Review

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Mercedes Zambrano-Soria , Gladys Alejandra Toledo-Ibarra * , Carlos Eduardo Covantes-Rosales , Victor Wagner Barajas-Carrillo , Isaias Rios-Jiménez , José Belisario Leyva-Morales , Migdalia Sarahy Navidad-Murrieta , Francisco Fabián Razura-Carmona , Manuel Iván Girón-Pérez *

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Pesticide Levels in Shrimp on Mexican Coasts

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Abstract: A review of pesticide residues detected in shrimp species of the Mexican Pacific and Gulf of Mexico coasts is presented. Most studies focus on monitoring organochlorine (OC) and organophosphate (OP) pesticides. The evaluated areas are mainly located in the northwestern zone of Mexico. Studies analyzing pesticides levels in shrimp of Mexico correspond to commercially important species, such as: *Penaeus vannamei*, *Penaeus stylirostris*, *Farfantepenaeus duorarum*, and *Trachypenaeus similis pacificus*. Extraction methods (sample preparation, extraction technique, solvent, and clean-up procedures) are presented, as well as chromatography and detector type used to quantify the analytes in the shrimp samples from the different ecosystems evaluated. Given that there is an under-evaluation of pesticides residues presence, there was a greater contribution of studies directed to geographical areas in the northwest of the country, with a monitoring gap in the Gulf of Mexico, as well as in the southern zone, considering that there are states that are among the main shrimp-producing entities. Hence, it is necessary to carry out recent evaluations, since the most current information is 17 years out of date, so presented data may not be a reflection of the current situation in the country.

Keywords: pesticides; organochlorines; organophosphates; chromatography; shrimp; food safety; seafood; pollution

1. Introduction

1.1. Shrimp farming in Mexico an Overview

White shrimp (*Peneaus vanameii*) is naturally distributed from the Gulf of Mexico to Peru, inhabiting estuaries, marshes, and oceans [1]. Globally, *P. vanameii* is the most produced shrimp species, reaching 53% of the harvest [2]. In Mexico, shrimp farming is practiced semi-intensively in ponds for 8-9 months; this production system gives a yield of one ton per hectare, although the industry continues to promote technification to increase yields [3]. In Mexico, white shrimp production is mainly dominated by the northwestern states of Sinaloa, Sonora, and Nayarit (Figure 1).

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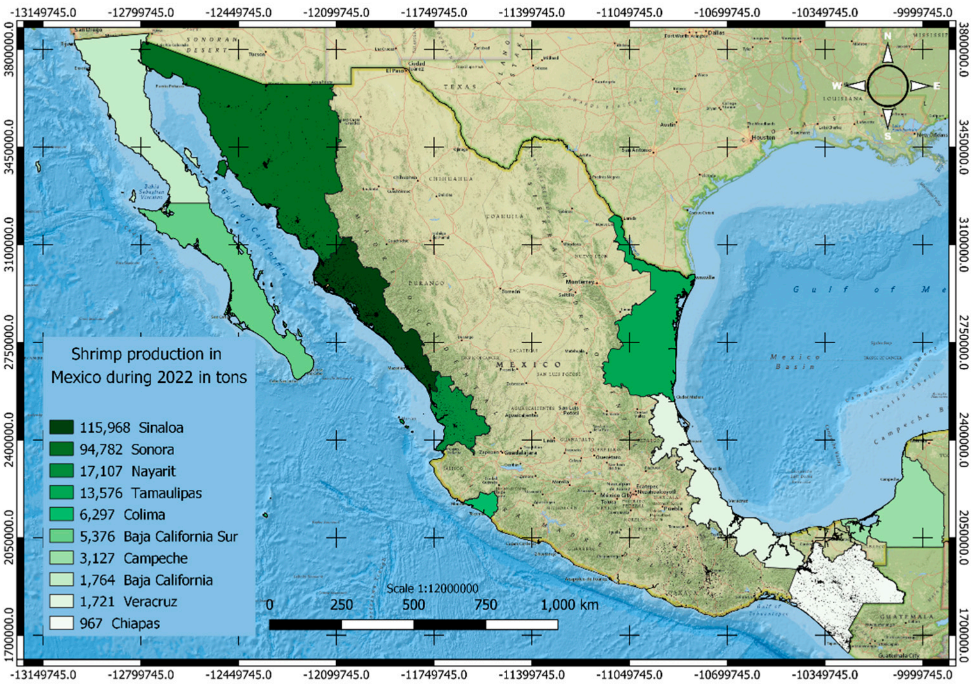

Figure 1. Shrimp production (tons) in Mexico in 2022.

Shrimp production in Mexico represented 270,000 tons in 2020, this activity is carried out through capture in estuaries and sea, as well as in shrimp farms, the latter being the most important since it represents 79.25% of the total [4]. In 2021, 262,000 tons were produced, leaving an economic impact of 277 million dollars for exports, reaching the 7th place in world production [5].

The beginnings of experimental shrimp farming in Mexico date back to the 1970s in Sonora, then it escalated to commercial farming in the 1980s, with white shrimp being farmed in the Pacific and Gulf of Mexico [6]. Subsequently, there has been an increase in the demand for land to establish shrimp farms, and this economic sector has grown at a significant rate of 5.5% per year [5].

Shrimp farming is carried out in areas where it competes with activities such as urban areas, industry, tourism, and agriculture. Therefore, land use in coastal areas is a phenomenon that inevitably overlaps, since the optimal locations for shrimp farms have not been historically selected, leading to environmental problems. As a result, the organism is exposed to pollutants such as pesticides, heavy metals, and water discharges with high organic matter load, becoming a risk for consumers [7].

2. Pesticides

Pesticides are any substance or mixture of substances, chemical or biological, used to repel, destroy or control pests. The word "pesticide" is a broad-term that includes insecticides, herbicides, fungicides, rodenticides, molluscicides, wood preservatives, and various other substances used for pest control. Pesticides also include plant growth regulators, defoliants, and desiccants [8, 9].

Pesticides can be classified according to several criteria such as functional groups, mode of action, toxicity, and chemical structure. In line with this, according to the type of target pest there are fungicides, insecticides, herbicides, and rodenticides [10, 11]. Besides, these substances are also categorized by source, either as chemical pesticides or biopesticides. Chemical pesticides are further divided into organochlorines (OC), organophosphates (OP), carbamates, pyrethroids, neonicotinoids, among others [8, 12].

It is generally accepted that pesticides play an important role in agricultural development since they can reduce agricultural products losses and improve affordable food yield and quality [11]. Pesticide use in agriculture goes back thousands of years, but pesticides have been used more widely since the 1940s due to the growth of synthetic chemical pesticides and the rapid development of biopesticides in the last decade. Today, there are more than a thousand pesticides on the market (including chemical, microbial, semi-chemical, and botanical pesticides) [13].

In addition, global pesticide production has increased at a rate of approximately 11% per year, from 0.2 million tons in the 1950s to more than 5 million tons in 2000 [12]. The use of pesticides has increased dramatically over the past 75 years and continues to increase. Approximately 2300 millions tons of pesticides are used annually worldwide [14]. Globally, the total pesticide use in agriculture will remain stable at 2.7 million tons of active ingredients in 2020. The global pesticide application rate per hectare of cropland was 1.8 kg/ha. Total trade in pesticides reached about 7.2 tons of formulated products with a value of USD 41.1 billion in 2020 [13].

Agriculture is the largest consumer (about 85% of world production) of pesticides for chemical pest control. In addition, pesticides are also used in public health activities to control vector-borne diseases (e.g., malaria and dengue), and unwanted plants (e.g., grasses and weeds) in ornamental landscaping, parks, and gardens [10].

Pesticides have different modes of action or ways of controlling target pests. Some herbicides can mimic the function of plant growth regulators, while others can effectively control the ability to convert light into food in plants. Similarly, a fungicide may interfere with cell division, while others may effectively slow the formation of certain compounds in the fungus. While a fungicide is used to control the growth of fungi, miticides, insecticides, and herbicides are used to control mites, insects, and weeds, respectively. Insecticides are capable of killing insects by direct contact (dermal entry), oral, and/or respiratory entry. Herbicides are used to kill plants by direct contact and/or by killing weeds when absorbed through the leaves, stems, or roots. Some pesticides are capable of moving into untreated tissues after being absorbed by plants or animals. Such insecticides or fungicides can enter treated plants to kill specific insects or fungi. Other pesticides have also been developed to affect the nervous system or act on the endocrine or hormonal systems of pests [10, 15].

Once pesticides are applied to a target crop or disposed of, these substances have the potential to enter the environment. Then, in the environment, pesticides can undergo processes such as transfer (or movement) and degradation. Pesticides move from the target site to other environmental media or non-target plants through transfer processes such as adsorption, leaching, volatilization, spray drift, and runoff [11]. The large amounts of pesticides that are left behind penetrate or reach non-target plants and environmental media. However, only 1% of all pesticides are effectively used to control insect pests on target crops [14].

The different types of chemicals show specific differences in environmental fate, for example, OC compounds such as DDT have low acute toxicity but show a significant ability to accumulate in tissues and persist to cause long-term damage [11]. Residues of OC are also generally transferred up the food chain, with implications for human health. The development of pest resistance to these chemicals urged for replacement with new and less persistent chemicals, such as OP, carbamate, and pyrethroid compounds, which are perceived to be more specific in pest control [12]. However, OP have been reported to be highly toxic to arthropods in general, which include insects but also shrimp, crabs, and other crustaceans, as well as vertebrates [16]. In addition, pyrethroids also have effects on insects and vertebrates [12].

In particular, pesticides accumulation in shrimp causes biochemical and physiological changes such as osmoregulation and enzymatic processes, decreased respiration rates, glycogen, and protein synthesis [17-19]. Similarly, Bamber *et al.* [20] observed a significant increase in the intensity of swimming activity in *Pandalus borealis* shrimp exposed to deltamethrin and azamethiphos. In other words, exposure to these OPs altered the mobilization capacity, which can be attributed to the mechanism of action of OPs through inhibition of the enzyme acetylcholinesterase, causing excessive accumulation of the neurotransmitter acetylcholine and cholinergic overstimulation [21]. Therefore, there is a risk that repeated pesticide discharges over time may lead to the displacement of shrimp populations [20].

In addition to the above, the physicochemical parameters of the environment can influence the toxicity of these compounds. In this sense, water salinity is a determining factor in the exposure of shrimp to pesticides, since in the case of diazinon (OP), it has been observed that the higher the

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salinity, the greater vulnerability of shrimp to the effects of this pesticide, which is observed by a limitation in the spatial distribution of organisms [22]. On the other hand, low salinity levels induce significantly higher toxicity of OP such as dimethoate and chlorpyrifos in postlarvae and juveniles of *P. vannamei* [23]. This situation must be taken into consideration because pesticide exposure is associated with various diseases such as cancer, hormone disruption, asthma, allergies, hypersensitivity, and neurodegenerative diseases [10, 24]. In this way, the contamination of aquatic systems by pesticide residues around the world has also repeatedly endangered aquatic food resources, fisheries, and aquaculture. As a result, pesticide contamination has polluted the environment and caused adverse human health effects [12].

3. Pesticide studies in shrimp in Mexico

Studies on pesticide prevalence of shrimp in Mexico are scarce and the most recent reports are from 2006. Most studies focus on monitoring OC and OP pesticides. The evaluated areas are mainly located in the northwestern zone of Mexico (Figure 1), among the ecosystems where the presence of pesticides in shrimp is reported are lagoon and/or estuarine systems in this zone, including coastal lagoons: Yavaros and La Atanasia-Santo Domingo in Sonora, Huizache-Caimanero, Teacapán, Santa María Bay, Altata-Ensenada de Pabellón, and Ohuira Bay in Sinaloa and the estuarine systems of San Cristóbal and Pozo-Rey in Nayarit [18, 25-32]. Reports from the southern part include the Tehuantepec Lagoon Complex in the state of Oaxaca and the Carretas-Pereyra and Chantuto-Panzacola in the state of Chiapas [33, 17,19]. Studies corresponding to the Gulf of Mexico are limited to the Palizada River area in the state of Campeche [34].

3.1.1. Organochlorine Pesticides Reported in the Mexican Pacific Ocean

Studies evaluating OC levels in shrimp from the Mexican Pacific correspond to commercially important species such as *P. vannamei*, *P. stylirostris*, and *T. s. pacificus*. These analyses date from 1983 to 2006, in which the following OC were reported: hexachlorobenzene (HCB), hexachlorocyclohexane (HCH) and its α, β, γ and δ isomers, heptachlor, heptachlor epoxide, endosulfan and its α, β isomers, endosulfan sulfate, aldrin, dieldrin, endrin, endrin aldehyde, alachlor-1254, chlordane, and dichlorodiphenyltrichloroethane (DDT) and its metabolites (Table 1).

Table 1. OC pesticide concentration in shrimp species from lagoon and/or estuarine systems in Mexico.

Pesticide	Concentration (ng g^{-1})	Shrimp	Location	Reference
HCH	1	*P. stylirostris* (without head and shell)	Huizache-Caimanero Lagoon, Sinaloa (Jan/ 1981)	[25]
heptachlor epoxide	0.34			
dieldrin	1.06			
DDT	0.55			
HCH	0.6	*P. vannamei* (without head and shell)	Huizache-Caimanero Lagoon, Sinaloa (Oct/ 1980)	
aldrin	0.68			
heptachlor epoxide	1.1			
dieldrin	1.88			
endrin	0.21			
DDT	0.33			
HCB	9	*P. vannamei*	Altata-Ensenada del Pabellón Lagoon, Sinaloa (1989)	[28]
p,p´-DDE	1.1			
dieldrin	1.1			
endosulfan sulfate	3			

aroclor-1254	2.7			
HCB	0.1		Altata-Ensenada del Pabellón Lagoon, Sinaloa (1991)	
β-HCH	1.3			
γ-HCH	0.08			
α- endosulfan	0.7			
p,p´-DDE	6			
dieldrin	1			
p,p´-DDT	0.5			
aroclor-1254	1.3			
DDMU	0.1			
heptachlor	19.6	*P. vannamei*	Altata-Ensenada del Pabellón Lagoon, Sinaloa (Dec/ 1997)	[18]
endosulfan sulfate	127.5			
DDE	20.5			
aldrin	2.6	*P. vannamei*	Altata-Ensenada del Pabellón Lagoon, Sinaloa (Sep/ 1998)	
α endosulfan	1.07			
endosulfan sulfate	1.9			
heptachlor	70.6	*P. vannamei*	Santa Maria Bay, Sinaloa (Dec/ 1997)	
dieldrin	15.6			
endrin	45.6			
endosulfan sulfate	106.8			
DDE	2.1	*P. vannamei*	Santa Maria Bay, Sinaloa (Sep/ 1998)	
endosulfan	11.67			
γ-HCH	BDL-132.0	*Penaeus sp*	Ohuira Bay, Sinaloa	[29]
δ-HCH	48.8-127.0			
heptachlor	18.0-127.0			
heptachlor epoxide	BDL-58			
α- endosulfan	47.0-2000.5			
DDE	19.0-29.0			
α- endosulfan	210.01	*P. vannamei*	Ohuira Bay, Sinaloa. Station 2(Sep/ 1996)	[27]
DDE	29.03			
heptachlor	126.04	*P. vannamei*	Ohuira Bay, Sinaloa. Station 4 (Sep/ 1996)	
α- endosulfan	200.44			
DDE	19			
γ-HCH	125.03	*P. vannamei*	Ohuira Bay, Sinaloa. Station 1 (Nov/ 1996)	
heptachlor	121.04	*P. vannamei*	Ohuira Bay, Sinaloa. Station 2 (Nov/ 1996)	
α- endosulfan	57.93			
γ-HCH	48.02	*P. vannamei*	Ohuira Bay, Sinaloa. Station 5 (Nov/ 1996)	
heptachlor	107.03			
α- endosulfan	194.14			
heptachlor	17.05	*P. vannamei*	Ohuira Bay, Sinaloa. Station 1 (Jan/ 1997)	
chlordane	112.51	*P. vannamei*	Ohuira Bay, Sinaloa. Station 3 (Jan/ 1997)	
γ-HCH	132.05	*P. vannamei*	Ohuira Bay, Sinaloa. Station 3 (Jan/ 1997)	
heptachlor	95.06			
α- endosulfan	59.73			

HCH	0.23	*P. stylirostris* (without head and shell)	Moroncarit Lagoon, Sonora (Jul/ 1980)	[25]
heptachlor epoxide	0.67			
dieldrin	3.87			
DDT	2			
HCH	1.71	*P. vannamei* (without head and shell)	Moroncarit Lagoon, Sonora (Jul/ 1981)	
aldrin	0.68			
heptachlor epoxide	1.1			
dieldrin	1.88			
endrin	0.21			
DDT	1.33			
HCH	0.11	*P. stylirostris* (without head and shell)	Yavaros Lagoon, Sonora (Oct/ 1980)	
heptachlor epoxide	0.21			
dieldrin	3.87			
DDT	0.85			
HCH	0.46	*P. stylirostris* (without head and shell)	Yavaros Lagoon, Sonora (Oct/ 1981)	
heptachlor epoxide	0.89			
dieldrin	0.62			
endrin	0.4			
DDT	0.8			
HCH	0.78	*T. s. pacificus* (without head and shell)	Yavaros Lagoon, Sonora (Oct/ 1981)	
heptachlor epoxide	1.24			
dieldrin	1.06			
α - HCH	1	*Penaeus sp*	Pozo Rey Estuary, Nayarit (1996-1997)	[32]
β-HCH	2.9 -7.9			
δ-HCH	15.37			
aldrin	0.9			
heptachlor epoxide	18.89			
α- endosulfan	9.54-13.33			
p,p′-DDE	0.98			
dieldrin	1.11			
endrin	9.24-12.25			
β- endosulfan	8.14			
p,p′-DDD	0.98- 25.45			
endrin aldehyde	2.45			
endosulfan sulfate	1.70- 8.99			
p,p′-DDT	3.02			
α - HCH	0.14	*Penaeus sp*	San Cristobal Estuary, Nayarit (1996-1997)	
β -HCH	9.0-33.49			
δ-HCH	0.7-13.49			
aldrin	4.05			
α- endosulfan	3			
p,p′-DDD	0.84-22.76			
endrin aldehyde	0.57			

DDT	1.53			
γ-HCH	0.2	*P. vannamei*	Sta. Rosa 1. Oaxaca	[33]
α- HCH	0.57		Sta. Rosa 2. Oaxaca	
γ-HCH	1.54			
δ-HCH	0.61			
heptachlor	0.2			
endosulfan sulfate	1.8			
α- HCH	1.5		Jaltepec 1. Oaxaca	
γ-HCH	6.71			
δ-HCH	2.77			
dieldrin	0.49			
endosulfan sulfate	2.27			
α - HCH	0.89		Jaltepec 2 A. Oaxaca	
γ-HCH	2.11			
δ-HCH	1.98			
heptachlor	1.83			
α- HCH	1.44		Jaltepec 2 B. Oaxaca	
γ-HCH	4.64			
heptachlor	5	*P. vannamei* (tissue)	Carreteras–Pereira Lagoon, Chiapas	[17]
p,p′-DDE	2			
HCH	2	*P. vannamei* (exoskeleton)		
p,p′-DDE	0.5			
δ-HCH	2.18	*P. vannamei* (exoskeleton)	Chantuto-Panzacola Lagoon, Chiapas (Feb/ 1995)	[19]
heptachlor	3.3			
p,p′-DDE	15.94			
heptachlor	4.66	*P. vannamei* (tissue)	Laguna Carretas- Pereyra Lagoon, Chiapas (Apr/ 1994)	
p,p′-DDE	1.97			
δ-HCH	1.54	*P. vannamei* (exoskeleton)		
p,p′-DDE	0.55			

BDL = below detection limit.

Most of the studies on the determination of OC in the Mexican Pacific correspond to the lagoon and/or estuarine systems of Sinaloa state (Figure 2). In the Huizache-Caimanero Lagoon, the presence of HCH, heptachlor epoxide, dieldrin, and DDT has been reported in *P. stylirostris and P. vannamei* species [25]. Galindo-Reyes *et al.* [26] analyzed shrimp from the Teacapan Estuary, where no OC residues were found. In Ohuira bay, there are two reports of OC analysis; on the one hand, Galindo-Reyes *et al.* [18] detected the following OC in shrimp samples DDE, HCH γ, chlordane, endosulfan α, and heptachlor, the latter two being the most abundant, and Osuna-Flores & Riva [29] also reported the occurrence of endosulfan α, heptachlor, DDE and HCH γ in the shrimp samples analyzed.

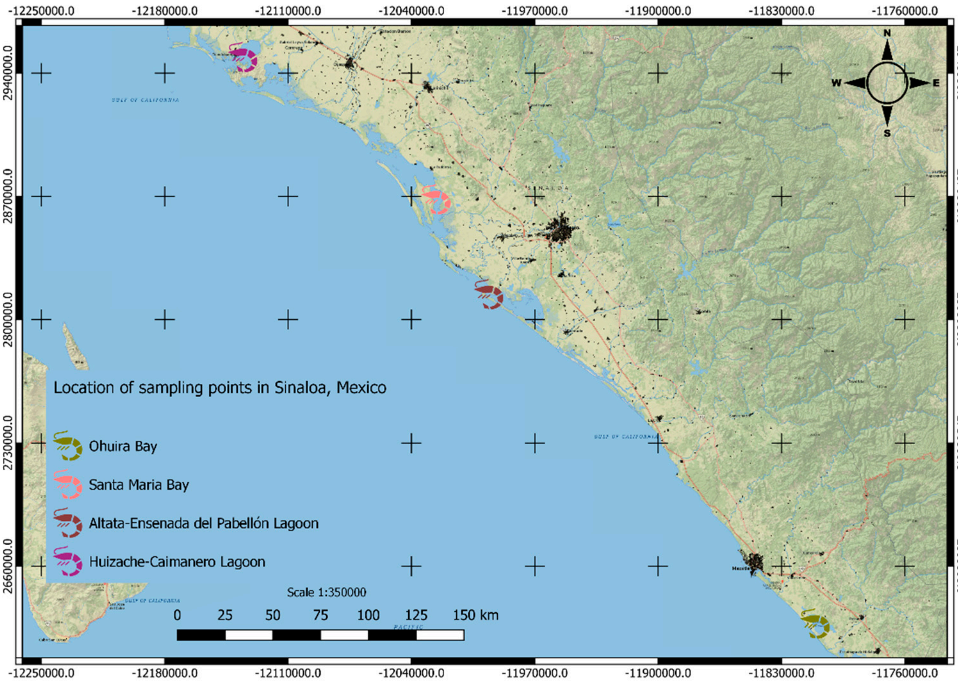

Figure 2. Reported sampling points for Sinaloa state.

In the Altata-Ensenada del Pabellón Lagoon system (Sinaloa), the following OC were detected in shrimp samples: HCB, β-HCH, γ-HCH, endosulfan *α*, *p,p´*-DDE, *p,p´*-DDT, dieldrin, and Aroclor-1254 [28], in addition to heptachlor, endosulfan sulfate, heptachlor epoxide, and DDE [18].

In Sonora, specifically in the Yavaros and Moroncarit lagoon systems (Figure 3), Rosales & Escalona. [25] reported: HCH, heptachlor epoxide, dieldrin, and DDT in three shrimp species (*P. stylirostris, P. vannamei,* and *T. s. pacificus*). Meanwhile, in the Atanasia-Santo Domingo Estuary, Burgos-Hernandez *et al*. [31] reported the presence of γ-HCH, dieldrin, endrin, and *p,p´*-DDD.

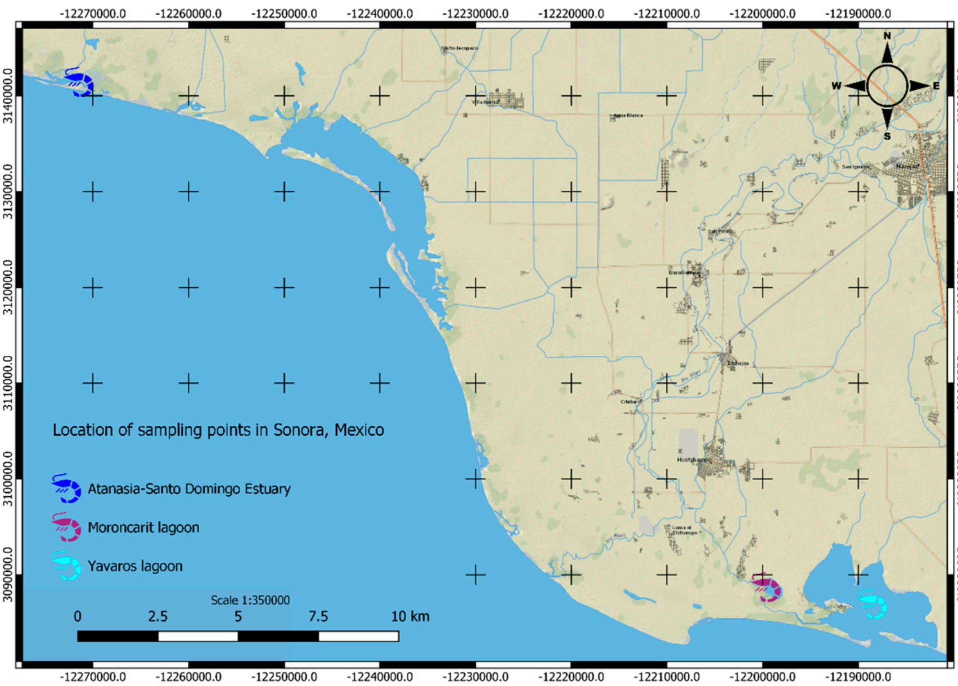

Figure 3. Reported sampling areas for Sonora state.

In the evaluation of the Pozo Rey and San Cristóbal estuaries in the state of Nayarit (Figure 4), OC were found in shrimp samples only in the Pozo Rey Estuary. There, 14 pesticide residues were

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detected (isomers α, β, y, δ of HCH, aldrin, heptachlor epoxide, endosulfan α, β, *p,p´*-DDE, *p,p´*-DDT, *p,p´*-DDD, dieldrin, endrin, endrin aldehyde, endosulfan sulfate) [32].

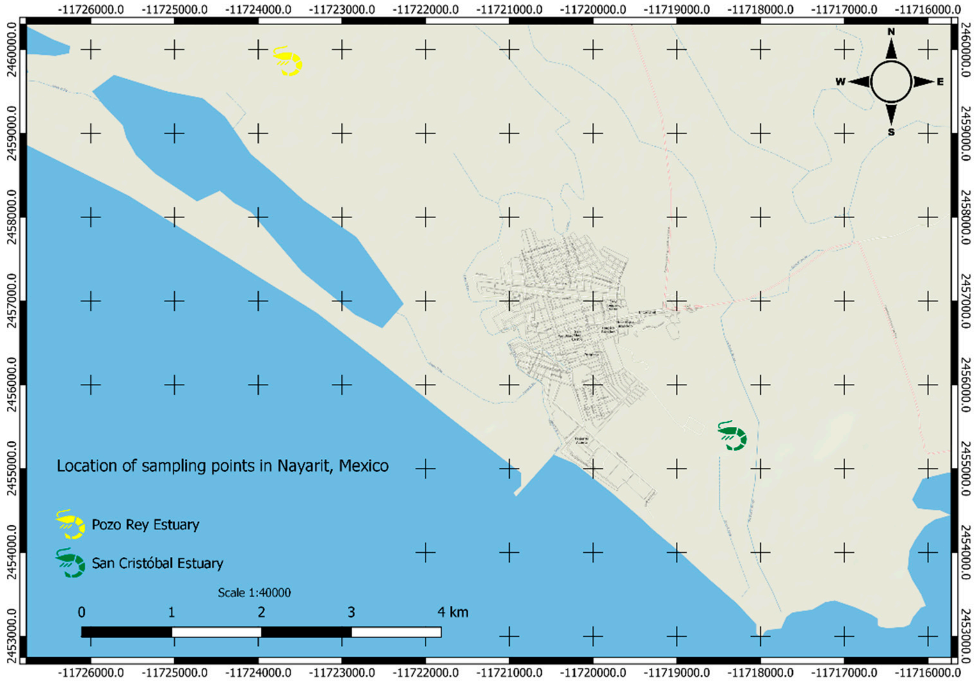

Figure 4. Reported sampling areas for Nayarit state.

Regarding southern Mexico, there are records of OC in shrimp from the Tehuantepec Lagoon Complex in Oaxaca state, specifically in the area of the western lagoon system of Jaltepec de la Mar and in the Lagartero de Santa Rosa de San Francisco de la Mar (Figure 5). At these sites, Bozada & Bejarano [33] reported the α, γ, and δ isomers of HCH, heptachlor, dieldrin, and endosulfan sulfate.

Figure 5. Reported sampling areas for Oaxaca state.

In the Carretas-Pereyra and Chantuto-Panzacola lagoons (Figure 6) located at Chiapas state, Rueda *et al.* [19] reported the presence of heptachlor and *p,p´*-DDE in the muscle and exoskeleton of shrimp from the Carretas-Pereyra Lagoons, while only HCH and *p,p´*-DDE were present in the exoskeleton. In the Chantuto-Panzacola Lagoon, OC was found only in the exoskeleton. Subsequently, in the same lagoon complex, Botello *et al.* [17] reported OC only in the exoskeleton, which is consistent with previous reports. While for the Carretas-Pereira Lagoon, the pesticides detected in muscle were heptachlor and *p,p´*-DDE and in exoskeleton δ-HCH and *p,p´*-DDE.

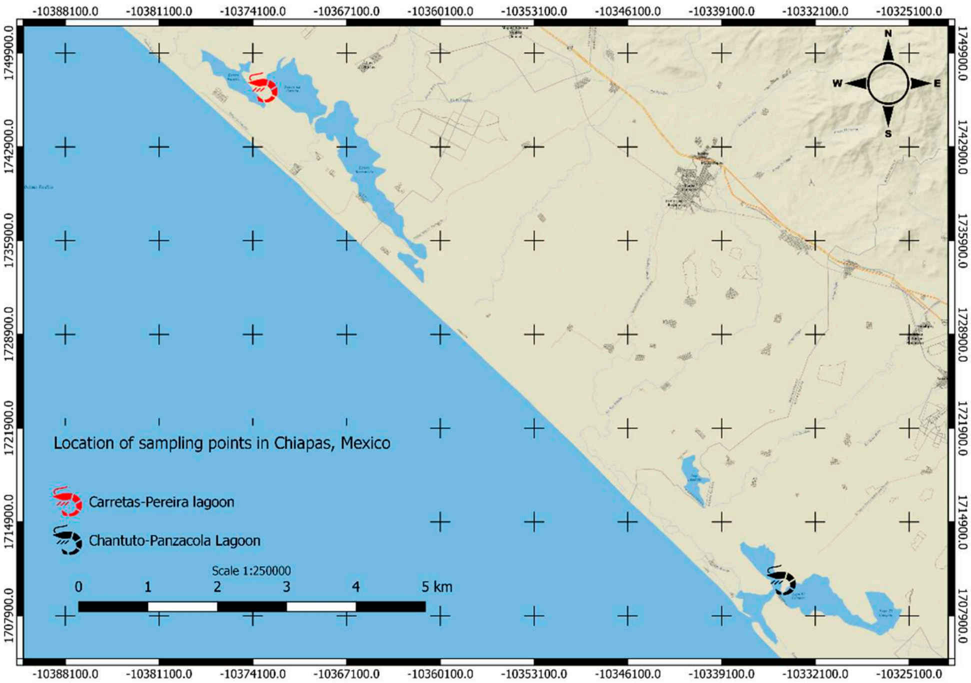

Figure 6. Reported sampling areas for Chiapas state.

3.1.2. Organophosphate pesticides reported in the Mexican Pacific Ocean

Regarding the presence of OPs in shrimp in the Mexican Pacific, the following have been reported: methyl parathion, chlorpyrifos, phorate, disulfoton, parathion, diazinon, malathion, and famphur (Table 2).

These studies correspond to shrimp samples from Ohuira Bay, Sinaloa, in which the pesticides methyl parathion, chlorpyrifos, and disulfoton, were detected [27,30]. The same is found in shrimp samples from the Atanasia-Santo Domingo Estuarie in Sonora, where chlorpyrifos, malathion, and parathion were reported [31].

Table 2. OP concentration in shrimp species from lagoon and/or estuarine systems in Mexico.

Pesticide	Concentration (ng g^{-1})	Shrimp	Location	Reference
methyl parathion	98.62	*P. vannamei*	Ohuira Bay, Sinaloa (Sep/ 1996)	[27]
methyl parathion	113.81	*P. vannamei*	Ohuira Bay, Sinaloa (Jan/ 1997)	
methyl parathion	103	*P. vannamei*	Ohuira Bay, Sinaloa (Oct/ 1997)	
chlorpyrifos	100-400	*Penaeus sp*	Ohuira Bay, Sinaloa	[30]
disulfoton	BDL-900			
phorate sulfoxide	BDL-400			
famfur	BDL-300			
chlorpyrifos	13	*Penaeus sp*	Atanasia-Santo Domingo Estuarie, Sonora	[31]

BDL = below detection limit.

3.2. Pesticides in the Gulf of Mexico

Information on OCs reported for shrimp species in the Gulf of Mexico is scarce. Information has been recorded from the state of Campeche, where the presence of these contaminants is evaluated in *Farfantepenaeus duorarum*, in which 11 OCs were found: α, γ, and δ isomers of HCH, Heptachlor, methoxychlor and DDTs (*o,p´*-DDD, *o,p´*-DDE, *o,p´*-DDT, *p,p´*-DDD, *p,p´*-DDE, *p,p´*-DDT) [35], and in *Penaeus setiferus* from the Palizada River the presence of Aroclor-1254 was detected [24].

4. Methods of extraction and identification of pesticides in shrimp in studies reported in Mexico

The studies carried out for the identification of pesticides are very old and use traditional extraction techniques that are currently rarely used and have been replaced by others that are simpler to perform and consume less time and reagents. In addition to being environmentally friendly due to the generation of less waste; on the other hand, although specific and/or selective detectors are still used today, the trend is the use of multi-residue methods coupled with mass spectrometry detectors in the different existing modalities because they allow more accurate identification of the contaminants to be evaluated under this method and the range of types of compounds that can be analyzed is wider.

Table 3 summarizes the extraction methods (sample preparation, extraction technique, solvent, and clean-up procedure), as well as the type of chromatography and detector used to quantify the analytes in the shrimp samples from the different ecosystems evaluated. In general, the samples undergo a drying process at 60 to 65 °C or freeze-drying with subsequent crushing for homogenization in a mortar and subsequent extraction with hexane for a period ranging from 4 to 8 hours. The extract is subjected to a clean-up procedure that consists of passing eluents through a column packed with various adsorbent materials used for the elimination of interferents, including silica gel (silicon dioxide), alumina (aluminum oxide), florisil (magnesium silicate), and anhydrous sodium sulfate, which are used alone or mixed in various proportions. Regarding the separation technique used, since these are volatile organic compounds, the one reported in the quantification of these pollutants is gas chromatography coupled to electron capture detectors (ECD) for organochlorine pesticides and to flame photometric detectors (FPD) and nitrogen-phosphorus detectors (NPD) for organophosphates; in addition, sometimes the use of mass spectrometry detector (MS) as a confirmation method is used.

This indicates the need for monitoring studies of pesticide residues in organisms from coastal ecosystems in Mexico, including shrimp, by using extraction and quantification techniques that allow the identification of pesticides of different chemical classes, considering both volatile and non-volatile pesticides and not only limiting them to those that can be determined by gas chromatography but extending them to the use of high-resolution liquid chromatography so that the current panorama of contamination of this type of agrochemicals in ecosystems of economic, social, and environmental importance in Mexico can be known.

Table 3. Methods of extraction and identification of pesticides in shrimp tissues.

Sample	Analyte	Area (location)	Extraction type	Extraction		Detection			Reference
				Solvent	Clean-up	Type of chromatography	Column	Detector	
Shrimp (*Penaeus vannamei and Penaeus stylirostris*) whole (without head and exoskeleton)	OC	Lagoon systems in northwestern Mexico	Soxhlet	Hexane	1^{st} deactivated alumina > Hexane 2^{nd} Deactivated silica > Hexane + 10% diethyl ether	GC	Chromosorb W/HP 80/100, 8% DC-200 y 6% QF-I	ECD ^{63}Ni	[25]
	OC	Teacapan Estuary Sinaloa (south)	Dry 60-65 °C Anhydrous sodium sulfate milling Soxhlet	Hexane	1^{st} alumina, 2^{nd} silica-gel and metallic copper	GC	4% OV-101 phase packed glass columns (2 mm x 2 m)	ECD	[26]
Shrimp (*Penaeus vannamei)*	OC and OP	Santa María Bay and Ensenada de Pabellon, Ohuira Bay, California gulf, Sinaloa, (northwest)	Dry 40-45 °C Soxhlet	Hexane	Silica gel/aluminum oxide/fluorisil/anhydrous sulfate column	GC	Restek-5x (fused silica, 30 m x 0.32 mm)	FID> OP ECD> OC	[18]
Shrimp (*Penaeus vannamei*)	Pesticides		Freeze-drying Soxhlet	Hexane	Silica gel/aluminum oxide/florisil column				[27]
Shrimp (*Peneaus spp*)	OC	Ohuira Bay	Dry Soxhlet	Hexane	Alumina column/ silica gel deactivated/ sodium sulfate	GC	Restek-5x (fused silica, 30 m x 0.32 mm)	ECD	[29]

Shrimp (*peneaus vannamei*)	OC and OP	Altata-Ensenada de Pabellon Sinaloa Lagoons, México	Soxhlet	Hexane	Inactivated Florisil	GC	Capillary column	ECD> OC FPD, NPD > OP Confirmation> MS	[28]
Shrimp (*Peneaus spp*)	OP	Ohuira Bay	Dry (60-65 °C) Mortar grinding Soxhlet	Hexane	Alumina column, silica/sodium sulfate/silica gel	GC	Restek RTX-5. 5 % diphenyl-95% dimethylpolysiloxane (30 m x 0.25 mm)	FID	[30]
Aquaculture shrimps	OC	Laguna La Atanasia-Santo Domingo, Cajeme, Sonora, Mexico	Dry (60-65 °C) Soxhlet	Hexane	Silica gel/aluminum oxide/fluorisyl/anhydrous sodium sulfate column	GC	Durabon 608 (30 mm × 0.32 mm)	ECD	[31]
	OC	Estuarine system (San Cristóbal and Pozo-Rey) San Blas coast, Nayarit, Mexico	Dry (60 °C) Mortar grinding Soxhlet	Hexane	Florisil column and anhydrous sodium sulfate	GC	Capillary column SPB-5 (30 m × 0.25 mm x 0.25 µm)	ECD ^{63}Ni	[32]
Shrimp (*Penaeus setiferus*).	OC	Palizada River, Campeche, Mexico (Gulf of Mexico)	Soxhlet (8h) Kuderna-Danish concentrator or Freeze-drying	Hexane	Florisil column	GC	Capillary column SE-54 (30 m×200 µm)	ECD	[34]
Shrimp (*Farfantepenaeus duorarum*)	OC	Campeche, Mexico	Soxhlet (8h)	Hexane/Dichloromethane	Column chromatography with	GC	ND	ECD	[35]

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	(Gulf of Mexico)	Kuderna-Danish concentrator		silica gel and alumina. Size exclusion column.	

Gas Chromatography (GC). Flame Ionization Detectors (FID). Electron Capture Detector (ECD), Photometric Flame Detector (FPD). Nitrogen-phosphorus detector (NPD). Mass spectrometry detector with electron impact detection and chemical ionization (MS), Not described (ND).

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5. Conclusions

The present review may not be a reflection of the current situation in the country, because there is an under-evaluation of the presence of pesticides, since there was a greater contribution of studies directed to geographical areas in the northwest of the country, with a lack of monitoring in the Gulf of Mexico, as well as in the southern zone, considering that there are states that are among the main shrimp-producing entities (Baja California, Baja California Sur, and Colima). In addition, it is necessary to carry out recent evaluations, since the most current information is 17 years out of date. Likewise, information on the toxic effect of pesticides on this type of crustacean is scarce, so it is necessary to carry out toxicity studies concerning the effects of growth, immunocompetence, and bioaccumulation/biomagnification in these organisms, as well as considering the environmental conditions in which they grow (temperature, salinity, pH, dissolved oxygen, among others).

Given the economic importance of shrimp, it is necessary to analyze the presence of pesticides, and the location of new shrimp farms should be carefully studied to avoid the use of water containing residues of these contaminants, thus preventing an economic disaster for shrimp farming, as well as exposing the population to pesticide residues ingested in the diet through their consumption, since one of the main routes of exposure is ingestion, which is a cause for concern for their presence in food.

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References

1. Food and Agriculture Organization of the United Nations (FAO). FAO Yearbook of Fishery and Aquaculture Statistics 2007; FAO, 2009. Available online: https://www.fao.org/documents/card/es/c/974997d3-409e-556b-808d-9f0c9f1d3022/ (accessed on 22 January 2023)
2. OECD Review of Fisheries. OECD publishing. 2017. Available online: https://one.oecd.org/document/TAD/FI(2017)14/FINAL/En/pdf
3. Vázquez-Vera, L.; Chávez-Carreño, P. Diagnóstico de la acuacultura en México; Fondo Mexicano para la Conservación de la Naturaleza, A.C: México, 2022. Available online: https://www.researchgate.net/profile/Leonardo-Vazquez-Vera/publication/361250469_Diagnostico_de_la_acuacultura_en_Mexico/links/62a63e6f55273755ebe7acfd/Diagnostico-de-la-acuacultura-en-Mexico.pdf
4. Comisión Nacional de Acuacultura y Pesca (CONAPESCA). Anuario Estadístico de Acuacultura y Pesca 2020. 2020. Available online: https://nube.conapesca.gob.mx/sites/cona/dgppe/2020/ANUARIO_ESTADISTICO_DE_ACUACULTURA_Y_PESCA_2020.pdf (accessed on 22 January 2023)
5. Servicio de Información Agroalimentaria y Pesquera (SIAP). Panorama Agroalimentario 2022. 2022. Available online: https://www.gob.mx/siap/acciones-y-programas/panorama-agroalimentario-258035 (accessed on 15 January 2023)
6. Instituto Nacional de Pesca. Acuacultura Camarón blanco del Pacífico. 2018. Available online:https://www.gob.mx/inapesca/acciones-y-programas/acuacultura-camaron-blanco-del-pacifico. (accessed on 28 April 2023)
7. Chávez Sánchez, M. C.; Higuera Ciapara, I. Manual de buenas prácticas de producción acuícola de camarón para la inocuidad alimentaria. Centro de Investigación en Alimentación y Desarrollo, A.C: Unidad

Mazatlán en Acuicultura y Manejo Ambiental y el Servicio Nacional de Sanidad, Inocuidad y Calidad Agroalimentaria, 2003. https://cesasin.mx/wp-content/uploads/2017/12/Cam-Manual-de-buenas-practicas-de-producción-acuicola-de-camarón-para-la-inocuidad-alimentaria.pdf

8. Abubakar, Y.; Tijjani, H.; Egbuna, C.; Adetunji, C. O.; Kala, S.; Kryeziu, T. L.; Ifemeje, J. C.; Patrick-Iwuanyanwu, K. C. Pesticides, History, and Classification. En Natural Remedies for Pest, Disease and Weed Control; Elsevier, 2020; pp 29–42. https://doi.org/10.1016/B978-0-12-819304-4.00003-8
9. Food and Agriculture Organization of the United Nations (FAO). Q&A on Pests and Pesticide Management. Food and Agriculture Organization of the United Nations, 2021. https://www.fao.org/newsroom/detail/Q-A-on-Pests-and-Pesticide-Management/en. (accessed on 15 January 2023)
10. Kim, K.-H.; Kabir, E.; Jahan, S. A. Exposure to pesticides and the associated human health effects. Sci. Total Environ. 2017, 575, 525–535. https://doi.org/10.1016/j.scitotenv.2016.09.009
11. Tudi, M.; Daniel Ruan, H.; Wang, L.; Lyu, J.; Sadler, R.; Connell, D.; Chu, C.; Phung, D. T. Agriculture Development, Pesticide Application and Its Impact on the Environment. Int. J. Environ. Res. Public Health 2021, 18 (3), 1112. https://doi.org/10.3390/ijerph18031112
12. Carvalho, F. P. Pesticides, environment, and food safety. Food Energy Secur. 2017, 6 (2), 48–60. https://doi.org/10.1002/fes3.108
13. Food and Agriculture Organization of the United Nations (FAO). Pesticides use, pesticides trade and pesticides indicators; FAO, 2022. https://doi.org/10.4060/cc0918en
14. Hayes, T. B.; Hansen, M.; Kapuscinski, A. R.; Locke, K. A.; Barnosky, A. From silent spring to silent night: Agrochemicals and the anthropocene. Elem Sci Anth. 2017, 5. https://doi.org/10.1525/elementa.246
15. Mnif, W.; Hassine, A. I. H.; Bouaziz, A.; Bartegi, A.; Thomas, O.; Roig, B. Effect of endocrine disruptor pesticides: a review. Int. J. Environ. Res. Public Health. 2011, 8(6), 2265-2303. https://doi.org/10.3390/ijerph8062265
16. Bernal-González, K. G., Covantes-Rosales, C. E., Camacho-Pérez, M. R., Mercado-Salgado, U., Barajas-Carrillo, V. W., Girón-Pérez, D. A., ... & Girón-Pérez, M. I. Organophosphate-Pesticide-Mediated Immune Response Modulation in Invertebrates and Vertebrates. Int. J. Mol. Sci.. 2023, 24(6), 5360. https://doi.org/10.3390/ijms24065360
17. Botello, A. V.; Rueda-Quintana, L.; Díaz-González, G.; Toledo, A. Persistent Organochlorine Pesticides (POPs) in Coastal Lagoons of the Subtropical Mexican Pacific. Bull. Environ. Contam. Toxicol. 2000, 64 (3), 390–397. https://doi.org/10.1007/s001280000013
18. Galindo-Reyes, J. G.; Fossato, V. U.; Villagrana-Lizarraga, C.; Dolci, F. Pesticides in Water, Sediments, and Shrimp from a Coastal Lagoon off the Gulf of California. Mar. Pollut. Bull. 1999a, 38 (9), 837–841. https://doi.org/10.1016/S0025-326X(99)00086-7
19. Rueda, L.; Botello, A. V.; Diaz, G. Presencia de plaguicidas organoclorados en dos sistemas lagunares del estado de Chiapas, México. Rev. Int. de Contam. Ambient. 1997, 13 (2), 55–61. https://www.revistascca.unam.mx/rica/index.php/rica/article/view/32823
20. Bamber, S.; Rundberget, J. T.; Kringstad, A.; Bechmann, R. K. Effects of simulated environmental discharges of the salmon lice pesticides deltamethrin and azamethiphos on the swimming behaviour and survival of adult Northern shrimp (Pandalus borealis). Aquatic Toxicology 2021, 240, 105966. https://doi.org/10.1016/j.aquatox.2021.105966
21. Lewchenko, V., Hariharan, P. C., Koski, W. S., & Kaufman, J. J. . Quantum chemical calculations for understanding and predicting toxicity. II. The phosphorylation step in the inhibition of ache by organophosphorus anticholinesterases. Int J Quantum Chem . 1982, 22(S9), 275-280. https://doi.org/10.1002/qua.560220725
22. Mena, F.; González-Ortegón, E.; Solano, K.; Araújo, C. V. The effect of the insecticide diazinon on the osmoregulation and the avoidance response of the white leg shrimp (Penaeus vannamei) is salinity dependent. Ecotoxicol. Environ. Saf 2020, 206, 111364. https://doi.org/10.1016/j.ecoenv.2020.111364
23. Pawar, A. P.; Sanaye, S. V.; Shyama, S.; Sreepada, R. A.; Dake, A. S. Effects of salinity and temperature on the acute toxicity of the pesticides, dimethoate and chlorpyrifos in post-larvae and juveniles of the whiteleg shrimp. Aquaculture Reports 2020, 16, 100240.https://doi.org/10.1016/j.aqrep.2019.100240
24. Mostafalou, S.; Mohammad, A. The link of organophosphorus pesticides with neurodegenerative and neurodevelopmental diseases based on evidence and mechanisms. Toxicology 409. 2018, 44-52. https://doi.org/10.1016/j.tox.2018.07.014
25. Rosales, M. T. L.; Escalona, R. L. Organochlorine residues in organisms of two different lagoons of Northwest Mexico. Bull. Environ. Contam. Toxicol. 1983, 30 (1), 456–463. https://doi.org/10.1007/BF01610160
26. Galindo-Reyes, J. G.; Guerrero Ibarra, M. A.; Villagrana Lizárraga, C.; Quezada Urenda, L. G. Contaminación por plaguicidas en agua, sedimentos, camarón y almeja, de dos ecosistemas costeros de Sinaloa, México. Trop. Ecol.1992, 33 (2), 172–180.

27. Galindo-Reyes, J. G.; Villagrana L., C.; Alvarez, G. L. Environmental Conditions and Pesticide Pollution of Two Coastal Ecosystems in the Gulf of California, Mexico. Ecotoxicol. Environ. Saf. 1999, 44 (3), 280–286. https://doi.org/10.1006/eesa.1999.1836
28. Carvalho, F. P.; Gonzalez-Farias, F.; Villeneuve, J. P.; Cattini, C.; Hernandez-Garza, M.; Mee, L. D.; Fowler, S. W. Distribution, Fate and Effects of Pesticide Residues in Tropical Coastal Lagoons of Northwestern Mexico. Environ Technol. 2002, 23 (11), 1257–1270. https://doi.org/10.1080/09593332308618321
29. Osuna-Flores, I.; Riva, M. C. Organochlorine Pesticide Residue Concentrations in Shrimps, Sediments, and Surface Water from Bay of Ohuira, Topolobampo, Sinaloa, Mexico. Bull. Environ. Contam. Toxicol. 2002, 68 (4), 532–539. 10.1007/s001280287
30. Osuna-Flores, I.; Riva, M. C. Plaguicidas organofosforados en camarones, sedimento y agua superficial de la Bahía de Ohuira, Topolobampo, Sinaloa, México. Afinidad 2004, 61 (513), 387–392. Available online: https://www.researchgate.net/publication/286073797_Organophosphorous_pesticide_in_shrimps_sediments_and_surface_water_from_bay_of_Ohuira_Topolobampo_Sinaloa_Mexico
31. Burgos-Hernández, A.; Zapién, M. G. L.; Madrid, M. L. A.; Sifuentes, C. O. G.; Gil, C. I. M.; Burgos, E. C. R.; Olivas, R. R. Presence of insecticides in shrimp farms adjacent to the sea of cortes: detection, quantification, and toxicity testing. Eur. Food Res. Technol. 2006, 222 (3-4), 380–384. https://doi.org/10.1007/s00217-005-0012-3
32. Robledo-Marenco, M. L.; Botello, A. V.; Romero-Banuelos, C. A.; Diaz-Gonzalez, G. Presence of persistent organochlorine pesticides in estuaries of the subtropical Mexican Pacific. Int. J. Environ. Pollut. 2006, 26 (1/2/3), 284. DOI: https://doi.org/10.1504/IJEP.2006.009112
33. Bozada, R. L. M.; Berajano, G. F. Los contaminantes orgánicos persistentes en el istmo mexicano 2006, Mexico: International POPs Elimination Network (IPEN). https://www.rapam.org/wp-content/uploads/2015/12/Los-Contaminantes-Istmo-Opti.pdf
34. Gold-Bouchot, G.; Silva-Herrera, T.; Zapata-Pérez, O. Chlorinated pesticides in the Rio Palizada, Campeche, Mexico. Mar. Pollut. Bull. 1993, 26 (11), 648–650. https://doi.org/10.1016/0025-326X(93)90505-E
35. Vidal-Martínez, V. M.; Aguirre-Macedo, M. L.; Del Rio-Rodríguez, R.; Gold-Bouchot, G.; Rendón-von Osten, J.; Miranda-Rosas, G. A. The pink shrimp Farfantepenaeus duorarum, its symbionts and helminths as bioindicators of chemical pollution in Campeche Sound, Mexico. J. Helminthol. 2006, 80 (2), 159–174. https://doi.org/10.1079/JOH2006358
36. Maia, M.L.; Delerue-Matos, C.; Calhau, C.; Domingues, V.F. Validation and Evaluation of Selected Organic Pollutants in Shrimp and Seawater Samples from the NW Portuguese Coast. Molecules 2021, 26 (19), 5774. https://doi.org/10.3390/molecules26195774