



REVISTA DE INGENIERIA DE LA FACULTAD DE INGENIERIA, UNIVERSIDAD NACIONAL DE COLOMBIA - BOGOTÁ

DYNA

ISSN: 0012-7353

ISSN: 2346-2183

Universidad Nacional de Colombia

Cárdenas-Izaguirre, Samuel Felipe; Márquez-Romance, Adriana Mercedes; Guevara-Pérez, Edilberto
Variation analysis of organochlorine pesticides in waters and sediments from a tropical river
DYNA, vol. 88, no. 216, 2021, January-March, pp. 203-209
Universidad Nacional de Colombia

DOI: <https://doi.org/10.15446/dyna.v88n216.86802>

Available in: <https://www.redalyc.org/articulo.oa?id=49668215026>

- How to cite
- Complete issue
- More information about this article
- Journal's webpage in redalyc.org

UNEN 

Scientific Information System Redalyc
Network of Scientific Journals from Latin America and the Caribbean, Spain and Portugal

Project academic non-profit, developed under the open access initiative

Variation analysis of organochlorine pesticides in waters and sediments from a tropical river

Samuel Felipe Cárdenas-Izaguirre, Adriana Mercedes Márquez-Romance & Edilberto Guevara-Pérez

Centro de Investigaciones Hidrológicas y Ambientales, Facultad de Ingeniería, Universidad de Carabobo, Venezuela. sfcardenas@uc.edu.ve, ammarquez@uc.edu.ve, eguevara@uc.edu.ve

Received: April 29th, 2020. Received in revised form: December 9th, 2020. Accepted: February 19th, 2021.

Abstract

In this paper, it is analyzed the temporal variation of organochlorine pesticides (OCPs) in water and sediments from a river influenced by the activity in an agricultural field in a tropical country during the period 2013-2016. The novelty consists of increasing the studies of concentrations of OCPs in water and sediments of rivers for contributing to establish thresholds of concentrations that allow to protect the biota in soils and waters. The mean values of the OCPs dissolved in water and sorbed on sediments varied as follows: p,p'-DDT (0.001 – 0.022 $\mu\text{g.L}^{-1}$), (0.1 – 8.24 $\mu\text{g.kg}^{-1}$), o,p'-DDT (0.001-0.021 $\mu\text{g.L}^{-1}$), (0.51 – 5.76 $\mu\text{g.kg}^{-1}$), p,p'-DDD (0.001-0.01 $\mu\text{g.L}^{-1}$), (0.14 – 1.96 $\mu\text{g.kg}^{-1}$), p,p'-DDE (0.001-0.027 $\mu\text{g.L}^{-1}$), (0.52 – 7.32 $\mu\text{g.kg}^{-1}$), o,p'-DDE (0.001-0.041 $\mu\text{g.L}^{-1}$), (0.2 – 5.52 $\mu\text{g.kg}^{-1}$), Aldrin (0.004-0.053 $\mu\text{g.L}^{-1}$), (0.23 – 8.22 $\mu\text{g.kg}^{-1}$), Dieldrin (0.001-0.032 $\mu\text{g.L}^{-1}$), (1.13 – 6.82 $\mu\text{g.kg}^{-1}$) and Endrin (0.001-0.008 $\mu\text{g.L}^{-1}$), (1.16 – 7.60 $\mu\text{g.kg}^{-1}$). The management of OCPs by the activity in the agricultural field is being controlled.

Keywords: agricultural land; Aldrin; Dieldrin; Endrin; DDT; organochlorine pesticides; sediment, water.

Análisis de la variación de plaguicidas organoclorados en aguas y sedimentos de un río tropical

Resumen

En este artículo, se analiza la variación temporal de los pesticidas organoclorados (POCs) en el agua y los sedimentos de un río influenciado por la actividad en un campo agrícola en un país tropical durante el período 2013-2016. La novedad consiste en aumentar los estudios de concentraciones de POC en agua y sedimentos de ríos para contribuir a establecer umbrales de concentraciones que permitan proteger la biota en suelos y aguas. Los POCs promedio disueltos en agua y sorbidos sobre sedimentos variaron de la siguiente manera: p,p'-DDT (0.001 – 0.022 $\mu\text{g.L}^{-1}$), (0.1 – 8.24 $\mu\text{g.kg}^{-1}$), o,p'-DDT (0.001-0.021 $\mu\text{g.L}^{-1}$), (0.51 – 5.76 $\mu\text{g.kg}^{-1}$), p,p'-DDD (0.001-0.01 $\mu\text{g.L}^{-1}$), (0.14 – 1.96 $\mu\text{g.kg}^{-1}$), p,p'-DDE (0.001-0.027 $\mu\text{g.L}^{-1}$), (0.52 – 7.32 $\mu\text{g.kg}^{-1}$), o,p'-DDE (0.001-0.041 $\mu\text{g.L}^{-1}$), (0.2 – 5.52 $\mu\text{g.kg}^{-1}$), Aldrin (0.004-0.053 $\mu\text{g.L}^{-1}$), (0.23 – 8.22 $\mu\text{g.kg}^{-1}$), Dieldrin (0.001-0.032 $\mu\text{g.L}^{-1}$), (1.13 – 6.82 $\mu\text{g.kg}^{-1}$) y Endrin (0.001-0.008 $\mu\text{g.L}^{-1}$), (1.16 – 7.60 $\mu\text{g.kg}^{-1}$). El manejo de POCs por la actividad en el campo agrícola está siendo controlando.

Palabras clave: tierras agrícolas; Aldrin; Dieldrin; Endrin; DDT; pesticidas organoclorados; sedimentos; agua.

1. Introduction

The study presents the temporal variation of the Organochloride Pesticides (OCPs) measured in a river influenced by the agricultural activities developed in a tropical country. Although the use of these pesticides has been banned in several countries, the results show that their metabolites continue to be found in environmental samples

due to their long half-life. The OCPs are synthetic pesticides that belong to the group of chlorinated hydrocarbon derivatives [1]. Some of these are considered persistent organic pollutants (POPs) that resist degradation and thus remain in the environment for years [2]. In human fats, the OCP's accumulation levels reached in proofs done on humans corresponded to the p,p'-DDE by comparing with other DDTs [3]. Regarding to fish fats, it has been found a

How to cite: Cárdenas-Izaguirre, S.F., Márquez-Romance, A.M. and Guevara-Pérez, E., Variation analysis of organochlorine pesticides in waters and sediments from a tropical river.. DYNA, 88(216), pp. 203-209, January - March, 2021

bioaccumulation factor, which can vary in the order to 10^4 to 10^5 in most of water bodies [3].

At the end of the 20th century, most of the studies were developed to characterize the concentration of DDT and its congeners on soils and sediments in agricultural land and rivers [4-10]. In these, the forms of DDTs sampled were p,p'-DDT and o,p'-DDT, the congeners mainly sampled were p,p'-DDD and p,p'-DDE. The measured concentrations of DDTs have commonly varied between 10^{-1} - 10^1 $\mu\text{g.kg}^{-1}$ dry weight for soils and sediments and 10^{-2} - 10^{-1} $\mu\text{g.L}^{-1}$ for water [4-10] (Table 1). From the beginning of 21th century to the present, the studies have extended the variety of OCPs examined in both, soils and water [11-34]. From 24 studies, 63% were made in soils and sediments (10^{-1} - 10^1 $\mu\text{g.kg}^{-1}$ dry weight), 29% in water and sediments (10^{-2} - 10^{-1} $\mu\text{g.L}^{-1}$, 10^{-1} - 10^1 $\mu\text{g.kg}^{-1}$ dry weight), 8% in water (10^{-2} - 10^{-1} $\mu\text{g.L}^{-1}$) [11-34] (Table 1).

In Venezuela, [35] characterized OCPs and physicochemical parameters in water and sediments of the Tucutunemo river. In water, total concentrations of OCPs varied in the order of 10^{-2} $\mu\text{g.L}^{-1}$, below the regulation of the Bolivarian Republic of Venezuela. In the sediments, the total concentrations of OCPs ranged in the order of 10^1 $\mu\text{g.kg}^{-1}$. This investigation presents the results of OCPs measured in water and sediments in the Tucutunemo river during the dry and rainy seasons for the period 2013-2016. The purpose implies to determine the levels of the concentrations of the OCPs in water and sediments of rivers for contributing to establish thresholds of concentrations that allow protecting the biota in soils and waters in tropical rivers.

2. Study area

The study area is the Tucutunemo river basin located in the central region of Venezuela (Fig. 1). The water and sediment monitoring stations on the river are three located in the zones of basin (Fig. 1): E1: $67^\circ 23' 26.485''\text{W}$ and $10^\circ 4' 46.74''\text{N}$, E2: $67^\circ 26' 1.54''\text{W}$ and $10^\circ 4' 25.33''\text{N}$, E3: $67^\circ 27' 45.907''\text{W}$ and $10^\circ 3' 23.173''\text{N}$. The land use and land cover detected are (Fig. 1): 1) vegetation (18.92 km^2 , 16%, 0.01), 2) agricultural (30.08 km^2 , 25%, 0.13), 3) degraded soil (69.95 km^2 , 59%, 0.28).

3. Methods

In this study, the method applied to analyze the temporal variation of organochlorine pesticides in the Tucutunemo river includes the following stages:

- Selection of monitoring stations of OCPs:** three water and sediment monitoring stations were selected from upstream of the basin to the 15000 m (E1), mean 10000 m (E2) and low 5000 m regarding to the outlet of basin (Fig. 1).
- Collection of samples of OCPs:** the water samples were collected in the middle of each cross section. The soil samples were captured from a layer of 10 cm in the river banks. In both cases, the samples were collected with a frequency of every six months, in two seasons: dry (April) and rainy (October) during the period 2013-2016.
- Analytical determination in the laboratory of OCPs:** For the determination and quantification of analytes, a gas

chromatograph with electronic capture detector, brand SHIMADZU, model GC-14B, was used in the laboratory of Environment Ministry. The OCPs involved are eight: p,p'-DDT (1,1,1-Trichloro-2,2-bis(4-chlorophenyl)ethane), o,p'-DDT (1,1,1-Trichloro-2-(2-chlorophenyl)-2-(4-chlorophenyl)ethane), p,p'-DDD (1,1,1-Trichloro-2-(2-chlorophenyl)-2-(4-chlorophenyl)ethane), p,p'-DDE (2,2-Bis(4-chlorophenyl)-1,1-dichloroethylene), o,p'-DDE (2-(2-Chlorophenyl)-2-(4-chlorophenyl)-1,1-dichloroethene), Aldrin (1,2,3,4,10,10-hexachloro-1,2,4 α ,5,8,8 α -hexahydro-1,4-endo,exo-5,8-dimetanonaftalina), Dieldrin (1,2,3,4,10,10-hexachloro-6,7-epoxi-1,4,4 α ,5,6,7,8,8 α -octahidro-1,4-endo,exo-5,8-dimetanonaftalina) and Endrin ($\text{C}_{12}\text{H}_8\text{Cl}_6\text{O}$). The limits of detection of the OCPs dissolved in water were of 0.001 $\mu\text{g.L}^{-1}$ and sorbed in sediments was of 0.01 $\mu\text{g.kg}^{-1}$ [36].

- Analysis of variation of OCPs:** the results of variation of OCPs were compared with other studies indicated in Table 1. The studies were selected in correspondence with the characterization of the OCPs dissolved in surface waters and sorbed on sediments from rivers during the period 1980-2020. The selected period began a decade above in which a group of OCPs were banned in the Stockholm Convention on Persistent Organic Pollutants in the early 1970s, including DDT and its metabolites likewise DRINs (Aldrin, Dieldrin and Endrin) [37-39]. The ban of OCPs was due to its harmful effects, including high environmental persistence, chemical stability, high lipophilicity, long-range transportation, chronic and acute toxicities, and bioaccumulation [37-39]. The OCP's statistical analysis consisted of estimating parameters such as mean and standard deviation for dry and rainy seasons during the period 2013-2016 (Tables 2 - 5).

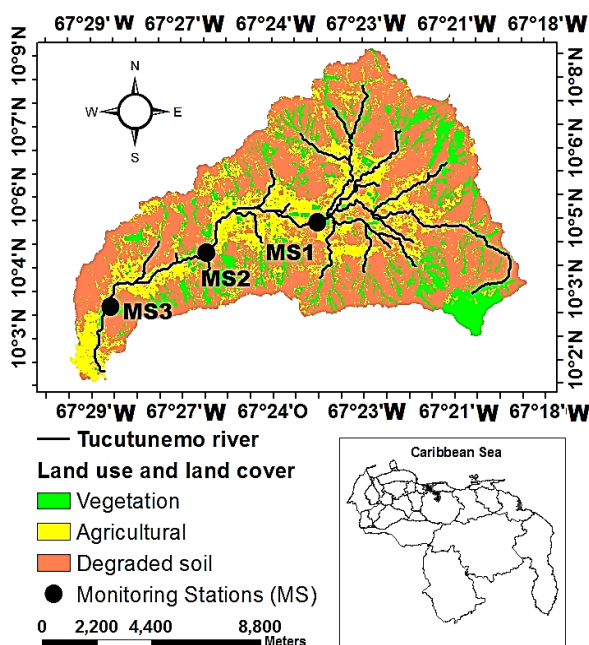


Figure 1. Land use and land cover in the Tucutunemo river basin, Venezuela. Source: The Authors

Table 1.

Comparison of organochlorine pesticides characteristics in water and sediments

Nº	Ref.	Type of OCP	Unit	Concentration ($\mu\text{g.kg}^{-1}$ dry weight)	Concentration ($\mu\text{g.L}^{-1}$)
1	[4]	1,2,3	1	3	
2	[5]	1,2,4	1	3	
3	[6]	1,3,4	1	3	
4	[7]	1,4,5,6,7	3	6	2
5	[8]	1,4	1	3	
6	[9]	1,3,4,6,8	1	3-7	
7	[10]	1	1	4	
8	[11]	1,3,4,7,8,9	1	3	
9	[12]	1	3	3	3
10	[13]	1,3,4,7,8,9	3	3	3
11	[14]	1,3,4	1	3-5	
12	[15]	1,3,4	1	3	
13	[16]	1,3,4,6	1	3	
14	[17]	1,3,4	2		1
15	[18]	1	1	3	
16	[19]	1	1	3	
17	[20]	1,3,4	3	3	3
18	[21]	1,3,4,6	1	1	
19	[22]	1,3,4,7,8,9	1	3	
20	[23]	1,3,4,7,8,9	1	3	
21	[24]	1,3,4,7,8,9	1	3	
22	[25]	1,2,3,4,5,6	2		1
23	[26]	1,4	3	3	2
24	[27]	1,3,4	1	3-4	
25	[28]	1,3,4,6	3	2	2
26	[29]	1,3,4,7,8,9	1	2	
27	[30]	1,3,4, 8,9	1	3	
28	[31]	1,3,4,7,8,9	1	3	
29	[32]	1,3,4,7,8,9	1	3	
30	[33]	1, 7,8,9	3	1	
31	[34]	1	3	1-2	

Type of OCPs: 1) p,p'-DDT, 2) o,p'-DDD, 3) p,p'-DDE, 4) o,p'-DDE, 5) o,p'-DDE, 6) o,p'-DDT, 7) Aldrin, 8) Dieldrin, 9) Endrin. B) Study unit: 1) Sediments, 2) Water, 3) Sediment and Water. C) Sediment concentration ($\mu\text{g.kg}^{-1}$ dry weight): 1) 10^{-3} - 10^{-2} , 2) 10^{-2} - 10^{-1} , 3) 10^{-1} - 10^0 , 4) 10^0 - 10^2 , 5) 10^2 - 10^3 , 6) 10^2 - 10^5 , 7) 10^5 - 10^7 . D) Water concentration ($\mu\text{g.L}^{-1}$): 1) 10^{-7} - 10^{-2} , 2) 10^{-2} - 10^{-1} , 3) 10^{-1} - 10^0 , 4) 10^0 - 10^2 , 5) 10^2 - 10^3 , 6) 10^2 - 10^5 .

Source: The Authors

4. Results

As a sample, the mean concentrations in the water of the Tucutunemo river for p,p'-DDT varied between 0.002 and 0.009 $\mu\text{g.L}^{-1}$ in dry season while these varied between 0.009 and 0.016 $\mu\text{g.L}^{-1}$ in rainy season (Table 2). The mean concentrations in water of the Tucutunemo river for Aldrin varied between 0.0023 and 0.034 $\mu\text{g.L}^{-1}$ in dry season while these varied between 0.004 and 0.013 $\mu\text{g.L}^{-1}$ in rainy season (Table 3). The mean concentrations in sediments of Tucutunemo riverbed for p,p'-DDT varied between 0.77 and 4.28 $\mu\text{g.kg}^{-1}$ in dry season while these varied between 1.87 and 7.66 $\mu\text{g.kg}^{-1}$ in rainy season (Table 4). The mean concentrations in sediments for Aldrin varied between 2.03 and 4.8 $\mu\text{g.kg}^{-1}$ in dry season while these varied between 3.19 and 7.61 $\mu\text{g.kg}^{-1}$ in rainy season (Table 5).

5. Discussion

5.1 Variation analysis of OCPs dissolved in waters of a tropical river with respect other studies.

By comparing the concentrations of the DDTs found in the water of the Tucutunemo river (Table 2), which varied

between 10^{-2} – and $10^1 \mu\text{g.L}^{-1}$ with those found in six studies (Table 1), ranging between 10^{-2} – $10^1 \mu\text{g.L}^{-1}$, it was found that the variation of the DDTs was not significant. The highest concentrations obtained in the water of the Tucutunemo river corresponded to p,p'-DDE by comparing with other DDTs (Table 2). The origin of p,p'-DDE in the water of the Tucutunemo river could be an anaerobic or aerobic biodegradation of p,p'-DDT or a mobility in the water-sediment interface from the sediments in the riverbed to water by a desorption process.

The concentrations of the DRINs obtained in the water of the Tucutunemo river resulted ranging from 10^{-2} to $10^1 \mu\text{g.L}^{-1}$, as it is shown in the Table 3, which were found lower in an order of 10 times than those shown in Table 1, which varied between 10^{-1} and $10^1 \mu\text{g.L}^{-1}$. The concentrations of the DRINs in the Tucutunemo river varied from the dry to the rainy seasons in the order of 10^{-1} . The highest values corresponded to Aldrin by comparing with other OCPs.

The technical-grade DDT is a mixture of three chemical compounds: p,p'-DDT (65-85%), o,p'-DDT (15-21%) and of very small amounts of o,o'-DDT (<4%) [37]. DDT can be biodegraded under aerobic and anaerobic conditions [37]. In vitro studies suggest that the ring excision stage of DDT requires the enzyme oxygenase to transform to DDE in the former stage under aerobic conditions [40]. The anaerobic conditions optimize the decomposition of DDT by catalysis performed due to the reductive dehalogenase enzyme to produce DDD [41].

The mechanism of reductive dehalogenation is hydrogenolysis, also known as hydrodehalogenation, which involves the replacement of a halogen atom by a hydrogen atom [41]. DDD has been used as a pesticide, but its use has been more limited compared to DDT [37]. The main forms of organochlorine pesticides such as DDT and DDD are being applied in the soils of agricultural plots of the Tucutunemo river basin.

Table 2

Statistical parameters of dichlorodiphenyltrichloroethane (DDT) concentrations in terms of its isomers and congeners in three water-sampling stations of the Tucutunemo river, Venezuela, during the period 2013-2016.

Sampling Campaign	Aldrin $\mu\text{g.L}^{-1}$	Dieldrin $\mu\text{g.L}^{-1}$	Endrin $\mu\text{g.L}^{-1}$
	μ	μ	μ
E1 April 2013	0.002	0.001	0.001
E1 April 2014	0.019	0.001	0.020
E1 April 2015	0.034	0.007	0.004
E1 April 2016	0.003	0.003	0.001
E1 October 2013	0.011	0.001	0.001
E1 October 2014	0.011	0.002	0.011
E1 October 2015	0.020	0.018	0.001
E2 April 2013	0.012	0.001	0.004
E2 April 2014	0.009	0.003	0.017
E2 April 2015	0.009	0.023	0.007
E2 April 2016	0.002	0.003	0.003
E2 October 2013	0.005	0.002	0.005
E2 October 2014	0.021	0.002	0.011
E2 October 2015	0.012	0.008	0.001
E3 April 2013	0.026	0.002	0.002
E3 April 2014	0.026	0.003	0.028
E3 April 2015	0.003	0.022	0.003
E3 April 2016	0.013	0.002	0.001
E3 October 2013	0.004	0.006	0.002
E3 October 2014	0.010	0.003	0.002
E3 October 2015	0.012	0.021	0.002

Source: The Authors

Once these pesticides are released into the air or onto crops, they can be subjected to three processes [41]: 1) transport, 2) transformation or 3) accumulation.

The deposition process can transport the pesticide from the air to the ground [37, 41]. The pesticide may be sorbed onto soil particles and retained some time. Once the soil particle is saturated with the pesticide, the excess can be returned by dissolution to the water that drains over the agricultural fields and transported to the water bodies as rivers and water reservoir, through a process known as desorption [41].

In the agricultural field of the Tucutunemo river basin, the sediment transport process has its origin in the water erosion. The terrain slope in the agricultural plots is less than 15% (Fig. 1). The water provided by the irrigation in the agricultural plots drains to the Tucutunemo river in a segment with a slope of the land from 6% upstream to 3% downstream close the outlet of the basin (Fig. 1). In the soil, microorganisms biodegrade DDT to its isomers such as DDE and DDD under anaerobic conditions [40]. Both DDT as its isomers are being transported to the Tucutunemo river dissolved in water or adsorbed in sediments. The Aldrin applied to agricultural plots can be subjected to 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 it is in an aqueous phase, the bioavailability of Aldrin is increased and a biochemical transformation can occur. It might be carried out by the microorganisms contained in the agricultural soil, converting Aldrin to Dieldrin [41]; according to which the oxygenase enzyme influences the metabolism by catalyzing the insertion of an oxygen atom present between doubly bound carbon atoms forming a triangular arrangement, known as epoxide [38,41]. This biodegradation could lead to a process of attenuation of Aldrin in the agricultural soils of the Tucutunemo river basin.

Table 3.

The concentrations of DRINs in three water-sampling stations of the Tucutunemo River, Venezuela, during the period 2013-2016.

Sampling Campaign	p,p'-DDT μg.L ⁻¹	o,p'-DDT μg.L ⁻¹	p,p'-DDD μg.L ⁻¹	p,p'-DDE μg.L ⁻¹	o,p'-DDE μg.L ⁻¹
	μ	μ	μ	μ	μ
E1 April 2013	0.002	0.002	0.001	0.003	0.002
E1 April 2014	0.009	0.005	0.007	0.008	0.006
E1 April 2015	0.009	0.004	0.001	0.001	0.004
E1 April 2016	0.010	0.002	0.001	0.005	0.004
E1 October 2013	0.014	0.007	0.002	0.004	0.007
E1 October 2014	0.014	0.011	0.003	0.012	0.008
E1 October 2015	0.016	0.001	0.001	0.006	0.009
E2 April 2013	0.004	0.010	0.002	0.002	0.006
E2 April 2014	0.005	0.029	0.012	0.007	0.003
E2 April 2015	0.005	0.010	0.002	0.002	0.003
E2 April 2016	0.003	0.004	0.001	0.004	0.002
E2 October 2013	0.009	0.006	0.002	0.004	0.006
E2 October 2014	0.011	0.011	0.009	0.012	0.015
E2 October 2015	0.015	0.001	0.001	0.013	0.021
E3 April 2013	0.005	0.007	0.005	0.004	0.004
E3 April 2014	0.003	0.045	0.012	0.007	0.003
E3 April 2015	0.003	0.010	0.001	0.001	0.003
E3 April 2016	0.002	0.001	0.003	0.004	0.003
E3 October 2013	0.006	0.006	0.006	0.009	0.006
E3 October 2014	0.007	0.010	0.009	0.010	0.022
E3 October 2015	0.008	0.004	0.004	0.004	0.026

Source: The Authors

The transport of the OCPs and its isomers in the Tucutunemo river has a trend to occur under a condition of steady flow. In the steady flow [42], the properties of the fluid do not depend on time. In the Tucutunemo river, the flow rate took values in the order of $10^{-2} \text{ m}^3 \text{ s}^{-1}$ between dry and rainy seasons for 2015 [35]. These three characteristics represented by two concentration gradients are an indication that the primary OCPs such as: p,p'-DDT, Aldrin, Dieldrin, and Endrin are being applied to agricultural soils permanently in the settlement of the Tucutunemo river basin.

5.2 Variation analysis of OCPs sorbed on sediments of a tropical river with respect other studies.

By comparing concentrations of DDTs sorbed in sediments of the Tucutunemo riverbed (Table 4), which varied between $10^{-1} - 10^1 \text{ μg.kg}^{-1}$ with those reported in 20 studies presented in the Table 1, ranging from 10^{-1} to 10^1 μg.kg^{-1} , it was found that the variation was not significant. The concentrations of DDTs in sediments were higher in the dry season than rainy season in an order from 2 to 6 times. The highest values were found for p,p'-DDT and p,p'-DDE (Table 4).

With respect to the concentrations of DRINs sorbed on sediments of the Tucutunemo river, these varied between 10^{-1} and 10^2 μg.kg^{-1} (Table 5). By comparing these results with nine studies shown in Table 1, in which, the DRINs sorbed on sediments varied from 10^{-1} to 10^1 μg.kg^{-1} , it was found that the riverbed contains concentrations higher than those shown in Table 1 in an order of 10^2 times. The concentrations of DRINs were higher in the dry season than rainy season in the order of 10 times. The highest values were found for Aldrin with regard to the remaining DRINs.

With regard to DRINs biodegradation, Aldrin is biodegraded to Dieldrin; due to influence of the oxygenase enzyme on microbial metabolism by catalyzing the insertion of an oxygen atom present between doubly bound carbon atoms forming a triangular arrangement, known as epoxide [39,40]. Endrin can degrade when exposed to high temperatures or light, forming mainly ketone and Endrin aldehyde and has low water solubility [41].

Although biodegradation and sorption-desorption processes might be occurring in the agricultural soils of the Tucutunemo river basin; the primary pollutants are not being attenuated, which means that there is a permanent and current use of the OCPs in the agricultural soils of the Tucutunemo river basin.

In the agricultural soils might be occurring chemical and biochemical processes such as retardation and biodegradation. The former would correspond to sorption / desorption processes, while in the latter, the main strategies used by microorganisms to feed OCPs would consist of the following metabolic pathways [41]: oxidation as epoxidation, reduction transformations as reductive dehalogenation and hydrolytic transformations such as dehydrohalogenation.

In agricultural soils, the main transport of OCPs occurs by water erosion and runoff. In the river, the transport nature of OCPs in waters and sediments can be given by processes of the type: advective, molecular diffusion, turbulent diffusion, and hydrological cycle as rainfall-runoff [41].

5.3 Variation analysis of OCPs dissolved in waters and sorbed on sediments of a tropical river with respect legislation.

In Venezuela, Sanitary Standard (1998) [43] regulates the maximum contaminant level in drinking water for OCPs as follows: DDT and its metabolites ($0.2 \mu\text{g.L}^{-1}$), Aldrin ($0.03 \mu\text{g.L}^{-1}$) and Dieldrin ($0.03 \mu\text{g.L}^{-1}$). By comparing the average OCPs measured in the water samples of the Tucutunemo river with legislation, it was found that the observed values are slightly lower than the maximum level for the OCPs established in the legislation.

With respect to the maximum level of OCPs in soil, the Department of toxic substances control of California Environmental Protection Agency in 2010 established the soil screening numbers (mg.kg^{-1} soil) for nonvolatile chemicals based on total exposure to contaminated soil: inhalation, ingestion and dermal absorption. By comparing the mean values of OCPs determined in sediments of river with environmental regulation of California Environmental Protection Agency [44], it was found that the observed values were lower than the maximum contaminant level for the OCPs established by the California human health screening levels, as a reference.

In general, the banned OCPs are being applied in many countries despite the prohibition of the Stockholm Convention [45]. In the agricultural fields of Tucutunemo river basin, the dose of applied OCPs would lead to the potential use in water and soils, implying that the management of the basin by the community of farmers is guaranteeing the protection of the means of soil, water and biota.

Table 4.

Concentrations of dichlorodiphenyltrichloroethanes (DDTs) in terms of its isomers and congeners in three sediment-sampling stations of the Tucutunemo river, Venezuela, during the period 2013-2016.

Sampling Campaign	p,p'-DDT $\mu\text{g.kg}^{-1}$	o,p'-DDT $\mu\text{g.kg}^{-1}$	p,p'-DDD $\mu\text{g.kg}^{-1}$	p,p'-DDE $\mu\text{g.kg}^{-1}$	o,p'-DDE $\mu\text{g.kg}^{-1}$
	μ	μ	μ	μ	μ
E1 April 2013	1.53	0.99	0.33	1.42	0.95
E1 April 2014	1.27	0.93	1.26	2.43	1.01
E1 April 2015	1.30	1.01	0.32	2.43	1.01
E1 April 2016	2.49	0.41	0.35	2.68	1.11
E1 October 2013	1.87	1.59	0.33	2.17	1.09
E1 October 2014	3.25	0.76	0.38	3.51	1.35
E1 October 2015	5.56	2.81	0.47	4.67	3.14
E2 April 2013	2.17	1.05	0.41	2.67	1.57
E2 April 2014	1.16	3.13	0.98	1.13	1.27
E2 April 2015	0.77	1.27	0.34	1.13	1.27
E2 April 2016	2.37	1.12	0.30	2.31	1.70
E2 October 2013	2.03	1.32	0.29	2.18	1.64
E2 October 2014	2.07	0.58	1.36	1.90	2.42
E2 October 2015	5.90	5.31	1.19	6.13	5.18
E3 April 2013	1.69	1.25	1.12	2.03	1.84
E3 April 2014	1.16	3.89	0.97	1.80	1.09
E3 April 2015	1.16	1.09	0.47	1.80	1.09
E3 April 2016	4.28	1.77	0.64	2.47	2.93
E3 October 2013	2.10	1.22	1.04	2.58	2.45
E3 October 2014	3.05	0.90	1.12	2.76	2.85
E3 October 2015	7.66	4.35	1.55	6.13	4.00

Source: The Authors

Table 5.

Concentrations of organochlorine pesticides in three sediment-sampling stations of the Tucutunemo river, Venezuela, during the period 2013-2016.

Sampling Campaign	Aldrin $\mu\text{g.kg}^{-1}$	Dieldrin $\mu\text{g.kg}^{-1}$	Endrin $\mu\text{g.kg}^{-1}$
	μ	μ	μ
E1 April 2013	2.79	0.99	1.15
E1 April 2014	3.46	2.89	1.73
E1 April 2015	3.46	1.40	2.59
E1 April 2016	3.98	1.26	1.24
E1 October 2013	3.19	1.14	1.39
E1 October 2014	5.21	1.61	1.68
E1 October 2015	5.46	3.12	2.06
E2 April 2013	2.03	1.17	1.15
E2 April 2014	2.57	4.37	1.29
E2 April 2015	2.57	2.99	5.91
E2 April 2016	4.80	2.75	1.18
E2 October 2013	3.75	1.16	1.69
E2 October 2014	5.56	3.33	1.90
E2 October 2015	5.84	4.73	2.46
E3 April 2013	3.16	1.62	1.31
E3 April 2014	2.15	2.55	4.03
E3 April 2015	2.15	6.58	6.82
E3 April 2016	4.37	2.54	2.01
E3 October 2013	3.65	1.69	1.62
E3 October 2014	4.67	3.57	1.31
E3 October 2015	7.61	6.16	7.43

Source: The Authors

6. Conclusions

This study has contributed to increase the knowledge about the characterization of OCPs in water and sediments in a tropical river. The characterization of OCPs in water and sediments resulted similar to those found on a sample of 31 studies, 68% of studies in sediments and soils, 26% studies in water and sediments at the same monitoring campaigns, and 6 % studies in water.

The organochlorine pesticides that include DDTs and DRINs are currently being applied to control insects in agricultural crops of a tropical basin. The temporal variation analysis of OCPs in water and sediments of river during the period 2013-2016 reveals that three processes could be occurring: 1) accumulation, 2) transformation (biodegradation) and 3) transport (agricultural runoff, diffusion-advection and sorption-desorption).

When comparing with the environmental regulation to control of drinking water and OCPs in soil, it was found that observed values of OCPs in water and sediments are lower than the environmental regulation thresholds.

References

- [1] Jayaraj, R., Megha, P. and Sreedev, P., Organochlorine pesticides, their toxic effects on living organisms and their fate in the environment. *Interdisciplinary Toxicology*, 9(3-4), pp. 90-100, 2016. DOI: 10.1515/intox-2016-0012.
- [2] Yadav, I.C., Devi, N.L., Syed, J.H., Cheng, Z., Li, J. et al., Current status of persistent organic pesticides residues in air, water, and soil, and their possible effect on neighboring countries: a comprehensive review of India, *Sci. Total Environ.* 511, pp. 123-137, 2015. DOI: 10.1590/S0102-311X2008000400005
- [3] Shi, L.L., Shan, Z.J., Kong, D.Y. and Cai, D.J., The health and ecological impacts of organochlorine pesticide pollution in China: bioaccumulation of organochlorine pesticides in human and fish fats,

- Human and Ecological Risk Assessment: an International Journal, 12(2), pp. 402-407, 2006. DOI: 10.1080/10807030500536843
- [4] Boon, J.P., Van Zantvoort, M.B., Govaert, M.J.M.A. and Duinker, J.C., Organochlorines in benthic polychaetes (*Nephtys* spp.) and sediments from the southern North Sea. Identification of individual PCB components. *Netherlands Journal of Sea Research*, 19(2), pp. 93-109, 1985. DOI: 10.1016/0077-7579(85)90013-4
- [5] Calamari, D., Bacci, E., Focardi, S., Gaggi, C., Morosini, M. and Vighi, M., Role of plant biomass in the global environmental partitioning of chlorinated hydrocarbons, *Environmental Science & Technology*, 25(8), pp. 1489-1495, 1991. DOI: 10.1021/es00020a020
- [6] Hussain, A., Maqbool, U. and Asi, M., Studies on dissipation and degradation of 14C-ddt and 14C-dde in Pakistani soils under field conditions, *Journal of Environmental Science & Health Part B*, [online]. 29(1), pp. 1-15, 1994. Available at: <https://www.tandfonline.com/doi/abs/10.1080/03601239409372853>
- [7] Abou-Arab, A.A.K., Gomaa, M.N.E., Badawy, A. and Naguib, K., Distribution of organochlorine pesticides in the Egyptian aquatic ecosystem, *Food Chemistry*, 54(2), pp.141-146, 1995. DOI: 10.1016/0308-8146(94)00153-V
- [8] Albanis, T.A., Danis, T.G. and Hela, D.G., Transportation of pesticides in estuaries of Louros and Arachthos rivers (Amvrakikos Gulf, NW Greece), *Science of the Total Environment*, 171(1-3), pp. 85-93, 1995. DOI: 10.1016/0048-9697(95)04667-5
- [9] Aigner, E.J., Leone, A.D. and Falconer, R.L., Concentrations and enantiomeric ratios of organochlorine pesticides in soils from the US corn belt, *Environmental Science & Technology*, 32(9), pp. 1162-1168, 1998. DOI: 10.1021/es970750h
- [10] Fernandez, M.A., Alonso, C., González, M.J. and Hernandez, L.M., Occurrence of organochlorine insecticides, PCBs and PCB congeners in waters and sediments of the Ebro River (Spain), *Chemosphere*, 38(1), pp. 33-43, 1999. DOI: 10.1016/S0045-6535(98)00167-2
- [11] Doong, R.A., Peng, C.K., Sun, Y.C. and Liao, P.L., Composition and distribution of organochlorine pesticide residues in surface sediments from the Wu-Shi River estuary, Taiwan, *Marine Pollution Bulletin*, 45(1-12), pp. 246-253, 2002. DOI: 10.1016/S0025-326X(02)00102-9
- [12] Feng, K., Yu, B.Y., Ge, D.M., Wong, M.H., Wang, X.C. and Cao, Z.H., Organo-chlorine pesticide (DDT and HCH) residues in the Taihu Lake Region and its movement in soil-water system: I. Field survey of DDT and HCH residues in ecosystem of the region, *Chemosphere*, 50(6), pp. 683-687, 2003. DOI: 10.1016/S0045-6535(02)00204-7
- [13] Zhang, Z.L., Hong, H.S., Zhou, J.L., Huang, J. and Yu, G., Fate and assessment of persistent organic pollutants in water and sediment from Minjiang River Estuary, Southeast China, *Chemosphere*, 52(9), pp. 1423-1430, 2003. DOI: 10.1016/S0045-6535(03)00478-8
- [14] Chen, L., Ran, Y., Xing, B., Mai, B., He, J., Wei, X., Fu, J. and Sheng, G., Contents and sources of polycyclic aromatic hydrocarbons and organochlorine pesticides in vegetable soils of Guangzhou, China, *Chemosphere*, 60(7), pp. 879-890, 2005. DOI: 10.1016/j.chemosphere.2005.01.011
- [15] Chen, S.J., Luo, X.J., Mai, B.X., Sheng, G.Y., Fu, J.M. and Zeng, E.Y., Distribution and mass inventories of polycyclic aromatic hydrocarbons and organochlorine pesticides in sediments of the Pearl River Estuary and the northern South China Sea, *Environmental Science & Technology*, 40(3), pp. 709-714, 2006. DOI: 10.1021/es052060g
- [16] Li, J., Zhang, G., Qi, S.H., Li, X.D. and Peng, X.Z., Concentrations, enantiomeric compositions, and sources of HCH, DDT and chlordane in soils from the Pearl River Delta, South China, *Science of the Total Environment*, 372, pp. 215-224, 2006. DOI: 10.1016/j.scitotenv.2006.09.023
- [17] Zhou, R., Zhu, L. and Chen, Y., Levels and source of organochlorine pesticides in surface waters of Qiantang River, China, *Environmental Monitoring and Assessment*, 136(1-3), pp. 277-287, 2008. DOI: 10.1007/s10661-007-9683-5
- [18] Guo, L., Qiu, Y., Zhang, G., Zheng, G.J., Lam, P.K.S. and Li, X., Levels and bioaccumulation of organochlorine pesticides (OCPs) and polybrominated diphenyl ethers (PBDEs) in fishes from the Pearl River estuary and Daya Bay, South China, *Environmental Pollution*, 152, pp. 604-611, 2008. DOI: 10.1016/j.envpol.2007.06.067
- [19] Wong, F., Alegria, H.A., Jantunen, L.M., Bidleman, T.F., Salvador-Figueroa, M., Gold-Bouchot, G., Ceja-Moreno V., Waliszewski S.M. and Infanzon, R., Organochlorine pesticides in soils and air of southern Mexico: chemical profiles and potential for soil emissions, *Atmospheric Environment*, 42(33), pp. 7737-7745, 2008. DOI: 10.1016/j.atmosenv.2008.05.028
- [20] Yu, M., Luo, X., Chen, S., Mai, B. and Zeng, E.Y., Organochlorine pesticides in the surface water and sediments of the Pearl River Estuary, South China, *Environmental Toxicology and Chemistry*, 27(1), pp. 10-17, 2008. DOI: 10.1897/07-055.1
- [21] Guan, Y.F., Wang, J.Z., Ni, H.G. and Zeng, E.Y., Organochlorine pesticides and polychlorinated biphenyls in riverine runoff of the Pearl River Delta, China: assessment of mass loading, input source and environmental fate, *Environmental Pollution*, 157(2), pp. 618-624, 2009. DOI: 10.1016/j.envpol.2008.08.011
- [22] Liu, Y., Song, C., Li, Y., Liu, Y. and Song, J., The distribution of organochlorine pesticides (OCPs) in surface sediments of Bohai Sea Bay, China, *Environmental monitoring and assessment*, 184(4), pp. 1921-1927, 2012. DOI: 10.1007/s10661-011-2089-4
- [23] El Nemr, A., Moneer, A.A., Khaled, A. and El-Sikaily, A., Contamination and risk assessment of organochlorines in surface sediments of Egyptian Mediterranean coast. *The Egyptian Journal of Aquatic Research*, 38(1), pp. 7-21, 2012. DOI: 10.1016/j.ejar.2012.08.001
- [24] Salem, D.M.A., Khaled, A. and El Nemr, A., Assessment of pesticides and polychlorinated biphenyls (PCBs) in sediments of the Egyptian Mediterranean Coast. *The Egyptian Journal of Aquatic Research*, 39(3), pp. 141-152, 2013. DOI: 10.1016/j.ejar.2013.11.001
- [25] Huang, Y., Xu, Y., Li, J., Xu, W., Zhang, G., Cheng, Z., Liu J., Wang Y. and Tian, C., Organochlorine pesticides in the atmosphere and surface water from the equatorial Indian Ocean: enantiomeric signatures, sources, and fate, *Environmental Science & Technology*, 47(23), pp. 13395-13403, 2013. DOI: 10.1021/es403138p
- [26] Kafizadeh, F., Assessment of organochlorine pesticide residues in water, sediments and fish from Lake Tashk, Iran, *Achievements in the Life Sciences*, 9(2), pp. 107-111, 2015. DOI: 10.1016/j.als.2015.12.003
- [27] El Nemr, A. and El-Sadaawy, M.M., Polychlorinated biphenyl and organochlorine pesticide residues in surface sediments from the Mediterranean Sea (Egypt), *International Journal of Sediment Research*, 31(1), pp. 44-52, 2016. DOI: 10.1016/j.ijsrc.2013.03.001
- [28] Lu, H. and Liu, W., Distribution characteristics of organochlorine pesticides in soil, water, and sediment from the Bahe River, China, *Environmental Forensics*, 17(1), pp. 80-86, 2016. DOI: 10.1080/15275922.2015.1133731
- [29] Ragab, S., El Sikaily, A. and El Nemr, A., Concentrations and sources of pesticides and PCBs in surficial sediments of the Red Sea coast, Egypt, *The Egyptian Journal of Aquatic Research*, 42(4), pp. 365-374, 2016. DOI: 10.1016/j.ejar.2016.09.007
- [30] Duodu, G.O., Goonetilleke, A. and Ayoko, G.A., Factors influencing organochlorine pesticides distribution in the Brisbane River Estuarine sediment, Australia, *Marine Pollution Bulletin*, 123(1-2), pp. 349-356, 2017. DOI: 10.1016/j.marpolbul.2017.09.022
- [31] Qu, C., Sun, Y., Albanese, S., Lima, A., Sun, W., Di Bonito, M., Qi, S. and De Vivo, B., Organochlorine pesticides in sediments from Gulfs of Naples and Salerno, Southern Italy, *Journal of Geochemical Exploration*, 195, pp. 87-96, 2018. DOI: 10.1016/j.gexplo.2017.12.010
- [32] Wang, W., Bai, J., Zhang, G., Wang, X., Jia, J., Cui, B. and Liu, X., Depth-distribution, possible sources, and toxic risk assessment of organochlorine pesticides (OCPs) in different river sediment cores affected by urbanization and reclamation in a Chinese delta, *Environmental Pollution*, 230, pp. 1062-1072, 2017. DOI: 10.1016/j.envpol.2017.06.068
- [33] Ogbeide, O., Chukwuka, A., Tongo, I. and Ezemonye, L., Relationship between geosorbent properties and field-based partition coefficients for pesticides in surface water and sediments of selected agrarian catchments: implications for risk assessment. *Journal of environmental management*, 217, pp. 23-37, 2018. DOI: 10.1016/j.jenvman.2018.03.065
- [34] Tham, T.T., Anh, H.Q., Trinh L.T., Lan, V.M., Truong, N.X., Yen, N.T.H., Anh, N.L., Tri T.M. and Minh, T.B., Distributions and

- seasonal variations of organochlorine pesticides, polychlorinated biphenyls, and polybrominated diphenyl ethers in surface sediment from coastal areas of central Vietnam, *Marine Pollution Bulletin*, 144, pp. 28-35, 2019. DOI: 10.1016/j.marpolbul.2019.05.009
- [35] Cárdenas, S., Marquez, A., Guevara, E. y Rey, D., Caracterización de plaguicidas organoclorados en agua y sedimentos en el río Tucutunemo, Venezuela. *Tecnología y Ciencias del Agua*, [en línea]. 9(5), pp. 131-169, 2018. Disponible en: <http://revistatyca.org.mx/ojs/index.php/tyca/article/view/1978>
- [36] APHA-AWWA-WPCF. Métodos normalizados para el análisis de las aguas potables y residuales. Preparado y publicado conjuntamente por: American Public Health Association, American Water Works Association, Water Pollution Control Federation. Ed. Díaz de Santos S.A., España, [en línea]. 2005. [Consultado: diciembre 10 de 2020]. Disponible en: <https://agris.fao.org/agris-search/search.do?recordID=US9335741>
- [37] Agency for Toxic Substances and Disease Registry. (ATSDR). Toxicological profiles of DDT, DDE and DDD. Draft for public comment, US Department of Health and Human Services, United State of America, [online]. 2019, 486 P. [date of reference, December 10th of 2020]. Available at: <https://www.atsdr.cdc.gov/toxprofiles/TP.asp?id=81&tid=20>
- [38] Agency for Toxic Substances and Disease Registry. (ATSDR). Toxicological profiles for Aldrin/Dieldrin, US Department of Health and Human Services, United State of America, [online]. 2002, 354 P. [date of reference, December 10th of 2020]. Available at: <https://www.atsdr.cdc.gov/ToxProfiles/tp.asp?id=317&tid=56>
- [39] Agency for Toxic Substances and Disease Registry. (ATSDR). Toxicological profiles for Endrin, Draft for public comment, US Department of Health and Human Services, United State of America, [online]. 2019, 202 P. [date of reference, December 10th of 2020]. Available at: <https://www.atsdr.cdc.gov/toxprofiles/tp89.pdf>
- [40] University of Minnesota Biocatalysis. (UMBBD). Biodegradation Database. DDT Pathway Map. USA, [online]. 1998. [date of reference, December 10th of 2020]. Available: http://umbbd.ethz.ch/ddt/ddt_image_map.html
- [41] Guevara E., Transporte y transformación de contaminantes en el ambiente y contaminación de las aguas. Ministerio de Agricultura y Riego, Lima, Perú, [en línea]. 2016. [consultado: diciembre 10 de 2020]. Disponible en: <https://hdl.handle.net/20.500.12543/3941>
- [42] Potter, M.C. and Wiggert, D.C., *Mecánica de fluidos*, 3^{ra}. Ed., Thomson Learning, México, 2007.
- [43] Ministerio del Ambiente y de los Recursos Renovables. Normas sanitarias de calidad del agua potable. *Gaceta Oficial de la República de Venezuela*, [en línea]. 1998. [consultado: diciembre 10 de 2020]. Disponible en: <http://www.fao.org/faolex/results/details/es/c/LEX-FAOC192714/>
- [44] California Environmental Protection Agency. Toxicity criteria for human health risk assessment regulation, US Department of Toxic Substance Controls, United State of America, [online]. 2019, 8 P. [date of reference, December 10th of 2020]. Available at: <https://dtsc.ca.gov/regis/toxicity-criteria-for-human-health-risk-assessment/>
- [45] Lallas, P.L., The Stockholm Convention on persistent organic pollutants. *American Journal of International Law*, 95(3), pp. 692-708, 2001. DOI: 10.2307/2668517
- S.F. Cárdenas-Izaguirre**, was born in Ecuador, in 1950. He received the BSc. Eng in Agronomic Engineering in 1991 at the Central University of Venezuela, MSc. in Environmental Engineering since 2002 and the PhD. student in Engineering at the University of Carabobo from 2016 to the present. From 1991 to the present, Samuel is professor of Statistical Methods in School of Commercial Administration at the University of Carabobo, Venezuela. From 2006, Samuel is member of the Center for Hydrological and Environmental Research (CIHAM-UC) belonging to the University of Carabobo.
ORCID: 0000-0001-8732-5075
- A.M. Márquez-Romance**, was born in Venezuela, in 1976. She received the BSc. Eng in Civil Engineering in 1999, the MSc. in Environmental Engineering in 2006 and the PhD. in Engineering in 2011. The three academic degrees were obtained at the University of Carabobo (UC), Venezuela. From 2002 to the present, Adriana is professor in School of Civil Engineering. From 2006, she is member of the Center for Hydrological and Environmental Research (CIHAM-UC) belonging to the University of Carabobo. From 2015 to the present, she has performing the role of CIHAM-UC Coordinator. From 2017 to the present, she is member of doctoral degree program in Engineering focused in Environmental Area at the UC. She is the author of three books, more than 20 scientific manuscripts, and more than 30 participations in scientist events to world, national and regional scales. In the area of remote sensing.
ORCID: 0000-0003-1305-5759
- E. Guevara-Pérez**, was born in Peru in 1943. In 1968 he received his BSc. Eng in Agricultural Engineering from the National Agrarian University, Lima, Peru. In 1970 he obtained his MSc. in Agricultural Engineering from Justus Liebig University, in 1972, his Dr. from Christian Albrechts University, Federal Republic of Germany; and in 1973. In 2007 he founded the Center for Hydrological and Environmental Research at the University of Carabobo (CIHAM -UC) being its Director until 2014. Since 2014 he has been a member of the National Water Court of the National Water Authority of Peru. Since 2017, Dr. Guevara has been a member of the National Academy of Engineering and Habitat of Venezuela. He is the author / co-author of 24 text and reference books, 130 publications in indexed technical journals and more than 100 articles refereed in national and international conferences.
ORCID: 0000-0003-2813-2147