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Chlorpyrifos and Dimethoate in Water and Sediments of Agricultural Drainage Ditches in Northern Sinaloa, Mexico

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Abstract

In northern Sinaloa state, Mexico, little is known on organophosphate pesticide transport and fate in agricultural drainage systems. Spatial and temporal variation of chlorpyrifos and dimethoate was assessed in two agricultural drainage ditches (Buenaventura and Burrión) and risk for aquatic life was estimated. Analysis was made by high performance liquid chromatography and risk estimates were determined following international reference frameworks. In water, the highest chlorpyrifos concentration in the Buenaventura ditch was 5.49 μg L^{-1}, and 3.43 μg L^{-1} in the Burrión ditch. Dimethoate was quantified only once in both ditches (0.44 μg L^{-1} and 0.49 μg L^{-1}). In sediment, chlorpyrifos was quantified only in the Burrión ditch (242 μg kg^{-1}). Chlorpyrifos concentrations surpassed water and sediment quality criteria, representing a hazard for environmental and human health, as both ditches discharge into the Gulf of California and are used for capture of commercial species such as the grey mullet (*Mugil cephalus*) and cauque prawn (*Macrobrachium americanum*).

Keywords Organophosphate pesticides · Water and sediment quality · Pollution · Environmental and human health

The Sinaloa state is one of the main vegetables and grain producers in Mexico. The most developed crops are maize, bean, potato, chickpea, safflower, wheat, sorghum, and vegetables (SIAP 2019). This region is distinctive for its highly technical agricultural practices and the presence of two agricultural cycles per year. Such agricultural practices include the use of pesticides for pest control and prevention. Martínez-Valenzuela et al. (2015), as well as Hernández-Antonio and Hansen (2011) point out that the most commonly used pesticide group in the northern region of the state is organophosphates, with chlorpyrifos, dimethoate, malathion, monocrotophos, and methyl parathion the most frequently applied. These pesticides vary in toxicity, from moderately toxic to extremely toxic to humans and wildlife, and difficult to degrade under natural environmental conditions (Nasrabadi et al. 2010). Chlorpyrifos and dimethoate are

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used in Sinaloa for pest control in grain and vegetable crops (Leyva-Morales et al. 2014). Both compounds are in Toxicity Group III; chlorpyrifos exhibits a high affinity to soil and sediment components, whereas dimethoate is highly water-soluble (INECC 2021a, b). Karam et al. (2004) point out that most pesticides used in the Sinaloa state have teratogenic action and affect the nervous, endocrine, and immunological systems, being considered potential generators of diseases such as cancer, asthma, and infertility. In this regard, improper pesticide use has been reported to imply a negative effect on the human being and the ecosystem, causing health problems and environmental deterioration (Benítez-Díaz and Miranda-Contreras 2013; Plenge-Tellechea et al. 2007). Pesticides migrate from crop terrains via adhesion to soil particles to agricultural drainages ditches, allowing them to move into aquatic ecosystems (Gebremariam et al. 2012). In the Sinaloa state, pesticide assessment in agricultural drainage ditches has found concentrations from a wide variety of chemicals (García de la Parra et al. 2012; Moeder et al. 2017). Most studies of organophosphate pesticides in agricultural drainage ditches have been performed in the central part of the state, and little is known on the movement and fate of these compounds in agricultural drainage systems in northern Sinaloa. Corn, beans, and chickpea are grown in this highly technified region; it is located within two of the largest irrigation districts (ID) in Mexico, ID 063 and ID 075 (CONAGUA 2018).This study aims to assess the spatial and temporal variation of chlorpyrifos and dimethoate, as well as estimate environmental risks for water, sediments and aquatic life in two agricultural drainage ditches located on ID 063 and ID 075 in Sinaloa, Mexico.

Materials and Methods

The study area comprises the lower part of the ditches Buenaventura and Burrión, both in agricultural areas of northern Sinaloa state, northwestern Mexico. The Buenaventura ditch is in the ID 075, in the lower part of the El Fuerte River basin. The Burrión ditch is in the ID 063, in the lower part of the Sinaloa River basin. The length and width of both drainage ditches is approximately 35 km and 10 m, respectively, and both discharge into the Gulf of California (Fig. 1).

Water temperature and pH were measured in July and November 2018, as well as in February and June of 2019. Measurements were made in four sampling stations with a multiparameter probe (YSI Professional Plus, Ohio, USA). Water samples for chlorpyrifos and dimethoate analysis were collected in 1 L amber glass bottles, from the first 20 cm of the water column, in the middle of the drainage ditch. Samples were stored at 4°C until analysis. Duplicates were made for quality control. Sediment samples from the upper 10 cm of the ditch bottom were taken and stored in glass containers and kept frozen for analysis (USEPA 1992). Prior to analysis, sediment samples were dried at 60°C and sieved with ≤ 2 mm sieve. Organic matter (OM) content in sediment was determined by the Walkley and Black (1934) method.

Extraction and analysis of chlorpyrifos and dimethoate in surface water followed method 614.1 of the US Environmental Protection Agency (USEPA 1992). One liter of water was poured into a 2 L separation funnel and 40 mL of methylene chloride were added; the funnel was shaken for 1 min. The funnel was allowed to stand for about 5 min

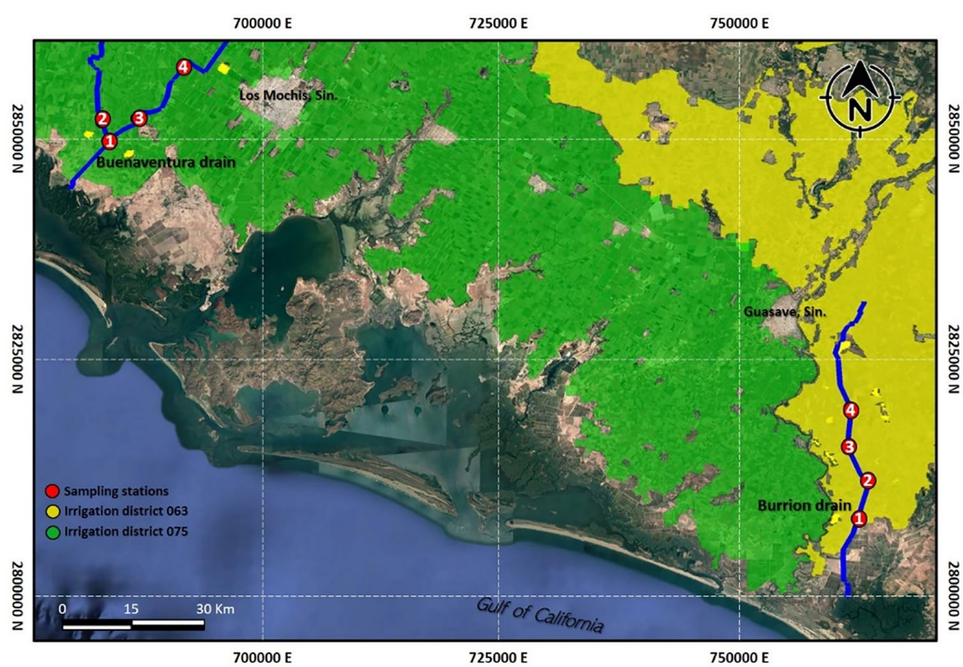

Fig. 1 Location of sampling stations within drainage ditches Buenaventura and Burrión

so that there was phase separation. The methylene chloride extract was collected in an Erlenmeyer flask. This process was repeated twice more. The extract was filtered through a 0.45 µm nylon membrane and evaporated in a rotatory evaporator at 45 ± 2°C in the vacuum. Once the extract was dried, it was resuspended in 1.5 mL of methanol and transferred to a 2 mL vial. For sediments, chlorpyrifos and dimethoate were extracted following the method described by Masís et al. (2008). Three extractions were performed at room temperature, with 25 g of sediment and 40 mL of methylene chloride and ultrasonic extraction for 15 min. The extract was filtered through a 0.45 µm nylon membrane. This fraction was evaporated and resuspended with 1.5 mL of methanol. Analysis was made by high performance liquid chromatography with UV–Vis detector (Shimadzu, model Prominence) and Kromasil C18 250 × 4.6 mm column. For the chromatographic analysis of chlorpyrifos, the mobile-phase was a mixture of water–methanol 20:80 (v/v) at a flow rate of 1 mL min^{-1}. Injection volume was 20 µL, and the column oven was set at 40°C. For dimethoate, the mobile-phase was a mixture of water–methanol 60:40 (v/v) at a flow rate of 1 mL min^{-1}. Injection volume was 20 µL, and the column oven was set at 35°C. Chlorpyrifos and dimethoate were detected at 247 nm and 220 nm, respectively. Compound identification was made from their retention times and quantification was based on peak height and area, as well as on comparison with reference standards (chlorpyrifos and dimethoate 99.5% and 98.3%, respectively; Chem Service, Inc.). Detection and quantification limits for chlorpyrifos were 0.054 and 0.153 µg L^{-1}, respectively. For dimethoate, the detection limit was 0.171 and quantification limit was 0.519 µg L^{-1}. Recovery of chlorpyrifos and dimethoate ranged from 89% to 105%.

Due to the lack of a framework of reference in Mexico, international frameworks of reference were used to assess aquatic life protection risks due to chlorpyrifos and dimethoate. For chlorpyrifos in water, the reference frameworks of the USEPA (1986) and the Canadian Council of Ministers of the Environment (CCME 2008) were used. For dimethoate in water, the reference framework used was that of the CCME (1993). Criteria established by Simpson et al. (2005) were used for determination of sediment quality for aquatic life protection. Shapiro–Wilk tests were performed to assess the normality of data and Duncan multiple range test was used to compare pesticide concentrations between ditches ($p \leq 0.05$).

Results and Discussion

In water, chlorpyrifos had the highest percent incidence in both Buenaventura and Burrión ditches, with 56.3% and 50.0%, respectively. Incidence of dimethoate was 6.25% in both ditches. In sediment, only chlorpyrifos was quantified in 25% of samples analyzed in the Burrión ditch. The highest concentrations in water were those of chlorpyrifos. In the Buenaventura ditch, chlorpyrifos ranged from 0.43 ± 0.20 to 5.49 ± 0.29 µg L^{-1}, whereas in the Burrión ditch, concentrations were between 0.70 ± 0.22 and 3.43 ± 0.69 µg L^{-1}. Dimethoate was quantified only once in both ditches. In the Buenaventura ditch, dimethoate concentration was 0.44 ± 0.11 µg L^{-1} and in the Burrión was 0.49 ± 0.08 µg L^{-1}. Only in sediments of the Burrión ditch chlorpyrifos was quantified, ranging from 151 ± 6.4 to 242 ± 17 µg kg^{-1}.

The highest average concentrations of chlorpyrifos and dimethoate (2.63 µg L^{-1} and 0.44 µg L^{-1}, respectively) were observed on February 2019, in waters of the Buenaventura ditch. This coincides with the period of highest agricultural activity in the ID 075. In the Burrión ditch, the highest average concentration of chlorpyrifos (2.66 µg L^{-1}) was observed in June of 2019, whereas the highest concentration of dimethoate (0.49 µg L^{-1}) was found in February of the same year. It is worth noting that the greatest application of pesticides in the main crops (maize, bean, and chickpea) within the study area coincides with the time where the highest chlorpyrifos concentrations were measured in both ditches. It also coincides with the irrigation season (February to May) of maize, the most extensive crop in the region, thus allowing pesticides to mobilize within irrigation surplus into agricultural drainage ditches. Dimethoate is highly soluble in water, whereas chlorpyrifos has a high adsorption affinity to soil particles and suspended particulate matter, which are transported within effluents (Gebremariam et al. 2012). The higher concentration of chlorpyrifos in June in the Burrión ditch was probably because the water level in the drain decreased in June (González-Márquez et al. 2014). Low water levels could have favored concentration increase within the drainage ditch. Monthly pesticide concentrations are shown in Table 1.

In the Buenaventura ditch, sampling station one had the greatest chlorpyrifos concentration (2.96 µg L^{-1}), whereas in the Burrión ditch the greatest concentration (3.43 µg L^{-1}) was found in sampling station four. Dimethoate was quantified in the same sampling stations of both ditches, with 0.44 µg L^{-1} in the Buenaventura ditch and 0.49 µg L^{-1} in the Burrión ditch. Only at the Burrión ditch sampling station one, located closest to the coastline, was chlorpyrifos quantified during the four samples. This indicates that there is a constant input of pesticide, either dissolved or adsorbed to particulate matter, into the lower part of the drain. In sediment, chlorpyrifos was only measured in the Burrión ditch, with an average concentration of 172 µg kg^{-1} in sampling station one and 97.8 µg kg^{-1} in sampling station two. The lack of detection of chlorpyrifos

Table 1 Chlorpyrifos and dimethoate in water (μg L^{-1}) and sediment (μg kg^{-1}) samples of Buenaventura and Burrión ditches (monthly averages)

Month	Buenaventura ditch				Burrión ditch			
	Water (μg L^{-1})		Sediment (μg kg^{-1})		Water (μg L^{-1})		Sediment (μg kg^{-1})	
	C	D	C	D	C	D	C	D
July 2018	Nd[d]	Nd	Nd	Nd	2.14[a,e]	Nd	Nd	Nd
November 2018	0.93 ± 0.30[e]	Nd	Nd	Nd	0.97 ± 0.30[c,e]	Nd	Nd	Nd
February 2019	2.63 ± 2.47[c,e]	0.44[a]	Nd	Nd	2.39[a,e]	0.49[a]	218 ± 25.2[b,f]	Nd
June 2019	1.05 ± 0.13[b,e]	Nd	Nd	Nd	2.66 ± 1.11[c,e]	Nd	151.8 ± 0.8[b,f]	Nd

[a]One value

[b]Mean of two values

[c]Mean of three values

[d]Mean of four values

[e]Above criteria for aquatic life protection: chlorpyrifos 0.041 μg L^{-1} (USEPA 1986), 0.002 μg L^{-1} (CCME 2008); Dimethoate 6.2 μg L^{-1} (CCME 1993)

[f]Above sediment quality criteria for aquatic life protection: chlorpyrifos 100 μg kg^{-1}, dimethoate 100 μg kg^{-1} (Simpson et al. 2005)

C Chlorpyrifos, *D* Dimethoate, *Nd* Not detected

in sediments of the Buenaventura ditch is probably related to OM content (Al-Ghadban et al. 1994), which was 43% lower compared to drainage Burrión. Average OM content in sediment was 1.71% ± 0.5% in drainage Buenaventura and 3.03% ± 0.3% in the Burrión ditch. Prevailing temperature (25° ± 2.5°) and pH (7.6 ± 0.5) in both ditches might have influenced chlorpyrifos degradation in sediments, as these conditions are favorable for microbial growth and physicochemical processes controlling transformation of chlorpyrifos, such as oxide-reduction and hydrolysis reactions (Getzin 1985; Macalady and Wolfe 1985).

When considering criteria for aquatic life protection, all samples where chlorpyrifos was quantified exceeded the criteria established both by USEPA (0.041 μg L^{-1}) and CCME (0.002 μg L^{-1}) protection guidelines. Therefore, such concentrations represent a risk for insects, crustaceans, and fish in both ditches and for the bays where they discharge. Tagatz et al. (1982) reported changes in marine plankton composition at chlorpyrifos concentrations greater than 0.1 μg L^{-1}. This is dangerous for seawater ecosystems, due to its impact on individual species and organism communities. In waters of the Lechuguilla and Navachiste bays, located in northern Sinaloa, Arellano-Aguilar et al. (2017) reported chlorpyrifos concentrations of 1.71 and 1.70 μg L^{-1}, respectively. In the Altata-Pabellones coastal lagoon, located in the central part of the state, Carvalho et al. (2002) revealed maximum concentrations of chlorpyrifos and dimethoate of 0.0048 and 0.021 μg L^{-1}, respectively; these authors found the highest concentration during the dry season, coinciding with the findings of this study. Moeder et al. (2017) described the presence of chlorpyrifos (0.082 μg L^{-1}) and dimethoate (0.413 μg L^{-1}) in surface waters of the agricultural ditch "La Michoacana" in the municipality of Culiacán, Sinaloa. García de la Parra et al. (2012) reported the presence of chlorpyrifos in sediments of an agricultural ditch in the Culiacán Valley (0.0009 μg kg^{-1}).

Moeder et al. (2017) point out that despite the semi-polar nature of chlorpyrifos, only marginal concentrations have been found in sediments due to its short half-life at the water–sediment interphase, which does not favor accumulation. Previously reported chlorpyrifos concentrations are not similar to those reported in this research. This difference may be due to variations in agricultural activities in the study area, as well as the types of crops established and pesticides used. Dimethoate concentrations found in the water of both ditches are below the criteria of 6.2 μg L^{-1} established by CCME (1993).

Pesticide concentrations in sediment were compared with the criteria of sediment quality for aquatic life protection established by Simpson et al. (2005). This criterion establishes a maximum permitted limit of 100 μg kg^{-1} for organophosphate pesticides. Chlorpyrifos was observed only in sediments of the Burrión ditch, with concentrations always greater than the reference limit in every month and station it was quantified. Results of this work indicate that migration of sediments with high chlorpyrifos concentrations might be a short- and long-term threat for aquatic ecosystems adjacent to the sites where the studied ditches discharge. Measurement of chlorpyrifos and dimethoate in the study area indicates the recent use and application of these compounds. Concentrations of chlorpyrifos in water did not show significative differences ($p \leq 0.05$) between the two ditches, which can be related to the similarity in crop types and agricultural cycles. Chlorpyrifos deserves most attention, according to its prevalence and concentration. However, both compounds may represent potential threats to adjacent aquatic ecosystems, as the acute toxic concentration for the most sensitive species is 0.001 μg kg^{-1}. It is important to point out that dimethoate levels were below the reference limits for protection of aquatic life. However, it should not be present in the natural environment at all. This study evidences the frequent presence of chlorpyrifos in water and sediments of two ditches in agricultural areas of northern Sinaloa state, Mexico. The presence of these pesticides implies that monitoring is essential to understand their transport, environmental fate, effects on ecosystems, and effects on public health, as both ditches are used to catch commercial species such as the grey mullet (*Mugil cephalus*) and cauque prawn (*Macrobrachium americanum*).

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