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Study the regional and seasonal variation of polychlorinated biphenyl in sediments of the Eastern AL-Hammar Marshes, Iraq

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Abstract Wetland sediments can become contaminated with contaminants that pose a risk to plants and animals and are present in groundwater and fresh surface water entering the wetland. The current study aims to detect PCB contaminants in the sediments of the Al-Hamar Marsh in southern Iraq from the winter season of 2021 until the fall season of 2022 during the day from five stations in the Al-Hamar Marsh, which are (1 - Al-Harir, 2 - Al-Mashab 3 - Al-Nakara, 4 - Baraka 1, 5 - Baraka 2). PCBs were analyzed by GC-MASS. The results showed that the highest rate of PCBs concentrations was (2.84) in the winter season and the lowest rate was (0.14 ng/g d. w). The concentrations of PCBs at the study stations ranged (2.34 ng/g d.w - 3.9 ng/g d.w) during the winter season. (0.01 ng/g d.w-3.7 ng/g d.w) during the spring, (0.01 ng/g d.w- 1.46 ng/g d.w) in the summer, and (0.02 ng/g d.w -5.78 ng/g d.w) during the summer. In the fall, the soil texture was measured and the results showed that the sediments of the Al-hammar marsh were silty clay deposits. This study is a first of its kind in the region and could be give available information and used as a baseline study in the futures.

Keywords: polychlorinated biphenyl, sediment, Al Hammar marshes, Iraq

1. Introduction

There are lakes and wetlands in the marsh area, which are divided by small islands. These include lakes with shallow and deep water, mudflats that frequently flood during times of high water, and stable, recurring marshes. (Pearce 2019). The entire marsh area is divided into three main sections: the Al-Hammar Marshes, Central Marshes, and Al-Hawizeh Marshes. Over time, notable changes have centered around these three key marsh zones. The Al-Hammar marshes extend from the eastern edge of the Shatt al-Arab River near Basrah city to the western edge of the Al-Nasiriyah Basin. Completely south of the Euphrates are they. (UNEP 2001). This marsh widened at its southernmost point, where a long stretch of mudshore was present. The estimated area of this marsh ranged from 4,500 km2 to 2899 km2. This marsh's water is shallow, eutrophic, and somewhat brackish due to its proximity to the Arabian Gulf. Its maximum depth is 1.8 meters, while its height is approximately 3 meters (AL-Atbee et al., 2019).

As contaminated water enters natural marshlands, pollutants are deposited there. Water quality is especially important for ecosystems and human health. The government dried up in the Central Marsh in the 1990s and then flooded it again in 2003. After restoration, the hydrology of the Central Marsh was altered, and only the Euphrates River has been affected by its intake (Fazza et al., 2021).

The sources of polychlorinated biphenyls (PCBs) in marshes are the presence of an electrical power plant nearby, the presence of oil fields spread widely in southern Iraq, and the fact that these environments are inhabited by the inhabitants of marshes who rely mainly on boats for transportation. Because they use fuel and motor oil to operate their boats, the spillage of these materials into the water causes the spread of these compounds, in addition to the drainage of agricultural land water to the marshes and the pesticides they contain that contain these dangerous toxic compounds.

There are medical studies on the effects of these compounds on human health, as they affect the human nervous system. They also cause cancer and can be transmitted from the milk of breastfeeding mothers to that of infants. However, in our article, we discussed the distribution, spread, concentrations, and sources of these compounds in the studied area.

1.1. Grine size

River research must focus on sediment parameters, which include chemical and physical characteristics, such as the pollutants absorbed by the sediment, the particle size distribution and the mineral composition (Hui and Shi, 2019).

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The distribution of particle sizes in sediment is one of the most important characteristics. Grain size is a useful tool for characterizing the geomorphic setting of a site, interpreting the geomorphic significance of fluid dynamics in the natural environment, and distinguishing between local and regional sediment transport mechanisms because it is a dominant controlling factor in sediment geochemistry. Clay has the highest surface area-to-volume ratio of any particle size class, making it the material of choice for the adsorption of cations from sources of pollution and mineral weathering (Das, 2013).

Rock weathering and soil erosion produce sediments, which are solid particles of inorganic or organic material that are carried and deposited by wind, water, or ice. They range in size from massive rocks to microscopic particles. Generally, the largest to smallest materials are employed first: boulders, cobbles, gravel, sand, silt, and clays. Sediments form as a result of the breakdown of rocks. They are carried by water for most of their journeys. The pieces are worn down throughout this process, losing their sharp edges and generally becoming rounder. The majority of lithogenic sediments are produced by land-based erosion (Al Dahaan, 2020).

1.2. Pollution with polychlorinated biphenyls (PCBs)

Many kinds of pollutants that are poisonous in certain amounts in aquatic environments and detrimental to all living things, including humans, contaminate water (Jaleel, 2020; Khalaf et al., 2021).

A class of chemical compounds with the formula C12H10, also known as spelled (C6H5)2, that are chlorinated and collectively referred to as polychlorinated biphenyls are referred to by the acronym "PCBs". Chemically, these compounds are made up of a diphenyl molecule (two rings of benzene joined by a single carbon–carbon bond) with one to ten chlorine atoms linked to a biphenyl via the formula C12H10-xClx, where X = 1–10. The hydrogen atoms in the diphenyl molecule are replaced by chlorine atoms to varying degrees. There are 209 congeners in the class of nonpolar hazardous chemical compounds known as PCBs (Adeyemi et al., 2009). Among PCBs, there are approximately 130 di- to deca-PCBs. Commercial goods and commercial oil mixtures may include 50 or more homogenous PCB chemicals (Wang and Zhong, 2011). All PCB congeners are lipophilic, have limited solubility in water, and become more susceptible to lipid buildup as the degree of chlorination increases. It typically bioaccumulates in organisms across all trophic levels, undergoes long-distance transmission, and settles in locations remote from emission sources. Furthermore, it is extremely hazardous and exists everywhere in ecosystems and among people (Al-Zabad, 2021).

PCBs are deposited in aquatic systems by the atmosphere because of their poor solubility in water and tendency to adhere to particles and sediments for a long time. Sediments can therefore serve as a naturally occurring sink for pollutants that resuspend themselves in different water layers. These events lead to an increase in the bioaccumulation of these pollutants as well as other dangerous substances in the food chain. At the apex of the food chain, they biomagnify, including humans. (Kelly et al., 2007; Iniaghe and Kpomah, 2022).

The concentration of PCBs in water bodies has recently become a concern for water quality. This is because after entering a lake or river, they cling to organic matter, which is subsequently concentrated in the sediments (Edjere and Iyekowa, 2017). These organic components are then consumed by aquatic animals that live in the sediment, such as crustaceans, snails, and phytoplankton, which can lead to fish ingesting these organisms and absorbing PCBs. Consequently, humans may consume PCB-contaminated fish, and because PCBs are lipophilic, they gradually bioaccumulate in human fatty tissues. (James and Kleinow, 2014).

1.3. Contamination of sediments with PCBs

Sediments are essential to the planet's cycle and are a major source of PCBs. Due to their low volatility and low water solubility, most of these heavy metals accumulate in sediments where they serve as environmental reservoirs and are continuously released over extended periods of time (Habeeb et al., 2015). Between 1965 and 1980, more than 10,000 tons of PCBs were produced; subsequently, these compounds were declared illegal. However, similar equipment is known to leak, which poses a greater risk in particular areas (Han et al., 2023a). Due to the limited solubility of PCBs in water, which results in a high adsorption coefficient in sediments and a high enrichment factor in aquatic species, the channels of direct waste dumping, nonpoint resource runoff, and home and industrial wastewater are all sources of PCBs in the river environment (Raghad et al., 2020). It has been hypothesized that PCBs associate with particulate matter in aquatic environments and then accumulate in underlying sediments (Qu et al.,2022; Farid et al., 2016).

PCB-containing products, leaky toxic landfills, and spills are the main drivers of PCB buildup in soil and sediment. Utilization and processing also induce volatilization, which can subsequently be carried out by dry and wet settling into lakes and seas. PCBs contribute to air pollution by volatilization and dispersion; however, because they decompose slowly and adhere to organic matter, they are most dangerous in soils and sediments. The primary method by which humans and wildlife are exposed to pollutants is through eating contaminated food (Brborić et al., 2019).

2. Materials and methods

2.1. Description of the study area

The Al-Hammar Marsh lies between the cities of Nasiriyah and Basrah, south of the Euphrates River (Figure 1). Before drying, the approximate area was 2,800 km2. Tributaries that sever from the Euphrates River provide it with water. Nevertheless, during the drying of the marsh in the 1990s, these tributaries rerouted off their original path (Partow, 2001). reeds and papyrus into two sections; the eastern portion is deeper than the western portion, which is very shallow. Because it is connected to the Shatt al-Arab River from the south via the Karmat Ali Channel, the remaining portion of the current research area was submerged in early 2003 and could not be returned to its previously submerged area. This area is known as the Eastern Hammar Seas. Because the waters of the Tigris and Euphrates Rivers do not drain into the Shatt Al-Arab, certain marine fish and shrimp species can reach the water for a variety of reasons.

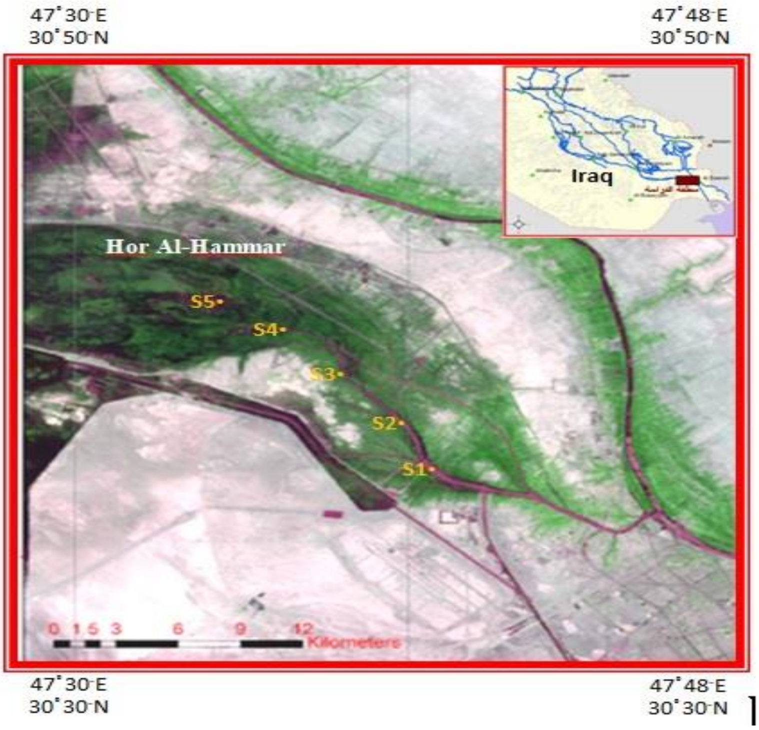

Figure 1 Sample locations.

2.2. Field Work

Samples were collected quarterly over the course of a year, starting from the winter season (2021) until the autumn season (2022) during the day from five stations in the Al-Hammar Marsh: 1-Al-Harir, 2-Al-Mashab 3-Al-Salal Junction, 4-Al-Nakara, 5-Baraka 1, and Baraka 2.

2.3. Sediment Samples

Sediment samples were collected from the study sites using a Van Veen grab sampler. After the samples were collected, the water was allowed to flow and exit, and the samples were kept in aluminum foil, labeled, and placed in a refrigerated box until they reached the laboratory, where they were dried, ground, and then sevied with a size (63 micron) sieve for analysis.

2.4. Grain size analysis (%)

The mean grain size analysis, shown in Figure 1, was carried out using the pipette method (Folk, 1974) for silt and clay grains and with standard sieves (63 µm pore size) for sand grains; then, the triangle texture was applied to describe the sediment texture.

2.5. Extraction of PCBs from sediments

After the sediment samples were brought to the laboratory, they were left to dry using a freeze dryer, after which foreign bodies and impurities were removed. The samples were subsequently ground using a FRITSCH mill and sifted through a sieve with holes of 63 µm. The method of Aganbi et al. (2019) was used to measure PCBs in the sediments as follows:

A total of 20 grams of sediment was taken and placed in a thimble, and PCBs were extracted using a Soxhlet Intermittent Extraction device. Afterwards, 100 ml of a mixture of hexane: methylene chloride (v/v1:1) was added for a period of 48 hours at a temperature not exceeding 40°C. Afterwards, the extract was left to cool. Afterwards, the saponification process was carried out for two hours with 15 ml of a 4-methanol potassium hydroxide solution, standard MeOH (KOH) (4 M), and left to cool. Afterwards, all the contents were transferred to the separating funnel, and 50 ml of hexane/methyl chloride (v/v1:1) was added. Afterwards, the separating funnel was shaken well, and the mixture was left for a period of time until it was separated into two layers. The bottom soaped layer was removed and discarded, and the unsoaped top organic layer containing PCBs was removed and subsequently passed through a chromatographic separation column containing glass wool at the bottom and above 2 grams of silica gel. The layer of alumina was topped with 2 grams to remove fatty acid residues, and above this layer, 2 grams of anhydrous sodium sulfate were used to remove water. The extract was collected in a glass container, labeled, left to dry, and then closed properly until measurement was performed by the GC-MASS device.

2.6. Blank samples

Blank solutions were prepared for each type of sample (sediment). The samples were analyzed in the same way for the purpose of estimating contamination that might occur as a result of using different chemicals or from laboratory conditions. In the case of small concentrations, the value of these concentrations is subtracted from the concentrations of the original samples. The standard methods for collecting samples were adopted, and the samples were transported and preserved for physical and chemical analyses according to the methods of the American Public Health Association (APHA, 2005).

2.7. Statistical analysis

The statistical program SPSS-22 was used for statistical analysis of the results of this study via analysis of variance (AVOVA) at a significance level of 0.05 and the least significant difference (LSD) test.

3. Results

3.1. Grain size

The results of the study showed that the marsh sediments consist of a mixture of sand, silt and clay. The lowest percentage of sand was recorded (9%) at Station 2, and the highest percentage reached (27%) at Station 4. For silt, the lowest percentage was recorded (60%) at Station 4, and the highest percentage reached (74%) at Station 1, while clay reached the lowest percentage. (11%) at Station 5 and the highest percentage (19%) at Station 2, as shown in Table 1 and Figure 2.

Table 1 Grain size values for the current study from winter 2021 to autumn 2022.

Stations	Grain size			Textures type
	Sand %	Silt %	Clay %	
st.1	12	74	14	Silty clay
st.2	9	72	19	Silty sand
st.3	20	65	15	Silty sand
st.4	27	60	13	Silty clay
st.5	25	64	11	Silty clay
Mean	18.6	67	14.4	
S.D	7.059745	5.215361924	2.6532998	

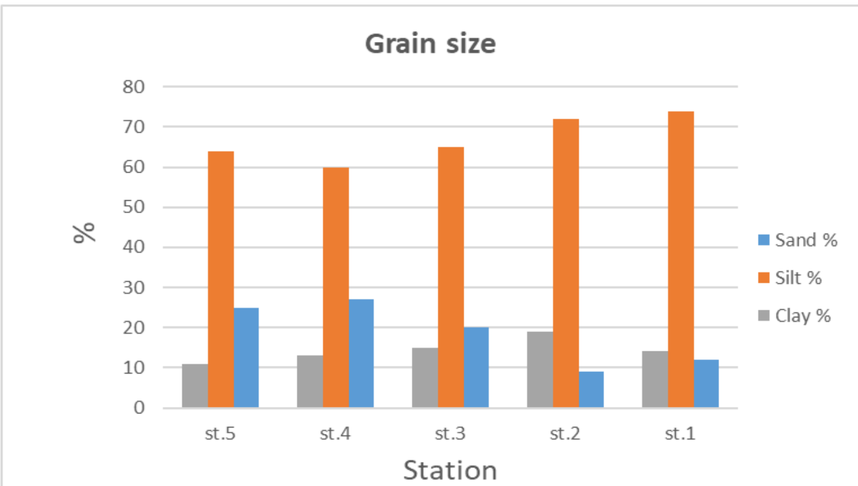

Figure 2 Grain size (%) in the sediments of the studied area.

This result was consistent with that of Balasim et al. (2013), who reported that the marsh sediments in their surface layers were deposited from the recent river sediments of the Tigris and Euphrates Rivers, in addition to the dust from desert storms, and that most of these sediments were composed of silt, sand and clay. The results of the study also agreed with the findings of Al-Badran (2006) and Atbee (2018), who indicated that the surface sediments of marshes consist of an upper layer characterized as a sandy alluvial with a depth of 7 cm.

3.2. PCBs in the sediments

The results showed that the highest mean PCBS concentration for the sediments was 2.84 ng/g d.w. at Station 1 in the winter season, while the lowest mean (0.14 ng/g d.w.) was observed at Station 5 in the summer season, as shown in Table 2 and Figure 3.

Table 2 Mean seasonal changes in PCBs (ng/g d.w.) in sediments from winter 2021 to autumn 2022.

Station	Winter	spring	summer	autumn
st1	2.84	2.03	0.45	1.41
st2	2.05	1.6	0.37	0.85
st3	1.04	1.54	0.34	0.84
st4	0.62	1.51	0.31	0.77
st5	0.34	1.24	0.14	0.71

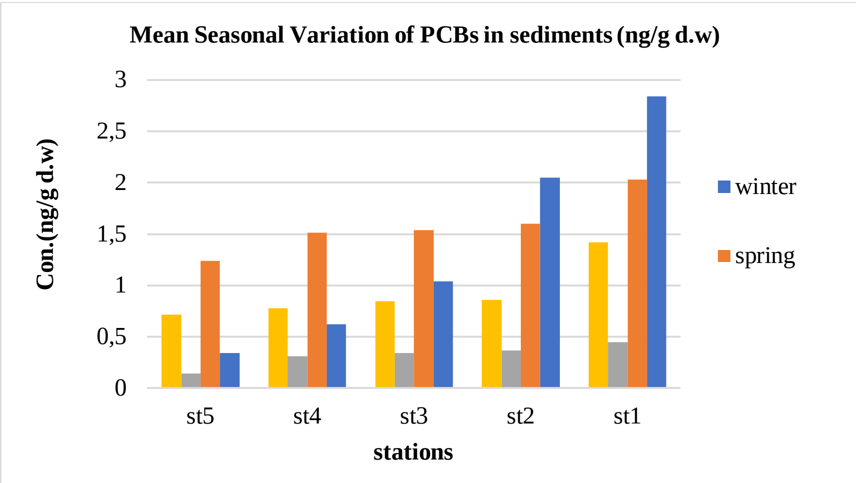

Figure 3 Mean seasonal variations in PCBs (ng/g d.w.) in sediments from winter 2021 to autumn 2022.

The winter results showed that the highest concentration of PCB141 (3.9 ng/g d.w.) occurred at Station 1, the highest mean PCB concentration (2.84 ng/g d.w.) occurred at Station 1, and the lowest mean concentration (0.34 ng/g d.w.) occurred at Station 5 (Table 3, Figure 4a and Figure 4b).

Table 3 Concentrations and types of PCBs (ng/g d.w.) in sediments during the winter season.

Compound name	st1	st2	st3	st4	st5
PCB 18	1.2	0.87	0.55	0.25	0.2
PCB-29(IS)	1.3	1.1	0.73	0.55	0.6
PCB 31	0.21	0.23	0.26	0	0
PCB 28	0.04	0.01	0.04	0.05	0.03
PCB 44	2.66	1.9	0.7	0.35	0.3
PCB 52	2.1	1.99	1	0.98	0.14
PCB 101	0.34	0.58	0.73	0.1	0.13
PCB 141	3.9	2.88	0.45	0.06	0.1
PCB 149	1.9	1.6	0.67	0.93	0.33
PCB 138	1.26	0.35	0.07	0.13	0
PCB 153	1.24	0.61	0.05	0.06	0.02
PCB 189	2.5	2.2	1.9	0.78	0.34
PCB 194	1.26	0.04	0.19	0.15	0.23
TOTEL	19.91	14.36	7.34	4.39	2.42
Mean	2.84429	2.05143	1.04857	0.62714	0.34571
±SD	1.0827	0.92442	0.50729	0.3533	0.17433

0=Not detected

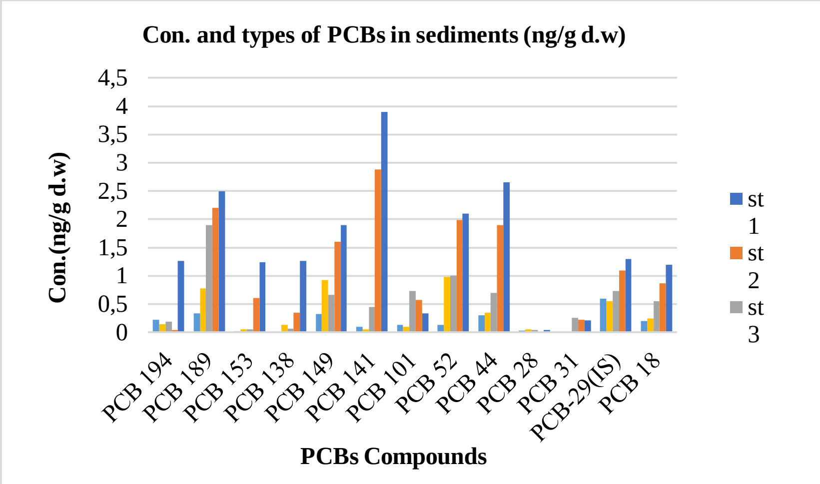

Figure 4 Concentrations and types of PCBs (ng/g d.w.) in sediments during the winter season.

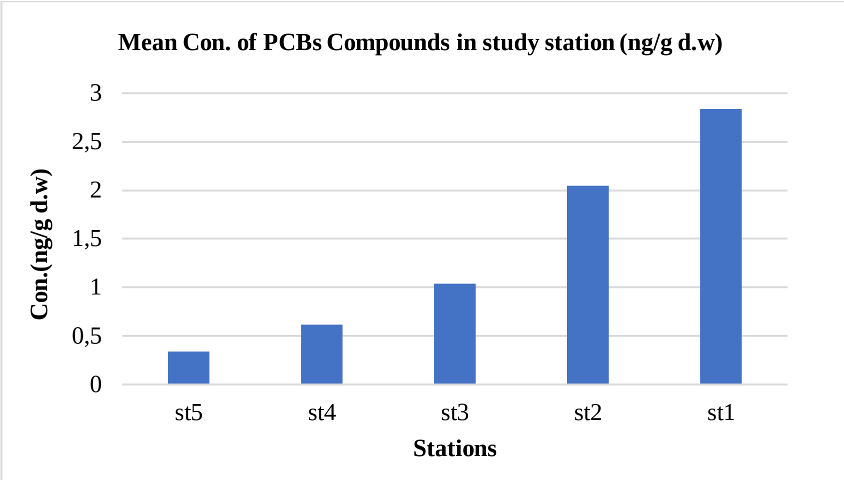

Figure 4b Mean concentrations of PCB (ng/g d.w.) compounds at the study stations during the winter season.

The spring results showed that the highest concentration of PCB101 (3.7 ng/g d.w.) occurred at station 2, and the lowest concentration of PCB-29 (IS) (0.01 ng/g d.w.) occurred at stations 1 and 3. The highest mean PCB concentrations (2.03 ng/g d.w.) occurred at station 1, and the lowest mean concentration (1.24 ng/g d.w.) occurred at station 5 (Table 4, Figure 5a and Figure 5 b).

Table 4 Concentrations and types of PCBs (ng/g d.w.) in sediments during the spring season.

Compound name	st1	st2	st3	st4	st5
PCB 18	1.39	0.16	0.05	0.06	0.13
PCB-29(IS)	0.01	0.1	0.01	0.08	0.06
PCB 31	1.73	1.42	1.51	2.27	0
PCB 28	0.27	0.13	0.13	0.12	0.12
PCB 44	0.08	0.02	0.02	0.01	0.02
PCB 52	2.14	0.69	0.83	0.99	2.61
PCB 101	3.43	3.7	3.24	2.92	2.52
PCB 141	0.16	0	0.42	0.12	0.07
PCB 149	0.12	0.31	0	0	0
PCB 138	1.53	1.27	1.42	0.74	0.49
PCB 153	1	0.93	0.83	0.63	0.27
PCB 189	0	0	0	0	0
PCB 194	2.33	2.49	2.29	2.66	2.4
Totel	14.19	11.22	10.75	10.59	8.69
Mean	2.03	1.6	1.54	1.51	1.24
±SD	1.105	1.36	1.029	1.082	1.06

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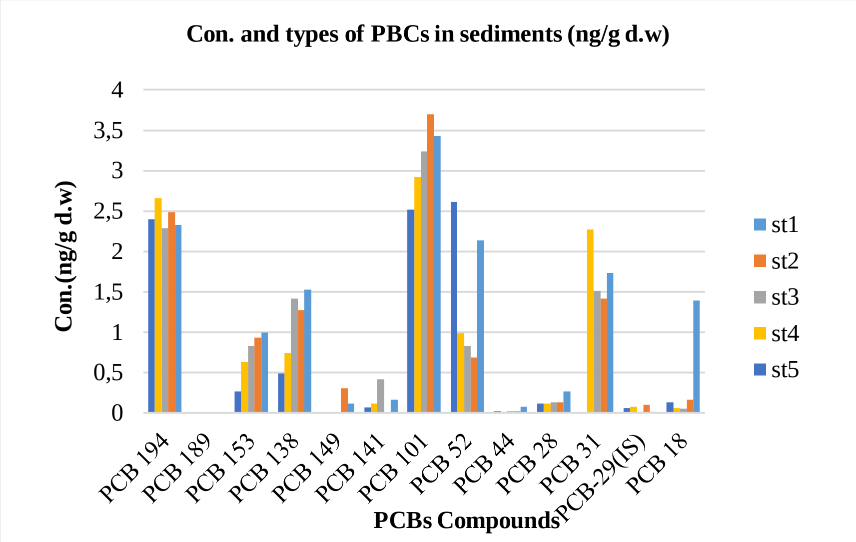

Figure 5a Concentrations and types of PCBs (ng/g d.w.) in sediments during the spring season.

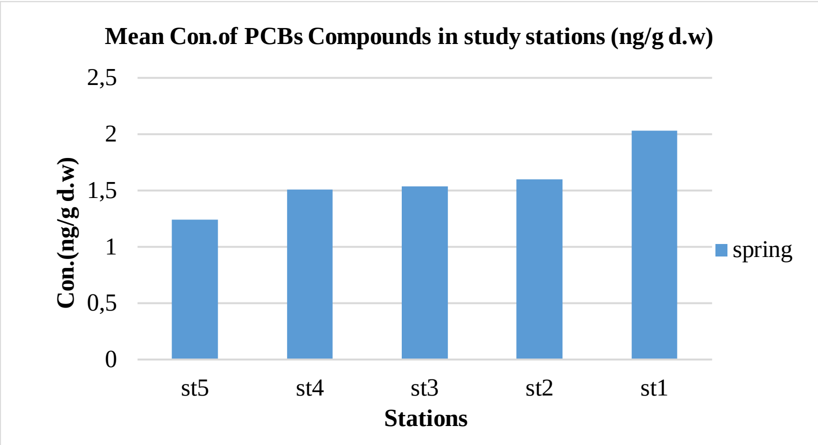

Figure 5b: Mean concentrations of PCB (ng/g d.w.) compounds at the study stations during the spring.

In the summer, the highest concentration of PCB 101 (1.46 ng/g d.w.) occurred at Station 2, and the lowest concentration of PCB 194 (0.01 ng/g d.w.) occurred at Stations 2 and 4. The highest mean PCB concentration (0.45 ng/g d.w.) occurred at Station 1, and the lowest mean concentration (0.14 ng/g d.w.) occurred at Station 5 (Table 5, Figure 6a and Figure 6b).

Table 5 Concentrations and types of PCBs (ng/g d.w.) in sediments during the summer season.

Compound name	st1	st2	st3	st4	st5
PCB 18	1.39	0.2	1.37	0.15	0.12
PCB-29(IS)	0.31	0.3	0.43	0.33	0.18
PCB 31	0.53	0.88	0.19	0.7	0.29
PCB 28	0	0	0	0	0
PCB 44	0.05	0.3	0.06	0.5	0.16
PCB 52	0.93	0.42	0.57	0.55	0.01
PCB 101	1.25	1.46	1.14	1.34	0.21
PCB 141	0.42	0.1	0.17	0.22	0.16
PCB 149	0	0	0	0	0.04
PCB 138	0.33	0	0	0	0
PCB 153	0.28	0.9	0.25	0.11	0.2
PCB 189	0.2	0.18	0.18	0.12	0.11
PCB 194	0.15	0.01	0.02	0.01	0.31
Totel	5.84	4.75	4.39	4.03	1.8
Mean	0.45	0.37	0.34	0.31	0.14
±SD	0.462	0.449	0.444	0.386	0.104

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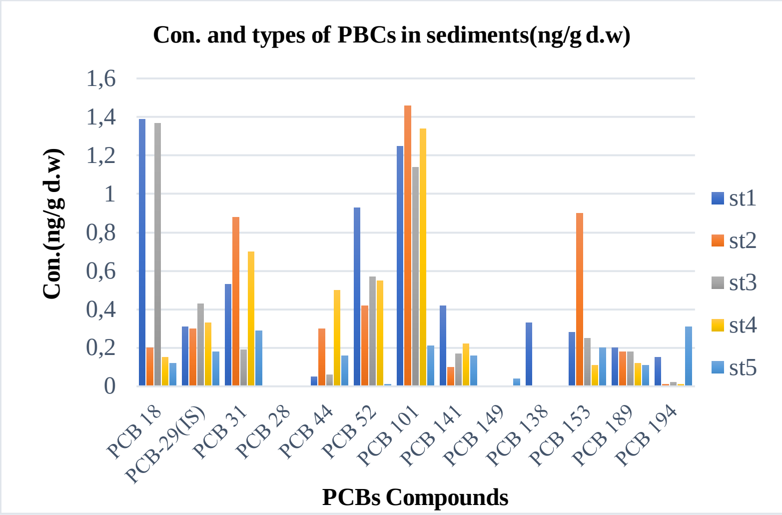

Figure 6a Concentrations and types of PCBs (ng/g d.w.) in sediments during the summer season.

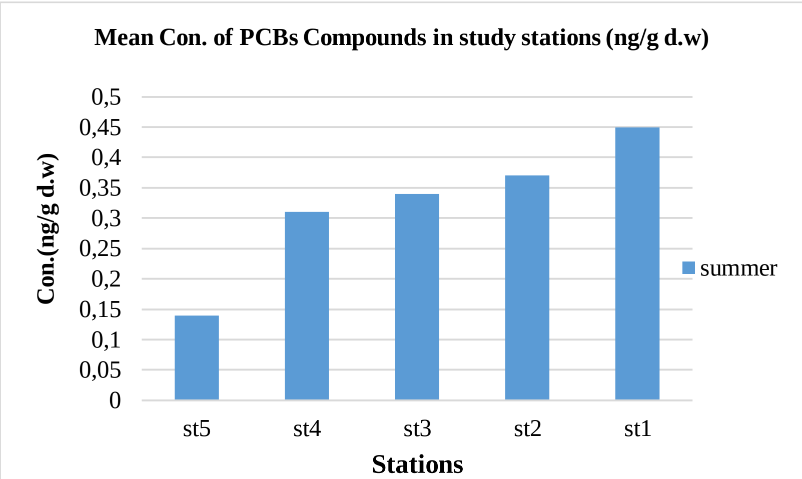

Figure 6b Mean concentrations of PCB (ng/g d.w.) compounds at the study stations during the summer season.

In the autumn season, the highest concentration of PCB 101 (5.78 ng/g d.w.) occurred at Station 2, and the lowest concentration of PCB 153 (0.02 ng/g d.w.) occurred at Station 1. The highest mean PCB concentration (0.45 ng/g d.w.) occurred at station 1, and the lowest mean concentration (0.14 ng/g d.w.) occurred at station 5 (Table 6, Figure 7a and Figure 7 b).

Table 6 Concentrations and types of PCBs (ng/g d.w.) in sediments during the autumn season.

PCB 18	st1	st2	st3	st4	st5
	1.53	1. 70	1.88	1.42	1.72
PCB 29	0.79	1.37	1.68	1.35	0.11
PCB 31	1.69	1.69	0.46	0.54	0.04
PCB 28	0.08	0.47	0.63	0.2	0.07
PCB 44	0.17	0.63	0.6	0.17	0.13
PCB 52	5.78	0.61	1.49	1.28	2.99
PCB 101	1.93	0.74	0.18	2.54	0.1
PCB 141	0.02	0.38	0.62	0.11	0.32
PCB 149	1.24	0.88	1.33	2.09	0.27
PCB 138	0.02	0.55	0.65	0.1	0.43
PCB 153	0.9	0.54	0.11	0.07	2.83
PCB 189	0.18	0.84	0.46	0.11	0.06
PCB 194	4.11	0.77	0.89	0.1	0.24
TOTAL PCBs	18.44	11.17	10.98	10.08	9.31
MEAN	1.418	0.859	0.844	0.775	0.716
±SD	1.734±	±0.382	±0.569	0.860±	±1.068

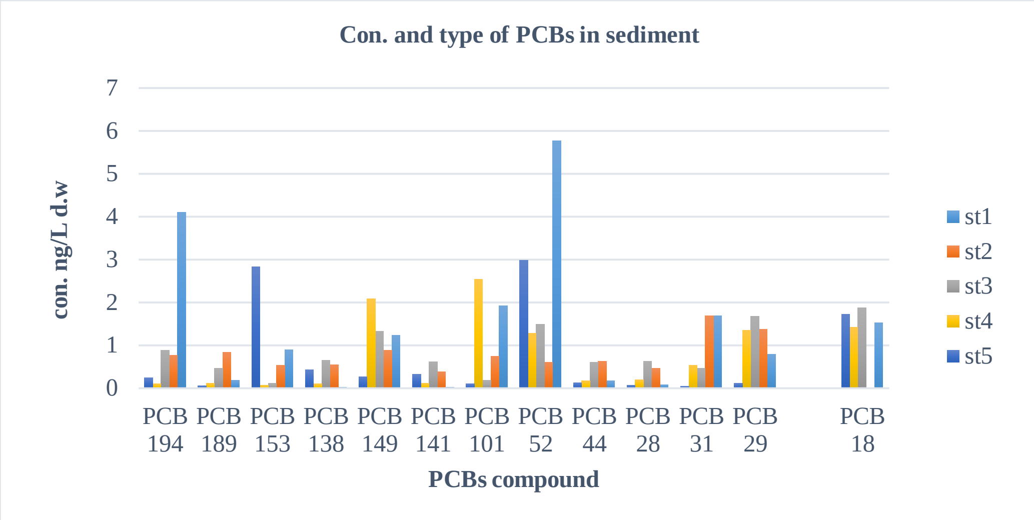

Figure 7a Concentrations and types of PCBs (ng/g d.w.) in sediments during the autumn season.

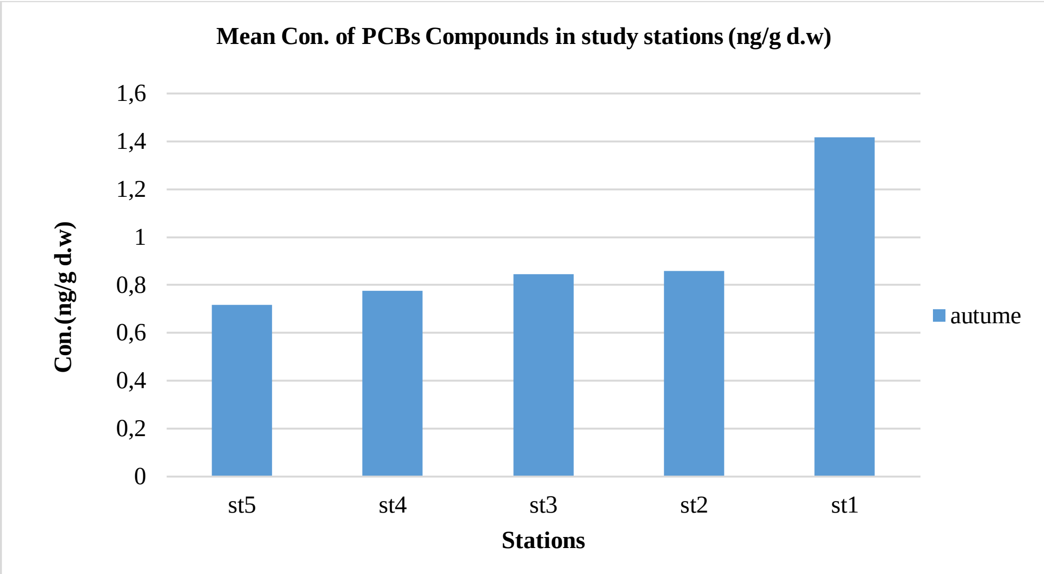

Figure 7b Mean concentrations of PCB (ng/g d.w.) compounds at the study stations during the autumn season.

4. Discussion

The results of the statistical analysis showed that there were significant differences ($p<0.05$) in PCB concentrations among the stations. The first station had the highest PCB concentration. Station 1 was the most polluted among the stations. The texture of the sediments at Station 1 may provide an explanation for this increase, as silty-clay sediments store chemicals in significant quantities, as the size of the sediment grains decreases as the sediments accumulate more material. According to Zabad (2021).

PCB values increased more in clay sediments than in sand. Additionally, a study by Barakat et al. (2013) suggested that a station's high concentration of chemicals may be related to its close proximity to the city. He found that sediments close to cities frequently have high quantities of PCBs because urban industrial regions are more exposed to PCB pollution than rural areas are, and vice versa.

Sediments play a significant role in the study of environmental pollution because they are a good indicator of the level of water pollution due to the high concentrations of PCBs they contain, which act as major environmental reservoirs for these pollutants in aquatic environments. These substances can leak gradually over time (Han et al., 2022). Water flow and organic matter can affect the amount of PCBs in sediments, which can affect the physical characteristics of PCBs, such as transit, migration, and adsorption. After they enter the aquatic environment, PCBs are concentrated in sediments.

This study agreed with the studies of Zabad (2021) and Sari et al. (2023), who recorded the highest concentrations of PCN compounds in sediments. A comparison of our data with those of previous studies of PCBs is shown in Table 7, which shows that our values are consistent with those of previous studies.

Table 7 Comparisons of the concentrations of PCBs in sediments in the present study with those in other studies worldwide.

Study area	country	concentration	Sources
Shuaiba Port	Kuwait	926 -132 ng/g	(Lyons *et al.*, 2015)
Jeddah coast	Saudi Arabia	15.63-0.58ng/g	(El-Aziz El-Maradny *et al.*, 2015)
Khor Musa	Iran	30.9-1.6 µg/kg	(Hassan *et al.*, 2013)
The Nile Rive	Egypt	2244-1461pg/g	(El-Kady *et al.*, 2007)
Bizerte lagoon	Tunisia	14.6-0.8 ng/g	(Barhoumi *et al.*, 2014)
Forcados River	Nigeria	202.3-2.7 µg/kg	(Iwegbue, 2016)
Haizhou Bay	China	6.27-1.33 ng/g	(Zhang *et al.*, 2014)
Arun River	Italy	200 - 10 µg/kg	(Bazzanti *et al.*, 1997)
Passaic River	America USA	4.7-1.1 mg/kg	(Wenning *et al.*, 1994)
Napoleon Bay	Uganda	1848-362 pg/g	(Ssebugere *et al.*, 2014)
Shatt al-Arab	IRAQ	27.75-4.48 ng/g	(AL-Zabad, 2021)
AL -Hamaer Marshes	IRAQ	0.14-2.84(ng/g d.w)	Present study

5. Conclusions

13 Polychlorinated biphenyls were detected in the sediment of five stations. The present study revealed variations in PCB concentrations among the different stations and different seasons of the year. There were good correlations between total organic carbon and the texture of the sediment with organochlorine pesticides, and these results could provide additional information for further studies in the future.

Ethical considerations

Not applicable.

Conflict of interest

On behalf of all the authors, the corresponding author states that there are no conflicts of interest.

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