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Residues of Organochlorine Pesticides in Soils from the Southern Sonora, Mexico

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Abstract Although, the Yaqui and Mayo valleys are the most important agricultural areas in Sonora, there is only limited data of the pesticides residue in soils in these valleys. This study measured the organochlorine pesticides (OCPs) in 234 soil samples (residential and agricultural) from 24 communities. The global results (mean, range) indicated that benzene hexachloride (19.2, ND-938.5 μg g^{-1}), endrin (6.6, ND-377.3 μg g^{-1}) and DDTs (36.45, ND-679.7 μg g^{-1}) were the dominant contaminants. Soil is one of the most important routes of exposure to OCPs in the population of southern Sonora and this study can be used to establish background levels of OCPs.

Keywords Organochlorine pesticides · Soil · Sonora

Soils are natural sinks for lipophilic organic compounds which adsorb to soil organic carbon and remain relatively immobile. DDT and the rest of persistent organochlorine pesticides OCPs) are found in soil samples from all regions of the globe and distributed throughout the environment (Vassilev and Kambourova 2006). Agriculture is the main activity carried out in the Yaqui and Mayo valleys of southern Sonora, Mexico where wheat, corn, vegetables, and cotton are the major crops (Rodriguez-Valle 2009). The south of Sonora was the birthplace of "Green Revolution" in the 1960s, focusing on increase production using hybrid varieties of maize and wheat. The utilization of pesticides added to the profits from the "Green Revolution", but created a dependency on these pesticides in modern agriculture of Latin America (Bejarano Gonzales 2002). By 2009, Sonora had 567,796 ha of agricultural land producing 3,401,038 tons mainly of wheat, potatoes, sorghum, watermelon, oatmeal and zucchini. This constituted 2.77% of the national production of Mexico (SAGARPA 2011) and is one of the pillars of the Sonoran economy.

In the past OCPs were liberally applied in this region resulting in the adsorption and absorption of toxic active ingredients into different matrixes such as soil and water reservoirs. Once pesticides enter the soil compartment, they can either degrade rapidly (e.g., within 15–30 days for some pesticides) or accumulate and persist for long periods of time. Depending on their half-life and organic carbon–water partition coefficient (Koc), OCPs can be potentially leached into groundwater and might alter the quality of water intended for human consumption. In addition, pesticides can be accumulated in fruits and vegetables as another route of exposure to humans. Pesticides residues in soil are another possible route of exposure for the population, especially in children because of their habits of playing on soil. Thus, the aim of the present work was to determine nine OCPs (BHC, lindane, aldrin, endrin, β-endosulfan, methoxychlor, p, p′-DDE, p, p′-DDD, p, p′-DDT) in soils from the Yaqui and Mayo valleys of southern Sonora, Mexico. Because this is the first study that focused on OCPs in soils in this region of the country the results of this research can be considered to establish background levels of OCPs in this matrix.

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Materials and Methods

The Yaqui and Mayo valleys are located geographically between the Gulf of California and the Sierra Madre Occidental; the availability of water for irrigation is from Yaqui and Mayo rivers. The average precipitation is 377.1 mm ± 127.4 mm for the Yaqui Valley and 272.1 mm ± 117.3 mm for the Mayo valley (Cruz-Medina 2006). Both the Yaqui and Mayo valley regions have modern systems of irrigation with 255,000 ha for the Yaqui valley and 116,000 ha for the Mayo valley in agricultural use (Villa-Ibarra et al. 2006; Cruz-Medina 2006).

To investigate OCPs incidence 183 residential soil samples and 51 agricultural soil samples were collected during 2007 from 24 localities in both valleys (15 in the Yaqui valley and 9 in the Mayo valley) (Fig. 1). The sampling sites in each community were laid out using the Google Earth 2007 program and then physically located at each locality using a Global Positioning System equipment (GARMIN Etrex model). The sampling was done according to Mexican Norm NMX-AA-132-SCFI-2006; each soil samples was obtained between 0 and 10 cm depth. All soil samples were collected using a hand auger, placed in paper bags, and stored at −20°C until analysis. The extraction of OCPs residues in soil was performed by matrix solid-phase dispersion (MSPD), according to Valenzuela-Quintanar et al. (2006). Briefly, the aluminum oxide was inactivated at 900°C for 12 h and then adjusted to 9% moisture (Mexican Official Norm NOM-021-ZOO-1995). Soil samples (0.5 g) were place in a mortar and ground with 0.6 g of aluminum oxide for the dispersion. For the purification of the sample, a 5 mL glass syringe was packed at the bottom with glass fiber and 2.6 g of aluminum oxide. The dispersed soil sample was added to the column and the OCPs in the sample were eluted

Fig. 1 Sampling locations of residential and agricultural soils in the Yaqui and Mayo valleys

with approximately 40 mL of hexane. The eluate was collected in a 50 mL conical glass tube. The eluate was evaporated to dryness with dry air using an N-EVAP (Organomation associates, Model 11155RT). The concentrate was reconstituted with 100 μL of hexane. All OCPs analyses included a blank sample or negative control (OCP-free soil), a sample added or positive control (soil fortified with 100 μL of a mixture of organochlorine pesticides known concentration) and a reagent blank. The samples were analyzed by GC analysis using an Agilent 7890A system equipped with electron microcapture detector (μCED) and 7683B Series Injector autosampler (Agilent Technologies) and with a DB-5 capillary column (30 m × 0.250 mm × 0.25 μm). Helium was used as the carrier gas at 2.3 mL min^{-1} under constant-flow mode. Helium was filtered with moisture, hydrocarbon and oxygen filters before entering the GC system. The oven temperature program was initial 110°C (1 min), final 280°C (2 min) (rate: 15°C/min up to 280°C). Injector temperature was 270°C operated in Splitless injection of a 1 μL.

Results and Discussion

A recovery study performed on 10 spiked replicates of the blank soil samples [2.0–20 ppb (μg/L)] showed an 81%–114% recovery with a coefficient of variation below 18%. The calibration curve for each pesticide was done from 0 to 30 ppb, getting regression coefficients (R^2) higher than 0.99. The detection limit for all compounds was between 0.2 and 0.5 μg g^{-1}.

BHC, lindane, aldrin, endrin, *β*-endosulfan, metoxichlor and DDTs (pp′-DDE, pp′-DDD and pp′-DDT) were detected in the soil samples (residential, n = 183 and agricultural, n = 51) collected at 24 localities in southern Sonora (Tables 1, 2). 75.21% of the samples (n = 176) were found to be contaminated with OCPs compounds. In general the concentrations of OCPs (sum of the 9 pesticides studied) found in soil ranged from non detected to 938.5 μg g^{-1}. All the OCPs were detected in the residential samples, but lindane only was detected in the residential soil from the Mayo valley (Table 2), while, as expected, all of the OCPs were found in the agricultural samples. For agricultural soil endrin and endosulfan were present in lower concentrations. BHC and DDTs were found to be the dominant contaminants. DDTs were predominant in both the residential (mean 46.8 μg g^{-1}, Table 2) and agricultural samples (mean 30.7 μg g^{-1}, Table 1). Contamination by OCPs of residential land resulted from poor agricultural practices (spraying of pesticides) as well as the change in land use (from agricultural to residential) which has become a common practice.

Lindane is still in use for the Ministry of Health in order to control lice. Endosulfan is the only organochlorine pesticide allowed in Mexico according to the Federal Commission for Protection against Health Risks (COFEPRIS) in crops. For endosulfan the highest value found was 124.0 μg g^{-1} (Table 1). However, DDTs contamination was 5.5 times higher with 679.7 μg g^{-1} despite its use being banned in the Mexico in 1999, after being heavily used for decades in agriculture and for the malaria control program (Yañez et al. 2004). This demonstrates the persistence of the DDTs in environmental matrices and therefore the potential risk to the health of populations living in this region either through direct contact with the ground or contamination of groundwater, which is the main

Table 1 Concentrations (μg g^{-1} dw) of OCPs in residential and agricultural soils from 15 localities in the Yaqui valley, Sonora

	Residential soil (n = 123)				Agricultural soil (n = 21)			
	Mean	SD	Minimum	Maximum	Mean	SD	Minimum	Maximum
BHC	10.5	37.2	ND	292.4	17.9	35.5	ND	143.1
Lindane	ND	ND	ND	ND	0.1	0.5	ND	2.1
Aldrin	0.5	3.3	ND	25.8	1.6	4.7	ND	15.9
Endrin	9.3	43.2	ND	377.3	1.5	7.1	ND	32.5
Endosulfan	0.6	4.2	ND	43.3	6.7	27.1	ND	124.0
Metoxichlor	0.4	2.5	ND	19.7	4.0	15.8	ND	71.7
p, p′-DDE	21.5	75.3	ND	621.3	11.2	18.0	ND	61.6
p, p′-DDD	4.9	22.4	ND	197.3	1.6	3.8	ND	13.3
p, p′-DDT	17.8	74.3	ND	679.7	17.9	36.4	ND	110.0
∑DDT	44.2				30.7			
Ratio 1	1.48				0.72			

Mean, SD, minimum and maximum were calculated assuming non detected (ND) measurements were equal to zero for statistical purpose

∑DDT = pp′-DDE + pp′-DDD + pp′-DDT

Ratio 1 = (p, p′-DDE + p, p′-DDD)/p, p′-DDT

Table 2 Concentrations (μg g^{-1} dw) of OCPs in residential and agricultural soils from 15 localities in the Mayo valley, Sonora

	Residential soil (n = 60)				Agricultural soil (n = 30)			
	Mean	SD	Minimum	Maximum	Mean	SD	Minimum	Maximum
BHC	37.5	143.1	ND	938.5	10.9	31.2	ND	127.9
Lindane	0.3	1.8	ND	13.9	0.1	0.6	ND	3.0
Aldrin	3.7	14.0	ND	74.0	3.6	9.4	ND	41.0
Endrin	8.9	28.3	ND	161.4	ND	ND	ND	ND
Endosulfan	0.9	5.0	ND	35.1	ND	ND	ND	ND
Metoxichlor	0.3	2.6	ND	20.0	0.5	2.9	ND	15.9
p, p′-DDE	21.6	43.2	ND	226.3	7.5	10.4	ND	42.2
p, p′-DDD	2.0	7.8	ND	39.3	1.9	5.7	ND	23.2
p, p′-DDT	23.3	57.3	ND	301.2	14.7	28.6	ND	120.4
∑DDT	46.8				24.1			
Ratio 1	1.01				0.64			

Mean, SD, minimum and maximum were calculated assuming non detected (ND) measurements were equal to zero for statistical purpose

∑DDT = pp′-DDE + pp′-DDD + pp′-DDT

Ratio 1 = (p, p′-DDE + p, p′-DDD)/p, p′-DDT

source of drinking water in these towns. The ratio of (p, p′-DDE + p, p′-DDD)/p, p′-DDT was used in this study as an indicator of residence time of p, p′-DDT in the environment. A value >1.0 indicates that the application was done in the past and a value <1.0 indicates a relatively recent application (Cheng et al. 2008). From residential soil samples a ratio of 1.25 was obtained indicating the DDTs residues are from past applications, but for the agricultural soils samples the ratio was 0.68 suggesting recent applications of this banned pesticide.

Similar incidence of contamination of soil with OCPs are seen around the world, Kumari et al. (2008) reported in soils from Hisar, Haryana, India residues of HCH varied from 0.002 to 0.051 μg g^{-1}, DDT from 0.001 to 0.066 μg g^{-1} and endosulfan from 0.002 to 0.039 μg g^{-1}. γ-HCH among HCH isomers, p, p′-DDE among DDT analogues and β-endosulfan among the endosulfan isomers were found to be the dominant contaminants, being consistent with that founded in our study. In the northern part of India Singh et al. (2007) demonstrated in both the soil and surface water samples that β- and δ-isomers of HCH were detected most frequently, whereas, methoxychlor was the least detected pesticide in the soil samples. However, methoxychlor was not detected in any of the surface water samples. In China studies related have been conducted; Hu et al. (2009) reported that high concentrations of DDTs were detected in soils around the two water reservoirs, which accounted for about 90% of the total OCP concentrations; in their study the mean concentration of total DDT was 0.00664 μg g^{-1}, and ranged from ND to 0.117 μg g^{-1}. However, our results are according with the earlier results. OCPs levels detected in our region were higher than in other regions of the world. Additionally our evidence suggesting recent applications of the banned pesticide, DDT, in agricultural soils. Due to the proximity of communities we studied to the agricultural field, soil can be a major exposure route of the people in these communities to the organochlorine pesticides.

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