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Research article

Temporal distribution and ecological risk assessment for pesticides in water from the north-central coastal zone of Sinaloa, Mexico

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ABSTRACT

Water contamination with pesticides is one of the major pollution problems in northwestern Mexico, and this is due to the extensive use of pesticides in agriculture. In this research, water samples of ten sampling sites (fishing grounds, beaches, and both) were analyzed in the search for 28 pesticides (organochlorines, organophosphates, pyrethroids, carbamates, among other chemical classes), supplemented with a calculation of the resulting potential environmental risk. Pesticides were separated from the matrix by liquid-liquid extraction and quantified by gas

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chromatography coupled to electron micro-capture (organohalogenated) and pulsed flame photometric detectors (organophosphates). In addition, the ecotoxicological risk of pesticides in algae, invertebrates, and fish was assessed, based on seawater pesticide concentrations using the Risk Quotient (RQ) and Toxic Units (TU) approach. The results showed 18 pesticides identified in the analyzed samples, where cypermethrin and chlorpyrifos were identified with the maximum concentrations of 1.223 and 0.994 μg L^{-1}, respectively. In addition, these two pesticides have been associated with acute toxic effects on algae, invertebrates, and fish. It is important to pay particular attention to the search for long-term alternatives to the use of chlorpyrifos and cypermethrin due to their high detection rates and the risks associated with their toxic properties. However, the adoption of alternative measures to synthetic pesticide control should be a priority, moving towards sustainable practices such as the use of biopesticides, crop rotation and polycultures.

1. Introduction

The current global agricultural production system is based on intensive agriculture in which a high use of chemical inputs (synthetic pesticides and fertilizers) and the practice of monocultures are notorious. Pesticides are used in a variety of sectors like food, health, forestry, industrial, agriculture and aquaculture. However, intensive use in agricultural activities associated with crop protection has been reported, which has caused the contamination of water bodies with acute and chronic effects on the environment and human health [1]. One of the most worrying aspects is the excessive use of pesticides which has led to a continuous entry and presence of these contaminants in the environment because they are transported from a targeted to a non-targeted area via adsorption, wastewater discharges leaching, volatilization, or infiltration/surface runoff [2–4]. Also, precipitation and excess irrigation (agricultural return flow) transport pesticides from the areas where they are applied to water system including marine aquatic ecosystems, where they can be accumulated by phytoplankton, aquatic invertebrates and fish that inhabit aquatic ecosystems and join the food chain and then pass to other fishes, birds and humans, etc. through the process known as biomagnification [3–5]. Consequently, marine aquatic ecosystems become the main receptors of pesticide concentrations, which are influenced by all productive activities carried out in terrestrial areas [6,7].

Currently, the trade and use of certain pesticides have been banned in several countries (e.g. Canada, France, Australia, United States, among others) [8]. However, recent studies have demonstrated that these compounds (e.g. endrin and their metabolites) continue to affect water bodies due to their high persistence in the environment, creating a global problem even in areas where pesticide applications are not carried out, where Mexico is no exception despite having established a ban on most pesticides of this type (organochlorine) since the 1970s [9,10]. As a result of this continuous application and potential for accumulation, pesticides have already been identified and quantified in various environmental matrices, including sediments from agricultural drains and coastal lagoons [11–14], agricultural drainage water [7,14], estuarine waters [7,12], and seawater [7], as well as in aquatic organisms such as fish [11], shrimp [11,12], and mollusks [11].

Various studies have documented that exposure to pesticides in organisms generates alterations in their metabolism, organ damage (e.g. liver, kidneys, gills, among others), oxidative stress, skeletal abnormalities, tumors, as well as the nervous system damage, effects on survival and development on algae, planktonic and benthic organisms, and death of individuals [15–20].

The north-central region of Sinaloa is no exception when it comes to pesticide use, as it stands out for its high national production of grains and vegetables, as well as livestock and fishery products [21–23]. During the development of these activities, a series of waste products are produced that can affect the environment. Among these, those derived from the use of pesticides in agriculture represent a serious problem [24,25]. Due to the coastal nature of Sinaloa, wastewater derived from the main economic activities in Sinaloa is discharged into the surrounding ecosystems and its final recipient is the water bodies of the Sinaloa Coastal Zone (SCZ). In the seawater of the north central SCZ, the main pesticides identified are organochlorines and organophosphates [7,11]. This presence is mainly attributed to their use in the agricultural sector [6,7]. García-Hernández et al. [25] carried out a study summarized the historical studies carried out over a period of 20 years (1998–2018) in the coastal zone of Mexico, regarding the presence of pesticides in different matrices, covering both the Mexican Pacific (north and south) and the Gulf of Mexico. However, these authors show a tendency to evaluate the impact of the presence of these pollutants mainly in sediment and organisms, leaving out the water component in most cases. In this sense, among the studies that report the presence of pesticides in water from ecosystems in the North Pacific region are those carried in the Huizache-Caimanero lagoon system, Sinaloa [26]; the Bay of Santa María, Sinaloa [27,28]; the Bay of Ohuira, Sinaloa [12,29,30], Navachiste Lagoon, Sinaloa, Mexico and Altata-Ensenada del Pabellon Lagoon System, Sinaloa, Mexico [7] (Table S1). The most recent study, prior to ours, dates from 2017 where Arellano-Aguilar et al. [7] analyzed the presence of organochlorine and organophosphate pesticides in water from rivers, drains, and lagoon systems (including some located in the study area) of the North Pacific (Table S1).

Since the study carried out by García-Hernández et al. [25] to date, we can affirm that the present study is one of the first to take up the monitoring of pesticides in water in the coastal zone of northwestern Mexico. Likewise, to date, no studies have been reported on the ecological potential risk assessment of pesticides in Sinaloa's coastal waters, despite the evidence of their presence. A simple and effective method to assess the environmental and toxicological risk of chemical substances is the Risk Quotient (RQ), which allows comparing the actual exposure of a substance with a reference concentration. It also provides information on a general scenario and a worst-case scenario at each study site [31,32]. RQ has been used to quantitatively assess the potential ecological risk of pesticides in

aquatic ecosystems in different parts of the world [31,33,34]. Furthermore, the utilization of RQ represents a viable instrument for the assessment of prospective risks at various trophic levels. It permits the evaluation of the cumulative effect of pesticide concentrations found in mixtures that could be related to biomagnification and bioaccumulation processes. This could reflect a greater impact on fauna at the top of the trophic network of aquatic ecosystems, such as birds, some fish and mammals [35]. Several studies have documented the implementation of potential risk assessment approaches with the objective of interpreting the concentrations of pesticides detected in marine environments around the world [36–38].

The objectives of this study were: 1) to determine pesticide concentrations in seawater in the north-central coastal zone of Sinaloa, Mexico, 2) to evaluate the temporal variation of pesticides (number and concentration) in seawater, and 3) to perform an ecotoxicological potential risk assessment at three trophic levels based on pesticide residues in the seawater.

2. Materials and methods

2.1. Study and sampling area

Mexico has more than 20 million hectares of agricultural land and Sinaloa is one of the Mexican states with 1.2 million hectares that are used for more than 50 different crops [39]. Sinaloa is a federative entity located in the northwest of Mexico, where the main economic activities are agriculture and fishing. Sinaloa's contribution to the value of national agricultural production is 10 %, ranking third at the national level. It is also considered the national leader in the volume production of red tomato, corn, and green chili, and ranks second nationally in potato and bean production [40]. The percentage of agricultural land with irrigation systems in the state is 78.8 % [41]. In terms of fish production volume, Sinaloa ranks second nationally and first in shrimp production [42].

The north-central region of Sinaloa is characterized by five Irrigation Districts (DRs), of which DR063: Guasave and DR010: Culiacan-Humaya are located adjacent to the study area [40]. Throughout the state of Sinaloa, including the municipalities (Angostura, Navolato, and Guasave) bordering the coastal area under study, agriculture is practiced during two agricultural cycles: autumn-winter (A-W) (October to March) and spring-summer (S–S) (April to September) [24,43–45].With reports of pesticide use, in Culiacan and Navolato, corresponding to 192.73 and 30.38 tons (t) of active ingredient (a.i.) for the A-W, and S–S cycles, respectively

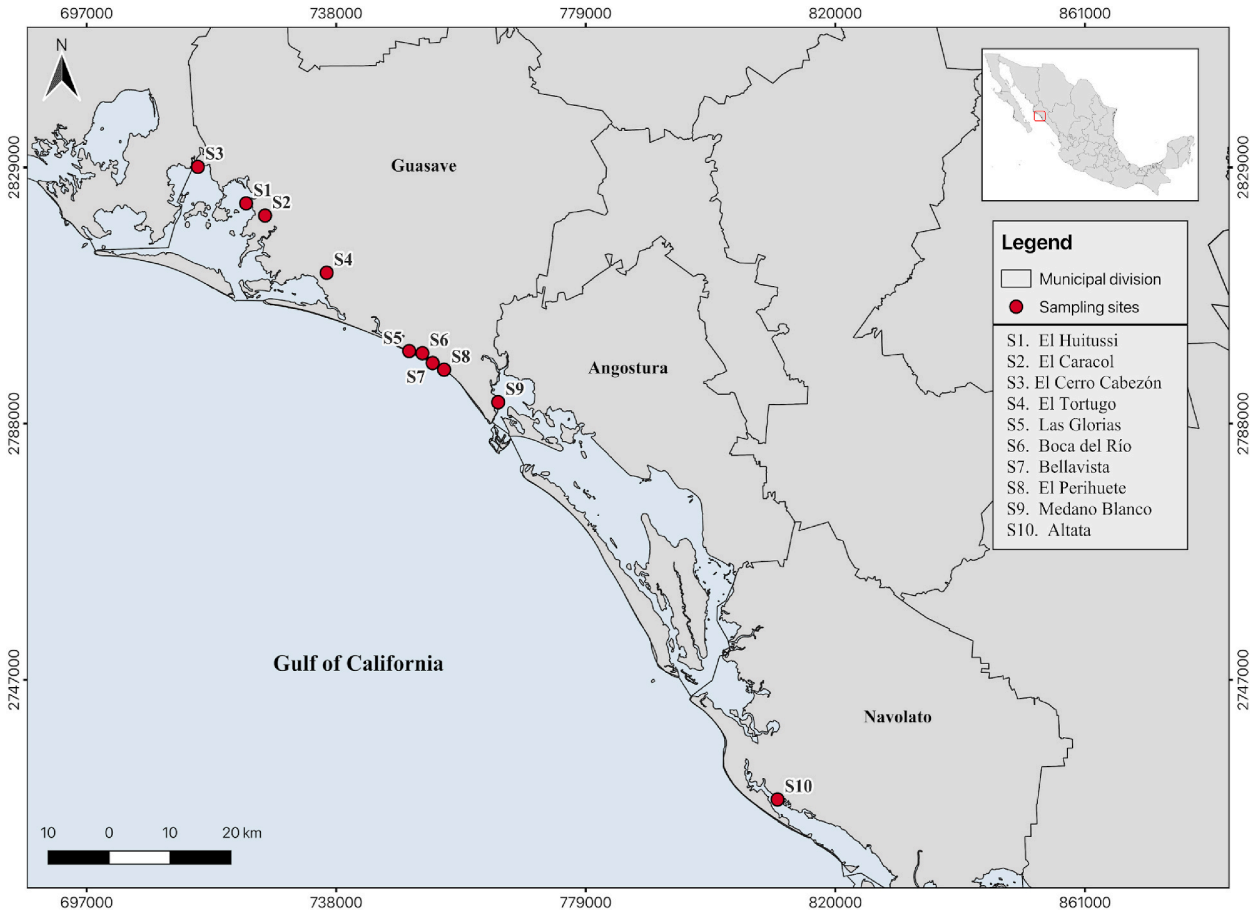

Fig. 1. Sampling sites in the coastal zone of Sinaloa, Mexico.

[24]. The main chemical classes used in Navolato and Culiacan are dithiocarbamates followed by bipyridyls, organophosphates, chloronitriles, pyrethroids, carbamates, organochlorines, and inorganic compounds [24,43–45]. For Guasave and Angostura, an annual use of 707 tons of a.i. is reported, with the dominant chemical classes being organophosphorus compounds followed by benzoic acid salts, and chlorophenoxy-derived substances [46].

In Navolato and Culiacan, the main active ingredients used include elemental sulfur, chlorpyrifos, dimethoate, glyphosate, mancozeb, chlorothalonil, paraquat, malathion, cypermethrin, oxamyl, endosulfan, dichlorvos, cupric hydroxide, naled, metam sodium, methomyl and captan [24,43,45]. While, in Guasave methamidophos, zeta-cypermethrin, abamectin, cyromazine, lambda cyalothrin, chlorpyrifos, pymetrozine, 2,4-D, dicamba, paraquat, benomyl, meptyl fluroxypyr and atrazine have been reported as the most widely used pesticides [46].

The municipality of Navolato has a territorial extension of 2,885 km^2, which represents 3.9 % of total area of the state of Sinaloa, with a coastline of 80 km. Two bays converge on its coasts: Altata and Santa Maria. The municipality is distinguished for being eminently agricultural (~153,563 ha) with the main agricultural crops being beans, corn, tomato, sugar cane, cucumber, green chili, and eggplant. In addition, fishing plays an important role, as Navolato has an extensive coastline, as well as a 523 km strip of federal zone and 9,700 ha of estuaries and stands out for the capture of species such as shrimp, clams, tope, mullet, sea bass, snapper, snook and sawfish [47]. The climate is warm sub-humid, dry, and semi-dry, the average annual temperature is around 25 °C and the rainy season occurs during the months of July to September, with an average annual rainfall of 790 mm [48]. On the other hand, the predominant economic activities in the municipality of Angostura are agriculture, fishing, and livestock, the first two being the most important. Agriculture corresponds to a surface area of 65,136 ha cultivated with an irrigation system and 5,519 ha of rainfed land. Its agriculture is modern and technified with high yields, traditionally producing soybeans, wheat, safflower, beans, corn, sorghum, and vegetables. Fishing is a second activity on which its economy is based and is mainly practiced in the communities of La Reforma, Costa Azul and Playa Colorada [49]. Finally, in municipality of Guasave the main economic activity is agriculture, other productive and service activities revolve around behavior of agricultural production. It has 200,000 ha of irrigated land where a wide range of agricultural products are cultivated, ranging from corn and wheat, to beans, rice, cotton, safflower, chickpeas, and vegetables; on the other hand, fishing has traditionally had an important contribution to economy of this municipality, where seven communities dedicated to fishing are located: El Cerro Cabezón, El Huitussi, El Caracol, El Coloradito, El Tortugo, La Pitahaya, and Boca del Río. The main products caught in these communities are shrimp, mullet, shark, mojarra, and sardine [50]. The climate is dry, warm, with a mean annual temperature of 25.1 °C, with a minimum and maximum of 2 and 44 °C, respectively. The rainfall regime is summer, with a percentage of winter rainfall between 5 and 10.2 % of the annual total. The average annual rainfall is 510.5 mm [51].

Therefore, sampling was carried out in the north-central coastal area, particularly in the municipalities of Angostura, Guasave, and Navolato that border the irrigation districts 010: Culiacán-Humaya and 063: Guasave, as well as human settlements (fishing grounds) and some beaches used for recreational purposes [48,52]. Ten sampling points were established, five of which corresponded to fishing grounds: El Caracol (S1), El Cerro Cabezón (S2), El Huitussi (S3), El Tortugo (S4) and El Perihuete (S5). Three to the beach area where recreational activities take place: Bellavista (S6), Las Glorias (S7) and Médano Blanco (S8). And two with both activities: Altata (S9) and Boca del Río (S10) (Fig. 1). Two sampling campaigns were conducted, one in May and one in August 2020, covering the dry and wet seasons, respectively.

Water samples (1 L per sample, two replicates per site) were collected manually from the shore at a depth of approximately 50 cm using an amber glass bottle and subsequently placed in a refrigerated cooler to be kept at 4 °C during transport to the laboratory [44]. The physicochemical parameters of water temperature, pH, conductivity, and salinity were measured in the field using a multiparametric probe (YSI Professional Plus, Ohio, USA) [14].

2.2. Standards and reagents

Analytical standards, with a purity of more than 98 %, for the following 73 pesticides acephate, acetamiprid, alachlor, aldrin, ametrine, atrazine, azinphos methyl, benzene hexachloride (BHC, alpha y beta), bifenthrin, cadusafos, carbaryl, carbendazim, carbofuran, chlordano (cis, trans and oxy), chlorfenapyr, chlorothalonil, chlorpyrifos, chlorpyrifos methyl, cyfluthrin, cypermethrin, deltamethrin, diazinon, dichlorvos (DDVP), dieldrin, dimethoate, disulfoton, endrin, endrin ketone, endosulfan alpha, beta and sulfate, esfenvalerate, ethion, ethoprophos, fenamiphos, fenitrothion, fenvalerate, fipronil, hexachlorobenzene (HCB), heptachlor, heptachlor epoxide, imidacloprid, lambda-cyhalothrin, lindane, malathion, metalaxyl, methamidophos, methomyl, methoxychlor, methyl parathion, metolachlor, metribuzin, mevinphos, myclobutanil, omethoate, pendimethalin, pentachloroaniline (PCA), pentachloronitrobenzene (PCNB), permethrin (cis and trans), pirimicarb, *p,p′*- DDD, *p,p′*- DDE, *p,p′*- DDT, propamocarb, propazine, pyriproxyfen, simazine, thiamethoxam, and trifloxystrobin were purchased from Chem Service Inc. (Pennsylvania, USA). The solvents, acetone, dichloromethane, and petroleum ether HPLC grade were provided by Control Técnico y Representaciones (CTR), S.A. of C.V. (Nuevo Léon, Mexico). NaCl, HCl, and NaOH, all ACS grade, were purchased from Sigma–Aldrich (Toluca, Mexico).

2.3. Extraction and cleanup/chemical analysis of pesticides

Once in the laboratory, the sample was filtered through Whatman #40 paper, and the pH was adjusted to 7.0 using HCl or NaOH 0.1 N. Once the sample has been filtered and the pH adjusted was saturated with 150 g of sodium chloride and a triple liquid-liquid extraction was performed with 60 mL of methylene chloride, stirring in a separatory funnel until dissolved and allowed to stand for 10 min to achieve phase separation (organic and aqueous phases). The extracts were combined and dried by passing through a filter containing anhydrous magnesium sulfate and collected in a 500 mL Kuderna-Danish concentrator attached to a 10 mL collection tube

and subsequent reconcentration of the extract in a concentric ring steam bath at 100 °C using 100 mL of petroleum ether and 50 mL of acetone, leaving the final extract in 1 mL of acetone for subsequent injection into the gas chromatograph [44].

2.4. Instrumental analysis and chromatographic conditions

Analyses were performed by gas chromatography coupled to micro-electron capture detector (μ-ECD) (organohalogenated compounds) and pulsed flame photometric detector (PFPD) (organophosphates). Standards and samples were automatically injected through an Agilent 7693 Autosampler into an Agilent 7890B Gas Chromatograph (Agilent Technologies, Palo Alto, USA) equipped with an Agilent VF-5 Pesticides 30 m × 0.25 mm x 0.25 μm capillary analytical column. The temperature ramp was programmed to maintain an initial temperature of 100 °C for 2 min, to increase to 170 °C at a rate of 20 °C min^{-1}, maintained for 1.25 min, and finally reach 275 °C at a rate of 4 °C min^{-1} maintained for 12 min. The injector and detector temperatures were 250 and 300 °C, respectively. The injection mode was split/splitless with a ratio of 10:1 and an injection volume of 2 μL. The total time for each run was 45 min. Nitrogen was used as carrier gas at a flow rate of 1.5 mL min-1 [53,54]. For the quantification of all compounds, the external standard method was used [55]; this was carried out using calibration curves at six concentration levels in the case of the analytes determined by GC-μECD, the levels were: 5, 10, 50, 100, 250 and 500 μg L^{-1}, starting from a stock solution of the standards mixture at a concentration of 2000 mg L^{-1}; whereas, for the analytes evaluated by GC-PFPD these were evaluated at the following concentration levels: 50, 100, 250, 500, 750 and 1000 μg L^{-1}, starting from a stock solution of the mixture of standards at a concentration of 1000 mg L^{-1}. If the compound identification was uncertain, the extract was analyzed for analyte confirmation using an Agilent 7890B Gas Chromatograph equipped with a 7000D TQ mass spectrometer detector and a model 7693 autosampler (Agilent Technologies, Palo Alto, USA) [54].

2.5. Quality control (QC)

For quality control during the analysis of the samples of each set, a blank sample (free of the pesticides of interest) was spiked with standards at a concentration of 5 ppm. Subsequently, the spiked samples were analyzed following the methodology previously described (sections 2.3 and 2.4). For each analyte, both the recovery percentage and coefficient of variation were evaluated according to the EURACHEM analytical method validation guide [56]. The results indicated recovery percentages between 85 and 97 %, while the coefficient of variation was between 5 and 11 %, which, according to the validation guide used as a reference and criteria established internally in the laboratory, indicates that the method is under control [57].

2.6. Ecotoxicological potential risk assessment for pesticide concentration in seawater

Ecotoxicological potential risk assessment based on seawater pesticide concentrations was evaluated using the Risk Quotient (RQ) and Toxic Units (TU) approach [58,59]. The RQ approach was used to analyze chronic effects, and TU to assess acute effects [60,61]. Both potential risk assessment approaches were carried out for three trophic levels of the aquatic ecosystem, these three were: 1) Algae: *Scenedesmus subspicatus, Raphidocelis subcapitata*, *Chlorella pyrenoidosa*, *Anabaena doliolum*, and *Selenastrum capricornutum*; 2) Aquatic invertebrates: *Daphnia magna*; and 3) Fish: *Oncorhynchus mykiss*, *Cyprinodon variegatus*, *Lepomis macrochirus*, and *Pimephales promelas*.

The RQ approach was carried out by comparing the general scenario (mean concentration) and the worst-case scenario (maximum concentration) of each pesticide in the samples with a toxicity reference value. For the assessment of possible chronic effects, the No Observable Effect Concentration (NOEC) is often used. The NOEC is a reference at which no adverse effects on aquatic organisms are expected [61]. However, if NOEC was not available, another value such as the effective concentration (EC_{50}) or lethal concentration (LC_{50}) was used. Toxicity reference values (NOEC, EC_{50} and LC_{50}) were obtained for each trophic level of the aquatic ecosystem from the Pesticide Properties Database developed by the Agriculture and Environment Research Unit (AERA) at the University of Hertfordshire [8]. The RQ values were calculated using equation (1):

$$RQ = \frac{MEC}{PNEC_{water}} \quad \text{Eq (1)}$$

MEC is the Measured Environmental Concentration. The predicted no-effect concentration (PNEC) was estimated from available toxicity reference values, with NOEC values taking precedence over any other reported acute toxicity values (EC_{50} or LC_{50}). However, in the absence of NOEC information, acute toxicity values were used. In this sense, an assessment factor (AF) was applied to all toxicity reference values used in this study (Table S2). This AF is a value that divides the PNEC value, considering the uncertainty inherent to the acquisition of laboratory toxicological data (unverified or verified data) and the type of toxicity reference value available (NOEC, EC_{50}, or LC_{50}), according to the Technical Guidance for Deriving Environmental Quality Standards of the European Commission [62]. The PNEC values were then divided by 1000 as an AF when at least one short-term test (LC_{50} or EC_{50}) was available at one trophic level. They were divided by 100 when data from long-term assays (EC_{10} or NOEC) with fish or aquatic invertebrates were available, and by 50 or 10 when two or three long-term assays (NOEC) were available [63]. Finally, potential chronic adverse effects were expected if the RQ value was >1, an intermediate risk if the value was between 0.1 and 1, and a low risk if the value was <0.1.

In addition, the RQ value per sampling site (RQ_{site}) was estimated using an additive approach with the RQ values obtained for each pesticide. According to equation (2):

$$RQ_{site} = \sum_{i=1}^{n} RQ_i \quad \text{Eq (2)}$$

Table 1
Pesticides detected (μg L^{-1}) by each sampling site in the seawater of the coastal zone of Sinaloa during dry and wet seasons.

Sites / Pesticide	1		2		3		4		5		6		7		8		9		10	
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
BHC		0.036	0.009			0.067	0.034	0.058	0.012	0.051	0.011	0.033		0.028	0.036		0.026	0.034	0.020	0.031
Chlorfenapyr	0.028					0.026		0.043	0.039						0.064			0.024	0.011	0.085
Chlorpyrifos	0.070	0.054	0.047	0.114	0.061	0.080	0.061	0.104	**0.994**	0.054	0.034	0.081		0.070	0.040	0.035		0.062	0.035	0.094
Cypermethrin			0.428		0.328		0.321		0.365		0.207	0.228	0.318	0.302	0.197	0.261	0.341	**1.223**	0.316	0.690
Dieldrin										0.015										
Endosulfan sulfate																			0.019	
Endrin				0.034				0.033												
Fipronil	0.025		0.020																	
Heptachlor			0.006				0.032	0.054	0.006	0.012	0.020		0.010		0.044		0.017		0.009	
Lindane							0.091													
Myclobutanil							0.072													
p,p'-DDE			0.007						0.010											
p,p'-DDT	0.0040				0.005				0.010											
Pendimethalin			0.057																	
Pentachloroaniline		0.054							0.012											
Pentachloronitrobenzene				0.008				0.025	0.022	0.015				0.021				0.015		0.020
Pirimicarb																	0.010			
Pyriproxyfen																				0.005

RQ_i is the risk quotient for each pesticide quantified in the samples. RQ_{site} assumed an additive approach with mean concentrations (general scenario), where the level of risk quotient for a sampling location was given by the toxic sum of each pesticide quantified at that location. Therefore, possible synergistic or antagonistic relationships between pesticides detected at the same site were not considered [64]. Similarly, the toxic contribution ($RQ_{contribution}$) of each pesticide was determined in the ecotoxicological potential risk assessment per sampling site, according to equation (3) [65]:

$$RQ_{Contribution} = \left(\frac{RQ_i}{RQ_{site}}\right) X\,100 \quad \text{Eq (3)}$$

The TU approach was carried out by comparing the concentration of each pesticide in the samples with acute toxicity reference values (EC_{50} and LC_{50}) at the three trophic levels. These acute toxicity reference values established the concentrations that could primarily affect growth, development, or survival at the trophic levels under study. The TU of each pesticide (TU_i) was determined using equation (4):

$$TU_i = \frac{MEC}{EC_{50}\ or\ LC_{50}} \quad \text{Eq (4)}$$

TU_i is the toxic unit for each pesticide quantified; MEC is the Measured Environmental Concentration in seawater samples; EC_{50} or LC_{50} are the effective and lethal concentrations, respectively, affecting 50 % of individuals when exposed to a given pesticide concentration [66]. Subsequently, the TU value per sampling site (TU_{site}) was obtained by summing the TU_i of each pesticide detected at this site [64]. The TU_{site} result was interpreted as follows: a value above 1 suggests a potential high risk of acute effects, and a value between 1 and 0.1 suggests a moderate potential risk of acute effects [67]. The difference between RQ and TU, when both use reference values for acute toxic effects (EC_{50} or LC_{50}), is that the TU method does not use an AF. Therefore, the threshold value is used directly,

Table 2
Pesticide concentrations in seawater in the north-central coastal zone of Sinaloa, Mexico.

Pesticide	Dry season (μg L^{-1})	Wet season (μg L^{-1})	Limit of detection	Limit of quantification
Range (n/cen) Mean ± SD	(n = 10)	(n = 10)	(μg L^{-1})	(μg L^{-1})
Benzene hexachloride (BHC)*	<DL-0.04 (3) 0.02 ± 0.01	<DL-0.07 (2) 0.04 ± 0.01	0.0005	0.0017
Chlorfenapyr	<DL-0.06 (6) 0.04 ± 0.02	<DL-0.08 (6) 0.04 ± 0.03	0.001	0.0033
Chlorpyrifos	<DL-0.99 (2) 0.17 ± 0.33	0.03–0.11 (0) 0.07 ± 0.02	0.001	0.0033
Cypermethrin	<DL-0.43 (1) 0.31 ± 0.07	<DL-1.22 (5) 0.54 ± 0.42	0.005	0.0165
Dieldrin*	<DL (10) –	<DL-0.01 (9) –	0.004	0.0132
Endosulfan sulfate*	<DL-0.02 (9) –	<DL (10) –	0.002	0.0066
Endrin*	<DL (10) –	<DL-0.03 (8) –	0.006	0.0198
Fipronil	<DL-0.02 (8) –	<DL (10) –	0.005	0.0165
Heptachlor*	<DL-0.04 (2) 0.02 ± 0.01	<DL-0.05 (8) –	0.001	0.0033
Lindane**	<DL-0.09 (9) –	<DL (10) –	0.006	0.0198
Myclobutanil	<DL-0.07 (9) –	<DL (10) –	0.005	0.0165
p,p'-DDE+	<DL-0.01 (8) –	<DL (10) –	0.001	0.0033
p,p'-DDT**	<DL-0.01 (7) 0.01 ± 0.003	<DL (10) –	0.001	0.0033
Pendimethalin	<DL-0.06 (9) –	<DL (10) –	0.001	0.0033
Pentachloronitrobenzene (PCNB)**	<DL-0.02 (9) –	<DL-0.03 (4) 0.02 ± 0.006	0.001	0.0033
Pentachloroaniline (PCA) +	<DL-0.01 (9) –	<DL-0.05 (9) –	0.001	0.0033
Pirimicarb	<DL-0.01 (9) –	<DL (10) –	0.001	0.0033
Pyriproxyfen	<DL (10) –	<DL-0.01 (9) –	0.001	0.0033

Range = minimum – maximum; arithmetic mean ± standard deviation; n = total samples; parenthesis = censored samples (cen); <DL = measurement below detection limit; - = There are no data due the quantification of that pesticide was determined in one or two samples; *Prohibited use; **Restricted use [75]; +Degradation product/metabolite.

whereas in RQ, the more acute effect values are used, the higher the AF value will be. The TU_{site} was obtained according to equation (5):

$$TU_{site} = \sum_{i=1}^{n} TU_i \quad \text{Eq (5)}$$

2.7. Data processing and statistical analysis

First, we compared the frequency of occurrence of pesticides between seasons using a one-way analysis of variance (ANOVA), considering that the assumptions of normality (Shapiro–Wilk test; $p = 0.17$) and homogeneity of variances (Levene test; $p = 0.26$) were met. Due to the presence of non-detected measurements, the basic statistics for each pesticide concentration were estimated using the Kaplan–Meier (K-M) method [68]. Temporal variation in pesticide concentrations was assessed using statistical analyses designed for censored data: the non-parametric K-M test was used to analyze pesticides with detection rates <50 %, and the parametric Maximum Likelihood Estimation (MLE) test was used for pesticides with detection rates >50 %. Pesticides with detection rates <20 % were excluded [68–70]. Due to the multiple comparisons made, the p-values were adjusted for the false discovery rate (FDR) [71,72]. All statistical comparisons were carried out in R v. 3.6.2 [73]. Analyses for censored data are considered the most appropriate in environmental contamination research, as they allow working with data that are below the detection limit, testing similar hypotheses to standard parametric tests for differences between groups, but avoiding the possibility of committing Type I error in comparisons [68–70].

3. Results and discussion

3.1. Occurrence of pesticides residues in seawater

At least two pesticides were detected in all samples. The highest number of pesticides was found in the sample from zone S5, a total of 8 during the dry season. In second place was S2 with 7 pesticides and in third place were S4 and S10 with 6 pesticides during dry and wet season sampling, respectively. The lowest number of pesticides found in the samples was at site S7 and S8, which presented two pesticides in the dry and wet season, respectively (Table 1).

The number of pesticides observed per site was variable, probably due to the nature of the site sampled. In this sense, the S5, S7, and S10 are not only impacted by the recreational activities practiced on the beach, but also by fishing in the inner bay and it is a receiving body for discharges from canals and agricultural drains that discharge their waters into the river that finally flows into the coastal area near the beach.

In the case of S8, only fishing activities have been reported and probably the presence of the compounds found is mainly due to historical contamination.

The pesticides with the highest percentage of detection during the study were chlorpyrifos (90 %), BHC (75 %), and cypermethrin (70 %) (Table 2). These results agree that the levels of some organochlorine pesticides are generally higher in semi-closed environments near highly anthropized areas, with intensive agricultural, industrial, commercial, or urban activities, according to Girones et al. [74], who analyzed the levels of organochlorine pesticides on the coasts and open waters of South America.

The use of these pesticides has been restricted in the USA and some European countries [8,26] because they cause serious health problems in humans, other terrestrial organisms, and aquatic organisms [27]. Therefore, detecting them in high concentrations in the samples analyzed is of great concern.

Pesticides reach water bodies by run-off, infiltration, and soil erosion, where they have been applied. They can also be mobilized by atmospheric transport, as well as by run-off during rainfall or agricultural irrigation, transported to water bodies, both surface and groundwater, and even contaminate coastal ecosystems [46]. It has been proven that the resuspension of the sediment caused by trawling allows the sediment from soft bottoms, such as silt and clay, to be moved to various areas by marine currents, while the thicker material with a greater settling speed can be deposited in the areas where trawling is carried out. In this sense, at sampling sites where fishing activities are carried out constantly, it has been reported that the resuspension of the sediment caused by trawling allows the sediment from soft bottoms such as silt and clay to be moved to various areas by marine currents, while the thicker material with a greater settling speed can be deposited in the areas where the trawling takes place, which could explain the presence of pesticides that tend to adhere to fine particles [54].

Arellano Aguilar et al. [7] and Girones et al. [74] state that the coastal zone is highly vulnerable to the presence of organic pollutants, such as pesticides, due to direct and indirect discharges from surface water bodies that flow into coastal lagoons and bays, the situation being more worrying when dealing with semi-closed systems, so that the dilution or dispersion of pollutants is limited.

3.2. Concentration of pesticides residues in seawater

The concentrations of 73 pesticides in the seawater samples were analyzed. Of the total number of pesticides analyzed, 28 were detected. Although only 18 were above the limit of quantification, of which fourteen pesticides were insecticides, three fungicides, and one herbicide. While, the pesticides alachlor (<0.33 μg L^{-1}), aldrin (<0.046 μg L^{-1}), bifenthrin (<0.16 μg L^{-1}), carbaryl (<0.19 μg L^{-1}), deltamethrin (<0.33 μg L^{-1}), endosulfan (<0.029 μg L^{-1}), endrin ketone (<0.19 μg L^{-1}), λ-cyhalothrin (<0.33 μg L^{-1}), metolachlor (<0.66 μg L^{-1}) and permethrin (<0.66 μg L^{-1}) were below the quantification limit and were omitted from the results (Table 2). The

pesticide residues detected in the present study (insecticides, fungicides, and herbicides) coincide with the types reported as most frequently used in several Mexican states such as Baja California [76], Coahuila and Durango [77], Nayarit [78,79], Sinaloa [24,80], Sonora [81,82] and Yucatán [83], although the proportion of use is variable in each of the Mexican states. However, the use of these compounds is higher in northwestern Mexico compared with the reported nationally which is about 30 % [84,85].

The concentrations and compounds reported in this study partially coincide with what has been previously reported in the ecosystems of the area, since mostly appear to reflect historical pesticide use in surrounding agricultural areas (Table S1). Likewise, the concentrations of some pesticides (dieldrin, endosulfan sulfate, endrin, heptachlor, *p,p'*-DDE and *p,p'*-DDT) in the present study were higher than those reported in the coastal waters of Indonesia [86].

In our study, although the compounds recorded in both highest frequency and concentration correspond to those reported in current use, the presence of those whose use is already restricted or prohibited according to Mexican regulations was also observed (Table 2) [10,80].

The maximum individual concentrations detected during the study are represented firstly by the insecticide cypermethrin in S9 with a concentration of 1.223 μg L^{-1} (wet season), secondly by the insecticide chlorpyrifos in S5 with a concentration of 0.994 μg L^{-1} (dry season), and thirdly by cypermethrin too, in S10 with a concentration of 0.690 μg L^{-1} (wet season) (Table 1). The concentrations obtained in this study of chlorpyrifos and BHC are higher than those obtained in other coastal areas [87].

Granados-Galván et al. [75] state that the concentration of pesticides in environmental samples, such as water, can be affected by several factors, both intrinsic (polarity, volatility, solubility, molecular weight, etc.) and extrinsic (physicochemical parameters, sampling time, among others). In this sense, Table S3 presents the salinity, conductivity, pH, and temperature values recorded during the two sampling seasons. The observed values correspond to those previously reported in seawater bodies close to the study area. For example, Montes et al. [13] reported in the Navachiste-Macapule lagoon system, for the dry season, an average salinity and temperature of 38 PSU and 30.6 °C, respectively; while, for the rainy season, the average salinity and temperature values were 37.6 PSU and 32.5 °C, respectively. No differences were observed regarding pesticide concentration between seasons. However, chlorpyrifos and heptachlor showed a higher concentration in the wet season, while PCNB in the dry season (Table 1).

The high frequency of occurrence of chlorpyrifos in seawater samples is attributed to the fact that, due to its low solubility in water, it is washed into the water column of rivers and agricultural drains that flow into lagoon systems and has been reported to possess high resistance to chemical degradation by hydrolysis and photolysis [88–91].

In the case of BHC, since it is an organochlorine pesticide, we assume that its high frequency of occurrence is attributed to its physicochemical properties since, despite its low solubility in water, it has a high octanol-water partition coefficient, which allows it to be persistent in the environment and liposoluble, in addition to its high affinity for organic matter means that, like other organochlorines, it accumulates in the sediments of aquatic ecosystems, so that the removal of sediments by marine currents or by the entry of spills into the system could lead to its incorporation into the water column [13,38,48,90]. Finally, the diverse presence of pesticides in the water of the coastal zone of the study area may be associated with their intensive use in agriculture in the neighboring irrigation districts, as well as their use in sanitary campaigns for disease vector control and the fact that some of them are used as intermediaries in the synthesis of other more complex pesticides [10,38,90].

Ávila-Díaz et al. [14] reported the coincidence between high concentrations of organophosphate pesticide residues (chlorpyrifos and dimethoate) in water from agricultural drains in the irrigation district 063, an area adjacent to the zone of Guasave, Sinaloa, Mexico, and the period of greatest agricultural activity (February), which therefore coincides with the peak of pesticide application and with the irrigation season (February to May) of maize, the crop with the largest surface area, and can be transported through the discharge of agricultural wastewater into the drains, and subsequently into the coastal area where it flows. These authors state that chlorpyrifos has a high adsorption as well as affinity for soil and suspended particles, which will usually be transported to nearby effluents through runoff or this compound is transported to groundwater through leaching, which could explain its high frequency and concentration in the present study.

3.3. Temporal distribution of pesticides in seawater

The total number of pesticides detected in seawater samples by season did not show significant differences ($P = 0.28$). BHC, chlorfenapyr, chlorpyrifos, cypermethrin, heptachlor, PCA, and PCNB were detected in both the dry and wet seasons. In the dry and wet season, 14 and 10 pesticides were detected respectively. Cypermethrin, chlorpyrifos, heptachlor, and BHC showed the highest detection rate in dry season samples with 90 % (9 samples), 80 % (8 samples), 80 % (8 samples), and 70 % (7 samples), respectively. In the wet season, chlorpyrifos and BHC showed the highest detection rate with 100 % (10 samples) and 80 % (8 samples), respectively (Tables 1 and 2).

On the other hand, only BHC, chlorfenapyr, chlorpyrifos, cypermethrin, heptachlor, and PCNB were statistically analyzed, because a detection rate of more than 20 % is required in the total samples. Chlorfenapyr and PCNB were analyzed using the parametric test of Maximum Likelihood Estimation test, as the data met the assumptions of normality and homoscedasticity of variance. BHC, chlorpyrifos, cypermethrin, and heptachlor did not have a normal distribution and they were therefore analyzed using the non-parametric Kaplan-Meier estimator test (Table S4). The six pesticides included in the statistical analysis with censored data to assess their temporal distribution did not show significant differences by season (Table S4).

Sinaloa has two agricultural cycles per year: 1) autumn-winter (A-W) from October to March, where the cultivation of export vegetables such as tomato, chili, cucumber, and eggplant predominates; and 2) spring-summer (S–S) from April to September, mainly dedicated to the cultivation of some grains such as maize and sorghum. During the first one, the highest peak of pesticide application has been observed in the area, which would explain that although there are no significant differences between the water monitoring

seasons in the coastal zone, in this study, the highest diversity of compounds has been observed in the dry season, probably due to the ability of these compounds to be transported and maintained in aquatic ecosystems [23,24,54].

According to Leal-Acosta et al. [54] during the rainy season, there is an increase in organic matter entrainment from runoff that reaches coastal systems. Therefore, there may be an increase in the input of pollutants to coastal systems. During this season, SCZ receives inputs from various surface water bodies through runoff from the Culiacan and Sinaloa rivers, which may favor the removal of fine sediments, allowing the release of compounds attached by entrainment to coastal systems, and incorporating them into the water column [13,19]. Additionally, Yogaswara et al. [86] indicate that the concentration and distribution of pesticides in coastal waters is due to physical hydrodynamic factors (tides, currents, wind, and riverine inputs) and their historical use.

However, some authors have observed that the presence and concentration levels of pesticides in Sinaloa's coastal ecosystems, at least in the case of coastal sediments, fluctuate depending on the seasons. Higher concentrations have been reported during the rainy season (July to October) and early dry season, mainly because runoff from agricultural drains surrounding these sites decreases during spring and early summer [13,39,48,92]. Similar results have been reported by Zheng et al. [93], on seasonal variation in the concentration of organochlorine pesticides in water samples in the western Pacific Ocean and the East China Sea.

3.4. Ecotoxicological potential risk assessment of pesticides in seawater

Chlorpyrifos and heptachlor were associated with a potential high chronic risk (RQ > 1) in algae at their maximum concentrations (worst-case scenario). For the aquatic invertebrates, chlorpyrifos and cypermethrin also represented a potential high chronic risk in both the worst-case and the general scenario. In addition, chlorfenapyr, heptachlor, and pyriproxyfen showed a potential high chronic risk in aquatic invertebrates only in the worst-case scenario. Finally, concentrations of chlorpyrifos, cypermethrin, endrin, and heptachlor showed an elevated potential chronic risk in fish in both the worst-case and general scenarios. Endosulfan sulfate also posed a potential high risk, but only in the worst case. Similarly, chlorpyrifos and heptachlor were the only pesticides that showed a potential chronically elevated risk at all three trophic levels (algae, aquatic invertebrates, and fish) (Table 3).

As can be seen, chlorpyrifos is the pesticide that is associated with a potential chronic elevated worst-case risk for all three trophic levels. However, a review of studies on the ecotoxicity of chlorpyrifos to aquatic organisms suggests that future studies should focus on the ecotoxicity of chlorpyrifos to marine organisms given the current lack of data [94]. These high concentrations are probably the cause of the frequent presence of chlorpyrifos in sediments and runoff waters of agricultural areas in the northern part of the state of Sinaloa [14]. Importantly, chlorpyrifos, heptachlor and cypermethrin were present at concentrations above those expected to cause chronic effects, sometimes tens, hundreds or even thousands of times the estimated chronic threshold. In a study reported by Girones et al. [74]on the ecotoxicological risk associated with the levels of some organochlorine pesticides in South America indicate that DDT levels in sediments, mussels and fish could cause damage to the structure and function of the community in the long term in the Bay of Guanabara, the coast of Lima, the Río de la Plata Estuary and other sites, In addition, the levels of lindane and endosulfan in the sediments could cause short or long-term damage to the biota in several coastal sites in southeastern Brazil and the coast of the Argentine Pampas.

Table 3
Results of ecological risk assessment using the Risk Quotient (RQ) on algae, aquatic invertebrates, and fish. The mean and maximum RQ for each pesticide represent the general and the worst-case scenarios, respectively.

Pesticides	Algae		Aquatic invertebrates		Fish	
	RQ		RQ		RQ	
	Mean	Max	Mean	Max	Mean	Max
Chlorfenapyr	–	–	0.6	**1.2**	0.2	0.5
Chlorpyrifos	0.1	**1.3**	**1.3**	**10.8**	**41.4**	**355.0**
Cypermethrin	0.3	0.9	**493**	**1529**	**657**	**2038**
Dieldrin	NA	0.2	NA	<0.1	NA	**12.2**
Endosulfan sulfate	NA	<0.1	NA	<0.1	NA	**3800**
Endrin	–	–	0.8	0.8	**4.6**	**4.6**
Fipronil	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Heptachlor	0.8	**2.0**	0.5	**1.3**	**3.0**	**7.8**
Lindane	NA	<0.1	NA	<0.1	NA	<0.1
Myclobutanil	NA	<0.1	NA	<0.1	NA	<0.1
p,p'-DDE	–	–	0.2	0.2	<0.1	<0.1
p,p'-DDT	–	–	0.1	0.2	<0.1	<0.1
PCA	–	–	0.2	0.3	<0.1	<0.1
PCNB	–	–	0.1	0.1	<0.1	<0.1
Pendimethalin	NA	0.2	NA	<0.1	NA	<0.1
Pirimicarb	NA	<0.1	NA	0.6	NA	<0.1
Pyriproxyfen	NA	<0.1	NA	**17.7**	NA	<0.1

Toxicological data used by trophic level: Algae: chronic 96 h NOEC and 72 h EC_{50}, aquatic invertebrate: chronic 21 days NOEC and 48 h EC_{50}, Fish: chronic 21 days NOEC. PCA: Pentachloroaniline, PCNB: Pentachloronitrobenzene. NA: There is no data because it was only determined once. Therefore, the maximum concentration was used as the worst-case scenario. -: Unavailable data for that trophic level. Bold number = RQ values with potentially high risk.

According to Rodríguez-Aguilar et al. [95], an ecotoxicological potential risk assessment on algae, macroinvertebrates, and fish, found that all three trophic levels show chronic effects, mainly due to the concentrations of different pesticides. Furthermore, they indicate that the use of RQ is a viable tool for risk assessment at different trophic levels. Through the processes of biomagnification and bioaccumulation, the impact of toxic substances has been greater on animals than they are at the end of the food chain, such as birds of prey and some fish [35].

Potential risk assessment by pesticide concentrations considering an additive model could generate a more realistic picture of the problem at each study site and determine the contribution of each pesticide to the risk level. It also allows information to be generated for the implementation of regulations on the sale and use of pesticides and public policies towards the use of more sustainable alternatives in food production [96]. Based on the additive RQ model, algae showed a high potential risk at sites 4, 8, and 9, while aquatic invertebrates and fish showed a high potential risk at all study sites.

The contribution of each pesticide in the additive RQ model was determined, and the results indicate that three pesticides (heptachlor, fipronil, and cypermethrin) contributed most to the potential risk assessment for algae. For aquatic invertebrates, four pesticides were identified (chlorpyrifos, cypermethrin, chlorfenapyr, and PCA). Finally, three pesticides (chlorpyrifos, endosulfan sulfate, and cypermethrin) were identified in the potential risk assessment for fish. The persistence of these pesticides makes their elimination difficult, leading to biomagnification and/or bioaccumulation processes. Ponce-Vélez and Botello [97] analyzed the trends of organochlorine pesticides (POC) in fish, crustaceans, and mollusks on the coast of Mexico, recording the presence of endosulfan sulfate, in the three biological groups evaluated. Similarly, studies by Karbalaei et al. [98] indicate that exposure of African catfish (*Clarias gariepinus*) to chlorpyrifos leads to significant changes in muscle protein content and amino acid and fatty acid compositions. Some studies have also reported that cypermethrin can affect aquatic organisms such as fish, amphibians, and some arthropods [99–102].

According to the above, cypermethrin was the pesticide that contributed most to the potential risk assessment in the study area, as it substantially influences each trophic level (Fig. 2). It has been reported that cypermethrin has a higher lipophilicity property, making fish the most subtle, penetrating and sensitive organism due to a higher absorption rate of cypermethrin in them. Furthermore, that exposure to cypermethrin induced hematobiochemical alterations in several fish species [103].

The results from the TU_{sites} showed that the detected pesticide concentrations could be associated with acute toxic effects mainly on aquatic invertebrates and fish. However, it is important to note that the additive process for determining risk for each site needs to be considered carefully, as the result may be biased if high percentages of the same pesticide are detected, especially in long-term and intensive studies. Study sites 2 to 10 showed elevated TU_{sites} values for aquatic invertebrates, while site 10 was the only one showing elevated values for fish, which provides important information to characterize the level of contamination at the study sites.

Therefore, according to the ecological potential risk assessment conducted in this study, the trophic level of aquatic invertebrates is the most vulnerable to the detected pesticide concentration, followed by the fish level and finally the algae level. According to Cao et al. [104] ecological risk assessment in seawater for pyrethroids indicated that pyrethroids pose a high risk to aquatic invertebrates and a lower risk to other marine organisms. Although the cumulative approach used in the Toxic Units analysis indicates a high risk of acute effects on aquatic invertebrates, the situation of pesticide contamination in an aquatic ecosystem is more complex because the relationships between pesticides in a mixture are not only cumulative but also antagonistic and synergistic, which can determine the toxicity of pesticides [105,106]. However, the results shown are important because the integrity of aquatic invertebrate populations could be affected and, as they are considered a basic component of river food webs, and indicators of good water quality. Their impact

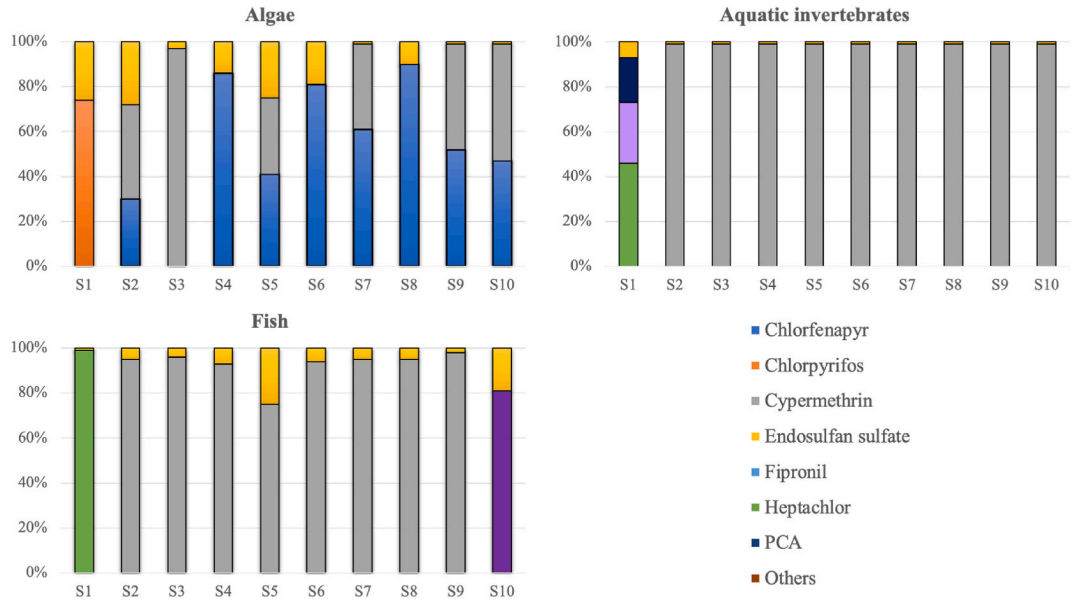

Fig. 2. Percentage contribution of the main pesticides detected per study site in the Risk Quotient (RQ) potential risk assessment.

may cause an ecological imbalance in more populations of aquatic trophic organisms and, consequently, in the structure of the aquatic ecosystem [107].

In this potential risk assessment of TU_{sites}, the major pesticide contributors are chlorpyrifos, cypermethrin, and endosulfan sulfate. Excluding the concentrations of these pesticides, no site showed a potential high-risk acute effect. Therefore, the risk shown is directly related to the presence of one of these three pesticides and not to the combination of multiple pesticides. This is consistent with the findings of Nowell et al. [108] and Covert et al. [109], who found that a small number of pesticides account for most of the toxicity in a sample, i.e. a small number of highly toxic pesticides overshadow the potentially additive effects of many pesticides. However, in other studies, such as those of Ccanccapa et al. [66] and Carazo-Rojas et al. [67], the risk was given by the sum of all the detected pesticides. This contradiction could be explained by the specificities of the study areas, related to the amount and heterogeneity of the productive activities carried out there and the type of agricultural activity (intensive or extensive). Furthermore, a study that analyzed the ecological risks associated with organochlorine pesticides in seawater, has demonstrated the importance of considering mixture risk assessments with the effects of phase-partitioning and seasonal changes for efficient oceanic risk management [110].

The results obtained in this study coincide with those published by Rodríguez-Aguilar et al. [95], since insecticides are the most influential pesticides detected in the ecological potential risk assessment, moreover, these insecticides are used in different activities such as agriculture, livestock, and domestic activities for pest control, so their use is widespread and not specific to a particular activity [103,111,112].

3.5. Limitations and future perspectives

A methodological limitation in the present investigation was that the analytical method used for the determination of the analytes only allowed the determination of the indicated compounds, since, due to lack of laboratory infrastructure, some of the pesticides reported as most used required a different type of extraction or a different and specific analytical determination (e.g. 2,4-D is determined by HPLC-UV, UPLC-MS/MS, or HPLC-DAD). Another limitation is that the study included only one year of monitoring (two seasons), so it would be necessary to extend it to a longer period to determine possible behavioral patterns or trends. In addition, the risk is assumed through toxicity data for model species at the laboratory level reported in databases, so it would be important in future studies to use native species of each trophic level for a better estimation of the risk to the aquatic ecosystem.

Finally, it should be noted that most species used in this study are freshwater species, due to the lack of relevant data for marine species. Therefore, the RQs obtained should be interpreted with caution, since possible interactions with sodium or chloride concentrations present in seawater are not included.

Moreover, further research is recommended to (1) investigate pesticide residues in other matrices such as sediments and organisms that obtaining allows a more complete picture of the problem in the studied area, (2) evaluate the intake of fishery products captured in the area that could present pesticide residues and, therefore, (3) evaluate the possible potential health risk from exposure to pesticides through the consumption of fishery products, obtained and consumed locally.

4. Conclusions

The analysis of pesticide concentrations in seawater of the coastal area of northwestern Mexico presented in this work is one of the first to address the environmental risk to aquatic ecosystems due to their presence. The pesticides detected are mainly of current used (chlorfenapyr, chlorpyrifos, cypermethrin, endosulfan, fipronil, myclobutanil, pendimethalin, PCNB, PCA, pirimicarb and pyriproxyfen). Their intensive use, both in terms of quantity and frequency, results in the presence of these compounds in a mixture.

The ecological potential risk assessment of pesticide concentrations in seawater, conducted in accordance with the RQ and TU approaches, revealed that the pesticide levels identified in these areas can exert toxic potential effects on marine algae, aquatic invertebrates, and fish. The RQ approach demonstrated that concentrations of chlorpyrifos and heptachlor may result in potential chronic effects on all three trophic levels (algae, aquatic invertebrates, and fish). Conversely, the TU approach demonstrated that the concentrations of chlorpyrifos, cypermethrin and endosulfan sulfate contributed most to the estimation of acute potential risk at each sampling site. Consequently, particular attention should be paid to the use and management of chlorpyrifos and cypermethrin due to their high detection rates in the total samples and the toxic potential effects in the biota.

Pesticide contamination of seawater in the coastal zone of northwestern Mexico is a problem that must be addressed with an integrated approach, considering economic, social, health, legal-institutional, political, and biophysical aspects, to progressively reduce their use and avoid environmental contamination, thus limiting exposure to living organisms. In addition, it is imperative to modify the prevailing system of agricultural production by transitioning towards alternative methodologies that utilize diminished or absent pesticide applications. This approach is founded upon traditional peasant knowledge, which fosters ecological and social relationships within a crop field, predicated upon a balance between ecological responsibility, economic viability, and social justice. However, the implementation of other important alternatives, such as the use of biodegradable pesticides, genetically modified crops, crop selection based on local conditions and laboratory grown crops, are all options to promote a transition to food production that is less harmful to the environment and human health.

Declaration of interest's statement

The authors declare no conflict of interest.

Data availability statement

Data will be made available on request.

CRediT authorship contribution statement

José Belisario Leyva-Morales: Writing – original draft, Validation, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Pedro de Jesús Bastidas-Bastidas:** Validation, Software, Resources, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Vilma del Carmen Salvatierra-Stamp:** Writing – review & editing, Writing – original draft, Visualization, Data curation. **Luis Carlos González-Márquez:** Validation, Conceptualization. **Yasser A. Davizon:** Writing – review & editing, Validation, Supervision, Conceptualization. **Henri Márquez-Pacheco:** Writing – review & editing, Supervision, Methodology. **Jesús Mateo Amillano-Cisneros:** Writing – review & editing, Visualization, Validation, Methodology. **Edgar Cruz-Acevedo:** Visualization, Supervision, Formal analysis, Data curation. **Bianca Anabel Amézquita-López:** Writing – review & editing, Validation, Formal analysis, Conceptualization. **Claudia Romo Gómez:** Writing – review & editing, Visualization, Supervision, Formal analysis. **Zamaria Yoselin De la Torre Espinosak:** Writing – review & editing, Visualization, Supervision, Investigation. **Brian Arturo Rodríguez-Aguilar:** Writing – original draft, Validation, Resources, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization.

Declaration of competing 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.

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Appendix A. Supplementary data

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