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RESIDUE ANALYSIS OF ORGANOCHLORINE AND ORGANOPHOSPHORUS PESTICIDES IN URBAN LAKE SEDIMENTS

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ABSTRACT: The knowledge of pesticide residual concentrations in the environment is important to understand the threats to the environment and human health, especially when natural resources are used for human consumption. In this context, this study aimed to assess the potential ecological risk and respective sources of sediment contamination by organochlorine and organophosphorus pesticides. The study site was an urban lake located in Cascavel city, western Paraná state, Brazil, where the history of land use and occupation in the urban environment is typically agricultural. Surface sediment samples were collected every three months from April 2010 to June 2013 at five different collection points, totaling 65 samples. Analyses showed that contamination by organochlorine pesticides is related to agricultural activities in the past, with a low ecological risk to benthic organisms. Conversely, organophosphorus pesticides presented a recent and continuous contamination from urban activities, with a risk coefficient, especially for disulfoton, indicating a significant potential adverse effect on organisms. However, in general, the obtained results did not indicate an immediate risk to public health.

KEYWORDS: agrochemicals, ecological risk, land use and occupation.

INTRODUCTION

The three main classes of synthetic organic pesticides are organochlorines (OCs), organophosphates (OPs), and carbamates (CBs). Largely used in agricultural activities, especially in the past, OCs have spread widely in the environment. In its turn, OPs have now been largely used because of their efficiency as an insecticide (Girard, 2013).

Nearly 95% pesticides reach other destinations than their target sites (Flaherty et al., 2013). In the environment, pesticides can undergo changes in chemical structure by biotic and abiotic processes, resulting in relatively harmless compounds, or even more toxic substances (Majumder & Das, 2016).

Soil pesticide mobility depends on several physical, chemical, and biological factors (Geronimo et al., 2014). The main route of pesticide spread is water, mainly through surface runoff, disseminating it from application areas to other places in the environment, such as water bodies and sediments (Masiá et al., 2013).

Sediments act as archives of environmental changes, and could, therefore, be used to assess contaminants dispersed in the atmosphere, water, and soil (El-Sayed et al., 2015; Remor et al., 2015; Bettinetti et al., 2016). These deposits act on water-column depletion or contamination due to sorption and desorption processes during the interaction among suspended particles, sediments, and water (Wu et al., 2013; He et al., 2015; Bettinetti et al., 2016).

Numerous researchers have assessed sediment contamination at different environments. Regarding OCs, Solé et al. (2013), Smalling et al. (2013), Pintado-Herrera et al. (2017), and Montuori et al. (2016) assessed sediments of coastal areas. Kuranchie-Mensah et al. (2012), Wu et al. (2013), Ogbeide et al. (2016), Oliveira et al. (2016), and Hunt et al. (2016) studied OCs on river

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sediments. In general, scientific studies on OP pesticides are scarcer than those on OCs. Among those with OPs, the most important are in river sediments (Masiá et al., 2015; Montuori et al., 2016; Hunt et al., 2016; Ccanccapa et al., 2016) and coastal area sediments (Smalling et al., 2013; Selvaraj et al., 2014; Montuori et al., 2015; Pintado-Herrera et al., 2017).

Even though lake sediments provide more information on pesticide contamination than those of river and estuarine deposits, they are still scarce (Li et al., 2015). Furthermore, the few already performed have only assessed large lakes, where agricultural activity is predominant in the surroundings. Accordingly, we can mention the studies of Zhao et al. (2010), Zhao et al. (2010), Kuranchie-Mensah et al. (2012), Wu et al. (2013), Yuan et al. (2013), Li et al. (2015), Bettinetti et al. (2016), and Hijosa-Valsero et al. (2016) in freshwater sediments, and those of Barakat et al. (2012b), Barakat et al. (2012a), Barakat et al. (2013), Kafilzadeh (2015), and Pinto et al. (2016) in saline water environments.

Notwithstanding, studies on sediments from urban lakes, whose use and occupation are typically agricultural, are scanty. In this context, this study aimed to assess the potential ecological risk and respective sources of sediment contamination by organochlorine and organophosphate pesticides.

MATERIAL AND METHODS

Study area

The studied lake is located in Cascavel, western Paraná state, Brazil (Figure 1), and presents a water mirror of 34 ha, a volume of 4,060,000 m^3, and drainage area of 650 ha. This lake was created in 1980, rectified in 1996, and dredged in 2010. Currently, land use and occupation in its drainage area are predominantly urban (70%), but with preservation areas (23%) (Cembranel et al. 2017).

Sample collection and preservation

Samples of about 2 kg of surface sediment (0 to 5 cm) were collected by using an Ekman dredger every three months, from April 2010 to June 2013. The sampling covered the four seasons, totaling 13 collections in five different points (Figure 1), totaling 65 samples. The location of points P1, P2, and P3 was determined considering water and soil inlet channels within the main drainage area. Point P4 was defined based on its greater depth, which promotes a major sediment accumulation. Point P5 was selected based on its location, near the lake discharge point, where lake sediments all accumulate. The samples were left to dry at room temperature, in an enclosed place. A Teflon sieve with a 63-µm mesh was used as recommended by Who (1982).

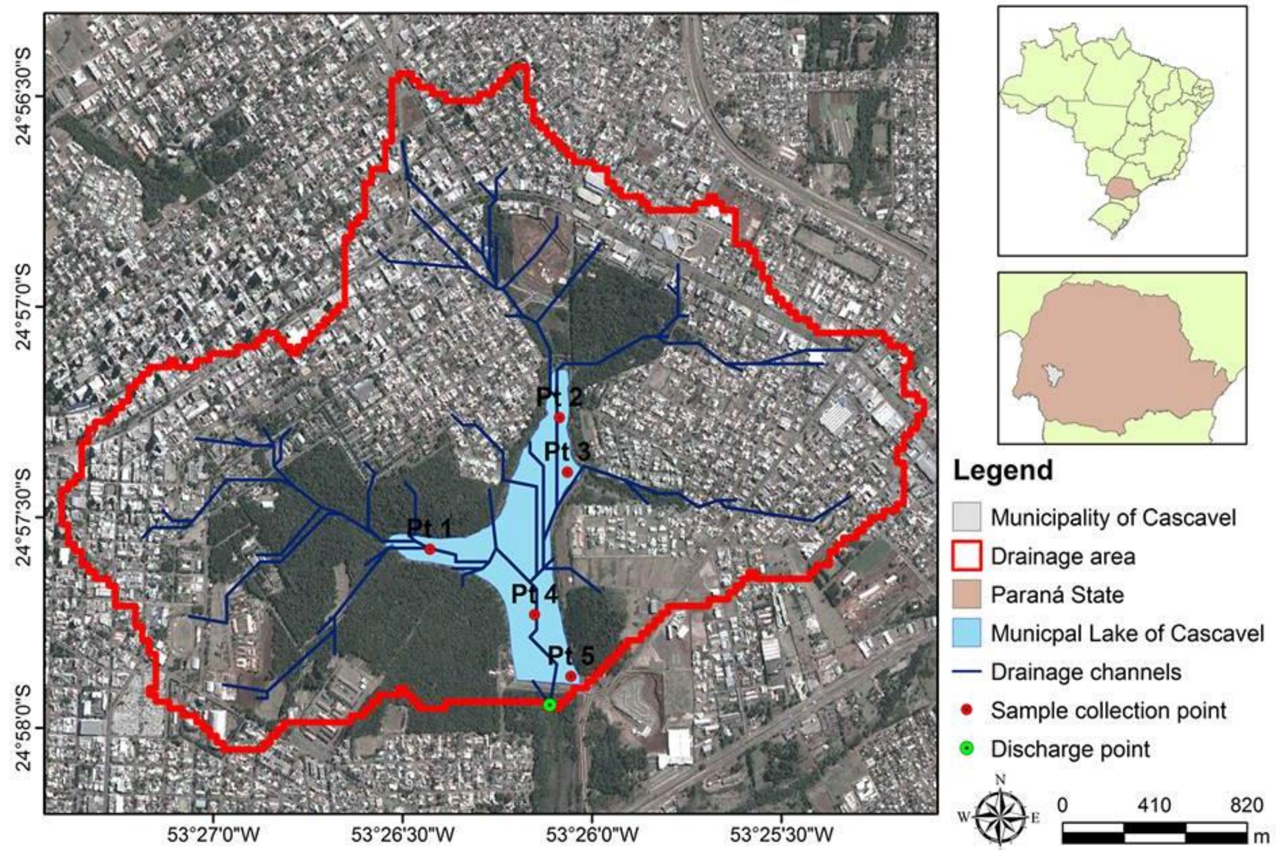

FIGURE 1. Location of the city of Cascavel, in Paraná state (Brazil), and location of the channels, drainage area, and sampling points in the lake.

Pesticides and analysis methods

The analyzed OCs were α-BHC, β-BHC, γ-BHC, δ-BHC, aldrin, DDD, DDE, DDT, dieldrin, endosulfan I (α), endosulfan II (β), endosulfan sulfate, endrin, endrin aldehyde, heptachlor, heptachlor epoxide, and methoxychlor. The analyzed OPs were azinphos-methyl, chlorpyrifos, disulfoton, ethoprophos, methyl parathion, O (2,4-dichlorophenyl), and ronnel (fenchlorphos). The methodology used for extracting, identifying, and quantifying the pesticides was based on Fernandes et al. (2013), by using the QuEChERS method with acetonitrile extraction. Reading was performed in a gas chromatograph coupled to a mass spectrometer (GC–MS).

Analytes were separated on a Restek's RTX$^{®}$-5MS capillary column (30 m × 0.25 mm × 0.25 µm). Column oven temperature was programmed as follows: initial temperature of 150 °C, with an increase of 4 °C/min until reach 300 °C, being held for 4 min, and a final run time of 41.5 min. Ion source temperature was 260 °C, with a detector interface temperature of 280 °C, injected a volume of 1 µL, and helium as carrier gas. OC and OP compounds were identified by comparing the retention time of ions with the standard used. Among the OCs, detection limit (DL) was 0.02 ng g^{-1} and quantification limit (QL) was 0.03 ng g^{-1}. Among the OPs, DL was 0.1 ng g^{-1} and QL was 0.2 ng g^{-1}.

Data analysis

Initially, a descriptive analysis of the data was applied to each collection point. The Tukey's test at 5% significance was applied in the analysis of spatial and temporal distribution. The data were classified by collection points (P1–P5) in the spatial distribution whereas, in the temporal distribution, the data were classified by climatic season (autumn, winter, spring, and summer) and collection year (2010–2013).

The historical analysis of land use and occupation of the drainage area was carried out using aerial images from the site in 1980, 1985, 1995, 2003, 2006, and 2013. Image dates were defined according to availability and confirmation of significant changes in land use and occupation. In the assessment of 1980, 1985, and 1995, we used aerial photos obtained in the city hall, generated by the companies *Esteio Engenharia e Aerolevantamentos S.A.* (1980) and *Engefotos S.A.* (1985 and 1995). Between 2003 and 2013, we used images from the Google Earth Pro. All images were georeferenced using the Georeferencing tool from the GIS ArcGIS 10.

Coordinates of control points were obtained through visual recognition by using the software Google Earth Pro of invariable targets. A digital elevation model from the project TOPODATA, developed by the National Institute for Space Research, was used for defining channels and drainage area. The extraction of channels and drainage area was performed using the toolset in the module Spatial Analyst Tools from the software ArcGIS 10. Initially, the drainage channels were generated for the entire image and, based on them, the discharge point was defined. Subsequently, the lake's drainage area was generated.

Land use and occupation were visually classified in four classes for all dates considered by using the software ArcGIS 10, as follows: forest, urban area, pasture, and agricultural area. Thus, the analyses were carried out by inferring about the quantities and percentage of variation of land use and occupation by category and year.

In the assessment of possible ecological risks caused by OCs (heptachlor epoxide, DDE, DDD, and DDT) contamination to organisms in sediments, the concentrations identified in the samples were compared to the guidelines of Long et al. (1995), Macdonald et al. (1996), and CCME (2002). In the determination of ecological risks caused by OPs (methyl parathion, disulfoton, and azinphos-methyl) compounds, the USEPA (2016) methodology was followed.

RESULTS AND DISCUSSION

Pesticides detected in sediment samples are described in Table 1. Concentrations varied over time and location of collection points. Some pesticides only had their presence identified. Although the use of OC pesticides is restricted to a few activities by the Ordinance No. 329 dated 9/2/1985 (ANVISA, 1985) due to their persistence, metabolites can be found mainly in the soil, sediments, and water (Tian et al., 2015; Garrison et al., 2014).

The metabolite heptachlor epoxide was quantified or identified in 29% of the total samples. At point P5, the site with the highest incidence of this metabolite, 46% of the samples were contaminated. The lowest contamination was observed at point P3, being detected in only two samples. The highest incidence of contamination at point P5 occurred possibly due to the location near the lake's discharge. This point at the lake is subject to a greater accumulation of sediments/pesticides from the whole lake due to the water flow. However, a reverse dynamics occurred at point P3, which is located in an area of small depth near the lakeshore, where water inlet from the surface runoff from a predominantly urban area occurs more strongly, limiting the concentration of sediment/pesticide particles. In studies developed by Barakat et al. (2013) and Kafilzadeh (2015), heptachlor epoxide was found more frequently when compared to our study. High levels of this metabolite, such as that observed in the studied lake, indicate an aged presence of heptachlor (Barakat et al., 2013).

DDT was quantified in 21% of the total samples, but it was not identified in the samples. At point P1, 38% of the samples were contaminated, making it the point of the greatest frequency of contamination. Point P1 is located in a lake appendix, a place with little water flow and water inlet through surface runoff, which is originated from a drainage area occupied by a forest. Thus, DDT incidence is possibly due to a contamination in the past. The metabolites DDD and DDE were not quantified in the samples. However, these metabolites were identified in 13% and 63% of the samples, respectively, considering the minimum detection limit. DDD was identified in 23% of the samples at point P4, which had the highest contamination level. DDE presence was identified at all collection points and in 100% of the samples at point P5.

In studies carried out by Zhao et al. (2010) and Li et al. (2015), DDT concentrations were higher than those of DDE and DDD, as observed in our study. However, these results are different from those found by Kuranchie-Mensah et al. (2012), Yuan et al. (2013), Wu et al. (2013), Bettinetti et al. (2016), and Hijosa-Valsero et al. (2016), in which DDE and DDD concentrations were higher when compared to DDT concentrations. DDE is a metabolite of DDT and a high proportion of this compound denotes a past use of DDT (Barakat et al., 2013). Thus, a DDE detection in 63% of the samples indicates an old contamination. Another method confirming this old contamination is the ratio DDT/(DDE + DDD) < 1 (Wu et al., 2013; Hijosa-Valsero et al., 2016; Oliveira et al., 2016), as observed in our study. However, DDT concentrations found in the samples could indicate contemporary contamination, which is possibly due to the dredging process carried out in the lake in 2010, causing a recirculation and movement of pesticide residues from the lower layers of sediments.

TABLE 1. Concentration of organochlorine and organophosphorus pesticides at collection points (ng g^{-1} d. w.).

Organochlorine pesticide

	P1				P2				P3				P4				P5			
Pesticide	$\bar{X}$	SD	Min	Max	$\bar{X}$	SD	Min	Max	$\bar{X}$	SD	Min	Max	$\bar{X}$	SD	Min	Max	$\bar{X}$	SD	Min	Max
Aldrin	n.d.	*	n.d.	n.d.	0.106	0.367	n.d.	1.378	n.d.	*	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.056	0.196	n.d.	0.734
DDD	<DL	*	n.d.	<DL	<DL	*	n.d.	<DL	n.d.	*	n.d.	<DL	<DL	*	n.d.	<DL	<DL	*	n.d.	<DL
DDE	<DL	*	n.d.	<DL	<DL	*	n.d.	<DL	n.d.	*	n.d.	n.d.	<DL	*	n.d.	<DL	<DL	*	n.d.	<DL
DDT	0.149	0.189	n.d.	0.394	0.088	0.160	n.d.	0.387	0.032	0.099	n.d.	0.374	0.061	0.142	n.d.	0.398	0.058	0.136	n.d.	0.384
Endosulfan II (β)	<DL	*	n.d.	<DL	n.d.	*	n.d.	n.d.	<DL	n.d.	n.d.	<DL	<DL	*	n.d.	<DL	<DL	*	n.d.	<DL
Heptachlor	0.008	0.015	n.d.	0.038	0.003	0.009	n.d.	0.033	0.005	0.012	n.d.	0.038	n.d.	0.000	n.d.	0.000	0.007	0.013	n.d.	0.037
Heptachlor epoxide	0.003	0.007	n.d.	0.025	0.009	0.021	n.d.	0.063	<DL	*	n.d.	<DL	0.154	0.283	n.d.	1.014	0.030	0.047	n.d.	0.155
Methoxychlor	0.010	0.036	n.d.	0.133	0.140	0.371	n.d.	1.411	0.011	0.037	n.d.	0.138	0.036	0.066	n.d.	0.182	0.053	0.067	n.d.	0.139

Organophosphate pesticide

	P1				P2				P3				P4				P5			
Pesticide	$\bar{X}$	SD	Min	Max	$\bar{X}$	SD	Min	Max	$\bar{X}$	SD	Min	Max	$\bar{X}$	SD	Min	Max	$\bar{X}$	SD	Min	Max
Azinphos-methyl	0.572	1.981	n.d.	7.435	1.145	2.685	n.d.	7.448	0.572	1.982	n.d.	7.438	2.289	3.434	n.d.	7.445	1.718	3.137	n.d.	7.445
Chlorpyrifos	n.d.	*	n.d.	n.d.	n.d.	*	n.d.	n.d.	n.d.	*	n.d.	n.d.	n.d.	*	n.d.	n.d.	0.321	1.112	n.d.	4.174
Disulfoton	1.573	2.871	n.d.	6.815	1.573	2.871	n.d.	6.815	2.097	3.146	n.d.	6.820	1.048	2.458	n.d.	6.814	3.145	3.397	n.d.	6.815
Ethoprophos	0.467	1.096	n.d.	3.048	0.474	1.113	n.d.	3.087	0.237	0.821	n.d.	3.081	0.233	0.808	n.d.	3.033	1.197	1.516	n.d.	3.351
Methyl parathion	2.902	3.134	n.d.	6.293	0.967	2.268	n.d.	6.288	2.899	3.132	n.d.	6.292	4.361	2.907	n.d.	6.316	4.360	2.907	n.d.	6.353
Ronnel fenchlorphos	0.193	0.353	n.d.	0.837	0.193	0.352	n.d.	0.837	0.064	0.223	n.d.	0.838	0.196	0.358	n.d.	0.879	0.516	0.408	n.d.	0.844

<DL = below the quantification limit; n.d. = not detected; * = not calculated; $\bar{X}$ = average of the 13 samples; SD = standard deviation; Min = minimum concentration; Max = maximum concentration; P1–P5 = collection points.

Among the assessed OCs, only for the metabolites heptachlor and DDT, the concentrations identified in the samples might have been originated from past agricultural activities, possibly before lake construction. OC compounds present stability to decomposition or degradation in the environment, i.e. they have a very low solubility in water and a high solubility in lipophilic environments (Spiro & Stigliani, 2009; Baird & Cann, 2011; Girard, 2013). Studies have shown that DDT is still found in high concentration in the biota at various locations around the world

(Kafilzadeh, 2015).

Organochlorines pesticides remain for a long time in sediments, soils, biota, and air, and may have a half-life of years or decades. Pesticide half-life corresponds to the time, in days, necessary for 50% of its initial dose to disappear. These compounds, when in aquatic and soil environments, adhere to the organic matter, avoiding the aqueous phase and soil solution, being accumulated in sediments due to its high octanol-water partition coefficient (Jones & Voogt, 1999; Girard, 2013; Barakat et al., 2013; Li et al., 2015).

Among the seven OP pesticides, six were found in the analysis (Table 1). In this group, there were no samples in which these pesticides were only identified, i.e. they were quantified or had no presence detected.

Methyl parathion was the pesticide most found, present in 49% of the total samples. At points P5 and P4, 69% of the samples contained this pesticide. At point P2, methyl parathion was found in only 15% of the samples. Galindo-Reyes et al. (1999) found concentrations higher than those observed in our study. Moreover, Ccanccapa et al. (2016) identified this compound with a low frequency and concentration.

Chlorpyrifos presented the lowest contamination index, being found in only one sample at point P5. Barakat et al. (2012b), Barakat et al. (2012a), Pinto et al. (2016), and Ccanccapa et al. (2016) found this pesticide in more than 50% of samples, with average concentrations higher than those identified in our study.

Among the OP pesticides, azinphos-methyl presented the highest concentration, being quantified in 16% of the total samples. Point P4 presented the highest number of contaminated samples whereas points P1 and P3 presented only one contaminated sample. In this sense, Masiá et al. (2013), Montuori et al. (2015), and Ccanccapa et al. (2016) observed a less frequent contamination by azinphos-methyl when compared to that identified in our study.

Disulfoton was found in 27% of the total samples, with an incidence at all collection points. Point P5 presented the highest contamination index, with 46% of the total samples contaminated with this pesticide. On the other hand, point P4 showed the lowest contamination index, with 15% of the samples contaminated with disulfoton.

Spatial and temporal analysis of pesticide concentrations

Among the OC pesticides, only the metabolite heptachlor epoxide showed a significant difference between collection points (Figure 2a) according to the Tukey’s test at 5% significance. The average sediment concentrations were statistically the same at points P2, P4, and P5, with the highest average concentration (0.154 ng g^{-1}) found at point P4.

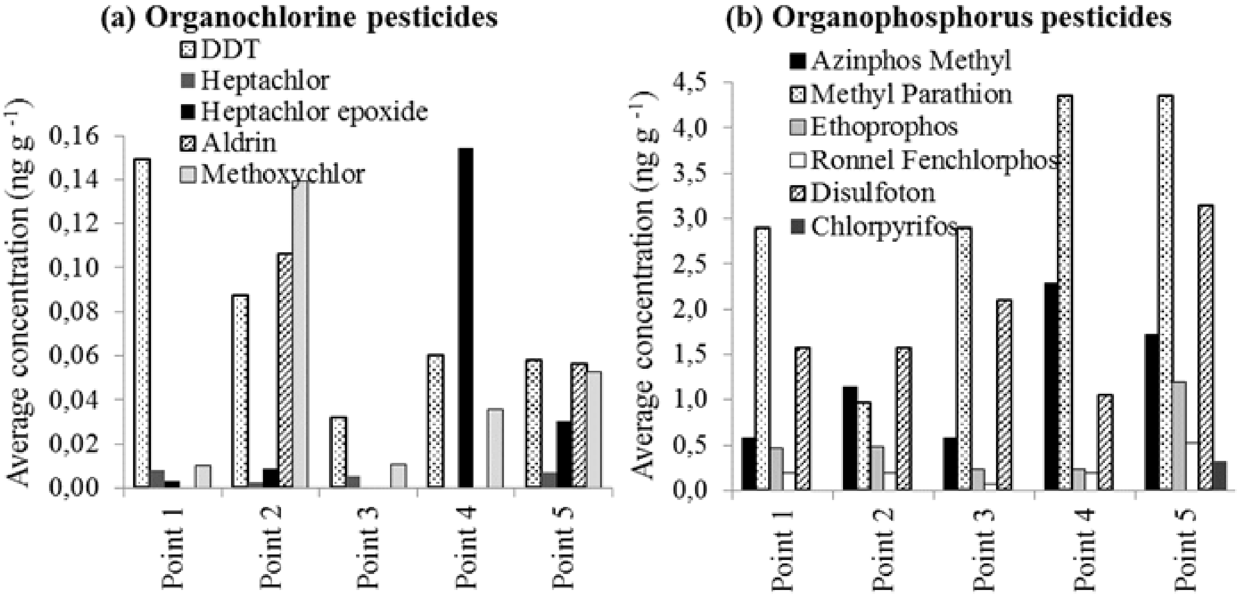

FIGURE 2. Pesticides found in sediments considering the collection points in the lake.

Among the OP pesticides (Figure 2b), ronnel fenchlorphos presented the highest average sediment concentration (0.516 ng g^{-1}) at point P5, statistically differing from those obtained at points P1, P2, and P4. Methyl parathion presented the highest average concentration at P4 (4,360 ng g^{-1}), statistically equal to the points P1, P3, and P5. The location of point P4, at the deepest site of the lake, and point P5, near the lake's discharge point, potentiated higher sediment concentrations due to the action of gravity (P4) and water flow (P5), leading to higher pesticide concentrations.

In the assessment of temporal distribution, OC compounds (Figure 3a) did not present average concentrations with statistically significant differences regarding the seasons by the Tukey's test (p 0.05). Among the OP pesticides (Figure 3b), disulfoton presented the highest average in the winter (4,089 ng g^{-1}), which is statistically equal by the Tukey's test ($p <0.05$) to that quantified in the sediments collected in the spring.

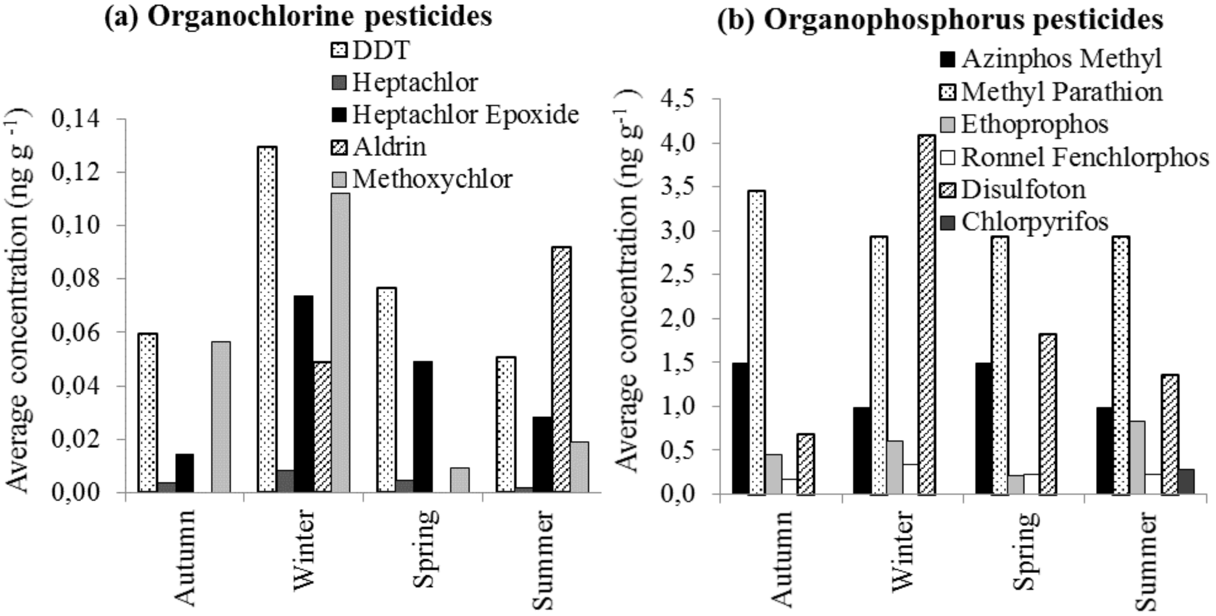

FIGURE 3. Pesticides found in sediments considering the climatic seasons.

The lake is located in a region where winter is characterized as a season with a lower rainfall. Rain directly interferes with the entry of water into the lake, interfering with the movement and sedimentation of particles contaminated by pesticides (Possavatz et al., 2014). Therefore, the average concentration of disulfoton in the winter was higher due to a lower water movement and higher sediment stability. In addition, the test performed by year of collection showed that the average concentrations of OC and OP pesticides did not present statistical differences by the Tukey's test ($p > 0.05$).

Influence of variation of land use and occupation

Lake's implantation occurred in a flooded soil area bordered by plots of soil with agricultural activities, pastures, forests, and a small urban area. In the years of 1980, 1985, and 1995, the plots of soil covered by agricultural activities corresponded to 7.19%, 6.89%, and 5.55% of the drainage area, respectively. The agricultural areas were extinguished from 2003, giving space to urban areas, forests, and pastures (Table 2). Between 1980 and 2013, significant transformations in land use in the drainage area occurred, being the most intense the exclusion of agricultural practices, which represented 7.19% of the area in 1980, not being identified from 2003. Another significant variation occurred in pasture areas, which occupied 11.52% of the area in 1980 and only 1.34% in 2013, characterizing the largest percentage difference between the analyzed categories. In absolute terms, the urban area increased 56.42 ha, which represents an increment of 8.67%. Forest areas increased by 5.11% from the lake's implantation until 2013.

TABLE 2. Land use and occupation between 1980 and 2013.

	Area and year of occupation (ha)					
Land use and occupation	1980	1985	1995	2003	2006	2013
Agriculture	46.74	44.83	36.10	–	–	–
Lake	–	35.02	33.78	32.90	33.17	34.38
Flooded soil	10.87	–	–	–	–	–
Forest	121.10	139.12	131.51	146.09	151.63	154.27
Pasture	74.96	32.07	25.53	34.43	19.92	8.78
Urban activity	396.81	399.43	423.55	437.04	445.75	453.03
Total area	650.466	650.466	650.466	650.467	650.466	650.466

Source: the authors.

Pesticide concentration in water and sediments of lakes is related to the amount and intensity of agricultural soil cultivated in the surroundings since pesticides are closely related to agriculture (Hijosa-Valsero et al., 2016). In this context, Table 2 shows that, even before lake's implantation, the drainage area presented a low occupation by agricultural activities (7.19%), which decreased over the years until a complete extinction between 1995 and 2003. In lakes, the most common route of entry of pollutants is the erosion of agricultural soils after irrigation or precipitation (Hijosa-Valsero et al., 2016). Therefore, the main contamination source was extinguished after the end of agricultural activities.

Despite the rapid degradation (Troeh & Thompson, 2007), OP pesticides have been frequently found in different studies (Hossain et al., 2013; Masiá et al., 2013; Abraham et al., 2014; Ccanccapa et al., 2016). In a study conducted by Cristale et al. (2013) with river sediments subject to different anthropogenic pressures, OP pesticides were omnipresent. In the river where the industrial and urban activities were more intense, the concentrations of OP pesticides were higher. Huizhen et al. (2011) identified OP pesticides in sediments in the urban area, while Chen et al. (2014) found relevant concentrations of OP pesticides at domestic and industrial wastewater discharge points. The study of Ccanccapa et al. (2016) with river sediment samples detected frequent OP contamination in agricultural and urban areas in the surroundings. OP inputs are originated from surface runoff and discharge from industrial wastewater, atmospheric deposition, and poor agricultural practices (Montuori et al., 2016). All these aforementioned studies evidence OP presence in sediments from sites with the influence of urban areas, as observed in our study.

Ecological risk assessment

Among the OC pesticides, the compound with the highest concentration in sediments was the heptachlor epoxide. However, in only one of the samples, taken from point P4, the concentration of 1.014 ng g^{-1} was higher than the threshold effect level (TEL) (Table 3), indicating that adverse effects may occasionally occur. This concentration at point P4 is possibly due to its location at the deepest point in the lake, where a greater particle accumulation due to the gravity action occurs. Another 16 samples presented concentrations lower than TEL, indicating a low probability of adverse effects.

TABLE 3. Assessment of ecological risks of organochlorine pesticides in sediments.

Pesticide	Variation in concentration (ng g^{-1})	TEL** (ng g^{-1})	PEL** (ng g^{-1})	ELR* (ng g^{-1})	ERM* (ng g^{-1})
Heptachlor epoxide	n.d. – 1,014	0.6	2.74	n.g.	n.g.
DDE	n.d. – p	2.07	374	2.2	27
DDD	n.d. – p	1.22	7.81	2	20
DDT	n.d. – 0.398	1.19	4.77	1	7

n.d. = not detected; p = not quantified; *according to Long et al. (1995) and Macdonald et al. (1996); C = concentration; C < ELR = adverse effects are rarely observed; ELR ≤ C < ERM = occasional adverse effects will occur; C ≥ ERM = adverse effects are likely to occur frequently; **according to CCME (2002); C < TEL = minimum level of effect, adverse effects rarely occur; TEL ≤ C ≤ PEL = adverse effects occur occasionally; C > PEL = possible adverse effects will occur frequently.

The metabolites DDE and DDD were not quantified in the samples, presenting any ecological risk. DDT was quantified in at least two samples at each collection point, totaling 14 contaminated samples, but at concentrations lower than the effect low range (ELR), in which adverse effects are rarely observed (Table 3).

In a study conducted by LI et al. (2015), DDT and its metabolites also did not represent a potential ecological risk to benthic organisms. In the study carried out by Barakat et al. (2013), the indices varied between samples, with and without potential ecological risk, different from the results obtained by Wu et al. (2013), who indicated a potential ecological risk for DDT.

For the assessment of the ecological risk of OP pesticides, methyl parathion and azinphos-methyl showed no significant risk to benthic organisms, with RQ < 1 (Table 4). However, disulfoton concentrations indicate a risk coefficient with a significant potential for an adverse effect on the organisms (Table 4). At all collection points, we observed at least two samples with pesticide concentrations at risk, totaling 18 samples under these conditions. Point P5 presented 33% of the total disulfoton samples with significant potential for adverse effect. Among the OP pesticides, the most researched is the chlorpyrifos, present in studies conducted by Weston et al. (2013), Li et al. (2013), Hunt et al. (2016), Nowell et al. (2016), and Xu et al. (2016). In our study, chlorpyrifos was identified in only one sample (4,174 ng g^{-1}), with a risk coefficient of 1.003, indicating a small potential for adverse effects.

TABLE 4. Assessment of ecological risks of organophosphorus pesticides in sediments.

Pesticide	Variation in concentration (ng g^{-1})	Average concentration (ng g^{-1})	LC_{50} (ng g^{-1})	RQ (maximum concentration)
Methyl parathion	n.d. – 6.352	3.097	6900[a]	0.920
Disulfoton	n.d. – 6.820	1.887	240[b]	28.41
Azinphos-methyl	n.d. – 7.447	1.259	21800[c]	0.341

According to USEPA (2016), RQ = MEC (ng g^{-1})/(LC_{50}/f); MEC = maximum concentration of pesticide in the samples (Cristale et al., 2013); LC_{50} = lethal pesticide concentration for 50% of the population on acute exposure; f = safety factor (1000); [a]LC_{50} for *H. azteca* (Weston et al., 2013); [b]LC_{50} for *G. lacustris* (ECOTOX, 2016); [c]LC_{50} for *A. tenuiremis* (Klosterhaus et al., 2003); RQ < 1.0 = no significant risk; 1.0 ≤ RQ < 10 = small potential for adverse effects; 10 ≤ RQ < 100 = significant potential for adverse effects; RQ ≥ 100 = potential adverse effects should be expected; n.d. = not detected.

The highest number of sediment samples (50%) contaminated with disulfoton with an RQ > 1 was observed in the winter, indicating a significant potential for adverse effects. The only sample of OC pesticides with adverse effects may occur occasionally was also collected in the winter. This season is characterized by the lowest precipitation index in the region. The dry season also presented the highest RQ in a study developed by Chen et al. (2014).

In a study conducted by Ccanccapa et al. (2016), OP pesticides also presented a great concern regarding the ecological risk among the analyzed pesticides. The potential ecological risk associated with OP pesticides should not be neglected, but monitored as they may cause potential damage to organisms from the benthic environment (Montuori et al., 2016).

However, the high octane-water partition coefficient and high solid/water ratio of hydrocarbons cause a low solubility in water, disfavoring their immediate use by organisms and promoting their accumulation in the solid phases of the environment (Johnsen et al., 2005). A precise determination of hydrocarbon effects on species is limited by the uncertainty in the quantification of receptor exposure (Quiñones-Rivera et al., 2003). The ecological risk analysis based on the amount of hydrocarbons does not necessarily indicate how much is available for absorption by the living organisms (Semple et al., 2004).

CONCLUSIONS

While OC pesticide analyses assigned the contamination to past agricultural activities, OP pesticide analyses indicated a recent and continuous contamination from urban activities. Overall, OC concentrations presented a low ecological risk to organisms in the benthic environment. On the other side, for OP pesticides, especially disulfoton, several samples showed a significant risk coefficient against organisms in the environment. In general, the results did not demonstrate an immediate risk to public health.

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