



# Analysis of organochlorine pesticides and polychlorinated biphenyls in tropical fruits and soils from Antioquia, Colombia and health risk assessment by consumption

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## ABSTRACT

Organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) are persistent organic pollutants (POPs) that accumulate in the food chain, persist in the environment, and pose health risks, even in small quantities from contaminated food, such as tropical fruits. This study assessed the levels of these pollutants in tropical fruits and soils from Antioquia, Colombia, and assessed the associated health risks by consumption. A total of 56 fruit samples (Hass avocado, cape gooseberry, and purple passion fruit) and 32 soil samples were collected from eight farms between March 2023 and January 2024. Samples were analyzed using gas chromatography coupled to mass spectrometry. Trace amounts between  $<0.0300$   $\mu\text{g}/\text{kg}$  and  $0.218$   $\mu\text{g}/\text{kg}$  of heptachlor and  $<0.0300$   $\mu\text{g}/\text{kg}$  and  $0.0662$   $\mu\text{g}/\text{kg}$  of gamma-chlordane in Hass avocado and purple passion fruit were founded. Furthermore, the levels of 4,4'-DDT were between  $1.07$   $\mu\text{g}/\text{kg}$  and  $90.2$   $\mu\text{g}/\text{kg}$  which were higher than 4,4'-DDE ( $0.223$   $\mu\text{g}/\text{kg}$  and  $28.8$   $\mu\text{g}/\text{kg}$ ) in the 18.8 % of the soils samples. The 4,4'-DDT/4,4'-DDE ratios were between 1.11 and 6.12, indicating a potential source of technical mixture of dicofol. PCBs were not detected in fruit samples, but were detected in 18.8 % of the soil samples. The levels found of these pollutants in fruits did not represent a risk to the population by consumption because hazard quotient was below 1.0 and the increased lifetime cancer risks were below  $10^{-6}$  and  $10^{-4}$ . These results suggest that fruits from La Unión, Antioquia, are not a significant source of exposure to OCPs and PCBs for the population. However, the presence of heptachlor and gamma-chlordane in fruit samples highlights the importance of ongoing monitoring. Furthermore, practical recommendations include periodic POPs monitoring in various foods and soils. This ensures food safety and promotes agricultural practices that minimize exposure to environmental contaminants.

## 1. Introduction

Persistent Organic Pollutants (POPs) are chemicals that remain in the environment for a long time, accumulate in the fatty tissues of living organisms through the food chain, and pose significant risks to both human health and the environment (Khairy et al., 2021), including carcinogenic and neurotoxic impacts, as well as adverse effects on reproductive and immune systems (Rokni et al., 2023). Moreover, they have been detected in various environmental compartments, including soil, sediments, atmosphere, and water (Bhutto et al., 2021; Güzel et al., 2022).

Chlorinated compounds, such as organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs), are among the most studied POPs

(Khairy et al., 2021). Many OCPs, including dichlorodiphenyltrichloroethane (DDT), hexachlorocyclohexane (HCH) (all isomers:  $\alpha$ -HCH,  $\beta$ -HCH,  $\gamma$ -HCH, and  $\delta$ -HCH), dieldrin, endosulfan I, endosulfan II, endosulfan sulfate, and cyclodienes, have been globally banned since the 1980s. However, certain OCPs, like DDT, are still used in limited quantities in some countries to control disease-carrying vectors. PCBs, first synthesized in 1881, were widely used from the 1940s to the 1970s in various industrial applications, such as paints, cement, dielectric oils, hydraulic fluids, plastic additives, sealants, adhesives, electrical insulators, refrigerants, and carbonless copy paper (Melymuk et al., 2022a). Their production declined significantly globally between the 1970s and 1980s due to increased awareness of their environmental and health risks (Megson et al., 2024). Although OCPs and PCBs were

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banned years ago, they have been found worldwide, even in remote regions such as the Arctic and Antarctic. Consequently, these two families of contaminants are included in the Stockholm Convention, an international treaty aimed at restricting and eventually eliminating the production, use, emission, and storage of POPs (Alshemmari, 2021). The Stockholm Convention was ratified in Colombia in 2009 through Law 1196 of 2008.

In recent years, the demand for tropical fruits has surged significantly. Fruits and vegetables are essential sources of nutrients and health-promoting phytochemicals, which play a crucial role in reducing the global incidence of nutritional deficiencies and providing protective antioxidants (Xiang et al., 2021). Among the key producers, Colombia stands out for its production and export of tropical fruits, such as cape gooseberry, purple passion fruit, and Hass avocado. These fruits are highly sought after in European and North American markets. As a result, Colombia has implemented international standards to ensure the safety and quality of its products.

Fresh fruits are essential in the daily diet due to their rich content of organic acids, sugars, vitamins, minerals, and other nutrients beneficial to health. They are globally appreciated for their delicious flavors and health-promoting properties (Joshi and Prabhakar, 2020; Slavin and Lloyd, 2012). However, OCP residues in fruits and soils have been reported worldwide (Chandra et al., 2021a; Mahmood et al., 2014; Odewale et al., 2022). For instance,  $\gamma$ -HCH (lindane) has been detected in the stems and leaves of plants, with concentrations of up to 585.82  $\mu\text{g}/\text{kg}$ . Heptachlor, in seven samples of tomato plants, ranged between 512.53 and 1173.8  $\mu\text{g}/\text{kg}$ . Dieldrin was found in rice stems (489.97  $\mu\text{g}/\text{kg}$ ). (Chandra et al., 2021a). Likewise, Qatar investigated OCP residues in fruits and vegetables, finding that 90 % of imported samples exceeded maximum residue limits (MRLs), heptachlor being the most detected pesticide (Al-Shamary et al., 2016a). Furthermore, the presence of OCPs in karst soil was investigated by analyzing 25 OCPs in karst soil near the Three Gorges Dam in China. Total OCP concentrations ranged from 0.161  $\mu\text{g}/\text{kg}$  to 0.431  $\mu\text{g}/\text{kg}$ , with p,p'-DDT and mirex being the most common compounds. (W. Chen et al., 2009). In studies conducted in Nigeria, concentrations of  $\sum$ 20 OCPs in agricultural soils were found to range from 5.8  $\mu\text{g}/\text{kg}$  to 395  $\mu\text{g}/\text{kg}$  (Tesi et al., 2020). Similarly, in China, DDT was predominant in agricultural land systems, with levels ranging up to 337  $\mu\text{g}/\text{kg}$  in agricultural soils and 22.8  $\mu\text{g}/\text{kg}$  in food crops (L. Chen et al., 2023).

In Colombia, several studies have reported the presence of OCPs in soils and fruits. For example, in Quindío, research on tomatoes and cape gooseberries found the highest concentrations of OCPs in these fruits. In tomatoes, the concentration of  $\alpha$ -HCH was 23.0  $\mu\text{g}/\text{kg}$  in the skin and 29.0  $\mu\text{g}/\text{kg}$  in the pulp, while aldrin was 32.0  $\mu\text{g}/\text{kg}$  in the skin and 17.0  $\mu\text{g}/\text{kg}$  in the pulp. In cape gooseberries, the concentration of HCH was 10.0  $\mu\text{g}/\text{kg}$  in the skin and 8.0  $\mu\text{g}/\text{kg}$  in the pulp, and endosulfan I was 161.8  $\mu\text{g}/\text{kg}$  in the skin and 112.3  $\mu\text{g}/\text{kg}$  in the pulp (Ávila-Orozco et al., 2017). Soil samples from the middle and lower basins of the Sinú River revealed significant levels of pesticide residues, including 4,4'-DDT ( $1.78 \pm 4.99 \mu\text{g}/\text{kg}$ ), 4,4'-DDD ( $3.55 \pm 8.27 \mu\text{g}/\text{kg}$ ),  $\alpha$ -chlordane ( $80.0 \pm 200.0 \mu\text{g}/\text{kg}$ ), and lindane ( $280 \pm 870.0 \mu\text{g}/\text{kg}$ ). Other residues, such as  $\beta$ -BCH ( $0.11 \pm 0.4 \mu\text{g}/\text{kg}$ ) and  $\beta$ -endosulfan ( $2.91 \pm 20 \mu\text{g}/\text{kg}$ ), were also detected (Caicedo-Rivas et al., 2022). Additionally, studies in the Bay of Cartagena showed total pesticide levels in sediments ranging from 0.83 to 33.67  $\mu\text{g}/\text{kg}$  (Duarte-Restrepo et al., 2021). In Sogamoso, total pesticide concentrations in soils ranged from 0.2142 mg/kg to 8.4977 mg/kg, while in sediments they ranged from 0.5696 mg/kg to 12.7682 mg/kg (Gallego et al., 2024). In the Magdalena River, pesticides were studied in sediments from 20 sites, with DDE being among the most abundant compounds, averaging  $0.66 \pm 1.38 \mu\text{g}/\text{kg}$  (Tejeda-Benítez et al., 2023). High levels of DDE have also been detected in breast milk from the Colombian population, with the highest concentration reaching 14,948  $\mu\text{g}/\text{kg}$  lipids (Rojas-Squella et al., 2013).

In addition, PCBs have been analyzed in citrus fruits and vegetables in the Jordan Valley, revealing significant differences in PCB

concentrations between species. Levels in citrus fruits ranged from 2.00  $\mu\text{g}/\text{kg}$  to 502  $\mu\text{g}/\text{kg}$ , suggesting potential atmospheric sources of contamination (Alrabadi et al., 2019). Furthermore, the distribution and composition of PCBs in soil-plant systems, particularly near electronic waste recycling sites, showed higher concentrations in rhizospheric soils (2.16  $\mu\text{g}/\text{kg}$ ) compared to non-rhizospheric soils (1.27  $\mu\text{g}/\text{kg}$ ). PCBs were also found to accumulate in plant tissues, with concentrations ranging from 4.02  $\mu\text{g}/\text{kg}$  to 14.5  $\mu\text{g}/\text{kg}$  in shoots and from 0.471  $\mu\text{g}/\text{kg}$  to 24.4  $\mu\text{g}/\text{kg}$  in roots, varying by plant cultivar (Luo et al., 2020). These findings suggest that low-chlorinated PCBs are more likely to accumulate and transfer within plants, a pattern confirmed by the relationship between the root concentration factor and the octanol-water coefficient. In addition, the enantiomeric fractionation of certain PCBs also varied between soil and plant tissues (Zhang et al., 2015). In Colombia, PCDD/Fs and dl-PCBs have been measured in consumer products, with levels up to 1710 pg WHO-TEQ/g of fat in oils and fish (Pemberthy et al., 2016). Additionally, PCBs were found in the breast milk of primiparous women, with PCB 153 being the most prevalent, at a median value of 7.30 ng/g lipids (Avila et al., 2022). However, there are no studies on PCB contamination in fruits and soils in Colombia. This highlights the need to begin monitoring these pollutants in the country to ensure food safety and protect ecosystems from potential exposure to contaminated soils.

Therefore, the objective of this study was to evaluate OCPs and PCBs levels in cape gooseberry (*Physalis peruviana*), purple passion fruit (*Passiflora pinnatistipula*), and Hass avocado (*Persea americana L. Hass*), as well as in the soils used for their cultivation. Additionally, health risk due to consumption was estimated. Monte Carlo simulations were conducted to evaluate the potential carcinogenic and non-carcinogenic risks associated with the concentrations of OCPs and PCBs present in the fruits. The results could be useful for environmental health policies to protect public health.

## 2. Materials and methods

### 2.1. Study area

The samples were collected in the municipality of La Unión, Antioquia, Colombia, which has a total area of 198 km<sup>2</sup>, with 62 km<sup>2</sup> of urban land and 136 km<sup>2</sup> of rural land. The municipality has a population of 21,475 inhabitants and is known for its agricultural production, including potatoes, cape gooseberry, Hass avocado, purple passion fruit, and strawberries. Additionally, its economy includes mining and livestock farming. This study included three Hass avocado farms (A1, A2, A3), three purple passion fruit farms (G4, G5, G6), and two cape gooseberry farms (U7, U8) (Figure S1).

### 2.2. Fruits sampling

Between March 2023 and January 2024, seven campaigns of sampling were conducted every 45 days, taking samples from all farms as follows: 21 samples of Hass avocado, 14 samples of cape gooseberry, and 21 samples of purple passion fruit. The weight of the sample taken was 500 g per bag. The samples were transported at  $25 \pm 5^\circ\text{C}$  to the laboratory of the Contamination and Diagnosis Control Group (GDICON) of the University of Antioquia. Homogenization of the samples was done with 200 g of dry ice using a Hobart GmbH, model CC34 (Offenburg, Germany). The homogenized samples were dried at  $25 \pm 5^\circ\text{C}$  for 15 days over aluminum foil. Afterwards, they were hermetically sealed in bags and stored at  $-20 \pm 2^\circ\text{C}$  until analysis. The sampling and pre-treatment of the samples were carried out in accordance with the protocol of the European Commission 2023/915 (EU, 2023), which establishes standardized procedures to ensure the accuracy and reliability of contaminant analysis in food. Specifically, it defines the minimum quantity of sample required, the appropriate conditions for transport and storage to prevent contamination or degradation, and the homogenization and

drying methods necessary to maintain sample integrity before analysis. The time between sampling campaigns corresponds to the harvest period of the crops

### 2.3. Soils sampling

Between March 2023 and January 2024, four sampling campaigns were conducted every 90 days, enabling the monitoring of changes in soil metal levels across different stages of plant growth. Two of these sampling campaigns took place during the wet season and two during the rainy season, allowing for an evaluation of precipitation effects on soil OCPs and PCBs levels. In total, 32 samples of soil were collected from the agricultural farms, distributed as follows: 12 samples of Hass avocado soil, 12 samples of Cape gooseberry soil, and 8 samples of purple passion fruit soil. Soil samples were collected by drilling at a depth of 0–40 cm using a soil auger suitable for soil extraction. The samples were then disaggregated, and foreign materials such as clasts, glass fragments, and/or debris were removed. The weight of the sample taken was 1000 g per bag, and the samples were transported at  $25 \pm 5^\circ\text{C}$  to the GDCON laboratory. The samples were dried at  $25 \pm 5^\circ\text{C}$  for 15 days over aluminum foil. The samples were stored at  $25 \pm 5^\circ\text{C}$ .

### 2.4. Standards and reagents

The standard pesticide solution used was Pesticide Mix AB #3 at a concentration of 2000  $\mu\text{g}/\text{mL}$ , which includes the following compounds: aldrin, alpha-hexachlorocyclohexane ( $\alpha$ -HCH), beta-hexachlorocyclohexane ( $\beta$ -HCH), gamma-hexachlorocyclohexane (lindane,  $\gamma$ -HCH), delta-hexachlorocyclohexane ( $\delta$ -HCH), gamma-chlordane, alpha-chlordane, 4,4'-DDD, 4,4'-DDE, 4,4'-DDT, dieldrin, endosulfan I, endosulfan II, endosulfan sulfate, endrin, endrin aldehyde, endrin ketone, heptachlor, heptachlor epoxide (B isomer), and methoxychlor, acquired from Restek (Bellefonte, PA, USA). The surrogate standard, 2-fluorobiphenyl, was purchased from Restek (Bellefonte, PA, USA) at a concentration of 2000 mg/L. The internal standard, pentachloronitrobenzene, was also from Restek (Bellefonte, PA, USA), with a concentration of 1000 mg/L. A working solution of pesticides was prepared at 1.0 mg/L in acetone. A 1.0 mg/L solution of 2-fluorobiphenyl in acetone was prepared, and all fruit and soil samples were spiked with 100  $\mu\text{L}$  of this solution. The calibration range used for sample quantification was 1.00–200  $\mu\text{g}/\text{L}$  (0.0300  $\mu\text{g}/\text{kg}$ –6.00  $\mu\text{g}/\text{kg}$ ) for fruits and 1.00–200  $\mu\text{g}/\text{L}$  (0.200  $\mu\text{g}/\text{kg}$ –40.0  $\mu\text{g}/\text{kg}$ ) for soils. The standard solution of PCB used was PCB-Mix 3 of 10 mg/L, which included the congeners PCB 28, PCB 52, PCB 101, PCB 118, PCB 138, PCB 153, and PCB 180 (indicator PCBs), acquired from Dr. Ehrenstorfer (Augsburg, Germany). Furthermore, certified PCB standards of PCB 81, PCB 77, PCB 123, PCB 114, PCB 105, PCB 126, PCB 169, PCB 189, PCB 167, PCB 156, and PCB 157 (dioxin-like PCB) were acquired from Dr. Ehrenstorfer (Augsburg, Germany). A solution of each dioxin-like PCB was made in acetone around 500 mg/L. A mix with all 18 PCB congeners was made at 1.0 mg/L in acetone. The labeled standard WP-LCS at 1.0 mg/L, including  $^{13}\text{C}_{12}$ -PCB 81,  $^{13}\text{C}_{12}$ -PCB 77,  $^{13}\text{C}_{12}$ -PCB 123,  $^{13}\text{C}_{12}$ -PCB 118,  $^{13}\text{C}_{12}$ -PCB 114,  $^{13}\text{C}_{12}$ -PCB 105,  $^{13}\text{C}_{12}$ -PCB 126,  $^{13}\text{C}_{12}$ -PCB 167,  $^{13}\text{C}_{12}$ -PCB 156,  $^{13}\text{C}_{12}$ -PCB 157,  $^{13}\text{C}_{12}$ -PCB 169, and  $^{13}\text{C}_{12}$ -PCB 189, was acquired from Wellington (Guelph, ON, Canada). A working mixture of labeled PCBs at 65  $\mu\text{g}/\text{L}$  in acetone was prepared, and all samples were spiked with 20  $\mu\text{L}$ . The calibration range used for sample quantification of PCBs was 1.00–300  $\mu\text{g}/\text{L}$  (0.0500  $\mu\text{g}/\text{kg}$ –15.0  $\mu\text{g}/\text{kg}$ ) for fruits and 1.00–300  $\mu\text{g}/\text{L}$  (0.00757  $\mu\text{g}/\text{kg}$ –2.27  $\mu\text{g}/\text{kg}$ ) for soils. All solutions were stored at  $-20 \pm 2^\circ\text{C}$ . For the extraction and clean-up process, the following were used: anhydrous sodium sulfate ( $\text{Na}_2\text{SO}_4$ ), magnesium sulfate ( $\text{MgSO}_4$ ), sodium acetate ( $\text{C}_2\text{H}_3\text{O}_2\text{Na}$ ), n-hexane (chromatographic grade), acetone (chromatographic grade), sulfuric acid ( $\text{H}_2\text{SO}_4$ ), and sodium hydroxide ( $\text{NaOH}$ ), acquired from Merck (Darmstadt, Germany); and alumina (Brockman I), Florisil (mesh, 100–200  $\mu\text{m}$ ), and silica (60 A, 230–400 mesh, 20–63  $\mu\text{m}$ ) acquired from Sigma-Aldrich (St.

Louis, MO, USA).

### 2.5. Extraction and clean-up

#### 2.5.1. Fruits

The OCP method consisted of weighing 1 g of dry sample in a 50 mL Falcon tube. Then, 10 mL of hexane: acetone (1:1), 20.0  $\mu\text{L}$  of the 2-fluorobiphenyl surrogate standard at 1 mg/L, 6 g of  $\text{MgSO}_4$ , and 1.5 g of  $\text{C}_2\text{H}_3\text{O}_2\text{Na}$  were added. Subsequently, the tube was stirred with a vortex for 1 minute. Then, the sample was centrifuged for 5 minutes at  $0^\circ\text{C}$  and 5000 rpm using a Boeco centrifuge model U-320R (Hamburg, Germany). The organic phase was transferred to a 50 mL volumetric flask. The extraction step was repeated twice each time. The organic extract was evaporated using a rotary evaporator Boeco RVO 400 SD (Hamburg, Germany) until  $\approx 1$  mL. The extract was cleaned up with a column bottom to top of 5 g of alumina, 5 g of silica, and 2 g of  $\text{Na}_2\text{SO}_4$ . The column was pre-conditioned with 15 mL of hexane, and the extract was eluted with 50 mL of n-hexane. Subsequently, the extract was evaporated until 1 mL and transferred to the chromatographic vial, where it was dried with a gentle nitrogen stream and reconstituted to 200  $\mu\text{L}$  with hexane. Finally, 20.0  $\mu\text{L}$  of PCNB at 10.0 mg/L was added. The vial was then ready for GC-MS analysis.

For extraction of PCBs, the method consisted of weighing 1 g of dry sample in a 50 mL Falcon tube. Then, 10 mL of hexane: acetone (1:1), 20.0  $\mu\text{L}$  of isotopically labeled standards at 65  $\mu\text{g}/\text{L}$ , 6 g of  $\text{MgSO}_4$ , and 1.5 g of  $\text{C}_2\text{H}_3\text{O}_2\text{Na}$  were added. Subsequently, the tube was stirred with a vortex for 1 minute. Then, the sample was centrifuged for 5 minutes at  $0^\circ\text{C}$  and 5000 rpm using a Boeco centrifuge. The organic phase was transferred to a 50 mL volumetric flask. The extraction step was repeated twice each time. The organic extract was evaporated using a rotary evaporator until  $\approx 1$  mL. The extract was cleaned up with a column bottom to top basic silica at 30 %  $\text{NaOH}$ , neutral silica, acidic silica at 40 %  $\text{H}_2\text{SO}_4$ , and anhydrous  $\text{Na}_2\text{SO}_4$ . The column was pre-conditioned with 15 mL of hexane, and the extract was eluted with 100 mL of n-hexane. Subsequently, the extract was evaporated until 1 mL and transferred to the chromatographic vial, where it was dried with a gentle nitrogen stream and reconstituted to 50  $\mu\text{L}$  with hexane. Finally, the vial was ready for GC-MS analysis.

#### 2.6. Soil

For extraction of OCPs and PCBs in soil, 1 g of dry sample was weighed in a 50 mL Falcon tube. Then, for OCP analysis, 20.0  $\mu\text{L}$  of 2-fluorobiphenyl surrogate standard at 1 mg/L was added, or for PCB analysis, 20.0  $\mu\text{L}$  of isotopically labeled standards at 65  $\mu\text{g}/\text{L}$  was added. Afterwards, 6 g of  $\text{MgSO}_4$ , 1.5 g of  $\text{C}_2\text{H}_3\text{O}_2\text{Na}$ , and 10 mL of hexane: acetone (1:1) were added. Subsequently, the tube was stirred with a vortex for 1 minute. Then, the sample was centrifuged for 5 minutes at  $0^\circ\text{C}$  and 5000 rpm. The organic phase was transferred to a 50 mL volumetric flask. The extraction step was repeated twice each time. The organic extract was evaporated using a rotary evaporator until  $\approx 1$  mL and transferred to the chromatographic vial, where it was dried with a gentle nitrogen stream. For OCP analysis, the vial was reconstituted to 200  $\mu\text{L}$  with hexane and 20.0  $\mu\text{L}$  of PCNB at 10.0 mg/L. For PCB analysis, the extract was dried and reconstituted to 50.0  $\mu\text{L}$  with hexane. Finally, the vials were ready for GC-MS analysis.

### 2.7. Instruments and gas chromatography coupled to mass spectrometry analysis

A gas chromatograph linked to a mass spectrometer (7890 A/5975 C) with a 7693 automatic sampler and a multimode inlet (MMI) (G3510A/G3511A) (Agilent Technologies, USA) was used to evaluate the sample extracts (fruits and soils). A ZB-35HT INFERNO column measuring 30.0 m x 0.25 mm x 0.25  $\mu\text{m}$  was utilized for OCPs (Phenomenex, USA). Splitless inlet mode was present. There was a 2  $\mu\text{L}$  injection volume.

290°C was the injection temperature. For 0.8 minutes, the split vent purge flow rate was 60 mL/min. After being at 60°C for one minute, the oven temperature was increased to 150°C at a rate of 15°C per minute and then to 320°C at a rate of 7°C per minute. The mass spectrometer's transfer line temperature was 320°C. The ion source temperature was 230°C, and the quadrupole temperature was 150°C. Electron ionization at 70 eV was used, and data acquisition on the mass spectrometer was performed in selected ion monitoring (SIM) mode (Table S1). With a purity of 99.999 %, helium was utilized as a carrier gas, flowing at a steady flow rate of 1.0 mL/min. 31 minutes was the chromatographic run time.

A ZB-5MS column, measuring 60.0 m x 0.25 mm x 0.25 µm (Phenomenex, USA), was utilized for PCB analysis. Splitless pulsation was the inlet mode. There was a 2 µL injection volume. 290°C was the injection temperature. For 0.8 minutes, the split vent purge flow rate was 50 mL/min, and for the next 0.5 minutes, the pressure was 50 psi. 140°C was the starting oven temperature, maintained for one minute. Following a one-minute hold, the temperature was escalated to 200°C at a rate of 20 °C/min, then to 280°C at a rate of 3 °C/min, and lastly to 320°C at a rate of 30 °C/min. The temperature of the transfer line was 320°C. 150°C was the quadrupole temperature, and 280°C was the ion source temperature. Electron ionization at 70 eV was used, and data acquisition on the mass spectrometer was performed in SIM mode (Table S2). Helium was used as the carrier gas at a constant flow rate of 1.5 mL/min with a purity of 99.999 %. The chromatographic run time was 33 min.

### 2.7.1. Validation and uncertainty

All methods used were validated, and the uncertainty of the measurement was estimated. The accuracy of the method was evaluated by considering both trueness (recovery) and precision (RSD). The validation parameters assessed included linearity, matrix effect, method detection limit (MDL), and method quantification limit (Chavan and Desai, 2022).

The linearity in both matrices was evaluated with three calibration curves using seven concentration levels in the range of 0.0300 µg/kg to 6.00 µg/kg for OCPs in fruits, 0.200 µg/kg to 40.0 µg/kg for OCPs in soils, 0.00757 µg/kg to 2.27 µg/kg for PCBs in fruits, and 0.0500 µg/kg to 15.0 µg/kg for PCBs in soils. The regression hypothesis using an analysis of variance (ANOVA) and the coefficients of determination ( $R^2$ ) was evaluated (European Commission, 2021). The matrix effect (ME) was evaluated by comparing the ratio between the slopes of calibration curves in solvent (hexane) and matrix using the following equation  $(a/b) \cdot 100$ , where a and b correspond to the slope in matrix and solvent, respectively. The acceptance criterion was  $\pm 20$  % (Zhou et al., 2022). MDLs and MQLs were estimated using the t99SLLMV approximation (Corley, 2003). Accuracy was assessed by using spiked samples at MQLs ( $n = 20$ ) and 10 MQLs ( $n = 20$ ) for OCPs in fruits and for PCBs in fruits and soils. For OCPs in soil, accuracy was evaluated by analyzing a certified reference material (Clay Loam Lot 015591) (CRM847–50G, Fluka). The acceptance criteria were relative standard deviation (RSD)  $\leq 20$  % and recovery percentages between 70 % and 130 % (U.S. Environmental Protection Agency, 2003).

Eq. (1) was then used to determine the uncertainty by combining the contributions of  $u_{treat}$ ,  $u_{trub}$ ,  $u_{cab}$ ,  $u_{vob}$ , and  $u_{um}$ . The expanded uncertainty is represented by U, the sample treatment factor is represented by um, the sample mass is represented by um, the relative standard uncertainty regarding the sample treatment factor is represented by  $u_{treat}$ , the relative standard uncertainty regarding the final volume is represented by  $u_{vob}$ , the coverage factor is represented by  $k = 2$ , and the trueness estimation for the relative standard uncertainty is represented by  $u_{tru}$ . (Mohamed et al., 2020).

$$U = k \sqrt{u_{cal}^2 + u_{vol}^2 + u_{um}^2 + u_{treat}^2 + u_{tru}^2} \quad (1)$$

## 2.8. Probabilistic Risk Assessment (PRA)

The risk by consumption of levels of OCPs and PCBs in the fruits of this study was estimated using a strategy of Probabilistic Risk Assessment (PRA) with Monte Carlo simulation (MCS). The risk was estimated in two scenarios, a non-carcinogenic one considering the hazard quotient (HQ) Eq. (2) and a carcinogenic one considering the lifetime cancer risks (LCR) Eq. (3).

$$THQ = \frac{EDI}{RfD} \quad (2)$$

$$LCRs = EDI * OSF \quad (3)$$

Where EDI, RfD, and OSF correspond to the estimated daily intake, the oral reference dose, and the oral slope factor, respectively. The EDI (mg/kg/day of body weight) was calculated using Eq. (4), in which, Cn represents the mean concentration of OCPs and PCBs in the fruits on a fresh weight basis (mg/kg) (log-normal distribution); IR ingestion rate (200 g/kg person/days) (log-normal distribution) (EPA, 1989); EFr is exposure frequency (365 days/year) (normal) (EPA, 1989); ED is exposure duration (70 years) (normal) (EPA, 1989); BW is the body mass, adult (70 kg) (log-normal distribution) (EPA, 1989); AT is the average time (365 days/year x number of exposure years) (EPA, 1989).

$$EDI = \frac{Cn * I * EFr * ED}{BW * AT} * 0.001 \quad (4)$$

The RfD was taken from IRIS for heptachlor. The RfD used was  $5.0 \times 10^{-4}$  mg/kg/day of body weight (IRIS, 1987). When the HQ value was less than 1 at the 95 % percentile, it indicated that the risk of non-carcinogenic effects was at a safe level. In contrast, when HQ was greater than 1, there was a probability of non-carcinogenic effects, with the probability increasing as this value increases (IRIS, 1987). The OSF was taken from IRIS. The amount of OSF used to heptachlor was 4.5 per mg/kg/day (IRIS, 1987). LCRs result is considered normal in the range between  $10^{-6}$  and  $10^{-4}$  (EPA, 1990). Values higher than  $10^{-4}$  indicated a carcinogenic risk. The MCS was performed with the package mc2d version 0.2.1 using 10000 iterations in the variables and 5000 iterations in the uncertainty.

## 2.9. Data treatment and statistics

All results are presented in µg/kg for fruits and soils. The values in which the results were <MQL were replaced by  $\frac{1}{2}$ MQL for descriptive analysis. All statistical analyses and graphs were performed using R 4.3.3 and RStudio 2024.04.2 + 764 software. In most cases, the Kruskal-Wallis nonparametric test (KW) using correction of the Benjamini-Hochberg method (BH) was used. When a KW-BH test was significant ( $p$ -value < 0.05) a post hoc Dunn test was performed as a pairwise comparison method. Finally, an analysis of variance (ANOVA) was performed to evaluate the regression hypothesis, and the Spearman method was used to evaluate the correlation and relationships between the data.

## 2.10. Quality assurance and control (QA/QC)

In each batch of samples analyzed, a control was performed using a laboratory blank of fruit and soil matrices to verify potential cross-contaminations during the extraction process. Furthermore, a laboratory fortified blank (LFB) was performed at the minimum report limit of 0.0300 µg/kg in fruits and 0.200 µg/kg in soils for OCPs, and 0.00757 µg/kg in fruits and 0.0500 µg/kg in soils for PCBs. The recovery percentages of LFB for OCPs ranged from 74.1 % (Aldrin) to 101 % (DDT) in fruits and from 74.6 % (DDE) to 116 % (Endosulfan I) in soils. For PCBs, recoveries in fruits ranged from 75.2 % (PCB-28) to 121 % (PCB-126), and in soils from 75.2 % (PCB-28) to 120 % (PCB-189).

Moreover, a laboratory-fortified sample matrix (LFM) was performed by duplicating at concentrations within the working range. The recovery percentages of LFM for OCPs ranged between 72.2 % (Aldrin) and 119 % (DDT) in fruits and between 73.3 % (DDE) and 113 % (DDT) in soils. For PCBs, recovery percentages ranged from 72.5 % (PCB-28) to 112 % (PCB-126) in fruits and from 73.5 % (PCB-52) to 114 % (PCB-153) in soils. The relative percentage difference (RPD) of LFM was below 20 % for both PCBs and OCPs.

### 3. Results and discussion

The methods used for the determination of OCPs and PCBs in fruit and soil samples were accurate because they had adequate precision and trueness (Wood, 1999). The validation results are shown in (Table S3) for OCPs and in (Table S4) for PCBs. The linearity was evaluated considering the coefficients of determination ( $R^2$ ) and the regression hypothesis through the ANOVA. The  $R^2$  for all compounds of the study was  $\geq 0.990$  in both solvent and matrix (Tables S3 and S4). Besides, the linear regression hypothesis ( $p < 0.05$ ) was demonstrated in solvent and matrix within the working range of all OCPs and PCBs. The compounds did not exhibit significant ME because all slope ratios calculated were below 20 %. This could be explained by the cleaning procedures used, which helped obtain purer extracts and reduced matrix interference (Rutkowska et al., 2018). Additionally, when analyzing non-polar compounds, the matrix effect is not likely to be significant (Bulaić Nevistić and Kováč Tomas, 2023). The polarity and stability of compounds are important factors influencing the degree of response change due to matrix effects. It turns out that highly polar compounds have a greater potential to interact with the active sites in the liner (Xu et al., 2021).

The MDLs for OCPs in fruits ranged from 0.00679  $\mu\text{g}/\text{kg}$  ( $\beta$ -BHC) to 0.00950  $\mu\text{g}/\text{kg}$  (4,4'-DDD), while the MQLs ranged from 0.0206  $\mu\text{g}/\text{kg}$  ( $\beta$ -BHC) to 0.0288  $\mu\text{g}/\text{kg}$  (4,4'-DDD). In soils, the MDLs varied between 0.0408  $\mu\text{g}/\text{kg}$  ( $\beta$ -BHC) and 0.0575  $\mu\text{g}/\text{kg}$  (4,4'-DDT), with MQLs ranging from 0.124  $\mu\text{g}/\text{kg}$  ( $\beta$ -BHC) to 0.174  $\mu\text{g}/\text{kg}$  (4,4'-DDT).

For PCBs in fruits, the MDLs ranged from 0.00122  $\mu\text{g}/\text{kg}$  (PCB 126) to 0.00172  $\mu\text{g}/\text{kg}$  (PCB 169), and the MQLs varied between 0.00371  $\mu\text{g}/\text{kg}$  (PCB 126) and 0.00523  $\mu\text{g}/\text{kg}$  (PCB 169). In soils, the MDLs were between 0.00810  $\mu\text{g}/\text{kg}$  (PCB 126) and 0.0114  $\mu\text{g}/\text{kg}$  (PCB 169), while the MQLs ranged from 0.0245  $\mu\text{g}/\text{kg}$  (PCB 126) to 0.0345  $\mu\text{g}/\text{kg}$  (PCB 169).

The MQLs of the OCPs in this study were similar in magnitude to those reported in other studies on fruits and soil (Bhutto et al., 2021; Chandra et al., 2021a; Khairy et al., 2021). In the case of PCBs, these compounds are analyzed less frequently in non-lipophilic matrices due to their high capacity for bioaccumulation in fatty tissues. For this reason, monitoring is preferred in matrices such as milk, meat products, and adipose tissue, among others (Pacyna-Kuchta, 2023). However, when compared with the limited studies available on fruits, we found that our MQLs were of the same magnitude (Güzel et al., 2022; Melymuk et al., 2022a, 2022b). This allowed us to monitor OCP and PCB levels in fruits at levels of magnitude similar to those reported previously. The recovery percentages for OCPs ranged between 73.3 % (Aldrin) and

122 % (Endosulfan sulfate) for fruits and between 72.8 % ( $\delta$ -BHC) and 125 % (Endosulfan aldehyde) for soils. For PCBs, the recovery percentages ranged between 72.2 % (PCB-28) and 128 % (PCB-118) for fruits and between 72.0 % (PCB-28) and 124 % (PCB-167) for soils. The RSDs were  $\leq 20$  % for both OCPs and PCBs in both matrices.

#### 3.1. OCPs in fruits

All results were below MQL (0.030  $\mu\text{g}/\text{kg}$ ) except for heptachlor and gamma-chlordane in Hass avocado and purple passion fruit. In Table 1, the concentrations found in A1, A2, A3 (Hass avocado farms), and G4 and G5 (purple passion fruit farms) are shown. However, the amounts found of heptachlor and gamma-chlordane were below the LMR of 10  $\mu\text{g}/\text{kg}$  (Codex, 2023). This indicates that analyzed fruits from La Union crops could be exported to the European Union as they satisfy European regulations regarding residuality of OCP; however, other pesticides that are used regularly on these crops must be monitored to guarantee their innocuity in terms of pesticide residues. That is because OCP has been banned in Colombia since the 1990s (Girones et al., 2020; Marrugo-Negrete et al., 2014). Therefore, OCPs residues are not expected to be found, in contrast to other pesticide families. The amounts found of heptachlor and gamma-chlordane could be associated with background levels in the country and region, which reflect the long-term persistence of OCPs in the environment (Kumar and Mukherji, 2018). While these compounds have been banned for decades, their continued presence in fruits might be due to historical contamination. Heptachlor and gamma-chlordane residues could still be detectable because of their persistence in the atmosphere or because they have been redeposited from previous applications (Gonzalez et al., 2003a). This phenomenon is not unique to Colombia. Heptachlor residues in fruits have been reported in several countries. For instance, in Qatar, heptachlor was found to be the most recurrent pesticide in all evaluated fruits, with a maximum concentration of 144  $\mu\text{g}/\text{kg}$  (Al-Shamary et al., 2016b). Furthermore, a study conducted on tomatoes found maximum heptachlor levels of 0.29  $\mu\text{g}/\text{kg}$  and  $\Sigma$  chlordane levels of 2.37  $\mu\text{g}/\text{kg}$ . Furthermore, it was that the same matrix contained maximum concentrations of 1.02  $\mu\text{g}/\text{kg}$ , 5.4  $\mu\text{g}/\text{kg}$ , and 0.32  $\mu\text{g}/\text{kg}$  for chlordane, hexachlorobenzene, and 4,4'-DDD, respectively (Wang et al., 2022a). Furthermore, heptachlor in seven samples of tomato plants ranged between 512.53 and 1173.8 ng/g (Chandra et al., 2021a). In this regard, other studies around the world have found residues of OCPs in fruits below MRLs, suggesting their low-level presence in these types of matrices and the persistence of these pollutants. For instance, levels of 4, 4-DDE and hexachlorobenzene in tomato samples in the ranges of 0.006 mg/kg - 1.09 mg/kg and 0.004 mg/kg - 0.007 mg/kg, respectively, have been found (Lozowicka et al., 2015). In addition, in a study on the detection of OCPs in vegetables and fruits in Bangladesh, chlordane was detected at maximum concentrations at  $2.09 \pm 0.27$   $\mu\text{g}/\text{kg}$  in tomato samples (Haile et al., 2023).

Thus, the residues of heptachlor and gamma-chlordane detected in Colombian fruits are likely indicative of continuing environmental contamination, possibly from the long-term persistence of these compounds in the atmosphere or background contamination from past

**Table 1**  
Results of OCPs in fruits.

OCPs	Sampling	A1	A2	A3	G4	G5
		Results ( $\mu\text{g}/\text{kg}$ ) $\pm$ U				
Heptachlor	Sampling 5	0.0735 $\pm$ 0.0176	0.0687 $\pm$ 0.0164	0.0855 $\pm$ 0.0205	0.0894 $\pm$ 0.0214	0.218 $\pm$ 0.0525
Gamma-chlordane		< 0.0300	< 0.0300	< 0.0300	< 0.0300	0.0662 $\pm$ 0.0112
Heptachlor	Sampling 6	0.145 $\pm$ 0.0348	0.0714 $\pm$ 0.0171	0.1805 $\pm$ 0.0434	< 0.0300	0.0721 $\pm$ 0.0173
Gamma-chlordane		0.0307 $\pm$ 0.00522	< 0.030	0.0322 $\pm$ 0.00547	< 0.0300	< 0.0300
Heptachlor	Sampling 7	< 0.0300	< 0.0300	< 0.0300	< 0.0300	0.0473 $\pm$ 0.00947
Gamma-chlordane		< 0.0300	< 0.0300	< 0.0300	< 0.0300	< 0.030

A: Hass avocado, G: Purple passion fruit.

agricultural practices in the country (Chandra et al., 2021b). These residues may have entered the fruits via atmospheric deposition or migration from nearby contaminated areas, especially in regions where these pesticides were once heavily used. Climatic factors such as temperature and rainfall, which influence the breakdown and movement of pollutants, could also contribute to the re-deposition of these contaminants in agricultural areas (Noyes et al., 2009). This emphasizes the need for ongoing monitoring of atmospheric contamination and historical pesticide residues to ensure the safety of agricultural products. Additionally, the global transport of POPs through atmospheric currents can contribute to the presence of these residues in Colombian fruits. These compounds, including heptachlor and gamma-chlordane, are known to undergo long-range atmospheric transport, traveling thousands of kilometers from their original sources before being deposited in distant regions through processes such as cold condensation and wet or dry deposition (Sakin et al., 2023). This phenomenon is particularly relevant in tropical and subtropical areas, where fluctuating temperatures and high humidity can facilitate the deposition and re-emission of these contaminants, further exacerbating their persistence in the environment (Alshemmari, 2021). The influence of global pollutant transport underscores the need for international cooperation in monitoring and regulating these hazardous substances.

In Fig. 1, concentrations of heptachlor and gamma chlordane in Hass avocado and purple passion fruit samples are shown. Heptachlor is a metabolite of chlordane and a constituent of industrial chlordane. As a result, it is not always evident from the identification of heptachlor or heptachlor epoxide compounds that heptachlor (or heptachlor epoxide) is the main effect (Kielhorn et al., 2006). Additionally, a positive correlation (0.639\*\*) between heptachlor and gamma-chlordane concentrations in Hass avocado, thus confirming the relationship that exists between both compounds (Xie et al., 2022). Spearman rank correlation coefficient (S) was used to assess their relationship. This method evaluates ranking agreement without assuming normality or equal variance, focusing on rank order differences rather than means. The null hypothesis (H0) posits no correlation between rank orders, with the coefficient ranging from  $-1$  to  $1$ , indicating correlation strength and direction (1 representing perfect positive,  $-1$  perfect negative). Hypothesis tests were conducted at a 95 % confidence level, using a significance level (P-value) of 0.05. A P-value less than 0.05 rejects H0, indicating a significant correlation between rank orders (Sedgwick, 2014).

Kruskal-Wallis tests did not show a significant difference ( $p > 0.5$ ) (Bon-Gang, 2018).

### 3.2. OCPs in soil

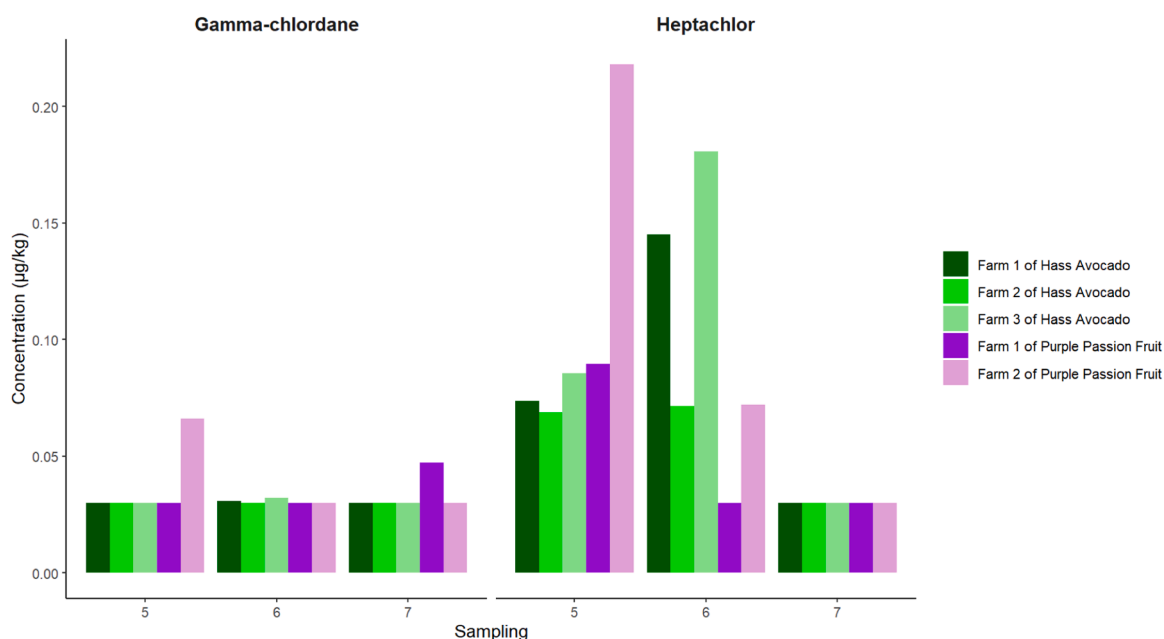
All results were below MQL (0.200  $\mu\text{g}/\text{kg}$ ) except for 4,4'-DDT and 4,4'-DDE in Hass avocado and purple passion fruit. In Table 2, the results of OCPs in soils are presented, showing the concentrations found in A1 (Hass avocado farms) and G5 (purple passion fruit farms).

The concentrations of 4,4'-DDT were higher than those of 4,4'-DDE in both soil samples. For example, in Sampling 3, the concentration of 4,4'-DDT was  $90.2 \pm 18.0 \mu\text{g}/\text{kg}$  in A1 soil, compared to  $81.1 \pm 14.4 \mu\text{g}/\text{kg}$  for 4,4'-DDE. In G5 soil, 4,4'-DDT had a concentration of  $32.2 \pm 6.44 \mu\text{g}/\text{kg}$ , while 4,4'-DDE was measured at  $28.8 \pm 5.14 \mu\text{g}/\text{kg}$ . These findings align with the general understanding that 4,4'-DDT can dechlorinate to 4,4'-DDE and reduce to 4,4'-DDD (Gong et al., 2020). The ratios of isomers of various organochlorine pesticides can indicate whether they are currently being applied or if their presence is due to degradation of products from past applications. A ratio of 4,4'-DDT to its metabolic products greater than 1 indicates current use, while a ratio less than 1 suggests past use (Wang et al., 2022b). In all the samples analyzed, the 4,4'-DDT / 4,4'-DDE ratio is greater than one, ranging from 1.11 to 6.12. Other studies have shown that DDT is an impurity of industrial dicofol with a greater contribution from 4,4'-DDT. It is reported that the ratio of 4,4'-DDT to 4,4'-DDE ranges from 3 to 7 (Pozo et al., 2017). This suggests that the presence of OCPs on the studied farm, where agrochemicals have never been used, is likely due to recent emissions resulting from

**Table 2**  
Results of OCPs in soil.

OCPs	Sampling	A1 Soil	G5 soil
		Results ( $\mu\text{g}/\text{kg}$ ) $\pm$ U	
4,4'-DDE	Sampling 3	$81.1 \pm 14.4$	$28.8 \pm 5.14$
4,4'-DDT		$90.2 \pm 18.0$	$32.2 \pm 6.44$
4,4'-DDE	Sampling 5	$1.23 \pm 0.219$	$0.562 \pm 0.103$
4,4'-DDT		$2.12 \pm 0.424$	$2.02 \pm 0.404$
4,4'-DDE	Sampling 7	$0.271 \pm 0.0484$	$0.223 \pm 0.0398$
4,4'-DDT		$1.66 \pm 0.334$	$1.07 \pm 0.214$

A: Hass avocado, G: Purple passion fruit.



**Fig. 1.** Concentration of Heptachlor and Gamma chlordane ( $\mu\text{g}/\text{kg}$ ).

atmospheric deposition of these pesticides (Gonzalez et al., 2003b).

Despite this potential for recent deposition, the persistence of these compounds in soil remains a significant concern. Fig. 2 presents the results obtained from the four soil samples, showing the concentrations of 4,4'-DDE and 4,4'-DDT at different sampling points. Overall, these findings are important because they demonstrate the persistence of these compounds in the environment and their slow degradation over time. Despite the ban on their use for several decades, the continued detection of 4,4'-DDE and 4,4'-DDT in soil samples suggests that these chemicals have a long environmental half-life, resisting natural degradation processes and potentially posing risks to ecosystems and human health (Singh et al., 2013). Their persistence can be attributed to their strong affinity for organic matter and their limited mobility in soil, which reduces their bioavailability but also slows down their breakdown (Zhang et al., 2015). Additionally, the gradual decrease in the concentrations of 4,4'-DDE and 4,4'-DDT in subsequent samples could indicate a natural remediation process, where microbial activity, photodegradation, or other environmental factors contribute to their slow transformation over time (Cui et al., 2024).

### 3.3. PCBs in fruits and soil

All fruit samples were below the MQL (0.00757 µg/kg), indicating that PCB contamination in the analyzed fruits was minimal or non-detectable. Research focusing on PCBs in fruits is scarce, partly due to the affinity of these compounds for fatty tissues, which makes their accumulation in low-lipid matrices less likely. However, studies conducted in Italy reported PCB concentrations in fruits and vegetables ranging from 33.39 to 10,130 pg/g of fresh weight (fw) for the sum of the 26 analyzed PCBs (Σ26 PCB) and from 14.86 to 4504 pg/g fw for the six indicator PCBs without dioxins (Ceci et al., 2022). These findings suggest that although PCBs can be present in plant-based foods, their levels tend to be relatively low, likely influenced by environmental deposition and plant uptake mechanisms.

In contrast, PCB contamination in soils has been more frequently reported due to their persistence and strong adsorption to organic matter (Šrédlová and Cajthaml, 2022). Table 3 presents the results of PCB concentrations found in soils from the studied areas, whereas other PCBs were detected below the limit of quantification (0.05 µg/kg). The

maximum sum of PCB concentrations in the analyzed soil samples was  $4.108 \pm 0.357$  µg/kg, a value significantly below the recommended threshold of 300 µg/kg for agricultural soils (Environment Canada, 2019).

It was observed that the purple passion fruit farm showed the highest concentration of PCBs, with levels exceeding the quantification limit for PCB 153, PCB 138, PCB 126, PCB 167, PCB 157, PCB 180, PCB 169, and PCB 189. Among these, PCB 153, PCB 138, and PCB 180 are commonly classified as indicator PCBs. In contrast, only PCB 123 was found to be present in the Hass avocado farm. In Figure S2, the sum of the PCB concentrations in the soil remains consistent over the last three samplings. Notably, our results indicate concentrations lower than those observed in other areas, such as the range of PCB concentrations reported in Korba (3.25 µg/kg–25.22 µg/kg) (Han et al., 2023).

Interestingly, the soil samples that tested positive for PCBs correspond to the same two farms that also tested positive for OCPs. This correlation suggests a possible relationship between the contamination of these soils by both types of POPs, reinforcing the idea that contamination in these two farms could be the result of regional atmospheric deposition, residual contamination from past industrial emissions, or long-range transport of these pollutants from urban or industrialized areas (Mao et al., 2021). Although PCBs were never intentionally applied in agriculture, their presence in these soils may originate from historical use in electrical transformers, hydraulic systems, and other industrial equipment, followed by gradual environmental dispersion (Valizadeh et al., 2021). Various potential sources of PCBs in industrial areas have been identified, including combustion processes, vehicle exhaust emissions, and industrial activities in general (Liu et al., 2020).

Following their release, PCB congeners partition into gaseous and particulate phases in the environment. It has been observed that congeners with lower chlorine content ( $Cl \leq 6$ ) tend to partition more into the gaseous phase compared to those with higher chlorine content ( $Cl \geq 7$ ) (Y. Wang et al., 2011). As a result, lower-chlorine congeners are more likely to experience long-range atmospheric transport from their site of origin to distant regions. However, our study's homogeneous pattern could be attributed to localized pollution sources, such as industrial emissions, waste incineration, or traffic-related PCB release, which contribute to short-range atmospheric movement and subsequent soil deposition (Erkul and Eker Şanlı, 2020). Additionally, PCBs can enter

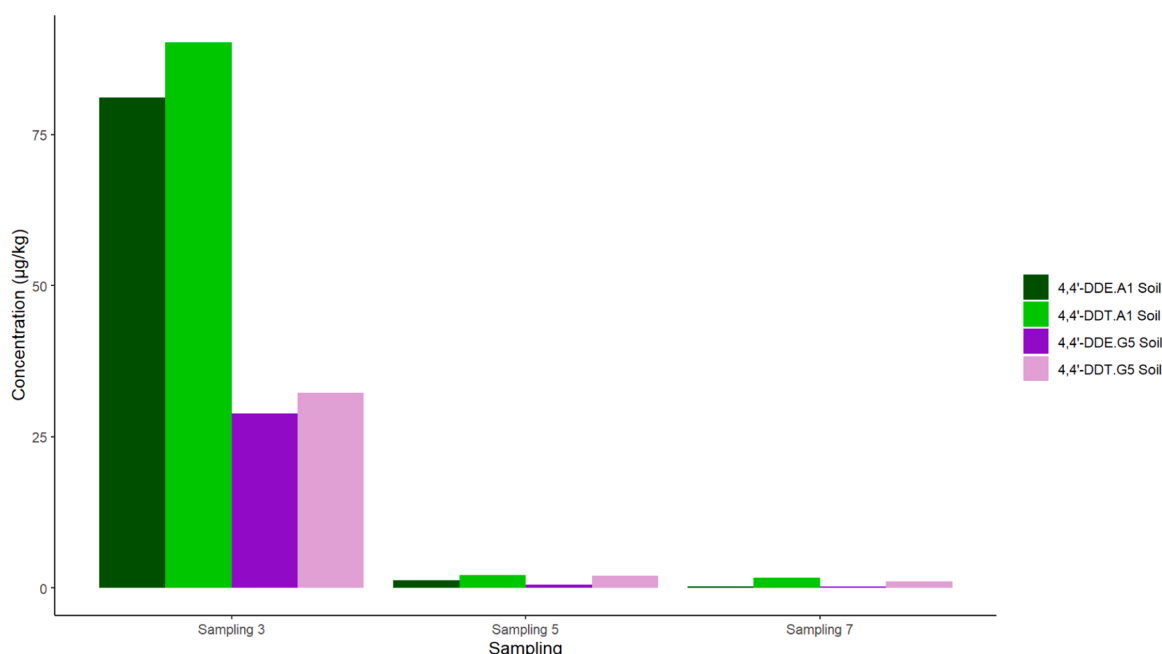


Fig. 2. Concentration of 4,4'-DDE and 4,4'-DDT in A1 and G5 soil samples (µg/kg).

**Table 3**  
Results of PCBs in soil.

Matrix	Sampling	PCB 123	PCB 153	PCB 138	PCB 126	PCB 167	PCB 157	PCB 180	PCB 169	PCB 189	ΣPCBs
Results (µg/kg) ± U											
A1	3	0.735 ± 0.167	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	0.735 ± 0.167
G5		< 0.05	0.129 ± 0.026	0.180 ± 0.039	0.223 ± 0.054	0.363 ± 0.087	0.280 ± 0.073	0.975 ± 0.253	0.708 ± 0.099	1.25 ± 0.188	4.108 ± 0.357
A1	5	0.735 ± 0.167	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	0.735 ± 0.167
G5		< 0.05	0.098 ± 0.020	0.125 ± 0.026	0.185 ± 0.044	0.568 ± 0.136	0.425 ± 0.111	0.545 ± 0.141	0.665 ± 0.093	1.13 ± 0.170	3.741 ± 0.302
A1	7	0.765 ± 0.174	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	0.765 ± 0.174
G5		< 0.05	0.267 ± 0.053	0.127 ± 0.026	0.203 ± 0.049	0.338 ± 0.081	0.215 ± 0.056	1.224 ± 0.318	0.702 ± 0.098	1.02 ± 0.153	4.096 ± 0.387

A: Hass avocado, G: Purple passion fruit.

the environment through improper disposal of contaminated equipment or leaks from old storage sites, which may explain their presence in non-industrial agricultural settings (Jones and De Voogt, 1999). This underscores the necessity of continuous monitoring and further research to determine whether these pollutants are being actively deposited in agricultural soils or if they are remnants of past contamination.

### 3.4. Monte Carlo Simulation (MCS)

This study employed MCS, a technique for handling uncertainty in parameter estimation (Jamshidi et al., 2021). In MCS, a range of possible values is assigned to each uncertain parameter using a probability distribution. The simulation iteratively samples values for each parameter, runs the model with these inputs, and records the outcomes. This process is repeated many times to produce a comprehensive distribution of potential results (Qin et al., 2021). Fig. 3 presents the results obtained for heptachlor, as this was the OCP most frequently detected and thus selected for this analysis.

The health risk is the possibility of developing cancer caused by exposure to a certain concentration of a chemical. Conditions that individuals would face with the exposures considered in this study (EPA/630/P-03/001F, 2005). In Fig. 3A, it is observed that there is no non-carcinogenic risk, as the HQ index value is less than one (IRIS, 1987). Furthermore, in Fig. 3B, it is evident that there is also no carcinogenic risk with the evaluated parameters, as the values fall within the acceptance criterion of  $10^{-6}$  and  $< 10^{-4}$  (EPA, 1990). Therefore, in both analyses, it can be affirmed that, at the 97.5th percentile, there is no health risk, whether carcinogenic or non-carcinogenic, associated with the consumption of the OCP levels found in the analyzed fruits. In other

studies, it has been observed that exposure to OCPs increases the risk of developing non-cancerous diseases in nearly half of the women studied. Additionally, it was found that approximately between 25 % and 75 % of the participants had a high risk of developing some type of cancer related to the concentrations of HCB and DDE present in their bodies (Rincón-Rubio et al., 2024). Similarly, exposure to heptachlor has also been associated with a significant non-cancerous risk. It has been reported that levels of exposure to heptachlor and dieldrin exceed the safety threshold, suggesting the possibility of adverse health effects for consumers (Akoto et al., 2015).

### 4. Conclusions

For the first time in the city of Unión, Antioquia, Colombia, OCPs and PCBs were monitored and quantified in fruits and agricultural soils. The results indicate that fruits are not a significant source of exposure to POPs for the population, as their levels in the samples were below of the regulated limits. However, the detection of heptachlor and gamma-chlordane in Hass avocado and purple passion fruit raises concerns and highlights the need for further research, as other foods in the city and country may contain higher concentrations of OCPs. The concentrations of OCPs found in soils suggest recent emissions of dicofol because of ratios of 4,4'-DDE and 4,4'-DDT corresponded to commercial mixture of it. The maximum concentration of total PCBs in soils was  $4.108 \pm 0.357 \mu\text{g}/\text{kg}$ , which was below the recommended threshold of  $300 \mu\text{g}/\text{kg}$  for agricultural soils, indicating that PCB contamination is not a concern in this area. To ensure food safety for the local population, it is crucial to continue conducting periodic monitoring, expanding the analysis to other food products. Practical recommendations include the

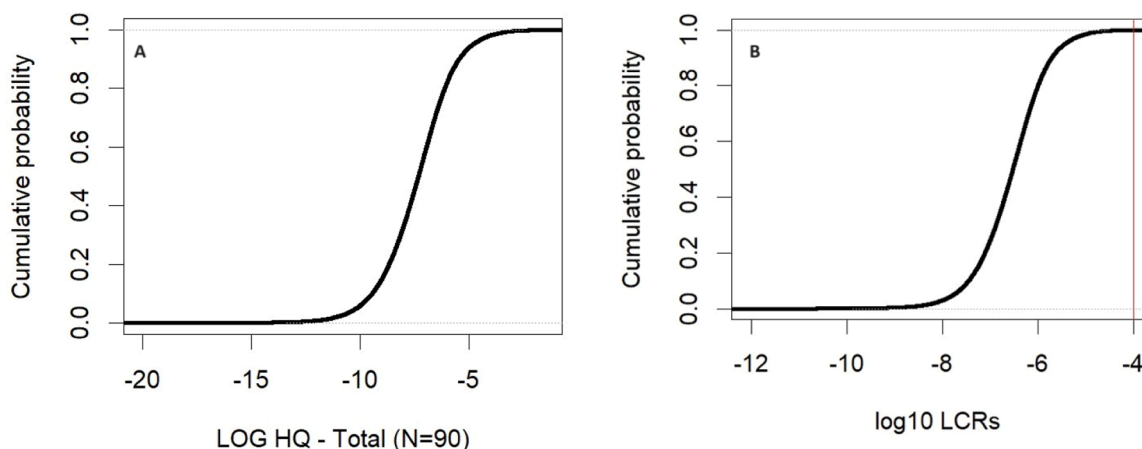


Fig. 3. Health risk 3A. non-carcinogenic risk assessment 3B. Carcinogenic risk assessment.



regular assessment of POPs in various foods and soils, allowing for the early detection and prevention of potential increases in population exposure. For policymakers and stakeholders, it is advisable to establish specific guidelines for monitoring POPs in Colombian agricultural products and to promote safe agricultural practices that minimize exposure to environmental contaminants.

### CRedit authorship contribution statement

**Gallego Sara:** Project administration, Conceptualization. **Avila Boris:** Project administration, Methodology, Conceptualization. **Peñuela Gustavo:** Supervision, Formal analysis, Conceptualization. **Castañeda Vargas Jovan Mateus:** Writing – original draft, Software, Formal analysis, Data curation, Conceptualization.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### Declaration

“All authors have read, understood, and have complied as applicable with the statement on "Ethical responsibilities of Authors" as found in the Instructions for Authors”

### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jfca.2025.107428](https://doi.org/10.1016/j.jfca.2025.107428).

### Data availability

Data will be made available on request.

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