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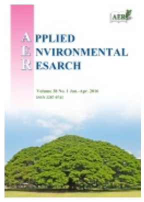

Assessment of Organophosphorus Pesticide Residues in Water and Sediment Collected from the Southern Caspian Sea

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Abstract

Pollution of water resources by uncontrolled pesticide use is a serious health and environmental issue. In this study, concentrations of three organophosphorus pesticides (diazinon, malathion, and azinphos-methyl) in water and sediment samples from five estuaries (Sefidrud, Chalus, Babolrud, Tajan, and Gorganrud) along the Caspian Sea were investigated. Samples were collected from surface water and sediment during summer to autumn, and pesticides were analysed by gas chromatography-mass spectrometry (GC-MS). Results indicated that salinity and turbidity in Gorganrud were higher (salinity: range 2–8%; turbidity: range 1–9%) compared to other stations. Higher diazinon (water: 0.08±0.06, sediment: 0.04±0.01), malathion (water: 0.09±0.06, sediment: 0.05±0.01) and azinphos-methyl (water: 0.1±0.08, sediment: 0.06± 0.02) concentrations were observed in the Tajan river compared to other stations. Mean concentrations of diazinon, malathion and azinphos-methyl pesticides were higher in the summer compared to the autumn. Azinphos-methyl concentrations were higher than sediment quality guidelines (SQGs), which warrants ongoing monitoring. Our research provides insights into the presence of organophosphate pesticides (OPs) in rivers that enter into the Caspian Sea. Further work to better understand the environmental pollution of OPs in the Caspian Sea is ongoing.

Keywords: Organophosphate pesticides (OPs); Diazinon; Malathion; Azinphos-methyl; Agriculture; Caspian Sea

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Introduction

Agriculture in the northern part of Iran is the largest sector contributing to the national economy, but requires application of huge quantities of pesticides to protect crops [1–2]. Rice is one of the most important crops grown in the northern part of Iran. Rice cultivation often occurs in areas close to important river basin which discharge into the Caspian Sea [3]. Pesticide use in agriculture in this region is estimated to be as high as 30×103 tons per year [4]. Flooding of rice and associated pesticides during the growing season contaminates surrounding river ecosystems by flushing pesticides into rivers [4–5].

Organophosphate pesticides (OPs) are agrochemicals that have been used extensively for decades [6–8]. Diazinon, malathion, and azinphos-methyl OPs are widely used in agricultural and non-agricultural activities and contaminate surface water resources via runoff into streams and lakes or via the lateral movement of chemicals via soil media to surface water bodies [3, 5, 9–11]. Diazinon, malathion, and azinphos-methyl are persistent contaminants, and are highly mobile in the environment [10]. Therefore, OP use on agricultural and urban areas has resulted in widespread pollution of aquatic ecosystems. As a result, pesticide concentrations in aquatic ecosystems have increased considerably due to inputs of industrial waste, sewage runoff and agriculture discharges [2, 12–13]. Diazinon, malathion and azinphos methyl are among the most widely used OPs applied during agricultural activities in northern Iran [3].

Several studies have reported that OPs accumulate in water, sediment and biota [3–4, 11]. Surface water contamination may have ecotoxicological effects for aquatic flora and fauna, as well as for human health if consumed [11, 14]. Sediments are ecologically important components of aquatic habitats, which play an important role in maintaining the trophic status of any water body. Highly polluted sediments can adversely affect ecological functioning of rivers due to persistence in the environment and long range transport [15–16]. Therefore, water and sediment are important sinks for pesticides introduced to aquatic organisms. Pesticides can be remobilized by microorganisms, consumed and retained by aquatic biota and consequently biomagnified through aquatic food webs to higher trophic levels [17–18]. In the tissues of animal-specific tissues, pesticides including diazinon, malathion, and azinphos-methyl are inhibitors of acetylcholinesterase enzyme and are also responsible for poisoning humans [19–21]. Acetylcholinesterase enzyme is a key enzyme in the nervous system and mainly found in the central nervous system, red blood cell membranes, and plasma [9, 23–24]. Therefore, inhibiting this enzyme causes changes in reproduction, environmental stress, leading to paralysis, convulsions and ultimately death of aquatic biota [24].

The Caspian Sea, the largest enclosed basin on the planet, is a unique system straddling several climate zones from continental to the Mediterranean due to its north-south orientation [25]. This coastline is now becoming increasingly polluted with massive loads of contaminants discharged into the Caspian Sea from various anthropogenic sources. Estuaries and coastal areas near human settlements or agricultural fields are the most heavily polluted [3, 26]. There are many cities with high agricultural activities around the Caspian Sea where many pesticides such as diazinon, malathion and azinphos-methyl are used to protect crops from pests. Pesticide pollution poses a serious threat for aquatic organisms and their consumers. Aquatic organisms, including fish, are among the most important food sources of humans, especially in coastal areas. Therefore, contamination of fish destined for human consumption poses potential human health impacts [27, 29]. Changes in nutritional parameters including skin gelatin, muscle protein content, amino acids and fatty acid compositions were reported in fish exposed to OPs [30–31].

Previous studies have reported the presence of persistent organic pollutants including pesticides in the Caspian Sea [2–3, 5, 16, 32–35]. Recently, diazinon concentrations was measured in the three rivers flowing into the Caspian Sea. Results showed mean diazinon concentrations (±SD) ranged from 41±76, 57±116, 76.5±145 ng L^{-1} in the Talar, Haraz, and Babolrud rivers, respectively [36]. In another study, mean diazinon concentrations in surface water ranged from 77.6 to 101.6 μg L^{-1} and mean malathion concentrations of ranged from 55.7 to 75.9 μg L^{-1} in the Babolrud river [37].

Despite extensive use of diazinon (which accounts for up to 60% of the total pesticide use in Iran), malathion and azinphos-methyl in these agricultural areas [26–27], limited studies exist about the distribution and concentration of these pesticides in the area. Therefore, monitoring of pesticide concentrations, and risk assessment of riverine ecosystems, is critical. This study measured diazinon, malathion and azinphos-methyl concentrations in surface sediment and water from five stations along the southern part of the Caspian Sea. The relationship between pesticide concentrations in sediment and water was studied. This was the first study to investigate diazinon, malathion and azinphos-methyl concentrations in the Sefidrud, Chalus, Tajan, and Gorganrud in Iran.

Materials and methods

1) Study area and sample collection

Sediment and water samples were obtained, Babolrud, Tajan, and Gorganrud (Figure 1). The green line near stations in this study show the basin of agricultural activity (particularly rice paddies) in this area (Figure 1). Sampling was conducted seasonally from summer (July, August, September) to autumn (October, November, December) 2019. Triplicate samples were collected from the water surface and sediment. A total of 60 sediment samples (3 replicates × 2 seasons × 5 stations) and water (3 replicates × 2 seasons × 5 stations) were collected. Random sampling was used to collect samples at each station. To prevent hydrolysis of pesticides in aqueous samples during transport to a laboratory, 50 mL methylene chloride solution was added to each sample. Sample containers were sealed by para-film, tagged and transferred to the laboratory for extraction. Environmental parameters such as temperature, pH, salinity and turbidity were analyzed by Standard Methods [38]. Thermometer and pH meters were used to determine temperature and pH. Also, turbidity and salinity were examined with nephelometry method and electrical conductivity, respectively.

Figure 1 Five sampling stations (bold points) in the Caspian Sea.

2) Pesticide laboratory procedures analysis

For extraction of diazinon, malathion and azinphos-methyl, dispersive liquid–liquid micro-extraction (DLLME) technique was used [39]. A 5 mL sample (water+analyte) mixed with 500 mL extraction solution (2 mL internal standard: chlorpyrifos 1,000 mg L^{-1}, 10 mL chloroform and 100 mL of acetone). The mixture was centrifuged for 5 min at 3,500 rpm. Afterwards, the upper of aqueous phase was collected by pipette and droplets were settled at the bottom of a conical tube and 1 μL injected into gas chromatography mass spectrometry (GC-MS) [40].

For extraction of diazinon, malathion and azinphos-methyl in sediment, a Soxhlet extractor was used. A 10 g sample was placed into a beaker containing 50 g anhydrous sodium sulfate (Merk, Germany) and mixed thoroughly. The sample mixture was transferred to an extraction thimble and placed in a Soxhlet extractor. The mixture was extracted with 150 mL of acetone: n-hexane (20:80 v/v) at 50°C for 4 h. Extracts were filtered, concentrated to 1 mL using a vacuum rotary evaporator. Raw extracts were then dissolved in 10 mL hexane (Merk, Germany) and passed through pre-conditioned octadecyl C-18 columns at a rate of 2 mL for cleaning. The column was washed with 1 mL, 30% methanol followed by 1 mL ultrapure water and allowed to dry. The sample was eluted with 0.5 mL aliquots of hexane 5 times to recover pesticide residues. Hexane in the sample was then allowed to evaporate off leaving the residue behind in the vial. The dried sample was dissolved in a 1 mL portion of hexane, mixed thoroughly with a whirl mixer and then transferred to auto sampler vials [40–41]. The GC-MS (6890N, AGILENT), with injection temperature of 250°C and phosphorous pesticide-specific detector (TSD) at 280°C and a sensitivity of 4×10^{-10} and the column temperature of 230°C, was calibrated and prepared for receiving samples. Since the basis of GC at the first stage was peaks identification and then amount determined, standards for pesticides were prepared and their retention time identified. Samples were then subsequently injected into the GC [43].

3) Quality assurance and quality control (QA/QC)

To check for solvent contamination, laboratory tubes, or equipment, procedural blanks were conducted. Background contamination was checked by blank samples. Method detection limits (MDLs) of pesticides were determined using a signal-to-noise ratio (S/N) of 3. No significant peaks of pesticides were found in solvent banks, and no significant peaks were found in procedural blank samples. Surrogate standards used to measure extraction efficiency for pesticides had recoveries of 97±4% and 95±6% for sediment and water, respectively. Pesticides in sediments had MDLs ranging from 0.01 to 0.05 ng g^{-1} dw and 0.01 to 0.03 ng L^{-1} for sediment and water, respectively. US EPA sediment quality guide-lines (SQGs) were applied to assess potential ecological risk of OPs in river sediments [44].

4) Statistical analysis

Before analyses, normality, and homogeneity of datasets were confirmed by Shapiro-Wilks and Levene's tests, respectively. Significant differences between pesticide concentrations at different stations were determined using one-way analysis of variance (ANOVA) followed by Duncan post hoc test. Pesticide concentrations were calculated in a milligram per kilogram dry basis (mg kg^{-1} dry weight), a probability of $p= 0.05$ was set to indicate statistical significance. Discriminant analysis, a dimension-reduction technique related to principal component analysis and canonical correlation was used to identify discrimination between estuaries. Spearman's correlation analysis was performed to confirm correlations between pesticides in water and sediment samples. All statistical analyses were performed with IBM SPSS Statistics (V. 23).

Results and discussion

1) Surface Water quality

Environmental parameters including temperature, pH, salinity and turbidity in five estuaries along the Caspian Sea showed in Table 1. Results indicate that the temperature varied from 9.9 to 29 °C in summer and autumn, which Gorganrud showed the highest temperature. pH ranged from 8.0 to 8.3 at all stations. Salinity varied from 4.90 to 11.5 ppt in the summer and autumn with the highest salinity detected in the Gorganrud station. Turbidity at all stations was between 219.3 to 583.3 NTU with the highest detected in the Gorganrud station. The highest environmental parameters were detected at the Gorganrud and Tajan stations, and the lowest were detected at the Sefidrud station. Weather conditions and sampling occurrence had a major effect on environmental parameters such as temperature. To avoid impacts of rain, most sampling was conducted during sunny or cloudy weather. Environmental parameters exhibited poor correlation with water quality of Gorganrud and Tajan rivers, which have been mostly affected by agricultural activities [10]. Therefore, our findings are critical for the basin's water resource management.

2) Concentrations of organophosphate pesticides in surface water

Mean concentration (mg L^{-1}), standard deviation (SD) and range of diazinon, malathion and azinphos methyl in water samples collected from five estuaries along the Caspian Sea are presented in Supplementary Material (SM) 1. Results show mean diazinon concentrations ranged from 0.04 to 0.08 mg L^{-1} across all stations. No significant differences were observed in diazinon concentrations in water across five stations (F=2.17, P= 0.78; Figure 2a). Malathion concentrations ranged from 0.01 to 0.09 mg L^{-1} across all stations. There was a significant difference in malathion concentrations at the Tajan and Sefidrud stations (F=2.94, P= 0.03), where Tajan and Sefidrud exhibited higher and lower malathion concentrations, respectively (Figure 2a). Azinphos-methyl concentrations ranged from 0.01 to 0.1 mg L^{-1} across all stations. Different stations showed significant differences in azinphos-methyl concentrations in water (F=6.47, P=0.01). Tajan and Babolrud stations exhibited the highest concentrations of azinphos-methyl. In contrast, Sefidrud and Gorganrud exhibited the lower azinphos-methyl concentrations (Figure 2a).

3) Concentrations of organophosphate pesticides in sediment

Mean concentration (mg kg^{-1}), standard deviation and range of diazinon, malathion and azinphos-methyl in sediment samples collected from five estuaries along the Caspian Sea are presented in SM 2. Results indicated that mean diazinon concentrations ranged from 0.03 to 0.05 mg kg^{-1} in sediment samples from all stations. There were significant differences in diazinon concentrations in sediments from Sefidrud, Babolrud, and Tajan (F=3.43, P=0.02). The highest diazinon concentrations were measured at Babolrud and Tajan and lowest concentrations were measured at Sefidrud. Mean malathion concentrations ranged from 0.03 to 0.05 mg kg^{-1} in sediment samples from all stations. No significant difference was observed in the concentration of malathion in sediment samples of different stations (F=2.07, P=0.81). High malathion concentrations were detected in Tajan. Mean azinphos-methyl concentrations ranged from 0.04 to 0.06 mg kg^{-1} in sediments from all stations. Significant differences in azinphos-methyl concentration in sediment samples from different stations were observed (F=17.52, P=0.001). Babolrud and Tajan exhibited higher azinphos-methyl concentrations in sediment samples compared to Gorganrud l (Figure 2b). The presence of diazinon, malathion and azinphos-methyl has previously been reported in water and sediment samples in Haraz River, Southern Caspian Sea basin [3]. Similarly, diazinon was previously reported in three major rivers flowing into the Caspian Sea [36].

Table 1 Environmental parameters in five estuaries along the Caspian Sea

		Sefidrud	Chalus	Babolrud	Tajan	Gorganrud
Temperature	Summer	27.9±0.4	28.0±0.8	27.6±0.4	27.1±0.2	29.0±0.8
(◦C)	Autumn	9.9±0.1	13.1±0.2	13.2±0.1	12.93±0.25	14.9±0.1
pH	Summer	8.2±0.0	8.2±0.0	8.1±0.0	8.1±0.0	8.03±0.0
	Autumn	8.3±0.0	8.2±0.0	8.0±0.1	8.01±0.07	8.0±0.1
Salinity (ppt)	Summer	10.8±1.2	8.5±2.3	7.8±0.3	10.1±1.5	11.5±0.1
	Autumn	5.9±1.1	9.7±2.8	5.3±1.4	4.90±1.72	11.2±0.1
Turbidity (NTU)	Summer	219.3±30.1	405.3±34.7	413.3±20.5	499.7±21.6	525.7±6.0
	Autumn	317.9±21.6	439.7±25.8	488.0±22.0	557.33±25.82	583.3±5.7

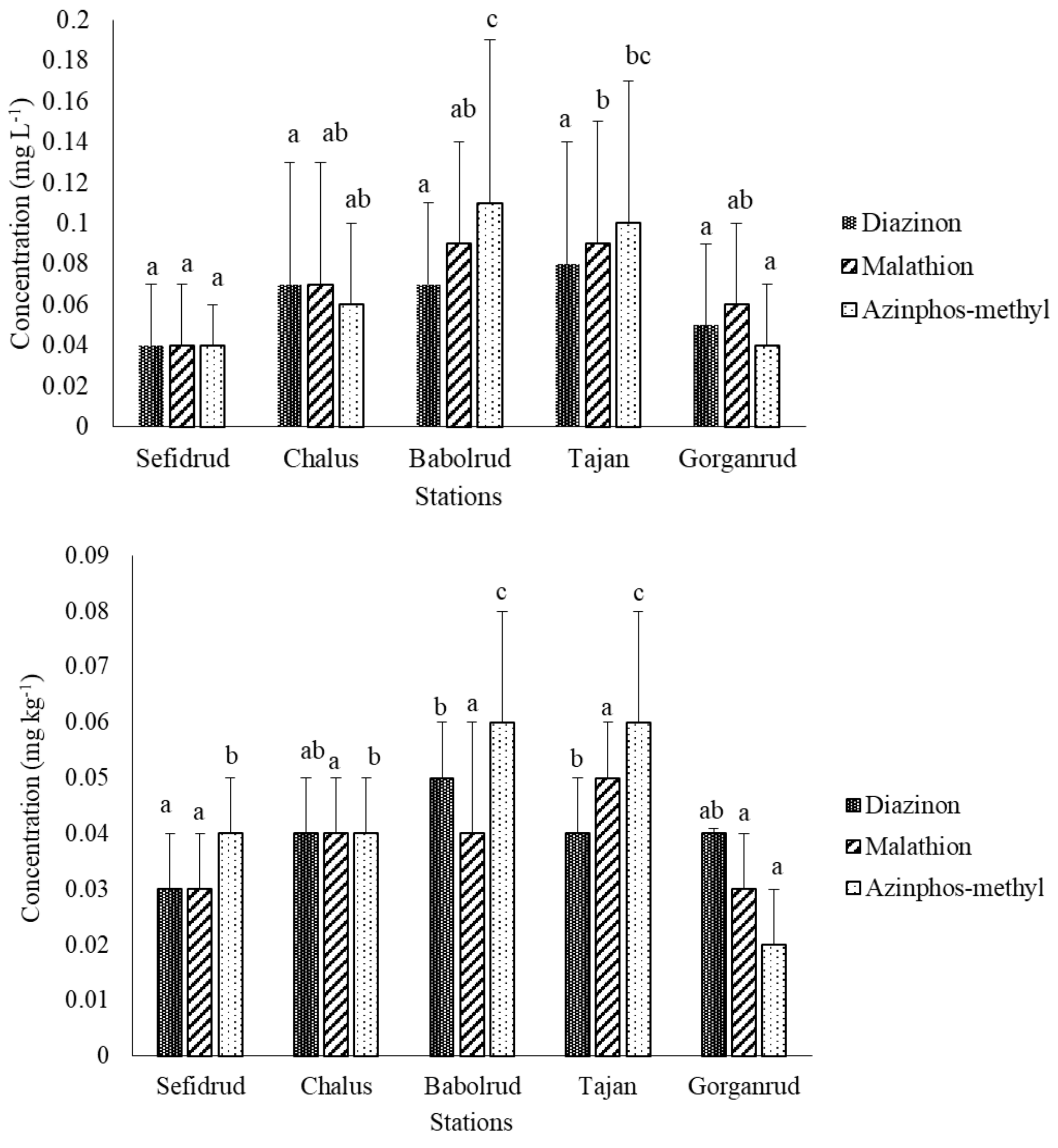

Figure 2 Comparison of OPs in a) water and b) sediment samples collected 5 stations in the Caspian Sea. The bars and errors represent means and standard deviations, respectively. Bars labeled with different letters are significantly different (one-way ANOVAs, P<0.05, Duncan's multiple range test).

Azinphos methyl concentrations were higher than other pesticides. Azinphos-methyl is one of the most toxic organophosphate pesticides due persistence in environment [10]. Bioavailability in the marine environment for azinphos-methyl pesticides is higher than diazinon and malathion. Shayeghi et al. [16] and Fadaei et al. [5] reported that azinphos-methyl pesticides were the most commonly used pesticids in agriculture around the Caspian Sea concentrations in the environment were higher than other pesticides. Similarly, Kafilzadeh [45] reported that azinphos-methyl had high concentrations among OPs in water and sediment in Caspian Sea. Higher azinphos-methyl concentrations compared to diazinon and malathion may be related to uncontrolled use, frequency of use, long-term effects, and high persistence of this pesticide in the environment.

4) Concentrations of organophosphate pesticides in different stations

The comparison between pesticides concentration in all stations showed that the highest concentration of pesticides was absorbed in the Tajan station (Figure 2a and b). Tajan River basin, located in the southern coast of the Caspian Sea along the Mazandaran province of northern Iran, is one of the most productive agricultural regions in the Middle East. Within the Mazandaran Province, a large quantity of pesticides is used to protect crops from pests [10]. Tajan River is one of pesticide polluted coasts of Caspian Sea, especially polluted of OPs, such as azinphos-methyl, malation and diazinon which are used as spray in gardens placed beside the river for control of pests on fruit trees. Azinphos-methyl, malation and diazinon, therefore, enter to the river directly or indirectly through the rain and wind. Environmental parameters such as turbidity was at higher in Tajan River, which showed presence of contaminants in this area.

Ebadi and Zare [18] showed OP concentration in Tajan River were higher than standards levels of FAO and WHO. Babaei [33] reported that Tajan River was a polluted area with a high concentration of OPs compared to other measured areas in the Caspian Sea. A high concentration of diazinon pesticides was reported in a study conducted by Ahmadi-Mamaqani et al. [46]. Similarly, a high level of pesticides in Tajan River was found by Kafilzadeh [45] compared to other rivers and estuaries along the Caspian Sea. Tajan River is one of the most important breeding habitats for sturgeon species and it provides spawning grounds for them. Therefore, high concentrations of pesticides pose threats to the Tajan river ecosystem and may accumulate in fish consumed by humans.

5) Comparison of organophosphate pesticides in summer and autumn

Mean±SD diazinon, malathion, and azinphos-methyl concentration in water samples in summer were 0.1±0.04, 0.11±0.05, and 0.11±0.06, respectively (Figure 3a). Additionally, mean±SD diazinon, malathion, and azinphos-methyl concentrations in water samples in autumn were 0.02±0.02, 0.03±0.02, and 0.03±0.02, respectively (Figure 3a). Results showed a significant increase of these pesticides in summer compared to autumn ($F=12.1$, $P=0.001$). In sediment samples, mean± SD diazinon, malathion, and azinphos-methyl concentrations were 0.04±0.02, 0.05±0.02, and 0.04±0.02 in summer, respectively. In autumn, mean±SD diazinon, malathion, and azinphos-methyl sediment concentrations were 0.04±0.01, 0.03±0.02, and 0.04±0.02, respectively (Figure 3b).

In Mazandaran province, widespread use of pesticides mainly occurs in rice paddy fields, during summer. Therefore, higher concentrations in summer compared to autumn may be due to increased use of pesticides [36]. A study monitoring of diazinon pesticides in soil and surface water of rice fields in northern Iran indicated the highest diazinon concentrations were reported in September, while diazinon was undetected in water in November [47]. Sediments may act as sink that tend to absorb of pollutants from water such as OPs that are easily accumulated in sediments. OPs can be incorporated by benthic organisms which can transform them to higher trophic levels through bioaccumulation and biomagnification [14].

Different pesticides in water and sediment samples can cause discrimination in different estuaries. Therefore, discriminant analysis was used to examine differences in pesticide pollutant loads between estuaries. Discriminant analysis show that Tajan and Babolrud estuaries have higher pesticide pollutant loads in Tajan and Babolrud estuaries compared to other estuaries (Figure 4).

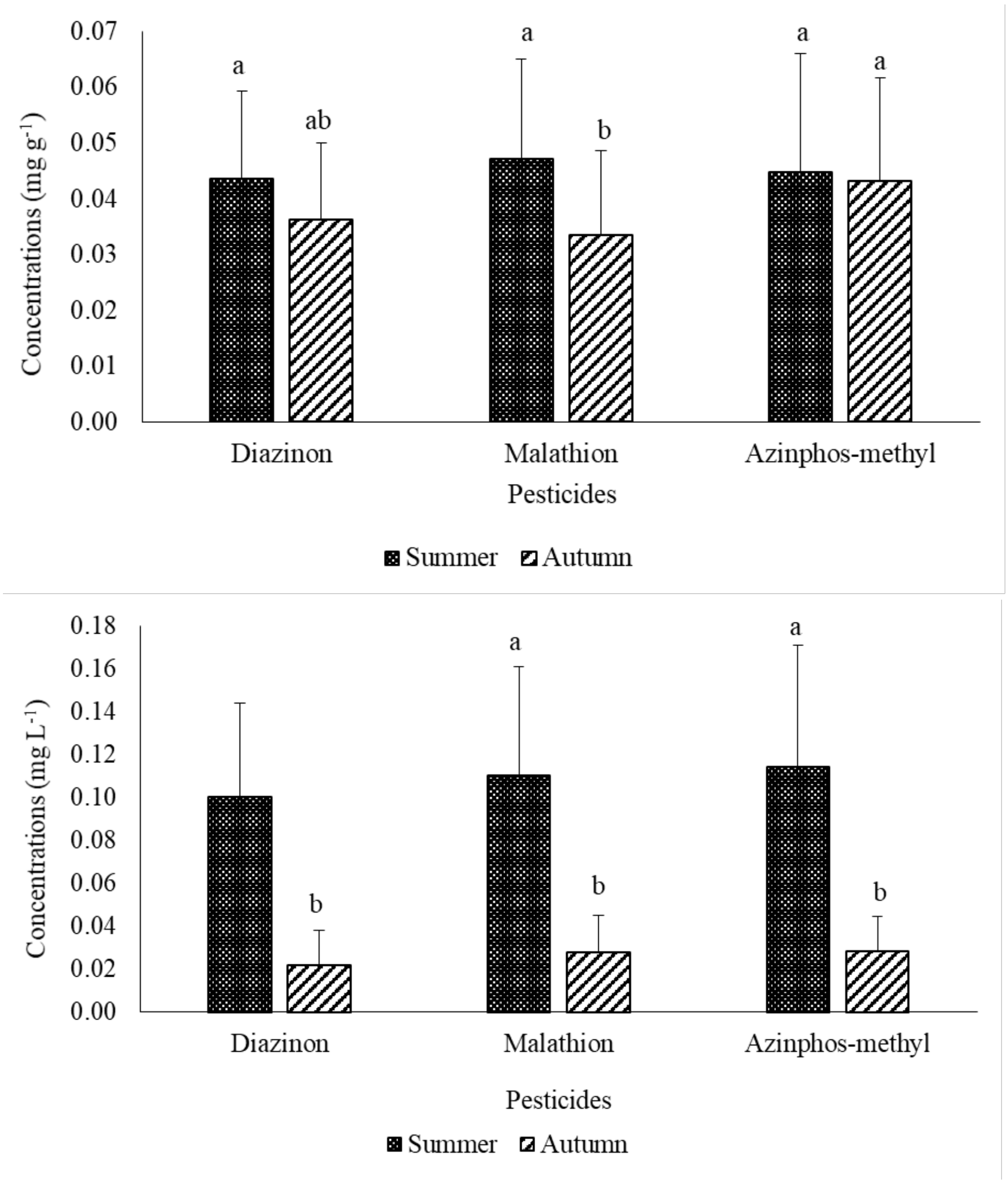

Figure 3 Comparison of mean±SD pesticides in a) water and b) sediment samples of Caspian Sea in summer and autumn (mg/L). Bars labeled with different letters are significantly different (one-way ANOVAs, P<0.05, Duncan's multiple range test).

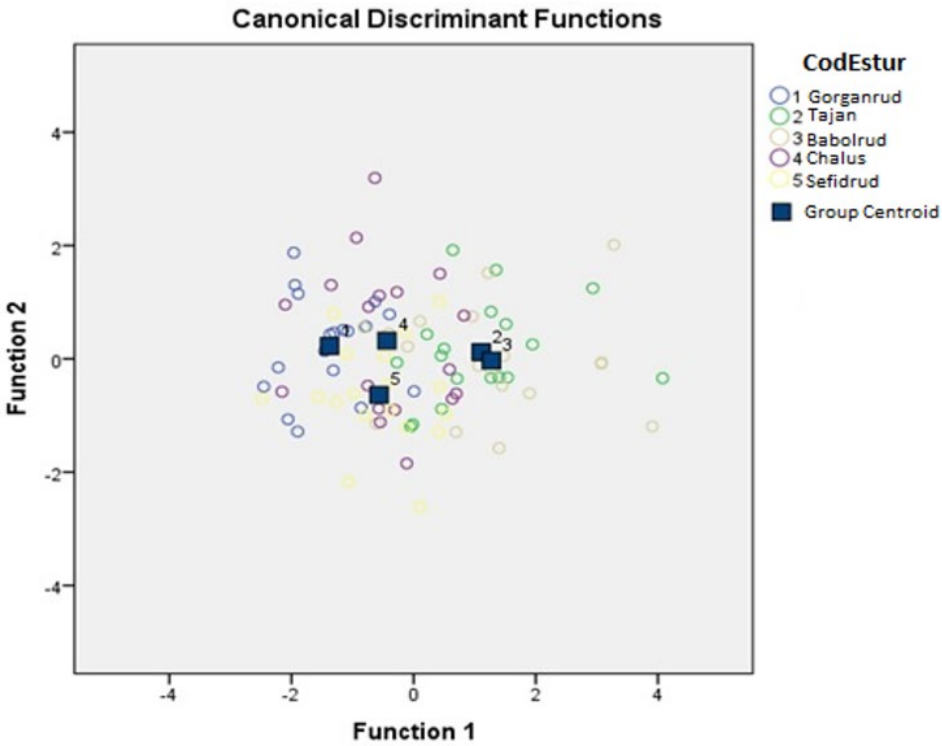

Figure 4 Discriminant chart based on mean pesticide concentrations between different estuaries.

6) Correlation analysis of organophosphate pesticides in water and sediment

Pearson correlation between diazinon, malathion and azinphos-methyl in water and sediment are presented in Table 2. Results indicate positive correlation between different pesticides in water and sediment. The highest correlation was between malathion with azinphos-methyl in water. Correlation between pesticides was higher in water compared with sediment. In contrary to this study, Kalantari and Ebadi [19] reported a high positive correlation between OPs in sediment in Tajan and Neka of Mazandaran Province. They reported that sources of OPs were similar, therefore there were positive correlations between different OPs. Kafilzadeh [45] showed there was a positive correlation between different OPs in water and sediment samples from Lake Tashk, Iran. Positive correlations between OPs reflect beginning the detoxification process, detoxification process, chemical form and the exact mechanism of pesticides [17].

7) Comparison of organophosphate pesticides in water and sediment in the world

An overview of OPs concentrations in water and sediment in different marine environments in world is presented in Table 3. The mean concentrations of diazinon, malathion and azinphos-methyl in water in this study are lower than the water samples in Hendo Khale River, Iran; Sacramento River in the USA, Kalamas River in Greece and Selangor River in Malaysia, but those concentrations are higher the comparison of Susquehanna River in the USA and Caspian Sea, Karun River and Lake Tashk in Iran. Therefore, OP concentrations in this study were lower compared with other countries, but concentrations were higher than previous studies reported in Iran. The mean concentrations of diazinon, malathion and azinphos-methyl in sediments in this study are lower the comparison of all studied pervious in Iran and other countries. SQGs standards showed levels of diazinon, malathion and azinphos-methyl in marine water were 0.82, 0.1 and 0.01, respectively [44]. In this study concentration of diazinon and malathion were below the SQGs standards, but the level of azinphos-methyl was higher than standards. Thus, Therefore, the health risk caused by azinphos-methyl in Caspian Sea cannot be ignored and the inputs of these contaminants should be controlled in the monitoring projects. Similarly, our recent study suggested low ecological risk of organochlorine pesticides based on SQGs in Gorgan Bay [50].

Table 2 Correlation between pesticides in water and sediment samples

	Water			Sediment		
	Diazinon	Malathion	Azinfos methyl	Diazinon	Malathion	Azinfos methyl
Diazinon	1	0.681**	0.698**	1	.212*	0.169
Malathion	0.681**	1	0.705**	0.212*	1	0.096
Azinfos methyl	0.698**	0.705**	1	0.169	0.096	1

Remark: * Correlation is significant at the 0.05 level. ** Correlation is significant at the 0.01 level.

Table 3 The comparison of OPs concentrations in water and sediment from various sites in the world

Location	Diazinon	Malathion	Azinphos-methyl	References
Water samles:				
Hendo Khale River, Iran	0.62	2.7		[29]
Sacramento River and San Joaquin River, USA	0.01–0.1		0.04–0.18	[48]
Susquehanna River, USA	0.028	0.03	0.07	[7]
Kurose River, Japan	0.002	0.04	0.09	[49]
Kalamas River, Greece	7.75	4.32	8.54	[11]
Selangor River, Malaysia	1.6–5.1	0.1–3.5	4.5–7.8	[8]
Caspian Sea, Iran	0.02	0.15	NR*	[33]
Babolrood River, Iran	0.07–0.1	0.05–0.07	NR	[5]
Karun River, Iran	0.02	NR		[39]
Lake Tashk, Iran	0.075	0.064	NR	[43]
Tajan River, Iran	0.08	0.09	0.1	
Gorganrud River, Iran	0.05	0.06	0.04	
Babolrud River, Iran	0.07	0.09	0.1	This study
Chalus River, Iran	0.07	0.07	0.06	
Sefidrud River, Iran	0.04	0.04	0.04	
Sediment samples:				
Hendo Khale River, Iran	1.5	3.2	NR	[29]
Sacramento River and San Joaquin River, USA	0.1–2.5		0.4–4.3	[49]
Susquehanna River, USA	0.3	0.8	1.4	[7]
Kurose River, Japan	0.4	0.7	1.3	[49]
Kalamas River, Greece	8.65	6.45	10.85	[11]
Selangor River, Malaysia	2.5–6.4	0.8–4.3	3.2–9.6	[8]
Caspian Sea, Iran	0.5	0.7	NR	[33]
Tajan River, Iran	0.04	0.05	0.06	
Gorganrud River, Iran	0.04	0.03	0.02	
Babolrud River, Iran	0.05	0.04	0.06	This study
Chalus River, Iran	0.04	0.04	0.04	
Sefidrud River, Iran	0.03	0.03	0.04	

* NR: Not Reported

The use of pesticides boost crop productivity, but there are now concerns about overuse of pesticides, mainly relating to contamination of water bodies and sediments consequent negative effects both on wildlife and human health. In humans and experimental animals, the accumulation of acetylcholine due to OP stressors result in cholinergic responses in peripheral (muscarinic and nicotinic) and central nervous system and neuromuscular junctions [21]. The Agency for Toxic Substances and Disease Registry (ATSDR) of toxicology has developed a mixtures program that includes trend analysis to identify mixtures of common contaminants found in environmental media and assessment of their joint toxicity and potential human exposures to mixtures of these chemicals. [21]. For example, the joint toxic action of diazinon and atrazine showed atrazine increased the toxicity of diazinon midge (*Chironomus tentans*) [21]. Combination of N, N-diethyl-m-toluamide (DEET), malathion and permethrin indicated higher toxicity compared their individual concentrations in rats [52].

Conclusions

This study measured the OP (diazinon, malathion and azinphos-methyl) concentrations in water and sediment samples from five estuaries along the Caspian Sea. Results showed that azinphos-methyl concentrations were higher than malathion and diazinon. Pesticide concentrations were higher in autumn compared to summer months. Positive correlations exist between different pesticides in water and sediment were observed. Therefore, bioavailability in the marine environment for azinphos-methyl pesticides were higher than diazinon and malathion. Tajan was the highest pesticide polluted river among stations measured in this study and thus, required ongoing monitoring. Further research is required to determine if pesticide concentrations reported in this study may contaminate fish consumed by humans.

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Data availability

All data generated or analyzed during this study are included in this published article.

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