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ANALYZING AND DISTRIBUTION OF POLYCHLORINATED BIPHENYLS (PCBs) IN SEDIMENTS ALONG SHATT AL-ARAB ESTUARY, IRAQ

The object of this research is the polychlorinated biphenyls (PCBs) in sediments along Shatt Al-Arab Estuary, Iraq. The study examines the problem of river PCB pollution. PCB effects on humans include cancer, impaired reproduction, neuro-developmental effects in infants, immunotoxicity and endocrine disruption. PCBs lead to liver damage and stimulate changes in the DNA sequence. The Shatt Al-Arab Estuary is formed in southern Iraq near Al-Qurna city after the confluence of the Tigris and Euphrates Rivers. The Shatt Al-Arab Estuary region is shared between Iraq and Iran. The Estuary receives pollutants when it is passing during Basrah City regions, due to industrial, agricultural and human activities which discharge the pollutants to the Estuary without treatment.

The concentrations of Σ13 PCBs compound in sediment samples were determined and analyzed at each site by using gas chromatography-mass spectrometry (GC-MS, Agilent). Six sites were chosen along Shatt Al-Arab Estuary. They are Al-Qurna (S1), Al-Deer (S2), Al-Qarma (S3), Al-Ashar (S4), Abi Al-Khasib (S5) and Al-Fao (S6), at Basrah city, south of Iraq. Sediment samples were collected seasonally, starting from Autumn season on September 2019 to summer season on July 2020. The Σ13 (PCB-18, PCB-29, PCB-31, PCB-28, PCB-44, PCB-52, PCB-101, PCB-141, PCB-149, PCB-138, PCB-153, PCB-189, and PCB-194) concentrations at the sediment samples ranged from 4.48 ng/g in Al-Deer site during summer season to 27.75 ng/g in Al-Ashar site during winter season for all selected sites. The Al-Deer site were found to have the lowest mean of PCBs its 0.345 ng/g and Al-Ashar site were found to have the highest mean of PCBs its 2.135 ng/g. PCBs concentrations in sediment samples during autumn, winter, spring and summer seasons ranged from 7.75 to 21.68 ng/g, 16.25 to 27.75 ng/g, 7.28 to 22.01 ng/g and 4.48 to 14.41 ng/g, respectively. The congener distribution patterns in these samples indicate the dominance highly chlorinated congeners (tri- and hexa-PCBs) in comparison with remaining others PCBs congeners. This project is the first of its kind in Basrah and all Iraq that reports PCB concentrations in the region and is considered a baseline study and can be used for subsequent studies.

Keywords: *sediments, Shatt Al-Arab Estuary, polychlorinated biphenyls, PCBs, seasonal variation, gas chromatography-mass spectrometry.*

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1. Introduction

The abbreviated term «PCBs» is the group of chlorinated organic compounds known as polychlorinated biphenyls (PCBs) that have the formula $C_{12}H_{10}$, sometimes written $(C_6H_5)_2$. The chemical formula is a molecule composed of 2 benzene rings bonded together (a single carbon-carbon bond) which may be replaced by up to 10 chlorine atoms related to biphenyl [1]. There are 209 congeners of PCBs, these congeners are numbered from 1 to 209 and differ in the number of chlorine atoms and their positions on the biphenyl (Fig. 1) [2].

PCBs are man-made organochlorines and are a class of hydrocarbons. PCBs are lipophilic congeners, accumulate in lipids with increasing chlorination, and have low solubility in water (hydrophobic) [3]. PCBs tend to bioaccumulate in organisms between all trophic levels [4]. PCBs cause high toxicity, biomagnifications and long-range transport. PCBs are ubiquitous in organisms, humans and all ecosystems [5]. PCB effects on humans include cancer, impaired reproduction, neuro-developmental effects in infants, immunotoxicity and endocrine disruption [6]. PCBs lead to liver damage [7] and stimulate changes in the DNA sequence [8].

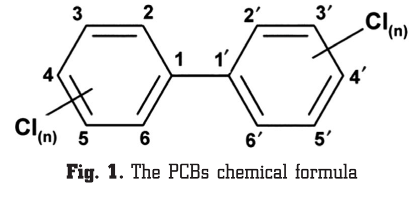

Fig. 1. The PCBs chemical formula

PCBs have been widely used as fully enclosed systems such as insulators in capacitors, transformers, and hydraulic fluids.

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Electrical capacitors contain up to 100 % and electrical transformers contain about 60–70 % of PCBs, these compounds are also used in open systems in small quantities such as carbon-free inks, copy paper, paint additives, adhesives, plastics and synthetic rubber. As well as its use in pesticides and lubricants [9]. The current sources of PCB emissions are volatilization from landfills containing damaged equipment and waste containing PCBs, accidents or fires which leads to release of large quantities of these compounds into the environment [10]. These compounds enter the environment through mishandling of damaged electrical equipment, leaks during refilling, and illegal disposal of waste containing PCBs into seas and oceans [11]. Most amounts of PCBs stick to molecules and sediments but small of the compounds remain in the water [12].

The Shatt Al-Arab Estuary is formed in southern Iraq near Al-Qurna city after the confluence of the Tigris and Euphrates Rivers. The Shatt Al-Arab Estuary region is shared between Iraq and Iran. The Estuary receives pollutants when it is passing during Basrah City regions, due to industrial, agricultural and human activities which discharge the pollutants to the Estuary without treatment, due to its flow and ecological nature the Estuary used as a sink for wastes [13].

The present study was aimed at determining the levels of PCBs for sediments in the Estuary in Basrah Governorate, southern of Iraq. This project is the first study that reports PCBs levels in Iraq. *The aim of research* was to estimate the levels and types of PCBs compounds at six sites from the cross of the Tigris and Euphrates Rivers in the Al-Qurna city to its estuary in the Arabian Gulf.

2. Materials and Methods

Sediment samples at six sites were collected seasonally in Shatt Al-Arab Estuary in Basrah city for the duration from autumn 2019 to summer season 2020 for estimation and analysis some of PCBs. The Global Positioning System (GPS) was used to fix the positions of these sites (Table 1). The sites are Al-Qurna (S1), Al-Deer (S2), Al-Qarma (S3), Al-Ashar (S4), Abi Al-Khasib (S5) and AlFao (S6), Fig. 2.

Standard methods were used to collect sediment samples according to the American Public Health Association (APHA), sediment samples were collected by Van Veen Grab sampler from the mid of the estuary and the water was allowed to flow out then kept in aluminum foil. All samples were transported in a cooling box to preserve the samples until transfer at the laboratory and performing laboratory analyzes. Sediment samples were dried at laboratory temperature for several days and grind by a grinding device then subsequently sieved by a sieve diameter of 63 microns [14].

PCBs were extracted from Sediment samples according to method of [15]. Soxhlet Intermittent Extraction was used to extract PCBs compounds. 20 grams of sediment dry weight (dw) were taken and put in a cellulose thimble. The Sediment samples mixture was subjected for 20 hours with 100 mL of Dichloromethan (DCM)/n-hexane (1:1 v/v) and saponification was performed for 2 hours. The separating funnel was used to separate the PCBs. The extract was purified on a column packed with Glass Wool, 2 grams of anhydrous Na_2SO_4, 2 grams of silica gel and copper powder (to remove sulfur) from bottom to top, then after the extract is put in a vial and saved until measurement by GC-MASS.

Table 1

Latitude and longitude of the locations in the study area

Location No.	Location name	Longitude andl
S1	Al-Qurna	N 31.00423° E047.44139°
S2	Al-Deer	N 30.80364° E047.58007°
S3	Al-Qarma	N 30.57691° E047.77744°
S4	Al-Ashar	N 30.51235° E047.84885°
S5	Abi Al-Khasib	N 30.46260° E048.00093°
S6	Al-Fao	N 29.98572° E048.46719°

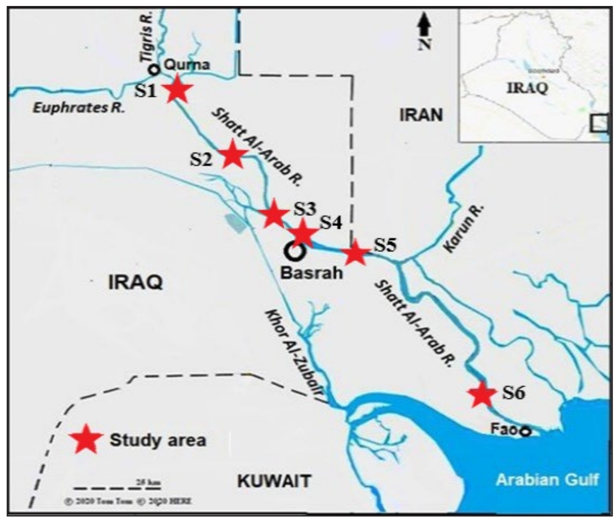

Fig. 2. The study sites

Statistical analysis: Analysis of Variance (One-way ANOVA) was applied by statistical software, Statistical Package for Social Science (SPSS) to identify the existence of spatial and temporal significant differences. The relationship between the parameters was calculated using Pearson's Correlation Coefficients.

3. Results and Discussion

The study showed that PCB compounds decreased during the summer while increased during the winter season. The levels of ∑13PCBs in sediment samples ranged from 4.48 ng/g in the Al-Deer site during summer to 27.75 ng/g in the Al-Ashar site during the winter season, the PCB levels in sediment are displayed in Tables 2–5.

The levels of PCBs in Al-Qurna site ranged between 5.32 to 16.25 ng/g, Al-Deer site levels ranged between 4.48 to 18.22 ng/g, Al-Qarma site ranged between 9.11 to 20.12 ng/g, Al-Ashar site, the values ranged between 14.41 to 27.75 ng/g, Abi Al-Khasib site ranged between 8.84 to 21.06 ng/g, and the values in Al-Faw site ranged between 7.11 to 23.53 ng/g (Fig. 3).

Table 2

Levels of PCBs (ng/g dw) in sediment during Autumn season

Compound Name	S1	S2	S3	S4	S5	S6
PCB-18	1.57	0.45	0.47	1.94	1.43	1.72
PCB-29	0.81	1.97	1.56	2.76	2.91	1.52
PCB-31	0.33	1.08	1.34	5.14	0.53	1.54
PCB-28	0.00	0.06	0.01	0.01	0.01	0.05
PCB-44	0.00	0.01	0.01	0.03	0.01	0.00
PCB-52	0.08	2.47	5.88	2.51	2.23	4.05
PCB-101	1.45	1.95	2.89	2.56	0.74	3.64
PCB-141	0.00	0.89	0.00	0.00	0.00	0.00
PCB-149	0.00	1.77	0.76	1.91	0.82	1.97
PCB-138	0.01	0.00	0.00	0.00	0.00	0.00
PCB-153	0.00	0.00	0.00	0.83	0.00	0.00
PCB-189	1.39	0.00	0.00	0.00	2.66	0.00
PCB-194	2.11	0.00	0.41	3.99	2.27	2.83
Total PCBs	7.75	10.65	13.33	21.68	13.61	17.32
Mean±SD	0.596±0.769	0.819±0.929	1.025±1.694	1.668±1.702	1.047±1.117	1.332±1.475

Table 3

Levels of PCBs (ng/g dw) in sediment during Winter season

Compound Name	S1	S2	S3	S4	S5	S6
PCB-18	1.88	1.38	1.67	0.76	0.64	0.62
PCB-29	0.00	2.71	2.53	2.97	2.75	2.55
PCB-31	4.43	2.76	3.18	0.91	1.53	1.87
PCB-28	0.00	0.01	0.00	0.00	4.49	0.12
PCB-44	0.01	0.01	0.02	0.03	0.06	0.03
PCB-52	3.98	2.64	2.98	7.19	4.04	6.87
PCB-101	2.63	2.09	2.72	0.83	1.13	2.79
PCB-141	0.72	0.00	2.07	9.83	0.83	0.14
PCB-149	0.87	0.91	1.25	0.52	1.59	2.93
PCB-138	0.78	0.73	1.73	0.00	0.00	0.00
PCB-153	0.00	0.00	0.00	0.00	1.45	0.00
PCB-189	0.00	2.11	0.00	2.86	0.00	2.93
PCB-194	0.95	2.87	1.97	1.85	2.55	2.68
Total PCBs	16.25	18.22	20.12	27.75	21.06	23.53
Mean±SD	1.250±1.538	1.402±1.180	1.548±1.196	2.135±3.053	1.620±1.466	1.810±1.982

Table 4

Levels of PCBs (ng/g dw) in sediment during Spring season

Compound Name	S1	S2	S3	S4	S5	S6
PCB-18	1.61	1.38	3.43	3.15	3.68	1.21
PCB-29	0.00	0.00	0.00	0.00	0.00	0.00
PCB-31	0.00	0.00	0.00	3.61	0.00	0.00
PCB-28	0.00	0.00	0.00	0.00	1.81	0.00
PCB-44	0.01	0.00	0.86	0.93	0.99	0.47
PCB-52	2.91	3.37	3.45	5.56	3.67	8.39
PCB-101	0.01	0.02	1.97	2.13	3.96	0.97
PCB-141	0.00	0.00	0.00	5.34	0.00	0.00
PCB-149	0.00	0.00	0.00	0.00	0.00	0.00
PCB-138	0.00	0.00	0.00	0.00	0.00	2.83
PCB-153	2.74	2.82	1.93	1.29	4.43	0.74
PCB-189	0.00	0.00	0.00	0.00	0.00	0.00
PCB-194	0.00	0.44	0.00	0.00	0.00	2.13
Total PCBs	7.28	8.03	11.64	22.01	18.54	16.74
Mean±SD	0.560±1.099	0.618±1.171	0.895±1.341	1.693±2.085	1.426±1.829	1.288±2.319

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Table 5

Levels of PCBs (ng/g dw) in sediment during Summer season

Compound Name	S1	S2	S3	S4	S5	S6
PCB-18	1.24	1.27	1.75	1.81	1.50	1.08
PCB-29	1.78	1.24	1.59	1.30	1.19	1.35
PCB-31	1.24	1.22	0.31	1.27	1.62	0.00
PCB-28	0.37	0.43	0.41	0.97	0.34	0.53
PCB-44	0.09	0.02	0.51	0.65	0.55	0.16
PCB-52	0.01	0.12	1.39	1.73	0.42	0.22
PCB-101	0.01	0.13	0.02	0.09	0.55	0.23
PCB-141	0.00	0.00	0.51	0.07	0.00	0.27
PCB-149	0.00	0.00	1.09	2.01	0.71	1.59
PCB-138	0.49	0.00	0.47	1.83	0.47	0.65
PCB-153	0.00	0.00	0.00	0.00	0.19	0.00
PCB-189	0.00	0.05	0.32	1.33	0.61	0.58
PCB-194	0.09	0.00	0.74	1.35	0.69	0.45
Total PCBs	5.32	4.48	9.11	14.41	8.84	7.11
Mean±SD	0.409±0.610	0.345±0.526	0.701±0.576	1.108±0.704	0.680±0.482	0.547±0.506

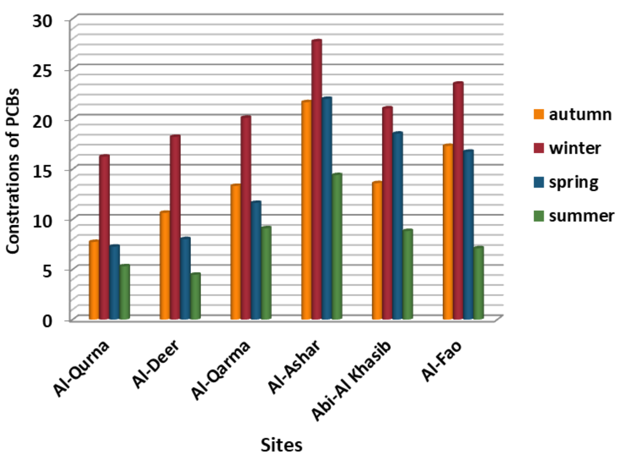

Fig. 3. Concentrations of PCBs at study sites

Significant differences $P \leq 0.05$ were found among seasons for PCBs compounds, The highest mean value 1.668 ng/g was recorded in Al-Ashar site, while the lowest mean value 0.596 ng/g was recorded in Al-Qurna site during the autumn season, The highest mean value 2.135 ng/g was recorded in Al-Ashar site, while the lowest mean value 1.250 ng/g was recorded in Al-Qurna site during the winter season, The highest mean value 1.693 ng/g was recorded in Al-Ashar site, while the lowest mean value 0.560 ng/g was recorded in Al-Qurna site during the spring season, The highest mean value 1.108 ng/g was recorded in Al-Ashar site, while the lowest mean value 0.345 ng/g was recorded in Al-Deer site during the summer season (Fig. 4).

The study of sediments has an important role in environmental pollution studies [16]. The sediments surface is important for studying the seasonal and regional changes of PCBs in the aquatic environment, most PCBs compounds in water tend to the adsorption rapidly on particles and suspended matter in the water column and then precipitate to the bottom due to their low water solubility (hydrophobic) [17]. Therefore, PCBs that reach the aquatic environment from urban and industrial pollutants areas, most of PCBs deposited in sediments and a small part remains in the water [18]. Most of PCBs are found in sediments due to their low solubility in the water. Persistent organic pollutants (POPs) such as PCBs are strongly bound to particles due to their hydrophobic properties and tend to accumulate in sediments [1, 19].

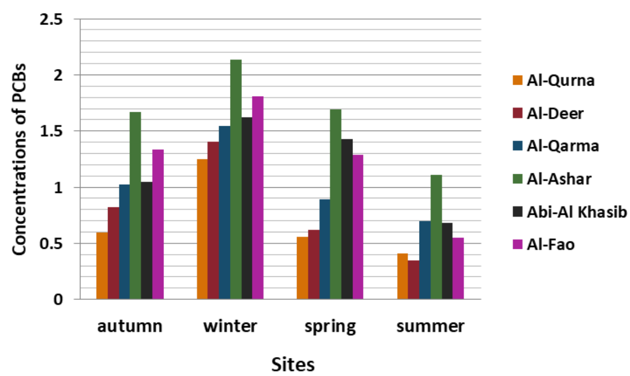

Fig. 4. Mean of PCBs Levels at study sites

The results of the study recorded that the highest concentration of PCBs in the sediments was 27.75 ng/g in Al-Ashar site during the winter season, then Al-Faw and Abi Al-Khasib sites respectively, while the lowest concentration was recorded 4.48 ng/g in Al-Deer site during the summer. The high concentrations of PCBs in Al-Ashar site during the winter may be attributed to the fact that the low temperature leads to a decrease in the evaporation and biodegradation processes by microorganisms [20]. The high death rates of algae, plants, phytoplankton, zooplankton, and their wastes containing these compounds increase the concentrations of PCBs in sediments, as well as the precipitation of PCBs from the air during rains, especially from industrial places, therefore, the PCBs accumulate in the sediments [21].

The high values of PCBs in Al-Ashar site may be due to its location near the city center and the main roads adjacent to the Shatt Al-Arab Estuary from the eastern and western sides, Al-Ashar site is affected by the Al-Khandaq, Al-Ashar and Al-Khora canals, these three channels drain the waste directly to the estuary without treatment, the water in these canals is contained many industrial pollutants, sewage pollutants and other types of waste [22]. The study of [5] referred that sediments near cities usually have high concentrations of PCBs, as urban industrial areas are more polluted than rural areas. PCBs Compounds that contain a high concentration of chlorine are more stable than compounds containing less chlorination [23]. As for the high levels of PCBs in Al-Faw and Abi Al-Khasib sites, due to the widespread oil transport ships, it's adding pollutants to the estuary through seepage and the washing processes. The study agreed with authors of [24] who mentioned the oil sources lead to an increase the PCBs levels, in addition to the Abadan refinery located on the eastern side and the Abu-Flous port on the western side in Abi Al-Khasib district which have a major role to adding many pollutants to the south of Shatt Al-Arab Estuary.

The levels of PCBs decreased during the summer season in Al-Deer and Al-Qurna sites, respectively, which may be due to the far from the center of Basrah city and the high temperatures that play an important role in the evaporation of these compounds, as well as, the biodegradation processes that often lead to the breakdown of PCBs by microorganisms are active in the sediment during the summer season. The process of removing chlorine from PCBs, especially highly chlorinated compounds, and converting them to less chlorinated compounds (mono to tri chlorine) is through microbial decomposition by microorganisms [25]. According to the United States Environmental Protection Agency guideline, the permissible limit of PCBs in sediments should be lower than 227 $\mu g \cdot kg^{-1}$.

Table 6 shows a comparison of the concentrations of the current study with previous international studies in sediment.

Table 6

Comparison of PCB concentrations of the current study with previous international studies

Reference	Concentration	Country of study	Study area
[26]	132.926 ng/g	Kuwait	Shuaiba port
[27]	15.6–0.58 ng/g	Saudi Arabia	Jeddah coast
[28]	30.9–1.6 µg/kg	Iran	Khor Musa
[29]	1461–2244 pg/g	Egypt	Nile River
[30]	0.8–14.6 ng/g	Tunisia	Bizerte lagoon
[31]	2.7–202.3 µg/kg	Nigeria	Forcados River
[32]	1.33–6.27 ng/g	China	Haizhou Bay
[33]	10–200 µg/kg	Italia	Arun River
[34]	1.1–4.7 mg/kg	USA	Passaic River
[35]	362–1848 pg/g	Uganda	Napoleon Bay
current study	4.48–27.75 ng/g	Iraq	Shatt Al-Arab Estuary

This project is the first study that reports PCBs levels in Iraq.

4. Conclusions

The study determined and analyzed the concentrations of ∑13 PCBs compound in sediment samples at each site by using gas chromatography-mass spectrometry (GC-MS, Agilent). Six sites were chosen along Shatt Al-Arab Estuary. They are Al-Qurna (S1), Al-Deer (S2), Al-Qarma (S3), Al-Ashar (S4), Abi Al-Khasib (S5) and Al-Fao (S6), at Basrah city, south of Iraq. Sediment samples were collected seasonally, starting from Autumn season on September 2019 to summer season on July 2020. The ∑13 (PCB-18, PCB-29, PCB-31, PCB-28, PCB-44, PCB-52, PCB-101, PCB-141, PCB-149, PCB-138, PCB-153, PCB-189, and PCB-194) concentrations at the sediment samples ranged from 4.48 ng/g in Al-Deer site during summer season to 27.75 ng/g in Al-Ashar site during winter season for all selected sites. The Al-Deer site were found to have the lowest mean of PCBs its 0.345 ng/g and Al-Ashar site were found to have the highest mean of PCBs its 2.135 ng/g. PCBs concentrations in sediment samples during autumn, winter, spring and summer seasons ranged from 7.75 to 21.68 ng/g, 16.25 to 27.75 ng/g, 7.28 to 22.01 ng/g and 4.48 to 14.41 ng/g, respectively. The congener distribution patterns in these samples indicate the dominance highly chlorinated congeners (tri- and hexa-PCBs) in comparison with remaining others PCBs congeners.

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Conflict of interest

The authors declare that they have no conflict of interest concerning this research, whether financial, personal, authorship or otherwise, that could affect the study and its results presented in this paper.

Financing

The study was performed without financial support.

Data availability

The paper has no associated data.

Use of artificial intelligence

The authors have used artificial intelligence technologies within acceptable limits to provide their own verified data, which is described in the research methodology section.

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