725	0.443	0.033	0.069
C32	0.723	0.556	0.062	0.025
C33	0.310	0.289	ND	0.315
C34	0.305	0.466	0.041	0.036
C35	0.070	0.301	0.026	0.059
C36	0.137	0.588	0.043	0.282
C37	ND	0.309	0.019	ND
C38	ND	0.020	0.109	ND
Total	10.906	4.513	3.998	1.734
odd	4.239	1.959	0.405	0.904
even	6.667	2.553	3.594	0.830
Pristane	ND	0.035	0.031	0.007
Phytane	0.041	0.079	0.097	0.059
Pr/ph	ND	0.446	0.318	0.117
CPI	0.636	0.767	0.113	1.088

3.3.2.3-N-alkanes in aquatic plants .

N-alkanes in *Phragmites australis*

Table (20) explain seasonal variations of total n-alkanes, odd and, even carbon number, pristane, phytane, CPI values and pri/phy ratio. Fig.(41) represent seasonal variations of total concentrations of n-alkanes in *P. australis*. The range of carbon chain length of n-alkanes in *P. australis* is C10 to C38. The total concentrations of n-alkanes in *P. Australis* ranged from 4.69 to 31.52 $\mu\text{g/g}$ dry weight during winter and summer respectively. Results of the present study that odd carbon number of n-alkanes was greater than even number at all seasons. Pristane and Phytane was detected during all seasons, Pristane /Phytane ratio ranged from 0.159 to 0.786 during autumn and winter respectively. CPI values ranged from 1.576 to 2.274 during winter and autumn respectively. The results indicate the origins of n-alkanes hydrocarbons in *P. australis* were biogenic and anthropogenic .

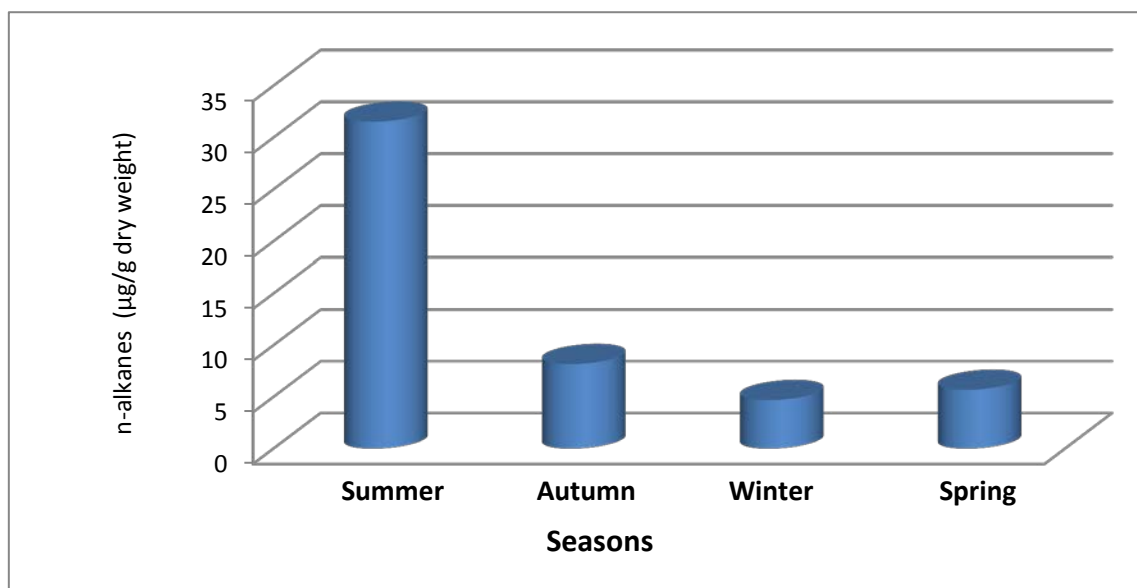


Fig (37):Seasonal variations of total n-alkanes($\mu\text{ g/g}$ dry weight) in *P. australis*

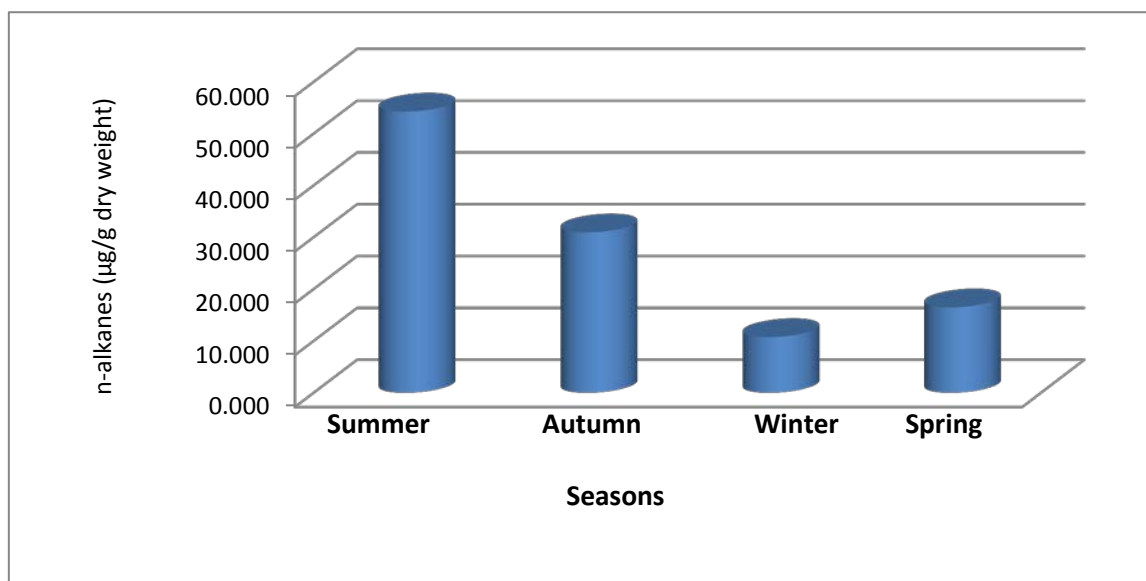
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Table(20): Seasonal variations of n-alkanes ($\mu\text{g/g d.w}$), pristine, phytane, odd carbon numbers, even carbon numbers, CPI values ,pri/phy ratio in *P. australis* .

Carbon NO.	Seasons			
	Summer	Autumn	Winter	Spring
C10	ND	0.013	ND	ND
C11	ND	ND	ND	ND
C12	ND	ND	ND	ND
C13	ND	ND	ND	ND
C14	0.005	ND	ND	ND
C15	0.018	0.004	ND	ND
C16	0.078	0.022	0.044	ND
C17	0.158	0.050	0.082	0.018
C18	0.369	0.163	0.178	0.075
C19	0.345	0.056	0.037	0.048
C20	0.426	0.134	0.203	0.108
C21	1.694	0.076	0.069	0.086
C22	0.319	0.116	0.244	0.136
C23	0.498	0.234	0.216	0.246
C24	0.553	0.195	0.172	0.198
C25	0.848	0.384	0.287	0.372
C26	0.844	0.231	0.185	0.207
C27	2.194	0.752	0.390	0.512
C28	1.684	0.335	0.240	0.322
C29	3.784	1.851	0.802	0.805
C30	2.106	0.544	0.078	0.263
C31	5.450	0.701	0.439	0.817
C32	0.630	0.176	0.059	0.111
C33	4.900	1.335	0.481	0.449
C34	2.195	0.190	0.075	0.126
C35	1.988	0.200	0.064	0.230
C36	0.236	0.150	0.343	0.526
C37	ND	0.032	ND	ND
C38	0.202	0.226	ND	0.028
Total	31.52	8.17	4.69	5.68
odd	21.877	5.677	2.868	3.583
even	9.647	2.496	1.820	2.100
Pri	0.535	0.034	0.109	0.015
Phy	0.823	0.215	0.139	0.049
Pri/Phy	0.650	0.159	0.786	0.298
CPI	2.268	2.274	1.576	1.706

N-alkanes in *Typha domingensis* :

Table (21) explain seasonal variations of n-alkanes, odd carbon, even carbon, pristane, phytane, CPI values and pri/phy ratio. Figure (42) represent seasonal variations of total concentrations of n-alkanes in *T. domingensis*. The range of carbon chain length of n-alkanes is between C₉ and C₃₈. The total concentrations of n-alkanes in *T. domingensis* ranged from 10.73 to 54.25 µg/g dry weight during winter and summer respectively. Results of the present study that odd carbon number of n-alkanes was greater than even number at all seasons. Pristane and Phytane was detected during all seasons, Pristane /Phytane ratio ranged from 0.204 during winter to 1.291 during spring respectively. CPI values ranged from 1.868 to 4.775 during summer and autumn respectively. The results indicate the origins of n-alkanes hydrocarbons in *T. domingensis* were biogenic source and few from them anthropogenic source.



Fig(38):Seasonal variations of total n-alkanes(µg/g dry weight)in *T. domingensis*

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Table(21) :Seasonal variations of n-alkanes ($\mu\text{g/g d.w}$), pristane ,phytane , odd carbon numbers ,even carbon numbers , CPI values ,pri/phy ratio in *T. domingensis*.

Carbon NO.	Seasons			
	Summer	Autumn	Winter	Spring
C9	0.197	ND	0.181	ND
C10	0.205	ND	0.006	ND
C11	0.042	ND	0.010	ND
C12	0.054	ND	0.009	ND
C13	0.031	ND	0.006	ND
C14	0.046	ND	0.044	0.006
C15	0.106	0.021	0.041	0.034
C16	0.321	0.021	0.023	0.341
C17	0.506	0.040	0.041	0.502
C18	0.738	0.126	0.167	0.619
C19	0.900	0.064	0.065	0.080
C20	1.810	0.175	0.162	0.490
C21	0.753	0.179	0.067	0.098
C22	0.661	0.390	0.160	0.398
C23	0.845	0.926	0.223	0.944
C24	1.318	0.951	0.348	0.779
C25	2.358	2.788	1.034	2.233
C26	1.817	0.850	0.359	0.593
C27	5.847	6.237	1.504	2.691
C28	2.309	0.896	0.481	0.184
C29	8.289	7.673	2.683	2.550
C30	2.754	0.717	0.316	0.373
C31	5.129	4.316	1.775	1.303
C32	1.542	0.170	0.132	0.155
C33	9.138	3.100	0.253	0.744
C34	2.697	0.197	0.050	0.075
C35	1.051	0.183	0.044	0.017
C36	0.634	0.377	0.183	0.663
C37	0.144	0.036	0.000	0.000
C38	2.008	0.483	0.357	0.591
Total	54.251	30.916	10.725	16.460
odd	35.335	25.562	7.928	11.194
even	18.916	5.353	2.796	5.265
Pri	0.802	0.074	0.045	0.662
Phy	0.981	0.067	0.219	0.513
Pri/Phy	0.818	1.093	0.204	1.291
CPI	1.868	4.775	2.835	2.126

N-alkanes in *Schoenoplectus littoralis* :

Table(22) explain seasonal variations of n-alkanes, odd carbon ,even carbon ,pristane ,phytane, CPI values and pri/phy ratio. Fig.(43)represent seasonal variations of total concentrations of n-alkanes in *S. littoralis*. The range of carbon chain length of n-alkanes is between C9 and C38. The total concentrations of n- alkanes ranged from 17.09 to 64.36 μ g/g dry weight during winter and summer respectively. Results of the present study that odd carbon number of n-alkanes was greater than even number at all seasons. Pristane and Phytane was detected of all seasons, Pristane /Phytane ratio ranged from 0.137 to 1.609 during autumn and spring respectively .CPI values ranged from 2.804 to 4.169 during winter and autumn respectively. The results indicate the origins of n-alkanes hydrocarbons in *S. littoralis* were biogenic and anthropogenic source .

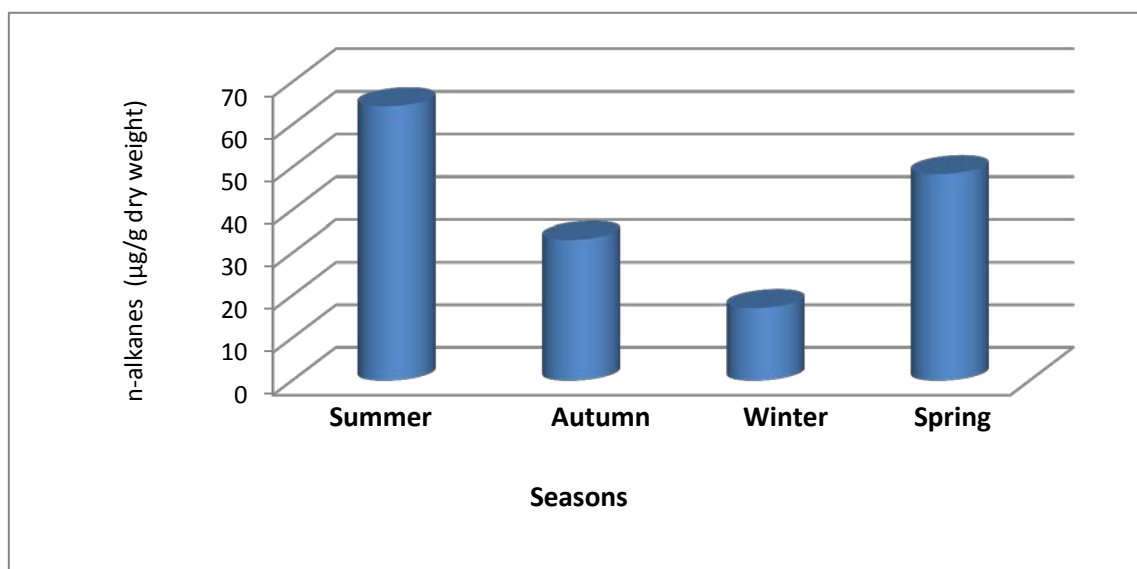


Fig.(39):Seasonal variations of total n-alkanes(μ g/g dry weight)in *S. littoral*

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Table(22) :Seasonal variations of n-alkanes ($\mu\text{g/g d.w}$), pristane ,phytane , odd carbon numbers ,even carbon numbers , CPI values ,pri/phy ratio in *S. litoralis*.

Carbon NO.	Seasons			
	Summer	Autumn	Winter	Spring
C9	0.006	ND	ND	0.096
C10	ND	ND	ND	ND
C11	ND	ND	ND	0.020
C12	ND	ND	ND	0.013
C13	ND	ND	0.006	0.013
C14	0.015	ND	ND	0.042
C15	0.037	0.025	0.040	0.092
C16	0.113	0.011	0.118	0.149
C17	0.236	0.055	0.106	0.166
C18	0.420	0.135	0.356	0.298
C19	0.368	0.048	0.100	0.182
C20	0.458	0.194	0.360	0.344
C21	3.543	0.295	0.377	0.433
C22	0.457	0.203	0.430	0.457
C23	1.245	0.721	0.691	1.405
C24	1.220	0.567	0.509	1.111
C25	3.359	2.252	1.495	3.601
C26	2.496	1.390	0.694	2.082
C27	11.790	10.460	4.257	11.466
C28	3.367	1.941	0.684	1.605
C29	12.506	9.284	2.896	8.347
C30	2.929	0.909	0.186	1.931
C31	4.300	1.615	1.415	6.154
C32	1.231	0.435	0.096	0.831
C33	7.707	1.698	0.956	4.406
C34	1.086	0.049	0.071	1.083
C35	4.131	0.214	0.256	0.421
C36	0.120	0.228	0.475	0.660
C37	0.029	0.043	ND	0.039
C38	1.190	0.345	0.513	0.984
Total	64.36	33.12	17.09	48.43
odd	49.257	26.712	12.595	36.841
even	15.102	6.407	4.492	11.590
Pri	0.432	0.024	0.140	0.220
Phy	0.557	0.178	0.267	0.137
Pri/Phy	0.776	0.137	0.525	1.609
CPI	3.262	4.169	2.804	3.179

N-alkanes in *Ceratophyllum demersum* :

Table (23) explain seasonal variations of n-alkanes, odd carbon ,even carbon ,pristane , phytane, CPI values and pri/phy ratio. Fig.(44)represent seasonal variations of total concentrations of n-alkanes in *C. demersum*. The range of carbon chain length of n-alkanes is between C13 and C38. The total concentrations of n- alkanes ranged from 5.23 to 40.85 $\mu\text{g/g}$ dry weight during winter and summer respectively. Results of the present study that odd carbon number of n-alkanes was greeter than even number except at winter season was found odd carbon number of n-alkanes lower than even number .Pristane and Phytane was detected during all seasons, Pristane /Phytane ratio ranged from 0.207 to 0.931 during spring and autumn respectively. CPI values ranged from 0.506 to 2.832 during winter and autumn respectively. The results indicate the origins of n-alkanes hydrocarbons in *C. demersum* were biogenic and anthropogenic source .

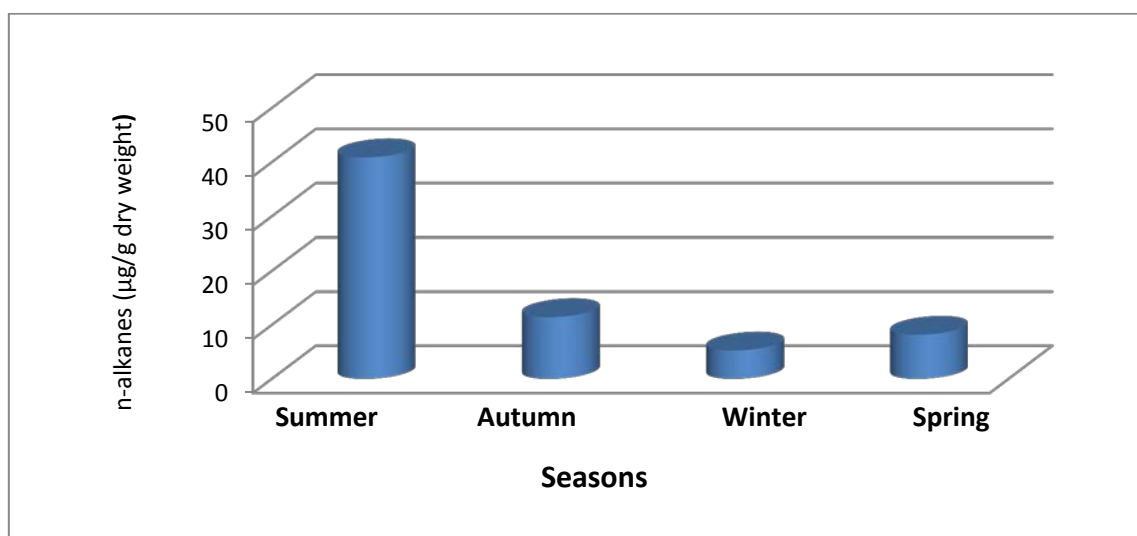


Fig (40): Seasonal variations of total n-alkanes ($\mu\text{g/g}$ dry weight)in *C. demersum*

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Table(23) :Seasonal variations of n-alkanes ($\mu\text{g/g d.w}$), pristane ,phytane , odd carbon numbers ,even carbon numbers , CPI values ,pri/phy ratio in *C. demersum*.

Carbon NO.	Seasons			
	Summer	Autumn	Winter	Spring
C13	ND	0.007	ND	ND
C14	0.006	0.008	ND	ND
C15	0.056	0.005	0.011	0.005
C16	0.205	0.028	0.132	ND
C17	0.584	0.117	0.279	0.050
C18	0.881	0.147	0.557	0.103
C19	1.030	0.127	0.085	0.087
C20	1.419	0.148	0.521	0.104
C21	4.789	0.092	0.043	0.131
C22	0.652	0.229	0.401	0.187
C23	0.601	0.182	0.121	0.224
C24	0.559	0.310	0.294	0.334
C25	0.672	0.290	0.319	0.374
C26	0.695	0.186	0.324	0.285
C27	0.904	0.295	0.226	0.395
C28	1.890	0.198	0.217	0.447
C29	4.436	0.472	0.168	0.458
C30	2.056	0.374	0.132	1.187
C31	2.369	0.987	0.221	0.478
C32	0.642	0.380	0.048	0.071
C33	8.725	5.521	0.238	2.522
C34	2.389	0.848	0.111	0.280
C35	0.729	0.216	0.045	0.152
C36	4.385	0.124	0.685	0.285
C37	0.149	0.127	ND	ND
C38	0.030	ND	0.051	ND
Total	40.854	11.417	5.229	8.159
odd	25.044	8.437	1.756	4.876
even	15.810	2.979	3.473	3.283
Pri	0.690	0.180	0.371	0.010
Phy	1.168	0.193	0.443	0.047
Pri/Phy	0.591	0.931	0.837	0.207
CPI	1.584	2.832	0.506	1.485

3.3.3-Polycyclic Aromatic Hydrocarbons (PAHs):

Sixteen PAHs compounds were identified in water, sediments and plants samples in the present study. They were divided into two groups depended on their molecular weight. The first group included the light (low molecular weight) compounds with two-three fused aromatic rings which consisting of six compounds: Naphthalene, Acenaphthylene, Acenaphthene, Phenanthrene, Fluorene and Anthracene. The second group included the heavy (high molecular weight) compounds with four or more fused aromatic rings consisting of ten compounds: Floranthene, Pyrene, Benzo(a)anthracene, Chrysene, Benzo(b) Flouranthene, Benzo(k) flouranthene, Benzo (a) Pyrene, Indeno (1,2,3,c,d) Pyrene, Dibenzo(a,h)anthracene, Benzo (g,h,i) Perylene.

3.3.3.1-PAHs in water :

The dominant light PAHs compounds in water were Acenaphthylene, Acenaphthene. Whereas, the dominant heavy PAHs compounds were Pyrene, Benzo(k)flouranthene, Indeno(1,2,3-c,d)pyrene, specially Benzo(k)flouranthene. Fig.(45) showed the percentage of PAHs compounds in water. The seasonal values of PAHs compounds in water at the studied stations were illustrated in tables (24-27).

At study period, the result show the concentration of PAHs compounds in water samples ranged from (2.44 ng/l) was founded at station 4 in spring season to (37.78 ng/l) was founded at station 1 in winter. Significant differences ($P \leq 0.05$) were found among seasons (Fig.46), the highest mean value (26.46 ng/l) was recorded in winter, while the lowest mean value (4.191 ng/l) was recorded in spring. While non-significant differences were found among stations (Fig.47).

In addition to results in the present study showed that HMW-PAHs (high molecular weight) compounds was more than LMW-PAHs (low molecular

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weight) compounds during study period in all stations except in station 4 during autumn and station 2 in winter were founded the that high molecular weight compounds was less than low molecular weight compounds .To determined the origins of PAHs in water sample according to the following ratios in tables (24-27), the LMW-PAHs/HMW-PAHs ratio was less than one in all stations during all seasons except at station(4) was more than one during autumn station 2 during winter, the results indicate that origin of these compound in water were pyrogenic in all stations while petrogenic in stations 2and4. The BaA/(BaA+Chr) ratio was disadvantage because most water sample had undetectable Benzo(a) anthracene value and the other samples had undetectable Chrysene values ,only few sample had Benzo(a) anthracene and Chrysene values together, because that the ratio ranged from 0.065 to 1 and indicate the source were few petrogenic and other source were pyrogenic.

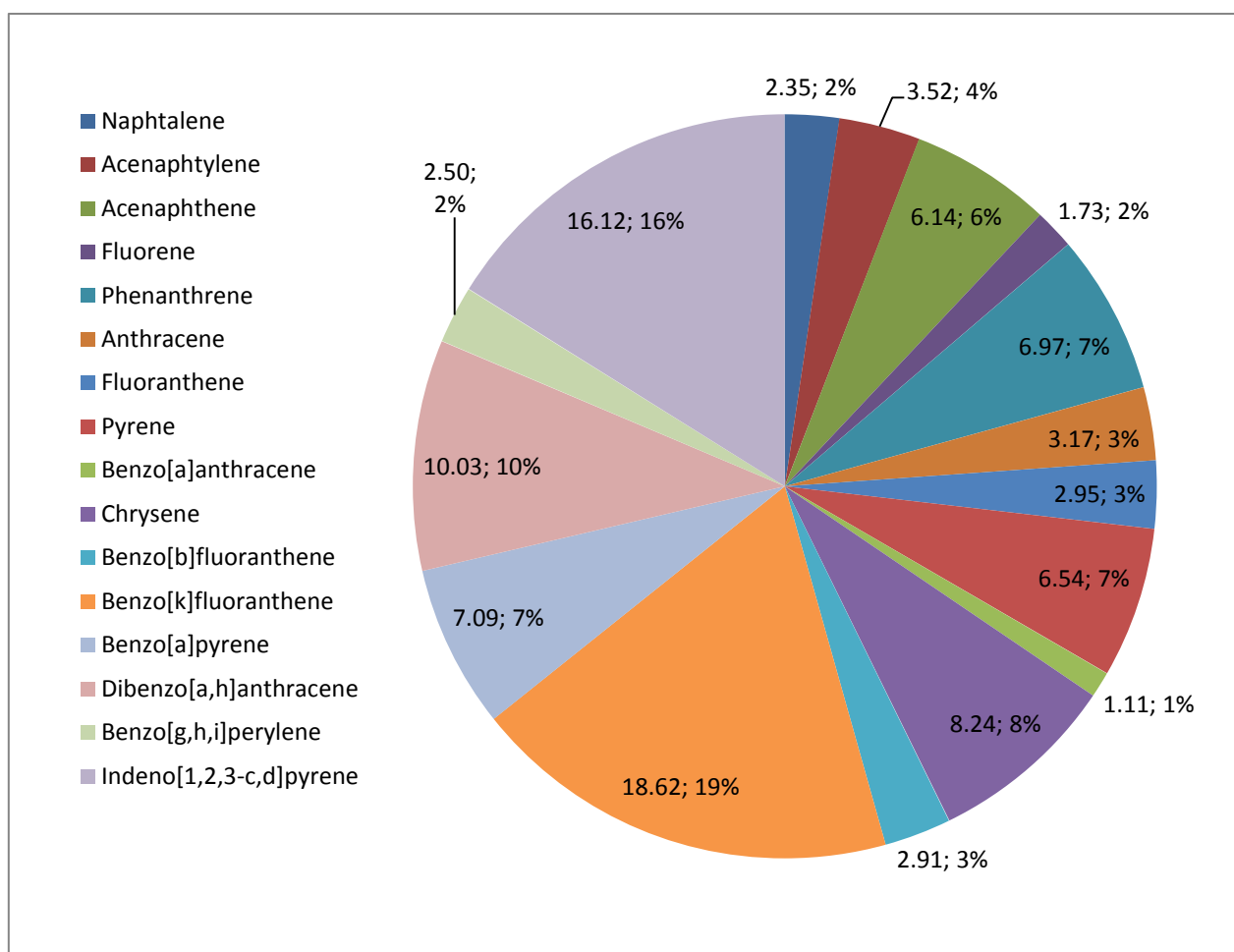


Fig.(41) : The PAHs compounds percentage in water samples during the studied periods.

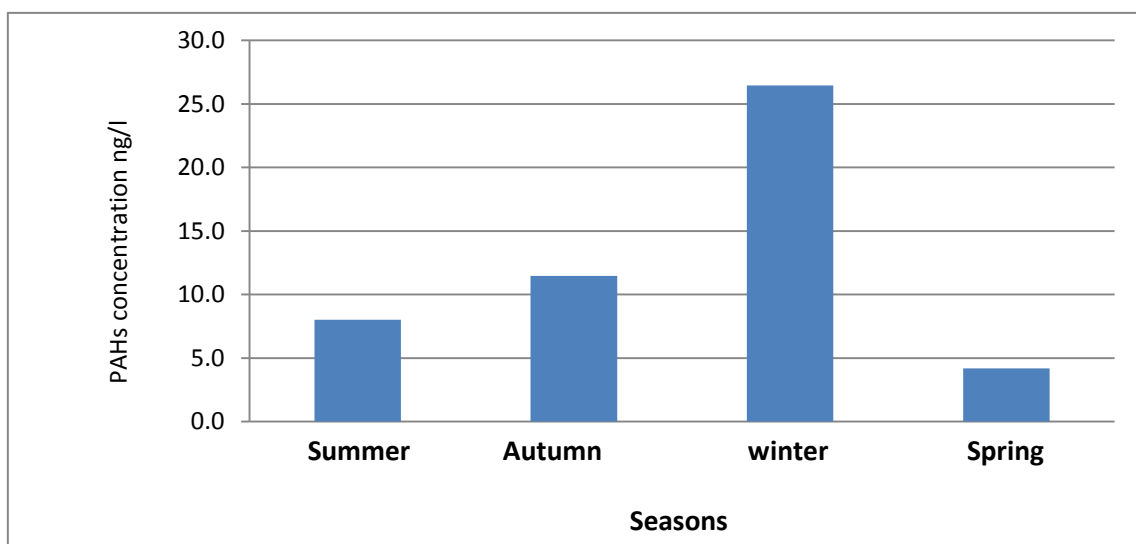


Fig.(42): Seasonal variations in total PAHs compounds (ng/l) in water samples during the studied periods.

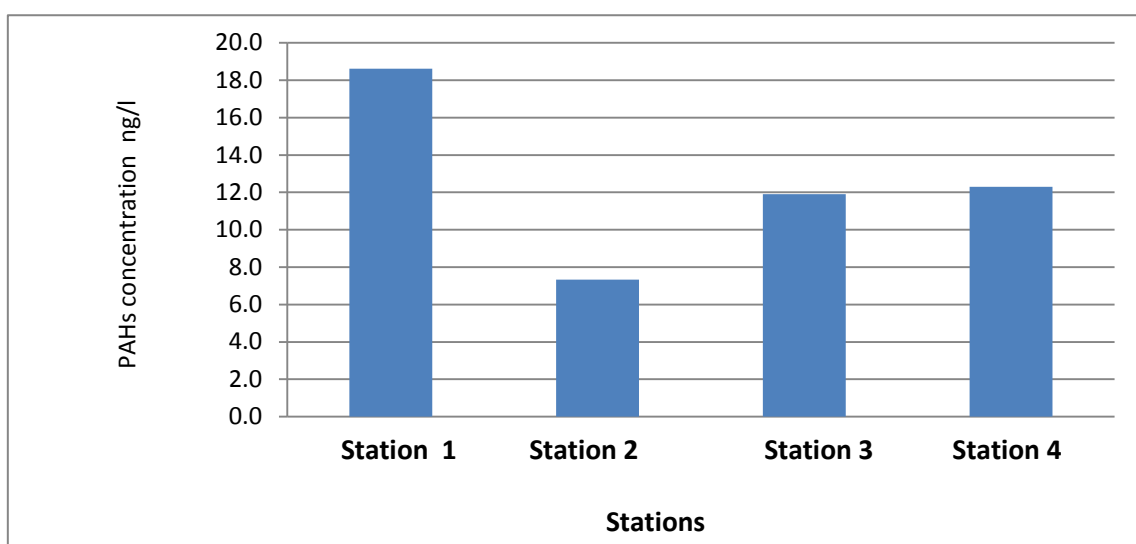


Fig.(43) : Spatial variations in total PAHs compounds (ng/l) in water samples at the studied stations.

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Table(24) :Concentrations of PAHs (ng/l) in water samples during summer season .

Compounds	Stations			
	St (1)	St (2)	St (3)	St(4)
Naphtalene	ND	ND	ND	0.464
Acenaphtylene	3.131	0.265	0.306	ND
Acenaphthene	ND	ND	0.981	0.382
Fluorene	ND	0.774874	ND	ND
Phenanthrene	ND	ND	ND	ND
Anthracene	3.515	ND	ND	ND
Fluoranthene	ND	ND	ND	ND
Pyrene	ND	ND	ND	0.049
Benzo[a]anthracene	ND	1.891	0.215	ND
Chrysene	ND	ND	3.084	0.032
Benzo[b]fluoranthene	1.832	ND	ND	ND
Benzo[k]fluoranthene	0.130	0.306	2.632	0.114
Benzo[a]pyrene	4.012	ND	ND	0.119
Dibenzo[a,h]anthracene	0.846	0.219	1.882	1.687
Benzo[g,h,i]perylene	ND	0.707	0.054	0.563
Indeno[1,2,3-c,d]pyrene	ND	ND	1.606	ND
Total	13.467	4.465	10.761	3.411
LPAHs	6.646	1.039	1.287	0.846
HPAHs	6.820	3.425	9.474	2.565
L/H	0.974	0.303	0.136	0.330
BaA/(BaA+Chr)	ND	0.561	0.065	ND

LPAHs /HPAHs

LPAHs : (Low Polycyclic Aromatic Hydrocarbons)

HPAHs : (High Polycyclic Aromatic Hydrocarbons)

BaA/(BaA+Chr) :(Benzo(a)anthracene/(Benzo(a)anthracene +Chrysene)

ND: not detected

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Table(25) :Concentrations of PAHs (ng/l) in water samples during autumn season .

Compounds	Stations			
	St (1)	St (2)	St (3)	St(4)
Naphtalene	ND	0.395	ND	0.050
Acenaphtylene	ND	ND	0.9206	1.389
Acenaphthene	2.367	0.990	1.092	1.046
Fluorene	ND	ND	ND	ND
Phenanthrene	1.175	ND	ND	6.152
Anthracene	ND	ND	ND	ND
Fluoranthene	ND	ND	ND	2.705
Pyrene	9.126	3.333	0.034	ND
Benzo[a]anthracene	ND	ND	0.035	0.032
Chrysene	ND	0.061	0.143	ND
Benzo[b]fluoranthene	0.476	ND	ND	ND
Benzo[k]fluoranthene	3.384	0.080	0.135	ND
Benzo[a]pyrene	ND	ND	0.119	0.052
Dibenzo[a,h]anthracene	ND	4.666	1.952	0.792
Benzo[g,h,i]perylene	0.577	0.644	0.530	0.608
Indeno[1,2,3-c,d]pyrene	ND	0.308	ND	0.528
Total	17.106	10.477	4.961	13.355
LPAHs	3.543	1.385	2.012	8.637
HPAHs	13.563	9.091	2.803	4.718
L/H	0.261	0.152	0.718	1.831
BaA/(BaA+Chr)	ND	ND	0.196	ND

ND :not detected

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Table (26) :Concentrations of PAHs (ng/l) in water samples during winter season .

Compounds	Stations			
	St (1)	St (2)	St (3)	St(4)
Naphtalene	1.048	ND	1.582	1.798
Acenaphtylene	0.475	ND	ND	0.290
Acenaphthene	5.294	ND	ND	ND
Fluorene	0.093	1.382	ND	ND
Phenanthrene	1.227	2.095	0.649	2.632
Anthracene	1.230	1.832	ND	ND
Fluoranthene	0.383	2.705	ND	0.036
Pyrene	0.599	0.254	ND	0.239
Benzo[a]anthracene	0.504	ND	ND	0.068
Chrysene	ND	ND	9.606	0.020
Benzo[b]fluoranthene	ND	0.596	1.473	1.123
Benzo[k]fluoranthene	17.879	ND	10.257	0.489
Benzo[a]pyrene	ND	ND	1.665	5.333
Dibenzo[a,h]anthracene	ND	1.042	0.229	ND
Benzo[g,h,i]perylene	ND	0.108	ND	ND
Indeno[1,2,3-c,d]pyrene	9.049	0.377	1.882	17.980
Total	37.780	10.390	27.642	30.006
LPAHs	9.367	5.309	2.231	4.719
HPAHs	28.413	5.081	25.112	25.287
L/H	0.330	1.045	0.089	0.187
BaA/(BaA+Chr)	1	ND	ND	0.775

ND :not detected

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Table(27):Concentrations of PAHs (ng/l) in water samples during spring season .

Compounds	Stations			
	St (1)	St (2)	St (3)	St(4)
Naphtalene	ND	ND	ND	ND
Acenaphtylene	ND	ND	ND	0.234
Acenaphthene	ND	ND	ND	ND
Fluorene	ND	1.353	ND	ND
Phenanthrene	ND	0.534	ND	ND
Anthracene	ND	ND	ND	ND
Fluoranthene	0.108	ND	0.194	ND
Pyrene	ND	ND	ND	ND
Benzo[a]anthracene	ND	ND	ND	ND
Chrysene	0.156	ND	ND	ND
Benzo[b]fluoranthene	ND	0.521	ND	0.023
Benzo[k]fluoranthene	ND	ND	0.745	ND
Benzo[a]pyrene	2.687	ND	ND	0.852
Dibenzo[a,h]anthracene	2.177	0.741	3.071	1.322
Benzo[g,h,i]perylene	0.875	0.816	0.214	ND
Indeno[1,2,3-c,d]pyrene	0.142	ND	ND	ND
Total	6.145	3.964	4.224	2.44
LPAHs	ND	1.887	ND	0.234
HPAHs	6.145	2.077	4.224	2.196
L/H	ND	0.908173	ND	0.107
BaA/(BaA+Chr)	ND	ND	ND	ND

ND: not detected

3.3.3.2-PAHs in sediments :

The dominant light PAHs compounds in sediments were Acenaphthene and Anthracene. Whereas the dominant heavy PAHs compounds in sediments were, Benzo(g,h,i)perylene , Indeno(1,2,3,c,d) Pyrene. Fig.(48) showed the percentage of PAHs compounds in sediments samples. The seasonal values of PAHs compounds in sediments at the studied stations were illustrated in tables(28-31)

The result show the concentration of PAHs compounds in sediments samples ranged from (6.56 ng/g dry weight) was founded at station 4 in spring season to (52.36 ng/g dry weight) was founded at station 4 in winter. Significant differences ($P \leq 0.05$) were found among seasons (Fig.49), the highest mean value (46.148 ng/g dry weight) was recorded in winter, while the lowest mean value (13.525 ng/ g dry weight) was recorded in spring. Non-significant differences were found among stations (Fig.50) .

The results of the sediments samples in the present study showed that HMW-PAHs (high molecular weight) compounds was more than LMW-PAHs (low molecular weight) compounds during study period in all stations except in station(4) during winter were founded the that high molecular weight compounds was less than low molecular weight compounds .To determined the origins of PAHs in sediments sample according to the following ratios in tables (28-31),the LMW-PAHs/HMW-PAHs ratio was less than one in all stations during all seasons except at station(4) was more than one during winter, the results indicate that origin of these compound in sediments were pyrogenic in all stations while petrogenic in station (4) .The BaA/(BaA+Chr) ratio was 0.018 at station 3 in autumn and (0.04,0.181 and 0.288) at stations 2,1and 3 respectively in summer which indicate the source was petrogenic ,but the BaA/(BaA+Chr) ratio in other stations and seasons was higher than 0.35 that indicate the source of PHAs was pyrogenic .

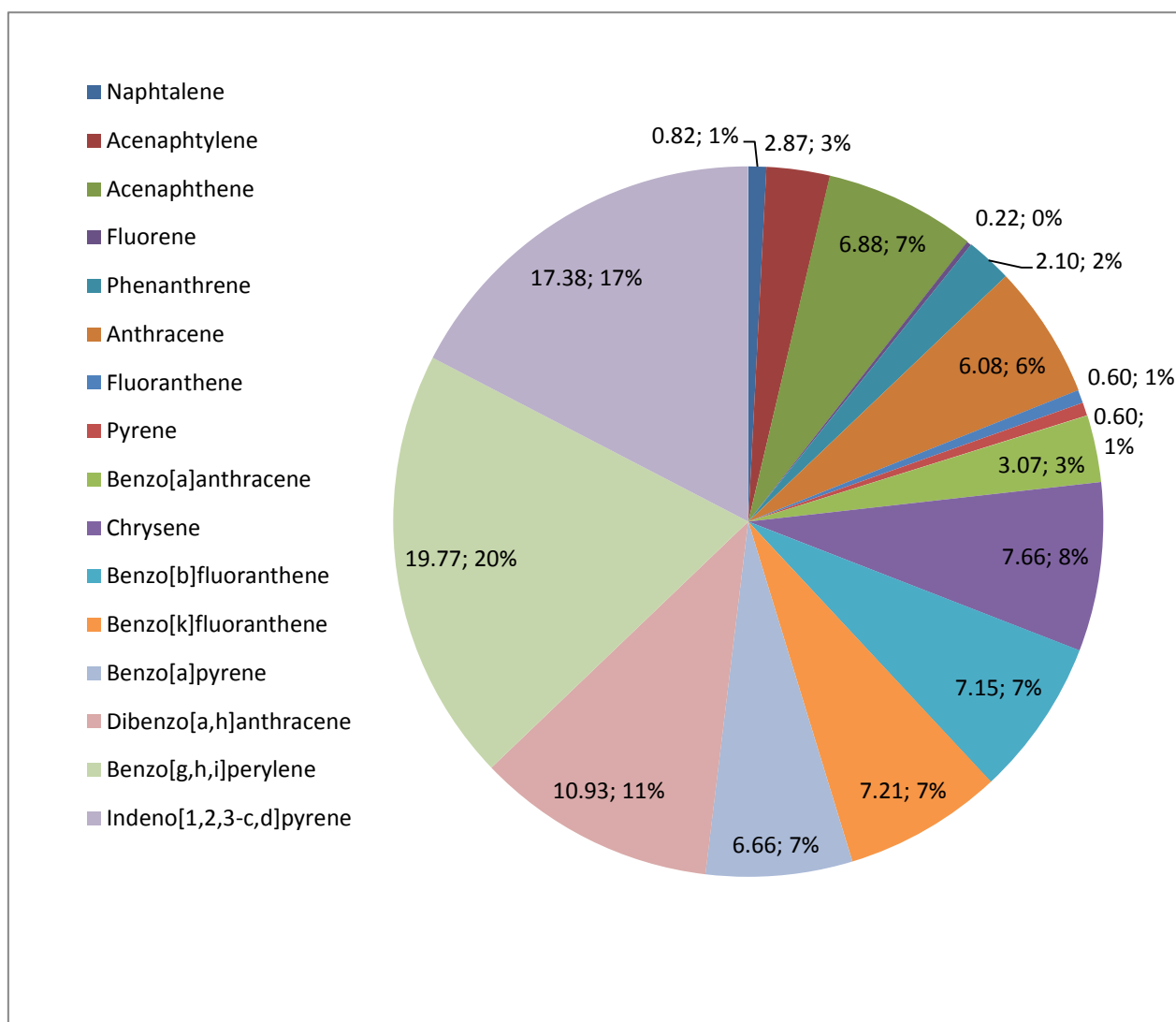


Fig.(44): The PAHs compounds percentage in sediments samples during the studied periods.

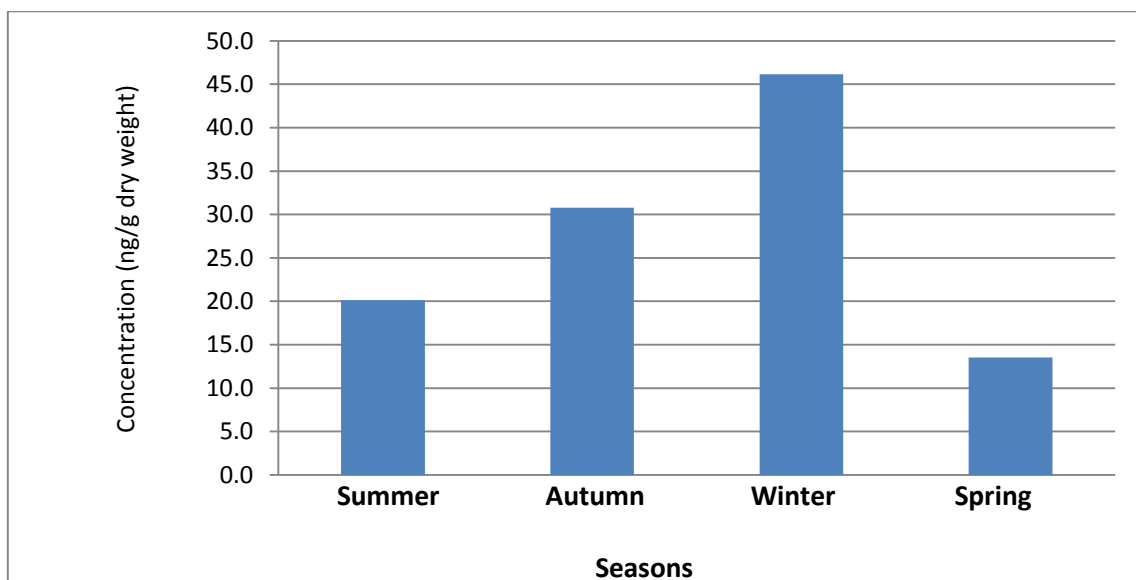


Fig.(45): Seasonal variations in total PAHs compounds (ng/g d.w) in sediments samples during the studied periods.

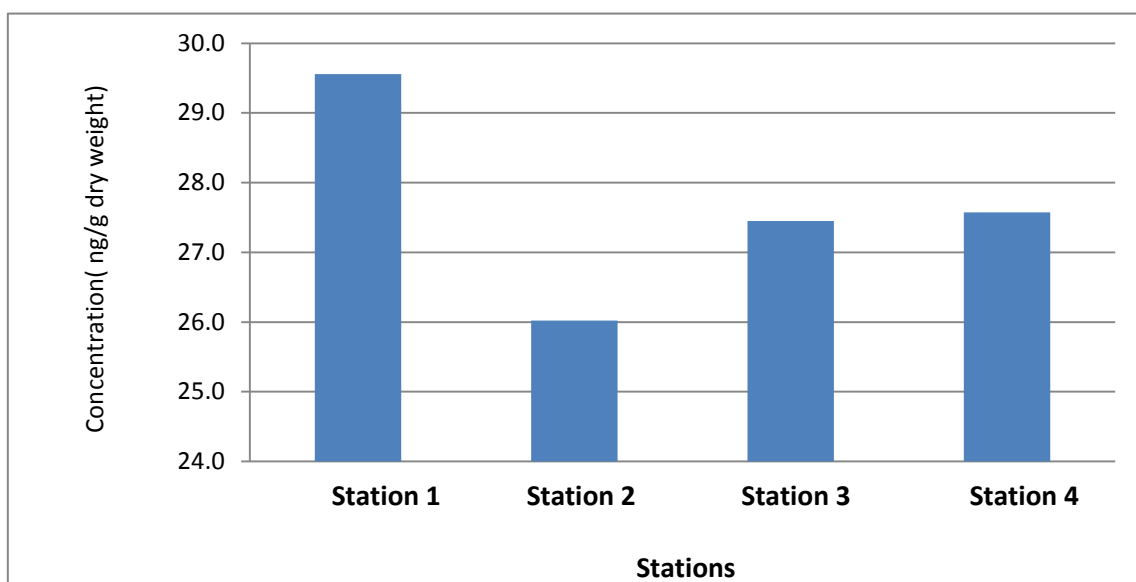


Fig.(46): Regional variations in total PAHs compounds (ng/g d.w) in sediments samples during the studied periods.

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Table(28): PAHs concentrations in sediments (ng/ g dry weight) at the studied stations during summer season.

Compounds	Stations			
	St (1)	St (2)	St (3)	St(4)
Naphtalene	ND	ND	ND	ND
Acenaphtylene	ND	ND	2.070	1.091
Acenaphthene	ND	0.847	ND	ND
Fluorene	ND	ND	ND	ND
Phenanthrene	3.522	0.115	ND	0.026
Anthracene	0.445	ND	0.063	0.085
Fluoranthene	ND	ND	ND	ND
Pyrene	ND	ND	0.023	ND
Benzo[a]anthracene	0.987	0.188	0.438	0.273
Chrysene	4.452	4.352	1.083	2.303
Benzo[b]fluoranthene	ND	ND	0.006	1.342
Benzo[k]fluoranthene	11.019	1.037	3.447	2.034
Benzo[a]pyrene	ND	3.221	0.023	0.462
Dibenzo[a,h]anthracene	6.096	ND	0.049	0.031
Benzo[g,h,i]perylene	ND	6.040	0.100	5.088
Indeno[1,2,3-c,d]pyrene	6.270	ND	5.064	6.881
Total	32.790	15.800	12.366	19.614
LPAHs	3.967	0.962	2.133	1.202
HPAHs	28.823	14.839	10.233	18.412
L/H	0.138	0.065	0.208	0.065
BaA/(BaA+Chr)	0.181	0.041	0.288	0.632

ND :not detected

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Table(29): PAHs concentrations in sediments (ng/ g dry weight) at the studied stations during autumn season.

Compounds	Stations			
	St (1)	St (2)	St (3)	St(4)
Naphtalene	ND	0.050	0.470	ND
Acenaphtylene	0.017	0.042	ND	0.031
Acenaphthene	ND	0.530	2.967	ND
Fluorene	0.571	0.055	ND	0.174
Phenanthrene	ND	0.441	ND	0.209
Anthracene	0.066	2.879	ND	0.037
Fluoranthene	ND	ND	0.252	0.289
Pyrene	0.005	ND	0.709	ND
Benzo[a]anthracene	0.416	0.198	0.258	0.765
Chrysene	0.216	0.253	13.782	0.416
Benzo[b]fluoranthene	3.200	0.046	8.390	ND
Benzo[k]fluoranthene	0.269	0.272	0.645	0.134
Benzo[a]pyrene	ND	4.881	3.960	1.114
Dibenzo[a,h]anthracene	4.148	2.634	0.249	0.286
Benzo[g,h,i]perylene	1.389	10.285	ND	12.423
Indeno[1,2,3-c,d]pyrene	13.353	0.103	13.582	15.883
Total	23.650	22.671	45.266	31.761
LPAHs	0.654	3.998	3.438	0.451
HPAHs	22.996	18.673	41.828	31.020
L/H	0.028	0.214	0.082	0.015
BaA/(BaA+Chr)	0.658	0.439	0.018	0.648

ND :not detected

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Table(30): PAHs concentrations in sediments (ng/ g dry weight) at the studied stations during winter season.

Compounds	Stations			
	St (1)	St (2)	St (3)	St(4)
Naphtalene	0.141	0.618	1.091	5.631
Acenaphtylene	ND	ND	ND	18.919
Acenaphthene	3.538	ND	ND	ND
Fluorene	ND	ND	ND	1.358
Phenanthrene	ND	3.564	ND	1.834
Anthracene	11.537	ND	ND	1.976
Fluoranthene	ND	ND	ND	1.438
Pyrene	ND	ND	0.106	4.194
Benzo[a]anthracene	ND	0.541	0.928	5.538
Chrysene	ND	0.354	0.901	2.490
Benzo[b]fluoranthene	0.479	15.072	ND	1.778
Benzo[k]fluoranthene	0.068	10.637	2.193	7.035
Benzo[a]pyrene	0.148	3.306	0.183	ND
Dibenzo[a,h]anthracene	12.887	1.349	ND	0.171
Benzo[g,h,i]perylene	18.867	ND	30.330	ND
Indeno[1,2,3-c,d]pyrene	1.291	10.887	1.211	ND
Total	48.956	46.329	36.943	52.362
LPAHs	15.216	4.182	1.091	27.742
HPAHs	33.740	42.147	35.852	24.621
L/H	0.451	0.099	0.030	1.127
BaA/(BaA+Chr)	ND	0.605	0.507	0.431

ND :not detected

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Table(31): PAHs concentrations in sediments (ng/ g dry weight) at the studied stations during spring season.

Compounds	Stations			
	St (1)	St (2)	St (3)	St(4)
Naphtalene	ND	ND	0.160	ND
Acenaphthylene	ND	4.946	ND	ND
Acenaphthene	ND	ND	2.506	1.218
Fluorene	0.143	ND	ND	ND
Phenanthrene	ND	ND	ND	ND
Anthracene	2.480	3.267	4.348	ND
Fluoranthene	ND	0.142	ND	ND
Pyrene	ND	ND	0.105	ND
Benzo[a]anthracene	0.403	0.361	0.38	1.241
Chrysene	0.136	0.264	0.088	0.791
Benzo[b]fluoranthene	ND	ND	ND	ND
Benzo[k]fluoranthene	ND	ND	ND	ND
Benzo[a]pyrene	1.106	0.177	4.359	ND
Dibenzo[a,h]anthracene	2.593	8.931	3.477	0.662
Benzo[g,h,i]perylene	0.522	0.347	ND	0.310
Indeno[1,2,3-c,d]pyrene	5.446	0.856	ND	3.125
Total	12.828	19.291	15.424	6.557
LPAHs	2.623	8.213	7.014	1.218
HPAHs	10.206	11.079	8.409	6.130
L/H	0.257	0.741	0.834	0.199
BaA/(BaA+Chr)	0.748	0.578	0.812	0.611

ND :not detected

3.3.3.3-PAHs in aquatic plants:

PAHs in *Phragmites australis*:

The total Concentrations of PAHs in *P. australis* are present in figure (51) and table (32) ranged from 54.42 ng/g d.w during spring to 86.66 ng/g d.w during summer .From the total PAHs, Acenaphtylene and Fluorene forms the grater ratio in light PAHs compounds, while Dibenzo (a,h) anthracene form the high ratio from heavy PAHs compounds. Results of the present study showed LMW- PAHs was greater than the HMW-PAHs during all seasons .To determined origin of PAHs in *P.australis* according to ratios in table(32),the results of LPAHs/HPAHs ratio recorded value more than one during all seasons, BaA/(BaA+Chr) rator ranged between 0.250 to 0.742 which referred that the origin of these compounds were shared pyrogenic and petrogenic , while the Phenanthrene/Anthracene ratio was less than ten in all seasons. this results indicates that the sources of PAHs in *P.australis* were mixed petrogenic and few as pyrogenic.

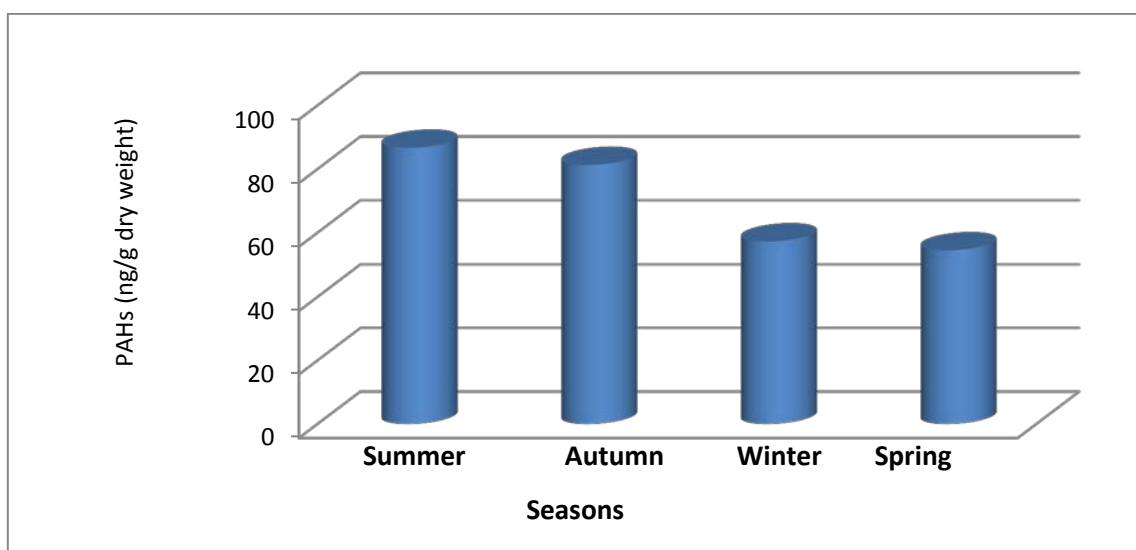


Fig (47) Seasonal variations of PAHs (ng/g d.w) in *P.australis*

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Table(32): Seasonal variations of PAHs (ng/g d.w) in *Phragmites australis*

Compounds	Seasons			
	Summer	Autumn	Winter	Spring
Naphtalene	0.792	9.902	ND	0.098
Acenaphtylene	14.972	16.490	19.615	16.970
Acenaphthene	8.954	6.504	ND	ND
Fluorene	18.121	5.952	6.234	13.327
Phenanthrene	0.343	2.595	0.308	0.216
Anthracene	2.922	3.235	2.251	3.944
Fluoranthene	0.120	0.171	0.269	ND
Pyrene	0.375	0.108	0.317	0.730
Benzo[a]anthracene	0.777	1.462	0.262	0.152
Chrysene	0.270	1.273	0.786	0.074
Benzo[b]fluoranthene	0.329	1.965	0.149	0.143
Benzo[k]fluoranthene	3.230	8.668	ND	2.150
Benzo[a]pyrene	1.442	2.496	ND	0.490
Dibenzo[a,h]anthracene	27.846	8.221	8.620	15.992
Benzo[g,h,i]perylene	5.613	0.311	0.413	0.134
Indeno[1,2,3-c,d]pyrene	0.552	11.921	18.004	ND
Total	86.658	81.273	57.226	54.419
LPAHs	46.103	44.678	30.658	34.554
HPAHs	40.555	36.595	28.819	19.865
L/H	1.137	1.221	1.064	1.739
BaA/(BaA+Chr)	0.742	0.535	0.250	0.673
Phenanthrene/Anthracene	0.117	0.802	0.137	0.055

ND :not detected

PAHs in *Typha domingensis*

The total Concentrations of PAHs *T. domingensis* are present in figure (52) and table (33) ranged from 37.02 ng/g d.w during spring to 80.54 ng/g d.w during summer. From the total PAHs, Acenaphtylene, Anthracene and Fluorene forms the greater ratio in light PAHs compounds, while Dibenzo (a,h) anthracene Benzo (k) Flouranthene, and Benzo (g,h,i) Perylene form the high ratio from heavy PAHs compounds . Results of the present study showed LMW-PAHs was greater than the HMW-PAHs during all seasons. To determined origin of PAHs in *T. domingensis* according to ratios in table (33), the results of LPAHs/HPAHs ratio recorded value more than one during all seasons, BaA/(BaA+Chr) ratio was more than 0.35, while the Phenanthrene/Anthracene ratio was less than ten in all seasons. this results indicates that the sources of PAHs in *T. domingensis* are mixed petrogenic and pyrogenic.

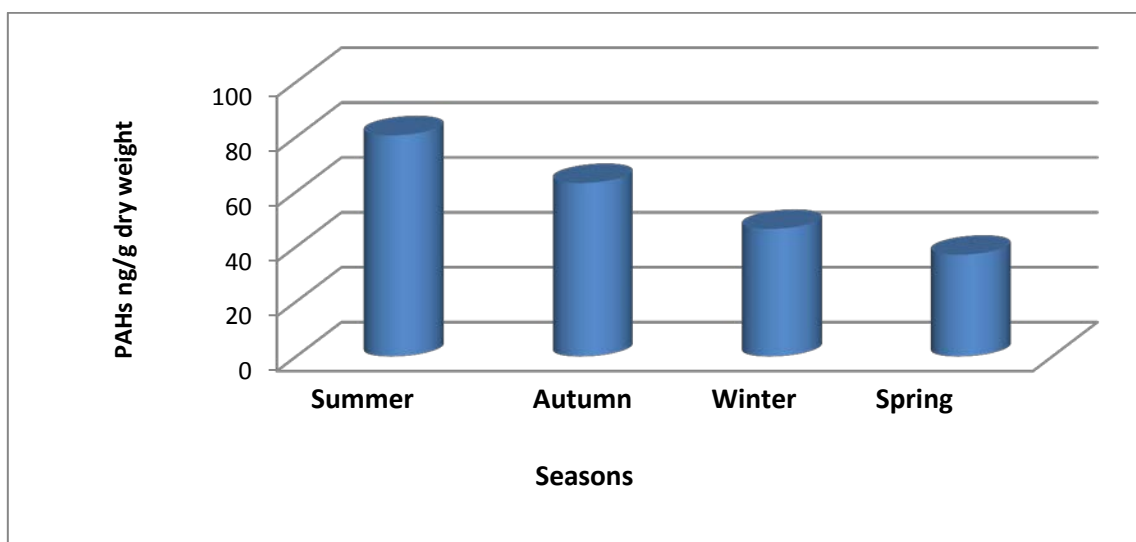


Fig. (48) Seasonal variations of PAHs (ng/g d.w) in *T. domingensis*

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Table (33):Seasonal variations of PAHs(ng/g d.w) in *Typha domingensis*

Compounds	Seasons			
	Summer	Autumn	Winter	Spring
Naphtalene	0.898	1.053	1.299	1.115
Acenaphtylene	21.813	4.663	3.784	0.415
Acenaphthene	ND	11.781	7.098	5.019
Fluorene	5.025	6.229	7.390	10.297
Phenanthrene	1.932	4.383	0.124	1.318
Anthracene	21.100	4.428	11.418	3.654
Fluoranthene	ND	ND	0.017	ND
Pyrene	0.067	2.232	2.978	0.815
Benzo[a]anthracene	0.713	0.257	1.506	1.245
Chrysene	0.227	0.285	0.327	0.119
Benzo[b]fluoranthene	0.703	0.071	0.201	0.186
Benzo[k]fluoranthene	2.513	10.849	8.205	2.118
Benzo[a]pyrene	0.493	0.945	0.607	0.144
Dibenzo[a,h]anthracene	7.373	8.072	1.009	10.240
Benzo[g,h,i]perylene	1.413	7.914	0.458	0.331
Indeno[1,2,3-c,d]pyrene	16.274	ND	ND	ND
Total	80.544	63.163	46.420	37.015
LPAHs	50.769	32.537	31.112	21.817
HPAHs	29.775	30.626	15.308	15.198
L/H	1.705	1.062	2.032	1.436
BaA/(BaA+Chr)	0.759	0.474	0.822	0.912
Phenanthrene/Anthracene	0.092	0.990	0.011	0.361

ND :not detected

PAHs in *Schoenoplectus litoralis*:

The total concentrations of PAHs *S. litoralis* are present in figure (53) and table (34) ranged from 6.32ng/g d.w during spring to 137.15 ng/g d.w during summer. From the total PAHs, Acenaphthylene and Anthracene forms the high ratio in light PAHs compounds, while Dibenzo (a,h) anthracene form the high ratio from heavy PAHs compounds. Results of the present study showed LMW-PAHs was greater than the HMW-PAHs during all seasons except in spring season LMW-PAHs was less than the HMW-PAHs. To determined origin of PAHs in *S. litoralis* according to ratios in table (34), the results of LPAHs/HPAHs ratio recorded value more than one during all seasons except in spring these ratio value less than one, BaA/(BaA+Chr) ratio ranged between 0.148 to 0.889, while the Phenanthrene/Anthracene ratio was less than ten in all seasons, this results indicates that the sources of PAHs in *S. litoralis* petrogenic and pyrogenic.

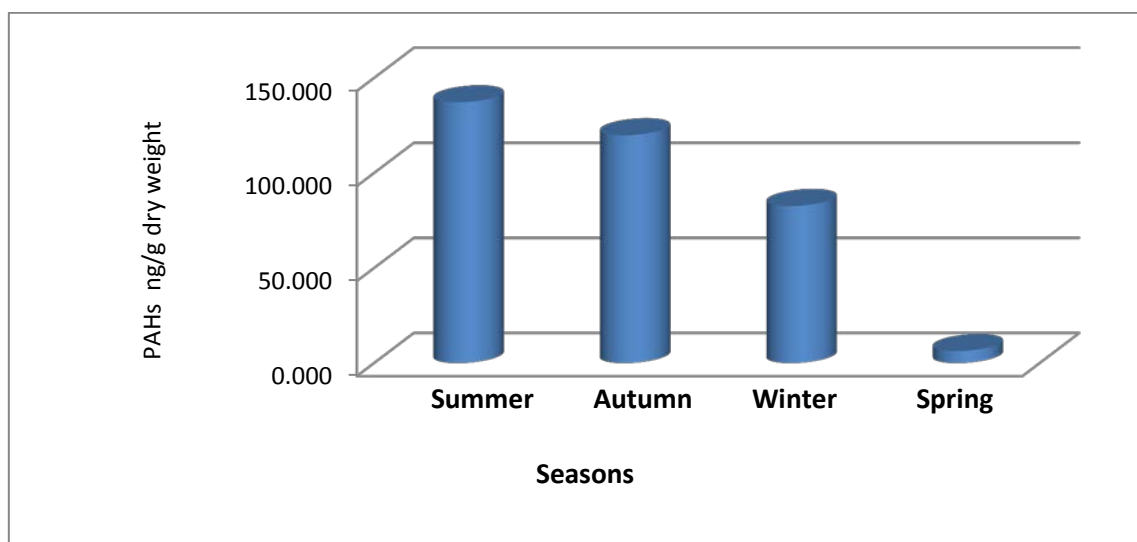


Fig (49) Seasonal variations of PAHs (ng/g d.w) in *S. litoralis*

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Table (34):Seasonal variations of PAHs(ng/g d.w) in *Schoenoplectus litoralis*

Compounds	Seasons			
	Summer	Autumn	Winter	Spring
Naphtalene	0.830	43.025	0.435	1.540
Acenaphtylene	63.005	4.630	26.967	ND
Acenaphthene	6.785	2.550	2.766	ND
Fluorene	8.186	20.745	1.861	ND
Phenanthrene	6.440	4.882	0.494	ND
Anthracene	32.124	10.548	27.963	0.067
Fluoranthene	0.245	ND	ND	ND
Pyrene	0.468	11.731	1.108	0.050
Benzo[a]anthracene	0.530	1.628	1.198	0.189
Chrysene	0.558	0.202	0.152	1.091
Benzo[b]fluoranthene	3.288	1.078	0.285	ND
Benzo[k]fluoranthene	0.961	3.053	3.542	ND
Benzo[a]pyrene	0.639	ND	2.524	ND
Dibenzo[a,h]anthracene	6.167	6.014	11.415	3.381
Benzo[g,h,i]perylene	6.091	4.196	1.898	ND
Indeno[1,2,3-c,d]pyrene	0.835	5.549	ND	ND
Total	137.153	119.828	82.608	6.318
LPAHs	117.370	86.378	60.486	1.606
HPAHs	19.783	33.450	22.123	4.712
L/H	5.933	2.582	2.734	0.341
BaA/(BaA+Chr)	0.487	0.889	0.888	0.148
Phenanthrene/Anthracene	0.200	0.463	0.018	ND

ND: not detected

PAHs in *Ceratophyllum demersum*:

The total concentrations of PAHs in *C. demersum* are present in figure (54) and table (35) ranged from 11.74 ng/g d.w during spring to 151.90 ng/g d.w during summer. From the total PAHs, Anthracene and Acenaphthylene forms the high ratio in light PAHs compounds, while Dibenzo(a,h)anthracene, Benzo (a) pyrene, and Indeno (1,2,3,c,d) pyrene form the high ratio from heavy PAHs compounds. Results of the present study showed LMW- PAHs was greater than the HMW-PAHs during all seasons. To determine the origin of PAHs in *C. demersum* according to ratios in table (35), the results of LPAHs/HPAHs ratio recorded a value more than one during all seasons, BaA/(BaA+Chr) ratio more than 0.35, while the Phenanthrene/Anthracene ratio was less than ten in all seasons, this result indicates that the sources of PAHs in *C. demersum* are petrogenic and pyrogenic.

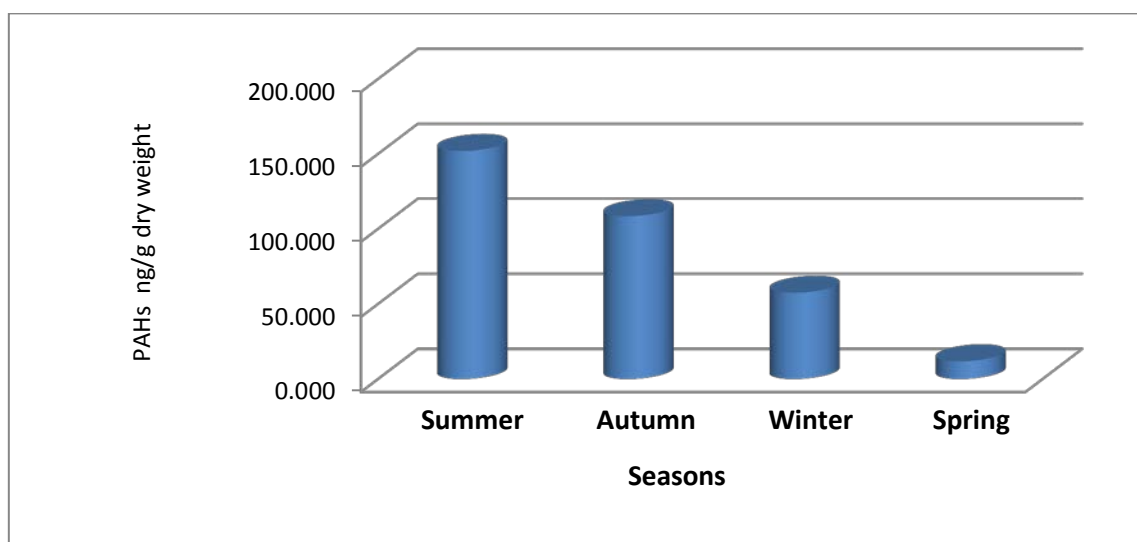


Fig (50) Seasonal variations of PAHs (ng/g d.w) in *C. demersum*

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Table (35): Seasonal variations of PAHs (ng/g d.w) in *Ceratophyllum demersum*

Compounds	Seasons			
	Summer	Autumn	Winter	Spring
Naphtalene	8.750	1.260	ND	0.216
Acenaphtylene	18.144	14.333	27.557	ND
Acenaphthene	8.341	6.428	7.396	5.696
Fluorene	11.368	16.755	10.033	ND
Phenanthrene	13.873	2.322	0.617	ND
Anthracene	37.751	25.567	1.095	ND
Fluoranthene	4.094	3.746	ND	ND
Pyrene	ND	1.295	0.014	0.311
Benzo[a]anthracene	0.221	11.236	0.348	0.179
Chrysene	0.202	0.252	0.624	0.217
Benzo[b]fluoranthene	0.093	1.979	0.009	ND
Benzo[k]fluoranthene	1.969	3.200	3.955	ND
Benzo[a]pyrene	0.373	6.743	0.480	ND
Dibenzo[a,h]anthracene	9.116	9.094	2.742	3.785
Benzo[g,h,i]perylene	7.013	4.216	0.689	1.333
Indeno[1,2,3-c,d]pyrene	30.589	ND	1.848	ND
Total	151.898	108.424	57.408	11.736
LPAHs	98.227	66.664	46.699	5.912
HPAHs	53.671	41.761	10.709	5.824
L/H	1.830	1.596	4.361	1.015
BaA/(BaA+Chr)	0.522	0.978	0.358	0.452
Phenanthrene/Anthracene	0.367	0.091	0.564	ND

ND :not detected

Chapter Four

Discussion

4.1 Physicals and Chemicals variables:

4.1.1-Temperature:

Temperature is a high-fluctuations environmental factor, which consider important parameter which regulated the biogeochemical processes in ecosystem (Mouillote *et al* .,2005). Each species growing best in optimum temperature range ,and this growth is reducing if the temperature below or above the optimum (Buttner *et al* .,1993;Al-Hejuje 2014).

In the present study the results showed seasonal variations in water temperature between summer and winter, this variations caused by variations in air temperature. Significant correlation ($r = 0.978$, $p < 0.05$) was found between water and air temperatures. The highest value recorded in summer that due to the long solar radiation and the length of the day period in the summer season. Also, water temperature depending on degree of shading caused by aquatic plants (Mohammed, 2007; Saleem, 2013).

The local variations in the temperature of water among stations may be due to the different in time of the sample at each station, turbidity, type of plants or they may be due to the different in the depth of water at each station, this finding is in agreement with Salman (2006).

4.1.2- Potential of Hydrogen ions (pH):

pH is an important factor to describing the chemical processes state in water, PH mean is a measure the concentration of hydrogen ion (H^+) in water(Wetzel, 2001). The pH values are affect by various factors such as temperature, the biological activity and CO_2 concentration ,the nature of climate and discharge of municipal and industrial waste waters (Sharma, 2014). Low pH value caused releasing of elements and toxic compounds from sediments to the water column and then into plants and other aquatic organisms (Van, 1999).

The range of pH in the present study indicated that water can be classified as slightly alkaline, it has being know that Iraq water mainly tend to be alkaline because present of carbonate and bicarbonate ions (Pradeep *et al.*.,2012), this result was agree with Al-Khafaji *et al.*(2012); and Al-Awady (2015).

There was a significant positive correlation between pH and temperature ($r=0.501$, $P<0.05$), and pH with salinity ($r=0.509$, $P<0.05$). This was confirmed by the results of the present study, which recorded that the highest value of pH was in the summer may be related to the high temperature and salinity of water which caused increasing the concentration of soluble salts (Odjadar and Okoh, 2010). While the lowest value of pH was recorded in the spring season, possibly due to the dilution factor by the increase in water levels and rainfall in this season(Kassim and Al-Saadi,1995), or may be due to the decomposition of dead organisms (specially aquatic plants), which lead to release carbon dioxide(acidification),ultimately reduce the pH value, this was in agreement with Varol *et al.*(2011).

4.1.3- Electrical Conductivity (EC) and Salinity(Sal.) :

Electrical conductivity and salinity is related to the water content of dissolve salt (Odum,1971).

Reid(1961) illustrated the limits on which surface water can be divided, salt water less than 0.5% is fresh water ,and 0.5 – 5% is oligohaline, whereas water with salinity between 5-18% is mesohaline. According to these classification, the present water can be classified as oligohaline.

The results of the present study showed highest levels of EC and salinity were recorded during summer ,that due to low water levels and an increase in evaporation rates. While, the lowest salinity and EC values were recorded in winter as a result of an increase in rainfall and higher water levels which caused dilution to the salt, in addition, decreasing of

evaporated processes during winter (Al-Bidhani,2014).These results was in agreement with Fahad (2006)and Qzar(2009).

4.1.4- Turbidity and Total Suspended Solids (TSS) :

The concentration and type of suspended material or colloidal matter control the turbidity and clearness of the water. Suspended matter consists of clay, silt, soluble organic compounds, fine particles of inorganic and organic matter, plankton and other microorganisms (Chapman ,1996).

The highest TSS concentration and turbidity during spring and winter in the present study may be attributed to increasing floods and rains at various places to the study areas which brings sand, clay and organic matters to the water column .The decomposition process which occur in sediments during spring season may be added large amounts of turbid matter to the aquatic environments. Also, the high values of turbidity may be due to the mixing processes resulting from the movement of boats which used in fishing, transport, and recreation that characterized the study areas (Al-Zaidi,2017). Positive significant correlation ($r=0.769$ at $p<0.05$) between turbidity and total suspended solid. The result was in agreement with (Jazza, 2009).

4.1.5-Dissolved Oxygen(DO) and Biological Oxygen Demand (BOD) :

Dissolved oxygen is an important parameter affecting aquatic organisms (Wetzel,2001). This is influence by number of physical and biological factors ,such us temperature, salinity and the amount of organic material, decomposition process (EL-Nemaki *et al.* 2008).

Increase in the water temperature, lead to evaporate gases from the water, including dissolved oxygen, and decreasing the dissolved oxygen level. Or as a result of the increased metabolic processes of aquatic organisms. In addition, pollution of water by sewage cause to the

consumption of large amounts of dissolved oxygen by bacteria, which work to decompose organic matter(Al-Awady ,2015).

Results showed highest values of dissolved oxygen was recorded in winter whereas the lowest values recorded during summer season ,this is because increasing of water temperature that lead the increasing to organic matter oxidation which cause consumption of dissolved oxygen in water during summer (Valdes and Real, 2004) .In contrast ,the maximum values was recorded in winter ,because of decreasing in temperature which lead to increase the dissolve gases in water(Lind,1979), a significant negative correlation was found between water temperature and dissolved oxygen level ($r = -0.854$, $P < 0.05$).

In addition ,the wind and rain , which increase the movement of water as well as dissolved oxygen ratios, also the effectiveness of photosynthesis by phytoplankton and aquatic plants which released oxygen to aquatic environment (Chapman, 1996).

BOD₅ value were fluctuated in water of marsh ,the lowest values were observed during winter season, while higher values during spring, this may be due to the decreasing biological degradation by bacteria and other microorganisms during low temperature and increasing during high temperature (Al-Shawi, 2006).Also, dead aquatic plants during late winter and beginning of spring (personal observation) caused more decomposer process during spring season, this explanation was in agreement with Al-Nagare (2009) and Mashkhool (2012).

4.1.6.Total Organic Carbon(TOC%) and Grain Size :

The terms clay, silt , and sand represents the size of the soil particles(Balasim, 2013). The grain size of Al-Chibayish marsh different in their percentage from station to another according to the geological origin and the effluent discharges. Generally, according to the texture compounds

Chapter Four: The Discussion

percentage, the sediments of Al-Chibayish marsh can be considered as silt-clay sediments .

The wastes of human and animal play an important role in increasing the content of organic carbon in sediment. The chemical and biological processes that take place in sediment greatly affect on the proportion of organic carbon (Balasim , 2013). The highest values was founded during winter related to high precipitation ratio of dead aquatic plants during winter, while the lowest during summer at all stations, is due to rise of temperature which stimulate microbial enzymes ,therefore the biodegradation processes generally increases with the increasing temperature (Foght *et al* .,1996 ; Ouyang,2003). TOC values showed negative significant correlation with water temperatures ($r=-0.627$ $p<0.05$). Result of the present study were in agreement with Al-Abadi (2011) and Maskhool (2012).

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Table(36)Comparison of the environmental factors in the present study at Al-Chibayish marsh with other previously studies .

W.T C	EC	Salinity	pH	TSS	DO	BOD	Turbid.	TOC%	References
	2.8-5.9		7.3-7.5					1.9-4.4	Al-bbawy(2009)
8.4-30.4		1.2-6.3	7.4-8.8						Abd (2010)
10.3-28.3	5.7-7.7	3.6-4.92	8.06-8.55	-	4.3-9.86		-	1.64-2.85	Mashkool(2012)
14-39	3.8-12.5	-	7.8-8.6	-			20.9-65.3	7.5-15	Al-Zaidi(2017)
10.5-33	4.53-6.15	2.5-3.4	7.24-8.15	1.68-97.22	0.7-7.75	0.75-3.5	1.3-50.55	9.93-13.49	Present study

4.2-The Heavy Elements:

4.2.1-Dissolved Phase :-

The total concentration of element in aquatic environment is not a good predictor of its bioavailability. Element speciation greatly affects element availability for aquatic organisms; only a part of the dissolved element is bioavailable (Al-Haidarey, 2009).

In the present study the concentrations of the studied heavy elements (Cd,Cr,Ni and Pb) as dissolved phase at most stations and seasons were below the permissible limits of drinking water according to the WHO limit (2011), and this result was in agreement with most studies done at marshes, this decreasing of elements concentrations in the studied area may be due to many factors such as: the lowest level and flowrate of water in the marshes, quantities and qualitative of plankton and suspended material that load in the water, complexion with organic matter and precipitate to the sediment, accumulation of element in aquatic plant (Harding and Whitton,1978 ; Al-Khafaji *et al.*, 2012 ; Al- Awady *et al.*,2015).

Decreasing of heavy elements in dissolved phase in the present study may be due to the removal of these elements by their deposition on suspended materials, sedimentation and/or removal by the organisms, especially aquatic plants. This finding was in agreement with Morris (1978) who noted that the heavy elements in the water are eventually separated into suspended matter, sediments or living organisms.

Negative significant correlations between Ni and Pb (Table 37) suggested that they had different pollutants origin, or they have different characteristics (Song *et al.*, 2010 ; Manoj *et al.*, 2012 ;Al-Hejuje, 2014). Also non- significant correlation between turbidity and each of elements may refer to the adsorption of these element on the turbid matters and reflect them as particulate matter.

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Table (37):The Pearson's correlation coefficients between dissolved heavy elements and different variables in Al-Ghibayish marsh.

elements	Cd	Cr	Ni	Pb
Cd	1			
Cr	-0.23	1		
Ni	-0.06	0.23	1	
Pb	0.28	-0.11	-0.73 **	1
pH	0.41	-0.09	-0.15	0.17
Salinity	-0.06	-0.20	-0.14	0.03
Turbi	-0.04	0.09	0.30	-0.32
TSS	-0.09	-0.47	-0.57 *	-0.38
Water Temperature	-0.34	-0.181	-0.48	0.47

** :Significant correlation at $P < 0.01$: * :Significant correlation at $P < 0.05$

Most of the studied elements, as dissolved form, showed non-significant differences among stations. The fluctuation of concentrations could be attributed to the interactions between some factors such as the aquatic plants and phytoplankton abundance which absorbed or adsorbed the ionic elements, the fuel burn emissions specially result from machines of fishing boats that released large amounts of lead and less amount of other compounds, that affect the concentrations of dissolved elements.

The dissolved phase of the studied heavy elements compared with the previous studies (Table 38) found that these concentrations were within the ranges in Al-Ghibayish marsh.

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Table(38): Comparison the mean concentrations of studied heavy elements in dissolved phase ($\mu\text{g/l}$) for the present study with the previous marshes studies.

Location Area	Cd	Cr	Ni	Pb	Reference
East Hammar marsh south of Iraq	0.22	-	-	6.04	(Qzar (2009)
Al-Hammar marsh south of Iraq	0.45	-	2.13	0.17	Al-Khafaji (2010)
Abu-Zariq Marsh South of Iraq	0.21	-	1.71	1.61	Al-Abadi (2011)
Al-Chibayish marsh south of Iraq	1.05		6.37	1.37	Al-Khafaji (2015)
Al-Chibayish marsh south of Iraq	0.057	2.029	0.555	2.965	Present Study

4.2.2-Particulate Phase :-

The heavy elements of the ecosystem are involved in a number of interactions, including absorption, the formation complexes and sedimentation, and these reactions affect the removal of elements from water column (Allen ,1993).

The partition between the elements in dissolved and suspended particulate matter determines their ultimate fate in the aquatic environment (Al-Awady *et al.*, 2015).

Some heavy elements in particulate phase negatively significant correlated with their concentrations in dissolved phase (Table 39), this could be due to the ability of suspended particulate to accumulated these elements from the surrounding water, causing decreasing concentration in dissolved phase and increasing concentration in particulate phase (Al-Hejuje, 2014).

As well, there were high particulate concentrations of most elements Cd , Ni, and Pb in summer compared to spring, this may be related to

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high growth rate of phytoplankton in summer which have the ability to accumulate heavy elements in their bodies and this cause to increased concentrations of heavy elements in particulate phase. In addition, high pH value leads to increased heavy elements in the particulate phase (Byrd *et al.*, 1990; Fang & Lin 2002). The high pH value tends to make the elements remain in the suspended materials and does not lead to the dissolution of the hydroxide ion of elements (Byrd *et al.*, 1990). This was confirmed by the results of the present study, where high concentrations of elements ,as particulate phase ,were founded in the summer while low concentrations in the spring , and this is consistent with many previous studies(Al-Haidarey,2009; Qzar,2009 ;Al-Awady,2015). The negative correlation coefficients between the concentrations of Ni or Cr in dissolve and particulate phase (Table 39) give an image that these elements was essential for the growth of phytoplankton which have the ability to accumulate these elements within their bodies (Al-Hejuje,2014). While, positively correlation coefficients between the concentrations of Pb or Cd in dissolve and particulate phase give an image that these elements was non-essential for the growth of phytoplankton ,therefore, the concentration of Pb or Cd in their bodies was dependent on and correlated to the concentration in dissolved surrounding water.

Table(39):The Pearson's correlation coefficients between heavy elements in particulate and dissolved phase and some variables measured in Al-Chibayish marsh .

Particulate	Cd	Cr	Ni	Pb
Dissolved				
Cd	0.08	0.17	-0.02	0.20
Cr	- 0.13	-0.20	0.16	-0.21
Ni	-0. 50 *	0.24	-0.29	-0.51 *
Pb	0.16	-0.16	-0.18	0.21

*: Significant correlation at $P < 0.05$

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The mean concentrations of all the studied heavy elements in particulate phase were greater than their concentrations in dissolved phase, this was attributed to the increased particulate matter in the water, which include living and non - living components. The particulate, which contain organic matter, colloids and element hydroxide, have large surface area therefore they can adsorb great concentrations of heavy elements from aquatic environments. So that, the increased the suspended matter in water cause to the transfer of elements from the dissolved to particulate phase (Warren and Zimmerman, 1994; Ogoyi *et al.*, 2011; Awady *et al.*, 2015), this finding was in agreement with Al-Hejuje (1997) and Habeeb *et al.* (2015).

The mean concentration of heavy element in particulate phase of the studied area was compared with the previous studies (Table 40) shown higher concentrations in the present study, this may be due to the elevated of turbidity level in the present area.

(Table 40) Acomparision between the mean of heavy elements concentrations in Particulate phase ($\mu\text{g/g}$ dry weight) in Al-Chibayish Marsh with the previous studies in marshes.

Study Area	Cd	Cr	Ni	Pb	References
East Hammar marsh south of Iraq	5.28	-	-	19.31	Qzar (2009)
Al-Hammar marsh south of Iraq	6.15	-	44	40.55	Al-Khafaji (2010)
Abu-Zariq Marsh South of Iraq	4.05	-	10.11	20.37	Al-Abadi (2011)
Al-Chibayish marsh south of Iraq	8.05	-	110.8	13.1	Al-Khafaji (2015)
Abo-Garak marsh	9.39	-	-	3.07	(Habeeb <i>et al.</i> (2015)
Al-Chibayish marsh south of Iraq	26.69	279.57	334.57	575.03	Present study

4.2.3-Sediments:-

Sediments consider as the final recipient of pollutants from natural and anthropogenic origin in aquatic environments (Hassan *et al.*,2010). Thus, they are represent as a good bio-indicator for water pollution. Also, the accumulation of elements in the sediment that result of long term exposure ,while the concentration of element in the water as dissolved is mainly result of recent contamination (Brankovic *et al.* ,2011)

A major part of the heavy elements, which enter the aquatic environment eventually settle down in the sediment, therefore the sediment act as archives for many pollutants such as heavy elements (Al-Khafaji ,2010). The high concentrations in sediments than in dissolved phase due to the strong binding affinity of heavy elements to the sediments (Al-Hejuje ,2014). In the present study, results shown that the concentrations of Cd and Pb in the exchangeable phase of sediments were higher than those in the residual phase of sediments (Tables 6 and 9), this finding could be a good evidence that there is an anthropogenic origin of pollutants which incorporated into the sediment from aqueous solution by processes such as adsorption and organic complication , this finding was in agreement with (Habeeb , 2015). Significant correlations between heavy elements in the sediments (Table 41) suggested that they had the same geochemical origin or behaviors (Song *et al.* , 2010 ; Manoj *et al.* , 2012).

Most heavy element in sediment positively significant correlated with clay particles and negatively correlation with the sand (Table 41) , this could be attributed to the sediment particles size which play an important role in the concentration and distribution of heavy element . Small particle size which have a large surface area ,such as clay and silt has an ability to accumulate higher concentration of heavy element because of these particles allowed to adsorption of element into their surface (Bentivegna *et al.*,2004) .

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Moreover, high concentrations of heavy elements in sediment as compared with the concentrations in the dissolved phase may be due to the increasing plant abundant at these stations in marshes which played an important role to increasing the heavy elements in the sediments, because plants work to reduce flow rate of water and this leads to deposit of suspended matter ,which containing high concentrations of heavy elements, to the sediments. The present results was in agreement with Mashkool (2012).

Table (41): The Perasons correlation coefficients between total heavy metals in sediments and the related variable measured in Al-Chibayish marsh .

Variables	Cd	Cr	Ni	Pb
Cd	1			
Cr	0.66 **	1		
Ni	0.33	0.78 **	1	
Pb	0.88 **	0.70 **	0.37	1
Sand %	-0.05	-0.24	-0.49 *	-0.15
Silt %	-0.09	-0.05	0.21	-0.07
Clay %	0.22	0.50 *	0.54 *	0.32
TOC %	0.09	0.14	0.16	-0.04

** : Significant correlation at $P < 0.01$; * Significant correlation at $P < 0.05$

The concentrations of heavy elements in surface sediment of the study area at Al-Ghibayish marsh was compared with the previous studies (Table 42) found that these concentrations were within the range of previous studies.

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Table(42):Comparison mean values of heavy elements concentrations in total sediment($\mu\text{g/g}$ dry weight) in the present study with the previous studies.

Studied Area	Cd	Cr	Ni	Pb	Reference
Some wetlands in south of Iraq	2.52-26.62	-	95.67-486.95	26.54-543.75	Mohmood(2008)
East Hammar south of Iraq	0.37	-	-	13.29	Qzar (2009)
Abu-Zariq Marsh South of Iraq	2.99	-	35.32	73.76	Al-Abadi(2011)
Al-Chibayish marsh south of Iraq	2.32	-	81.25	5.1	Mashkool(2012)
Al-Chibayish marsh south of Iraq	0.69	102.65	121.70	39.62	Present study

4.2.4- Heavy elements in aquatic plants

The level of environmental contamination could be reflect by organisms that have the capability to take up elements proportionally to their concentration in the surrounding environment, this is associated to organisms that accumulate the elements independently as their physiological needs because they do not have the capacity to discriminate between different elements(Brankovic *et al.*,2011). Because the aquatic plants have the ability to absorb the heavy elements from water column and sediments and accumulate them in their tissues, therefore, the aquatic plants use as a good monitor and biological indicators for element pollution in the aquatic ecosystem (Cheng 2003).

The result showed non significant differences at (P 0.05) in the concentration of heavy elements among the studied stations, this may due

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to that plants of these stations exposure to same type of pollutants such as oil split from boats ,sewage and chemicals used for fishing .

While the concentration of heavy elements in tissues of plants showed different among seasons, that due to many environmental factors such as the different ability of aquatic plant possess to accumulate element in their tissue , and the uptake of the element which depended on plant species and the difference in the age state of plants , this finding was in agreement with Cardwell *et al.*(2002) and Mahmood (2008) how found that there were specific seasonal differences in the concentration of element in studied aquatic plants. Anther reason for such concentration was the available element in water or sediment, different pollution source, growth form of plant and the physical-chemical factors such as pH, salinity and TSS (Saygideger *et al.*,2004; Habeeb *et al.*,2015). The variation of plant species contents may be due to the way of stored element ,many plant species stored elements in their stems or at their roots. Also, the accumulation of elements in aquatic plants tissues are affected by the depth of the water column (Oudeh *et al.*,(2002).

The results showed that the aquatic plants differ in their accumulation of heavy elements according to the above reasons as the following order:

Ceratophyllum demersum > *Phragmites australis* > *Typha domingensis* > *Schoenoplectus litoralis* .

Comparison of total element uptake by the studies plants showed the higher uptake and absorbent of all elements from various concentrations was occurred by the submergent species *Ceratophyllum demersum* , that may be due to the nature of the plant that have the ability to absorb this element from surrounding water and sediments ,and the surface area of the plant branches that twigs over anumber of other species (Zaki *et al.*,2016). Al-Mayah (2016) pointed that *Ceratophyllum demersum* specie fully adaptable to aquatic life, so they are rootless and most of the

plant's body is busy with branches leaves ,which has the function of stabilizing the plant as it grows into the depths of the sediments . The present result was in agreement with (Al-Awady *et al*,2015; Zaki *et al*,2016 and Hanef, 2016) they found the concentrations of element in this specie was more than their concentrations in other aquatic plants.

The different in accumulation may be due to the different accumulation mechanisms of heavy elements in the aquatic plants tissue which including : linked the toxic elements to the cells walls in the roots or stem which prevents transmission to the vegetable sap, or it is expels to non-sensitive place in the cells and storing in air vacuoles (Memom *et al*.,2001). Cobbet (2000) pointed out that the tolerance of the plant to the high levels of elements may be due to binding these elements to peptides which containing the thiol group(-SH group) and this called phytochelatins , or through the elementlothioneins that are proteins found in the plant cell plays an important role in the removal of toxicity by binding to the elements in the cell (Rauser,1999).

According to (Memon,2001) phytochelatins and elementlothioneins in plants cell form complexes with heavy elements and translocate them into the air vascular . This is a mechanism of hyperaccumulation heavy elements in plants .

The studied plants were characterized by their absorption of elements higher than the concentration in water, but less than those in the sediments (Table 11). It is clear that the concentration of heavy elements is not necessarily related to those of sediments, Stoltes and Greger (2002) pointed that it is not necessary to link the mineral concentration in the plants with their levels in the sediments while the results disagreement with Al-Saad *et al* .(1994) and Al-Tae (1999) who showed that the elements concentration in the tissues of the plant is higher than in the surrounding water or sediment. The low concentration of elements within

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the plants tissues as compared to the sediments in this study may be due to the variation of accumulation mechanism (Marseille *et al* , 2000).

The results of the statistical analysis showed some correlations among the elements that absorbed by the studied aquatic plants (Table 43). A positive significant correlation between Cd and each of Ni and Pb . Also, Cr significantly correlated with Ni .Other elements has shown non-significant correlation with each others. These results, in turn, confirm that the accumulation of elements in plants is variation by different elements and plants species.

Also (Table 43) showed negative significant correlation between the total suspended solid matter in water and the concentration of heavy elements in plant tissue ,this result may be due to the suspended solid material consists of different organic and inorganic matter , and most of them hold on the particles surfaces. Organic material in the water column have the ability of binding the heavy elements (Balkis *et al*,(2010).

Table (43) Pearson correlation coefficients between heavy elements concentration in plant samples and with total suspended solid matter in water.

	Cd	Cr	Ni	Pb
Cd	1			
Cr	0.44	1		
Ni	0.49*	0.62*	1	
Pb	0.69**	0.37	0.33	
TSS	-0.75*	-0.50*	-0.78*	-0.10

Generally ,this study showed that the highest concentrations for heavy elements was in particulate phase ,followed by the sediments, then the aquatic plants and the lowest concentrations was recorded in the

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dissolved phase , and these results were in agreement with Mashkool (2012).

Table(44) :Comparison mean metal concentrations in aquatic plants($\mu\text{g/g}$ dry weight) in Al- Chibayish marsh with the other previous studies.

Study Area	Study Area	Cd	Cr	Ni	Pb	References
Al-Hammar marsh	<i>C. demersum</i>	0.90	-		0.78	Awad <i>etal</i> ,(2008)
Al-Chibayish marsh	<i>P.australis</i>	1.75	-	67	3.4	Mashkool(2012)
	<i>T.domingensis</i>	1.37	-	59.75	2.97	
Al-Chibayish marsh	<i>T.domingensis</i>	1.35	-	54.5	3.72	Al-Khafaji(2015)
Al-Chibayish marsh	<i>P.australis</i>	0.20	5.27	4.21	6.19	Present study
	<i>T.domingensis</i>	0.20	3.96	3.05	5.60	
	<i>S.litoralis</i>	0.20	4.58	3.49	4.31	
	<i>C. demersum</i>	0.51	9.73	51.44	9.99	

4.2.5-Heavy Elements Pollution Indices:

4.2.5.1-The Heavy Elements Pollution Index(HPI):

The HPI value is less than the maximum threshold value of 100 as proposed by Reza and Singh (2010) This result indicates that the influence of the four studied elements on the marshes water quality is not alarming because it's below the permissible limits of drinking water according to the WHO (2011).

The concentrations of the four heavy elements in Al- Chibayish marsh water at all stations were found to be low and within guideline levels recommended (Appendix 2). This result was disagreement with Al-Hejuje (2014) who founded HPI value at Shatt Al-Arab river alarming

because it's higher than the permissible limits of drinking water according to the WHO (2011), thus considered that river as polluted with heavy elements, this may be due to the different characteristics of these two ecosystems (river and marsh). Also, the Shatt Al-Arab river received heavy organic pollutants through its branches at Basrah city that have high level of heavy elements in addition to the shipwrecks in shatt Al-Arab river (Al-Hejuje *et al.*,2017). Ewaid (2016) recorded the HPI value was (98.6) in Al- Gharraf river water slightly below the critical value100 for drinking water.

4.2.5.2- The Geo-accumulation Index (I_{geo}) :

The I_{geo} values can be used effectively to determining the extent of heavy element accumulation in sediments .The I_{geo} grades for the surface sediments in the present study differ from element to element and from station to station. According the I_{geo} values the sediments at all the studied stations were considered as unpolluted with Cd and Pb ,but unpolluted to moderately polluted with Cr , and moderate to moderately-strongly polluted with Ni .This could be due to the high concentrations of these elements in surface sediments that exceeded the world surface rock average according to CBSQG (2003) values (Appendix 3).The present result was in agreement with Al-Sabah and Aldhahi (2017)who found that the sediments of Auda marsh was unpolluted with Zn , Fe, Cu and Pb , While disagreement with Al-Haidarey *et al*(2010)who found that the sediments of Al-Hawizeh Marshes were suffering from moderately to strongly contaminate with the As ,Cd, Cr, Co ,Cu and Pb according to I_{geo} values. The different in results may be due to the different in the studied areas characteristics and different the studies periods.

4.2.5.3-Bioaccumulation Factor (BAF):

Bioaccumulation factor can turn out to be important tools to identify hyperaccumulator species ,because bioaccumulation factor is refers to the

species efficiency to accumulate heavy elements into their tissues from the surrounding environment (Ladisalas *et al.*, 2012). Willson and Pyatt(2007) state the plants with BAF greater than 100 have potential to act as hyperaccumulator and indicator of pollution .

From the result of present study it is clear that BAF values varied from one plant species to another ,and also from one element to another. Generally ,the BAF for *Ceratophyllum demersum* species was highest values (>100)for all studied elements, therefore, *Ceratophyllum demersum* can be used as hyperaccumulator and bioindicator for heavy elements pollution , whereas the other studied species that showed low BAF values (<100) for studied elements can't be classified as hyperaccumulators .

The present study reveals the tendency of aquatic plants to bioaccumulate heavy elements. The concentration of Cd in the studied plant (0.2-0.51µg/g dry weight)was non phytotoxic. Whereas the concentration of Cr (3.96-9.73 µg/g dry weight) indicating as high phytotoxic for the studied plant , whereas the concentration of Nickel (3.05-51.44 µg/g dry weight), Lead (4.31-9.99 µg/g dry weight) indicating as phytotoxic for the studied plant (Kabata-Pendias,2011). Aquatic plants considered as biological filters which directly effect the remover of heavy elements in any aquatic ecosystem .

4.3 – The Hydrocarbons:

4.3.1 - Total Petroleum Hydrocarbons (TPHs):

4.3.1.1 – TPHs in water:

Hydrocarbons reach to the aquatic environment from a number of sources, including bio-synthesis by living organisms, especially aquatic plants, or their entry from adjoining lands and the atmosphere (GESAMP,1993;Al-Bidhani,2014).

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Distribution and concentrations of petroleum hydrocarbons are a good indicator for the study state of the aquatic environment .It can indicate the source of the pollutant that deserve special emphasis or needs more control (Talal ,2008;Jazza,2015).

Results of the present study showed the highest levels of TPHs in water during winter ,while the lowest levels observed during summer, which indicates the effect of temperature on the removal most of hydrocarbons from water (Al-Saad, 1995). Temperatures affect in two main directions, the first one is to increase evaporation, in this process, carbon compounds with low molecular weights evaporate as well as the breakdown of carbon compounds which have high molecular weights (Law, 1981). The second affect of temperature including increase the enzymatic activity of microorganism that use oil as an important source of organic carbon (Shamshoom *et al* ., 1990). Harnstrom *et al* (2009) demonstrated that about 20 to 50 % of hydrocarbon compounds will be lose during evaporation processes, also the increase of enzyme activity of microorganisms increasing when temperature in the range 30 C° to 40 C° (Leahy and Colwell,1990) .

The other factor is photo-oxidation, which results in the breakdown of oil compounds in the water column, so that this process is very important to change these compounds into simple ones(Ehrhardt and Patrick ,1993).

In addition high levels of TPHs were showed during winter this may be attributed to the increase fall of airborne from atmosphere during rain of these compounds which occur during winter , and to use a high amounts of wood and hydrocarbons compounds for heating or other uses (Al-Saad ,1995).

The result of this study was in agreement with Al-Khatib (2008) and Jazza (2015),a negative significant correlation between TPHs and each

of water and air temperature respectively ($r=-0.606$ and $r=-0.574$ at $p<0.05$).

4.3.1.2-TPHs in sediments :

Pollutants in the aquatic environment reach the sediments either by direct deposition due to their high weight or carrying with water currents to long distances and then precipitate according to decreasing velocity of currents (Aboul-Kassim and Simoneit,1995;Al-Khatib,2008). Also these compounds enter living organisms through the food chains and eventually reach the sediment during death of living organisms(Al-Saad,1995). The pollutants in aquatic ecosystem tend rapidly to adsorption on particulates and suspended substances in the water column ,then sink to the bottom(Al-Hejuje,2014). In the present study there was a positive significant correlation between TSS and TPHs in sediments ($r=0.566$ at $p<0.05$).This result was in agreement with Jazza (2015), for those reasons the concentrations and distribution of TPHs in water column are very low as compared with these concentrations in sediments .

The seasonal distribution of TPHs in sediments shows that the highest level was recorded during winter ($52\mu\text{g/g}$) at all stations and the lowest levels was during summer ($21.17\mu\text{g/g}$). That may be attributed to low temperature during winter which lead to decrease the evaporation and biodegradation processes by microorganism in sediments .Also the rate of organic matter sedimentation and the solubility of hydrocarbons affect by water temperature (Al-Dossari ,2008), as well as the high death of aquatic plants and phytoplankton during winter which cause to increase hydrocarbons concentrations in sediments (Al-Timari *et al* ., 2003 ; Al-Imarah *et al* ., 2006a), so we found that there is a positive significant correlation between TOC% and TPHs in sediments ($r=0.808$ at $p<0.05$). Whereas the total hydrocarbons concentration was decrease during

summer season due to elevated air and water temperatures(Al-Dossari ,2008). A negative significant correlation between TPHs and temperature of air and water ($r=-0.516$ and $r=-0.520$ at $p<0.05$) respectively. This result was in agreement with (Al-Khatib,2008 and Al-Taie ,2013). The TPH in the present study was compared with the previous studied and found they were located within the ranges (Table 46).

4.3.1.3- TPHs in aquatic plants :

Plants are the most important components of the ecosystem because they are the main source of energy, on land, marine or fresh water (Richardson and Hussain , 2006). Aquatic plants, accumulate chemical compounds such as hydrocarbons, so they are used as bio- indicators to identify environmental changes in the region(UNEP, 2001).

The results of the present study showed that there was variation in the concentrations of TPHs. The total concentrations of hydrocarbons at all studied aquatic plants were highest in the summer and the lowest in the winter, this may be due to the fact that summer is considered as the growth season of the plant(Al-Imarah *et al.*,2006b).

The sequence of total hydrocarbon compounds accumulation in the aquatic plant specie was follow:

Typha domingensis > *Ceratophyllum demersum* > *Schoenoplectus litoralis* > *Phragmites australis*.

It can be observed that there was a variation in the concentrations of TPHs in different species of aquatic plants ,these variations may be attributed to the different abilities of plants specie to accumulate of certain pollutants from the environment. Also the accumulation processes of pollutants may depend on some physical and chemical properties like temperature, pH , salinity, dissolved oxygen and

concentration of nutrients in the surrounding environment (Thomas *et al.*, 1984 ; Al-Saad ,1994).

Boehm and Quinm (1998) confirmed the difference in plant species ability to concentrate hydrocarbons is related to the volume of fatty tissue of each plant, this difference depends on the type of plant which are considered lipophilic on accumulation in fatty tissue. (Talal,2008)

In the present study noticed the concentration of TPHs within plant tissues are higher than their concentrations in water , which is consistent with the study of (Al-Saad, 1996 and Talal,2008).

4.3.2-The Normal Alkanes (N-alkanes):

4.3.2.1- N-alkanes in water:

Eliphatic compounds are an important part of hydrocarbons , N-alkanes inter the aquatic environment by different ways such us the geochemical factors, anthropogenic source, biosynthesis by aquatic organisms and biodegradation for plankton and aquatic plants (Al-Saad,1996).

The results showed that seasonal variations in the concentrations of n-alkanes was found in the water of Al-Chibayish marsh which were higher in winter than in summer season ,this due to the high temperature in summer season lead to increase the evaporation of low molecular weight hydrocarbons and also stimulation biodegradation processes of organic matter by different microorganisms (Al-Saad and Al-Timari ,1993).While the low temperature in winter season lead to decrease the evaporation and biodegradation processes to the hydrocarbon compounds(Al-Saad ,1995), also increasing the use of fuel in heating during winter season (Al-Khatib ,2008 and Jazza ,2015) .In addition found the large numbers of fishing and transportation boats in the studied station which release a lot of hydrocarbons from exhaust engine oils to the environment (Rushdi *et al* .,2006 and Al-Bidhani,2014).This results was in agreement with Al-Khatib (2008) and Jazza (2015).

The presence of odd carbon numbers is due to algae and phytoplankton (Al-Saad,1995). Law *et al* (1994) and Cripps (1995) pointed that the source of the odd carbon (C15,C17,C19)compounds in the aquatic environment is due to present of phytoplankton and algae. While, abundance of odd carbon n-alkanes C25,C27,C29 and C31 had been used as monitor to organic material which derive from terrestrial plants (Zhao *et al* ., 2003 and Sakaria et al .,2008). In addition ,Al-Saad and Al- Timari (1994) pointed that the source of odd compounds (C17 -C 21) in the Iraq marsh water is due to the present of diatoms. Also Tynni (1983) explained that the diatoms are the source of the normal alkanes with the even carbon number .While the source of C22 and C24 were from bacterial activities (Al-Khatib ,2008 and Talal,2008).

The undetectable values of C10 – C15, and the low values of C16- C17 may be due to the fact that the low molecular weight n-alkanes such as C9-C15 in water to evaporate easily or has the ability to decompose by microorganisms , while the high molecular weight n-alkanes such as C33-C36 , which is more resistant to biodegradation , has the ability to settle down to the sediments. This finding was in agreement with Al-Hejuje (2014).

A number of indices such as carbon preference index (CPI) and the ratio of Pri/Phy had been calculated to recognize the sources of n-alkanes in water samples. most stations have CPI around or less than one number referred to anthropogenic origin of n-alkanes in water, while other stations have CPI greeter than one number indicating biogenic source of n-alkanes, such as bacteria, phytoplankton and aquatic plants. Another indicator of the n-alkanes source is the ratio of the isoprenoids pristane and phytane . Pristane is usually found in zooplankton, while phytane is reported as a normal component of oil (Guerra-García *et al.*, 2003). Also the (pristane and phytane) came

indirectly from aquatic biomolecules like chlorophyll (Al-Hejuje, 2014). When pristane/phytane ratio low than one number referred to anthropogenic origin, and the ratio greater than one referred to biogenic origin. Because most samples in the present study have undetectable values for pristane and /or phytane at most periods, therefore shows the disadvantage of this index in water samples for Al-Ghibayish marsh, the same conclusion have been arrived by (Al-Hejuje, 2014).

4.3.2.2- N-Alkanes in sediments:

The surface layer of the sediments is important for studying the seasonal and regional variations of hydrocarbons and the types of n-alkanes in the aquatic environment, because about 56% of hydrocarbons in water are adsorbed to suspended particles according to their low solubility in water (Al-Saad, 1995). High values of n-alkanes in the sediments were noticed as compared with the water column values.

Generally the total concentrations of n-alkanes in sediments during summer were less than in winter. This may be due to rising temperature during summer which plays an important role in the evaporation processes of these compounds. Also biodegradation processes which occur by the sediments microorganism was stimulated during summer season. Although hydrocarbon compounds biodegrade over a wide range of temperatures, the rate of biodegradation generally decreases with decreasing temperature (Al-Dossari, 2008). This result was in agreement with Al-Khatib (2008) and Talal (2010).

The carbon chain length of n-alkanes in the sediments samples was ranged from C₁₆ to C₃₈, various carbon number of n-alkanes in sediments may come from different biological sources such as plankton which produce a simple mixture of hydrocarbons dominated by short chain of odd carbon C₁₅, C₁₇ and C₁₉ (Goutx and Saliot, 1980; Gogou *et al.*, 2000).

Al-Saad and Al-Timari(1994) pointed to the diatoms which responsible for (C15-C21) in the sediments of Iraqi south marshes. while the source of high molecular weight (C23- C31) where from vascular higher plant wax(Al-Saad ,1995; Al-Khatib *et al.* ,1998 and Rusdi et al.,2006) , Whereas, the main origin of long chain even carbon numberes C20-C30 in sediments are related to bacterial activity (Simoneit ,1993 ;Al-Timari ,2001 ;Al-Khatib ,2008). Same conclusion have been reached by Rushdi *et al.*(2006) in sediments of southern Iraqi marshes.

The CPI values at most stations were more than one number, according to high value of odd carbons chains, indicating biogenic source of n-alkanes like from bacterial activity, algae and wax of vascular higher plant leaves (Pearson and Eglinton 2000; Meyer, 2003; Medeiros and Bicego, 2004; Gao *et al.*, 2007).while other Location like St 1,2,3 in winter and spring also St4 in summer and autumn, which have CPI less than one number referred to anthropogenic origin.

There were non-significant correlation ($p>0.05$) between the n-alkanes in sediments and each of TOC% or the sediments texture compounds (silt ,clay and sand). This result was in agreement with (Al-Hejuje,2014) and (Al-Saad *et al* ,2015) who found that non-significant correlation between the n-alkanes in sediments and each of TOC% and the sediments texture compounds (silt, clay and sand), this may be due to another factors affect

The concentration of n-alkanes in the present study was compared with previous studies as shown in (Table 46), and found it is within the rang.

4.3.2.3- N-Alkanes in aquatic plants:

The carbon chain length of n-alkanes in the aquatic plants sample was ranged from C9 to C38, observation the high concentration of odd carbon number n-alkanes and high molecular weight, it is distinguished

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characteristic of higher plants. Generally, results of this study exhibited that plants had a high proportion of odd carbon number comparative to even carbon number at all seasons which are derived from bacteria, fungi, phytoplankton and zooplankton . These results was in agreement with Al-Khatib (2008) and Abed Ali (2013).

The results showed that all CPI values were greater than the number one at all stations and seasons that indicate the origin of n-alkanes were biogenic , except for the *Ceratophyllum demersum* plant species, where the value of carbon less than one (0.506) during winter season which indicate the anthropogenic origin. While the ratio of pr/ph ranged from 0.137 to 1.809 for all studied plant and that indicate the origin of most compounds were anthropogenic and few from biogenic.

The results of the present study showed that the aquatic plants differ in their accumulation of n-alkanes compounds as in the following order:

Schoenoplectus litoralis > *Typha domingensis* > *Ceratophyllum demersum* > *Phragmites australis* .

This variations may be attributed to different of plant species abilities to accumulate and concentrated these compounds which depend on the type of plant and some physo- chemical properties in the ecosystem like pH, temperature , concentration of nutrients ,salinity and dissolved oxygen (Thomas *et al* ., 1984 ; Al-Saad *et al* ,1994). Also, it may be due to the mechanisms of each plant to detoxified the n- alkanes compounds, or the production of some n-alkanes compounds as a secondary metabolites. The concentration of the n-alkanes in aquatic plants of the present study was compared with previous studies as shown in (Table47) .

4.3.3 - Polynucleic Aromatic Hydrocarbons (PAHs):

4.3.3.1-PAHs in water:

The environmental pollution with aromatic compounds is mainly related to the anthropogenic sources which are the main source in the aquatic environment compared to the natural sources (Zakaria *et al.*, 2002; Yan *et al.* , 2012).

The results showed that there are two types of the PAHs compounds in water column: The low molecular weight (2-3 fused aromatic rings) predominated with Acenaphthylene ,Acenaphthene mainly originated from fuel combustion activities indicated a pyrogenic source (Budzinsky *et al.*, 1997) . The second type is the high molecular weight (4 and more fused aromatic rings), predominated with Benzo(k) flouranthene ,Dibenzo(a,h)anthracene ,Benzo(g,h,i)perylene, which are lipophilic and least dissolved in water.

The increasing in the total concentration of PAHs compounds in autumn and winter is due to the fact that aromatic compounds that are input to the environment are higher in autumn and winter due to the increasing in burning fuel and wood which using in heating during winter (Al-khatib, 2008). As well as the low rate of evaporation processes to the PAHs compounds in the winter and decreasing the effectiveness of different microorganisms in degradation processes of these compounds with low temperatures (Al-Tamari *et al.*, 2003). Whereas the low concentrations in the spring and summer are attributed to the warm climate of Iraq in summer, as high temperatures causing evaporate the PAHs compounds in water (Al- Saad, 1998). The high temperatures also stimulate the microorganisms to break down these compounds, especially the low molecular weights (Al-Tamari, 2000). In addition, the oxidation processes due to the long period of brightness and intensity of solar radiation (Al-Tamari *et al.*, 2003), as well as the

high rainfall in the spring, where the dilution factor has an important role in decreasing the concentrations.

To determine the source of PAHs in water samples according to the ratio of LMW-PAHs to HMW-PAHs (LMW/HMW) had been used to distinguish between pyrogenic and petrogenic, the result showed this ratio was less than one at all stations and seasons, which detected to the pyrogenic origin derived from incomplete combustion of fuel, except at station 4 was more than one during autumn which coming from petroleum compounds origin.

In addition to that BaA/(BaA+Chr) ratio ranged from 0.065 to 1.00 that indicated the petrogenic and pyrogenic origin. The present study shows the disadvantage of this index in water samples because most samples have undetectable values for Benzo(a)Anthracene and /or Chrysene at most periods.

Of the recorded results, it is clear that the source of the PAHs compounds in the water is petrogenic and pyrogenic, and these result was in agreement with Al-Khatib(2008).

4.3.3.2-PAHs in sediments :

The study of sediments had an important role in the studies of environmental pollution (Al-Khatib,1998). It provides a good guide to the state of water pollution, therefore, sediments represent a main reservoir of PAHs in the aquatic environment (Perra *et al.*,2009;Qiu *et al.*.,2009).

The concentrations of PAHs in the sediment tend to be higher than in water sample (Appendix 5), these attributed to the ability of hydrophobic PAHs compound to adsorb on the suspended particulate in water column and then sink to the sediments (Zhou *et al.*,2000), the same result was reached by (Al-Hejuje,2014) in the water and sediments of the Shatt al-Arab river. This association between PAHs and particulate

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matter or the accumulation by fatty organisms caused to decrease the concentrations of PAHs compounds in water column compared with them in sediments .

The results showed that the lowest concentrations recorded during spring , while the highest concentrations recorded during winter ,this may be due to the climatic condition effect photo-oxidation, volatilization and low degradation during the cold season, lead to elevated levels of these compounds during winter, also precipitation which are significantly high in winter because increase using of fuel forms and burning in the winter season (Mohammed ,2007;Al-Khatib,2008).While raise of temperature in spring ,lead to increase the evaporation rate and also affect the biodegradation, which is higher than winter season (Boyd *et al.*, 2001),generally the rate of evaporation and biodegradation increase with increasing of temperature and vice versa ,there for the highest degradation rates generally occurs in the temperature range from 20 to 30C° in some freshwater environments(Bartha and Bossert ,1984).This finding was in agreement with (Al-Khatib,2008 ; Jazza,2015). as well as the high rainfall in the spring, where the dilution factor has an important role in decreasing the concentrations(Al-Bidhani,2014).

For the purpose of identifying the source of PAHs compounds in the sediments, the ratio of low molecular weight compounds to the high molecular weights was calculated. The result was less than one number, this indicates the source of PAHS compounds in the sediments was pyrogenic resulting from fuel combustion processes from oil and its derivatives as well as waste oils and fumes derived from fishing and transport boats that ultimately reach the sediments, except at station 4 the ratio was more than one during winter this indicates the origin of PAHS compounds petrogenic which coming from petroleum

compounds. BaA/(BaA+Chr) ratios at stations 1 and 2 during summer as well as station 3 during autumn were less than 0.2 indicating that PAHs were mainly originated from pterogenic sources. While other stations the ratio of BaA/(BaA+Chr) were more than 0.35 indicating that PAHs were originated from pyrogenic sources derived from combustion fuel in its forms. It is clear that the sources of PAHs compounds in the sediments of Al-Chibayish marsh are (pyrogenic and pterogenic). Result of the present study are in agreement with Al-Khatib(2008). The concentration of PAHs compounds in the present study was compared with previous studies as shown in (Table 46), and found it is within the range.

4.3.3.3-PAHs in aquatic plants :

The results noticed that lower molecular weight PAHs in studied plants was more than higher molecular weight PAHs during all seasons, this may be attributed to the fact that PAHs compounds with low molecular weight have more solubility in water compared to PAHs compounds with high molecular weights (Dahle *et al.*,2003), Thus entering the tissues of the plants by absorbing water from the sediments and water column (Hsu,2004). That is in agreement with (Al-Khatib ,2008), whereas disagreement with (Jazza,2015).

The highest levels of PAHs compounds in aquatic plants were recorded during summer, whereas the lowest levels during spring season, the seasonal variations may be due to that summer season is considered as a growth period for these plants because of high temperature, long period of solar radiation and the abundance nutrients compared with other seasons, this will lead to increase photosynthesis processes and absorption the PAHs compounds from water column and sediments (Hsu, 2004 ; Al-Khatib ,2008;Jazza ,2015).

The results of the study show that the aquatic plants differ in their accumulation of PAHs compounds as the following order:

Ceratophyllum demersum > *Schoenoplectus litoralis* > *Phragmites australis* > *Typha domingensis* .

There are differences in the concentration of PAHs compounds among studies aquatic plants ,these variations may be attributed to the lipid compounds of each plant species ,the nature of growth substrate for each plants, tolerance of each species for environmental conditions , and surface area that affect the rate of accumulation of plants (Hassan *et al.*,2016) .To determine the origin of PAHs in aquatic macrophytes study according to ratios (tables 32-35), the results of this study revealed that LMW-PAHs/HMW-PAHs ratio was more than one during all seasons, which indicate that the sources of PAHs in these species were petrogenic (Vrana *et al.*, 2001),except the *Schoenoplectus litoralis* species the sources of these compounds were pyrogenic . BaA/(BaA+Chr) ratio was more than 0.35 which indicate that the origins of PAHs in all species were pyrogenic .While Phenanthrene /Anthracene ratio in all species were less than ten number which indicated the origin of PAHs compounds were pyrogenic (Sander *et al.*,2002) .

From the results the source of PAHs compounds in the studied plants is a mixed of petrogenic and pyrogenic. Al-Khatib (2008) also reached to the same result when analyses aquatic plants samples collected from Al-Howaiza marsh. The concentration of PAHs in the aquatic plants of the present study was compared with previous studies as shown in (Table 47).

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Table(45): comparison between total hydrocarbons($\mu\text{g/l}$). n-alkanes($\mu\text{g/l}$), and PAHs (ng/l) content in water for the present study with the other previously studies .

Studied Areas	Total Hydrocarbons ($\mu\text{g/l}$)(Dissol+partic.)	n-alkane ($\mu\text{g/l}$) (Dissol+partic)	PAHs (ng/l) (Dissol+partic)	References
Southern of Iraq marshes	0.6-46.82			Al-Imarah <i>et al.</i> (2006)
Hor Al-Howaiza	1.005-11.965	1.143 - 34.461	1-50.8	Al-Khatib(2008)
Hor Al-Hammar	0.411-0.824	3.64 - 4.40		Talal (2008)
Southern of Iraq marshes	0.012-0.037			Al-Saad <i>et al.</i> ,(2009)
Al-Chibayish marsh	1.91-6.79	0.32 - 2.98	2.435-37.780	Present study

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Table (46): comparison between of total hydrocarbons. n-alkanes($\mu\text{g/g}$), and PAHs (ng/g) content in sediments for present study with the other previously studies .

Studied Areas	Total Hydrocarbons ($\mu\text{g/g}$)	n-alkane ($\mu\text{g/g}$)	PAHs (ng/g)	References
Southern of Iraq marshes	15.17 -103.80			Al-Imara <i>et al.</i> (2006)
Hor Al-Hammar	0.485 -1.128	6.53-31.46		Talal (2008)
Hor Al-Howaiza	4.057 -47.335	3.43-42.38	0.1-145.8	Al-Khatib(2008)
Southern of Iraq marshes	0.030-0.96			Al-Saad <i>et al.</i> ,(2009)
Euphrates River /Nasiriya city	4.74-12.32	3.43-42.38		Abed Ali (2013)
Al-Chibayish marsh	2.98-17.98	0.62-29.75	6.55 -52.36	Present study

Table (47): comparison between of total hydrocarbons. n-alkanes($\mu\text{g/g}$), and PAHs (ng/g) content in aquatic plants for present study with the other previously studies.

Studied Areas	Total Hydrocarbons ($\mu\text{g/g}$)	n-alkane ($\mu\text{g/g}$)	PAHs (ng/g)	References
Hor Al-Hammar		5.53-11.45		Al-Saad <i>et al.</i> ,(1996)
Hor Al-Hammar	1.712-2.260	3.99-6.59		Talal (2008)
Hor Al-Howaiza	3.31-14.147	4.832-41.45	0.1-81.4	Al-Khatib (2008)
Euphrates River		0.451-2.215		Abed Ali (2013)
Al-Chibayish marsh	5.248-30.680	4.688-64.359	6.318-151.899	Present study

Conclusions:

- 1-Noticeable increase in the upper limits of EC , Turbidity and TSS, values of Al-Chibayish marsh.
- 2-The concentrations of heavy metals in particulate phase were higher than those in dissolved phase , sediments and aquatic plants.
- 3- The ability of aquatic plants to accumulate heavy elements and hydrocarbons higher than the concentration in the dissolved phase , thus an indicator of the use of aquatic plants in the process of treatment of pollutants.
- 4-The concentrations of heavy elements and hydrocarbons compounds in sediments higher than those in water column indicated that the sediments acted as a sink and source for these compounds.
- 5-HPI values referred to unpolluted water of Al-Chibayish marsh with heavy elements according to impermissible values of dissolved Cd , Cr , Ni and Pb.
- 6-According to Igeo values , the sediments of Al-Chibayish marsh can be classified as unpolluted with Cd and Pb , while unpolluted to moderately polluted with Cr , and moderate to moderate- strongly polluted with Ni.
- 7- The possibility of using the studied aquatic plants, especially *Ceratophyllum demersum* species act as indicating to the contamination of heavy elements in the aquatic environment
- 8-The carbons chain length of n-alkanes in water , sediment and aquatic plants samples were ranged from C9 to C38, and the odd carbon number chain were dominant in the studied aquatic plants.
- 9-The PAHs compounds in Al-Chibayish marsh, can be divided into two major groups (Low Molecular Weight (LMW) that consist of 2-3 fused rings , and High Molecular Weight(HMW) that consist of 4 and more fused rings, and the LMW compounds were dominant in the studied aquatic plants.
- 10- From the CPI index and Pristine/Phytane values , the source of n-alkanes hydrocarbons in Al-Chibayish marsh was biogenic and anthropogenic .Also according the LMW/HMW, Phenanthrene/Anthracene and BaA/(BaA+Chr) ratio, the source of PAHs compounds in the water, sediments and aquatic plants were pyrogenic and petrogenic.

Conclusions and Recommendations

11-The hydrocarbons concentrations were within the permissible values and Al-Chibayish marsh was considered as unpolluted with hydrocarbons compounds .

Recommendations :

- 1- Monitoring the water quality in Al-Chibayish marshes constantly to monitor the negative changes and find suitable solutions for them.
- 2- Attention to aquatic plants and awareness to show their importance to the aquatic environment and use it as an effective tool to show the pathways and accumulation of various types of pollutants.
- 3- Studying other types of aquatic plants to determine their ability to accumulate environmental pollutants.
- 4- Studying other type of pollutants in water , sediments, and aquatic organisms such as pesticides and radioactive .
- 5- Environmental laws should be enacted in order to reduce the use of chemical toxins in the process of fishing, and there should be a reduction of oil spilt from the boats.
- 6- The marshes can be use as a large area to treat the heavy elements and hydrocarbons compounds using aquatic plants .

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Appendices

Appendix 1: The world and the Iraqi Permissible values for drinking and irrigation water as compared with the present study .

Parameters	Units	WHO (2004, 2011)	US-EPA (2012)	Iraqi systems for rivers maintains (2011)	Ayers and Westcot (1985) for Irrigation water resources	Present study
Water Temperature	°C	-	-	-	20-30	10.5 - 33
pH		6.5 -8.5	6.5 – 8.5	6.5 – 8.5	6.5- 8.4	7.24 – 8.15
Electrical Conductivity (EC)	mS/cm	-	0.25	-	0.7	4.53 – 6.5
Turbidity	NTU	5	5	<5	-	1.3 – 50.55
Total Suspended Solids (TSS)	mg/l			50	-	1.68 -97.22
Dissolved Oxygen (DO)	mg/l	5	-	>5	-	0.7 -7.75
Biological Oxygen Demand (BOD ₅)	mg/l	5	-	<3	-	0.75-3.51

Appendix 2: The World and the Iraqi Permissible values for heavy metals in water as compared with the present study.

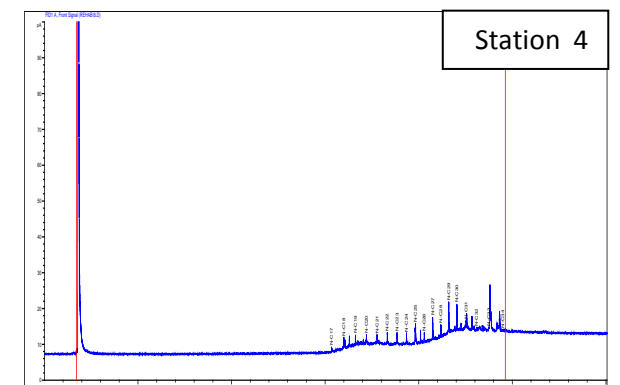
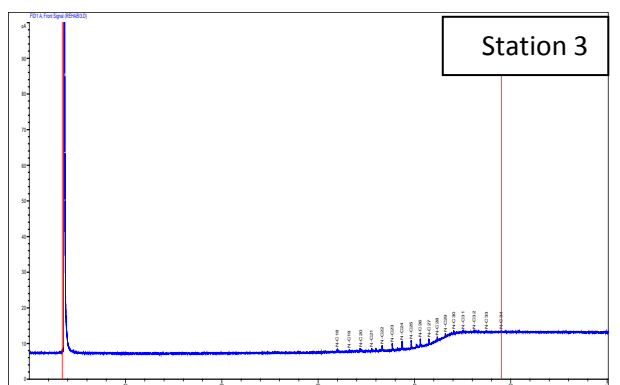
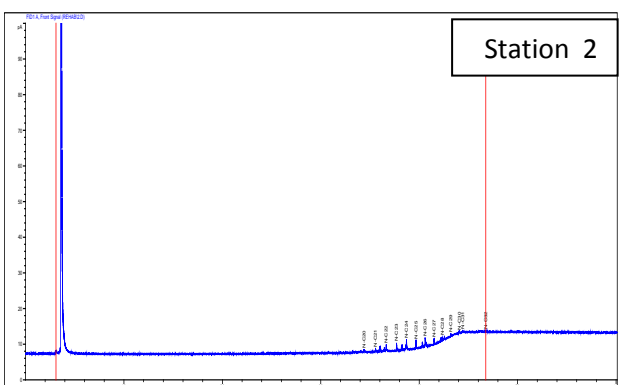
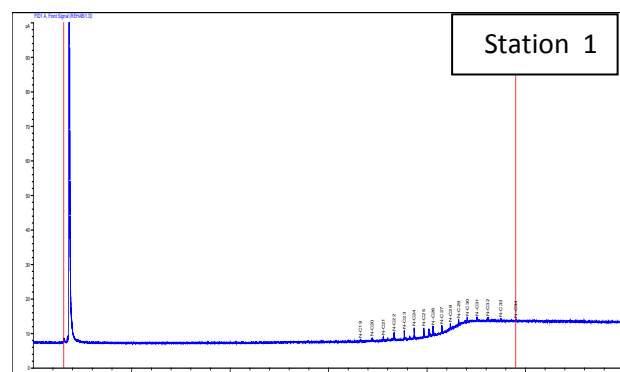
Parameters	Units	WHO(2004 , 2011) for drinking and domestic purposes	Present study
Cadmium	µg/l	3	0.06
Chromium	µg/l	50	2.03
Nickel	µg/l	70	0.56
Lead	µg/l	10	2.97

Appendix 3: The World and the Iraqi Permissible values for heavy metals in the sediments as compared with the present study.

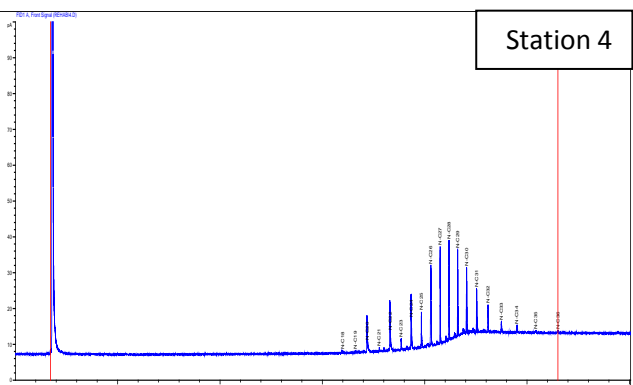
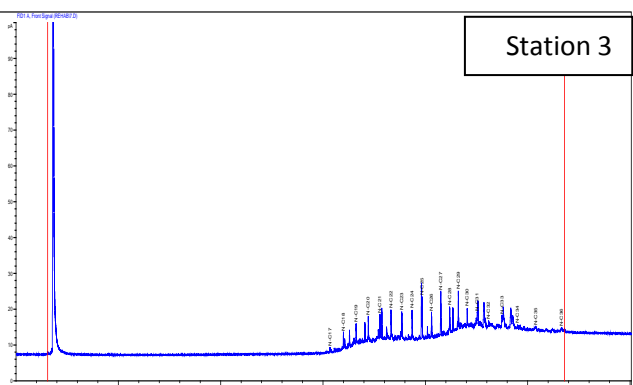
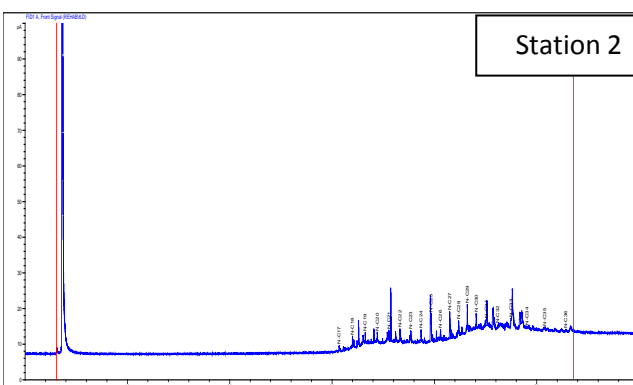
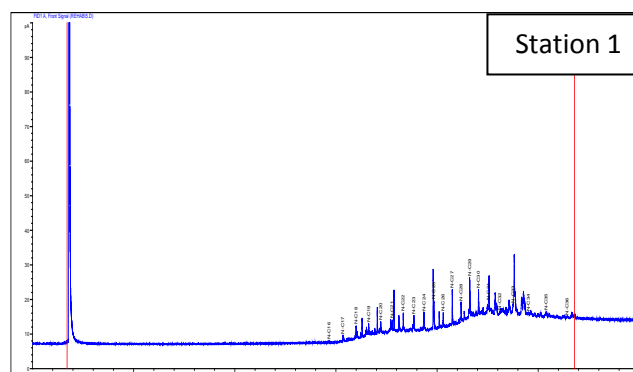
Parameters	Units	CBSQG (2003)	Present study
Cadmium	µg/g	0.99	0.69
Chromium	µg/g	43	102.65
Nickel	µg/g	23	121.70
Lead	µg/g	36	39.62

Appendix 4 :Chromatograms of N-alkanes in water and sediments samples of the studied stations during summer season .

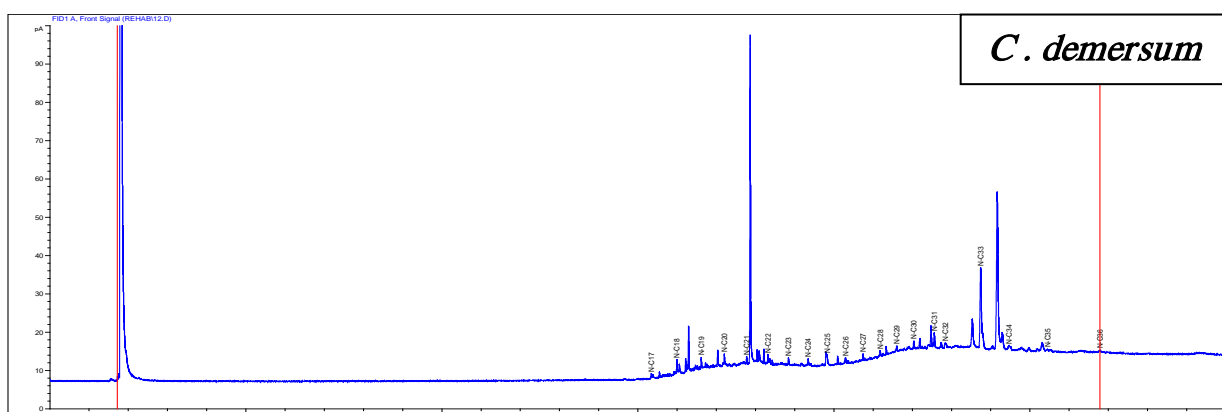
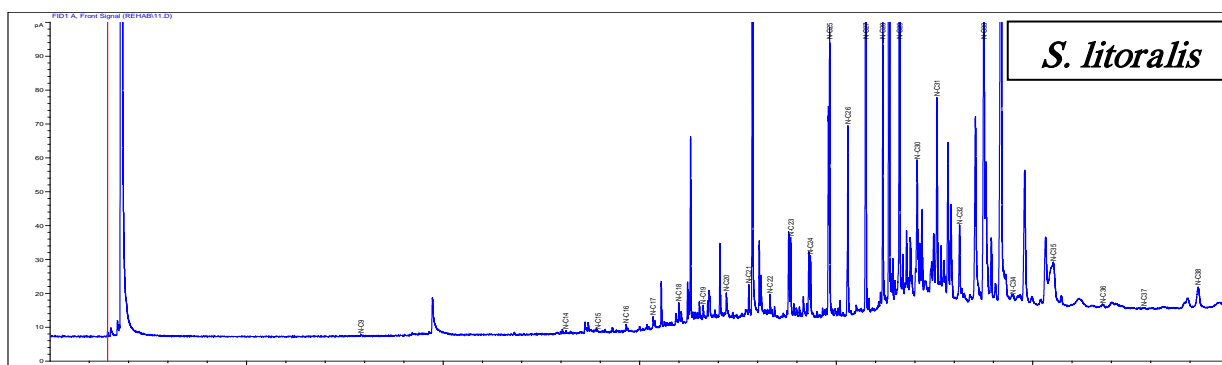
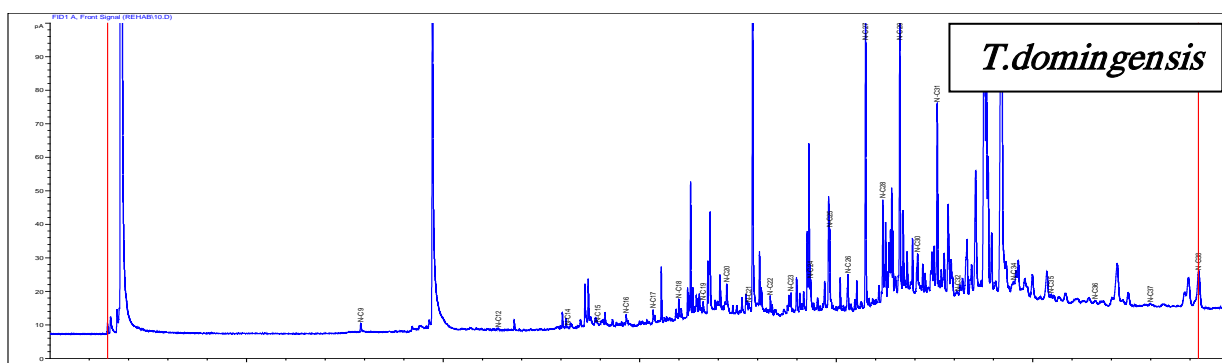
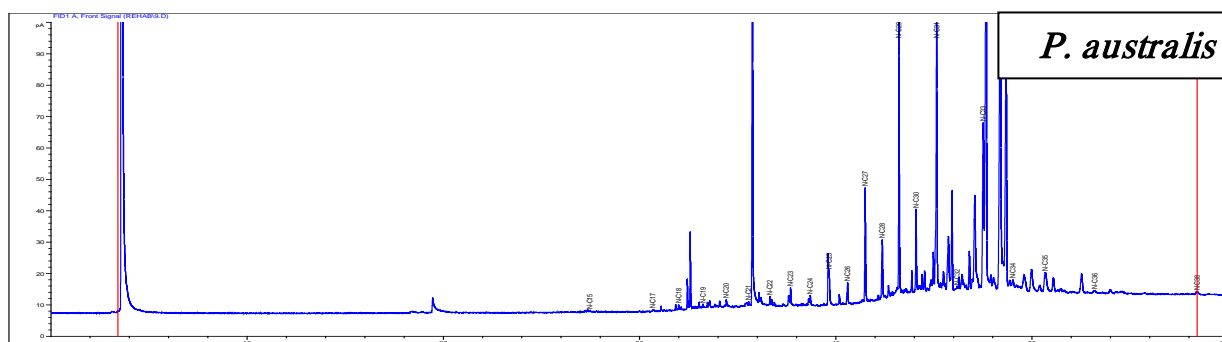
Water samples



Sediments samples

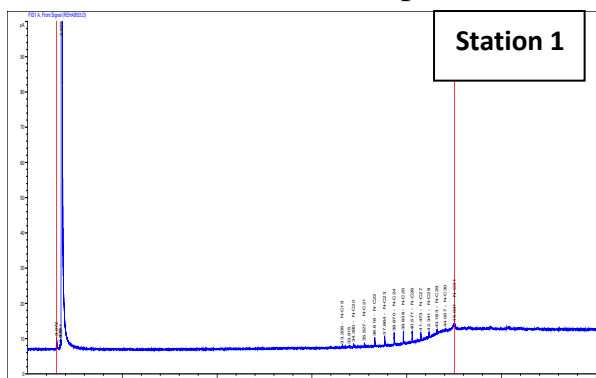


Appendix 4 :Chromatograms of N-alkanes in aquatic plants samples during summer season .

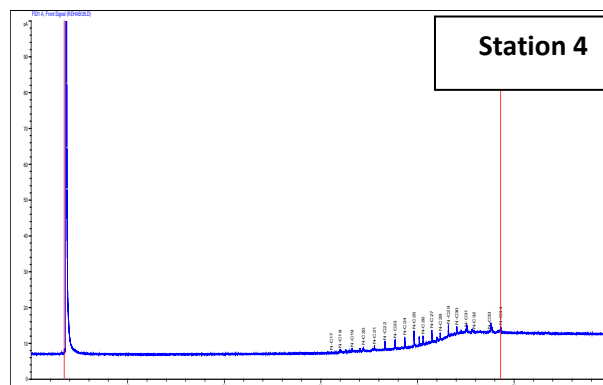
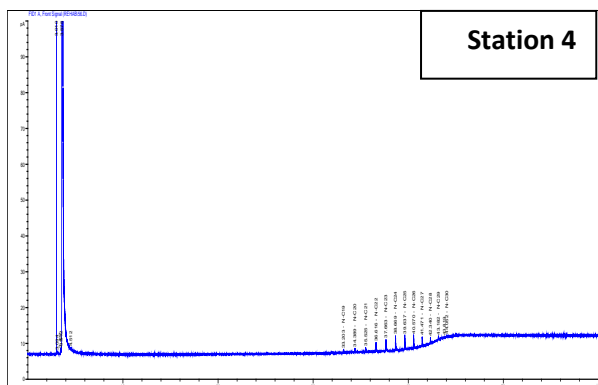
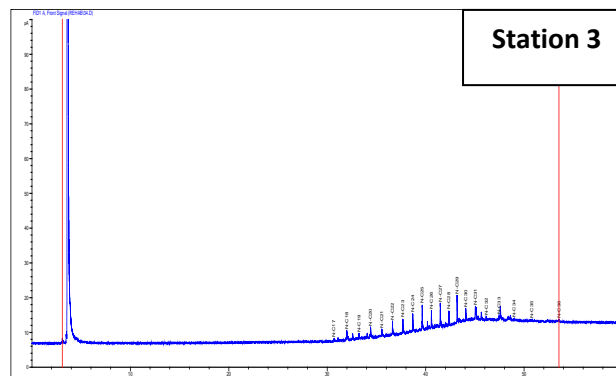
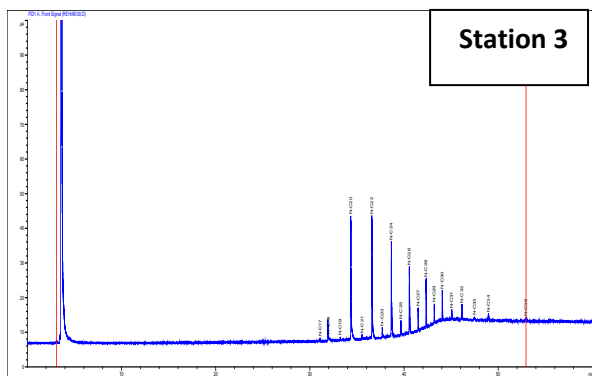
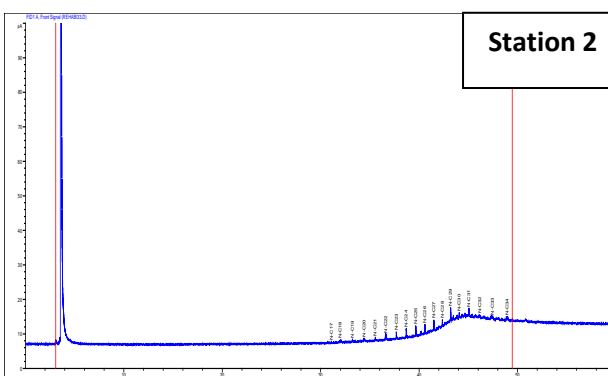
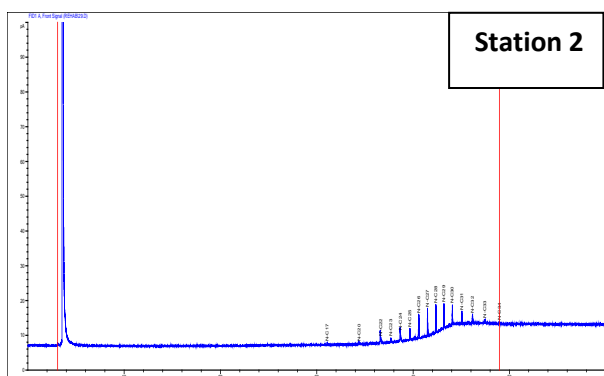
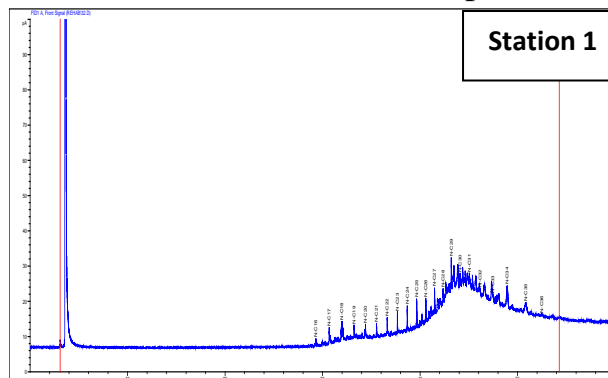


Appendix 4 :Chromatograms of N-alkanes in water and sediments samples of the studied stations during autumn season.

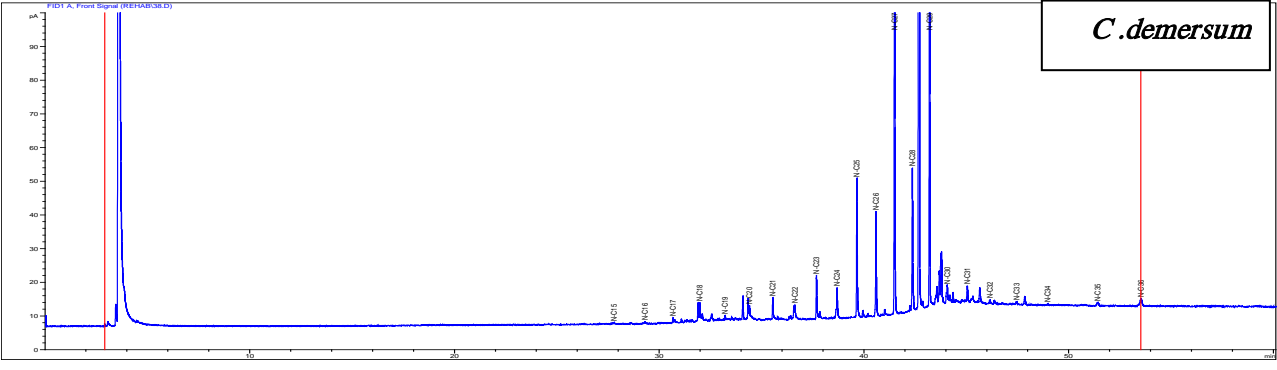
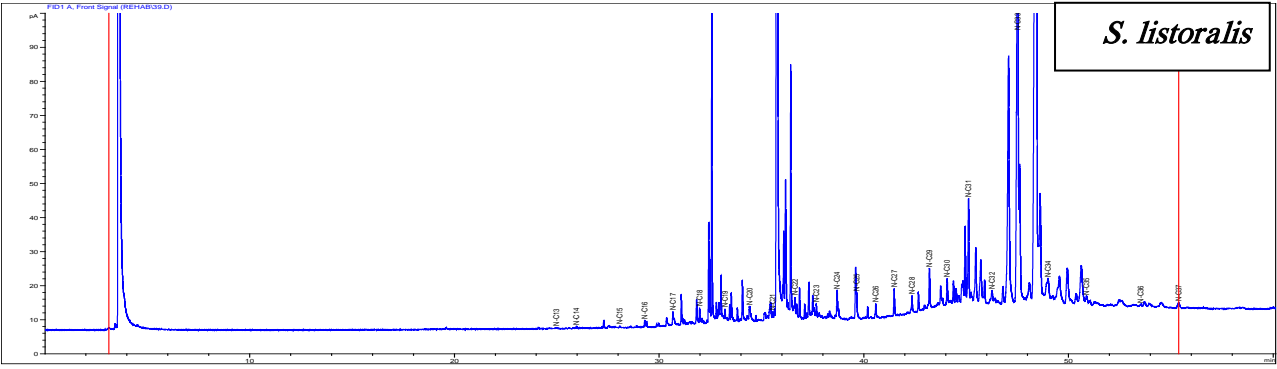
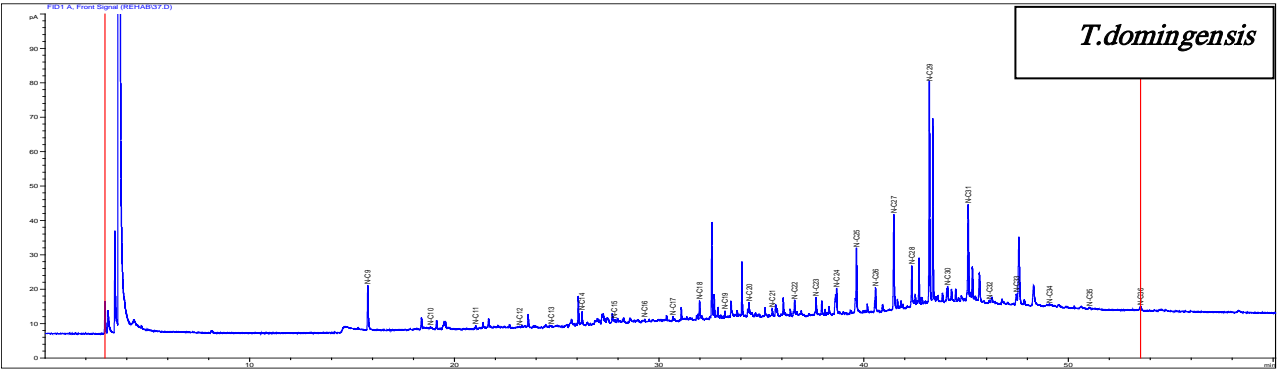
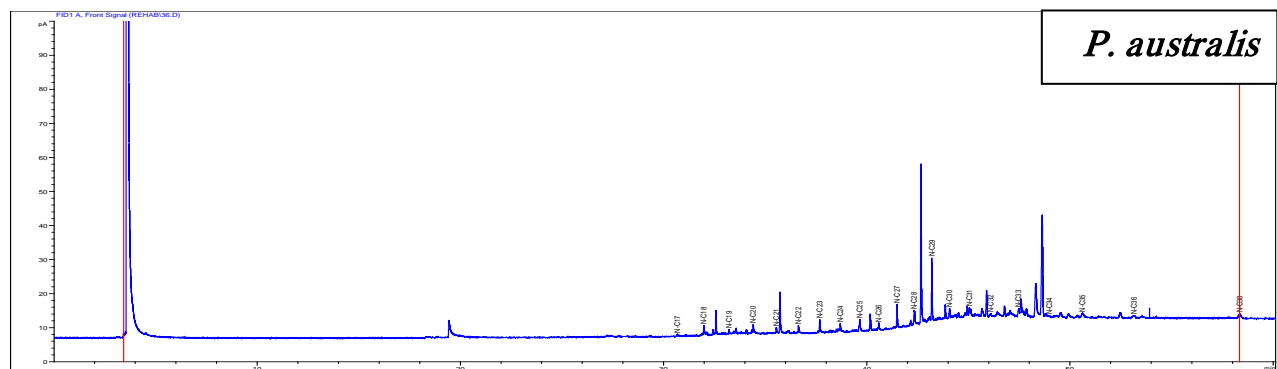
Water samples



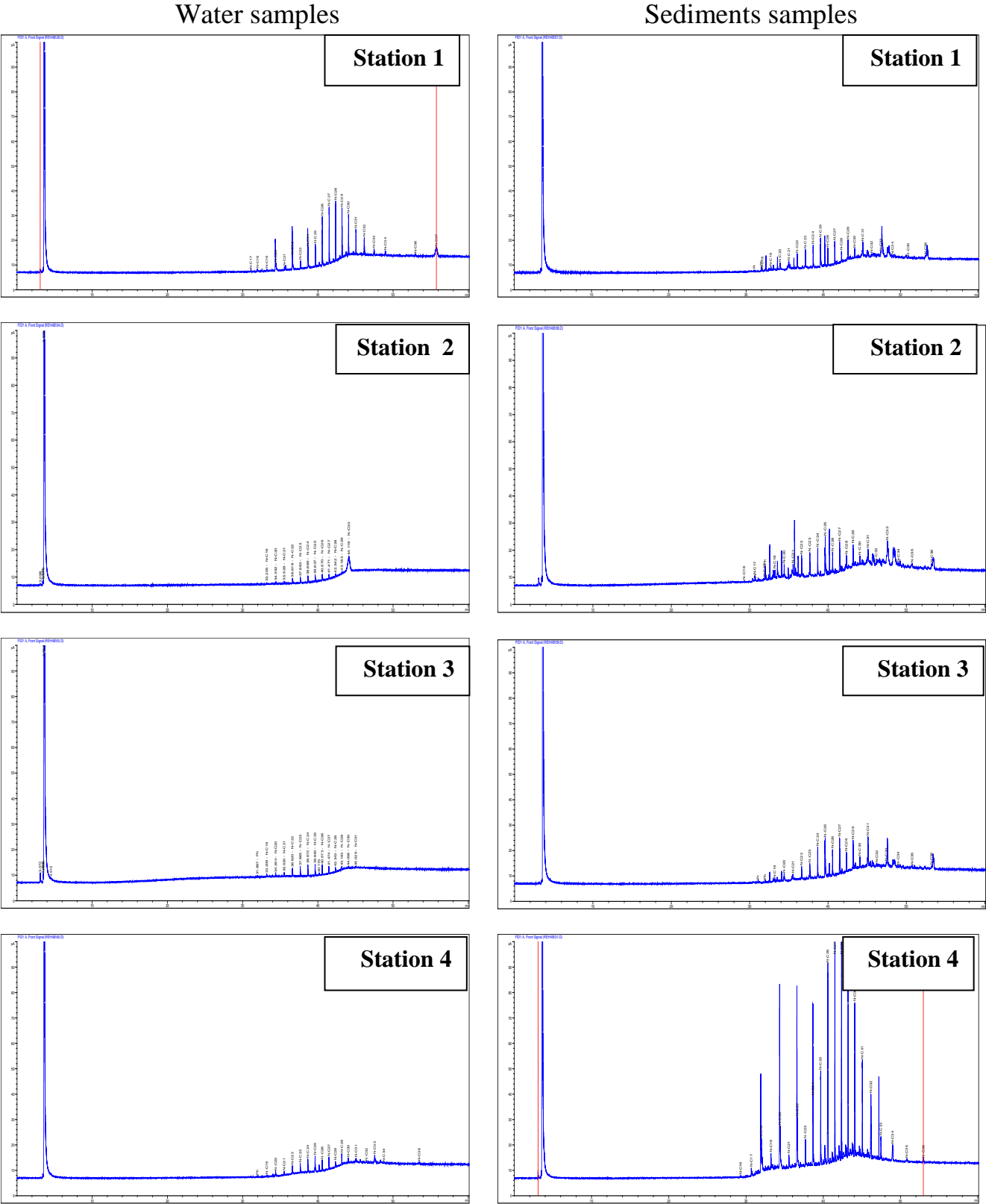
Sediments samples



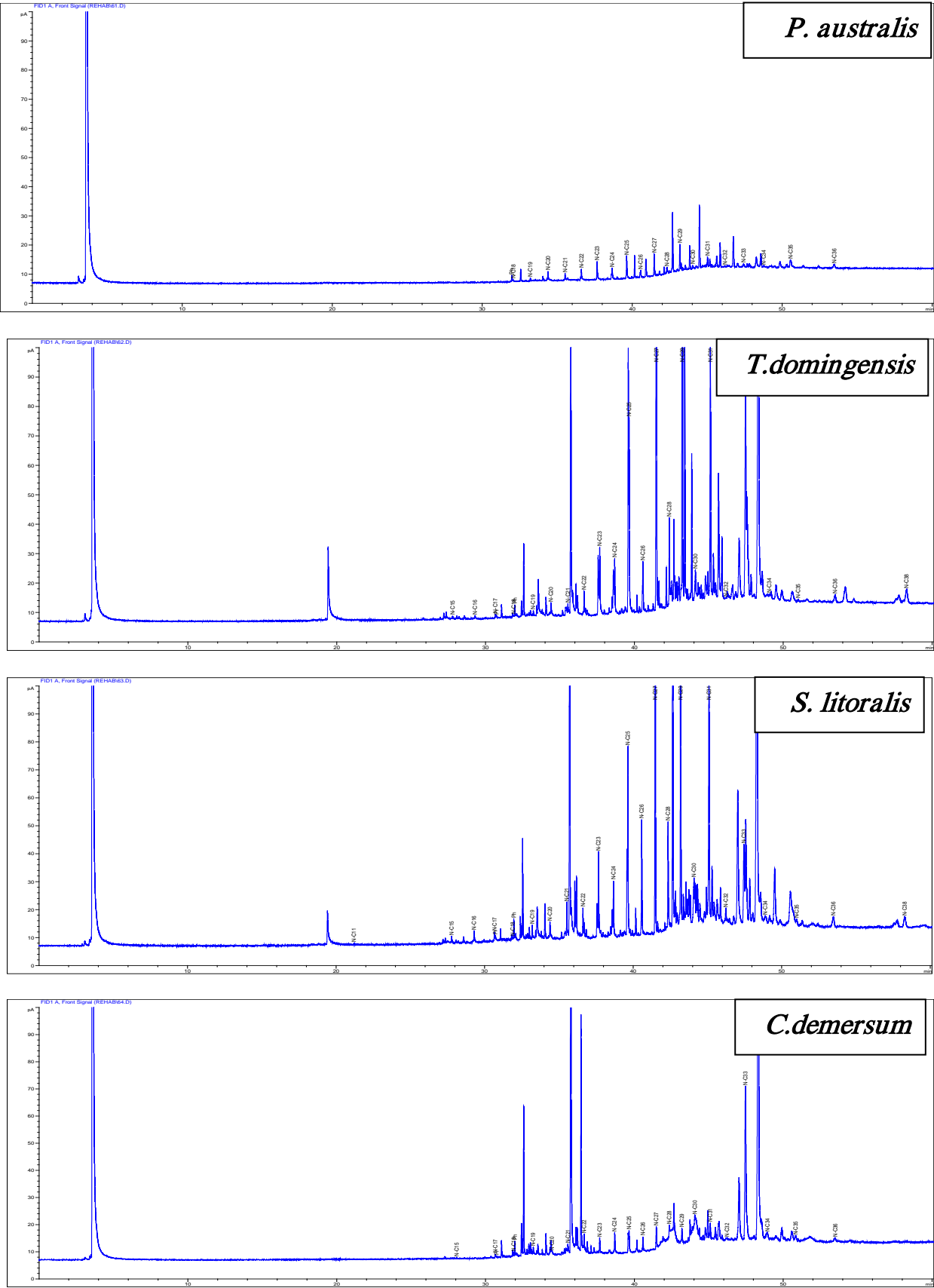
Appendix 4 :Chromatograms of N-alkanes in aquatic plants samples during autumn season



Appendix 4 :Chromatograms of N-alkanes in water and sediments samples of the studied stations during winter season.

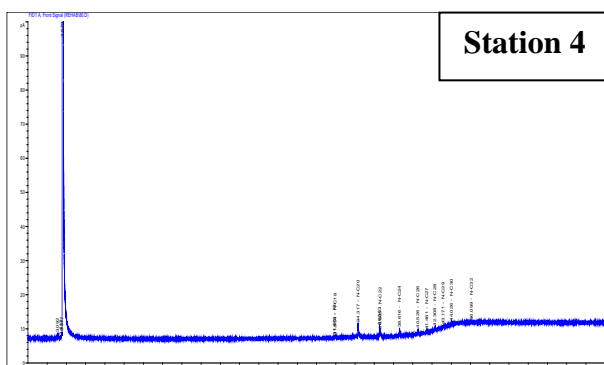
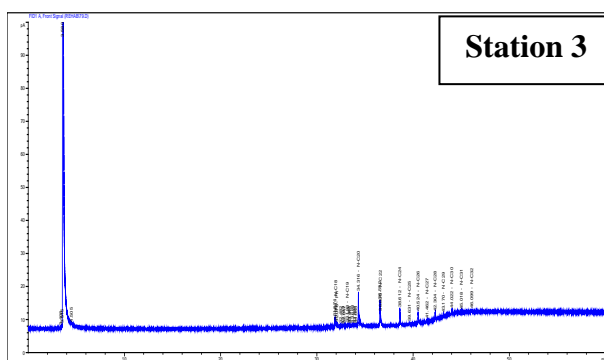
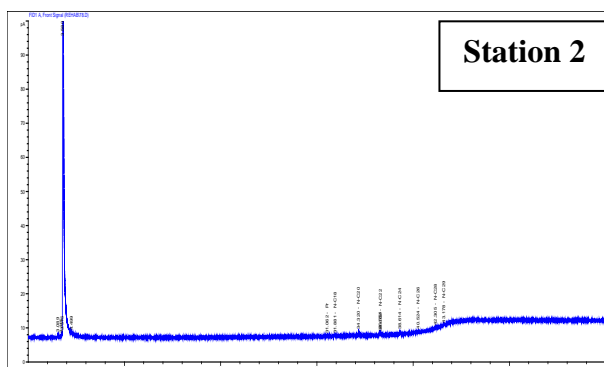
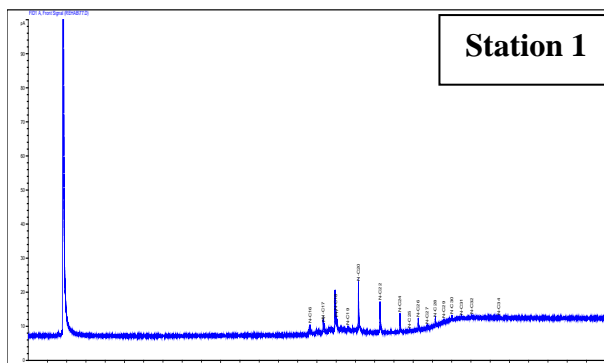


Appendix 4 :Chromatograms of N-alkanes in aquatic plants samples during winter season

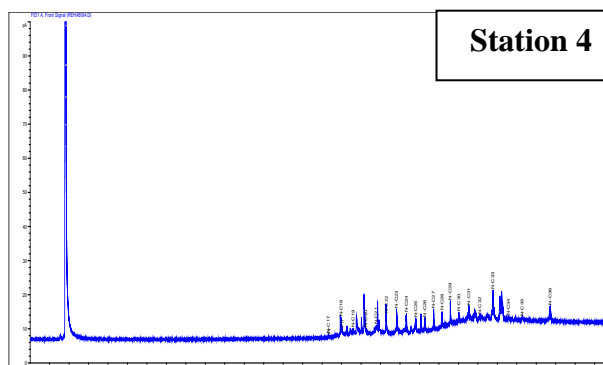
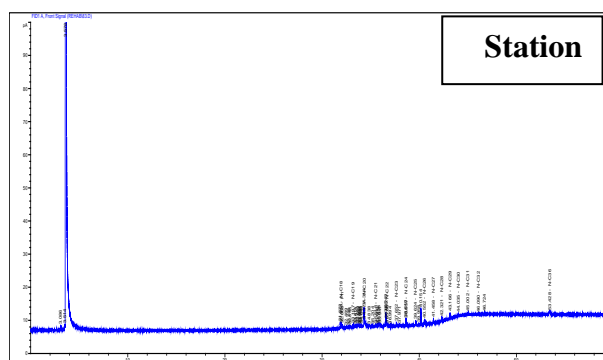
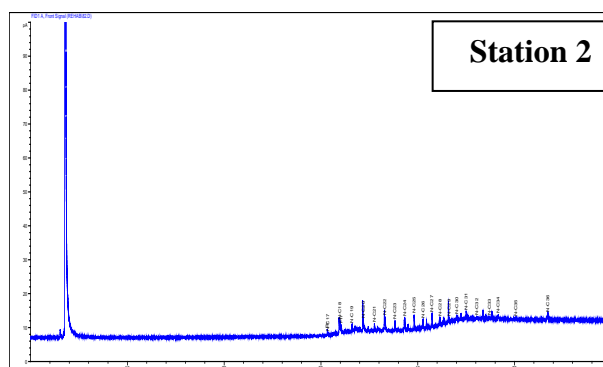
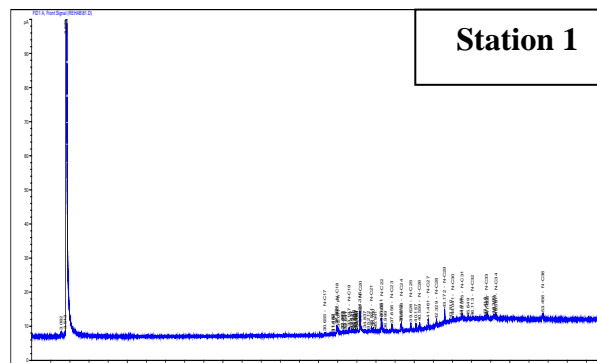


Appendix 4 :Chromatograms of N-alkanes in water and sediments samples of the studied stations during spring season.

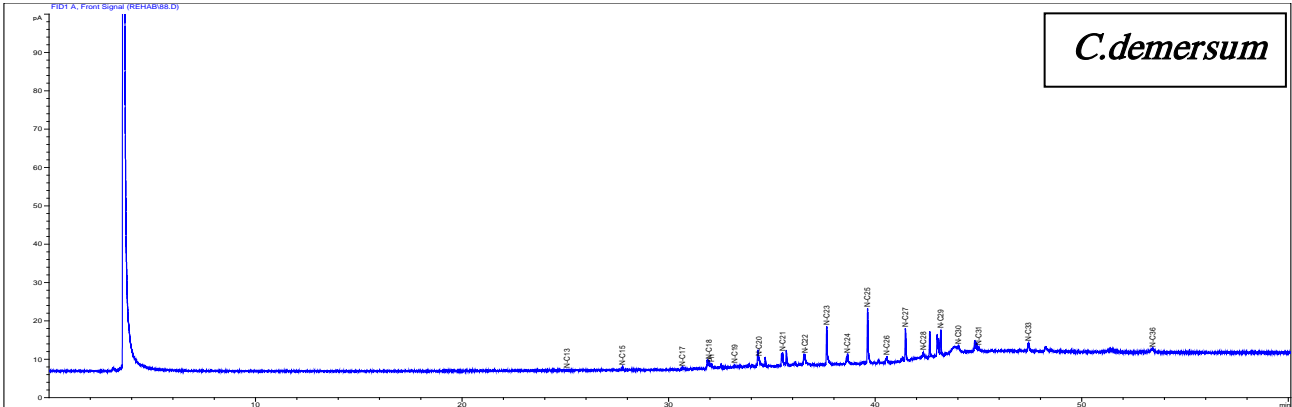
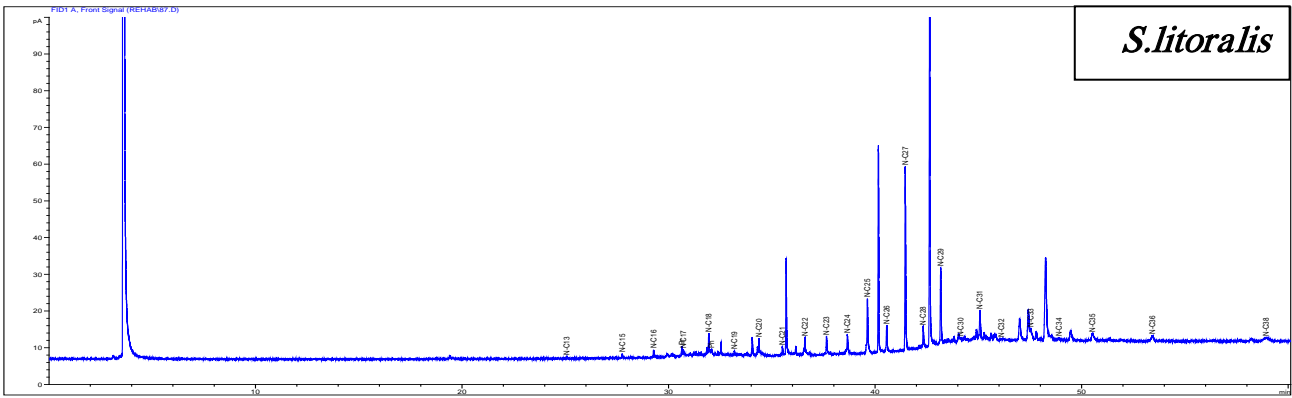
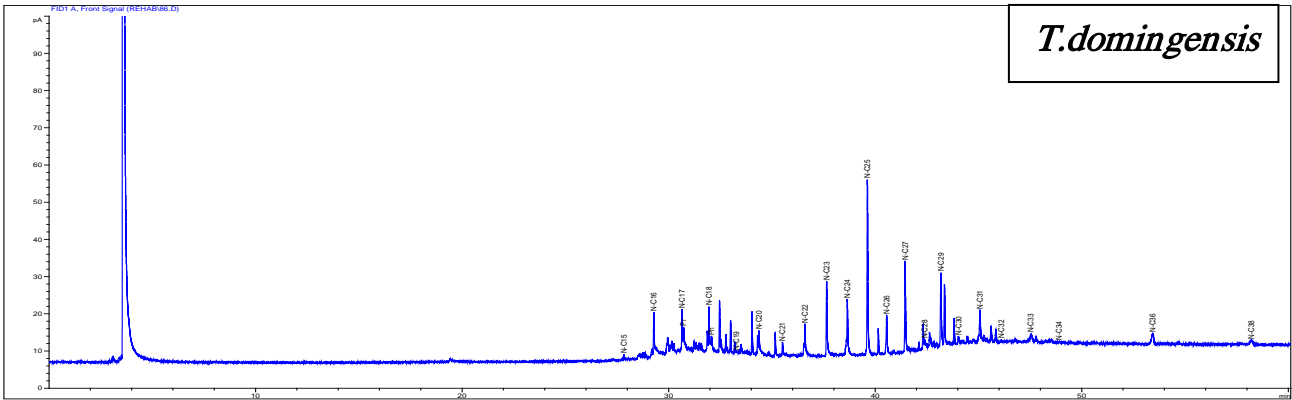
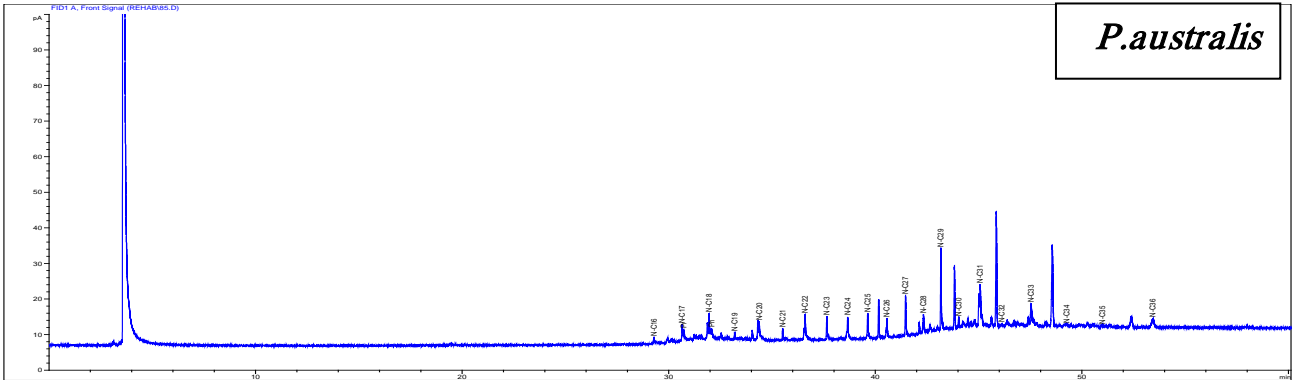
Water samples



Sediments samples

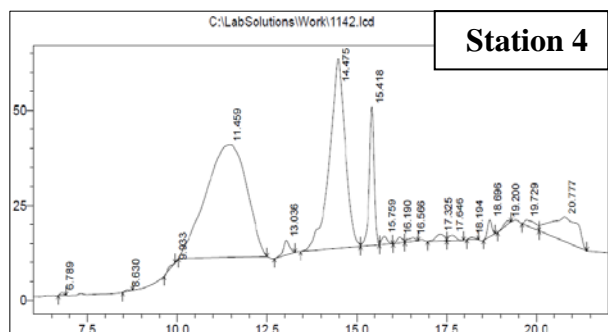
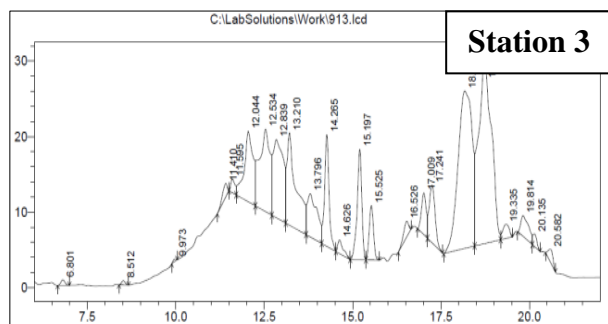
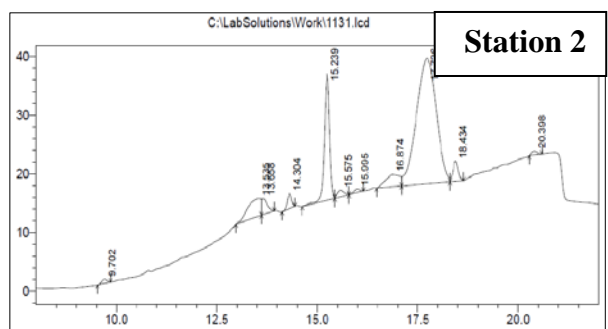
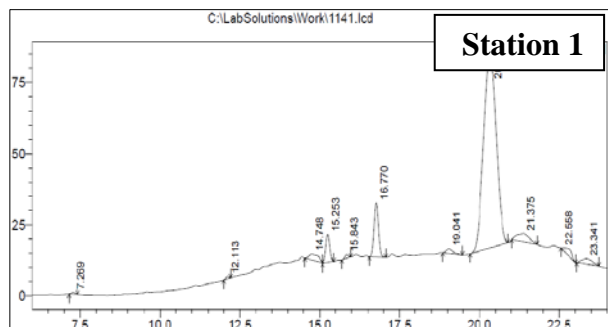


Appendix 4 :Chromatograms of N-alkanes in aquatic plants samples during spring season

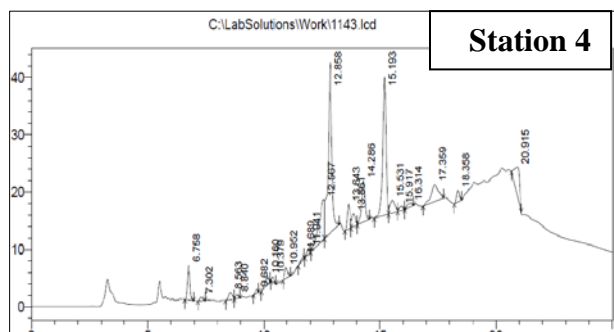
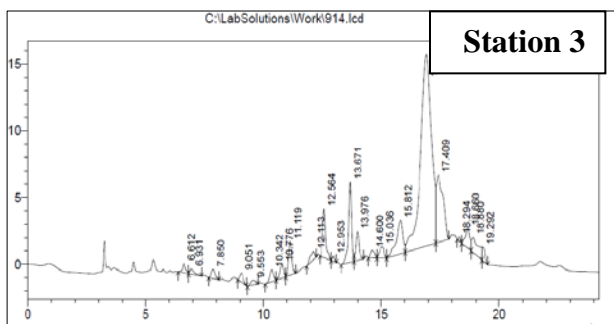
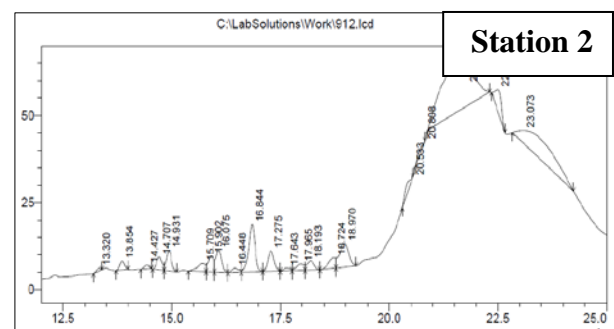
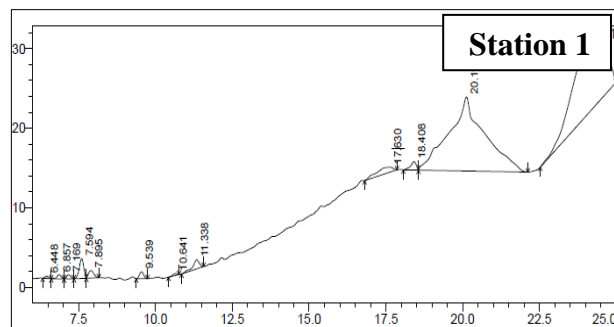


Appendix 5 :Chromatograms of PAHs compounds in water and sediments samples of the studied stations during summer season.

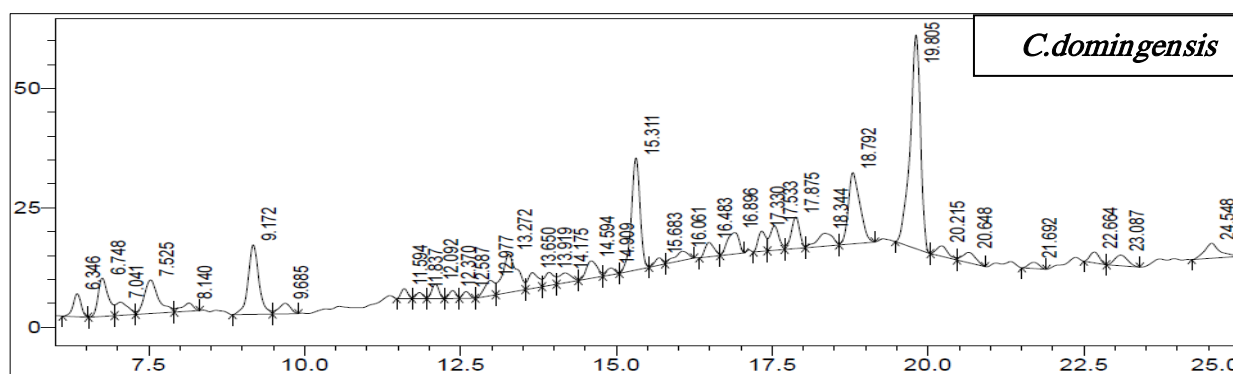
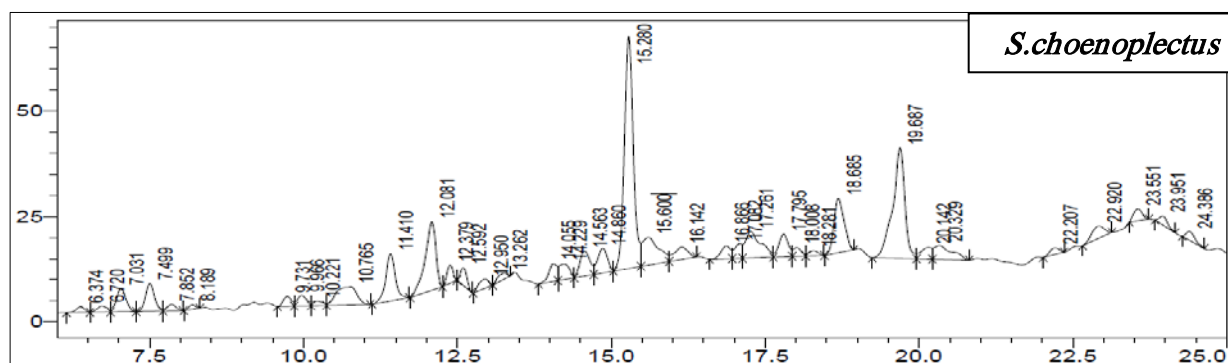
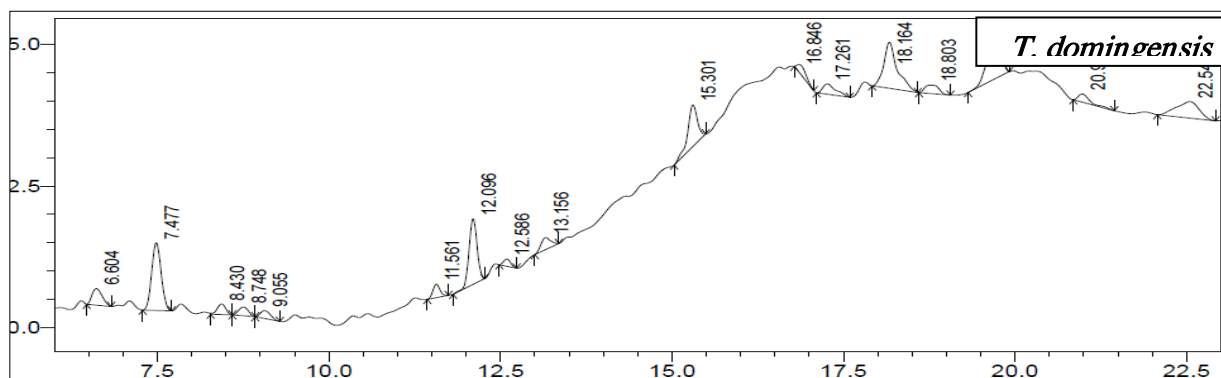
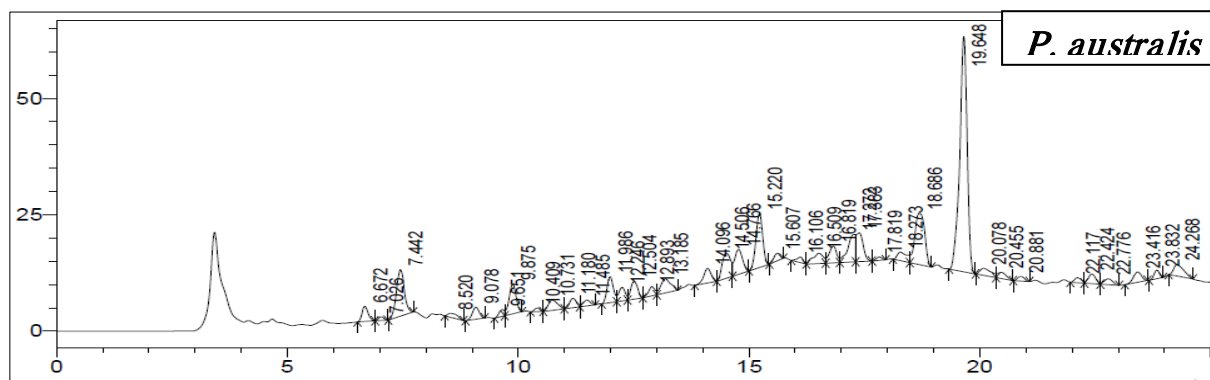
Water samples



Sediments samples

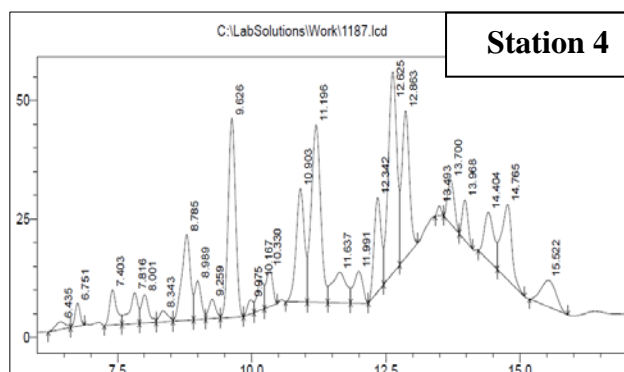
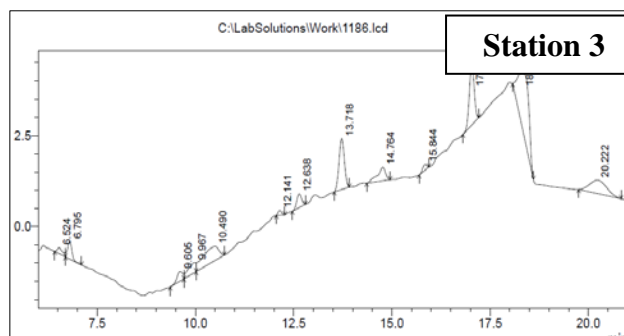
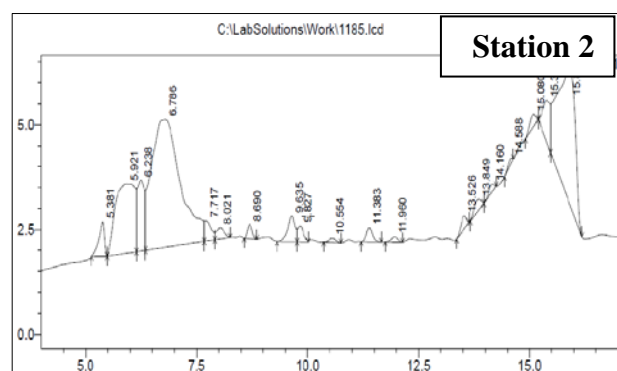
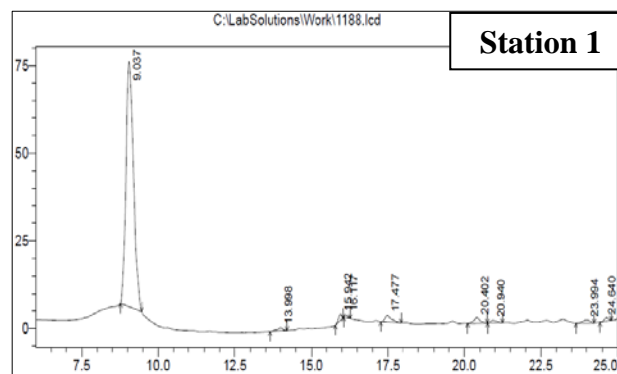


Appendix 5 :Chromatograms of PAHs compounds in aquatic plants samples during summer season .

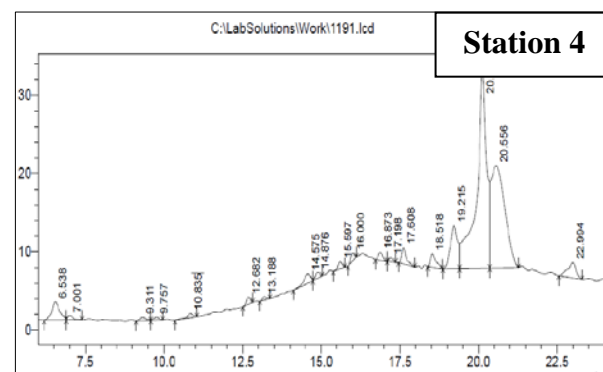
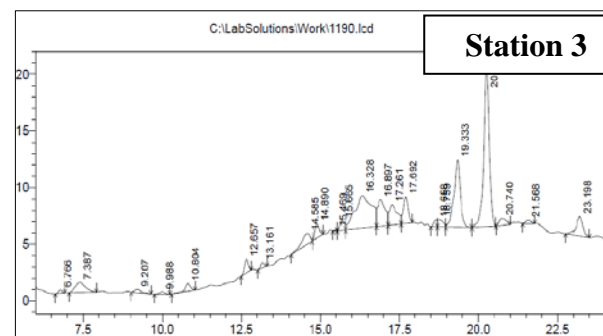
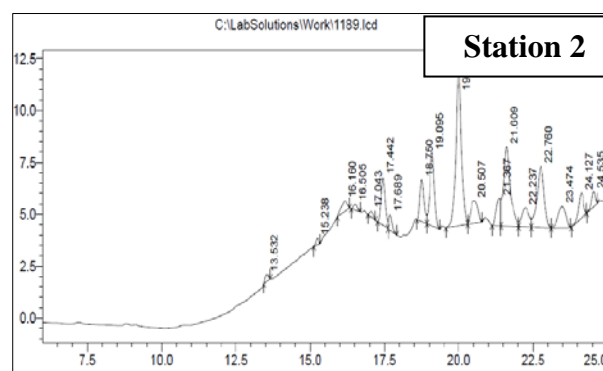
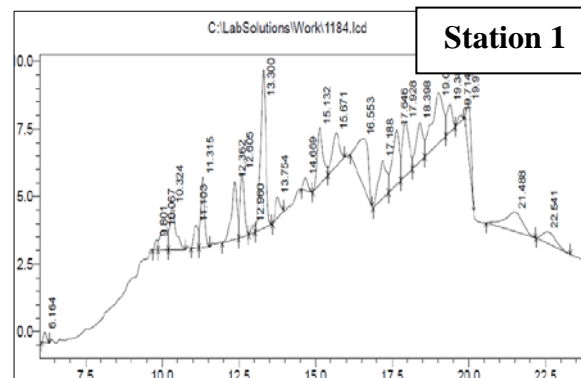


Appendix 5 :Chromatograms of PAHs compounds in water and sediments samples of the studied stations during autumn season .

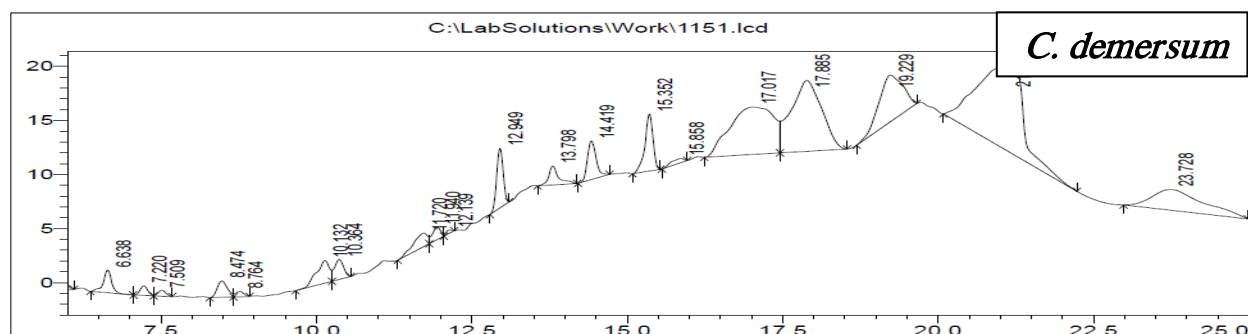
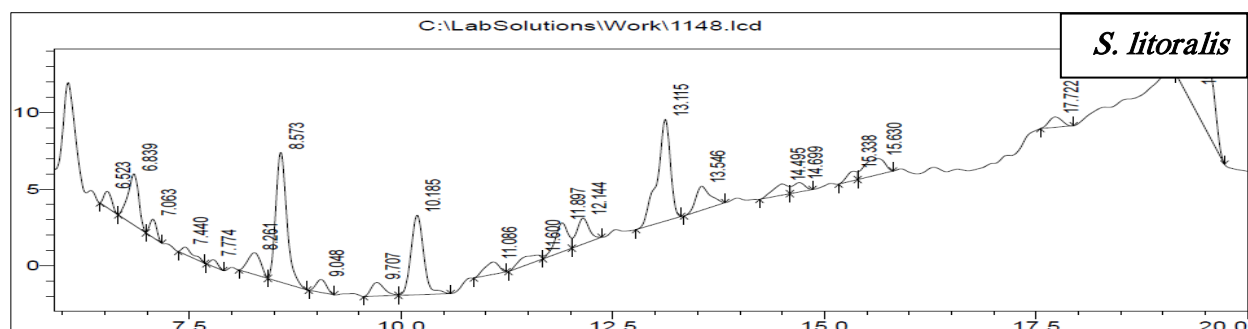
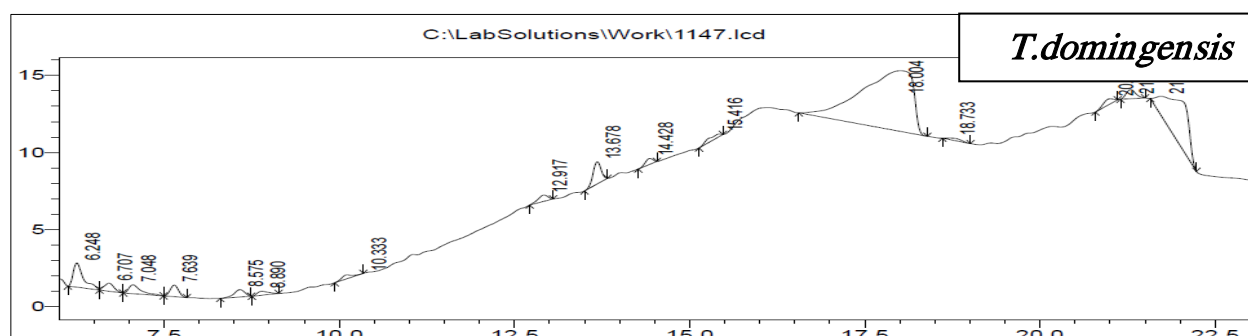
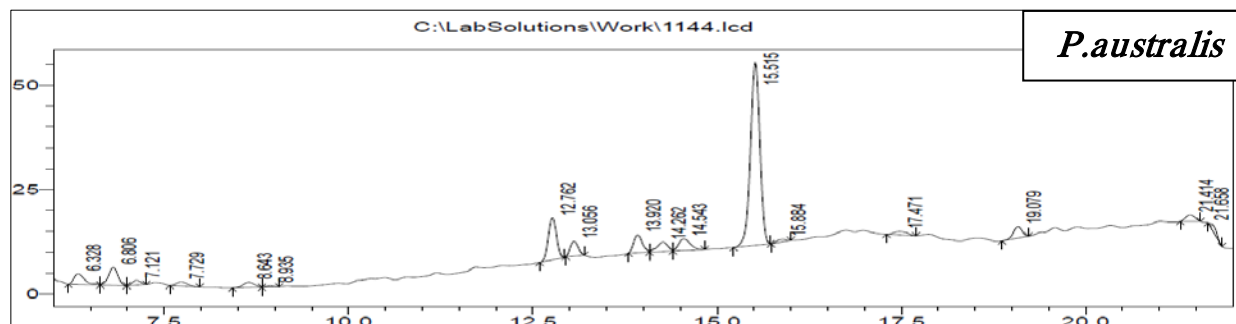
Water samples



Sediments samples

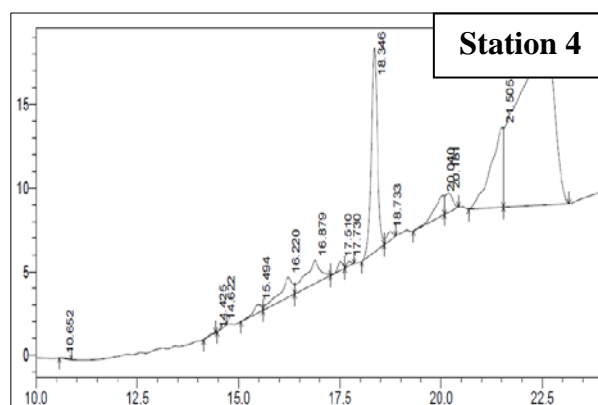
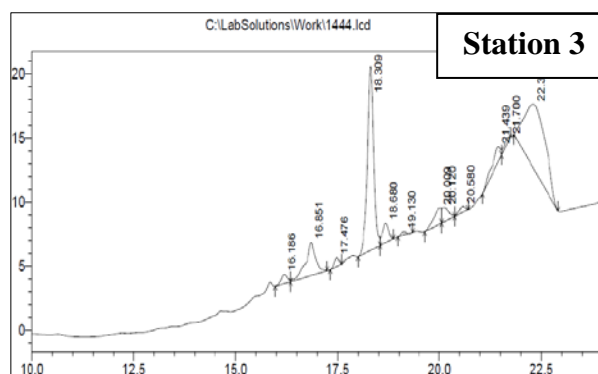
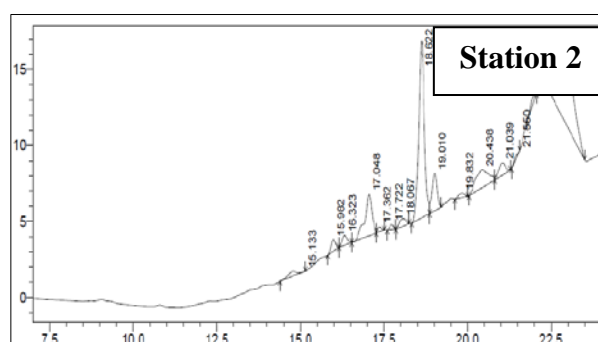
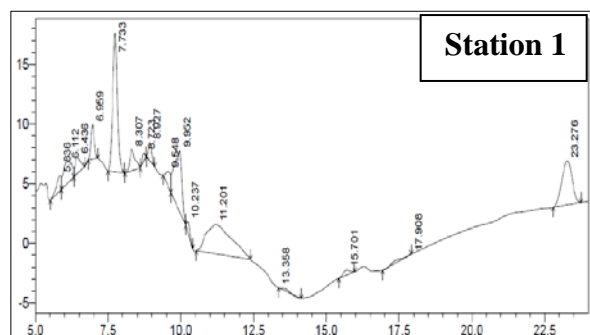


Appendix 5 :Chromatograms of PAHs compounds aquatic plants samples during autumn season .

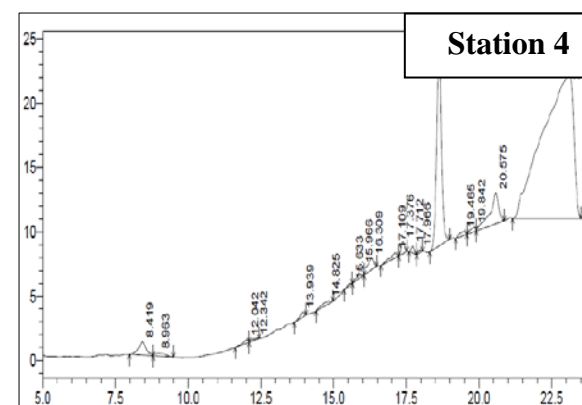
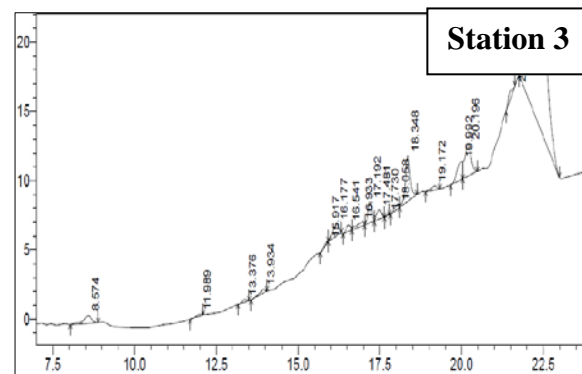
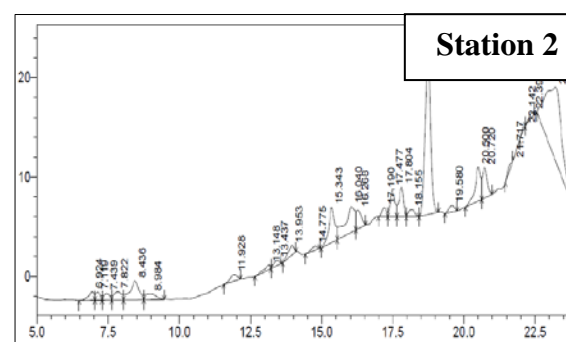
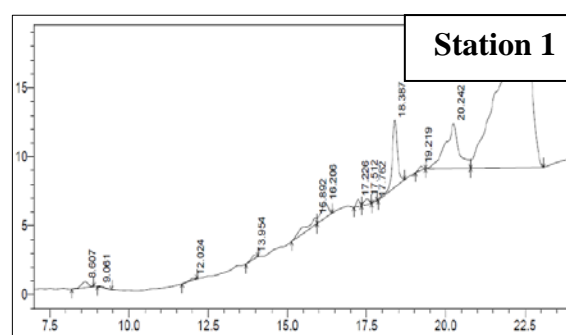


Appendix 5 :Chromatograms of PAHs compounds in water and sediments samples of the studied stations during winter season .

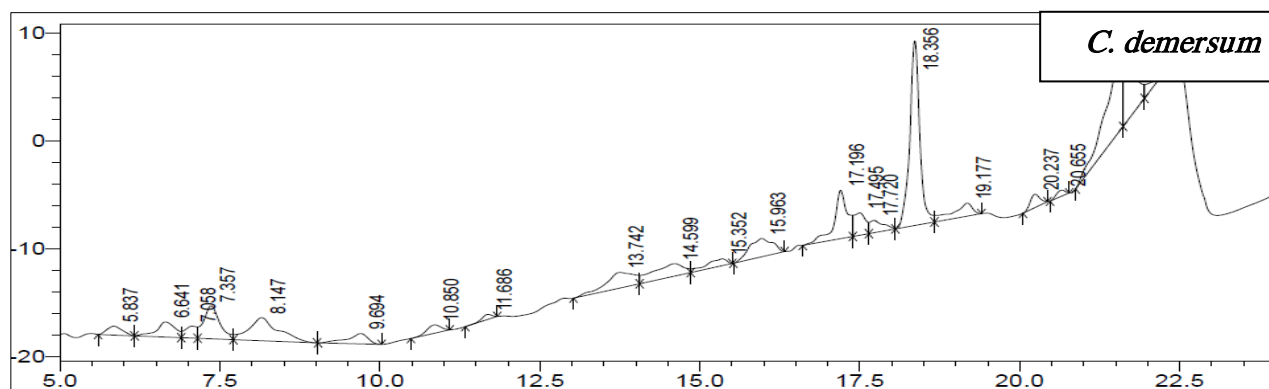
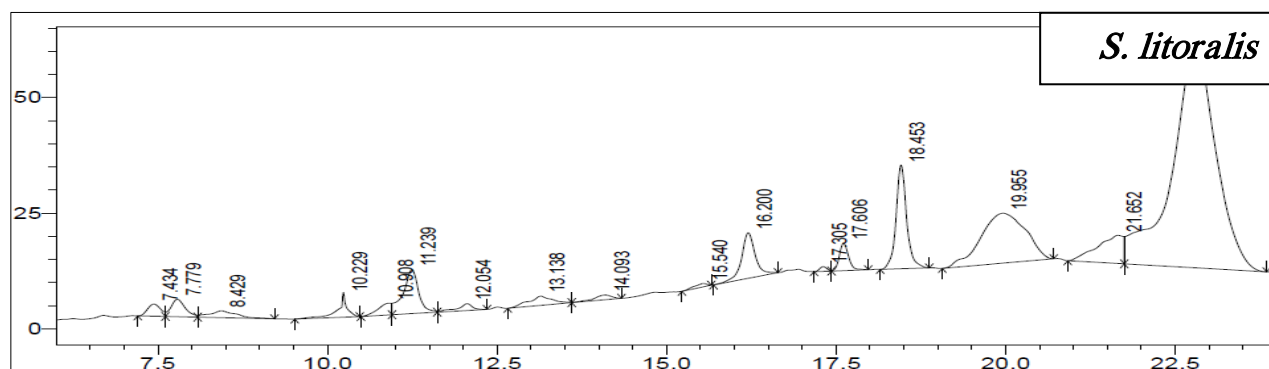
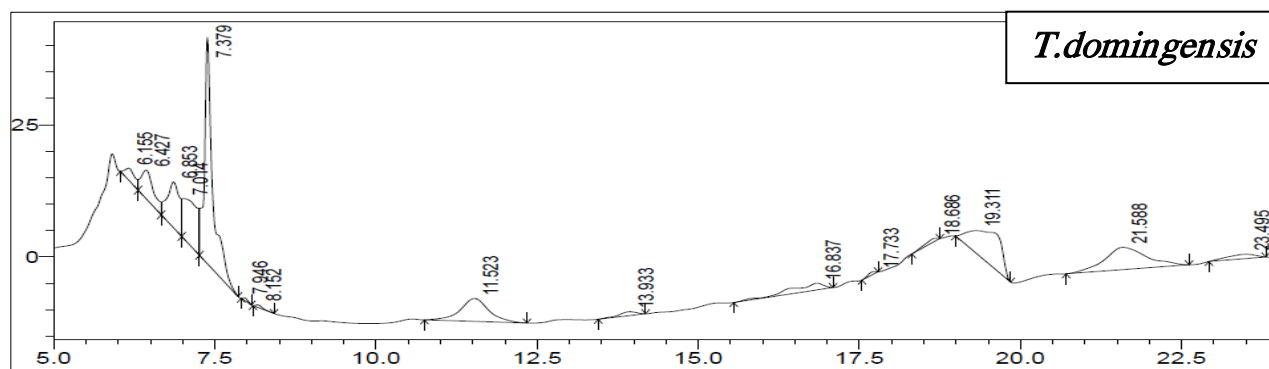
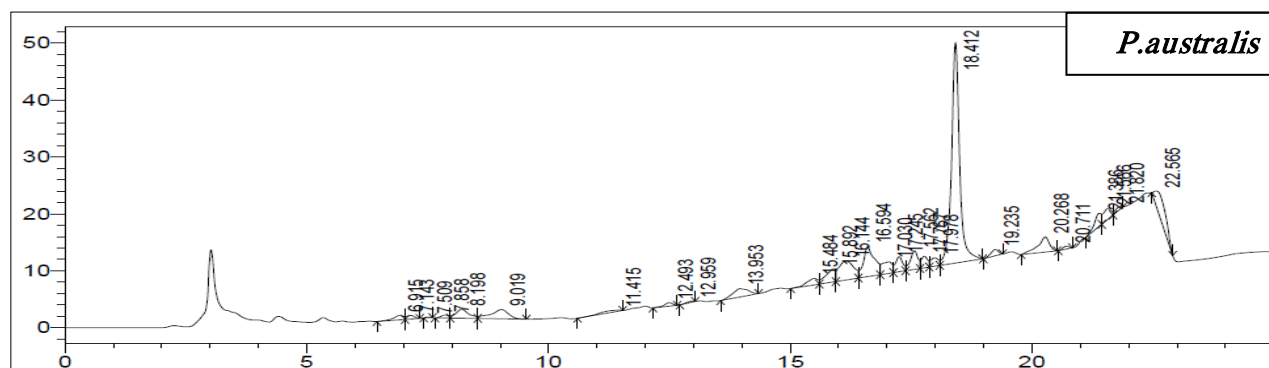
Water samples



Sidements samples

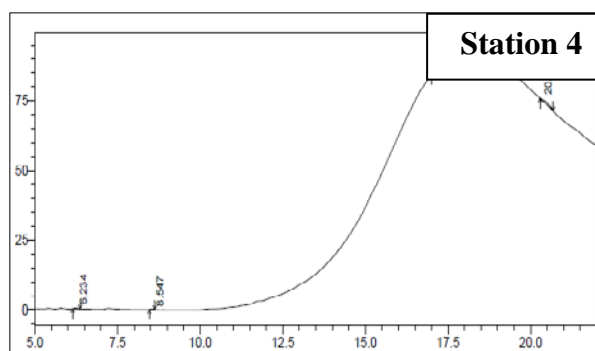
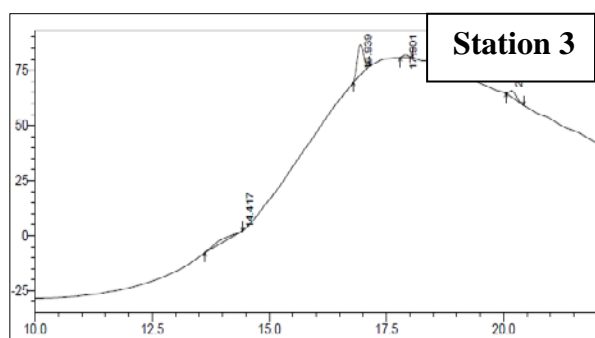
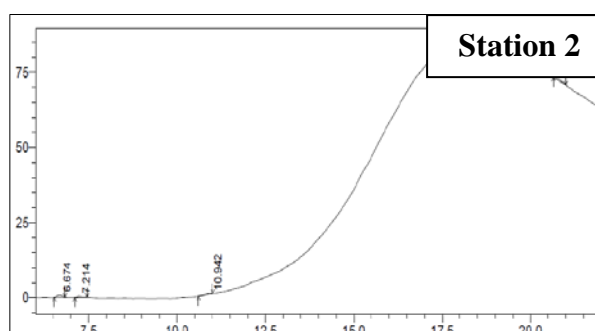
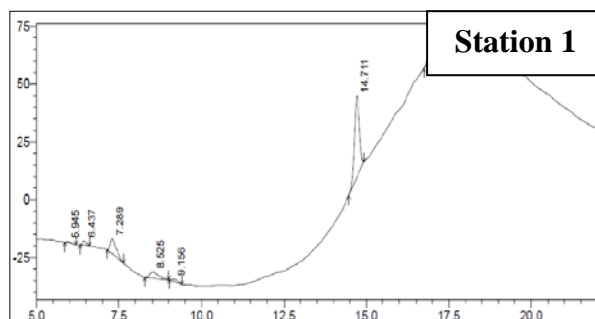


Appendix 5 :Chromatograms of PAHs compounds aquatic plants samples during winter season .

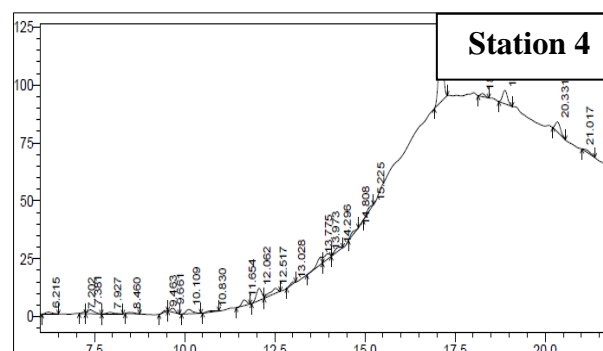
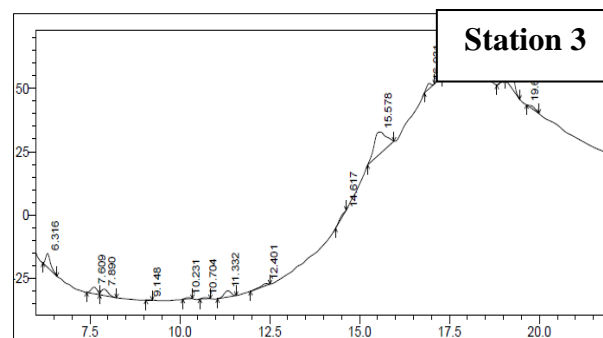
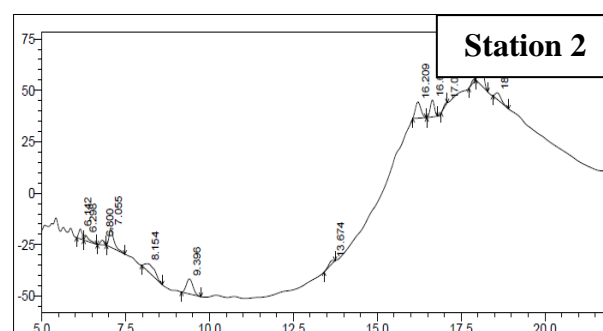
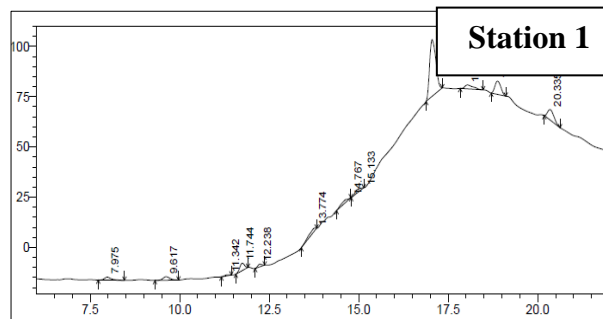


Appendix 5 :Chromatograms of PAHs compounds in water and sediments samples of the studied stations during spring season.

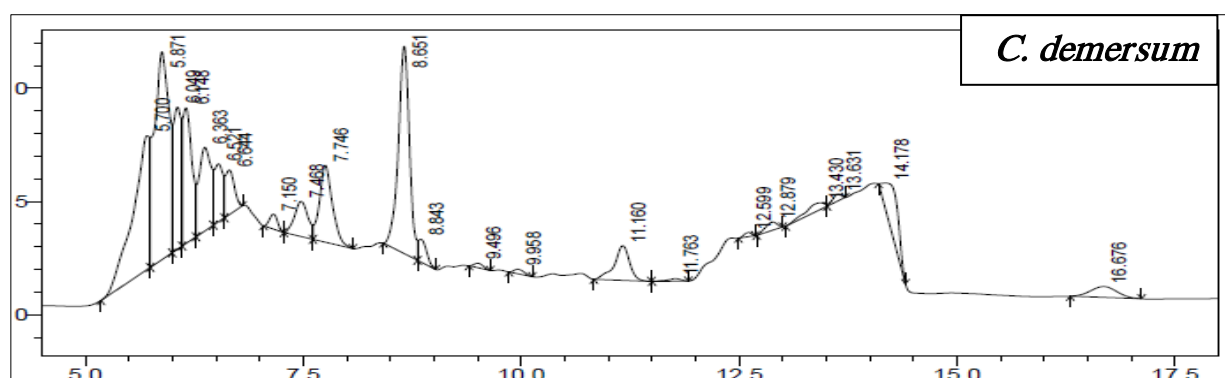
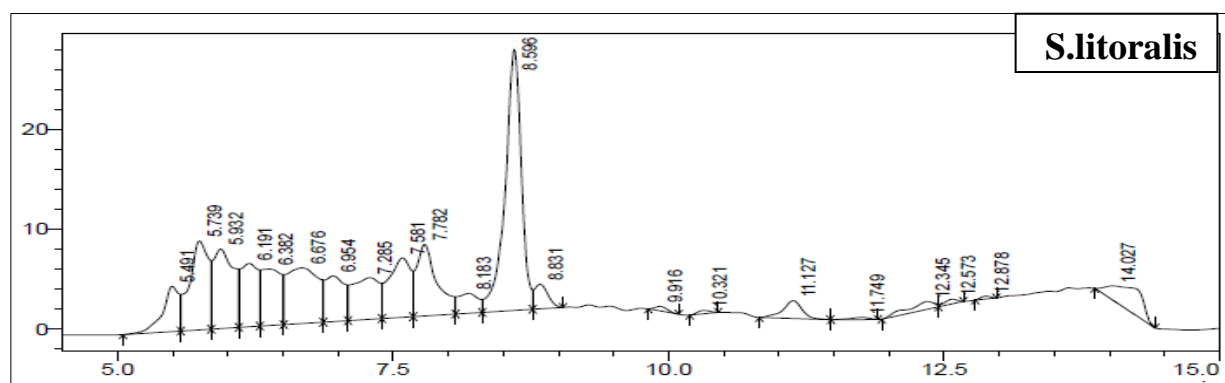
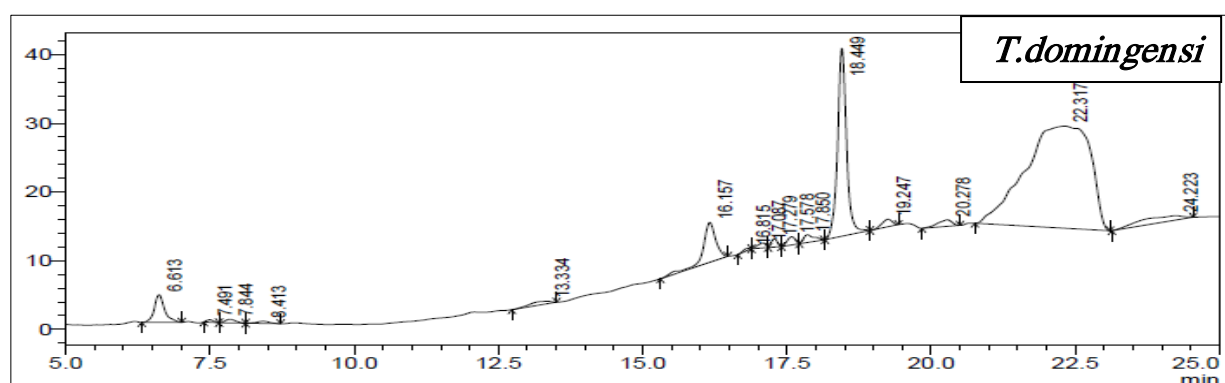
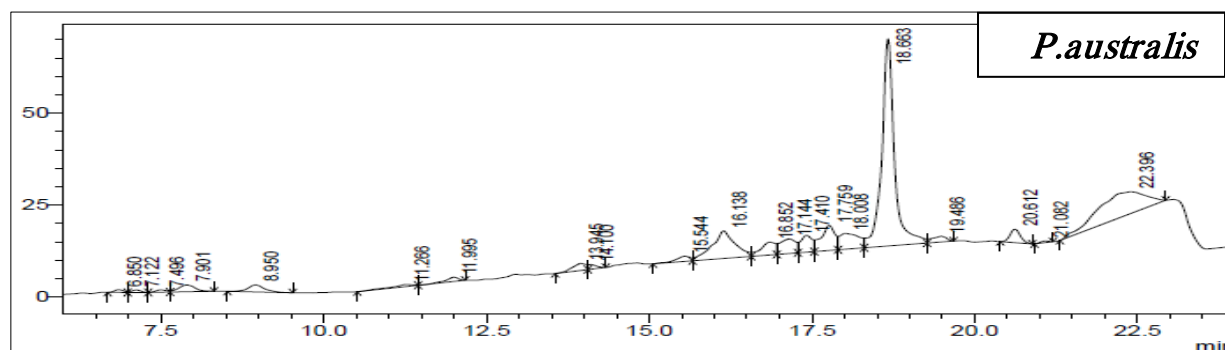
Water samples



Sidements samples



Appendix 5 :Chromatograms of PAHs compounds aquatic plants samples during spring season .



الخلاصة

جمعت عينات الماء والرسوبيات والنباتات المائية السائدة (الغاطسة: الشمبلان *Ceratophyllum demersum*) والبارزة (القصب *Phragmites australis* و البردي *Typha domingensis* , والجلان *Schoenoplectus litoralis*) فصليا من اربعة محطات تم اختيارها في هور الجبايش في محافظة ذي قار جنوب العراق ، المحطة الاولى (ابو سوباط) ، المحطة الثانية (البغدادية 1) ، المحطة الثالثة (البغدادية 2) ، المحطة الرابعة (الحماره) للفترة الممتدة من اب 2017 الى نيسان 2018 ، لتحديد تراكيز بعض العناصر الثقيلة (الكاديوم Cd، الكروم Cr ،النكل Ni والرصاص Pb) وتم قياس هذه العناصر في الطورين الذائب والعالق (المتبادل والمتبقي) في عينات الماء، والطورين المتبادل والمتبقي لعينات الرسوبيات . كما تم حساب دليل التلوث بالمعادن الثقيلة (HPI) لوصف تلوث المياه بالمعادن الثقيلة ودليل التراكم الجيوكيميائي (I-geo) لوصف تلوث الرسوبيات بالمعادن الثقيلة ودليل التراكم الحيوي (BAF) للعناصر الثقيلة في النبات المائية. كما تضمنت الدراسة تحديد تراكيز ومنشأ المركبات الهيدروكاربونية في الماء ، الرسوبيات والنباتات المائية في هور الجبايش .

كذلك تم قياس بعض العوامل البيئية (درجة حرارة الهواء والماء ، الاس الهيدروجيني ، الملوحة ، التوصيلية الكهربائية ، العكورة، المواد الصلبة العالقة الكلية، الاوكسجين المذاب و المتطلب الحيوي للاوكسجين) أضافة الى قياس نسجة التربة والكربون العضوي الكلي في عينات الرسوبيات .

أوضحت النتائج كما يلي: درجة حرارة الهواء (14-47)°م، بينما درجة حرارة الماء (10.5-33)°م ، الاس الهيدروجيني (7.24-8.15)، الملوحة (2.5-3.4) وحدة ملوحة عملية PSU، التوصيلية الكهربائية (6.15-4.53) مليسيمنز/سم، العكارة (1.3-50.55) وحدة عكارة نفلومترية، المواد الصلبة العالقة الكلية (0.75-3.5) ملغم /لتر، الاوكسجين المذاب (0.7-7.75) ملغم /لتر، المتطلب الحيوي للاوكسجين (0.75-3.5) ملغم /لتر ، بينما نسجة الرسوبيات : الرمل (1-24) %، الغرين (59-86) %، والطين (7-25) % ومحتوى الرسوبيات من المواد العضوية الكلية (9.93-13.49) % .

أوضحت النتائج بأن معدل تراكيز العناصر الثقيلة في الطور الذائب كانت:

(0.06 ، 0.56، 2.03، 2.97) مايكغم / لتر للعناصر على التوالي ، بينما في الطور المتبادل من المواد العالقة كانت: (14.47 ، 53.97 ، 90.91 ، 332.78) مايكغم /غم وزن جاف على التوالي ، وفي الطور المتبقي من المواد العالقة كانت: (12.21 ، 225.6 ، 243.66 ، 242.25) مايكغم /غم وزن جاف على التوالي ، وتراوح قيم HPI المسجلة (4.39-12.51) وأشارت الى عدم تلوث مياه المحطات بالعناصر الثقيلة مقارنة بالحدود المسموح بها عالميا لهذه العناصر بشكل ذائب بالماء.

أما في الرسوبيات فقد كان معدل تركيز العناصر في الطور المتبادل من الرسوبيات :

(0.41 ، 19.70 ، 46.37 ، 25.20) مايكغم /غم وزن جاف على التوالي ، وفي الطور المتبقي من الرسوبيات كانت التراكيز كما يلي (0.27، 82.95، 75.32، 14.41) مايكغم /غم وزن جاف على التوالي . بالاعتماد على قيم دليل التراكم الجيوكيميائي (Igeo) ، توصف رسوبيات هور الجبايش بانها غير ملوثة بالكاديوم والرصاص ، وغير ملوثة – متوسطة التلوث بالكروم ، و متوسطة – شديدة التلوث بالنكل .

في النباتات المائية، كانت معدل تراكيز العناصر الثقيلة في نبات القصب :

(0.20، 5.27، 4.21، 6.19) مايكغم /غم ، نبات البردي كانت(0.20، 3.96، 3.05، 5.60) مايكغم /غم ،نبات الجولان (0.20، 4.58، 3.49، 4.31) مايكغم /غم ،بينما كانت في نبات الشمبلان الغاطس(0.51، 9.73، 51.44، 9.99) مايكغم /غم لكل من الكادميوم ،الكروم ،النكل والرصاص على التوالي .بالاعتماد على دليل التراكم الحيوي فأن نبات الشمبلان كان اعلى النباتات تراكما للعناصر المدروسة .

حددت تراكيز الهيدروكربونات النفطية الكلية في عينات الماء ،الرسوبيات والنباتات المائية باستخدام جهاز الفلورة ، وشخصت المركبات الالفاتية (الالكانات الاعتيادية) والمركبات الهيدروكربونية الأروماتية متعددة الانوية باستخدام جهاز كروماتوغرافيا الغاز (GC) وجهاز كروماتوغرافي السائل العالي الاداء (HPLC) على التوالي .اوضحت النتائج ان تراكيز الهيدروكربونات النفطية الكلية في عينات الماء كانت تتراوح ما بين(1.91 – 6.79) مايكغم /لتر وفي الرسوبيات (2.98- 17.98) مايكغم /غم وزن جاف بينما كانت تراكيز الهيدروكربونات الكلية في النباتات المائية (5.99-34.91)،(30.68- 5.25)،(7.78-30.74)،(9.01-34.29) مايكغم /غم وزن جاف لكل من نبات القصب ،البردي ،الجولان والشمبلان على التوالي .

كانت تراكيز المركبات الالفاتية (الالكانات الاعتيادية) في عينات الماء (0.32-2.98) مايكغم /لتر وفي الرسوبيات (0.62-29.75) مايكغم /غم وزن جاف. بينما كانت تراكيز المركبات الالفاتية في النباتات المائية (4.69-31.52)، (10.73-54.25)، (17.09-64.36)، (5.23-40.85) مايكغم /غم وزن جاف . وكانت اطوال سلاسل المركبات الالفاتية في عينات الماء والرسوبيات تتراوح ما بين C38-C16 بينما في النباتات المائية فقد تراوحت ما بين C9 -C38 .

تراوحت تراكيز المركبات الهيدروكربونية الاروماتية في الماء (2.44-37.78) نانوغرام /لتر وكانت المركبات الاكثر تواجد هي الاسينافثالين والاسينافثين (كمركبات خفيفة) والبنزو(k) فلورنثين و أندينو(1,2,3-c,d)بايرين (كمركبات ثقيلة) .اما في الرسوبيات فقد تراوحت التراكيز بين (6.56-52.36) نانوغرام /غم وزن جاف وكانت المركبات الاكثر تواجد هي الاسينافثين والانثراسين (كمركبات خفيفة) والبنزو(i,h,g)بيريلين و الاندينو (1,2,3-c,d)بايرين (كمركبات ثقيلة) .بينما كانت تراكيز المركبات الاروماتية في النباتات المائية :

القصب(54.42-86.66) والبردي (37.02-80.54، والجولان(6.31-137.15)، والشمبلان (-151.90، 11.74) نانوغرام /غم وزن جاف .

باستخدام قيم دليل تفضيل الكربون ونسبة البرستين /الفيتين فقد اعطت دلالة واضحة على ان مصدر الالكانات الاعتيادية في مياه ،رسوبيات والنباتات المائية في هور الجبايش كانت احيائية وبشرية .بينما كانت نسبة تراكيز المركبات ذات الاوزان الجزيئية الواطئة الى تراكيز المركبات ذات الاوزان الجزيئية العالية ونسبة البنزو(a)انثراسين /(البنزو(a)انثراسين +جايرسين)ونسبة الفينانثرين /الانثراسين اعطت دلالة على ان مصدر هذه المركبات في الماء ،الرسوبيات والنباتات المائية هو ناتج من احتراق الوقود ومن مصدر نفطي .



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جامعة البصرة
كلية العلوم

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رسالة مقدمة الى

مجلس كلية العلوم – جامعة البصرة

وهي جزء من متطلبات نيل درجة ماجستير علوم في علوم الحياة

(التلوث البيئي)

من قبل

((رحاب سالم خزعل العطبي))

بكلوريوس علوم – علوم حياة (1995)

بأشراف

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