Dichloro-Diphenyl-Trichloroethane (DDT) and Endosulfan in Sediments of Sabancuy Lagoon, Campeche, Mexico

Miguel Angel Ramírez-Elías¹*, Atl Victor Córdova-Quiroz¹, Julia Griselda Cerón-Bretón¹, Rosa María Cerón-Bretón¹, Jaime Rendón-von Osten², Javier Hipólito Cortés-Simón³

¹Facultad de Química, Universidad Autónoma del Carmen, Ciudad del Carmen, México
²Centro de Ecología, Pesquerías y Oceanografía del Golfo de México (EPOMEX), Universidad Autónoma de Campeche, Campeche, México
³Secretaría de Marina, V Zona Naval, Estación de Investigación Oceanográfica, Cd del Carmen, Campeche, México
Email: mramirez.unacar@gmail.com

Received 10 November 2015; accepted 12 January 2016; published 15 January 2016

Copyright © 2016 by authors and Scientific Research Publishing Inc.
This work is licensed under the Creative Commons Attribution International License (CC BY).

Abstract
DDT and Endosulfan are persistent organic compounds which have been prohibited and their use has been limited in agricultural activities due to their toxicity, persistence and bioaccumulation potential. The use of DDT in fumigation campaigns against endemic diseases transmitted by vectors of malaria and dengue was prohibited in Carmen Island, Campeche, Mexico since 1995. In the surroundings of Sabancuy Lagoon, many and diverse agricultural activities are carried out and it is a common practice to use organ-chlorine pesticides as endosulfan. In order to know the levels of these compounds in this area, a sediment sampling campaign was carried out in ten sampling points randomly located within the Sabancuy Lagoon, Campeche and considering one reference sampling point located 2 km away from Sabancuy Lagoon within the Mexican Gulf. Three metabolites were identified in sediments samples belonging to DDT’s family: (4,4'-DDD; 4,4'-DDE; 4,4'-DDT) and Endosulfan’s family (Endosulfan I, Endosulfan II y Endosulfan sulfate). Higher concentrations in DDT’s family were found for 4,4'-DDD, followed by 4,4'-DDE and 4,4'-DDT. Endosulfan’s family showed the following order for concentrations: Endosulfan II > Endosulfan I > Endosulfan sulfate. Mean concentration for Σ-DDT and Σ-Endosulfan in Sabancuy Lagoon sediments was twice higher than those found in other studies carried out in Términos Lagoon, Campeche, Mexico in 2002.

Keywords
Organochlorine Pesticides, Pollution, Sabancuy, Coastal Lagoons

*Corresponding author.

1. Introduction

Dichloro-Diphenyl-Trichloroethane (DDT) and Endosulfan are persistent organic compounds which belong to the organo-chlorine pesticides family (POC), compounds of great concern around the world for its chronic toxicity, persistence and bioaccumulation [1]. Such compounds represent potential threats to ecosystems and human health [2] [3]. POC’s are known to persist in the environment long after its application and are able to experience atmospheric transport over long distances [4]-[8]. Chemical structure for DDT’s isomers and Endosulfan’s isomers is showed in Figure 1 and Figure 2, respectively [9] [10].

Although their production, use and disposal have been regulated or banned in most developed countries today they are still used in many developing countries [11]. In North America, POC’s continue being detected in the environment despite its use was banned some decades ago [7].

In 2005, Mexico ranked sixth in the world for the use of DDT, accumulated in agriculture and was ranked in the fifth place for its use in the field of public health [12]. In 2003, it was estimated that between 1969 and 1979, 9000 tons of POC’s were used, being the most popular DDT, toxafen, hexachloro-benzene, and endrin, among others [13]. Díaz-Barriga and collaborators reported similar trends: an annual usage of more than 4000 tons of DDT between the end of 1950’s and the beginning of 1960’s, followed by decrease and increase periods (especially due to its use in order to control of vector diseases) and showing a reduction in the end of 1990’s [14].

![Figure 1. Chemical structures for DDT’s isomers: (a) DDT, (b) DDE and (c) DDD.](image1)

![Figure 2. Chemical structures for Endosulfan’s isomers: Endosulfan I (α), Endosulfan II (β) and Endosulfan sulfate.](image2)
The Environmental Cooperation Commission for North America [15] reported that the usage of DDT with public health purposes was reduced from 1,400 tons in 1993 to less than 600 tons in 1999. Under the Regional Action Plan for North America (PARAN), México agreed to eliminate in a gradual way the use of DDT for 2002 year; however, its complete elimination was accomplished in 2000 year [16][17].

An air quality study was carried out in Chiapas, México, during the period from 2000 to 2001 [18][19] and other studies were carried out in Belize and Central America, from 1995 to 1996 [20] and from 2000 to 2001, respectively [19]. All these studies reported high levels of DDT in those places; high levels of aldrin and dieldrin in Belize; and important concentrations of toxafen and endosulfan in Chiapas [7].

Coastal lagoons and estuaries are ecosystems that are affected in a negative form for POC’s whose source is related to the urban growth, development, industrial and agricultural activities among others [21]. In coastal zones, the final destiny of persistent organic is aquatic bodies and coastal ecosystems [1][22][23]-[26]. Las lagunas costeras del Golfo de México se encuentran entre esos ecosistemas [1][26]. Sabancuy Lagoon has an approximate area of 32 km² and it belongs to a lagunar system named Términos-Pom-Atasta-Dead River. This lagoon is cursory with 1.5 m deep, and the mean channel through in a longitudinal and adjacent way to the continental edge with depths of up to 2 m [27].

DDT and Endosulfan were used until 1995 in the surroundings of Sabancuy Lagoon mainly in agricultural activities and fumigation campaigns against endemic diseases transmitted by vectors such as malaria and dengue. The most used pesticides in the past were DDT (99% of the total volume), malation and fention. Particularly, in Campeche these pesticides were applied approximately in 25% of the total volume applied in the Southeast region of Mexico [1]. Currently, the use of pesticides has been increased in an uncontrolled way in the agricultural sector in developing countries, due to the need to raise the performance of new farmland and accelerate the production of fruits, vegetables, legumes and grasses; in order to satisfy the population demand in a global, regional and local levels; generating pollution of pesticides in sediments.

Under favorable conditions, sediments are sinks of POC, which can be resuspended and lead to a second round of water pollution [28]. Therefore, POC residues in pore water, suspended particles and sediments can provide valuable records that denote potential pollution and environmental hazards [3][29].

Regarding to agricultural activities, in the cultivation of chile (Capsium annuum), the most used pesticides are malation, endosulfan and metamidofos, with a treated surface of almost 100%. Most of the pesticides are applied in their whole (almost 90%) between May and September being more intensive in chile cultivation though rice cultivation has the higher crop area and application rates [30].

Sabancuy climate is humid tropical warm type, which favors the main activities of the population, such as fishing and golf, with the rainiest month usually occurring in summer, with a maximum temperature of 36°C and an annual average of 26°C and an average temperature of the coldest month about 18°C with a variation of 5°C - 7°C [31].

In the surroundings of Sabancuy Lagoon, agricultural activities are carried out considering different types of crops being the most important the papaya, Jalapeño chile jalapeño and vegetables cultivation; these activities contribute in a great manner in lixiviate of organochlorine pesticides such as DDT and Endosulfan, mainly. Therefore, the objective of this study was to determine the concentration levels of DDT and Endosulfan present in sediments of Sabancuy Lagoon, in Campeche, Mexico.

2. Materials and Methods

Sabancuy Lagoon is located within Carmen City municipality in Campeche, México, at the northeast Términos lagoon (18°48′35″N and 19°02′25″N and 91°06′43″W and 91°26′56″W) (Figure 3). Sabancuy lagoon has a permanent natural communication with sea at the northeast and has communication at southwest with La Aguada and Términos lagoons. Sabancuy lagoon is additionally separated from the Gulf of Mexico by a sandy barrier parallel to the coast [27].

A strategic sampling was established considering the continental shelf of Sabancuy Lagoon, where the collection of superficial samples of sediment was carried out. This sampling included the urban bank within the lagoon and a reference sampling site located out of the lagoon. Eleven stations were considered which were distributed along the lagoon in the following manner: six stations were located before the continental shelf; three were located after the continental shelf where the urban influence is more evident, and one station was located in the mouth of the lagoon (where the bridge that connects the island with the continental zone is located) and fi-
nally, a reference station was located in the outer edge of the Sabancuy Lagoon, at 2 km away from the Mexican Gulf (Figure 3).

The collection of superficial samples of sediment was carried out using a dredge Van Veen, collecting them in a direct way, in amber glass bottles previously treated, which were stored at low temperature (4°C) and sent to the lab for analysis. Sediment samples were frozen and subsequently lyophilized with a Labconco Freeze Dry System. Once they were lyophilized, these were screened with a 0.5 µm i.d. sieve mesh. The compounds of DDT and Endosulfan were determined for three seasons, according to the technique described by Sericano [32] and recognized by the National Status and Trends Program of the National Oceanic and Atmospheric Administration’s (NOAA) in the laboratory of Environmental Sciences, College of Chemistry, University of Carmen City (UNACAR).

DDT and Endosulfan were quantified by gas chromatography using a Perkin-Elmer Gas Chromatography equipment XP Model with a capillary column CP-Sil 5 CB (with 100% dimetil-polisiloxan, 25 m × 0.15 mm, and 1.2 µm internal diameter), in a Split less mode and with an electron capture detector (ECD) [33]. Injector temperature was of 250°C and temperature in ECD was of 375°C. Temperature program conditions were the following: 240°C for one minute, then temperature was increased until 270°C and it was maintain for two minutes, and finally, temperature was increased until 320°C and maintained for one minute. Nitrogen was used as carrier gas at 50 psi pressure at 32.4 ml·min⁻¹.

**Statistical Analysis**

Statistical analysis was carried out using the non-parametric Kruskal Wallis statistical test in order to know if there were significant differences among groups and between mean values for DDT and Endosulfan, for the three seasonal sampling using the software Statistical 7.0 [34].
3. Results and Discussion

The results are presented for DDT and Endosulfan grouped in families with the same molecular weight or degradation product in the following way:

Dichloro-Diphenyl-Trichloroethane (DDT) $\Rightarrow$ $\Sigma$DDTs = (4,4’-DDD + 4,4’-DDE + 4,4’-DDT).

Endosulfan $\Rightarrow$ $\Sigma$-Endosulfanes = (Endosulfan I + Endosulfan II + Sulfate Endosulfan).

3.1. Temporal variation for Dichloro-Diphenyl-Trichloroethane (DDT).

DDT’s family in superficial sediments of Sabancuy Lagoon showed a maximum concentration for 4,4’-DDD of 1.920 ng·g$^{-1}$ during June (dry season) and a minimum value of concentration of 1.066 ng·g$^{-1}$ during February (norths season); therefore, significant differences among seasons were found ($P < 0.05$). The highest inter-quartil rank was obtained for June which was typical for the dry season with a median of 1.900 ng·g$^{-1}$ and a mean value of 1.715 ng·g$^{-1}$ de 4,4’-DDD (Figure 4(a)).

Regarding to 4,4’-DDE, this compound showed too significant differences among seasons ($P < 0.05$), with a maximum concentration 1.912 ng·g$^{-1}$ during June (dry season) and a minimum value of 0.572 ng·g$^{-1}$ during October (rainy season).

Figure 4. Temporal variation for (a) 4,4’-DDD; (b) 4,4’-DDE; (c) 4,4’-DDT; (d) $\Sigma$-DDTs expressed in ng·g$^{-1}$. 
The highest inter-quartile rank was obtained during dry season with a median of 0.613 ng g\(^{-1}\) and a mean value of 0.965 ng g\(^{-1}\) for 4,4’-DDE (Figure 4(b)). 4,4’-DDT did not show significant differences among seasons, the maximum concentration was of 1.449 ng g\(^{-1}\) and the minimum value was of 0.644 ng g\(^{-1}\) during October (rainy season). The highest inter-quartile rank was obtained during dry season with a median of 1.152 ng g\(^{-1}\) and a mean value of 1.043 ng g\(^{-1}\) for 4,4’-DDT (Figure 4(c)). The statistical analysis of Σ-DTT showed significant differences (P < 0.01) among the months for each sampling season. Maximum and minimum concentrations for Σ-DTT were 3.907 ng g\(^{-1}\) and 3.460 ng g\(^{-1}\) during June and rainy season, respectively (Figure 4(d)). The highest interquartile-range was obtained for October with a median of 3.521 ng g\(^{-1}\) and a mean value of 3.593 ng g\(^{-1}\) for Σ-DTT.

DDT’s were characterized by presenting the highest concentrations in June during the dry season and the lowest values in October during the rainy season; mainly in Sabancuy bridge zone where there is a greater flow of saline and fresh waters, during all the seasons (Nonths, dry and rainy). The maximum concentrations for 4,4’-DDD and 4,4’-DDE during dry season (June) were found in sampling site 3 (1.92 ng g\(^{-1}\)) and sampling site 10 (1.9123 ng g\(^{-1}\)), respectively. ΣDDT’s concentrations were high too in the same sampling site with a maximum value of 3.9073 ng g\(^{-1}\). Therefore, according to the obtained results, degradation products of DDT’s compounds family showed significant differences (P < 0.05 in both, sampling sites and climatic periods. Figure 5 shows obtained chromatograms for DDT’s isomers (4,4’-DDD; 4,4’-DDE; 4,4’-DDT).

On the other hand, 4,4’-DDT had its maximum concentration (1.449 ng g\(^{-1}\)) in October during the rainy season with a minimum value of 0.644 ng g\(^{-1}\). Higher concentrations for DDT’s during dry season could be attributed to an increase in concentration in sediments due to they are sparingly soluble in water and highly persistent. Gil and Vale found a mean concentration of 2.27 ng g\(^{-1}\) for Σ-DDT in sediments of Tagus estuary (Portugal) [35], which are lower than those found in this study (Σ-DDT= 3.61 ng g\(^{-1}\)) for sediments of Sabancuy Lagoon. On the other hand, a study carried out in 2004 in sediments of the Dongting Lagoon in China [36], reported the following mean values: 1.29 ng g\(^{-1}\) de 4,4’-DDD, 2.0 ng g\(^{-1}\) de 4,4’-DDE and 1.43 ng g\(^{-1}\) de 4,4’-DDT; comparing these values with those reported in the present study, it can be observed that in sediments of the Sabancuy Lagoon, 4,4’-DDE and 4,4’-DDT showed lower concentrations but it was found a higher concentration for 4,4’-DDD. Likewise, mean concentration for Σ-DDT Dongting Lagoon in China was of 5.31 ng g\(^{-1}\), greater than that found in Sabancuy Lagoon in Campeche, Mexico (3.61 ng g\(^{-1}\)).

Marine Secretary of Mexico (SEMAR) carried out a study in the Términos Lagoon System in Campeche, Mexico, it was found a mean value for Σ-DDT of 1.9466 ng g\(^{-1}\) [37], which is lower than the found value in Sabancuy Lagoon (3.6142 ng g\(^{-1}\)). According to the concentrations found in the Términos Lagoon [37] and comparing with those found in the present study, individual pesticides concentrations were quite lower. However, values for Σ-DDT and Σ-Endosulfan’s in Sabancuy Lagoon were 1 - 2 times higher than those reported for

---

**Figure 5.** Typical obtained chromatograms for DDT’s isomers (4,4’-DDD; 4,4’-DDE; 4,4’-DDT) and Endosulfan’s isomers detected in Sabancuy Lagoon, Campeche, Mexico.
Términos Lagoon probably due to an intensive use of DDT (since 1995) by the health sector and health jurisdiction of Carmen Municipality in campaigns against vectors such as dengue and malaria.

3.2. Temporal Variation of Endosulfan

Statistical analysis indicates that Endosulfans (I, II and sulfate) showed significant differences \( (P < 0.05) \) among months and seasons.

Endosulfan’s family in sediments of Sabancuy Lagoon showed a maximum concentration for Endosulfan I in June with a value of 0.7036 ng·g\(^{-1}\) (dry season) and a minimum of 0.5251 ng·g\(^{-1}\) in October (rainy season). Likewise, the highest interquartile-range was obtained in June with a median of 0.698 ng·g\(^{-1}\) and a mean value of 0.658 ng·g\(^{-1}\) for Endosulfan I (Figure 6(a)).

For Endosulfan II, maximum concentration was of 0.713 ng·g\(^{-1}\) in June (dry season) and a minimum value of 0.511 ng/g was found in October (rainy season). The highest interquartile-range was obtained in October with a median of 0.528 ng·g\(^{-1}\) and a mean value of 0.565 ng·g\(^{-1}\) for Endosulfan II (Figure 6(b)).

Sulfate Endosulfan presented a maximum concentration of 0.678 ng·g\(^{-1}\) and a minimum value of 0.584 ng·g\(^{-1}\) in February (Norths season). The highest interquartile-range was obtained in June, during dry season, with a median of 0.673 ng·g\(^{-1}\) and a mean value of 0.656 ng·g\(^{-1}\) for Sulfate Endosulfan (Figure 6(c)). Statistical analysis for \( \Sigma \)-Endosulfanes presented significant differences \( (P < 0.01) \) among the different months for each climatic period. Maximum concentration for \( \Sigma \)-Endosulfanes was obtained in February with a value of 1.956 ng·g\(^{-1}\) and a

![Figure 6](image-url)
minimum value of 1.779 ng·g⁻¹ was obtained during the rainy season (Figure 6(d)). The highest interquartile-range was found in June with a median of 1.922 ng·g⁻¹ and a mean value of 1.907 ng·g⁻¹ for Σ-Endosulfanes.

Endosulfanes family are commonly used in pests control in agricultural activities [38], being their use more intensive during dry season in June, this is attributed to an increase in their concentration in sediments due to they are poorly soluble in water and very persistent at higher temperatures. Maximum concentration for Endosulfan I was of 0.7036 ng·g⁻¹ (in sampling site 3) and Endosulfan II presented its maximum value (0.7137 ng·g⁻¹) in sampling site 11, and the highest interquartile-ranges were found in dry season in sampling site 5. Both Endosulfan sulfate as Σ-Endosulfanes presented their minimum and maximum concentrations during February in sampling site 6 with values of 0.6784 ng·g⁻¹ and 1.9562 ng·g⁻¹, respectively. Figure 5 shows obtained chromatograms for Endosulfan’s isomers detected in Sabancuy Lagoon.

Therefore, according to obtained results, Endosulfanes family showed significant differences (P < 0.05) among sampling sites and climatic periods. In 1999, mean concentrations for Endosulfan I (0.048 ng·g⁻¹), Endosulfan II (0.128 ng·g⁻¹) and sulfate Endosulfan (0.067 ng·g⁻¹) were reported in sediments of Naranjo-Paso Caballos Lagoon in Nicaragua [22]. Comparing these results with those found in this study (0.642, 0.573 and 0.641 ng·g⁻¹), respectively, it can be observed that there is a higher concentration for the Endosulfanes in Sabancuy Lagoon. On the other hand, in the study reported for Términos Lagoon in Campeche, Mexico, a mean value of 1.663 ng·g⁻¹ was found for Σ-Endosulfanes [37]. Comparing the found results in this study (1.857 ng·g⁻¹) with those reported for Términos Lagoon study, it can be observed that higher concentrations for Σ-Endosulfanes were found in Sabancuy Lagoon probably due to its application and intensive use in the production of agricultural products as papaya and chili.

4. Conclusion

Endosulfanes family was dominant in dry season showing significant differences (P < 0.05) among sampling sites and climatic periods. Mean concentration for Endosulfanes presented the following relative abundance: Σ-Endosulfanes > Endosulfan I > Endosulfan sulfate > Endosulfan II. Likewise, DDT’s family was dominant and showed their maximum concentrations during dry season. As maximum concentrations for degradation products of DDT such as 4,4’-DDD and 4,4’-DDE are higher than the maximum concentrations for 4,4’-DDT, it can be concluded that its application in health campaigns against vectors such as malaria is not recent. It means that probably these compounds have been accumulated in the Lagoon during the last years. This agrees with the provided information by Sanitary Sector No. 3 of Carmen City, Campeche, indicating that DDT has not been used since 1995.

References


Handbook of Environmental Chemistry

Delta.


