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ORGANOCHLORINE PESTICIDES IN WATERS OF THE CHACAHUA-PASTORIA LAGOON SYSTEM

José Rafael Contreras Hinojosa
Instituto Nacional de Investigaciones
Forestales, Agricultural and Livestock
Research. Experimental Field Valles
Centrales of Oaxaca, Villa de Etla, Oaxaca

José Antonio Cueto Wong
Instituto Nacional de Investigaciones
Forestales, Agricultural and Livestock
Research. La Laguna Experimental Field
Matamoros, Coahuila

Adán Hernández Hernández
Instituto Nacional de Investigaciones
Forestales, Agricultural and Livestock
Research. Experimental Field Valles
Centrales de Oaxaca, Villa de Etla, Oaxaca

Rafael Guajuardo Panes
Instituto Nacional de Investigaciones
Forestales, Agricultural and Livestock
Research. Cotaxtla Experimental Field
Cotaxtla, Veracruz

Finland Barbosa Moreno
Instituto Nacional de Investigaciones
Forestales, Agriculture and Livestock
Research. Experimental Field Valles
Centrales de Oaxaca, Villa de Etla, Oaxaca

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Abstract: In waters of the Chacahua and Pastoría lagoons, sampling was conducted in surface and subsurface water in 2017 and 2018, in order to detect the presence of organochlorine insecticides. The presence of the ten pesticides evaluated was detected, Chlordane was the one for which the highest values were detected with 53 ng L^{-1} , despite the fact that this type of pesticides stopped being used more than 30 years ago. Because these pesticides are hydrophobic, they tend to concentrate in sediments, which is why sampling should consider sediments and interstitial water in addition to the water column. Parallel to the above, because these pesticides accumulate in soil and plants, strategies should be implemented to control the sources of entry into water bodies.

Keywords: DDT, Endrin, concentration, sediment, sediments

INTRODUCTION

Coastal lagoons formed at the end of the ice age as a result of sea level rise during the Holocene and Pleistocene (Kjerfve, 1994), within a process of eustacy (Bianchi, 2007). They cover 13% of the world's coastline, from the tropics to the polar regions (Caumette *et al.*, 1996). They are areas of relatively shallow depth, which are completely or partially separated from the sea by a sand barrier, implemented above the high tide level (high tide) by wave action (Bird, 2008). They are generally oriented parallel to the coast and salinity can vary from that of a freshwater coastal lake to a hypersaline lagoon, depending on the hydrological balance (Kjerfve, 1994). From a geomorphological point of view, the term coastal lagoon is applied where the width of the connection with the sea at high tide is less than one-fifth (20%) of the total length of the barriers (Bird, 1982). The waters of coastal lagoons generally have a high primary productivity due to the photosynthetic activity of autotrophic organisms (plants, algae, bacteria) capable of transforming CO_2 into organic matter (Forti, 1966), from which the secondary productivity or production of the organisms that inhabit these bodies of water, such as fish, mollusks, arthropods, among others, is derived (Alvarez-Borrego, 1994; Yáñez-Arancibia *et al.*, 1993). Mexico's coastline is 11,122 km long (INEGI, 2021), 70% of which is exposed to the Pacific Ocean. There are approximately 125 coastal lagoons in the country, defined as areas that are below the medium-high sea level and have permanent or ephemeral communication with the sea, but are protected by some type of barrier (Lankford, 1977). The "Lagunas de Chacahua" are included in the Convention on Wetlands of International Importance, in RAMSAR site 1819, which covers 17,424 ha (RAMSAR, 2023) and are located in the Pacific Ocean within a Natural Protected Area, belonging to the municipality of Villa de Tututepec de Melchor Ocampo. The lagoon system is made up of two large bodies of water called Laguna Chacahua and Laguna Pastoría, the latter being dominant in size.

Figure 1 shows an overview of the watersheds that supply water to the lagoons.

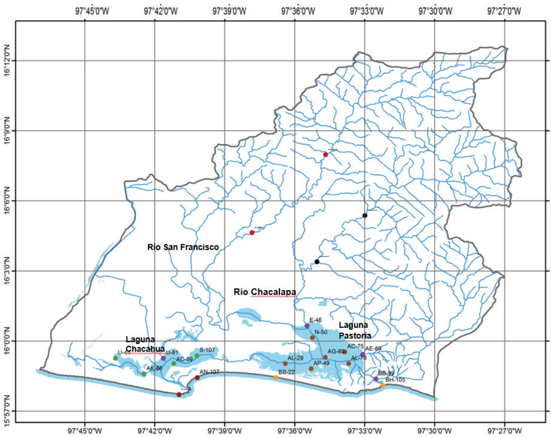

Figure 1.- The lagoon system and sampling points.

All around the lagoons there is vegetation, mainly red mangrove *Rhizophora mangle* (Agraz Hernández *et al*., 2015), which functions as a protective barrier against hurricanes and as a nesting ground for local and migratory birds, as well as a shelter for lizards and reptiles. The body of water has a 2.5 km long "open-air" thinning, which keeps the two lagoons together and thus allows boat traffic. However, on both sides of this thinning there is mangrove vegetation where water and fauna are allowed to flow. At one time, each lagoon had a connection to the sea, however, currently only the connection to the Chacahua lagoon is open, with an approximate width of 60 meters, while the connection to the Pastoría lagoon maintains an obstacle in the form of a sand barrier 2-3 meters high above the average maximum height of the sea with an approximate extension of 100 meters. Sea waves in the vicinity of the lagoons reach an average height of 1 to 1.5 meters and are sequenced approximately every 15-20 seconds.

As a large body of water, the tidal effect is perceived due to the rotation of the earth and the effects of the moon and the sun. An analysis of the tideograms from the tide gauge station in Puerto escondido, Oax. for the month of October 2024 (tide-forecast.com, 2024), indicate that there are two high and two low tides, their type is Semidiurnal Mixed, with an approximate amplitude of 80-1.20 and 55-85 cm for the high and low periods, respectively, in a cycle of 24.83 hours, which is considered a lunar day (Bowers and Roberts, 2019) and this range allows it to be classified as micromareal (Kirby, 1992).

Due to the closure of the Pastoria Lagoon's connection to the sea, the dominant ebb and flow of water is through the opening of the Chacahua Lagoon. Apart from the sea waters, the lagoon waters during the rainy season are fed by the runoff generated by the Chacalapa and San Francisco rivers, and at the end of the rainy season, the rivers practically dry up.

The estuaries of these rivers are wetlands, with different types of vegetation, with marshes and swamps, which are subject to tidal fluctuations and the meeting and mixing of fresh water from the rivers with salt water from the sea and receiving sediment from their basins and also of marine origin (Bird, 2008), which hinders direct flow into them. In addition to these inflows, an irrigation unit that takes water from the Verde River allows irrigation of crops located within the wetland on the Chacahua Lagoon side. While on the Pastoría lagoon side, by Cerro Hermoso, Oax., in the rainy season water enters from a wetland that extends from Río Grande, Oax. In the Pastoría lagoon area, subsurface water inflow is observable, known locally as pozas, which are an important source of nitrogen and carbon in the primary production of the coastal lagoons (Andrisoa *et al*., 2019).

Because the waters of the rivers do not come into direct contact with the waters of the sea, the saline intrusion is partially mixed, with higher salinity values near the connection with the sea (Savenije, 2005), therefore, the water in the lagoons is brackish. Due to the organic and inorganic sediments in the lagoons, the flow of water through the rivers and the ebb and flow of seawater through the tides, as well as the variation in depth of the tides, among other things, the waters generate colors ranging from the turquoise blue of the sea to dark green colors, associated with foul odors. Around the lagoons there are four towns with less than 2,500 inhabitants: El Zapotalito, La Pastoría, Cerro Hermoso and Chacahua, the first three of which are associated with Pastoría Lagoon.

Coastal lagoons, among other things, function as a natural trap for materials transported by rivers and the sea, some visible in physical form, such as sediment and floating organic and inorganic material, as well as in solution, such as detergents, pesticides, and heavy metals, among others. The sedimentation of these materials with silts and clays is concentrated in inactive areas within the lagoons where energy sources such as tides, waves and currents are minimized (Martens, 1982). Considering obstacles by mudflats, sediment input to lagoons can be by material moving in a two-phase flow (bottom lift and suspension), as well as those that once suspended, rest in suspension during complete transport (Gyr and Hoyer, 2006).

Within the material that comes in solution or adhered to organic and inorganic particles, among others, are pesticides, classified based on the type of pest they combat, thus we have fungicides, algaecides, herbicides, insecticides, nematicides and molluscicides, which generally refer to chemically synthesized products (Stenersen, 2004).

In the human body, pesticides can be metabolized, excreted, stored or bioaccumulated in body fat and damage is associated with dermatological, neurological, carcinogenic, reproductive, genetic, cardiovascular, respiratory, endocrine and gastrointestinal problems (Nicolopoulou-Stamati *et al*., 2016).

It should be noted that some pesticides are hydrophobic and tend to be sorbed by suspended particulate matter and retained at the bottom of aquatic systems by sedimentation (Pinto *et al*., 2016). Due to the effect of dissolved organic matter (particles < 0.45 μm), an increase in solubilization of pesticides by dissipation is considered, in addition to an increase in their degradation by microbial co-metabolism when increased by the presence of more readily biodegradable organic matter (Pinto *et al*., 2016).

Pesticides are grouped by chemical families (Stenersen, 2004) and include organochlorines, organophosphates, carbamates, inorganic salts and pyrethroids, among others. In the case of insecticides, they are generally for agricultural use, eliminate pests and reach the soil directly or by runoff from leaves and stems (Matthews, 2006). Some can be degraded by organisms, while others can also be degraded by biotic processes (Hamilton, 2003), but their availability is influenced by sorption to different types of organic matter, however, excess water can promote dilution effects (Pinto *et al*., 2016).

Collaterally, insecticides affect other organisms, including humans. This collateral effect is associated with their drift at the time of application and direct damage to other insects, their entry into humans and animals can be via the skin, ingested or inhaled. The presence of insecticides in soil is associated with their solubility in water, the octanol to water partition coefficient ratio and their half-life (Sabzevari and Hofman, 2022), as well as the pesticide's affinity to adsorb to organic carbon and soil minerals, such as clays, oxides and hydroxides (Peña *et al*., 2016). In the soil, insecticides degrade and are transformed into other products, which can be equal or more toxic than the original insecticide, while chemical reactions of photolysis, hydrolysis, oxidation and reduction, as well as microbial reactions are involved in their degradation (Sabzevari and Hofman, 2022).

As their name indicates, organochlorine insecticides are composed mainly of chlorine atoms inserted in different positions in the carbon and hydrogen rings; their mode of action is to affect the nervous system; they have the advantage of their persistence, so that they control pests for a longer period of time (Matthews, 2006). They tend to be hydrophobic and are present at very low levels in the water column, and are persistent because they are resistant to abiotic and microbial degradation in water and sediment and to the metabolism of aquatic and terrestrial organisms (Nowell *et al*., 1999).

Their residues tend to be accumulated in some animals at the end of the food chain and despite being banned, residues are still found in soils and waters (Matthews, 2006) and their residual effects still persist, their presence in women has been detected in breast milk (Chávez-Almazán *et al*..., 2018), in adult men they are related to breast and prostate cancer (Xu *et al*., 2010), as well as Parkinson's disease, especially heptachlor epoxide (Webster Ross *et al*., 2019). In animals, in the food chain, the presence of these pesticides in predatory birds promotes eggshell thinning, which leads to egg breakage and, therefore, a reduction in hatching (Matthews, 2006).

These pesticides are listed as priority hazardous substances, with Endrin being the most dangerous for having a Lethal Dose 50 (LD_{50}) of 3 mg kg^{-1} , while for Dichlorodiphenyltrichloroethane (DDT) it is 87 (Pinto *et al*., 2016), this being the most representative of organochlorine insecticides, since it is the insecticide that has saved the most lives by effectively controlling diseases transmitted to humans by insect vectors (Stenersen, 2004) and for its impact in this area, its discoverer was awarded the Nobel Prize in Medicine (Rowe Davis, 2014). Its effectiveness, Matthews (2018) frames it in the case of Ceylon, where in 1948 there were 2.8 million cases of Malaria and by 1964 only 30 cases had been reported.

This pesticide began to be used since the 1940's in a gradual way in the states of the Mexican Republic in the fumigation of homes against insect vectors, later and until the end of the 1980's, when its production in Mexico ended, it was also used for the control of crop pests (Fernández Bravo *et al*., 2020) as well as the rest of the pesticides, especially Endosulfan, which was the last of this group to be withdrawn from the market in 2011 (United Nations, 2011).

Under the premise that organochlorine insecticides were the first to appear in Mexico and that their use was agricultural and domestic and that by leaching and surface runoff they ended up in the lagoons; however, their availability in the waters may be subject to adsorption processes, both in soils and organic matter, mainly clay and humus content (Barceló and Henion, 2003) and in order to characterize the water quality of the lagoons in terms of the content of this type of insecticides, analyses were performed in the water column in both lagoons, in 2017 and 2018.

MATERIALS AND METHODS

Water analyses were performed by a laboratory registered with the Mexican Accreditation Entity (EMA) based on the chemical analysis methods proposed by the United States Environmental Protection Agency (EPA, 1996). These insecticides were Aldrin, Alpha-BHC, Beta-BHC, Chlorothalonil, Chlordane, DDT, 4,4-DDD, 4,4-DDE, Dieldrin, Endosulfan, Endosulfan sulfate, Lindane, Heptachlor, Heptachlor epoxide, Hexachlorobenzene, Methoxychlor, and Mirex. Of these pesticides, the United Nations Environmental Program (UNEP) through the Stockholm Convention proposed to eliminate them, while DDT has a worldwide use restriction, however, it is still used to combat the vectors that transmit Malaria and Leishmaniasis in tropical regions of Asia and Africa (UNEP, 2022).

In the water of the lagoons, quadrants were delimited to try to make the samplings equidistant and because the Pastoría lagoon is larger, a greater number of sites were sampled in this one and all these analyses were carried out in two campaigns.

	Sampling point and position				
	CHA-U81* Superficial	PAS-E46** Surface	PAS-BB99 Superficial	PAS-AE89 Surface	PAS-AE89 Background
Aldrin	0.5058	0.5058	0.5058	0.5058	0.5058
Heptachlor	0.5053	0.5053	0.5053	0.5053	0.5053
Heptachlor epoxide	0.5056	0.5056	0.5056	0.5056	0.5056
Lindane	0.5058	0.5058	0.5058	0.5058	0.5058
Chlordane	53	53	53	53	53
Methoxychlor	0.5050	0.5050	0.5050	0.5050	0.5050
4,4-DDDD	0.5063	0.5063	0.5063	0.5063	0.5063
4,4-DDE	0.5058	0.5058	0.5058	0.5058	0.5058
D.D.T.	0.5058	0.5058	0.5058	0.5058	0.5058
Dieldrin	0.5058	0.5058	0.5058	0.5058	0.5058
alpha-BHC	0.5058	0.5066	0.5066	0.5066	0.5066
beta-BHC	0.5050	0.5050	0.5050	0.5050	0.5050
Endosulfan II	0.5050	0.5050	0.5050	0.5050	0.5050
Endosulfan sulfate	0.5058	0.5058	0.5058	0.5058	0.5058
Hexachlorobenzene	0.5405	0.5405	0.5405	0.5405	0.5405
Endrin ketone	0.50	0.50	0.50	0.50	0.50
Chlorothalonil	0.5376	0.5376	0.5376	0.5376	0.5376
Mirex	0.8282	0.8282	0.8282	0.8282	0.8282

Table 1.- Insecticide content in water (ng/L). 24/10/2017.

*PAS: Pastoría Lagoon. **CHA: Chacahua Lagoon.

	Sampling point and position		
Insecticide	CHA-U81* CHA-U81* CHA-U81* CHA-U81* CHA-U81* CHA-U81 Superficial	PAS-BB99** Superficial	PAS-E46 Superficial
Aldrin	0.5058	0.5058	0.5058
Heptachlor	0.5053	0.5053	0.5053
Heptachlor epoxide	0.5056	0.5056	0.5056
Lindane	0.5058	0.5058	0.5058
Chlordane	53	53	53
Methoxychlor	0.5050	0.5050	0.5050
4,4-DDDD	0.5063	0.5063	0.5063
4,4-DDE	0.05058	0.05058	0.05058
D.D.T.	0.05058	0.05058	0.05058
Dieldrin	0.5058	0.5058	0.5066
alpha-BHC	0.5066	0.5066	0.5066
beta-BHC	0.5050	0.5050	0.5050
Endosulfan II	0.5050	0.5050	0.5050
Endosulfan sulfate	0.5058	0.5058	0.5058
Hexachlorobenzene	0.5405	0.5405	0.5405
Endrin ketone	0.50	0.50	0.50
Chlorothalonil	0.5376	0.5376	0.5376
Mirex	0.8282	0.8282	0.8282

Table 2.- Insecticide content in water (ng/L). 16/01/2018.

*PAS: Pastoría Lagoon. **CHA: Chacahua Lagoon.

RESULTS AND DISCUSSION

Tables 1 and 2 show the results of the samplings carried out. In the first instance, it can be seen that these organochlorine pesticides are present in both lagoons, despite the fact that they ceased to be used more than 30 years ago.

In the two sampling stages, the highest concentration value corresponded to Chlordane with 53 ng/L while the content of the metabolite 4,4-DDDD was higher than the original pesticide (DDT). These concentration values are considered low compared to the results of other studies, thus, Vazquez Botello *et al.* (2020) summarized results of the presence of organochlorine insecticides in sediments of three coastal lagoons of the Gulf of Mexico, finding minimum and maximum values of 0.18 and 36.2 ng g^{-1} , respectively. Zhou *et al.* (2000), when sampling the presence of organochlorines in waters in a bay in China, found concentrations ranging from 6.6 to 32.6 ng/L and indicated that the concentrations in pore water are one or two orders of magnitude higher than in surface waters, which implies that these contaminants prefer to remain in the sediment rather than in the water, in addition to the fact that the concentrations of these pesticides decrease with salinity. Thus, Dueri *et al.* (2008) indicate that it is not advisable to diagnose the presence of pesticides at different depths of the water column and suggest that sampling in the sediment and interstitial water should be added.

CONCLUSIONS

From the analysis of water samples from the lagoons, the results indicate the presence of organochlorine pesticides, both those that have been used directly in domestic and agricultural activities, as well as their metabolites, in the case of DDT and Endosulfan. It is presumed that these pesticides ended up in the waters of the lagoons through runoff from the highlands, which is why the movement of soil and vegetation masses should be reduced to the maximum to reduce the risk of these and other pesticides entering the water bodies and, in the best case scenario, to control punctual and diffuse runoff.

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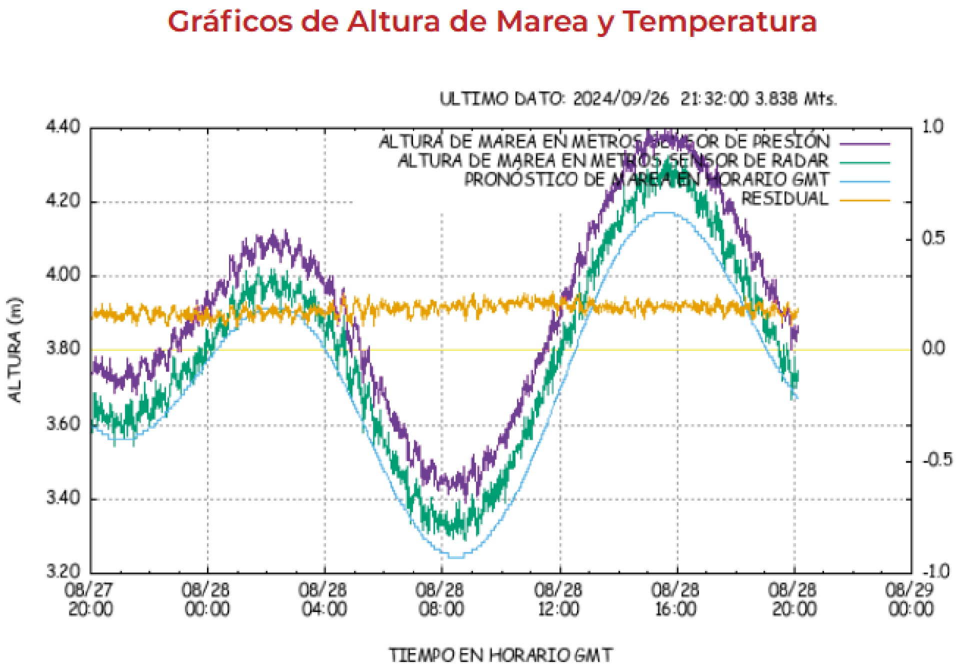

Acapulco Tide Gauge Station, Gro.

https://oceanografia.semar.gob.mx/Templates/grafnum_acapulco.html