

Evaluation of Occurrence and Health Risk of Organochlorine Pesticides in Sediments of the Department of Bolivar, Colombia

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Organochlorine pesticides such as Dichlorodiphenyltrichloroethane (DDT) and hexachlorocyclohexane (HCH) were widely used in agriculture and vector disease control worldwide. Despite its ban in production and application since the 1970s in many countries, its residues in water, air and soil have been reported. Organochlorine pesticides have been proposed as possible carcinogens. In Colombia, organochlorine pesticides were used for many years in agriculture and for vector control. Currently, its waste continues to be found in environmental and biological matrices. The objective of this study was to determine the concentrations of organochlorine pesticides in sediments of freshwater bodies in the department of Bolivar, Colombia and to evaluate the risk of cancer from organochlorine pesticides for adults and children. Pesticide concentrations were determined in sediments at six sites of the main freshwater body in the department of Bolivar, Colombia. Dichlorodiphenyldichloroethylene (DDE), a degradation product of DDT, was the most recovered pesticide. Heptachlor and heptachlor epoxide represented an increased risk for cancer in children and adults in this study. This study can provide a reference for the management and control of pesticides at the regional level and to support public health programs.

1. Introduction

Pesticides are inherently toxic substances that are used in agricultural, residential, and commercial settings as they offer several benefits, including increasing crop production and controlling vector-borne diseases (Zúñiga et al., 2022). Three billion kilograms of pesticides are used worldwide each year, of which only 1% of the total effectively controls insect pests on target plants. The remaining large amounts of pesticides penetrate or reach non-target plants and environmental media (Tudi et al., 2021).

Organochlorine pesticides are highly stable, a characteristic that makes them valuable for their residual action against insects and at the same time dangerous due to their prolonged storage in mammalian fat. Within this group of insecticides are DDT, benzene hexachloride (BHC), chlordane and dieldrin. These compounds caused a revolution in the fight against insects, due to their wide range or spectrum of action and their low cost (Ponce et al., 2006). Among its characteristics are its persistence, potential for bioaccumulation, chronic toxicity with possible negative impacts on humans and wildlife. Despite the restriction of their use, they can still be detected in the environment and species (Zhao et al., 2016). Organochlorine pesticides are resistant to microbial degradation and their half-life varies from several months to several years. They can be transported over long distances, and their presence can even be detected in the Arctic (Carvalho 2017).

Although organochlorine pesticides were banned many years ago due to their physical and chemical characteristics, even today, an important part of the population is influenced by direct and indirect contamination by these substances. Colombia is no stranger to this reality, due to the widespread use of organochlorine pesticides, used for many years in agriculture and for vector control (Zhao et al, 2016).

2. Methodology

2.1 Sample collection

The sampling sites were selected considering various aspects such as the anthropogenic activity existing in the area and ease of access. Sampling was carried out between November 1 and 10, 2013. At each of the sites, four sediment subsamples were taken approximately 50 m from the shore through a grab sampler to complete approximately 1.0 kg of a composite sample. The collected samples were placed in polyethylene bags, stored at 4 °C until transfer to the laboratory and stored at -20 °C. The samples were then subjected to freeze-drying at -50 °C and -0.019 mbar to remove moisture. The freeze-dried pellets were crushed and sieved to <63 µm and kept at -20 °C.

2.2 Analysis of pesticides

2.2.1 Chemicals

All samples were analyzed for organochlorine pesticides, including aldrin, Heptachlor epoxide Iso B, trans chlordane, cis chlordane, 4,4'-DDE, endrin, dieldrin, 4,4'-DDD, Endosulfan sulfate, 4, 4'-DDT, Endrin ketone, methoxychlor, heptachlor, α -BHC, β , δ -BHC. Pesticide standards were purchased from Phenova (Golden, CO, USA) and Sigma Aldrich (St. Louis, MO, USA). Internal standards (ISTD) were purchased from Wellington Laboratories Inc (Ontario, Canada). Pesticide stock solutions (50 mg/L) were prepared by dissolving the appropriate amount in residual quality isooctane. Octadecylsilica (C18) was obtained from Agilent Technologies (Santa Clara, CA, USA). MgSO₄, NaCl, LC/MS grade acetonitrile, and isooctane for pesticide residue analysis were purchased from Fisher Scientific (Pittsburg, PA, USA). NANOpure™ Barnstead International (Dubuque, IA) was used in all experiments.

2.2.2 Extraction and cleaning of QuEChERS sediments

The procedure followed in this work was based on the QuEChERS method described by (Payá et al., 2007). Briefly, 4 g of homogenized lyophilized pellet was weighed into 50 mL centrifuge tubes. Ten mL of water was added to the sample and stirred for 1 min. Then 10 mL of acetonitrile was added and the mixture was vortexed for 1 min. After that, 4 g of MgSO₄ and 1 g of NaCl were added to adjust the phase separation, the mixture was stirred vigorously and stirred for 1 min and centrifuged at 3400 rpm for 8 min. For cleanup by dispersive solid phase extraction, an aliquot (4 mL) of the organic phase was transferred to a 15 mL centrifuge tube already containing 12.5 mg of C18, 25 mg of PSA and 150 mg of MgSO₄ per ml of extract. The tube was closed, vortexed vigorously for 1 min, and centrifuged for 8 min at 3400 rpm. The supernatant was passed through a 0.2 µm PTFE filter. Subsequently, the filtered supernatant was evaporated to dryness and reconstituted with 1 mL of isooctane. An aliquot of the extract was added with 12.5 µL, of 500 ng/mL spiking solution. This spiked sample was used as a single-point standard addition for quantification.

2.2.3 GC/MS/MS Analysis

Analysis was performed on a Thermo Scientific Trace GC Ultra coupled to a TSQ Quantum XLS mass spectrometer. The separation was performed on a DB-5HT column (30 m × 0.25 mm inner diameter × 0.10 µm film thickness; Agilent Technologies). The temperature program was set at 60 °C (held for 1 min), increased to 160 °C at 15 °C/min (held for 2 min), then increased to 190 °C at 2.2 °C/min and finally increased to 290 °C at 50 °C (held for 3 min). The ionization energy of the MS was 70 eV, the transfer line temperature was 280 °C, and the ion source was 200 °C. Samples were injected (3 µL) using a programmable temperature vaporization injector in split less mode, which was set at 89 °C with a split flow of 125 mL/min and a split less time of 1.4 min. The flow rate was 1 mL/min with helium as carrier gas. The QqQ mass spectrometer was operated in the selected reaction monitoring (SRM) mode. Two mass transitions were acquired for each target compound, one of which was used for quantification.

2.3 Health Risk Assessment

In general, people are exposed to organochlorine pesticides through three main routes: direct ingestion, dermal absorption, and inhalation that can be estimated according to the Exposure Factors Handbook (USEPA, 1997). The Chronic Daily Intake (CDI, mg/kg/day) of chemicals in soils or sediments through non-dietary ingestion, dermal contact, and inhalation can be calculated according to the following equations:

$$CDI_{ing} = \frac{C_s \times IR_{ing} \times EF \times ED}{BW_a \times AT_c} \times 10^{-6} \quad (\text{Equation 1})$$

$$CDI_{der} = \frac{C_s \times SA \times SAF \times ABS \times EF \times ED}{BW \times AT_c} \times 10^{-6} \quad (\text{Equation 2})$$

$$CDI_{inh} = \frac{C_s \times IR_{inh} \times EF \times ED}{PEF \times BW \times AT_c} \quad (\text{Equation 3})$$

where C_s is the concentration of pesticides in sediments (mg/kg); the ingestion rate (IR_{ing}) is 100 mg/kg for adults and 200 mg/kg for children; the inhalation rate (IR_{inh}) is 10.9 m³/d for children and 17.5 m³/d for adults; The exposure frequency (EF) is 350 days/year; the duration of exposure (DE) is 30 years for adults and 6 years for children; the exposed area (SA) is 5,700 cm² for adults and 2,800 cm² for children; the adherence factor (SAF) is 0.07 mg/cm² for adults and 0.2 mg/cm² for children; the dermal absorption factor (ABS) is chemically specific and the particle emission factor (PEF) is 1.36 × 10⁹ m³/kg (USEPA, 2002). Body weight (BW) is 70 kg for adults and 20 kg for children; and the average time (AT) is 2190 days for children and 8760 days for adults (USEPA, 2011).

Carcinogenic risk is the probability that an individual will develop any type of cancer during his or her lifetime due to exposure to carcinogenic hazards. In our study, the cancer risk for an individual throughout their life was calculated according to the following equation (USEPA, 2011):

$$CR = CDI \times SF \quad (\text{Equation 4})$$

Where SF is the carcinogenicity slope factor (mg/kg/day)⁻¹ (Table S4, USEPA, 2002). If multiple carcinogenic toxicants are present, the cancer risk from all compounds and routes of exposure is summarized:

$$CR = \sum_i CR_i \quad (\text{Equation 5})$$

In general, risk ratios between 1.0 × 10⁻⁴ and 1.0 × 10⁻⁶ are considered acceptable (USEPA, 1989), while those greater than 1.0 × 10⁻⁴ are suggested to represent a risk carcinogenic to humans.

2.4 Data analysis

For statistical data analysis, Excel 2010 software (Microsoft Inc., Seattle, WA, USA) was used to prepare tables and graphs.

3. Results and discussion

3.1 Presence of organochlorine pesticides in sediment samples

In Colombia, there is a high consumption of pesticides, although the records are inaccurate. FAO estimates suggest that Colombia used more than 37.7 thousand tons of pesticides in 2018, ranking 18th among the top pesticide users worldwide (FAO 2020). Organochlorines were used for many years in Colombia, and although their use is currently prohibited, their biochemical characteristics, which make them resistant to degradation, mean that their residues are still found in various environmental matrices

The most abundant pesticides in the sediments were 4,4'-DDE (1.14 ± 2.35 ng/g), followed by 4,4'-DDT (0.40 ± 0.59 ng/g) and 4,4'-DDD (0.41 ± 0.74 ng/g) and found at sampling site M3. In which one of the biggest environmental problems is the deterioration of bodies of water due to the appropriation of agricultural productive spaces that do not obey the criteria of sustainability and the inappropriate use of agrochemicals.

The other chlorinated compounds apart from the DDT metabolites that were also found in the other sampling sites on a smaller scale reflect the agricultural activity of the regions of the department of Bolívar and its history regarding the use of pesticides for the cultivation of products such as cotton, which was the main product of those regions for more than 30 years.

Hazardous pesticides associated with global cotton production represent a substantial threat to global freshwater resources. Hazardous cotton pesticides are now known to contaminate rivers in USA, India, Pakistan, Uzbekistan, Brazil, Australia, Greece and West Africa (EJF and Pesticide Action Network UK. 2019). Other authors have reported the presence of compounds related to DDT in Cartagena Bay and the Rosario Islands (Menzies et al. 2013), in the vicinity of some of the sampling sites.

The concentrations of pesticides in the analyzed samples are shown in Table 1.

Towards the coastal areas of Colombia, studies have also been carried out where similar concentrations of organochlorine compounds described here have been found, especially in crop areas in water, sediments and organisms, which reflects the need to pay attention to organochlorine pesticides in the soils of the study area (Calva and Torres 1998; Garces and Espinosa 2011).

Table 1: Concentration of pesticides in sediments.

Pesticide	M1	M2	M3	M4	M5	M6	$\bar{x} \pm SD$
α -BHC	0	0	0.27	0	0	0	0.04 \pm 0.11
β . δ -BHC	0	0	0.26	0	0	0	0.04 \pm 0.10
Heptachlor	0	0	0.23	0.03	0.03	0.01	0.05 \pm 0.089
Aldrin	0	0	0.28	0	0	0	0.04 \pm 0.11
Metolachlor	0.06	0.06	0.31	0.1	0.1	0.08	0.11 \pm 0.09
Heptachlor Epoxide ISO B	0	0.01	0.24	0.02	0.03	0.02	0.05 \pm 0.0084
<i>trans</i> -chlordane	0.06	0.05	0.46	0.06	0.05	0.05	0.12 \pm 0.16
<i>cis</i> -chlordane	0.04	0.04	0.39	0.05	0.04	0.04	0.1 \pm 0.142
Dieldrin	0	0	0.41	0	0	0	0.06 \pm 0.16
4.4'-DDE	0.17	0.14	5.94	0.23	0.16	0.22	1.14 \pm 2.35
Endrin	0	0	0.23	0	0	0	0.03 \pm 0.09
4.4'-DDD	0.07	0.1	1.93	0.13	0.12	0.15	0.41 \pm 0.74
Endosulfan sulfate	0.04	0.05	0.27	0.1	0.06	0.06	0.09 \pm 0.08
4.4'-DDT	0.03	0.21	1.97	0.06	0.11	0.06	0.40 \pm 0.59
Endrin ketone	0	0	0.35	0	0	0	0.05 \pm 0.14
Methoxychlor	0	0	0.23	0.06	0.06	0.03	0.06 \pm 0.08

3.2 Cancer Risk Assessment

The CDI and CR values for ingestion, dermal exposure, and inhalation due to each chlorinated pesticide for children and adults are listed in Tables S1 to S12 in Supplementary Material. A CR between 10^{-6} and 10^{-4} indicates a potential risk, while a CR greater than 10^{-4} suggests a potentially high health risk. A CR less than 10^{-6} expresses security (Chen and Liao, 2006; Peng et al., 2011; Huang et al., 2014; Ogbeide et al., 2016). Applying Equation 5 to the CR calculated for each compound and exposure route, the CR of each sediment sample is shown in Table 2.

In 4 out of 6 samples analyzed there is a potential risk of cancer for children and adults. The most dangerous routes of exposure are the skin route and ingestion. The pesticides that contributed the most to these risks were heptachlor and heptachlor epoxide. Aldrin, DDT, Dieldrin, heptachlor, heptachlor epoxide are classified as group B2 carcinogens by EPA (EPA, 1998).

Children are at greater risk from exposure because they are likely to ingest dirt while playing, and their body weights are lower, which may result in higher doses of hazardous substances per unit of body weight (Peng et al., 2012).

Although the pesticides present in the sediments do not present a high risk of cancer, it is necessary that some actions be taken to prevent dangerous effects on the health of the population that lives in these areas.

Table 2. Cancer risk for children and adults through different routes of exposure

Sampling sites	Children CR				adults CR			
	Ingestion	Inhalation	Dermal exposure	RC global	Ingestion	Inhalation	Dermal exposure	RC global
M1	7.05E ⁻⁰⁷	5.59E ⁻¹¹	1.97E ⁻⁰⁷	9.03E ⁻⁰⁷	5.04E ⁻⁰⁷	3.24E ⁻¹¹	5.03E ⁻⁰⁸	5.54E ⁻⁰⁷
M2	1.12E ⁻⁰⁶	1.83E ⁻⁰⁹	6.47E ⁻⁰⁶	7.59E ⁻⁰⁶	1.65E ⁻⁰⁵	1.06E ⁻⁰⁹	1.65E ⁻⁰⁶	1.82E ⁻⁰⁵
M3	7.35E ⁻⁰⁵	5.44E ⁻⁰⁹	1.92E ⁻⁰⁵	9.27E ⁻⁰⁵	4.90E ⁻⁰⁵	3.15E ⁻⁰⁹	4.89E ⁻⁰⁶	5.39E ⁻⁰⁵
M4	2.37E ⁻⁰⁶	5.34E ⁻⁰⁹	1.89E ⁻⁰⁵	2.12E ⁻⁰⁵	4.81E ⁻⁰⁵	3.10E ⁻⁰⁹	4.81E ⁻⁰⁶	5.30E ⁻⁰⁵
M5	2.48E ⁻⁰⁶	1.52E ⁻⁰⁹	5.37E ⁻⁰⁶	7.86E ⁻⁰⁶	1.37E ⁻⁰⁵	8.82E ⁻¹⁰	1.37E ⁻⁰⁶	1.51E ⁻⁰⁵
M6	1.94E ⁻⁰⁶	1.29E ⁻⁰⁹	4.56E ⁻⁰⁶	6.50E ⁻⁰⁶	1.16E ⁻⁰⁵	7.49E ⁻¹⁰	1.16E ⁻⁰⁶	1.28E ⁻⁰⁵

3. Conclusions

All sediment samples had concentrations of DDT and its metabolites, which indicates historical contributions, since this insecticide used to control malaria, dengue, Chagas disease and yellow fever, was banned in Colombia in 1994. The absorption of DDT in sediments and its slow degradation allows organochlorine pesticides residues to continue to be found in freshwater resources, with the potential risk to health. Heptachlor and heptachlor epoxide represented a greater risk for cancer in children and adults in this study, with children being more sensitive, therefore, local authorities should take actions to reduce organochlorine pesticides contamination in the environment. Such studies are necessary for strengthening environmental monitoring, ecosystem management, and legislative initiatives.

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