Distribution, Source finding, ecological hazard assessment and water-sediment exchange rate of polychlorinated biphenyl compounds (PCBs) in South Pars Industrial Zone, Iran

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Abstract

South Pars Industrial Zone is located near an Assaluyeh city on the coast of the Persian Gulf and is known as the energy capital of Iran. In this study, environmental and health effects due to PCB components had an assessment. In this study, 10 air stations, 10 seawater, and sediments stations were systematically selected and sampled in two seasons. Air, seawater and sediment pollution made by polychlorinated biphenyls (PCBs) were evaluated. Seawater-sediment exchange conditions using the fugacity coefficient reviewed. PCB levels in marine sediments, seawater, and air-based on the analysis of the obtained data were 107.33-172.92 ng / g, ND-135.68 µg / l, and ND-4.4 ng / m³, respectively. The highest concentration was observed in the vicinity of refineries, petrochemicals, and petroleum export facilities. These values had increased significantly compared to values of studies, conducted in similar areas. The sources were electrical wastes, storage sites, power generation units, and wastewater treatment. The ecological risk of seawater was assessed to be high, while sediment risks were reported with a low to moderate risk range. The heavier compounds with more chlorine were moved from sediments to seawater and, showed that seabed acted as a secondary source of sea pollution. Lighter compounds with less chlorine moved toward the sediments, from the seawater, and the seabed acted as a sink for these compounds. It is suggested for the area to be continuously monitored while engineering and management measures should be adopted to improve the situation and also prevent the spread of pollution.

Highlights

- Spatial distribution of PCBs in South Pars region.
- First PCBs ecologic risk assessment in South Pars Industrial Zone coastal sediment.
- The seabed acts like a sink for low-chlorine PCB compounds
- Sediments act as a secondary source for high-chlorine PCB compounds
- Significant increase in pollutants, especially carcinogenic compounds, was shown in the vicinity of industrial units.

Introduction

Polychlorinated biphenyls compounds (PCBs) because of their special properties have long been produced under various brands (e.g. Aroclor oil) in industrialized countries and were widely used in industries such as heat exchangers, pesticides, cosmetics, hydraulic lubricating oils, dyeing, plastics, paints, adhesives, carbonless copy paper, capacitors, transformer oils, circuit breakers and fluorescent lamps(Erickson et al. 2011).

Although initially thought by manufacturers to be harmless, the widespread adverse effects on human health and the environment have been reported including embryonic abnormalities, fetal stillbirth, accumulation in the leaves and roots of plants, microorganisms' body, fish, suffocation, and malnutrition, false satiety of turtles, birds, and animals.

These compounds were identified as the main cause of cancer due to their properties such as hydrophobicity, carcinogenicity, the tendency to fat, and stability in the environment as organic environmental pollutants with very high toxicity potential (Aghadadashi et al. 2019Löf et al. 2016). All compounds of PCBs have been announced to be carcinogenic by the US International Environmental Protection Agency (Farrington. 2020). Following the disclosure of high levels of pollution and their effects on human and environmental health, their production were proscribed since 1972 and excluded from global consumption by the international community in 1977(Maung et al. 2021).

However, there is still their potential or possible entry into the environment since they are available in huge amounts in warehouses and various devices. Currently, 83% of produced PCBs are still remaining and need to be removed according to the estimates of the United Nations Environment Program (UNEP)(EPA. Mahmoudi et al. 2020). Contamination with PCB compounds is not limited to a specific geographical location; air, water, soil and sediment pollution is observed by these compounds worldwide. Contamination with PCB compounds is not limited to a specific geographical location, air, water, soil and sediment pollution is observed by these compounds worldwide. (Sakizadeh. 2020) The following are some examples.

In 2009, a study on an area of 19 km in London reported the concentration of PCBs in urban soil to be 9-2600 µg/kg, which was higher than that in other similar cities In a study conducted on a coastal industrial area in Turkey in 2017, PCB concentration values of air, seawater, and coastal sediments were found 104-20083 pg/m³, 880pg/l, and 2.7–2450 ng/g dry weight (ng/g.dw), respectively. The predominant transfer of these pollutants was observed from seawater to air(60.6%) in the vicinity of industrial units(Odabasi et al. 2017)

Nozar et al. measured the PCB level in the coastal sediments of the northern Persian Gulf and announced that 10.3% and 2.9% of the obtained concentrations were higher than the effects of Range-Low (ERL) and the effects of Range-Median (ERM), respectively(Nozar et al. 2014) The level of PCB contamination in the fish of Lark Coral Island in the Persian Gulf was reported by Ranjbar et al. to be in the range of 2.95–7.95 ng / g body weight.(Ranjbar Jafarabadi et al. 2019) In 2009, the concentrations of PCBs in coastal water and sediments in the southwest of the Persian Gulf were reported 8-7375 ng/l and 50 – 3.4 µg/g, respectively (Zahed et al. 2009). (Zahed et al. 2009).

In studies on coastal sediments of Bahrain, the highest concentration (0.88 ng/g.dw) was observed in the vicinity of refineries (Bersuder et al. 2020). In a study on the contamination of plastic resin pellets (plastic waste) on the coasts of Iran-Qatar-UAE, during the years 2010–2018, the concentration of PCB was in the

range of 54–624 ng/g-pellet, and the highest contamination was observed near the coasts of Bushehr and Bandar Abbas. (Alidoust et al. 2021).

Pars gas field in the Persian Gulf is located 105 km from the nearest coast of Iran. The discovery and exploitation of this field has led to the establishment of oil, gas and petrochemical industries along with ancillary facilities in the region. Industrial development has also been accompanied by population growth and an increase in transportation services in the region.

The South Pars Industrial Zone is bounded on the south by the Persian Gulf and on the north by the mountains. Vast and pollutant industries, such as petrochemical complexes, gas refineries, power plants, storage tanks, and export wharves are located near the urban fabric (Samadi Kuchaksaraei et al. 2021).

Since the abovementioned industries and facilities can be the sources of production and release of PCBs to air, soil, and coasts, it is essential to investigate the destructive effects of sustainable organic compounds on health (Danesh et al. 2021). Arfaei Nia et al. were the first to measure PCB concentrations in coastal sediments of Assaluyeh. To the best knowledge of the authors, there has not been similar studies conducted on the ecological hazards and source finding of PCBs in the air and coasts of the South Pars Industrial Zone (SPIZ).

On the other hand, it is necessary to re-measure and update the data on air, sediments, and seawater considering the passage of 5 years from a previous study on sediments and since a remarkable number of refineries, petrochemicals, and related facilities have been running in the area.

Measurements of PCB concentrations in seawater and air, ecological risk assessment, source identification, and determination of exchange in liquid-air/liquid-sediment phases were the innovations of this study which were done in SPIZ for the first time, the results of which can be a reference for further studies.

The five main objectives of this research are: 1) measuring the levels and profiling of PCBs attached to dust particles in the air, seawater, and coastal sediments of the region, 2) determining the origin of PCBs, 3) ecological hazard assessment of PCBs, 4) providing local distribution maps of PCBs, and 5) an investigation of the pollution transfer process between air-seawater and seawater-sediments.

Materials And Methods

Study area

The study area of SPIZ (Fig. 1) along the Persian Gulf coast in the south of Iran comprises a combination of light and heavy industries including 10 gas refineries, seven petrochemical complexes, electricity power plants, storage tanks, and export facilities. With geographical coordinates of 27.53438 to 27.41403 N and 52.25648 to 52.67028 E and an approximate area of 521.5 km², this area is connected to the Nayband National Park in the east and to Kangan city in the west.

An area of 100 km² of Assaluyeh city is located in the above area. The study area has been built by a combination of industrial and urban uses (Mahmoudi et al. 2020).

Selection of the site and the sampling method

A systematic sampling model was selected due to the low concentrations of PCBs which aimed at investigating the effects of SPIZ on the regional ecosystem and also factors such as sources of pollution, depth, and distance of human and industrial activities (Batley et al. 2016). Ten stations were selected for sampling sediments and water in the coastal area, and 10 stations were chosen for air sampling in the minimum possible distance in the coastal zone (Odabasi et al. 2017). According to the climatic conditions of the region, samples were taken in winter and summer 2019.

In the westernmost point of the study area, Shirino coastal village was selected as a control station as it was very distant from the related industries and activities. It is noteworthy that the village is used by oil, gas, and petrochemical companies for housing the employees (Ahmad et al. 2019; Jalilisadrabad et al. 2020).

Preparation of air samples

Air was sampled randomly in each station from a height of 1.56 m above the ground by an SKC pump (model 9001-3011) with a flow of 20 L min⁻¹ for 24 h every week in a three-month period. The sample size was in the range of 28-30 m³. Particulate matter was collected using polyurethane filters and an average weight of 15 g. To avoid cross-contamination, separate forceps were used to remove each filter (Yang et al. 2021).

Preparation of water and sediment samples

To inactivate microorganisms in the water that could feed on volatile organic compounds and reduce their concentrations, hexane/dichloromethane solution in a ratio of 70 to 30 (10 ml in each sampling bottle depending on the volume of vessels) was injected into the solution in sampling bottles. Sediment samples were collected in sterile plant bags and aluminum foil. The temperature was stabilized using two cold boxes with a volume of 20 l. Before sampling, the ice gels of each cold box were frozen at -18 °C for 48 h. (Almeda et al. 2013).

Due to the measurement of PCBs, care was taken to use equipment and materials that did not contain chlorine compounds, and the glass was filled slowly due to the volatility of the compounds.

Sampling points were determined by the Global Positioning System (GPS) (Nozar et al. 2014). For sampling of sediments, Van Veen Grub type sampler with approximate dimensions of 55 × 30 × 22 cm (made of stainless steel) and mass of 5 kg was used. Water samples were taken from a depth of 5-10 cm of the sea by dark glass bottles. In each sampling, 10 l and 500 g of water and sediments were sampled, respectively (Hoseyn Khezri et al. 2018). The depth of the sea was between 3 and 20 m at the time of sampling (Odabasi et al. 2017).

The measured physicochemical parameters of water and sediments were salinity, temperature, pH, and turbidity, and the evaluated physical parameters of air were wind speed, humidity, and air temperature.

Laboratory tests

The selected laboratory vessels were of the Pyrex type. Before transferring the samples to the laboratory, the vessels were thoroughly washed with 75 °C water and dishwashing liquid. The dishes were then immersed in a dilute dishwashing liquid solution for 8 hours. The vessels were after that rinsed with 50 °C water at least 10 times and then placed in hexane-impregnated aluminum foil. Finally, the vessels were heated in an oven at 50 °C for 4 h (Sari et al. 2020).

Filters containing airborne particles were immediately transferred to the laboratory and incubated at a temperature of < 4 °C. After washing the filters containing particulate matter, the compounds were extracted using a Soxhlet system with a capacity of 1000 ml flask. Hexane was selected as the main solvent with a purity of 99.99% (Mercier et al. 2012).

The frozen precipitate was first crushed by a mortar and then sieved using a 250 µm pore sieve, then; 20 g of the samples were transferred by fingers without using a hand. For this purpose, aluminum foil was wrapped around the fingers and the sample was transferred using forceps and also one ml of the standard internal solution of PCB 198 and PCB 29 with a concentration of 20ng / ml were added to the finger. The extraction was performed for 8 hours by adding some boiling stone and 250 ml of hexane / dichloromethane solution (50:50 ratio). (Benson et al. 2020)

PCBs in seawater were extracted by the DLLME method. In the first step, 5 ml of the sample solution was poured into a test tube with a conical end, followed by a quick addition of 500 µl of acetone with 10 µl of Chloro benzene using a syringe with a capacity of 500 µl to create a cloudy state in the sample. This was done to create a wide contact surface between the solvent range and the aqueous medium.

In the next step, the sample was centrifuged at 5000 rpm for 2 min. Chloro benzene droplets were then taken from the bottom of the test tube (Rezaei et al. 2008) The organic matter (OM) content was determined by the weighing method, through heating at 600 °C for 4 h (Wang et al. 2011)

To prepare the standard peak, 1 ml of internal standard solution was used instead of the sample. The Soxhlet-extracted sample was concentrated to a volume of 15 ml by a rotary evaporator at 27 °C, dried over anhydrous sodium sulfate, and made to a volume of 1 ml with nitrogen (Benson et al. 2020).

Desulfurization using copper powder

The copper powder was used for the removal of free sulfur and existing mercaptans. To do this, 20 g of copper powder was combined with concentrated hydrochloric acid in an Erlenmeyer in such a way to completely cover the surface of the copper powder. The Erlenmeyer was then shaken and transferred to an ultrasonic bath. This procedure was repeated after 10 min. The acid was emptied on the copper

surfaces, and fresh acid was added again to the copper surfaces. The acid was replaced by repetition for 4 times.

After the fourth step, the acid was replaced with distilled water, and the copper was shaken again and transferred to an ultrasonic bath for 10 min. This procedure was repeated to neutralize the pH of the mixture. It was then washed with acetone and transferred to an ultrasonic bath, which was repeated 4 times.

The copper particles were then transferred to the hexane solvent. After adding copper to the samples, sulfur was removed from the sample by changing the copper color after 12 h (Pérez-Fernández et al. 2019Rezaee et al. 2006).

Injection of PCB samples into a GC device

By an automatic sampler, Samples were injected into a GC / MS Agilent-7890 B and a mass detector (5977 A MSD) with a DB-5MS chromatogram column to obtain the mass spectrum. The results were compared with a standard reference calibration. The temperature program (for PCB) first reached 150 ° C, followed by 210, 270, and 280 ° C with slopes of 12, 3, and 20 ° C in three stages. The carrier gas was also helium (Wang et al. 2011)

Quality control and guarantee

The reliability of the observed results and quality control were examined by the following procedures. The tests were performed using devices with a valid calibration certificate approved by accredited authorities according to the standards of the Department of Environment of Iran. All sampling and testing instruments were washed with water, purified water, ACE, and PE.

An alternative standard solution with specific concentrations was prepared for PCBs and added to each sample and the blank sample to calculate the recovery efficiency before the extraction step. Each sample was repeated twice. The recovery efficiency for PCBs was 75.4%-115.2%, and the obtained data were acceptable without the need for correction.

The accuracy of the analysis using the applied materials was ensured by preparing a blank sample whose composition was read below the limit of detection (LOD). Standard PCB solutions were used to construct GC/MS calibration curves with five calibration points at concentrations of 10, 50, 100, 250, and 500 ng/ml. Linear responses ($r^2 > 0.999$) were reported afterward. The LOD and limit of quantitation (LOQ) were measured by three times a signal-to-noise ratio (Sari et al. 2020) and consider 0.33,1

Statistical analysis

Data were analyzed by IBM SPSS ver.22 and 2010 Microsoft Excel software. The calculated indices were standard deviation, mean, and median. The normality of data was verified using statistical tests such as Shapiro-Wilk. Non-parametric synonymous tests were used when data were highly dispersed (non-

normal). The effect of seasons on data distribution was assessed using the one-way analysis of variance (ANOVA) at a significance level of 0.05.

Preparation of zonation maps

Spatial distribution maps of pollutant concentrations were prepared by ArcGIS 10.2 software using exploratory geostatistics interpolation analysis of Kriging method.

Ecological risk

Two conventional methods were used to assess the ecological risk:

1. Calculation of ERI ecological risk index for seawater

The ecological risk assessment index in this formula is equal to the sum of the ecological risks (E) of all PCB in a sample (Eq. 1).

$$ERI = \sum E_r^i$$

$$E_r^i = T_r^i C_f^i$$

$$C_f^i = C_0^i / C_n^i$$

In this formula, the number T is the toxicity factor, which equals 40 by default for PCBs. The C_f number is the contamination factor obtained by dividing the concentration of a particular PCB by the reference dose or C_n equal to 0.01 mg/L or 10 ng/g.dw For PCB numbers, ER numbers of < 40, 40–70, and > 70 mean low, moderate, and high risks, respectively (Iwegbue et al. 2020).

Sediment quality guidelines (SQGs)

SQGs were widely used to assess sediment risk in marine environments with the development of biological effects database for sediments (BEDS). ERL and ERM indicate that the probability of biological effects is < 10% and > 50%, respectively. Concentrations below ERL, between ERL and ERM, and above ERM indicate seldom, occasional, and frequent occurrence of adverse biological effects, respectively (Cao et al. 2020 Li et al. 2017)

Water and sediment exchange

The exchange state of PAHs and PCBs in water and sediments is calculated and analyzed using the

fugacity fraction (ff): $ff = \frac{K'_{oc}}{K'_{oc} + K_{oc}}$, where (K_{oc}) and (K'_{oc}) are the Organic carbon normalized

partitioning coefficients and in situ sediment-water partitioning coefficient, respectively. K'_{oc} is obtained based on this equation:

$$K'_{oc} = c_s / (c_w \times f_{oc})$$

Concentrations of sediment (C_s) and water (C_w) are obtained as ng/L, and f_{oc} is the fraction of organic carbon, the relationship of which with the fraction of organic matter (f_{om}) is $f_{oc} = f_{om} / 1.8$

The K_{oc} ratio is an experimental value based on laboratory simulations, it was tried to use the numbers obtained in similar studies, including PCBs. If the ratio is not available, it can be predicted based on the n-octanol-water partition coefficient (K_{ow}) (Zhao et al. 2021)

Based on the experimental results, is obtained by the following linear-logarithmic relationship:

$$\log K_{oc} = a \cdot \log K_{ow} + b$$

In this study, the values of $a = 1.04$ and $b = -0.61$ were used based on a similar study on PCBs (Zhang et al. 2013).

In the chemical partition of water and organic matter phases, K_{ow} is a key parameter that can be extracted from sources such as the Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals/Mackay and the US EPA EPI Suite™ which contains the properties of more than 40,000 chemicals.

The result of the abovementioned fraction is analyzed as:

$ff < 0.3$ Means the movement of pollutants from water to sediments creating a so-called sink state.

$0.3 < ff < 0.7$ means that the pollutant is in an equilibrium state between the water and the sediment, and $0.7 < ff$ means that the pollutant moves toward seawater from sediments, with sediments playing a role as the second source of pollution spread in water.

Source identification

To analyze the source, the characteristics and share of environmental PCB sources were calculated using the Unmix EPA model.

In principle, the Unmix EPA model can be characterized by the following equation:

$X_{ij} \equiv \sum_k f_{ik} G_{kj}$, where x_{ij} is the type of i concentration in sample j , f_{ik} is the species concentration in source k , and G_{kj} is the share of source k in sample j . The main logic of the aforementioned model is to create a chemical balance between the outputs of the sources received in the sample. The signal/noise index is one of the source acceptance criteria in the software and presents important items (e.g. stability error) in the final report. Information about this model is detailed in the Unmix6 EPA Principles and User Guide (EPA. 2007)

Results And Discussion

Air

In the cold season, the total concentrations of PCB were in the ranges of 3-3.63 and 2.82–4.42 ng/m³ in urban and industrial areas, respectively. These numbers decrease significantly in the warm season. The highest concentration of PCB153 (3.24 ng/m³) was measured in the air adjacent to the industrial area. These values are higher than those reported in Dalian, China, and lower than those of the Aliaga Industrial Zone, Turkey.

Among homologs, the highest concentration (3.24 ng/m³) was recorded for Hexa-PCB in the vicinity of petrochemical complexes, and the highest percentages of low-chlorine PCB (49.45% and 40%) were measured in stations 7 and 8 (residential areas), respectively.

The highest percentages of perchlorate compounds (84.77% and 87.07%) were estimated in the stations adjacent to petrochemical complexes and urban areas, respectively. The compounds were distributed uniformly based on the number of chlorides in the study area, and no significant difference was observed between values recorded close to industrial units and urban areas. The results are summarized in Table 1 and Fig. 2

Table 1
Statistical report of the concentration of PCB congeners in the study area in $ng_{PCB} / M3$

Component	Industrial station				Residential stations			
	Range	Mean	Median	SD	Range	Mean	Median	SD
PCB 28	0.18–1.11	0.54	0.32	0.36	0.23–0.58	17.89	13.99	10.96
PCB 52	0.17–0.88	0.49	0.30	0.31	0.22–1.54	33.29	31.35	21.55
PCB 101	0.21–0.78	0.53	0.72	0.26	0.48–1.45	32.55	24.96	21.62
PCB 138	ND-1.27	0.60	0.51	0.42	ND-0.39	15.51	14.37	6.89
PCB 153	0.25-3.24	1.17	0.78	1.06	0.23–0.52	9.48	7.72	9.42
PCB 194	ND-0.36	0.19	0.22	0.12	ND-0.88	15.20	12.31	13.99
PCB 195	ND-0.35	0.22	0.25	0.12	ND-1.33	21.15	12.25	25.52
$\sum PCBs$	2.82–4.42	3.72	3.81	0.54	3-3.63	156.75	161.66	27.69

Seawater

The test results of water samples were reported in ppb or µg/L. In table no.2 is shown the results obtained based on the type of compounds in terms of the range of variations (minimum/maximum, average,

median, and standard deviation). The highest concentration of PCBs was observed in station 2 located near the outlet of export tanks of chemical products. Among PCBs, the highest pollutant concentrations belonged to PCB 101 (40.18 ppb) in winter and PCB194 (194 ppb) in summer. Figure 3 shows the spatial distribution of PCB compounds in seawater.

Table 2
Distribution of PCBs in seawater in cold and hot seasons according to the type of compound

Component	Winter				Summer			
	Range	Mean	Median	SD	Range	Mean	Median	SD
PCB18	N.D	-	-	-	ND- 1.73	0.20	0.03	0.51
PCB 31	ND- 3.70	0.7	0.00	1.4	ND- 1.21	0.29	0.12	0.35
PCB 44	ND- 30.38	8.65	3.98	10.88	ND- 1.04	0.18	0.04	0.31
PCB 52	ND- 35.77	13.06	7.10	11.41	ND- 0.54	0.11	0.00	0.21
PCB 101	ND- 40.18	11.29	3.19	14.48	ND- 1.45	0.22	0.08	0.41
PCB 141	ND- 1.60	0.16	0.00	0.48	ND	-	-	-
PCB 149	ND- 3.27	1.22	0.82	1.30	ND	-	-	-
PCB 138	ND- 16.33	3.27	0.00	6.53	ND- 0.81	0.14	0.05	0.24
PCB 153	ND- 3.81	0.87	0.14	1.43	ND- 4.91	0.95	0.25	1.53
PCB 189	ND- 3.20	0.63	0.00	1.26	ND	-	-	-
PCB194	ND	-	-	-	ND- 12.25	2.30	0.29	4.09
PCBs	ND- 135.68	39.85	16.62	48.21	ND- 22.29	4.38	0.94	7.33

Sediments

The test results of sediment samples were reported in ppb or ng/g dry weight. Tables 3 summarizes the results obtained based on the type of compounds in terms of the range of variations (minimum/maximum, average, median, and standard deviation). PCB18 (43.6 ppb) in winter and PCB44 (566 ppb) in summer reached the highest concentrations of PCBs. Among the stations, the highest concentration of PCBs was estimated in station 6 located near the outlets of refineries to the sea. Examination of the results based on homologs of PCBs indicates the predominance of compounds with less chlorine content. The average decreased but the cumulative level of pollution increased compared to the results of a previous study. It seems that the pollution is distributed locally along with the formation of foci of contamination (Arfaeina et al. 2017) Fig. 4 shows the spatial distribution of PCB compounds in the area sediments.

Table 3
Distribution of concentration of PCB compounds in coastal sediment cold and hot seasons according to station number

Component	Winter				Summer			
	Range	Mean	Median	SD	Range	Mean	Median	SD
PCB 18	ND- 43.57	13.48	6.91	15.06	ND-2.00	0.30	0.00	0.64
PCB 31	ND	-	-	-	ND	-	-	-
PCB 28	ND-1.97	0.38	0.00	0.76	ND	-	-	-
PCB 44	ND-10.85	4.47	4.52	4.17	ND-566.00	56.60	0.00	169.80
PCB 52	ND	-	-	-	ND-3.00	0.80	0.00	1.25
PCB 105	ND-3.45	2.00	1.90	0.91	ND-14.00	1.60	0.00	4.18
PCB 141	ND	-	-	-	ND	-	-	-
PCB 149	ND	-	-	-	ND	-	-	-
PCB 138	ND-5.09	1.47	1.86	1.51	ND	-	-	-
PCB 151	ND-5.26	1.76	1.80	1.76	ND	-	-	-
PCB 180	ND-5.09	1.41	0.91	1.68	ND-11.00	1.10	0.00	3.30
PCB 194	ND	-	-	-	ND	-	-	-
PCBs	5.68–54.42	24.98	20.63	15.41	ND-579.00	60.40	1.50	172.94

Control station

The results of the control station (Table 4) show much lower values than those of the other stations but they are more than the studies on similar areas in the Persian Gulf (Bahrain). Concentrations in air and sediments increase significantly with the change of seasons.

Table 4
Control station results

Ecological risk	Concentration range		Media
	Summer	Winter	
	ND	ND-1.45 ng/M3	Air
Low	ND-7.56	ND- 6.45 µg/L	Seawater
Low	ND- 2.00	ND- 5.26 ng/g.dw	Coastal sediment

Source identification (sediments)

Based on the sedimentation rate of the study area in the Persian Gulf, the collected sediment sample can represent several years of introduced pollutants (Veerasingam et al. 2021); hence, the source of sea pollution was determined based on the results of sediments.

The results were modeled using Unmix EPA software. According to the analysis of the first source, high-chlorine compounds (PCB105, PCB131, PCB151, and PCB180) were predominant at 68.1%. These compounds contain a high percentage of commercial compounds, PCB1254 and PCB1260, which are used in various applications such as power converters, gas distribution turbines, hydraulic fluids, adhesives, tires, heat transfer systems, wax diluents, and carbonless papers (Information, 2021).

This source can be attributed to industrial units such as power plants and industrial wastewater treatment units, and petrochemical complexes and refineries. In source 2, the majority of pollutants (93.4%) belonged to low-chlorine compounds (PCB18, PCB28, and PCB44), which make up a high percentage of arcolor1016 and are mostly used in capacitors and electrical insulators.

The highest concentrations of low-chlorine PCB compounds were detected in station 3 located near the outlet of petrochemical complexes. These results deserve consideration given the extensive construction of the abovementioned complexes (Dumanoglu et al. 2017). Source 2 can be considered a place for the disposal of electrical waste. The results are summarized in Table 5 and Fig. 5.

Table 5. Sources compositions

Species	Source 1	Source 2
PCB 18	1.690	11.900
PCB 28	-0.024	0.530
PCB 44	1.030	3.080
PCB 105	1.200	0.595
PCB 138	1.530	-0.010
PCB 151	1.500	0.496
PCB 180	1.590	-0.027
PCBs	8.440	16.500

Seawater ecological risk

The ecological risk of each station was determined using the concentrations of PCBs in water samples by relationships1, 2, and 3. The calculated risk of the area ranged from 23 to 218. High, moderate, and low risks were found in six, three, and one stations, respectively, with an average risk of 100. The highest level of risk was observed adjacent to the outlets of industrial companies to the sea, which is higher than that measured around the Larak Island in the Persian Gulf.

SQGs

According to the indicators defined in the instructions, the ecological risk level of sediments was in the medium range in station 6, and the rest of the sampled stations were evaluated in the low range. The seabed results currently show less pollution than those of seawater. The ecological risk is slightly lower in the northern Persian Gulf and is fairly higher than that of the shores of Bahrain on the shores of the Persian Gulf (Table 6).

Table 6
The component ERL and ERM for PCBs

Component	ERL	ERM	Current study	
			Min.	Max.
Total PCBs	0.023	0.18	0	0.0597
ERL - Effect Range Low; ERM - Effect Range Median Long (Burton. 2002)				

The exchange flow of the seawater/sediment interface

The fugacity index was calculated and reported at each station using the results of the concentrations of PCBs in sediments and seawater as well as related formulas. Based on these results, low-chlorine compounds (e.g. PCB52 and PCB44) mostly precipitated from seawater to sediments, and the seabed played the role of a sink for these compounds. Medium-chlorine compounds (e.g. PCB 105) were in equilibrium in some stations. Heavier compounds (e.g. PCB180 and PCB194) often entered seawater from sediments, and sediments are actually the secondary source of seawater pollution with compounds having more chlorine content.

Similar studies

A better understanding of pollution in the study area is obtained by examining the records of studies on PCBs in coastal industrial areas worldwide, particularly those with similar climatic-industrial conditions. As shown in Table 7, the maximum concentration increased relative to the previous study in the area (sediments), but a decrease in the average indicates the formation of local pollution masses.

The concentration increased compared to those of the northern Persian Gulf, the coast of the Persian Gulf near Bahrain, and mangrove forests near the Assaluyeh region. This pollution can endanger the ecosystem of mangrove forests. The obtained concentration is lower than that of a similar coastal industrial zone in Turkey. The prevailing transfer process from the seawater phase to air in the vicinity of the outlets of industrial complexes is similar to the mentioned industrial zone.

Table 7
Similar studies

Reference	Ecological risk	Concentration range	Environment	Study area
(Arfaeinia et al. 2017)		Max:74062pg/g Industrial Ave. 514.32 urban Ave. 144.67pg/g.dw	sediment	Assaluyeh Iran
(Nozar et al. 2014)	%10.3 > ERL %2.9 > ERM	sediment: 2.5–462(ng/g.dw)	sediment	North Persian Gulf
(Ranjbar Jafarabadi et al. 2019)	Toxicity indicators within the permissible level (WHO)	Seawater:0.97-3.1ng/L Sediment:2.95-7.95ng/g.dw	sediment & seawater	Around Lark Island - Iran
(Odabasi et al. 2017)	—	sediment:2.7–2450(ng/g.dw) seawater:880-50829(pg/L) air:104-20083pg/M3	Air& sediment and seawater	Aliaga industrial region, Turkey
(Behrooz et al. 2009)	-	Seawater:8-375ng/L Sediment:3.4– 50.2 µg /g.dw	Seawater& sediment	Southwest Persian Gulf-Iran 2009
(Bersuder et al. 2020)	According to the SQGs index was low	The highest concentration (0.881 ng / g.dw) was observed in the vicinity of refinery output	sediments	Bahrain-Persian Gulf coast
(Alidoust et al. 2021)	–	54-624ng/g Pellet The highest concentration was observed in the vicinity of Bushehr and Bandar Abbas industrial cities	Plastic resin pellets (plastic waste)	Persian Gulf Coasts (Iran, Qatar and United Arab Emirates) 2010–2018
(Montuori et al. 2020)		Water:4.1-48ng/L Sediment:4.3-64.3ng/g.dw	water sediment	Volturno River in southern Italy 2017–2018
(Zhong et al. 2020)	Low	106.7 to 270.0 pg./g.dw	sediment	Liaohe Estuary china

Conclusion And Recommendations

Based on the obtained data, the range of PCB concentrations in the marine sediments, water and air particulate matter, were 107.33-172.92 ng/g.dw, ND-135.68 µg/L, and ND-4.4 ng/m³, respectively. Most of these concentrations were measured near the refineries, petrochemical industries, and oil export facilities,

indicating the impacts of these industries on the pollution. This level of pollution increased significantly in winter.

The concentrations increased compared to studies from the northern Persian Gulf, Bahrain coasts, and mangrove forests near the study area. The sources of these compounds were electrical waste, their storage sites, power generation units, and wastewater treatment units. Different conditions were found in the study of seawater and sediment exchange so that heavier compounds with more chlorine moved from sediments to the seawater and the seabed played the role of a secondary source of sea pollution.

Lighter compounds with less chlorine moved to sediments from the seawater, and the seabed acted as a sink for these compounds. Given the mentioned exchange conditions, seawater seems to be the main source of pollution in the study area, and a part of the pollutant enters the air and the other part precipitates in the seabed; these conditions are intensified by such phenomena as sunlight, windstorms, and precipitation.

The ecological risk of seawater was assessed in high and polluted conditions, while better conditions currently exist in sediments with a low-medium range of risk. The observed role of seabed in precipitating part of the pollution suggests the very high probability of increasing the concentration of PCBs and the related ecological risk level in sediments.

It is suggested to continuously monitor and adopt engineering and management measures to improve and prevent the spread of pollution and perform complementary measurements on water and sediments of mangrove forests and native aquatic fish used by local people. Since the pollutant concentrations are used in the gas phase, it is recommended to use passive sampling methods in air sampling to investigate the exchange conditions.

Declarations

Author contribution

Fazel Amiri and Tayebbeh Tabatabaie: conceptualization, methodology, writing-reviewing and editing. Alireza Ghadrshenas: sample preparation and chemical analysis. Abdul Rahim Pazira: writing-reviewing, and editing.

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Conflicts of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Some or all data, models that support the findings of this study are available from the corresponding author upon reasonable request.

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Figures

Figure 1

Study area (South Pars Industrial Zone)

Figure 2

Distribution of PCBs in the air of the cold season study area

Figure 3

Spatial distribution of seawater PCBs in the study area

Figure 4

Spatial distribution of PCBs in the study area sediment

Figure 5

Figure 6

Chart of fugacity index of the common surface of water and sediments of PCB compounds in the coastal stations of the study area