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Concentrations of Polychlorinated Biphenyls (PCB) in Water of the Southern Part of Tigris River-Iraq

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ABSTRACT

Polychlorinated Biphenyls(PCB) contamination has spread throughout the world due to its high stability and tendency to accumulate in the bodies of living organisms resulting in serious health effects on organisms.Water samples were collected from four stations along the southern part of the Tigris River during the period from autumn (2022) to summer (2023) to determine the concentrations of PCB compounds. Twelve compounds of PCBs were identified in the study areas; namely, PCB153, PCB149, PCB141, PCB138, PCB101, PCB52, PCB44, PCB31, PCB28, PCB18, PCB194, PCB189 one dioxin-like PCB compound appeared (PCB189). The concentrations of total PCBs in water samples ranged from (1.2ng/L) during the winter to (18.8ng/ L) during the autumn season; these compounds recorded the highest level in the upper station compared to the lower stations. This may be due to human activities, household wastes and neighboring agricultural lands that use fertilizers and pesticides as sources of PCB compounds.

INTRODUCTION

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Environmental pollution is one of the serious problems facing communities around the world since ancient times, especially in poor communities; this problem forms a direct threat in terms of its impact on human health and the resources (**Al-Hejuje***et al.*, **2015**).Components that transition from useful elements to harmful pollutants lose much of their natural role in ecosystems (**Saadoun**, **2018**). Water pollution is a major problem that is increasingly complicated by the release of pollutants directly or indirectly from domestic, industrial and agricultural waste water, production, refining and transportation of crude oil (**Al-Hejuje**, **2014**). Certain pollutants exhibit high chemical stability, resisting decomposition or breakdown. This characteristic contributes to their widespread and complex dissemination (**WHO/IPCS**, **1993**).

The term PCBs refers to the group of chlorinated organic compounds known as polychlorinated biphenyls. These are synthetic aromatic compounds formed by replacing hydrogen atoms on a biphenyl molecule (two benzene rings bonded together by a single

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carbon-carbon bond) with 1 to 10 chlorine atoms. The chemical formula for PCBs is C12H10-xClx, where x ranges from 1 to 10 (**Apitzet al., 2006**).

PCBs are a family of hydrophobic chlorinated compounds characterized by high degradation resistance and are characterized by toxicity, bioaccumulation properties and widespread distribution in the environment (**Wang** *et al.*,2019). However, bans and evidence showing that concentrations of these toxic substances in the environment have decreased (**USEPA**, 1997). PCBs contamination has spread throughout the world due to its high stability and tendency to accumulate in the bodies of living organisms aligned with serious health effects on wildlife, humans and organisms (Ahlborget al., 1995). PCB was classified as persistent organic pollutants (POPs), and its production and use in 1978 was regulated worldwide under the United States federal law (**Porta, 2002**).

PCBs are not naturally occurring compounds; they are associated with commercial manufacturing, storage, use, and disposal. These chemicals do not have natural sources and can be unintentionally formed from thermal and chemical processes (Li *et al.*, 2013). PCBs are man-made chlorine organic liquid substances; their shape is often crystalline, and the pure ones are colorless with an aromatic smell, and they do not crystallize at low temperatures (WHO/IPCS,1993). PCBs are characterized by low flammability and are chemically stable and have a distinctive physical property that they are capable of electrical insulation (Koppe & Keys, 2001). Production of PCBs has recently been ceased due to their numerous health and environmental risks. However, these chemicals can still be found in various industrial applications, particularly in old power plants that previously used PCB-containing oil. PCBs are also present in some old capacitors, transformers, and other devices (Lauby-Secretan *et al.*, 2013).

Due to the lack of studies that address the distribution and spread of polychlorinated biphenyls (PCBs) in Iraqi waters in general and river waters in particular, the dangers of these pollutants are detected in the neighborhoods. Hence, the current study aimed to study the concentrations, seasonal and localized changes of PCBs compounds in the waters of the southern part of the Tigris River.

MATERIALS AND METHODS

The study area is located in the southern part of the Tigris River from the borders of Maysan Governorate to the borders of Basra Governorate represented by Qurna City. The Tigris River in this region is one of the most important surface water sources for the governorates of Basra and Maysan. In the current study, four stations (Al-Majar, Qal'at Saleh, Al-Uzair and Al-Qurna) were selected to collect water samples in the southern part of the Tigris River (Fig. 1).



Fig. 1. Current study stations

Water samples were collected from four stations along the southern part of the Tigris River seasonally (two months per season) during autumn 2022 to the summer 2023 at the beginning of the day. Water samples were collected using opaque glass bottles of 5 liters, with a depth of 25cm below the surface of the water during the reflux period for measuring PCBs. Ten milliliters of chloroform were added to each sample in the field to stabilize the sample.

The method outlined in **USEPA** (2006) for extracting PCB compounds from water samples was followed as follows: initially, a water sample of 5 liters was mixed with 100ml of hexane:dichloromethane in a 1:1 ratio for 30 minutes using a mixer device. Subsequently, 500ml of the sample was transferred to a 1-liter separation funnel, and 20ml of extraction liquid (dichloromethane) was added to the sample. The separation funnel was thoroughly shaken for 10-15 minutes, after which it was left undisturbed for 10 minutes to allow the complete separation of the two phases, the aqueous phase and the organic phase.

The organic phase was then passed over a glass column of approximately 20cm in length. The column contained a glass wool at the bottom, followed by 2g of silica gel, 2g of alumina, and 2g of anhydrous sodium sulfate (Na2SO4), in that order from bottom to top. The extract was collected, and the sample was transferred from the glass flask after concentration to a glass container (vial). It was then left to evaporate in the air until completely dry, and the container was sealed tightly. The samples were stored until the PCB compounds were measured using gas chromatography-mass spectrometry (GC-MS) analysis.

Statistical analysis

The statistical program (SPSS) Statistical Package for Social Science was used using the analysis of variance (ANOVA test-one way) under a significant level of 0.05. The correlation coefficient (r) was extracted to find the extent of the relationship between the physical and chemical variables of water and the concentrations of PCBs in water.

RESULTS

The present study revealed the presence of various PCB compounds in the water samples. Twelve PCB compounds were identified in the study areas, specifically PCB153, PCB149, PCB141, PCB138, PCB101, PCB52, PCB44, PCB31, PCB28, PCB18, PCB194, and PCB189. These types were detected across the water samples collected. Among all the samples, one dioxin-like PCB compound, 189PCB, was observed. Tables (1- 4) display the concentrations of PCB compounds (in ng/L) in the water samples from the study stations during the four seasons, spanning from autumn 2022 to summer 2023.

Table 1. PCB concentrations (ng/ L) in the water of the study stations during the autumn season

Compound name	AL-Majar	Qal'at Saleh	Al-Uzair	Al-Qurna
PCB18	0.98	0.13	0.17	0.26
PCB31	2.26	0.34	0.36	0.22
PCB28	2.47	0.3	0.29	0.25
PCB44	1.68	0.08	0.22	0.27
PCB52	1.33	0.34	0.1	0.23
PCB101	0.29	0.24	0.24	0.23
PCB141	1.51	0.4	0.33	0.64
PCB149	1.63	0.33	0.33	0.34
PCB138	2.11	0.29	0.26	0.45
PCB153	1.96	0.76	0.52	0.47
PCB189	0.9	0.27	0.12	0.19
PCB194	1.69	0.45	0.32	0.21
TOTAL PCBs	18.8	3.92	3.27	3.76

Compound name	AL-Majar	Qal'at Saleh	Al-Uzair	Al-Qurna
PCB18	0.15	0.12	0.13	0.12
PCB31	0.04	0.08	0.11	0.04
PCB28	0.08	0.12	0.3	0.09
PCB44	0.04	0.04	0.05	0.09
PCB52	0.05	0.06	0.23	0.38
PCB101	0.13	0.08	0.09	0.06
PCB141	0.05	0.09	0.19	0.12
PCB149	0.25	0.09	0.2	0.08
PCB138	0.11	0.13	0.1	0.12
PCB153	0.23	0.06	0.07	0.33
PCB189	0.02	0.13	0.06	0.07
PCB194 TOTAL PCBs	0.03 1.2	0.38 1.38	0.15 1.65	0.31 1.8

Table 2. PCB concentrations (ng/ L) in the water of study stations during the winter season

Table 3. PCB concentrations (ng/ L) in the water of study stations during the spring season

Compound name	AL-Majar	Qal'at Saleh	Al-Uzair	Al-Qurna
PCB18	0.2	0.37	0.26	0.12
PCB31	0.23	0.21	0.14	0.17
PCB28	0.22	0.28	0.17	0.17
PCB44	0.14	0.21	0.05	0.07
PCB52	0.23	0.05	0.06	0.11
PCB101	0.23	0.15	0.11	0.1
PCB141	0.04	0.1	0.08	0.05
PCB149	0.05	0.04	0.06	0.07
PCB138	0.23	0.18	0.03	0.1
PCB153	0.2	0.05	0.1	0.05
PCB189	0.25	0.13	0.3	0.19
PCB194	0.17	0.11	0.06	0.16
TOTAL PCBs	2.19	1.88	1.42	1.35

Compound name	AL-Majar	Qal'at Saleh	Al-Uzair	Al-Qurna
PCB18	0.38	0.21	0.19	0.06
PCB31	0.22	0.18	0.25	0.15
PCB28	0.02	0.19	0.15	0.16
PCB44	0.11	0.08	0.06	0.32
PCB52	0.17	0.15	0.34	0.02
PCB101	0.04	0.02	0.35	0.33
PCB141	0.11	0.08	0.24	0.11
PCB149	0.12	0.16	0.08	0.35
PCB138	0.08	0.24	0.03	0.14
PCB153	0.2	0.15	0.16	0.04
PCB189	0.13	0.2	0.17	0.13
PCB194	0.18	0.02	0.04	0.13
TOTAL PCBs	1.78	1.69	2.08	1.93

Table 4. PCB concentrations (ng/ L) in the water of study stations during the summer season

The concentrations of total PCBs in water samples ranged from 1.2ng/ L during winter to 18.8ng/ L during the autumn season in Al-Majar station. In Qalat Saleh station, the concentrations ranged between 3.9 & 1.38ng/ L, while in Al-Uzair station, it ranged between 3.27 & 1.41ng/ L, whereas the range in Al-Qurna station fluctuated between 3.76 & 1.35ng/ L (Fig. 2).



Fig. 2. Seasonal and local variations of total PCB compounds (ng/L) in the water of the studied stations.

The results of the statistical analysis using one-way ANOVA showed that there were no significant differences between the study stations (P> 0.05) in all PCBs, except for PCB18 which showed significant differences, as PCB18 recorded the

highest concentration (0.98 ng/L) in Al-Majar station and the lowest concentration (0.06 ng/L) in Al-Qurna station.

DISCUSSION

All compounds recorded their highest concentration in the autumn season, while compounds (PCB31, PCB189, PCB138, PCB101, PCB44) recorded their lowest concentration in the winter season. The compounds (PCB52, PCB141, PCB153, PCB149) recorded their lowest concentration in spring, while compounds (PCB194, PCB28) recorded their lowest concentration in the summer season.

Compared to natural sources, human activities (Anthropogenic) sources are the main sources of pollution of the aquatic environment, as PCBs reach the aquatic environment through multiple sources, including soil erosion in adjacent lands and rainfall on the aquatic environment (Hartet al., 1993).

Al-Majar station showed a rise in the concentrations of PCBs compounds in the water compared to other stations; this may be due to human activities, household waste and neighboring agricultural lands that use fertilizers and pesticides as sources of PCBs compounds. Al-Qurnaand Qal'at Saleh stations have moderate concentrations, and this rise can be explained by the presence of extensive human activities near the stations and also the use of fishing boats where they are used by residents of the areas surrounding the stations, as well as the amount of sewage water discharging into the river from houses built near the banks of the river that increases the concentrations of PCBs in aquatic environment.

These pollutants are released into the water through transportation, loading, unloading, leakage, car wash water, oil tanks, and oil drains, especially car oils. It was noted that there are oil exchange shops near the Tigris River, which drain oils, wash and discharge into the Tigris River, as well as electrical transformer oils and many oils of the electrical appliances containing PCBs, in addition to the presence of a regulator (dam) Oala'at Saleh, and all combined play a major role in the accumulation of pollutants there. Hence, this study showed a high level of high-chlorine PCBs in the northern part of the Tigris River at Al-Majar, and then Qal'atSalih station, while low chlorine PCBs predominate as we move to the southern part and reach Al-Uzair station and Al-Qurna station, since the concentrations were lower compared to stations in the upper part of the river. These results agree with the study of Karawiand Sabra (2012), which concluded that in the Lattakia River, the concentrations of PCBs is elevated due to the sewage, oils, human activities and added that highly chlorine compounds prevail in the northern part of the study stations, compared to the study stations in the southern part. Despite the presence of the use of these compounds, the quantities of PCBs remain in the water and exist as persistent organic pollutants and may cause problems for the environment.

The highest levels of PCBs in the water were recorded during the autumn season, while the lowest levels were recorded during the winter season; this may be due to the fall of dead plant leaves that carry PCBs, in addition to the fact that human activities can have a role in increasing PCBs, as well as many trips, tourism activities, and the use of fishing boats in or near the study stations during the autumn season. This study coincides with the study of **Montuori** *et al.* (2016) who concluded that, the concentrations of PCBs are high due to the high concentrations of agricultural pesticides in the Volturno River in southern Italy. The compound PCB28 recorded the highest value (2.47ng/L) in the

autumn season, while PCB44 recorded the lowest concentration (0.08ng/L) during the same season.

In winter, the concentrations of PCB compounds decreased, and this may be due to the increase in the amount of rain and the increase in water level in the Tigris River due to released huge amounts of water from neighbored countries (Turkey and Iran), and thus the increase in the volume of water and the mitigation process of pollutants, including PCBs, as well as the speed of water flow that transports pollutants and reduces their concentrations. Furthermore, the decrease in water temperatures during winter caused these lipophilic compounds to be absorbed by the organic matter suspended in the water column; this conclusion concurs with that recorded in the study of **Swackhamer and Skoglund (1993)**. The process of adsorption by suspended particles in the water column into sediment is a major process in which PCBs are transformed from the water column into sediments, and this was confirmed in the study of **Verbrugge and Patrick (1995)** and **Al-Zabadet al. (2021)**, matching the findings of the current study. Adsorption processes and the conversion of PCB compounds from a dissolved to a precipitate increase with the increase in the contents of organic matter, mud and fine particles in the water (**USEPA**, **1980**).

The lower concentrations of PCBs observed during summer and spring could be attributed to the rising temperatures of these periods. Temperature impacts the presence of PCBs in water in two distinct ways. Firstly, the increase in temperature can enhance the enzymatic activity of microorganisms utilizing organic carbon including PCBs as a significant energy source (**Shamshoomet al., 1990**). Secondly, higher temperatures lead to increased evaporation, a process through which PCBs tend to dissipate more in flowing water and estuaries. This evaporation process might be a significant factor in reducing PCB levels in the water. Research indicates that PCBs can decrease by approximately 20-50% when enzymatic activity of microorganisms intensifies and during the evaporation process at temperatures ranging between 30 & 40°C (Leahy & Colwell, 1990).

CONCLUSION

Through this study, it was found that there are temporal and local changes in the concentrations of PCBs in the water of the Tigris River. It was noted that the lowest concentrations of PCBs was found in summer and spring seasons, while the highest concentrations was found in the winter season; this was attributed to the use of fertilizers during winter season.

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