

## Characterization of organochlorinated pesticides in water and sediments, Tucutunemo River, Venezuela

### Abstract

This research intends to characterize Organochlorinated Pesticides (OCPs) and physicochemical parameters in water and sediments in the Tucutunemo River; information, which will serve to subsequently develop a pollutant transport model. A total of 36 simple samples of water and sediments were collected and analyzed every six months in three monitoring stations in 2015. The Tucutunemo River basin covers an area of 116.67 km<sup>2</sup>, of which 13.75 km<sup>2</sup> is cultivated agricultural land. The OCPs were characterized by chemical analysis, using a gas chromatograph with electron capture detector. It was calibrated with 14 OCPs, eight of which were detected, including: aldrin, dieldrin, p.p'-DDD, p.p'-DDE, p.p'-DDT, endrin, o.p'-DDE and o.p'-DDT. In water, total OCP concentrations varied from 0.073 to 0.098 µg l<sup>-1</sup>, below the regulation of the Bolivarian Republic of Venezuela, which proposes 200 µg l<sup>-1</sup>. The average of the highest concentrations of OCPs detected in water were: aldrin, 0.021 µg l<sup>-1</sup>; dieldrin, 0.022 µg l<sup>-1</sup>; and p.p'-DDT, 0.011 µg l<sup>-1</sup>. Except for p.p'-DDT, the ranges were lower than those proposed by the EPA of 1.300, 0.730 and 0.001 µg l<sup>-1</sup>, for aldrin, dieldrin and DDT, respectively. In the sediments, the total concentrations ranged from 13.340 to 45.910 µg kg<sup>-1</sup>. The highest average concentrations were aldrin (4.508 µg kg<sup>-1</sup>) and dieldrin (4.169 µg kg<sup>-1</sup>). In sediments, analysis of variance detected significant differences (p < 0.05) for some of the OCPs.

**Keywords:** Characterization, organochlorinated pesticides, water, sediments, Tucutunemo River.

Received: 28/06/2017

Accepted: 14/03/2018

## Introduction

On a global scale, the issue of pesticides is of concern to researchers and institutions that regulate the contamination of water bodies because of their harmful effects on people, animals and benthic organisms (Jones & Voogt, 1999). It is estimated that almost two-thirds of the water used by man is used for agriculture, while the need for fresh water to sustain life on Earth is increasingly. However, the use of pesticides has increased considerably over the last 35 years, reaching rates of increase of 4 to 5.4 percent in some regions (FAO, 2002).

The United Nations Environment Program (PNUMA, 2012) declares that water is essential for all ecosystems, both aquatic and terrestrial, which is due to the fact that it is subject to high levels of competition among users. Agricultural activity as a major consumer of pesticides and fresh water is the main cause of the degradation of water resources. In low-income countries, OCPs pose health risks through multiple exposures in a relatively short period of time, risks which are often elevated by inappropriate use and a lack of regulatory control. These pesticides do not dissipate easily and can remain in the environment for a long time. Thus, the evaluation of 72% of extensive rivers and 56% of lake area demonstrates the polluting effects of agriculture (FAO, 1997; Del Puerto, Suárez, & Palacio, 2014; FAO, 2015).

Currently, persistent and bioaccumulative OCPs are found in agricultural soils, including DDT, Toxaphene, aldrin and dieldrin, which are banned in many countries in accordance with the Stockholm Convention. For example, annual results on the trend of pollution in Europe, America and Asia report that pesticide residues still persist in coastal sediments that originated in river basins, due to soil erosion, surface runoff and water discharges from rivers that transport significant amounts of OCPs in the environment (Carvalho, 2006; Carvalho, 2017).

As an illustration, the case of the Montrose Chemical Corporation of California has been reported, which operated for 35 years and produced approximately 800 000 tons of DDT. This company constituted a point source of pollution that extended to a radius of 2 km, with even more distant effects from its effect on ocean sediments on the floors of the continental platform of the Palos Verde Bay (EPA, 2003; EPA, 2009).

OCPs are organochlorinated pesticides that are basically formed by carbon and hydrogen skeletons to which chlorine atoms bond. They were widely used from 1940 to 1970 in agriculture and insect control (Stoker & Seager, 1980; EPA, 2009). Meanwhile, the water provided by rain and irrigation extracted from the wells produces water erosion that transports the surface layer of cultivated soils to the Tucutunemo River,

where the samples were collected. A variety of contaminants were detected, among which the following OCPs were found: aldrin, dieldrin, p.p'-DDD, p.p'-DDE, p.p'-DDT, endrin, o.p'-DDE and o.p'-DDT. Compounds such as DDT, once present in the riverbed, can be incorporated into biota, water, and sediments, causing health problems for agricultural equipment operators and their families (FAO, 2002; Astiz, 2012).

In addition, OCPs tend to present transboundary transport and dispersion. In this sense, the pollution scenario identifies an instant point source with a piston-type flow that disperses the pollutant to other latitudes through water, sediments and air. It is then detected in a wide range of environmental settings. The shortcomings of the transboundary water pollution control and monitoring programs in the Danube River basin are related to a lack of accepted guidelines on water quality and differences in sampling methods and data interpretation. Similarly, the Tucutunemo River originates in the state of Aragua and then flows into Guárico state, affecting the quality of the water in the Camatagua reservoir. This type of contamination, punctual or diffuse, poses a threat to human health and the overall environment (Literathy, 1997; Kuranchie-Mensah *et al.*, 2012; Del Puerto *et al.*, 2014; Guevara, 2016).

In Venezuela, OCPs began to be used frequently in the 1940s. For example, DDT was first introduced in 1945 to control malaria and yellow fever. Later, in 1960, DDT was applied for agricultural purposes under the impetus of the Agrarian Reform. It is also reported that between 1975 and 2003 roughly 8 600 tons of OCPs were imported into the country, identified as: DDT, aldrin, Hexachlorobenzene, Chlordane, Toxaphene, Heptachlor, dieldrin and endrin (Ministerio del Poder Popular para el Ambiente, 2006; Isea, Huerta, & Rodríguez, 2009).

The Tucutunemo River basin is located in the state of Aragua, in an agricultural sector having strategic importance as the first producer of certified corn and sorghum seed for more than 20 years (Pérez & Nieves, 2004; Pineda, Machado, Casanova, & Vilorio, 2006)). After the signing of the Stockholm Convention and its ratification in 2005, according to the Official Gazette 38 098, agriculture in Venezuela and the Tucutunemo River basin was modified by the prohibition of the use of OCPs, such as: aldrin, dieldrin, endrin, Chlordane, DDT, Heptachlor, Mirex and Toxaphene, Polychlorinated Biphenyls (PCB), dioxins and furans (Gil, 2006). The water in the Tucutunemo River does not receive purification treatment along its course, though it is collected and treated

to meet the needs of towns and Caracas (Hidroven, 2012; Hidroven, 2013).

As a reference for this research, results are included of OCPs found by Romero in water and sediments in the Lake of Valencia basin, in the state of Carabobo. That study found concentrations of metabolites of DDT, Lindane, Heptachlor and their epoxides, which varied in water from 0.015 to 0.060  $\mu\text{g l}^{-1}$  and in sediments from 2.50 to 8.00  $\mu\text{g kg}^{-1}$  for sampling campaigns conducted in July and November 2001, respectively (Romero, 2002).

Within this context, it is necessary to consider the United Nations Report that projects attaining a sufficient supply of good quality water by the year 2025, to benefit the entire population on the planet (PNUMA, 1977). However, to contribute to this projection and preserve the hydrological, biological and chemical functions of ecosystems, so that human activity conforms to the limits of the capacity of nature, the present study is aimed at characterizing organochlorinated pesticides and physicochemical parameters in the water and sediments of the Tucutunemo River. The results of this research can provide valuable information for regulators of water companies, as well as for farmers in the region, farm managers, the chemical industry, consultants and researchers on a global scale, who are interested in the quantification and dynamics of OCPs in water bodies.

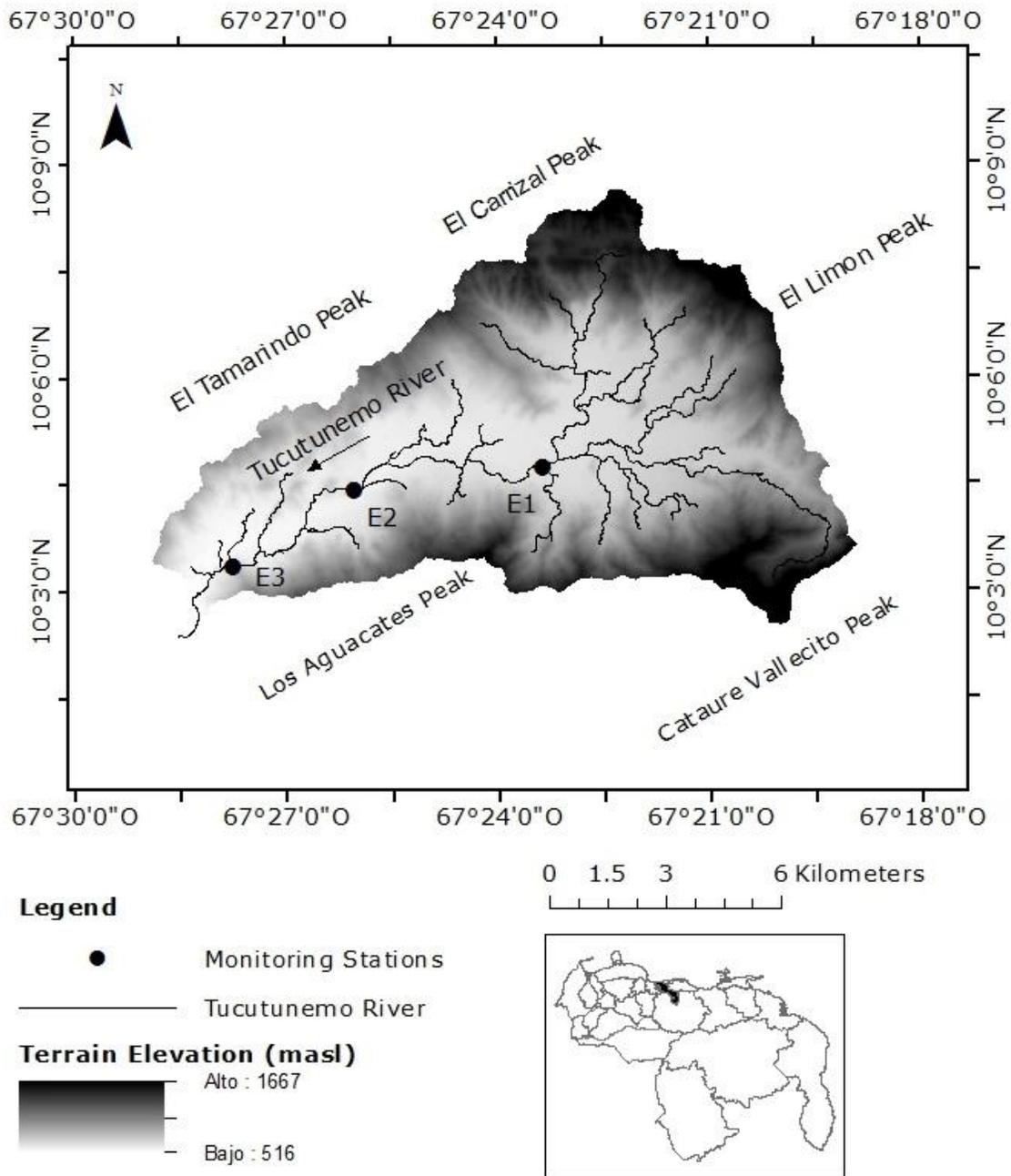
## Materials and Methods

### Study area

The study area is the Tucutunemo River basin, located in the Zamora municipality of the state of Aragua, in central Venezuela. The projected coordinates obtained with a GPS system (Global Positioning System) are: North 1 110 000 - 1 123 000 and East 666 000-685 000.

The investigation was carried out in the Tucutunemo River (Figure 1); where the monitoring stations are located, identified by their UTM coordinates and altitude, as follows: Station 1 (E1), N 1 115 667–E 676

612, altitude 593 meters above sea level (masl); Station 2 (E2), N 1 114 377–E 672 058, altitude 565 masl; and Station 3 (E3), N 1 112 747–E 668 331, altitude 534 masl, located in the localities of El Espinal, El Cortijo and La Lagunita, respectively. These are strategic points in the basin, where there is agricultural activity. The Tucutunemo River transports water regularly throughout the year, which flows from Station 1 to Station 3, with an average flow at Station 3 of  $0.076 \text{ m}^3 \text{ s}^{-1}$ . In these stations, samples of water and sediments were collected to measure OCPs and physicochemical parameters during the months of April and October 2015. It is observed that the basin has an elevation that varies from 1 690 to 590 masl.

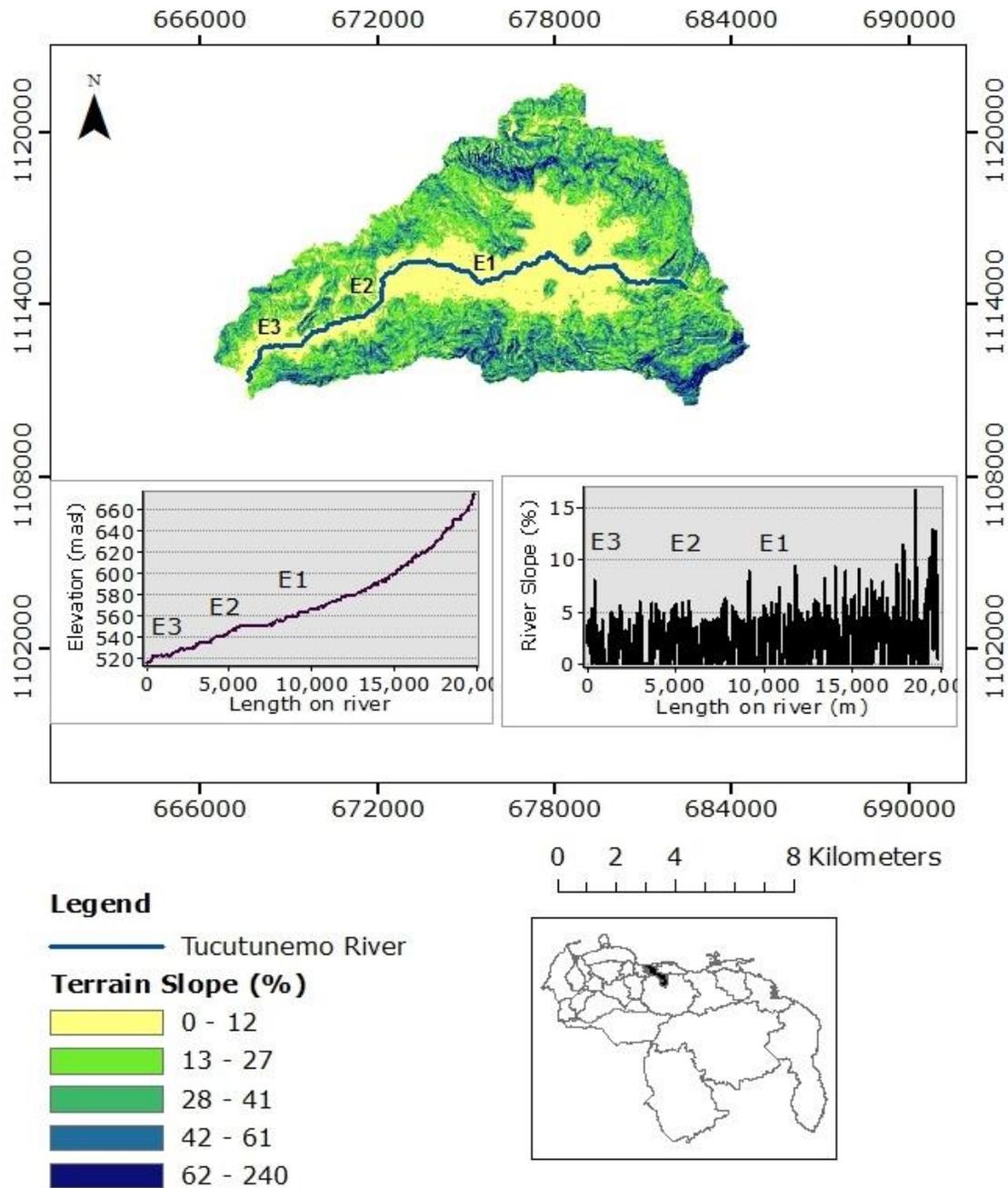


**Figure 1.** Monitoring stations on the Tucunemo River, Zamora municipality, Aragua state, Venezuela.

The digital elevation model known as ASTER GDEM (Advance Spaceborne Thermal Emission and Reflection Radiometer Global Digital

Elevation Model) is a product of METI and NASA, downloaded from the Earth Explorer satellite image portal ([https:// earthexplorer](https://earthexplorer)).

Figure 2 shows the geomorphological characteristics that influence the transport of OCPs, such as: slope of the Tucutunemo River basin, longitudinal profile of terrain elevations along the river axis and profile of the channel's slopes (%) with an indication of the OCP measurement stations. The zonal statistics of the observed slope classes (%) were extracted with the ArcGIS V.10 program and are associated with the coverage area as follows: 0 and 12%: 35 km<sup>2</sup> (31%); 13 and 27%: 29 km<sup>2</sup> (25%); 28 and 41%: 30 km<sup>2</sup> (26%); 42 and 61%: 16 km<sup>2</sup> (14%); 62 and 240%: 4 km<sup>2</sup> (4%).

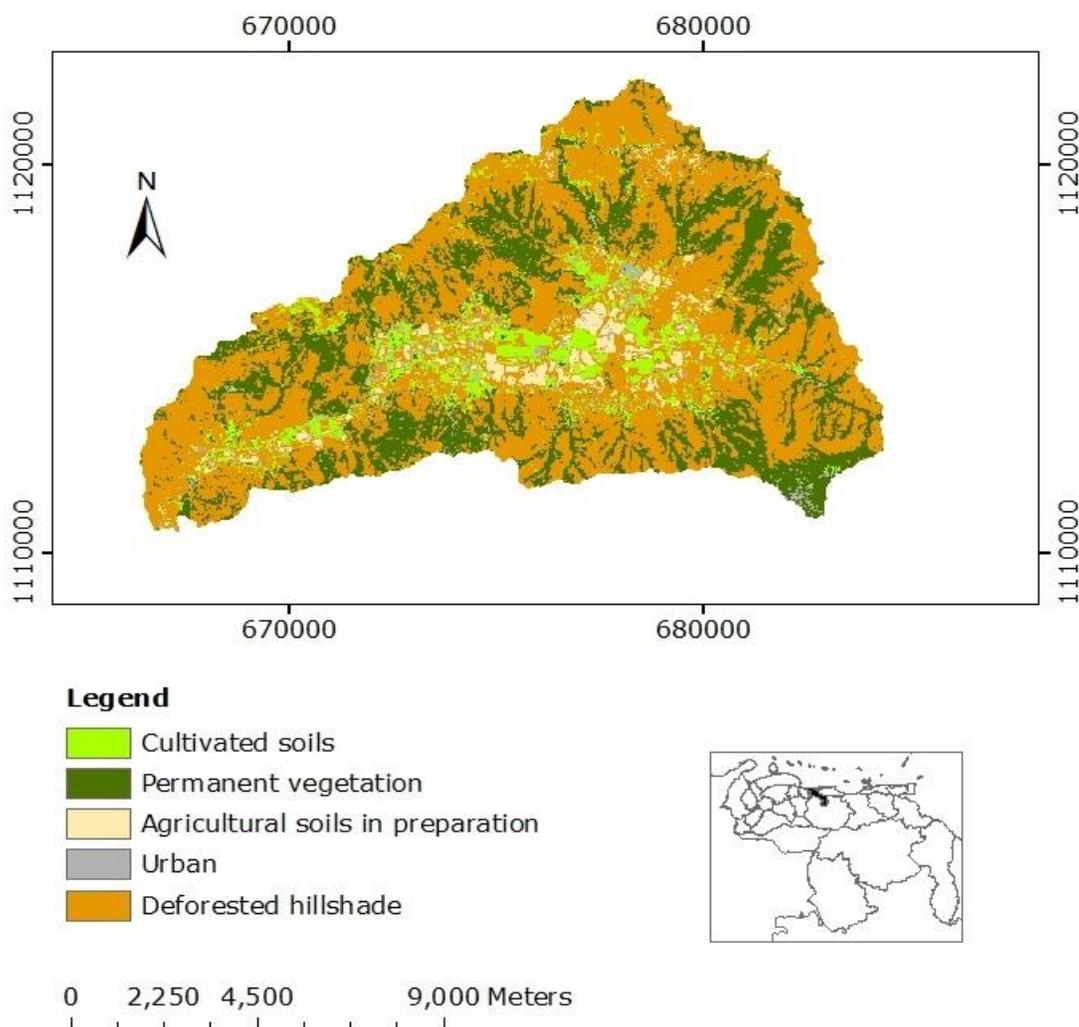


**Figure 2.** Land slope of the Tucutunemo River basin, including longitudinal profile of terrain elevations (masl) on the river axis and slope profile (%) of the channel, with indication of OCP measurement stations.

The elevation and slope profiles of the river channel are presented along with the OCPs measuring stations, which are located from the outlet to

the headwaters approximately as follows: E3: 1 000 m, 3%; E2: 5 000 m, 6% and E1: 10 000 m, 8%. In general, the slope profile shows that the slope of the river bed varies between 0 and 8% along at least 15 km of the river from the outlet to the head of the basin, which is considered slight, according to Guevara and Cartaya (2004).

For an overview of the agricultural activity in the Tucutunemo River basin, Figure 3 presents a land use and land cover map obtained by applying a supervised classification method to an image of the Landsat 8 satellite, from April 30, 2015, obtained from the US Geological Survey.



**Figure 3.** Map of land use and coverage in the Tucutunemo River basin, Zamora municipality, Aragua state, Venezuela.

The land use and land cover extracted from ArcGIS V. 10 indicate the following distribution in terms of area: 1) cultivated soils: 8.87 km<sup>2</sup> (7.6%); 2) perennial vegetation: 26.67 km<sup>2</sup> (31.09%); 3) agricultural soils in preparation: 4.23 km<sup>2</sup> (4.93%); 4) urban: 2.77 km<sup>2</sup> (3.23%) and 5) deforested hillsides: 58.73 km<sup>2</sup> (68.52%).

According to this information, cultivated soils and agricultural soils in preparation can be integrated in a single cartographic unit, identified as "agricultural soils," with an area of 13.75 km<sup>2</sup>, equivalent to 11.79% of the total area, estimated as 116.67 km<sup>2</sup>. According to the climatological information available, the study area has an average annual rainfall of 890.2 mm, which is divided into two notable periods: rainy and dry. The rainy period includes the months from May to October and the dry period from November to April. It has a warm climate, with temperatures ranging between 20 ° and 35 ° C, depending on the intensity of the winds and the presence of clouds (Olivar, Mijail, Pedrique, & Rossmar, 2006).

## **Monitoring for the Determination of OCP in Water and Sediments**

One-liter amber glass jars with plastic lids were used to collect the water samples. They were previously washed and sterilized, and provided by the Environmental Quality laboratory of the Ministry of Popular Power for Habitat and Housing Ecosocialism, in Maracay, Aragua state. The samples were collected in the Tucutunemo River every six months during both the dry and the rainy seasons, from April 15 to October 15, 2015 respectively. To determine the variability of the OCPs in the samples, the water tests were repeated every three days, so that in each season 9 simple samples of water were collected, that is, 3 samples per station with 3 repetitions in each of them. The water samples were obtained manually in the center of the cross-section of the river, at half the depth of the channel. In total, in the dry and rainy seasons, 18 water samples were collected and the concentration of OCPs was determined. in  $\mu\text{g l}^{-1}$ . The instrumental detection limit for pesticides in water was  $0.001 \mu\text{g l}^{-1}$ .

The sediment samples were collected in the same way as the water samples, from April to October, with a total of 18 simple samples, which

were taken at each monitoring station, on both banks of the channel, with a spatula, in a thin surface sheet, with an approximate weight of 500 g. They were placed in clean plastic bags of 2 kg capacity and identified as follows: Tucutunemo River, SEDIMENTS: E1, M1, 04-15-2015.

For the determination and quantification of analytes, a gas chromatograph was used, with electronic capture detector, brand SHIMADZU, model GC-14B, catalog number 122-1332 and THK 2673335 film. The conditions for the analysis of each sample were detector temperature of 320° C, injector temperature of 280°C and column temperature of 230° C, according to criteria in Training Manual No. 430 / 1-74-012 (Bicking, Olin, & King, 1974), Manual for the Determination of Residues for Organochlorinated Pesticides in Water (Covenin, 1987) and Standard Methods (APHA-AWWA-WPCF, 2002).

The chromatograph was calibrated with a set of 14 OCPs that in the past were used in the cultivation plots in the Tucutunemo River basin, namely: aldrin, Lindane,  $\alpha$ -BHC,  $\beta$ -BHC, p.p'-DD, p.p'-DDE, p.p'-DDT, dieldrin, endrin, Heptachlor, Heptachlor epoxide, o.p'-DDD, o.p'-DDE and o.p'-DDT. From this group, eight OCPs were selected, which were regularly determined to have detectable concentrations, allowing for statistical analysis. These OCPs were: aldrin, dieldrin, p.p'-DDD, p.p'-DDE, p.p'-DDT, endrin, o.p'-DDE and o.p'-DDT. The detection limit for the OCPs in sediments was 0.01  $\mu\text{g kg}^{-1}$ .

## **Determination of Physicochemical Parameters in Waters in the Tucutunemo River**

Physicochemical parameters were determined in each station, in the dry and rainy periods of the year 2015, using international standard methods. The elements that were measured and are related to the OCPs studied in the water from the Tucutunemo River are: a) flow, b) pH, c) electrical conductivity and d) total, dissolved and suspended solids.

## **Statistical Analysis**

The statistical analyses included 1) the ranges, compiled from minimum and maximum values of the OCP levels detected, 2) the average, and 3) the standard deviation of the samples in each station. For cases with no variability in OCP among the samples, the range and the standard deviation was assigned a value of "0." However, in these cases, the range shown in the tables identifies the same value as the minimum and maximum levels detected at the corresponding station. The analysis of variance was applied to the data, which identified variability in order to determine significant differences in the mean OCP measured at each sampling station. All tests are statistically significant for  $p < 0.05$ .

## Results and discussion

### Physicochemical parameters

Table 1 presents the results of the physicochemical parameters that are related to the OCP in water from the Tucutunemo River. As a sample of these results, total solids (TS) are presented, which increased from Station 1 to Station 3 from 278 to 483  $\text{mg l}^{-1}$  in the dry period and from 435 to 470  $\text{mg L}^{-1}$  in the rainy period. The total suspended solids (TSS), varied in the dry season from 44 to 93  $\text{mg l}^{-1}$ , and in the rainy season from 81 to 91  $\text{mg l}^{-1}$ . The mass load (ML) of total solids generated in the agricultural process in the Tucutunemo River basin corresponds to 4 101.41  $\text{kg day}^{-1}$ , which equals a mass value of 1 497 013.92  $\text{kg year}^{-1}$ .

**Table 1.** Physical chemical parameters measured from Station 1 to Station 3 during the dry and rainy periods in the Tucutunemo River, year 2015.

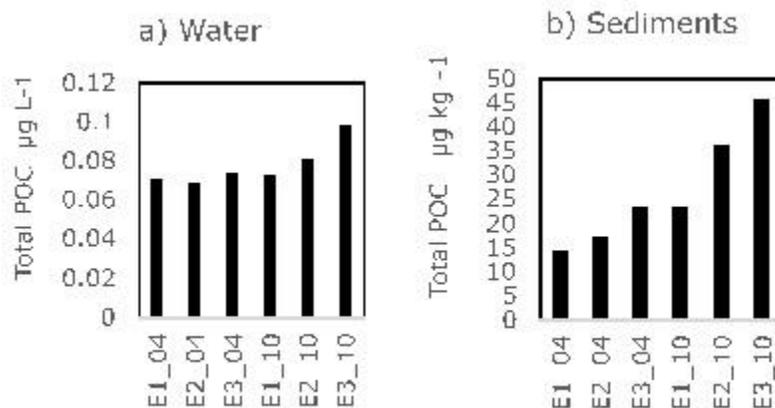
Parameters	Dry period: April 2015	Rainy period: October 2015
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	<b>E1</b>	<b>E2</b>	<b>E3</b>	<b>E1</b>	<b>E2</b>	<b>E3</b>
Flow ( $\text{m}^3 \text{s}^{-1}$ )	0.028	0.047	0.051	0.044	0.062	0.101
Reynolds No. ( $> 4000$ )	3 088 000 000	4 011 860 317	6 568 800 000	3 867 530 159	5 789 815 873	7 859 830 688
pH	7.03	7.05	7.15	7.1	7.05	7.06
Electric conductivity, EC ( $\mu\text{S cm}^{-1}$ )	467	730	783	705	699	708
Total solids, TS ( $\text{mg l}^{-1}$ )	278	454	483	435	459	470
Total Suspended Solids, TSS ( $\text{mg l}^{-1}$ )	44	89	93	82	91	81
Totals dissolved solids, TDS ( $\text{mg l}^{-1}$ )	234	365	390	353	368	389
ML. Total solids ( $\text{kg day}^{-1}$ )	672.538	1 843.603	2 128.291	1 653.696	2 458.771	4 101.408
ML. Suspended Solids ( $\text{kg day}^{-1}$ )	106.445	361.411	409.795	311.731	487.469	706.838
ML Dissolved Solids, ( $\text{kg day}^{-1}$ )	566.093	1 482.192	1 718.496	1 341.965	1 971.302	3 394.570

ML: Mass load.

## Distribution of total OCPs in water and sediments

Figure 4 shows the results obtained for the total OCPs in water ( $\mu\text{g l}^{-1}$ ) and sediments ( $\mu\text{g kg}^{-1}$ ) for the Tucutunemo River in the dry and rainy periods for 2015. On the x-axis the coding is presented according to the station, followed by the month of monitoring. As an example, the sequence E1\_04, E2\_04 and E3\_04 corresponds to Station 1 (E1), Station 2 (E2) and Station 3 (E3) in the month of April (04) or dry period, respectively. The total OCP residues are presented on the y-axis.



**Figure 4.** Concentrations of total OCP: a) measured in water ( $\mu\text{g l}^{-1}$ ) and b) in sediments ( $\mu\text{g kg}^{-1}$ ) in three stations on the Tucutunemo River, corresponding to the year 2015, Zamora municipality, Aragua state, Bolivarian Republic of Venezuela.

In general, the total OCPs measured in water from the Tucutunemo River show an accumulation tendency from station 1 to 3 and from the dry to the rainy period (Figure 4a). In this case, the OCPs measured in water ranged from 0.073 to 0.078  $\mu\text{g l}^{-1}$  during the dry period and from 0.075 to 0.098  $\mu\text{g l}^{-1}$  during the rainy period. This variation represents an 6.85% increase in total OCP during the dry period and 30.67% during the rainy period. To compare these results, Zhou, Zhu, Yang and Chen (2006), who studied waters from the Qiantang River in China, report total OCPs varying from 0.008 to 0.269  $\mu\text{g l}^{-1}$ . These concentrations are higher than those registered in the Tucutunemo River. Although the increase in the total OCPs in water is evident both in the dry and rainy periods, during both periods the total OCPs in water were less than 200  $\mu\text{g l}^{-1}$ , which is the maximum limit allowed by the Venezuelan regulations established in decree 883 of the Bolivarian Republic of Venezuela (1995). Therefore, the Tucutunemo River water is classified as sub-type 2A, that is, it is suitable for the irrigation of vegetables for human consumption. However, the total OCPs found in the waters of the Tucutunemo River would be alarming if they were evaluated with the freshwater quality criteria by the Environmental Protection Agency (EPA) for DDT and its metabolites, which establishes 0.001  $\mu\text{g l}^{-1}$  as a critical limit for a 24-hour average (EPA, 2003; EPA, 2016).

Meanwhile, the total OCPs in sediments (dry weight) shown in Figure 4b varied from Station 1 to Station 3 from 13.340 to 25.063  $\mu\text{g kg}^{-1}$  during the dry period and from 27.323 to 45.910  $\mu\text{g kg}^{-1}$  during the rainy

period. As a comparison of total OCP concentrations in sediments, in the Guanting reservoir in Beijing, where a total of 21 OCP were analyzed, the concentrations varied from 5.250 to 33.400  $\mu\text{g kg}^{-1}$  ( Xue, Zhang, & Xa, 2006), which are lower than those found in the rainy period in the Tucutunemo River, where the OCP contributions found in the sediments responded to the drainage of agricultural land from the effect of rainfall or irrigation water from wells.

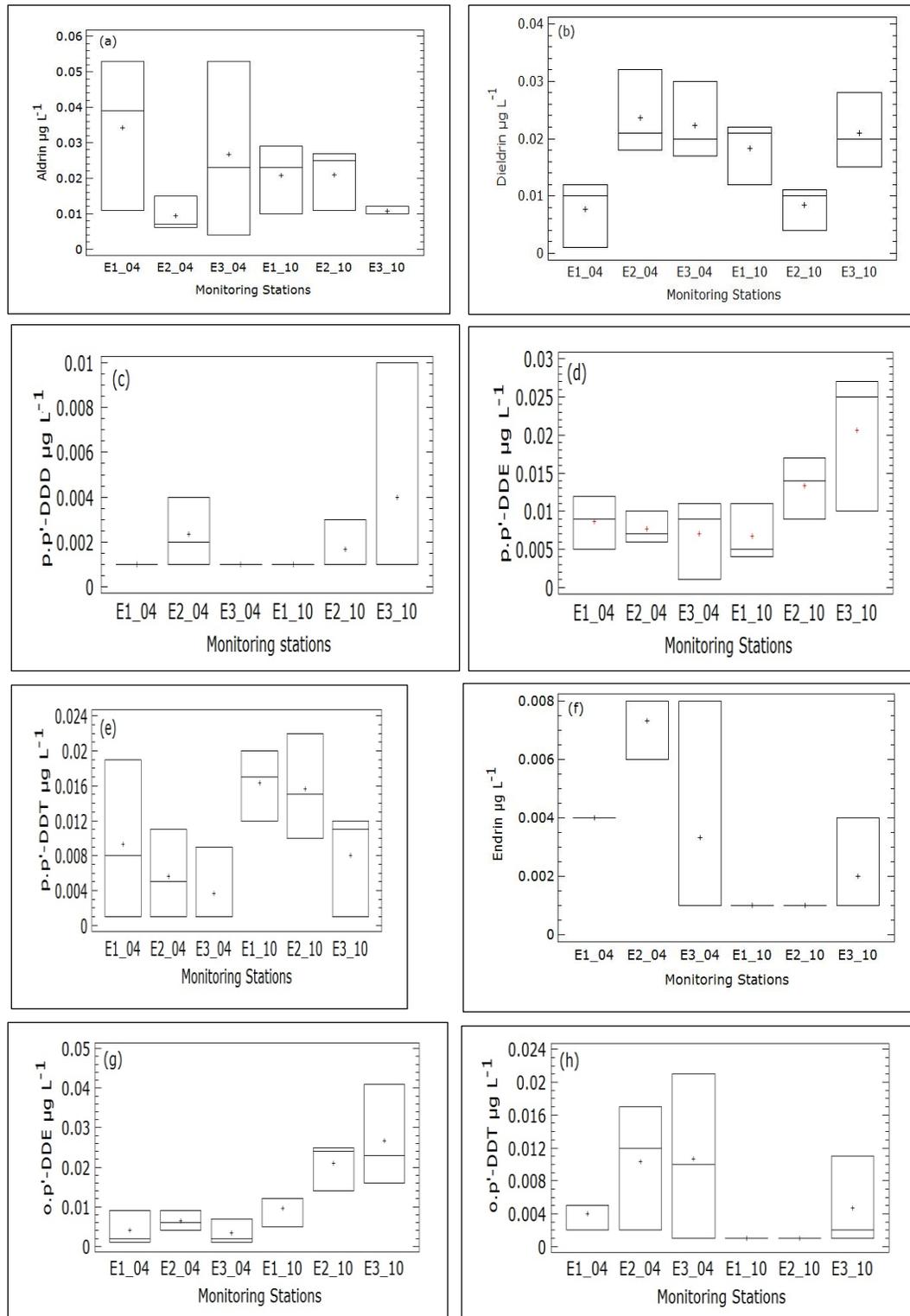
The notable difference between the OCP residues in water versus those in the sediments is due to the fact that these compounds are hydrophobic with a high affinity given the tiny sediment particles ( Elder & Weber, 1980; Guevara, 2016). In addition, the increase in total OCP residues in sediments during the dry season is probably due to the lower flow of the river, which contributes to greater sedimentation of the soil's microparticles and the sorption of the pesticides in them.

## Individual OCPs in water and sediments

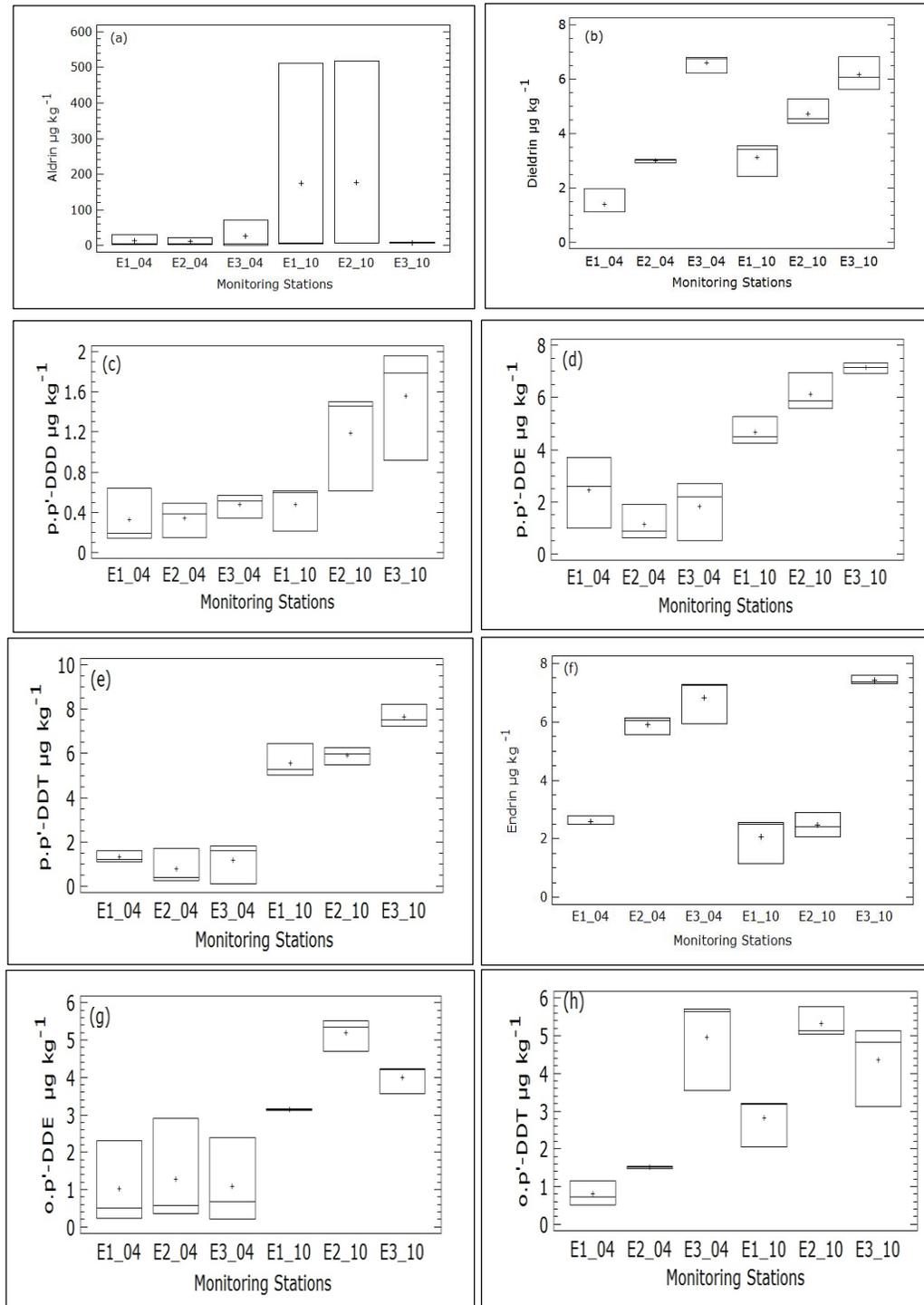
Figure 5 and Figure 6 show the individual results of the OCPs in water ( $\mu\text{g l}^{-1}$ ) and sediments ( $\mu\text{g kg}^{-1}$ ) from the Tucutunemo River, using the same coding applied in Figure 4. Each component in each graph in Figure 5 and Figure 6 shows a box, whose ends represent the interquartile range. The data's variability, asymmetry, arithmetic average sign (+) and median or dividing line are shown within each box, representing measures of central tendency. The results for aldrin in water and sediments from the Tucutunemo River are shown in Figure 5a and Figure 6a. In water, a higher concentration of aldrin is observed in the dry season with respect to the rainy season, varying between 0.004 and 0.053  $\mu\text{g l}^{-1}$  and from 0.010 to 0.029  $\mu\text{g l}^{-1}$ , respectively. In Figure 5a and Figure 6a, the box diagrams overlap, indicating that there are no significant differences in the concentrations of aldrin found in water and sediments among measuring stations and between climatic periods for 2015. By comparing the values of the aldrin in the water from the Tucutunemo River with those found for aldrin in the Densu River in the Republic of Ghana, whose range of variation is reported as between 0.010 and 0.020  $\mu\text{g l}^{-1}$  (Kuranchie-Mensah *et al.*, 2012), the concentration of aldrin in water from the Tucutunemo River is found to be higher than that of the Densu River. Also, Astiz (2012) reports concentrations of aldrin in water from the Cataniapo River in Venezuela

in the range of 0.019 to 0.072  $\mu\text{g l}^{-1}$ , which is higher than the Tucutunemo River. Although aldrin is prohibited in Venezuela, due to the shortage of alternative pesticides, some farmers in the Tucutunemo River basin still use it, at their own risk, in their agricultural work. It is stated that in Venezuela, the use of OCPs is prohibited, therefore they are not sold or marketed.

In the sediments, it is observed that the interval varies between 0.23 and 8.22  $\mu\text{g kg}^{-1}$ . The variability within the samplings is greater in the dry season compared with the rainy season. A tendency towards stability was observed in the concentrations of aldrin in the sediments, with a slight increase towards the E3 station. The cultivation area is adjacent to the Tucutunemo River, as shown in Figure 2 and Figure 3, and therefore it is possible to infer that aldrin is being applied to agricultural soils and is transported by runoff and water erosion to the Tucutunemo River on an ongoing basis.



**Figure 5.** Concentrations of POC ( $\mu\text{g l}^{-1}$ ), in water samples in the Tucutunemo River during 2015: a) aldrin; b) dieldrin; c) p,p'-DDD; d) p,p'-DDE; e) p,p'-DDT; f) endrin; g) o,p'-DDE, and h) o,p'-DDT.



**Figure 6.** Concentrations of POC in sediments ( $\mu\text{g kg}^{-1}$ ), in the Tucutunemo river during 2015: a) aldrin; b) dieldrin; c) p,p'-DDD; d) p,p'-DDE; e) p,p'-DDT; f) endrin; g) o,p'-DDE, and h) o,p'-DDT.

The source of the aldrin in the river water can be found in the interaction of the soil-water environment. The aldrin applied to agricultural land can undergo chemical and biochemical processes: retardation and biodegradation, respectively. In the case of biodegradation, once the aldrin has been desorbed from the agricultural soil towards the solution-mass and is in an aqueous phase, its bioaccessibility is increased and a biochemical transformation can take place, carried out by the microorganisms contained in the agricultural soil from aldrin to dieldrin. Thus, the enzyme oxygenase influences the metabolism by catalyzing the insertion of an oxygen atom present between double-bond carbon atoms in a triangular form, known as epoxide (Vogel, Criddle, & McCarty, 1987; Guevara, 2016). This biodegradation could lead to reducing aldrin in the agricultural soils of the Tucutunemo River basin, but only when the application of these OCPs has ceased, which is unlikely.

The results for dieldrin in water and sediments from the Tucutunemo River are presented in Figure 5b and Figure 6b. As can be seen, for water, most of the box diagrams overlap (Figure 5b), which represents stability in the occurrence of dieldrin concentrations; being slightly lower in the E1 and E2 monitoring stations located upstream from E3 located in the flattest area of the basin at approximately 1 000 m from the outlet, on the Tucutunemo River axis where the slopes range from 0 to 3% (Figure 1 and Figure 2). dieldrin concentrations tend to increase during each dry or rainy period, from 0.004 to 0.053  $\mu\text{g l}^{-1}$ , similar to that found for aldrin (Figure 5a), given the rapid recovery of dieldrin concentrations in water between consecutive climatic periods in 2015. This is an indication that farmers are directly applying this OCP to the agricultural land on an ongoing basis.

Regarding the sediments, the results of dieldrin in sediments are presented in Figure 6b, where it is observed that from measuring station E1\_10 to E3\_10, the concentration increases from 1.13 to 6.82  $\mu\text{g kg}^{-1}$  recurrently during the dry and rainy periods. This implies that the dieldrin is not being eliminated at the point source located in the agricultural soils of the Tucutunemo River basin.

As a reference, 0.01 to 0.03  $\text{mg kg}^{-1}$  of dieldrin has been found in agricultural soils in the municipality of Pueblo Llano, according to Uzcategui, Araujo and Mendoza (2011).

The origin of dieldrin can be from two sources: a product synthetically created as a commercial pesticide or a "daughter product" generated as a result of the biodegradation of aldrin, as mentioned above. In both

cases, its presence in agricultural land is a result of controlling pests in crops, with possible application in past and present times in the agricultural settlement of the Tucutunemo River basin (Guevara, 2016). The results of p.p'-DDD found in the water and sediments of the Tucutunemo River are presented in Figure 5c and Figure 6c. In water, Figure 5c shows the box diagrams varying in orders of magnitude between 0.001 and 0.010  $\mu\text{g l}^{-1}$ . The box diagrams overlap so there is no statistically significant difference in the p.p'-DDD concentrations found among monitoring stations and between climatic periods. The concentration in the E3 station has a slightly increasing trend due to being located in the flatter areas of the river where the slope varies between 0 and 3%, with molecular diffusion and sorption processes occurring in the solid particles in the soil of the Tucutunemo River bed (Figure 2).

With respect to sediments, the concentration of p.p'-DDD in sediments is shown in Figure 6c, which ranges from 0.14 to 1.96  $\mu\text{g kg}^{-1}$ . The box diagrams show most of these overlapping, which represents stability in the occurrence of p.p'-DDD concentrations in the sediments; being slightly lower in measuring stations E1 and E2 located upstream of E3, which is located in the flattest area of the basin, approximately 1 000 m from the outlet on the axis of the Tucutunemo River, where the slopes vary between 0 and 3% (Figure 1 and Figure 2). This fact implies that the p.p'-DDD is being applied on an ongoing basis at the point source located in the agricultural land in the Tucutunemo River basin.

As a reference, p.p'-DDD has been found in the agricultural soils of Pueblo Llano, in concentrations ranging between 0.04 and 0.83  $\text{mg kg}^{-1}$  (Uzcátegui, Araujo, & Mendoza, 2011). The compound p.p'-DDD is a pesticide and also a degraded form of p.p'-DDT (ATSDR, 2002; Álvarez & Guevara, 2003).

It can result from a biochemical transformation caused by the anaerobic microorganisms contained in the agricultural soil from p.p'-DDT, whose process involves a reductive dehalogenation of the hydrogenolysis type, also known as hydrodehalogenation. This mechanism involves the replacement of a halogen Cl atom by a hydrogen atom (ATSDR, 2002; University of Minnesota, 2003; Guevara, 2016).

The results of p.p'-DDE found in water and sediments from the Tucutunemo River are presented in Figure 5d and Figure 6d. In water, Figure 5d shows that p.p'-DDE varies from 0.001 to 0.010  $\mu\text{g l}^{-1}$ . The box diagrams overlap, so there is no statistically significant difference in the concentrations of p.p'-DDE among sampling stations and between consecutive climatic periods. In addition, the concentration in the E3

station has a slightly increasing trend, due to being located in the flatter areas of the river, where the slope varies between 0 and 3%, with molecular diffusion and sorption processes occurring in the solid particles of the soil in the Tucutunemo River bed (Figure 2).

In sediments, the results of p.p'-DDE are shown in Figure 6d; varying between 1.9 and 6.8  $\mu\text{g kg}^{-1}$ . Most box diagrams overlap, which represents a concentration of p.p'-DDE in sediments that tends to be stable in the dry season, while in the rainy season, the tendency of the concentration is ascending from E1 to E3. This suggests that the p.p'-DDT is being applied on an ongoing basis at the point source located in the agricultural land in the Tucutunemo River basin. As a recent reference, p.p'-DDE has been found in the agricultural soils of Pueblo Llano in concentrations from 0.01 to 0.56  $\text{mg kg}^{-1}$  (Uzcátegui *et al.*, 2011).

The p.p'-DDE compound is a "daughter product" of p.p'-DDT formed by a biochemical transformation, where a neighbor hydrogen atom and a halogen are removed as ions with the concurrent formation of a double bond, through a process called dehydrohalogenation. This reaction can also occur spontaneously in water without the need for biological catalysis (ATSDR, 2002; Guevara, 2016).

In particular, the p.p'-DDD in Figure 6c and the p.p'-DDE in Figure 6d show similar patterns in relation to the median concentration of the OCP, with values that increase from the category E1\_04 to the category E3\_10. In addition, asymmetry can be seen, which is expressed as the deviation between two observable statistics in the box diagrams that measure the central tendency of the data, such as the arithmetic average and the median. In this sense, it can be observed in the box diagrams that, if the arithmetic average coincides with the median, there is no bias. If the arithmetic average (+) is above the median then there is positive asymmetry; or if the arithmetic average (+) is below the median then there is negative asymmetry. In Figure 6c, the bias of p.p'-DDD values is positive and in some cases bias is not found; while in the categories of p.p'-DDE (Figure 6d), the asymmetry is variable, resulting in positive in some instances and negative in others.

However, despite having a bias of the arithmetic average with respect to the median, this is not statistically significant; thus it can be said that the data conform to a normal distribution function. The latter is an assumption that is used to perform an analysis of variances of the arithmetic averages obtained from the OCP samplings among the measurement stations in the dry and rainy periods of 2015. This

guideline extends to the rest of the analysis of the box diagrams of the OCPs included in the study.

The results of p.p'-DDT found in waters and sediments from the Tucutunemo River are presented in Figure 5e and Figure 6e. In water, Figure 5e shows that the p.p'-DDT ranges from 0.001 to 0.020  $\mu\text{g l}^{-1}$ . The box diagrams overlap so there is no statistically significant difference in the concentrations of p.p'-DDT in the water from the Tucutunemo River among sampling stations and between consecutive climatic periods. Figure 6e shows the results of p.p'-DDT in sediments varying between 0.1 and 8.24  $\mu\text{g kg}^{-1}$ .

The box diagrams overlap so there is no statistically significant difference in the p.p'-DDT concentrations in Tucutunemo River waters among sampling stations and between consecutive climatic periods. In addition, the concentration of OCP in sediments has a slightly increasing trend in the E3 station due to being located in the flatter areas of the river, where the slope varies between 0 and 3%, and molecular diffusion and sorption processes occur in the solid particles of the soil in the Tucutunemo River bed (Figure 2). This implies that the p.p'-DDT is being applied on an ongoing basis at point sources located on the agricultural land in the Tucutunemo River basin.

As a recent reference, 0.04 and 0.99  $\text{mg kg}^{-1}$  of p.p'-DDT has been found in agricultural soils in the municipality of Pueblo Llano, according to Uzcátegui *et al.* (2011). The origin of p.p'-DDT in the river water is based on the interaction of the soil-water environment. The p.p'-DDT applied to agricultural soil can undergo two processes: retardation and biodegradation.

In the case of biodegradation, once the p.p'-DDT has been desorbed from the agricultural soil towards the mass-solution and is in an aqueous phase, its bioaccessibility increases and a biochemical transformation can result from the microorganisms present in the agricultural soil, converting from p.p'-DDT into its "daughter products" such as p.p'-DDD and p.p'-DDE, as described above, which exhibit uniformity and seasonality, and are biodegraded by hydrodehalogenation and by dehydrohalogenation, respectively.

This biodegradation could reduce p.p'-DDT in agricultural soils in the Tucutunemo River basin only if the application of this OCP has ceased, which is unlikely.

Figure 5f and Figure 6f show the results of endrin found in water and sediments from the Tucutunemo River. In water, Figure 5f shows that endrin varies between 0.001 and 0.008  $\mu\text{g l}^{-1}$ . Box diagrams overlap so

there is no statistically significant difference in endrin concentrations in among sampling stations and between consecutive climatic periods.

Figure 6f presents the results of endrin in sediments, which shows an increasing concentration from 1.16 to 7.6  $\mu\text{g kg}^{-1}$  recurrently during the dry and rainy periods from the upstream measurement station E1\_10 to E3\_10 located near the outlet of the basin. This implies that endrin is being applied on an ongoing basis at a point source in the agricultural land in the Tucutunemo River basin.

As a recent reference, 0.01 and 0.04  $\text{mg kg}^{-1}$  of endrin has been found in agricultural soils in the municipality of Pueblo Llano, according to Uzcátegui *et al.* (2011). endrin in the river's water results from the interaction of the soil-water environment. endrin can degrade when exposed to high temperatures or light, forming mainly ketone and endrin aldehydes, and has low water solubility (ATSDR, 1996).

Figure 5g and Figure 6g show the results of o.p'-DDE in water and sediments. In water, Figure 5g shows that 0.001 to 0.041  $\mu\text{g l}^{-1}$  of o.p'-DDE has been found in the water of the Tucutunemo River. In sediments, Figure 6g shows the results of the pesticide o.p'-DDE in the form of boxes, present increasing concentrations from 0.2 to 5.52  $\mu\text{g kg}^{-1}$ .

The concentration of o.p'-DDE in sediments shows stable and low values during the dry period from category E1\_04 to E3\_04, compared with the rainy season. In the rainy season, there is an increase in concentration from category E1\_10 to E3\_10. Most of the box diagrams overlap, showing that the concentrations of o.p'-DDE tend to be stable along the river during the dry and rainy seasons. A slight increase in E3 tends to occur due to being located in the flatter areas of the river, where the slope varies between 0 and 3% (Figure 2). This fact implies that the o.p'-DDE is currently being applied on an ongoing basis in the agricultural settlement of the Tucutunemo River basin.

The o.p'-DDE is a degraded form of p.p'-DDT (ATSDR, 2002; Álvarez & Guevara, 2003). As a recent reference, 0.04 and 0.99  $\text{mg kg}^{-1}$  of p.p'-DDT has been found in agricultural soils in the municipality of Pueblo Llano, according to Uzcátegui *et al.* (2011). The o.p'-DDE is a "daughter product" of p.p'-DDT resulting from a biochemical transformation, where a neighbor hydrogen atom and a halogen are removed as ions with the concurrent formation of a double-bond, through a process called dehydrohalogenation. This reaction can also occur spontaneously in water without the need for biological catalysis (ATSDR, 2002; Guevara, 2016).

In general, regarding the characterization of the OCPs in waters and sediments from the Tucutunemo River, no statistically significant differences have been found ( $p = 0.05$ ) in the concentrations of all OCP included in this study, given that the box diagrams show overlap, with a slight increasing tendency in OCP concentrations in water and sediments towards the E3 measuring station.

This station is located 1 000 m away from the outlet on the river axis and constitutes the flattest area of the Tucutunemo River basin, where the slopes of the channel vary between 0 and 3%, affecting OCP transport predominantly by molecular diffusion. Given this tendency, the nature of the flow of the OCP and its degraded forms can be characterized by three conditions: 1) uniform flow along the river ( $dC/dx = 0$ ), 2) incompressible flow along the Tucutunemo River ( $dC / dx = 0$ ), 3) and steady flow ( $dC/dt = 0$ ).

In the uniform flow, the properties of the fluid remain constant throughout the flow field. In the incompressible flow, the density of each particle of the fluid remains relatively constant as it travels through the entire flow field. In steady flow, the properties of the fluid do not depend on time (Potter & Wiggert, 2003). These three characteristics, represented by two concentration gradients, are an indication that the primary OCPs, such as aldrin, dieldrin, p.p'-DDT and endrin, are being applied to agricultural soils on an ongoing basis in the settlement of the Tucutunemo River basin. There are also strains of microorganisms in the agricultural soils of the Tucutunemo River basin that are capable of degrading the primary forms of the OCP into dieldrin, p.p'-DDD, p.p'-DDE and o.p'-DDE.

Although biodegradation is occurring in the agricultural soils of the Tucutunemo River basin, which is a form of elimination by biotransformation of the structure of the organic compounds represented by the OCP, the primary pollutants are not being reduced since the three flow characteristics of the pollutants observed in the Tucutunemo River (an indirect source) suggest ongoing and current use in the agricultural soils of the Tucutunemo River basin. Chemical and biochemical processes such as retardation and biodegradation are occurring in the agricultural soils. The former involves sorption / desorption.

And in the latter, the main strategies used by microorganisms to feed OCPs consist of the following transformation routes: oxidation as epoxidation, reduction transformations as reductive dehalogenation and hydrolytic transformations such as dehydrohalogenation. In agricultural soils, the transport of OCPs occurs as a result of water erosion and

runoff. In the river, the nature of OCP transport in waters and sediments can be characterized by the following processes: advective, molecular diffusion, turbulent diffusion, and hydrological cycle as rain-runoff (Guevara, 2016).

Table 2 and Table 3 present the results of the OCP levels in water, measured during the dry and rainy periods in three stations in the Tucutunemo River. For each OCP, the range, mean and standard deviation of the observed measurements are presented for each station. At the end of each OCP, the  $F$  and  $p$  values are presented to evaluate the statistical significance of the means of each station based on an analysis of variance, evaluated with a confidence level of 95% (significant for  $p < 0.05$ ).

Table 2 shows the summary of the analysis of variance for OCP residues in water during the dry period, expressed in  $\mu\text{g l}^{-1}$ . To test the statistical significance of the OCP means, the analysis of variance showed a  $p$ -value greater than 0.05 in the case of aldrin, p.p'-DDD, p.p'-DDE, p.p'-DDT, endrin, o.p'-DDE and o.p'-DDT. This verifies that there are no statistically significant differences among the means of these OCPs, in the water from the sampling stations, with 95% confidence level; except for dieldrin with a probability of 0.048 ( $p < 0.05$ ), which confirms statistically significant differences among the means of dieldrin during the dry period, measured at the three stations (95% confidence level).

**Table 2.** Summary of the Analysis of Variance for the results of OCP residues in water, expressed in  $\mu\text{g l}^{-1}$ , from three stations in the Tucutunemo River, during the dry period, April 2015.

OCP	Station 1		Station 2		Station 3		F Value	p Value
	Rank	Mean $\pm$ TD	Rank	Mean $\pm$ TD	Rank	Mean $\pm$ TD		
Aldrín	0.011 – 0.053	0.034 $\pm$ 0.021	0.006 – 0.015	0.009 $\pm$ 0.005	0.004 – 0.053	0.027 $\pm$ 0.025	1.352	0.328
Dieldrín	0.001 – 0.012	0.008 $\pm$ 0.006	0.018 – 0.032	0.024 $\pm$ 0.007	0.017 – 0.030	0.022 $\pm$ 0.007	5.254	0.048
p.p'-DDD	0.001 – 0.001	0.001 $\pm$ 0.000	0.001 – 0.004	0.002 $\pm$ 0.002	0.001 – 0.001	0.001 $\pm$ 0.000	2.286	0.183
p.p'-DDE	0.005 – 0.012	0.009 $\pm$ 0.004	0.006 – 0.010	0.008 $\pm$ 0.002	0.001 – 0.011	0.007 $\pm$ 0.005	0.142	0.871
p.p'-	0.001 –	0.009 $\pm$	0.001 –	0.006 $\pm$	0.001 –	0.004 $\pm$	0.580	0.590

DDT	0.019	0.009	0.011	0.005	0.009	0.005		
Endrín	0.004 – 0.004	0.004 ± 0.000	0.006 – 0.008	0.007 ± 0.001	0.001 – 0.008	0.003 ± 0.004	2.340	0.177
o.p'- DDE	0.001 – 0.009	0.004 ± 0.004	0.004 – 0.009	0.006 ± 0.003	0.001 – 0.007	0.003 ± 0.003	0.630	0.566
o.p'- DDT	0.002 – 0.005	0.004 ± 0.002	0.002 – 0.017	0.010 ± 0.008	0.001 – 0.021	0.011 ± 0.010	0.790	0.498

DT = typical deviation;  $F$  = significance test;  $p$  = probability value;  $n = 9$

**Table 3.** Summary of the Analysis of Variance for the results of OCP residues in water, expressed in  $\mu\text{g l}^{-1}$ , from three stations of the Tucutunemo River during the rainy season, October 2015.

OCP	Station 1		Station 2		Station 3		$F$ Value	$p$ Value
	Rank	Mean ± TD	Rank	Mean ± TD	Rank	Mean ± TD		
Aldrín	0.010 – 0.029	0.021 ± 0.010	0.011 – 0.027	0.021 ± 0.009	0.010 – 0.012	0.011 ± 0.001	1.807	0.243
Dieldrín	0.012 – 0.022	0.018 ± 0.006	0.004 – 0.011	0.008 ± 0.004	0.015 – 0.028	0.021 ± 0.007	4.578	0.620
p.p'-DDD	0.001 – 0.001	0.002 ± 0.001	0.001 – 0.003	0.002 ± 0.001	0.001 – 0.010	0.004 ± 0.005	0.788	0.497
p.p'-DDE	0.004 – 0.011	0.007 ± 0.004	0.009 – 0.017	0.013 ± 0.004	0.010 – 0.027	0.021 ± 0.009	3.772	0.087
p.p'-DDT	0.012 – 0.020	0.016 ± 0.004	0.010 – 0.022	0.016 ± 0.006	0.001 – 0.012	0.008 ± 0.006	2.152	0.197
Endrín	0.001 – 0.001	0.001 ± 0.000	0.001 – 0.001	0.001 ± 0.000	0.001 – 0.004	0.002 ± 0.002	1.000	0.422
o.p'-DDE	0.005 – 0.012	0.010 ± 0.004	0.014 – 0.025	0.021 ± 0.006	0.016 – 0.041	0.027 ± 0.013	3.069	0.121
o.p'-DDT	0.001 – 0.001	0.001 ± 0.000	0.001 – 0.001	0.001 ± 0.000	0.001 – 0.011	0.005 ± 0.006	1.331	0.333

DT = Typical deviation;  $F$  = Significance test;  $p$  = probability value;  $n = 9$ .

In Table 3, a summary of the analysis of variance is presented to demonstrate the statistical significance of the means of the OCP in water during the rainy period. The table shows that there are no statistically

significant differences between the means of the OCPs in the sampling stations, with a 95% confidence level ( $p > 0.05$ ).

Table 4 and Table 5 include a summary of the analysis of variance obtained for each OCP measured in sediments, expressed in  $\mu\text{g kg}^{-1}$ , during the dry and rainy periods at three stations in the Tucutunemo River. As can be seen in Table 4, the highest concentrations of OCP in sediments, during the dry period, correspond to the pesticides aldrin, dieldrin, p.p'-DDE and endrin, which register the most significant ranges: 2.100 to 5.200; 6.220 to 6.800; 1.000 to 3.700 and 5.940 to 7.290  $\mu\text{g kg}^{-1}$ , respectively.

**Table 4.** Summary of Analysis of Variance for the results of OCP residues in sediments ( $\mu\text{g kg}^{-1}$ ), from three stations in the Tucutunemo River, during the dry period, April of 2015.

OCP	Station 1		Station 2		Station 3		3	4
	1	2	1	2	1	2		
Aldrín	2.1 – 5.2	3.407 ± 1.582	0.230 – 5.200	2.577 ± 2.497	0.710 – 4.900	2.150 ± 2.382	0.280	0.764
Dieldrín	1.1 – 1.9	1.407 ± 0.479	2.920 – 3.050	3.000 ± 0.068	6.220 – 6.800	6.587 ± 0.319	188.610	0.000
p.p'-DDD	0.140 – 0.640	0.323 ± 0.275	0.150 – 0.490	0.340 ± 0.173	0.340 – 0.570	0.473 ± 0.119	0.506	0.626
p.p'-DDE	1.000 – 3.700	2.433 ± 1.358	0.610 – 1.900	1.130 ± 0.680	0.520 – 2.700	1.807 ± 1.142	1.060	0.404
p.p'-DDT	1.100 – 1.600	1.300 ± 0.265	0.240 – 1.700	0.777 ± 0.803	0.100 – 1.800	1.167 ± 0.929	0.422	0.674
Endrín	2.490 – 2.780	2.593 ± 0.162	5.550 – 6.130	5.730 ± 0.633	5.940 – 7.290	6.827 ± 0.768	42.711	0.000
o.p'-DDE	0.240 – 2.300	1.017 ± 1.120	0.350 – 2.900	1.277 ± 1.411	0.200 – 2.400	1.093 ± 1.157	0.035	0.966
o.p'-DDT	0.510 – 1.160	0.800 ± 0.331	1.480 – 1.540	1.513 ± 0.031	3.540 – 5.700	4.960 ± 1.230	27.436	0.001

DT = Typical deviation;  $F$  = Significance test;  $p$  = probability value;  $n = 9$ .

1: Range; 2: Mean±SD; 3: *F* Value; 4: *p* Value.

**Table 5.** Summary of the Analysis of Variance for the results of OCP residues in sediments ( $\mu\text{g kg}^{-1}$ ), from three stations in the Tucutunemo River, during the rainy period, October 2015.

OCP	Station 1		Station 2		Station 3		<i>F</i> Valor	<i>p</i> Valor
	Rank	Mean $\pm$ SD	Rank	Mean $\pm$ SD	Rank	Mean $\pm$ SD		
Aldrín	5.020 – 6.250	5.463 $\pm$ 0.683	5.180 – 6.260	5.843 $\pm$ 0.581	7.110 – 8.220	7.610 $\pm$ 0.563	10.536	0.011
Dieldrín	2.420 – 3.550	3.127 $\pm$ 0.616	4.370 – 5.270	4.730 $\pm$ 0.476	5.610 – 6.820	6.163 $\pm$ 0.612	21.188	0.002
p.p'-DDD	0.210 – 0.610	0.473 $\pm$ 0.228	0.610 – 1.500	1.190 $\pm$ 0.503	0.920 – 1.960	1.557 $\pm$ 0.558	4.436	0.066
p.p'-DDE	4.250 – 5.270	4.670 $\pm$ 0.533	5.590 – 6.940	6.133 $\pm$ 0.712	6.930 – 7.320	7.137 $\pm$ 0.196	16.676	0.004
p.p'-DDT	5.020 – 6.430	5.567 $\pm$ 0.756	5.470 – 6.250	5.900 $\pm$ 0.396	7.220 – 8.240	7.660 $\pm$ 0.524	11.342	0.009
Endrín	1.160 – 2.550	2.067 $\pm$ 0.786	2.080 – 2.890	2.460 $\pm$ 0.407	7.320 – 7.600	7.430 $\pm$ 0.149	99.836	0.000
o.p'-DDE	3.120 – 3.170	3.143 $\pm$ 0.025	4.690 – 5.520	5.187 $\pm$ 0.438	3.560 – 4.230	4.000 $\pm$ 0.381	42.711	0.000
o.p'-DDT	2.050 – 3.210	2.813 $\pm$ 0.661	5.050 – 5.760	5.310 $\pm$ 0.391	3.120 – 5.120	4.353 $\pm$ 1.079	8.143	0.020

DT = Typical deviation; *F* = Significance test; *p* = probability value; *n* = 9.

During the rainy season, the concentrations of these same pesticides were even higher, the most significant of which were: aldrin from 7.110 to 8.220; dieldrin from 5.610 to 6.820; p.p'-DDE from 6.930 to 7.320; and endrin from 7.320 to 7.600  $\mu\text{g kg}^{-1}$  (Table 5). The group of OCP previously identified represents 62.29% of the total OCP detected in sediments from the Tucutunemo River.

The analysis of variance to evaluate the statistical significance of the means of the OCP during the dry period (Table 4) includes probabilities less than 0.05, as in the case of dieldrin, endrin and o.p'-DDT. This confirms that there are statistically significant differences between the means of these OCPs in three stations (confidence level of 95%).

Comparing the total OCP concentration in sediments in the Tucutunemo River (range from 13.340 to 45.910  $\mu\text{g kg}^{-1}$ ) with the total OCP

concentrations found in the Da-han and Erh-jen rivers in Taiwan (0.2 to 14.8 and from 0.6 to 29.5  $\mu\text{g kg}^{-1}$ ), there is evidence of a higher concentration of total OCPs in the Tucutunemo River compared to the Da-han and Erh-jen rivers in Taiwan (Doong, Sun, Liao, Peng, & Wu, 2002).

During the rainy period (Table 5), the results of the analysis of variance show that, except for the p.p'-DDD, the whole OCP group examined has statistically significant differences between the means of the OCP ( $p < 0.05$ ) measured in three stations (95.0% confidence level). This increase in OCP residues in sediments in the rainy season is related to the increase in water runoff and the affinity of OCP for the fine soil particles through which the pesticides are transported (Elder & Weber, 1980).

## **Effects of OCP Residues in Water, Fishes and Humans**

Tanveer, Hashmi and Menon (2015), in a study of bioaccumulation of OCP in water and sediments in the Mahi River (India) explain that these pesticides have a negative impact on biota and humans, which consume contaminated water and fish. Therefore, the characterization of OCP in rivers provides relevant information, which contributes to the control of the projection presented by PNUMA (1977), whose goal is to provide good quality water by 2025.

## **Comparison of OCP Residues in Water with International References**

Table 6 shows an overview of OCP levels detected in rivers in Asia and Africa. This table also contains reference values from recognized institutions that have reported critical limits of OCPs in water. In addition to the results found in the Tucutunemo River, OCP is reported by researchers such as Zhang, Jun, Gang and Huasheng (2004);

Kuranchie-Mensah *et al.* (2012); Yang, Shihua, Jiaquan, Chenxi and Xinli (2013), who did similar studies and also detected concentrations of OCP in water. For example, in the case of aldrin, the concentration detected in the water from the Tucutunemo River was greater than that found in the Densu and Tonghui rivers. The other OCP records were lower than those detected in the rivers presented in Table 6.

**Table 6.** Comparison of levels of OCP in water ( $\mu\text{g l}^{-1}$ ) from several rivers worldwide and reference values by the Bolivarian Republic of Venezuela, Australia and WHO.

OCP ( $\mu\text{g l}^{-1}$ )	Tucutunemo River (annual average) Venezuela 2015	Jinjiang River. (DDTs level) China 2013	Densu River, Weija Site (average 2 stations) Ghana 2012	Tonghui River (average 8 stations) China 2004	RV (total OCP) Venezuela	RV (Guideline values) Australia 2011 (Australian Government, 2011)	RV WHO 2011
Aldrin	0.021	–	0.013	0.011	200	0.01	0.03
Dieldrin	0.017	–	nd	nd		0.01	0.03
Endrin	0.003	–	0.015	nd		–	–
p,p'-DDE	0.011	0.004	0.015	0.016		0.06	2.0
p,p'-DDT	0.011		0.019	0.020		0.06	2.0

RV = reference value; – = No information; nd = not detectable.

OCP concentrations in the Tucutunemo River were comparable with the reference values from Venezuela, Australia and WHO, observing that the OCP detected in the waters from the Tucutunemo River were lower than those established for fresh water by countries and institutions such as the Bolivarian Republic of Venezuela, Australia and WHO, except for aldrin and dieldrin, whose concentrations were higher than the Australian reference values of  $0.01 \mu\text{g l}^{-1}$  (Australian Government, 2011).

## Conclusions

The study identified and quantified eight OCPs detected in water and sediments from the Tucutunemo River, which are: aldrin, dieldrin, p.p'-DDD, p.p'-DDE, p.p'-DDT, endrin, o.p'-DDE and o.p'-DDT. The concentrations of these OCPs varied, observing higher levels in sediments. In water, OCP concentrations were low due to their hydrophobic nature and to adsorption by retention of OCPs on the surface of soil microparticles or dissolved organic molecules. However, due to the turbulent type of flow in the river and the decrease in the slope of the channel from Station 1 to Station 3, the concentration of OCP in sediments, during both climatic periods, was higher during season 3 (3% slope). The OCPs detected in water and sediments come from agricultural activity in the Tucutunemo River basin. The levels of OCP found in the waters and sediments from the Tucutunemo River were lower than the reference values established by international agencies, which confirms that this water is not a risk to the environment. It is recommended that research institutes, universities, the Ministry of People's Power for Eco-development-Habitat of Venezuela and international organisms such as UNEP, WHO, EPA, ATSDR, identify critical areas and systematically monitor ecosystems subject to severe environmental impacts caused by OCP, in order to take environmental sanitation measures.

### **Acknowledgments**

We thank the technical staff of the Center for Hydrological and Environmental Research of the University of Carabobo (CIHAM-UC) and the Environmental Quality Laboratory of the Ministry of Popular Power for Eco-development, Habitat and Housing of the State of Aragua, for their cooperation in obtaining of satellite images, sample processing, chemical analysis and determination of OCP residues.