Environmental and Biological Monitoring of Organochlorine Pesticides in the City of Salamanca, Mexico

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Abstract

The former Tekchem Industrial Unit located in the city of Salamanca, Mexico, constitutes an environmental liability in which the presence of high levels of organochlorine pesticides (OCPs) has been reported. In the present study, levels of OCPs were quantified using gas chromatography – mass spectrometry in 52 soil samples and in 88 blood samples from school-age children in the city of Salamanca. A median concentration of 70.6 ng/g (6.93 - 3276) was obtained for total OCPs in soil, while for the total sum of dichlorodiphenyltrichloroethane (DDT) the value was 49.6 ng/g (6.93 - 3276). In children, the median level of the total sum of OCPs was 390 ng/g lipid (7.34 - 14895), and for the total sum of DDT was 175 ng/g lipid (<LOD - 14802). The OCPs that resulted in highest concentrations in soil were DDT and its metabolites, as well as aldrin and heptachlor epoxide; while in blood the highest levels corresponded to 4,4'-DDT and its metabolites, followed by heptachlor and heptachlor epoxide. The spatial distribution of the concentrations of OCPs in soil shows that the facilities of Teckchem may be a significant potential source for the dispersion of these compounds towards the metropolitan area of Salamanca. The results obtained in the present study demonstrate the presence of OCPs in soil and in child population, providing important bases to study the problem from a broader perspective, while reiterating the importance of continuing efforts to generate resolute and precautionary measures with respect to the environmental liability of Tekchem.

1. Introduction

Persistent organic pollutants (POPs) are a group of chemical compounds of mainly synthetic origin, which have been widely used for various purposes. The problem surrounding these substances lies in their toxicity to both humans and biota, and their persistence in the environment, since due to their physical and chemical characteristics, their degradation is slow, causing them to remain for long periods of time in environmental compartments such as soil, sediment, air and water, as well as in the adipose tissue of living beings in which they can carry out bioaccumulation and biomagnification processes (Ashraf 2017; Magulova and Priceputu 2016; UNEP 2020).

Generally, POPs include pesticide compounds for agricultural and residential use, compounds used in industrial chemical processes, while others are unintended by-products (UNEP 2020). Exposure to these substances has been associated with various effects on human health (Guo et al. 2019), such as endocrine disruption (Schecter 2012), decrease in birth weight (Cabrera-Rodríguez et al. 2019), neurological problems (Berghuis et al. 2015; Rocha-Amador et al. 2009) and an increased risk to other conditions such as cancer, diabetes, obesity, hypertension and cardiovascular diseases (Ennour-Idrissi et al. 2019; Ljunggren et al. 2014; Vafeiadi et al. 2015; Yang et al. 2017). Children are particularly susceptible to the effects of these types of environmental pollutants because they may be exposed through various routes, including specific routes such as breast milk. In addition, their state of development can lead to windows of vulnerability, so that children can be exposed at different stages of their growth, manifesting late effects (World Health Organization 2006).

Organochlorine pesticides (OCPs) correspond to a group of semi-volatile and highly persistent POPs, characterized by having carbon and chlorine atoms united in their structure. These compounds have been widely used in past decades, in the agricultural sector and as controls for disease-transmitting vectors in tropical countries (Ali et al. 2020; Jayaraj et al. 2016; Sparling 2016). Currently, the production and use of most OCPs is regulated under the Stockholm Convention agreements, whose objective since its launch in 2001 is to protect human health and the environment from POPs. Regarding OCPs, the regulatory instrument establishes the prohibition for their manufacture and use, with only dichlorodiphenyltrichloroethane (DDT) being part of the restricted use category for countries with prevalence of endemic vector-borne diseases (Magulova and Priceputu 2016; UNEP 2020).

OCPs can enter the environment in different ways, mainly by direct application, also through the discharge of waste contaminated with these substances into landfills, and through the discharge from the factories where they are synthesized (Jayaraj et al. 2016). Human exposure to these compounds can occur via ingestion, inhalation, or dermal absorption (Genuis et al. 2016; Jayaraj et al. 2016). Soil has been shown to be one of the most important exposure routes to POPs in general, as it serves as a reservoir from which these compounds can migrate to other environmental matrices and enter the food chain (Bidleman and Leone 2004; Cai et al. 2008). Therefore, soil can be considered as one of the most important sources of exposure for the human population (Herrera-Portugal et al. 2005).

As part of biomonitoring in various places in Mexico, there are studies that have evidenced the presence of OCPs in different environmental matrices, biota and in human population, in relation to scenarios that involve agricultural and industrial activities, unregulated solid waste deposits, and endemic malaria zones (Cantu-Soto et al. 2011; Díaz-Barriga Martínez et al. 2012; Domínguez-Cortinas et al. 2013; Espinosa-Reyes et al. 2012; Flores-Ramírez et al. 2016, 2017; González-Mille et al. 2010; Martínez-Salinas et al. 2011; Orta-García et al. 2016; Pérez-Maldonado et al. 2013, 2014, 2010; Perez-Vazquez et al. 2015; Sánchez-Osorio et al. 2017; Torres-Dosal et al. 2012; Trejo-Acevedo et al. 2009, 2012).

The city of Salamanca, located in the state of Guanajuato, in central Mexico, is characterized by its industrial and agricultural development. There is a particular case related to contamination by OCPs in the place: the facilities and surroundings of the former Tekchem Industrial Unit, in which organochlorine and organophosphate pesticides were manufactured, among other dangerous compounds. The company operated between 1943 and 2007, however, to date there is a problem of soil and groundwater contamination due to the inadequate management of processes and waste during most of the production stages (Albert and Jacott 2015; Beltrán Hernández et al. 2019). An environmental risk assessment study at the site showed that the soil is mostly contaminated by OCPs, representing approximately 70% of the identified compounds, with DDT and its metabolites being found in the highest concentrations (SEMARNAT 2018).

To date, the impact of the compounds present in the facilities of the former Tekchem Industrial Unit is still little known, in terms of their dispersion towards the surrounding areas, and the possible contamination of other environmental matrices, as well as the exposure that may occur in human population. In context with what has been previously described, the objective of this study is to quantify levels of OCPs in soil and in school-age children from the city of Salamanca, Mexico.

2. Materials And Methods

2.1 Study setting and population

A cross sectional observational study was performed in Salamanca city, Mexico, based on the history of industrial activity of the municipality, assessing environmental and biological samples in order to estimate exposure to OCPs. Salamanca city is in the central part of Guanajuato state, with an area of 774 km^2 and a population of 135,874 people in the municipal seat. The climate of the place is characterized by being semi-warm with rain in summer, with an average temperature of 19.3 ° C and a rainfall of 600 to 800 mm per year (Sistema Meteorologico Nacional, n.d.). For environmental monitoring, soil samples were taken covering the entire metropolitan area of the municipality, following the protocol established by the Official Mexican Standard NMX-AA-132-SCFI-2006 (SCFI, 2006). For biological monitoring, four elementary schools located in the metropolitan area were selected: “Eduardo Soto”, “Luis G. Araujo”, “Mártires de Cananea” and “Xidoo”, counting with a total participation of 88 children. Inclusion criteria were as follows: informed and voluntary consent signed by parents or guardians; apparently healthy children; residence in the city not less than one year; and 12-hour fasting to avoid variability in blood lipid levels. The parents or guardians responded to a carefully designed questionnaire for health, habits and exposure data concerning children, which was conducted by trained personnel; their address was also requested to obtain the georeferencing of children’s homes. It is important to mention that of the schools sampled, the one attended by each child is the closest to his or her home. The children were measured to obtain weight and height, and blood samples were taken. The body mass index (BMI) for age was calculated as an anthropometric indicator for children, and this parameter was categorized based on the z-score cut-offs established by the World Health Organization (WHO) Growth Reference Data for 5-19 years (WHO, n.d.). The study was approved by the Institutional Committee of Bioethics in Research of the University of Guanajuato.

2.2 Environmental sample collection

A detailed sampling was carried out according to the specifications of the Official Mexican Standard NMX-AA-132-SCFI-2006 (SCFI, 2006), to determine the volume of soil contaminated by OCPs. In this way, sampling areas of 600 m x 600 m were established, and the sampling points were selected with the support of Geographic Information Systems (GIS), thus recording the georeferencing of each one. The samples were taken in outdoor surface soils with a shovel, covering up to a depth of 5 cm and collecting a quantity of 1 kg of the material at each point. A quantity of 52 samples were obtained, which were stored in aluminum foil inside valve bags, at a temperature of -20 ° C until analysis.

2.3 Biological sample collection

Blood samples were taken from the antecubital vein in 8 mL vacuum tubes without anticoagulant, to obtain serum. The samples were centrifuged at 1200 x g for 10 minutes, and serum was transferred to Eppendorf tubes and stored at -80 ºC until analysis.

2.4 Extraction of OCPs in soil

The extraction of the analytes was carried out based on the extraction method Soxhlet (3540C) of the Environmental Protection Agency of the United States (EPA, 1996). 0.2 g of soil was weighed and placed in extraction thimbles (Whatman) inside the chamber. 130 mL of dichloromethane (J.T. Baker) was used as a solvent in a flat-bottomed round flask, to which 25 ppb of PCB 141-C13, DDT-C13 and HCH-C13 were added as surrogate standards. The system was kept at reflux for 10 hours, on the basis that every 40 minutes an extraction cycle is carried out. The obtained extract underwent two evaporation processes, first on a rotavapor at 30 ºC up to a volume of 3-4 mL, to subsequently clean with 2 mL of hexane, three times; and second using a nitrogen flow until obtaining an approximate volume of 2 mL. The analytes were solid phase extracted using florisil cartridges previously conditioned with a mixture of hexane / acetone 1:1 (Karal) and eluted with 6 mL of hexane (J. T. Baker). The eluate was recovered in a conical tube and then evaporated with a stream of nitrogen at 37 ° C until a volume of 100 µL was obtained, which was transferred to a 150 mL insert and the final volume was adjusted with hexane (J.T. Baker). The insert was placed in a vial and stored at -10°C for further analysis by gas chromatography.

2.5 Extraction of OCPs in blood

First, the lipids were extracted from each blood sample according to method described by Ryan et al., 1997, for which 2 mL of separated plasma as above were placed in a previously weighed round tube. Then 25 ppb of surrogate standards PCB 141-C13, DDT-C13 and HCH-C13 (CAMBRIDGE ISOTOPE) were added to the sample, and it was stored for 48 hours at -20 ° C. The mixture was thawed at room temperature and 0.5 mL of formic acid (J. T. Baker) and 3 mL of isopropyl alcohol (J. T. Baker) were added. A 1: 1 ethyl ether / hexane (J. T. Baker) solution was added to the contents of the tube and then centrifuged at 3000 rpm for 3 minutes. The upper phase was recovered, to which 2 mL of a 1% KCl (J. T. Baker) solution was added and centrifuged to recover the upper phase again. The entire process was repeated two more times and the three extracted phases were recovered in a conical glass tube previously weighed, to finally be brought to dryness under a stream of nitrogen at 37 ° C, until obtaining a constant weight. The lipid content in the sample was determined by gravimetry.

The extraction of OCPs was carried out based on (Sugawara et al., 2002.) and (García-Nieto et al., 2010). The lipid samples obtained as previously indicated were dissolved in 3 mL of hexane (J.T. Baker), then the solution was transferred to a tube round to which 2 mL of H_2SO_4 (J. T. Baker) were added. The mixture was incubated for 10 minutes at room temperature and centrifuged at 3000 rpm for 3 minutes, to later recover the upper phase in a conical tube, while the lower phase was extracted two more times with 3 mL of hexane (J.T. Baker). The three extracts corresponding to each sample were pooled in the conical tube and then concentrated to a volume of 2 mL under a nitrogen stream at 37 ° C. The analytes were extracted with florisil cartridges, exactly as described in paragraph 2.4.

2.6 Quantitative analysis of OCPs

The quantification of the analyzed compounds was carried out on a Perkin Elmer Clarus 500 gas chromatograph coupled to a Perkin Elmer Clarus 560S mass spectrometer (Waltham, MA, USA). A 30 m x 0.32 mm ID Elite-5 MS column with 0.25 µm film thickness was used. The oven temperatures were as follows: initial at 100 ° C (2 min), final at 310 ° C (ramps: 20 ° C / min to 200 ° C, 7 ° C / min to 270 ° C / min, and 15 ° C / min up to 310 ° C for 6 min), the injector temperature at 270 ° C with 30 mL / min splitless, the transfer line at 300 ° C and the mass detector at 225 ° C. Helium was used as carrier gas at a linear speed of 1.5 mL / min. Under these conditions the retention times of each compound were determined. A standard mixture (Sigma Aldrich) of 13 OCPs was used: α-, β- and γ-HCH, heptachlor, heptachlor epoxide, aldrin, dieldrin, endrin, 2,4'-DDD, 4,4'-DDD, 4,4'-DDE, 2,4'-DDT and 4,4'-DDT in octane starting from a concentration of 100 ppb to generate the calibration curve.

Blood OCPs concentrations were adjusted to lipid content, determined as described above.

Limit of detection (LOD) is defined as the arithmetic mean of a hexane blank, added with 25 ppb of surrogated standard, adding three times the standard deviation. If no chemical was found in the blanks, the LOD was defined as the Instrumental Detection Limit (IDL), which was estimated by injecting low concentrations of target analytes until a small peak was obtained with a signal-to-noise

ratio of ~ 3: 1. The values obtained were: 0.01ppb for the compounds α-, β- and γ-HCH, heptachlor, heptachlor epoxide, aldrin, dieldrin and endrin for the compounds 2,4'-DDD, 4,4'-DDD, 4, 4'-DDE, 2,4'-DDT and 4,4'-DDT was 0.4ppb.

The concentrations of the compounds 2,4’-DDT, 4,4’-DDT and 4,4’-DDE were used to calculate the DDT/DDE ratio, both in soil and blood samples (only in samples with values above the LOD) (Tavares et al., 1999).

2.7 Development of concentration distribution maps of the total OCPs

Concentration distribution maps of the total sum of OCPs both in soil and blood in the Salamanca metropolitan area were elaborated through the program QGIS 3.16.6 (Alkmaar, The Netherlands), using the georeferencing data of the soil sampling points, and the corresponding to the homes of the children who participated in the study. The distribution is shown in percentiles, so that each color represents the concentration quartile to which the sample belongs (green: quartile 1; light green: quartile 2; orange: quartile 3; red: quartile 4). The maps included the locations of the schools, and of some industrial sites of possible influence for the presence of the pollutants, such as the Tekchem property, the thermoelectric power plant of the Federal Electricity Commission (CFE) and the refinery Ing. Antonio M. Amor (RIAMA) of PEMEX company.

2.8 Statistics

A descriptive analysis of the data set for both soil and blood OCPs concentrations was performed, calculating mean, standard deviation, minimum, maximum, percentiles, frequencies and distribution. For analysis purpose, if the concentration value of a sample was less than LOD for any compound, then it was replaced by LOD/2 (Cohen & Ryan, 1989). OCPs concentration values did not show a normal or lognormal distribution (Kolmogorov-Smirnov test), so the results are described with the median and range. All analyzes were performed using GraphPad Prism 8.0.1 statistical package (San Diego, CA, USA).

3. Results

Table 1 shows the descriptive characteristics of the children participating in the study, in terms of their anthropometric data, as well as certain habits or risk activities. The mean age was 10 years, ranging from 6 to 15 years; 53% of children were female, while 47% were male. Regarding BMI for age, 60% of children had a normal or healthy value, while 24% were overweight, 15% obese and 1% underweight (WHO n.d.). In addition, an average of approximately 8 years of residence of children in the city of Salamanca was reported, ranging from 1 to 15 years. With respect to risk activities, 92% of parents or guardians mentioned the use of household pesticides (insecticides or rodenticides), and 22% smoke inside the house.

Table 1
General characteristics of participating children

Characteristic	
Age (years) [a]	10.0 ± 1.67 (6.00 - 15.0)
Female (%) [b]	53
Male (%) [b]	47
Height (cm) [a]	139 ± 10.8 (113 – 165)
Weight (kg) [a]	37.2 ± 11.4 (18.4 - 72.5)
BMI for age (kg/cm^2) [a]	18.8 ± 3.71 (12.0 - 28.1)
Underweight (%) [b c]	1
Normal (%) [b c]	60
Overweight (%) [b c]	24
Obesity (%) [b c]	15
Number of years living in the city [a]	7.73 ± 3.38 (1.00 - 15.0)
Use of pesticides at home (%) [b]	92
Someone smoking inside the home (%) [b]	22

[a] Mean ± standard deviation; maximum and minimum values are shown in parenthesis. [b] Relative frequencies as percentages. [c] Cut-offs according to the growth reference data for 5-19 years established by the WHO (z-scores) (WHO n.d.)

Table 2 shows the statistical distribution parameters of both the individual soil OCPs concentrations and their total sum, in addition to the sum of total DDT, and DDT/DDE ratio. All the measured OCPs were detected to a certain extent, highlighting 2,4'-DDD that was detected in almost all the samples (96.2%). It is followed by 4,4'-DDT and 4,4'-DDD with detection percentages close to 90 and 85%, respectively. 2,4'-DDT, 4,4'-DDE, heptachlor epoxide and aldrin were also detected in significant percentages, all above 50%. The compounds γ-HCH, heptachlor and endrin were detected in less of 50 % of the samples.

Table 2
OCPs concentrations in soil from Salamanca, Mexico

Compound	Mean	SD	Min	Percentiles				Max	% Detected
				25	50	75	90		
γ-HCH	1.79	4.65	<LOD	<LOD	<LOD	<LOD	8.15	20.7	23.1
Heptachlor	4.59	6.96	<LOD	<LOD	<LOD	10.2	17.1	24.2	34.6
Heptachlor epoxide	5.06	5.58	<LOD	<LOD	4.06	9.10	13.1	21.9	51.9
Aldrin	3.72	2.96	<LOD	<LOD	4.25	6.14	7.47	9.11	67.3
2,4'-DDT	13.4	35.3	<LOD	<LOD	7.32	10.5	23.1	241	63.5
4,4'-DDT	23.7	81.1	<LOD	9.99	11.3	13.4	21.3	593	88.5
4,4'-DDE	88.9	250	<LOD	<LOD	8.19	41.3	207	1474	63.5
2,4'-DDD	38.7	136	<LOD	7.06	10.7	20.6	44.5	968	96.2
4,4'-DDD	46.5	193	<LOD	5.36	9.19	17.2	76.6	1389	84.6
Endrin	4.13	12.5	<LOD	<LOD	<LOD	<LOD	21.0	55.6	11.5
Total OCPs	230	563	6.93	41.8	70.6	160	346	3276	—
Total DDT	211	561	6.93	27.1	49.6	144	346	3276	—
DDT/DDE ratio	2.01	4.39	0.09	0.30	1.04	1.60	2.31	23.1	—

Concentrations are shown in ng/g. SD: standard deviation; Min: minimum; Max: maximum. % detected: percentage of samples with concentrations above the limit of detection 0.01ppb for compounds α-, β- and γ-HCH, heptachlor, heptachlor epoxide, aldrin, dieldrin and endrin for compounds 2,4'-DDD, 4,4'-DDD, 4, 4'-DDE, 2,4'-DDT and 4,4'-DDT was 0.4ppb. <LOD: value below limit of detection.

For the total sum of OCPs in soil, a median concentration of 70.6 ng/g (6.93 - 3276) was obtained, while for the total sum of DDT it was 49.6 ng/g (6.93 - 3276). As for the individual OCPs, those that resulted in highest median levels were 4,4'-DDT (11.3 [<LOD – 593] ng/g) and 2,4'-DDD (10.7 [<LOD – 968] ng/g). 4,4'-DDD and 4,4'-DDE resulted with similar median levels (9.19 [<LOD – 1389] ng/g and 8.19 [<LOD – 1474] ng/g, respectively). 2,4'-DDT was found to have a median level of 7.32 ng/g (<LOD – 241). The lowest median concentrations corresponded to aldrin (4.25 [<LOD – 9.11] ng/g) and heptachlor epoxide (4.06 [<LOD – 21.9] ng/g). γ-HCH, heptachlor and endrin median concentrations resulted below the LOD. With respect to the DDT/DDE ratio in soil, a median value of 1.04 (0.09 - 23.1) was obtained.

On the other hand, Table 3 shows the statistical distribution of the concentrations of OCPs measured in children's blood and their total sum, as well as DDT total sum and DDT/DDE ratio. Like OCPs in soil, all the compounds measured in the children also showed positive detection levels. In this case, it is noteworthy that heptachlor was detected in 100 % of the samples. Regarding DDT and its metabolites, only 4,4'-DDE, 4,4'-DDD and 4,4'-DDT were detected in significant percentages (82, 60 and 58 %, respectively). Heptachlor epoxide was also detected at a significant level (57%). The compounds γ-HCH, aldrin, endrin, 2,4'-DDT and 2,4'-DDD were detected in less of 50 % of the samples.

Table 3
Blood OCPs concentrations in children from Salamanca, Mexico

Compound	Mean	SD	Min	Percentiles				Max	% Detected
				25	50	75	90		
γ-HCH	1.44	2.90	<LOD	<LOD	<LOD	1.45	5.92	14.3	29.5
Heptachlor	199	567	2.02	16.9	47.1	141	485	4975	100.0
Heptachlor epoxide	201	1029	<LOD	<LOD	13.7	92.5	307	9576	56.8
Aldrin	4.58	15.5	<LOD	<LOD	<LOD	1.13	11.0	90.9	25.0
Endrin	96.1	494	<LOD	<LOD	<LOD	27.0	90.1	3755	34.1
2,4'-DDT	97.8	391	<LOD	<LOD	<LOD	37.8	210	3111	38.6
4,4'-DDT	433	1257	<LOD	<LOD	20.2	188	1411	7577	58.0
4,4'-DDE	579	1686	<LOD	10.7	70.6	283	923	9719	81.8
2,4'-DDD	21.4	67.8	<LOD	<LOD	<LOD	12.3	47.5	438	28.7
4,4'-DDD	128	326	<LOD	<LOD	15.0	80.9	289	1841	60.2
Total OCPs	1761	3625	7.34	77.6	390	1282	5380	14895	---
Total DDT	1259	3064	<LOD	14.9	175	829	2474	14802	---
DDT/DDE ratio	1.98	2.01	0.05	0.924	1.72	2.19	3.81	11.3	---

Concentrations are shown in ng/g lipid. SD: standard deviation; Min: minimum; Max: maximum. % detected: percentage of samples with concentrations above the limit of detection 0.01ppb for compounds α-, β- and γ-HCH, heptachlor, heptachlor epoxide, aldrin, dieldrin and endrin for compounds 2,4'-DDD, 4,4'-DDD, 4, 4'-DDE, 2,4'-DDT and 4,4'-DDT was 0.4ppb. <LOD: value below the limit of detection.

Regarding the total sum of OCPs in children's blood, the median concentration was 390 ng/g lipid (7.34 - 14895), while for the total sum of DDT the value was 175 ng/g lipid (<LOD – 14802). Of the individual compounds analyzed, the one with the highest median concentration was 4,4'-DDE (70.6 [<LOD – 9719] ng/g lipid), followed by heptachlor (47.1 [2.02 – 4975] ng/g lipid), 4,4'-DDT (20.2 [<LOD – 7577] ng/g lipid), 4,4'-DDD (15.0 [<LOD – 1841] ng/g lipid) and heptachlor epoxide (13.7 [<LOD – 9576] ng/g lipid). γ-HCH, aldrin, endrin, 2,4'-DDT and 2,4'-DDD had median concentrations below the LOD. For the DDT/DDE ratio in children's blood, the median was 1.72 (0.05 - 11.3).

Figure 1 shows the spatial distribution of total OCPs concentrations in soil, grouped by quartiles. It can be observed that the highest concentrations tended to be present around the site of the former industrial unit Tekchem, towards the east and southeast of the city of Salamanca, while lower concentrations predominated in the north and west. On the other hand, the spatial distribution of total OCPs concentrations in children is depicted in the map in Figure 2. In this case, a more heterogeneous distribution of concentrations can be seen, resulting in higher levels in children living in the north and west of the city than in children living in the area around Tekchem.

4. Discussion

The city of Salamanca, Mexico is well known for its history of environmental pollution, as it is a center of industrial activity at the national level. Such activities, when not carried out based on regulatory standards, or when this does not exist, unfortunately leads to problems associated with the introduction of dangerous substances into the environment, with the risks involved. One of the most worrying cases, which so far has no definitive solution, is the presence of environmental liabilities within the vicinity of the former Tekchem Industrial Unit, which, when in operation, manufactured a wide range of OCPs and other synthetic chemical compounds. The environmental liabilities generated were the result of an accumulation of several years due to inconveniences in

terms of waste disposal. Previous studies have characterized the polluting substances in the site, mainly reporting the presence of OCPs, which constitute 70% of the polluting mass (Beltrán Hernández et al. 2019; SEMARNAT 2018).

In this study, levels of γ-HCH, heptachlor, heptachlor epoxide, aldrin, endrin, as well as DDT and its metabolites were detected and quantified in soil and in school-age children in the city of Salamanca. Said compounds correspond to those that have been identified in the environmental liabilities of Tekchem (SEMARNAT 2018). DDT and its metabolites were the compounds that showed the highest levels of concentration in soil, followed by aldrin and heptachlor epoxide (Table 2). Comparing the total DDT concentration obtained in our study with the Canadian Environmental Quality Guideline, which establishes a maximum value of 700 ng/g of total DDT for residential soil (Canadian Council of Ministers of the Environment 1999), we find that the level did not exceed this value. The California Human Health Screening Levels guide, on the other hand, establishes a maximum value of 1900 ng/g for 4,4'-DDT, 2000 ng for 4,4'-DDE, and 2300 ng/g for 4,4'-DDD (California Department of Toxic Substances Control 2020), which were not exceeded in the soil samples analyzed. In the case of aldrin, the same guide establishes a maximum value of 3300 ng/g for residential soil, so that the levels obtained in this study did not exceed this limit.

In our country, monitoring studies have been carried out on OCPs in soil, mainly in agricultural areas and in those with a high prevalence of vector-borne diseases such as malaria. The total DDT concentration obtained in this study was higher than the levels reported in urban soil of San Luis Potosí (6.10 ng/g) (Perez-Vazquez et al. 2015), and in the Mexicali Valley (20 ng/g) and the Yaqui Valley (3.6 ng/g) in northwestern Mexico (Sánchez-Osorio et al. 2017). In this last work mentioned, lower heptachlor epoxide levels (Mexicali Valley: 0.013 ng/g; Yaqui Valley: 0.022 ng/g) (Sánchez-Osorio et al. 2017) were also reported compared to ours. Another study performed in soil from communities from Tabasco reported lower levels of total DDT compared to ours (median concentrations ranged from 4 to 38 ng/g), except for the community Cardenas whose level was higher (91 ng/g) (Torres-Dosal et al. 2012). In another monitoring carried out in urban soils of Chihuahua, the range of total DDT values (2 – 141.7 ng/g) was lower than that of our study (Díaz-Barriga Martínez et al. 2012). On the other hand, Orta-García et al. (2016) found higher median levels of total DDT (79.5 ng/g) compared to the present study, in urban soil from Monterrey. Likewise, the levels within the resulting range for total DDT in soil from various communities in Chiapas (2 – 26,980 ng/g) exceeded the maximum value obtained for total DDT in our study (Martínez-Salinas et al. 2011).

Cantu-Soto et al. (2011) reported ranges with very high levels of OCPs with respect to those obtained in the present work, in residential soils of the Yaqui Valley (4,4'-DDT: <LOD - 679,700 ng/g; 4,4'-DDE: <LOD - 621,300 ng/g; 4,4'-DDD: <LOD - 197,300 ng/g; aldrin: <LOD - 25,800 ng/g) and the Mayo Valley (4,4'-DDT: <LOD - 301,200 ng/g; 4,4'-DDE: <LOD - 226,300 ng/g; 4,4'-DDD: <LOD - 39,300 ng/g; aldrin: <LOD - 74,000 ng/g), in southern Sonora, Mexico.

Comparing with soil monitoring for OCPs in other countries, we found that the ranges obtained in this study had higher levels than the resulting maximum concentrations in urban soils in Pristina, Serbia (DDT: 2.41 - 18.8 ng/g; DDE: 1.19 - 30.5 ng/g; DDD: 0.97 - 8.38 ng/g; aldrin: 1.94 - 3.28 ng/g) (Gulan et al. 2017). Likewise, the maximum total DDT value from our study was higher than that reported in agricultural soils from Wuhan, China (<LOD - 1198 ng/g), while on the other hand aldrin range resulted in higher values than our maximum value obtained (<LOD - 21.56 ng/g) (Zhou et al. 2013). Another study performed in agricultural soil from Shanghai, China, reported maximum values for total DDT and heptachlor epoxide (0.44 – 247.45 ng/g and <LOD – 4.78 ng/g, respectively) lower than those from our study, while for aldrin was obtained a similar range (<LOD – 6.62 ng/g) (Jiang et al. 2009).

With respect to the levels of OCPs in the infant population, the compounds that resulted in the highest concentrations were 4,4'-DDT and its metabolites, as well as heptachlor and heptachlor epoxide (Table 3). By comparing our results with the median concentrations obtained in the German Environmental Survey for Children and Adolescents (GerEs) 2014-2017 for 4,4'-DDT (1.94 ng/g lipid), 4,4'-DDE (26.7 ng/g lipid) and 4,4'-DDD (1.88 ng/g lipid) (Bandow et al. 2020), we can see that our levels exceed the previous ones by 10, 2.6 and 8 times, respectively. On the other hand, the Fourth National Report on Human Exposure to Environmental Chemicals (population aged 12 to 19) reports heptachlor epoxide and 4,4'-DDT as undetectable, while for 4,4'-DDE the median concentration was 93.6 ng/g lipid (CDC 2009), slightly exceeding our found median value.

As well as in soil, in our country monitoring has also been carried out in children exposed to OCPs. Flores-Ramírez et al. (2017) reported a median value of 4,4'-DDE slightly lower than ours (58.77 ng/g lipid), in children living near contaminated sites in Mexico. Another study in children from pollution hot spots in Mexico showed median levels of DDE (387 ng/g lipid) and DDT (189 ng/g lipid) higher than ours, while heptachlor epoxide was not detected (Trejo-Acevedo et al. 2009). Studies conducted in children in

malaria-endemic areas of the country show levels of DDT and its metabolites that far exceed those in this study. In Chiapas and Oaxaca, in southeastern Mexico, median levels of total DDT ranged from 11,353.8 ng/g lipid to 34,189 ng/g lipid between three assessed communities (Pérez-Maldonado et al. 2013). In Quintana Roo, in southern Mexico, median levels of DDT of 5,646 ng/g lipid and DDE of 39,934 ng/g lipid were found, while heptachlor epoxide was not detected (Trejo-Acevedo et al. 2012). In children from Chihuahua, ranges with higher levels than those in our study were reported, both for DDT (711 - 68, 669 ng/g lipid) and for DDE (271 - 170,596 ng/g lipid) (Díaz-Barriga Martínez et al. 2012).

Regarding monitoring in other countries, OCPs levels in children from our study were higher than those found in children in South Korea (heptachlor: <LOD; heptachlor epoxide: <LOD; 4,4'-DDT: 3.2 ng/g lipid; 4,4'-DDE: 44.7 ng/g lipid; 4,4'-DDD: <LOD) (Park et al. 2016). The ranges we obtained in this study for 4,4'-DDT and 4,4'-DDE include values that exceed the maximum concentrations reported in children from Canada (4,4'-DDT: 2.3 - 62.7 ng/g lipid; 4,4'-DDE: 5.6 – 1864.4 ng/g lipid) (Turgeon O'Brien et al. 2012). On the other hand, Windham et al. (2010) reported a median 4,4'-DDE value of 101.5 ng/g lipid in US girls, which is slightly higher than that obtained in our study.

The DDT/DDE ratio for soil resulted in a median value of 1.04, while in children it was 1.72. According to Tavares et al. (1999), a value of this ratio ≥ 1 indicates the recent incorporation of DDT into the environment, which is usually due to recent applications. The half-life time for DDT in terms of its persistence in the environment is 2 to 15 years, depending on the factors that are present in the site influencing its degradation (ATSDR 2019; Jayaraj et al. 2016). According to the previous studies performed both in soil and children, the concentrations of OCPs obtained in our study were lower, in general, than those reported in endemic areas of malaria, where large amounts of these compounds were applied in the past, mainly DDT (Díaz-Barriga et al. 2003). However, in the case of OCPs in blood, they are higher compared with baseline levels from general population data, such as those from the GerEs (Bandow et al. 2020). In the case of Tekchem, DDT was discontinued in 1997, however, as mentioned above, to date residues are present within the facilities, which are likely dispersing to the soils of the urban area of Salamanca, and this would explain the value obtained for DDT/DDE ratios in both soil and children, indicating both present and past exposure to DDT (Tables 2 and 3).

In our study, heptachlor was detected in 100% of children, however, in soil it was not detected significantly (less than 50% of the samples). It is important to mention that very few studies have reported levels of heptachlor and heptachlor epoxide in the human population, and in most cases, these compounds are not detected. Morgan et al. (2014) quantified heptachlor in various environmental media such as soil, dust, outdoor air and indoor air, finding the highest levels in air, mainly in indoor environments. The same study determined that the predominant route of exposure for this compound in preschool children was inhalation of air both outdoors and indoors (98%) (Morgan et al. 2014). This could explain our findings, in terms that in the case of heptachlor the soil is not the main route of exposure.

About the spatial distribution of the total sum of OCPs quantified in soil (Figure 1), it is noted that the highest concentrations were determined in the vicinity of Tekchem, so in this case there is a well identified source for the emission of these substances into the environment, and thus for human exposure. However, it is important to consider the possible influence of other OCPs sources that may be contributing to the concentrations of OCPs found in Salamanca soil. On the other hand, this type of compounds have the characteristic that they can be transported by the wind and travel great distances, being later in places distant to their origin (Heidelore Fiedler 2002; Sparling 2016). In the case of the total sum of OCPs in blood, the spatial distribution is interesting (Figure 2), since the highest concentrations were mainly identified in the northern area of Salamanca, however, there are also high concentration points in the vicinity of Tekchem. This variability in distribution could be explained by the different routes of exposure through which OCPs can be incorporated into the infant population. Although outdoor soil is one of the most important routes of exposure to OCPs (Herrera-Portugal et al. 2005), other routes such as food, breast milk and indoor soil and dust can also contribute significantly, which were not considered in this study. For example, it has been established that high concentrations of OCPs in indoor spaces, and longer residence times, can increase exposure to these pollutants up to 1000 times compared to outdoor exposure (Hwang et al. 2008). Another important point to consider in our study is the mobility of children within the city, which could also explain the variability in the spatial distribution of OCPs. Finally, as already mentioned, although the compounds studied are subject to either prohibition or restriction regulations (Stockholm Convention), unfortunately to date they are still dispersed globally and ubiquitously, regardless of their origin (Sparling 2016).

We cannot know specific risks to the health of children with the results obtained in our study, because cut-off levels have not been established for the compounds studied. However, various health effects associated with exposure to OCPs have already been

reported in infant populations (Segal and Giudice 2019; Vrijheid et al. 2016).

Our work has several limitations, such as sample size, and the fact that other exposure routes to quantify compounds were not considered. In addition, due to the cross-sectional nature of the study, there may be biases in terms of spatio-temporal variability of the concentrations of the compounds analyzed, both in soil and in children.

5. Conclusion

The results of the present exploratory study demonstrated the presence of OCPs both in the soil and in school-age children in the city of Salamanca, Mexico. The spatial distribution showed that, in the case of soil, the highest concentrations of OCPs could be related to the presence of environmental liabilities in the Former Tekchem Industrial Unit. In the case of children, the fact that the highest concentrations were identified at different points in the city could suggest the influence of other routes of exposure -besides soil-, and the mobility of children within the city inherent in their activities.

Despite the limitations, this study provides relevant information regarding the presence of OCPs in Salamanca, Mexico, while providing the basis for future research in which the problem can be addressed from a broader perspective. This includes the study of other routes of exposure, as well as the presence of compounds in other environmental media that could serve as potential additional sources of OCPs to the population of the city, mainly to children, who are especially vulnerable towards exposure to environmental pollutants. It also reiterates the importance of continuing efforts to generate effective and precautionary measures with respect to the case of environmental liability Tekchem.

Declarations

6.1 Funding

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6.2 Conflicts of interest

The authors declare not competing interests

6.3 Availability of data and material

The creation of tables and databases was carried out which are available upon request for anyone who requests it.

6.4 Authors' contributions

Israel Castro-Ramirez: His participation was in environmental sampling, data collection in the laboratory, preparation of tables of results and writing

Diana Olivia Rocha-Amador: The researcher participated in the biological sampling, participation management, communication and dissemination of results, also carried out the preliminary review of manuscript.

Tania Ruiz-Vera: The researcher participated in the statistical analysis of data and writing.

Jorge Alejandro Alegría-Torres: The researcher participated in the review and quality of biological monitoring results.

Gustavo Cruz-Jiménez: The researcher participated in the review and quality of the environmental monitoring results.

Israel Enciso-Donis: His participation was in biological sampling, obtaining laboratory data.

Rogelio Costilla-Salazar: The researcher participated in the management of financial resources, review of laboratory results, review of manuscript

6.5 Ethics approval

The document is in attachment to manuscript 1

6.6 Consent for publication

The document is in attachment to manuscript 2

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Figures

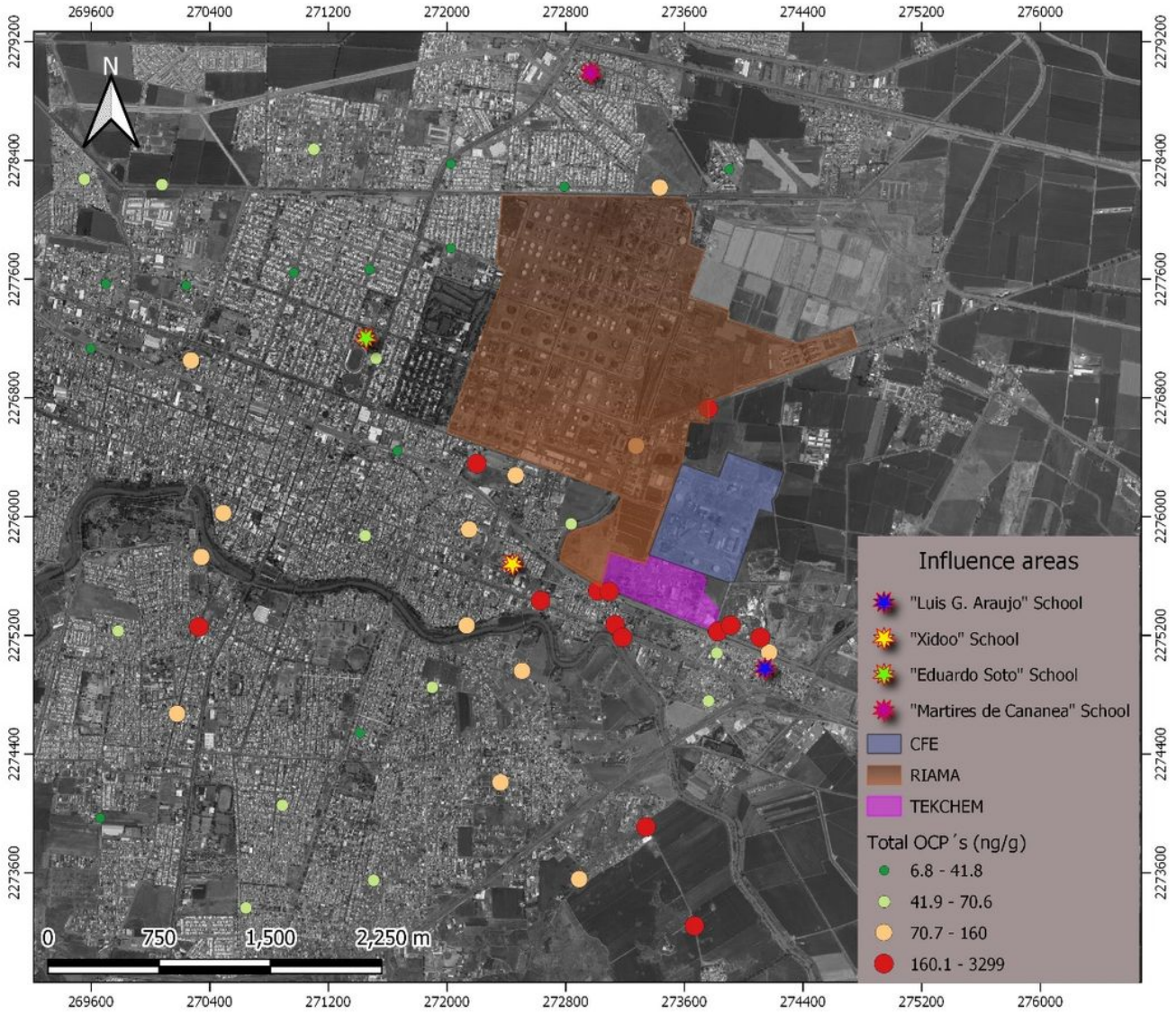

Figure 1

Spatial distribution of total OCPs concentrations in soil. The points correspond to the georeferencing of the sample. Each color represents the concentration quartile to which the sample belongs (green: quartile 1 [6.93 – 41.8 ng/g]; light green: quartile 2 [41.9 – 70.6 ng/g]; orange: quartile 3 [70.7 - 160 ng/g]; red: quartile 4 [160.1 - 3299 ng/g]).

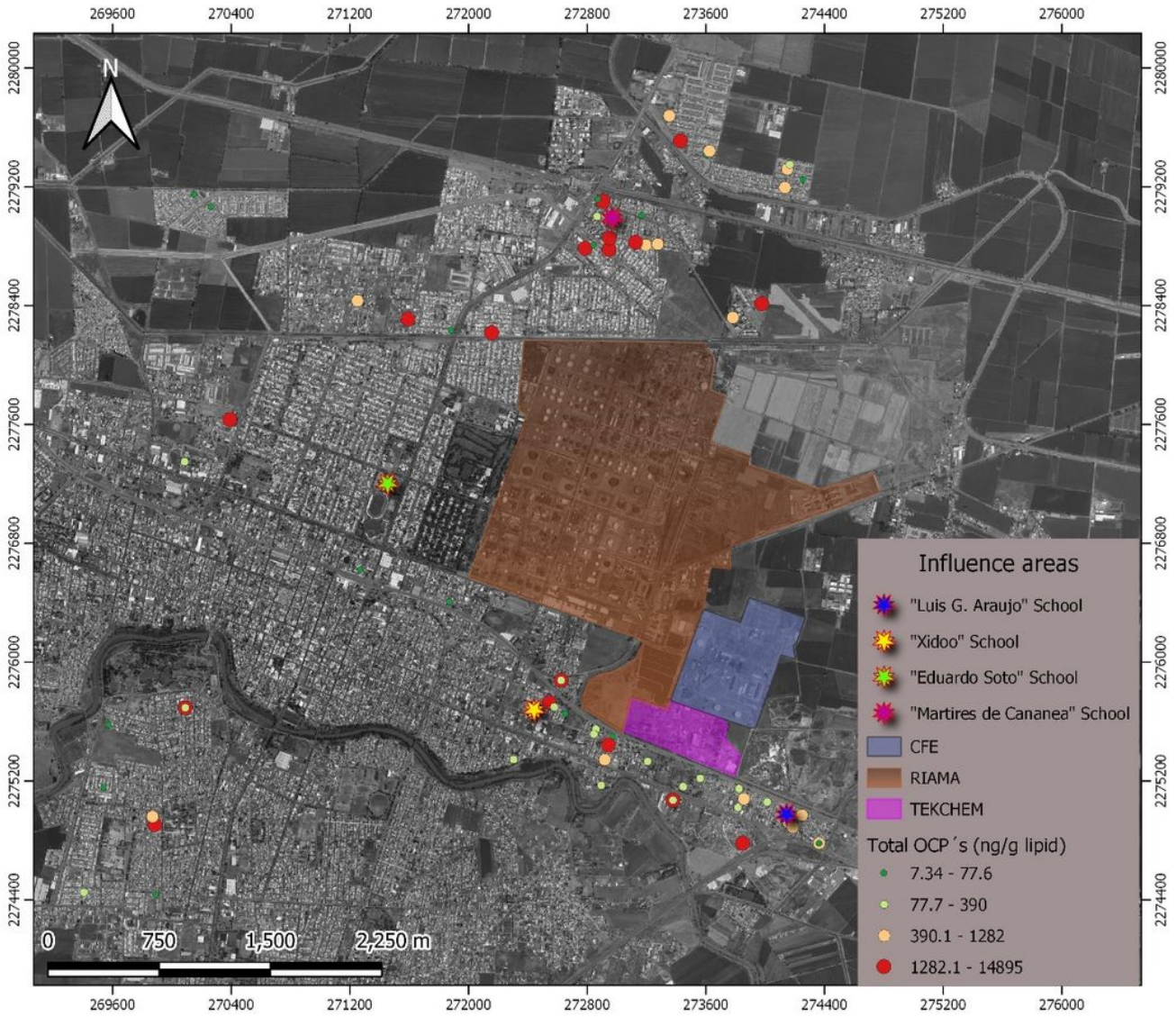

Figure 2

Spatial distribution of total OCPs concentrations in children's blood. The points correspond to the georeferencing of each participant's home. Each color represents the concentration quartile to which the sample belongs (green: quartile 1 [7.34 – 77.6 ng/g lipid]; light green: quartile 2 [77.7 - 390 ng/g lipid]; orange: quartile 3 [390.1 - 1282 ng/g lipid]; red: quartile 4 [1282.1 - 14895 ng/g lipid]).