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Agrochemical loading in drains and rivers and its connection with pollution in coastal lagoons of the Mexican Pacific

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Abstract The state of Sinaloa in Mexico is an industrialized agricultural region with a documented pesticide usage of 700 t year^{-1}; which at least 17 of the pesticides are classified as moderately to highly toxic. Pollutants in the water column of rivers and drains are of great concern because the water flows into coastal lagoons and near-shore waters and thereby affects aquatic organisms. This study was done in four municipalities in the state of Sinaloa that produce food intensively. To investigate the link between pollution in the lagoons and their proximity to agricultural sites, water was sampled in three coastal lagoons and in the rivers and drains that flow into them. Seawater from the Gulf of California, 10 km from the coast, was also analyzed. Concentrations of nutrients, organochlorines, and organophosphorus pesticides were determined. Nutrient determination showed an unhealthy environment with N/P ratios of <16, thus favoring nitrogen-fixing cyanobacteria. The organochlorine pesticides showed a clear accumulation in the coastal lagoons from the drains and rivers, with ΣHCH showing the highest concentrations. In the southern part of the region studied, pollution of the coastal lagoon of Pabellones could be traced mainly to the drains from the agricultural sites. Accumulation of OC pesticides was also observed in the Gulf of California. Tests for 22 organophosphates revealed only five (diazinon, disulfoton, methyl parathion, chlorpyrifos, and mevinphos); diazinon was detected at all the sites, although methyl parathion was present at some sites at concentrations one order of magnitude higher than diazinon.

Keywords Organochlorine pesticides · Organophosphorus pesticides · Nutrient loading · Coastal lagoons · Agricultural pollution · Mexican Pacific · Sinaloa · Gulf of California

Introduction

The increased use of pesticides and synthetic fertilizers in intensive agriculture has adversely affected food safety and the environment. According to the Global Environment Facility, the greatest threat to aquatic systems is chemical contamination. In Mexico in 2013, 37,455 t of pesticides per hectare was applied (FAO 2016). Furthermore, several pesticides banned in other countries for their toxicity to humans, pollinators, and the environment continue to be used in Mexico and are still allowed in the official catalog of pesticides issued by the Inter-Secretariat Commission for the Control Process and Use of Pesticides, Fertilizers and Toxic Substances (CICLOPAFEST 2002). Owing to the lack of regulation and monitoring, there is no detailed information on the use of these substances and it is difficult to monitor their effects. Within Mexico, Sinaloa is a highly industrialized agricultural state with >1,250,000 ha of croplands

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(SIAP and SAGARPA 2015) and ranks first in grain production. Food production is concentrated in the municipalities of Guasave, Ahome, Culiacan, and Navolato. Hernandez and Hansen (2011) reported the use of agrochemicals in Sinaloa to be ~700 t year^{-1}, including 17 pesticides considered by WHO (2009) to be moderately to highly toxic. This intensive use of agrochemicals has polluted water bodies and sediments in the area between the Culiacan River and the Pabellones lagoon, where pollution by ammonia and total phosphorus in the 1990s was reported (Guerrero Galván 1998). In other areas of the Culiacan valley, pollution by organic compounds such as methyl parathion, disyston, malathion, and the persistent organic pollutants lindane, endrin, DDT, and hexachlorocyclohexane (HCH) has also been reported (CEC Commission for the Environmental Cooperation 2009). The environmental consequences include their bioaccumulation in the food web and alteration of aquatic ecosystems in both fresh and coastal waters. For example, shrimp farms, an important activity for the state, have been affected by the presence of agrochemicals such as organochlorine pesticides (HCH, endosulfan, chlordane, heptachlor, aldrin, dieldrin, and endrin); organophosphates (dichlorvos, diazinon, parathion-methyl parathion, malathion, chlorpyrifos, and ethion); PCB-28, PCB-138, and PCB-52 isomers; and fipronil in sediments (García-de la Parra et al. 2014). More recently, Vargas-Gonzalez et al. (2016) showed the bioaccumulation of organochlorine pesticides in clams in coastal lagoons of the Gulf of California.

Regarding fertilizers, the most frequently used have been urea, monoammonium phosphate, and ammonium gas (González-Farias et al. 2014). Overloading of both nitrogen and phosphorus has been associated with altered biogeochemical cycles as well as eutrophication and dead zones close to coastal areas (Dìaz et al. 2009). Phosphorus in particular is often the key factor in freshwater environments, while nitrogen is a pollutant that extends into seawater and is therefore the nutrient of concern in coastal water pollution (Khan et al. 2014). Although algal blooms can be a natural phenomenon caused, for example, by seasonal changes in the mixing of the water column, in the availability of light, or in the rise of nutrients from the deep ocean (Lewitus et al. 2012), they can also be caused by anthropogenic nutrient overload (Heisler et al. 2008). The coast of Mexico, together with the rest of the western coast of North America, has been suffering from harmful algal blooms at least since 1979 (Lewitus et al. 2012), but this has rarely been studied on the coasts of the Mexican Pacific Ocean.

This study aimed to determine the nutrient and agrochemical loading in surface water bodies of the northern region of Sinaloa, where pollution from agricultural activity affects the environment both in rivers and in coastal lagoons; previous papers (Montes et al. 2012; Osuna-Flores and Riva 2002; Carvalho et al. 2002) have focused on sediments, but a water-orientated study will help to assess the possible bioavailability of the pesticides for the aquatic organisms (farmed and naturally occurring) in the region. In this paper, we focus on the rivers El Fuerte, Sinaloa, and Culiacan and three wastewater drains from agricultural fields in the northern region of Sinaloa, as well as on seawater samples from the Gulf of California.

Materials and methods

Selection of sampling stations was based on the degree of land cover by agriculture adjacent to drains and rivers that discharge directly into coastal lagoons; this sought to assess the influence of these inland sources on the coastal lagoons.

Sampling encompassed four municipalities in the state of Sinaloa with important food production: Ahome, Guasave, Navolato, and Culiacan. The sampled sites were three replicates, all within 100 m of each other, taken from each of the stations, e.g., three rivers, three agricultural drains and three coastal lagoons (Fig. 1). All drains were made of concrete, and no municipal discharges were apparent. Additional samples were taken from three sites in the Gulf of California (10 km off the coast of the El Fuerte river at a depth of 10 m). Fieldwork was conducted in August 2015 as a single event.

Seven water quality variables were registered in triplicate with a multiparameter device for each sampling site (Hanna Instruments HI9828): dissolved oxygen (DO), pH, temperature, conductivity, salinity, total dissolved solids, and redox potential. Surface water samples were collected in a van Dorn bottle at half the water column depth. Samples were stored in 4-L amber crystal bottles. Samples for nutrient analysis (ammonium, nitrate, nitrite) were collected in 1-L high-density polypropylene bottles and were filtered through a 10-nm pore membrane before measurement. All samples were transported and stored at 4 °C until analysis.

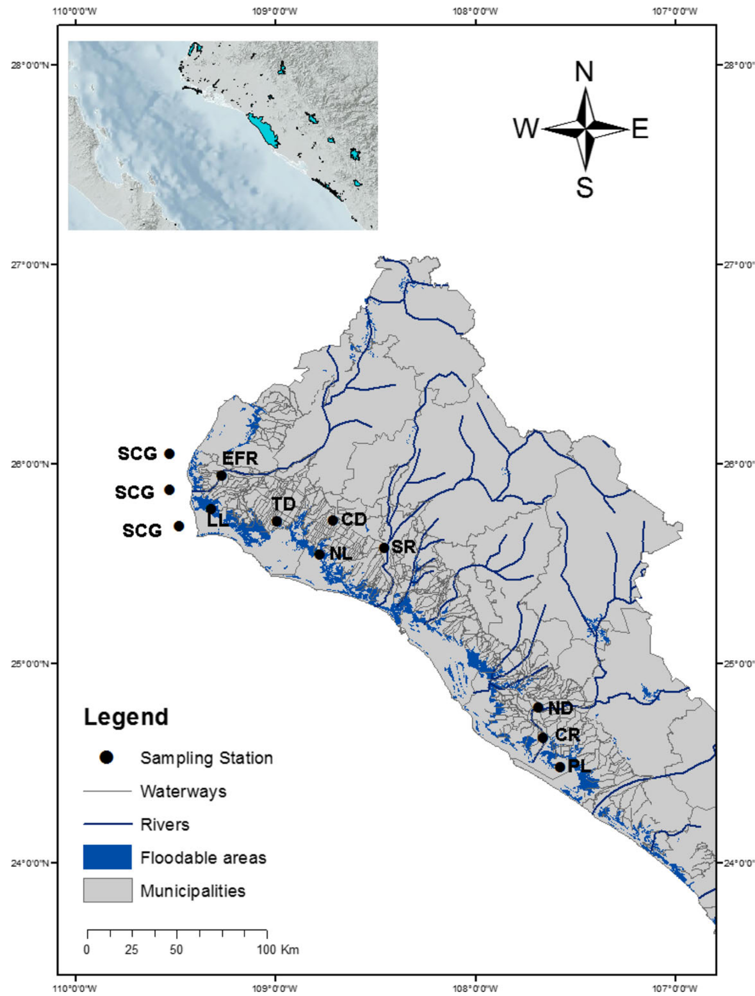

Fig. 1 Sampled stations in the northern region of Sinaloa. *SCG* Gulf of California South, *EFR* El Fuerte river, *TD* Topolobampo drain, *SR* Sinaloa river, *CR* Culiacan river, *LL* Lechugillas lagoon, *PL* Pabellones lagoon, *NL* Navachiste Lagoon, *CD* Cortinez drain, *ND* Navolato drain

Ammonium, nitrate, nitrite, and phosphorus in the rivers and drains were measured by photometric multiparameter meter (Hanna Instruments 83214). Nitrite and nitrate in the coastal lagoons were measured with an EXO2 multiparameter sonde from YSI Inc. (China). Organochlorine pesticides (OC) in water samples were determined by liquid-liquid extraction (EPA 351OC) and gas chromatography (Agilent HP 5890), equipped with an electron capture detector (GC-ECD) coupled to a specialized OC column (Restek Rtx CL-11141 Pesticides and RTX 11324 Pesticides CL-30, 0.32 mm ID and 0.25 μm thick). GC conditions were as specified in EPA 8081B: briefly, the carrier gas was helium with an injector temperature of 225 °C in split/splitless mode, a detector temperature of 300 °C, the ramp initiated at 100 °C held for 2 min, then 100 to 160 °C at 15 °C/min, followed by 160 to 270 °C at 5 °C/min to a final temperature of 270 °C. Determination of concentrations used the standards DDT, DDE, DDD, aldrin, dieldrin, aldehyde endrin, heptachlor, epoxide heptachlor, α-HCH, β-HCH, γ-HCH (lindane), δ-HCH, α-endosulfan, β-endosulfan, and endosulfan sulfate (Pesticide mixture 5, Chem Service). Organophosphorus pesticides (OP) were determined by liquid-liquid extraction (EPA 3510c) using a gas chromatograph (Agilent 6890) equipped with a nitrogen-phosphorus detector (CG-NPG) coupled to an OP-specific column (Restek Rtx OPP-11243 Pesticides 30 m, 0.25 mm ID, and 0.25 μm thick). Determination of their concentrations used the standards dichlorvos (DDVP), mevinphos, demeton O and S, tributyl phosphate, ethoprophos, phorate sulfoxide, naled, diazinon, disulfoton, methyl parathion, chlorpyrifos (Dursban), fenchlorphos (Ronnel), fenthion, trichloronate, tetrachlorvinphos (Stirofos), tokuthion (prothiofos), merphos, sulprofos, fensulfothion, azinphos-methyl

(Gusathion), and coumaphos from Restek Analytical Reference Materials Catalog 32277 OP Pesticide Calibration Mix A32277. The recoveries for all pesticides ranged from 87 to 100% for a prepared solution with OC and OP standards in distilled water, and relative standard deviations (RSDs) did not exceed 5.7%. Experimentally, the method limit of detection (LOD) was acquired by sevenfold extraction of the smallest standard mixture added of each pesticide through the whole procedure, where the LOD was calculated as $LOD = 3 \times RSD \times$ mean concentration detected (SANCO/3131/2009) with blank subtraction when necessary.

Results and discussion

Physicochemical parameters

In general, the rivers and drains had slow flows and high concentrations of suspended solids. Riparian vegetation was abundant on the rivers as well on the lagoons. In rivers and drains (Table 1), temperatures ranged from 31 to 34 °C with dissolved oxygen levels in the range of 4 to 5 mg L^{-1} and pH between 6.6 and 7.2. Drains were generally slightly acid. Conductivity, salinity, and total dissolved solids were higher in the rivers than in drains, with the highest being in the El Fuerte river. Negative redox potentials in all samples indicated reducing environments, particularly in the Culiacan river and Navolato drain. These physicochemical properties of water bodies can greatly influence the toxicity of pollutants (McCarty and Mackay 1993). Required values of dissolved oxygen, pH, and temperature have been established in the National Guideline for surface water quality (Ley Federal de Derechos 2016); only the Topolobampo drain had values slightly lower than specified for dissolved oxygen.

Nutrients

At every station, at least one sample exceeded the maximum allowed by the Mexican guidelines for the protection of aquatic life for both fresh and coastal waters (Table 2). There was also a clear accumulation of nitrate and ammonium, which suggests impairment of the nitrogen cycle; this is concerning, since shifts in abundance of a single nitrogen species can greatly reduce biological diversity. In general, wide nutrient ranges were found in the rivers compared with those in the drains, suggesting that the rivers have a more dynamic distribution of the nutrients among the various compartments of the system (soil, surface water, groundwater, sediments, and atmosphere) and the main environmental variables that modulate the chemical equilibria. Drains have less sediment and no riparian processes (Burt et al. 1999; Ranalli and Macalady 2010), and hence had narrower ranges of nutrient concentrations (Table 1). Although nutrient load was expected to be higher in the drains than in the rivers, this was not observed; this suggests that nutrient loading in the coastal lagoons can be carried from both rivers and drains. Nitrate and nitrite concentrations in the coastal lagoons were an order of magnitude lower than in the rivers and drains, and did not exceed the Coastal Water Aquatic Life Protection guidelines. However, even these relatively low levels are likely to encourage algal blooms. O'Neilland et al. (2015) found that NO_3-N concentrations of <0.1 mg L^{-1} can under certain conditions lead to excessive growth of opportunistic algae; indeed, between March and August, blooms of *Gymnodinium catenatum* are common in lagoons on the Mexican Pacific coast such as Pabellones (Band-Schmidt et al. 2010). Piñon et al. (2009) found that nutrients from several sources are being used by macroalgae in the harmful algal blooms on these coasts, although it is not known whether this reflects the direct influence of the nitrogen loads or whether the algae are selective with regard to the nitrogen chemical species.

As for phosphorus, phosphate species were, as expected, dominant. For most lakes, streams, reservoirs, and estuaries, concentrations of >100 μg total P L^{-1} are unacceptably high and even 20 μg L^{-1} can be a problem (Correll 1998). The values recorded in this study were below this threshold.

Overall, the nutrient imbalances recorded here may affect the river environment, and this in turn could affect the coastal lagoons. The nitrogen/phosphorus ratio was <16 at all sites; hence, nitrogen was in deficit, and these low ratios indicate conditions favorable for nitrogen-fixing cyanobacteria. The N/P ratios in these rivers were between 6.1 and 1.8; according to Downing (1992), N/P ratios between 3.3 and 0.8 are characteristic of sediments of oligotrophic and eutrophic lakes and effluents from sewage and septic tanks. As for the drains, their range of 0.7 to 1.0 falls outside the N/P values of 20 from agricultural watersheds and of 7.9 on average for fertilizers suggested by Downing (1992), and so these drains may reflect more than solely agricultural inputs.

Table 1 Physicochemical parameters recorded at the sampling stations in rivers and drains of Sinaloa, August 2015

		Dissolved oxygen (mg/L)	pH	Temp. (°C)	Conductivity (μS/cm)	Total dissolved solids (ppm)	Salinity (PSU)	REDOX potential (ORP: mV)
El Fuerte river	Average	5.03	7.11	32.18	1533.75	674.50	0.67	−153.65
	Minimum	4.83	7.03	32.18	1524.00	670.00	0.66	−156.60
	Maximum	5.41	7.14	32.19	1537.00	676.00	0.67	−147.20
Sinaloa river	Average	4.98	7.20	34.14	839.00	357.50	0.34	−142.00
	Minimum	4.93	7.20	34.12	835.00	356.00	0.34	−144.10
	Maximum	5.07	7.20	34.14	841.00	358.00	0.34	−141.00
Culiacan river	Average	5.35	7.30	32.47	683.50	337.50	0.29	−375.36
	Minimum	4.62	6.80	31.48	107.00	47.00	0.04	−414.30
	Maximum	6.45	7.51	33.29	1000.00	554.00	0.43	−143.50
Topolobampo drain	Average	4.13	6.67	31.39	291.25	117.38	0.10	−136.15
	Minimum	3.12	6.48	30.74	250.00	11.00	0.01	−153.20
	Maximum	5.20	6.86	31.93	331.00	149.00	0.14	−118.40
Cortinez drain	Average	5.29	6.75	32.79	164.25	71.63	0.07	−206.85
	Minimum	5.06	6.65	32.26	145.00	63.00	0.06	−278.00
	Maximum	5.47	6.97	33.15	178.00	77.00	0.07	−136.60
Navolato drain	Average	5.89	7.34	32.77	284.75	123.88	0.12	−417.64
	Minimum	5.46	7.27	32.11	234.00	103.00	0.10	−420.90
	Maximum	7.49	7.35	33.43	331.00	143.00	0.13	−411.40
LFD thresholds[a]	Fresh water	5.0	6.5 to 8.5	Ambient temperatures ±1.5	–	–	–	–
	Coastal water	5.0	6.0 to 9.0	Ambient temperatures ±1.5	–	–	–	–

[a] (Ley Federal de Derechos 2016)

Organochlorine pesticides

Unlike nutrients, which could be influenced by natural sources, pesticide residues in water can be directly used to assess the impact of agricultural activities in nearby areas. In Mexico, five pesticides have been banned (aldrin, dieldrin, endrin, mirex, chlordecone), five others are allegedly not marketed and are in the process of being banned (chlordane, lindane, DDT, PFOS more usually sulfluramide and endosulfan), and six others have never been approved for use (heptachlor, HCB, toxaphene, pentachlorobenzene, and α- and β-HCH). All of these were detected in this study and in previous studies of the area (Montes et al. 2012; Galindo et al. 1997; Gonzales-Farias et al. 2002). In this study, OC pesticides were present in all samples except those from the Sinaloa and Culiacan rivers (Table 3). Endosulfan is banned in some countries for its high level of toxicity. Lindane (γ-HCH), detected in Lechuguilla lagoon and in the Gulf of California, is listed as a carcinogen (group 1) by IARC WHO (Loomis et al. 2015) and is restricted in Mexico according to the official catalog of pesticides (CICLOPAFEST 2002). A related compound, δ-HCH, showed high concentrations in several of the samples, probably due to its high mobilization, since desorption experiments have shown preferred association of the α and β isomers with particulate matter, and elevated dissolution of γ, δ, and ε HCHs (Berger et al. 2016). Indeed, Granados-Galván et al. (2015) found δ-HCH to be the pesticide residue with the highest concentration in the muscle tissue of a population of snapper (*Lutjanus* sp.) in Navachiste lagoon.

Samples from the Pabellones lagoon showed a greater number of organochlorine pesticides (HCH, endrin, endosulfan, methoxychlor, DDT, epoxide heptachlor, *cis*-chlordane, and dieldrin) than from other coastal

Table 2 Concentrations of nutrients (mg L^{-1}) in water of the sampled stations

	(NH_3-N)	(NO_3-N)	(NO_2-N)	(PO_4)	(P)	(P_2O_5)	N/P
El Fuerte river	*0.05–0.15*	1.6–7.10	ND–4	ND–1.1	*0.37*	ND–1.0	6.1
Topolobampo drain	*0.15–0.24*	ND	2–4	ND–0.2	*ND–0.09*	ND–0.2	1.0
Sinaloa river	*0.15–3.90*	ND	2–10	0.9–7	*ND–2.3*	ND–5.2	1.8
Cortinez drain	*ND–0.09*	1.10–1.14	3–5	ND–2.3	*ND–0.80*	ND–1.7	0.8
Culiacan river	*0.02–0.13*	ND	2–4	0.1–1.4	*0.03–0.47*	0.61–1.0	3.5
Navolato drain	*0.14–0.36*	ND–2.30	ND–3	0.7–1.2	*0.27–0.35*	0.56–0.9	0.7
Pabellones coastal lagoon[b]		<0.02	<0.01				
Navachiste coastal lagoon[b]		<0.05	<0.042				
Lechuguilla coastal lagoon[b]		<0.04	<0.01				
Fresh water[a]	0.06	–	–	–	0.05	–	
Coastal water[a]	0.01	0.04	0.01	–	0.01	–	

Values in italics are the concentrations exceeding the water quality guidelines

ND not detected

[a] Maximum permissible limits for the protection of aquatic life (National Water Commission 2009)

[b] Measured with multiparameter sonde

lagoons; this may be attributable to heavy precipitation in the area 24 h before the sampling in Pabellones, since this could have increased the dragging and resuspension of pesticides accumulated in the sediments. Contaminants in water, even in drinking water, have been associated with flash floods (Yard et al. 2014), so episodes of rain might increase the flow of pesticides into the ocean.

In two or more stations, endrin, endosulfan sulfate, and heptachlor epoxide exceeded the thresholds recommended by the Water Rights Act (Ley Federal de Derechos 2016) for the Protection of Aquatic Life in Freshwater, Brackish or Coastal Water Ecosystems (Table 3). Nevertheless, this is only an exploratory study and systematic monitoring of the area is needed.

An overview of the OC pesticides in the drains, rivers, and coastal lagoons (Fig. 2) showed an accumulation in the lagoons, with ΣHCH showing the highest concentrations and dieldrin the lowest. Coastal areas are particularly vulnerable to direct or indirect discharges of organic pollutants where dilution and/or dispersion is limited, for example, in semi-enclosed bays and in lagoons such as the ones in this study. Unexpectedly, even in the Gulf of California at 10 km from the coast and at 10 m depth, OC pesticides including HCH, endosulfan, and endrin were present; these were presumably derived from runoff of agricultural pesticides, which suggests that there was also nutrient runoff.

To assess OC loads to the coastal lagoons, directly related water bodies within a given crop area were examined. For example, in the southern part of the study area, concentrations of the OC pesticides were higher in the three sampled sites in Pabellones lagoon than in two of the sampled sites in Navolato drain and Culiacan river (Fig. 3); therefore, in the lagoon, there was a clear accumulation of the HCH, endrin, and DDT families.

In the central part of the study area, where the Sinaloa river and Cortinez drain surround the crop area, the OC pesticide concentrations suggest a weak relationship with OC pesticides in Navachiste lagoon (not shown); in that case again, ΣHCH would be transported by Cortinez drain to the coastal lagoon. Montes et al. (2012) also found ΣHCH to be the most abundant OC pesticides in sediments in this area; however, in their study, methoxychlor was the second most abundant whereas in the present study, endrin was the second most abundant, closely followed by methoxychlor.

Concentrations of endrin aldehyde in water were high in Navachiste and Pabellones lagoons and the sea sample from the Gulf of California, which could suggest that endrin is not from recent applications; this contrasts with the findings of Montes et al. (2012), but their analysis was of sediments, where degradation of organic compounds can be slower (Carvalho et al. 2002). As for endosulfan, only Lechuguilla and Navachiste lagoons showed high concentrations of its degradation products, while the sea sample showed low concentrations, so it is difficult to determine whether there has been a recent application of this product. For the persistent

Table 3 Organochlorine pesticides maximum concentration found in surface water (μg L^{-1})

	El Fuerte river	Culiacan river	Sinaloa river	Topolobampo drain	Cortinez drain	Navolato drain	Lechuguilla lagoon	Navachiste lagoon	Pabellones lagoon	Gulf of California	LOD
α-HCH	ND	ND	ND	ND	ND	ND	ND	ND	ND	3.6	0.01
β-HCH	ND	ND	ND	ND	ND	ND	ND	0.1	0.2	0.1	0.01
γ-HCH	ND	ND	ND	ND	ND	ND	0.1	ND	ND	0.2	0.01
δ-HCH	6.8	ND	ND	5.2	6.5	1.6	10.6	7.9	22.1	4.9	0.01
Endrin ketone	ND	ND	ND	ND	ND	ND	0.2	0.1	0.1	0.1	0.28
Endrin aldehyde	ND	ND	ND	0.4	0.1	ND	ND	3.7	2.0	2.9	0.28
Endrin	0.1	ND	ND	ND	ND	ND	*0.1*	*0.5*	*0.7*	*0.5*	0.01
Endosulfan sulfate	ND	ND	ND	ND	ND	ND	0.10	*0.8*	ND	*0.8*	0.03
β-Endosulfan	ND	ND	ND	ND	0.1	ND	0.1	0.7	ND	1.0	0.01
α-Endosulfan	ND	ND	ND	ND	ND	ND	ND	0.1	0.4	0.1	0.01
Methoxychlor	0.3	ND	ND	0.4	0.3	ND	0.8	1.1	0.7	*0.5*	0.01
pp′DDT	ND	ND	ND	ND	ND	ND	0.3	0.6	0.2	0.9	0.03
pp′DDE	ND	ND	ND	ND	ND	ND	ND	0.5	0.8	ND	0.01
pp′DDD	ND	ND	ND	ND	ND	ND	ND	*0.7*	ND	ND	0.58
Heptachlor epoxide	ND	ND	ND	ND	ND	ND	ND	*0.7*	*0.6*	0.1	0.01
cis-Chlordane	ND	ND	ND	ND	ND	ND	ND	0.7	0.3	ND	0.02
Dieldrin	ND	ND	ND	ND	ND	ND	ND	0.2	ND	ND	0.01

Italicized entries indicate values that exceeded thresholds recommended by the Water Rights Act for the Protection of Aquatic Life in Freshwater, Brackish or Coastal Water Ecosystems (Ley Federal de Derechos 2016)

LOD limit of detection, *ND* not detected

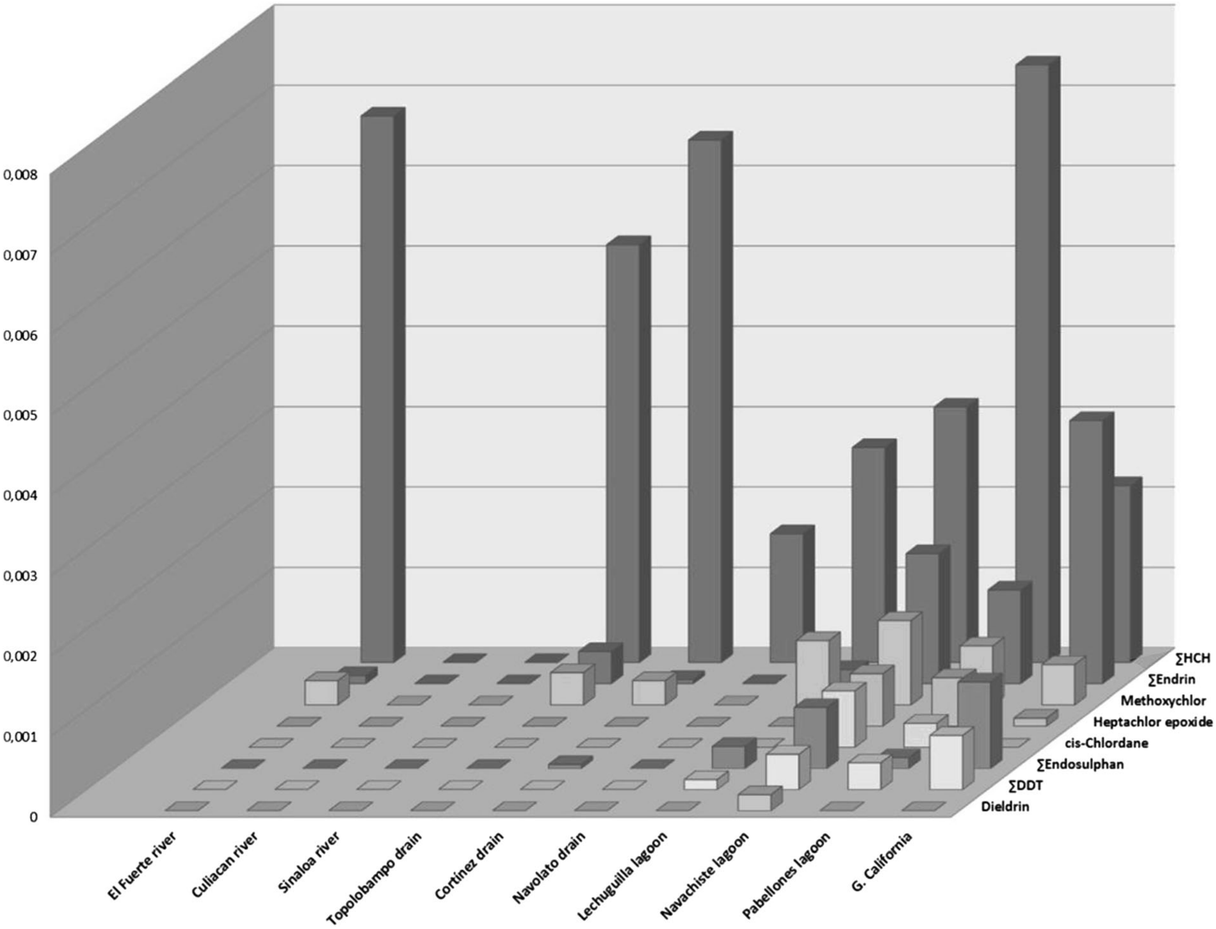

Fig. 2 Graph showing the sum of the OC family of pesticides in all rivers, drains, coastal lagoons, and coastal water in milligrams per liter

organochlorine pesticide DDT, Carvalho et al. (2002) reported a DDT/DDE ratio >1, indicative of a recent application of DDT in the region or at least before 2002, the last year in which cotton was intensively grown in Sinaloa with high usage of DDT. The DDT/DDE ratio of >1 in our results for Lechuguilla and Navachiste lagoons could suggest recent usage; however, these results are not conclusive and intensive monitoring would be necessary to prove recent usage of DDT.

Organophosphorus pesticides

Organophosphorus pesticides are less persistent in the environment than organochlorine pesticides. However, they are much more toxic and have been linked to a number of adverse health effects in humans and other vertebrates. They show acute toxicity, neurotoxicity, immunotoxicity, mutagenicity, and teratogenicity (Vittozzi et al. 2001; Arellano-Aguilar and Macías-Garcia 2008). The organophosphate pesticides reported to have been used in Sinaloa show a predominance of products containing methyl parathion, chlorpyrifos, phosmet, azinphos-methyl, or methamidophos (Hernández-Antonio and Hansen 2011; García-de la Parra et al. 2014; Gonzales-Farias et al. 2002; Leyva Morales et al. 2014). However, of the 22 organophosphates sought in this study, only five were detected (diazinon, disulfoton, methyl parathion, chlorpyrifos, and mevinphos) (Table 4). Diazinon appeared in all the stations sampled, with 96 μg L^{-1} being the highest concentration detected. The second most frequent was chlorpyrifos, followed by methyl parathion with concentrations an order of magnitude higher than those of the other two. Owing to its toxicity and wide use, chlorpyrifos has been classified by the European Commission as a substance requiring priority surveillance

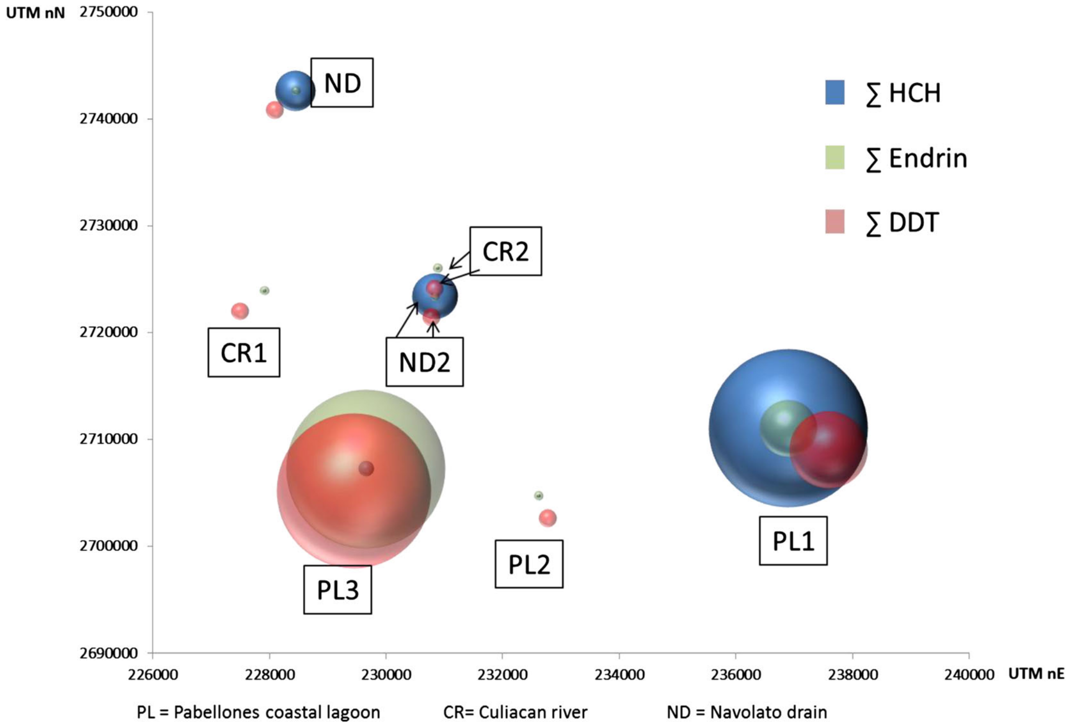

Fig. 3 Bubble chart showing accumulation of the pesticides from Navolato drain and Culiacan river into Pabellones lagoon

with an annual average Environmental Quality Standard (EQS) set at 30 ng L^{-1} for surface water (European Commission 2013), a standard exceeded in our river and drain samples.

No clear increase of OP pesticides toward the coastal lagoons could be traced, although higher concentrations of diazinon and methyl parathion in the rivers than in the drains (Fig. 4) suggested a higher contribution of these pesticides by the rivers than by the drains. This lack of an identifiable link between OP pesticides in the coastal lagoons and their associated rivers and drains could be due to their low persistence in the environment. Nevertheless, OP pesticides diazinon and chlorpyrifos were detected in the Gulf of California, 10 km from the coast

Table 4 Organophosphorus pesticide mean concentrations in the sampled sites in micrograms per liter.

	Diazinon	Disulfoton	Methyl parathion	Mevinfos	Chlorpyrifos
G. California	13.07	ND	ND	ND	1.50
El Fuerte river	26.05	ND	209.24	ND	4.86
Culiacan river	96.33	0.72	113.39	ND	ND
Sinaloa river	33.34	ND	ND	ND	ND
Topolobampo drain	25.53	ND	ND	ND	ND
Cortinez drain	18.19	ND	ND	ND	1.97
Navolato drain	22.85	ND	ND	ND	ND
Lechuguilla costal lagoon	19.44	ND	ND	ND	1.71
Navachiste coastal lagoon	12.68	ND	ND	ND	1.70
Pabellones coastal lagoon	19.02	ND	ND	ND	1.39
LOD	0.12	0.10	0.88	0.46	0.29

ND not detected, *LOD* limit of detection

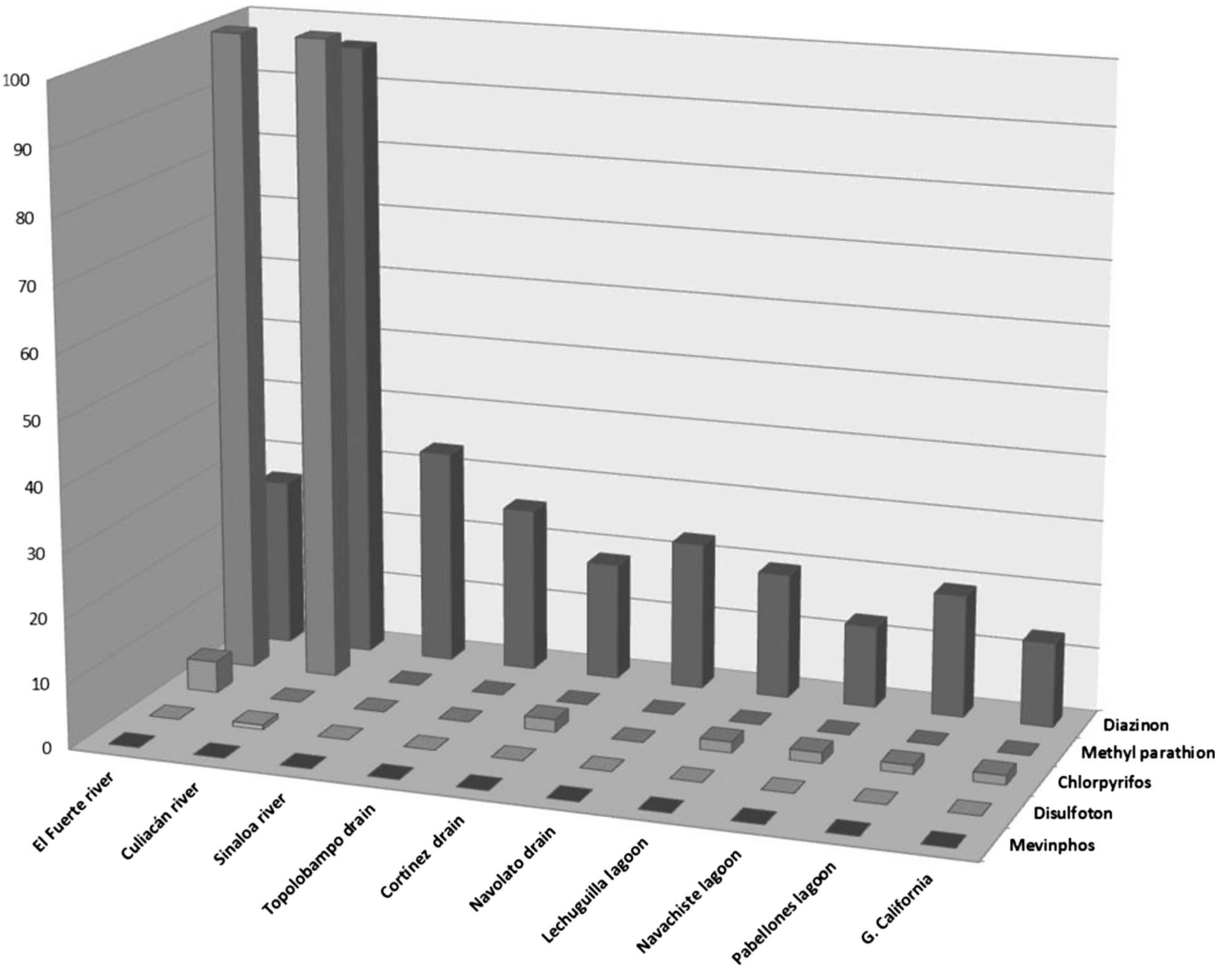

Fig. 4 OP pesticides at all the sampled sites of the northern region of Sinaloa in micrograms per liter.

and at 10 m depth, at concentrations at the same order of magnitude as in rivers and drains. Their concentrations were considerably higher in the El Fuerte and Culiacan rivers than in the Sinaloa river and other sampled stations. Methyl parathion exceeded 100 μg L^{-1} in the El Fuerte and Culiacan rivers. There has been a shift toward the use of OP pesticides in the region (Carvalho et al. 2002), and the presence of OP pesticides in ocean water and the high concentrations of OP pesticides in the rivers indicate just how intense the recent use of these pesticides has been.

Although Mexico lacks monitoring programs to assess the impact of agriculture, results from this and previous studies highlight the consequences for the environment and human health that could arise from the use of pesticides; this problem must be addressed by all responsible parties.

Conclusions

Along the Mexican coastline bordering, the Pacific Ocean and the Gulf of California are highly productive agricultural areas. However, agrochemical pollution could significantly affect other economic activities such as fisheries, or could have serious consequences for humans and the environment. Toxic algal blooms in coastal lagoons can also be associated with high input of nutrients from agroindustry. Water carries bioavailable water-soluble pollutants from the land to the coast. The present study found that both pesticides and nutrients could be transported by superficial water drains and rivers, ultimately to reach coastal lagoons and the ocean. In terms of nutrients, every sampled site had at least one replicate that exceeded the maximum allowable for the protection of aquatic life. The broad range of nutrient concentrations in the rivers suggested a dynamic distribution through the various compartments of the system, with riparian processes occurring in rivers but not in the drains.

Several banned organochlorine pesticides such as endosulfan, HCH, and chlordane were detected in the water bodies. Navachiste lagoon showed the presence of most of the OC pesticides; nevertheless, the pesticides accumulated in all the lagoons and in the coastal site. In the southern part of the studied area, OC pesticides can be traced to the rivers and clearly to the related Navolato drain. Organophosphorus pesticides were detected in higher concentrations than the organochlorine pesticides, although no clear accumulation to the lagoons could be identified, probably because their persistence in the environment is lower. Diazinon was detected in all sites and at high concentrations, with chlorpyrifos being the second most detected OP pesticide, and methyl-parathion being detected in two of the three rivers at very high concentrations.

This study (1) contributes to description of the interconnection between water systems in Sinaloa in relation to agrochemicals and nutrients that could affect the integrity of coastal ecosystems, (2) identifies sites where it is necessary to establish permanent environmental monitoring programs in accordance with the Stockholm Convention, and (3) emphasizes an area on the Mexican coast where environmental problems have been neglected.

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