Organochlorine pesticides in agricultural soils of the main agricultural valleys of Baja California, Mexico

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Introduction

Organochlorine pesticides (OCPs) was extensively used in Mexico since the 1950s, mainly for pest control, agricultural activities, as well as vector control for dengue and malaria [1]. Between 1969 and 1979, in Mexico were used approximately 9000 tons/yr of OCPs of which 7800 tons/yr was produced locally. During this period, the most widely OCPs used were DDT, toxaphene, lindane (g-HCH), and endrin [1,2]. Li and Macdonald ranked Mexico in sixth place in the world for DDT usage in agriculture and public health programs [3]. Baja California (B.C.) is one the most important agricultural areas in northwest Mexico with great economic dynamism among the primary economic activities as fishing, agriculture and mining. The Mexicali Valley and the Coastal Zone are their two large areas of primary production. Within the agricultural activities, the production of onions, tomato, wheat, cotton and alfalfa for plantings, grapes for wine, as well as strawberries, and scallions, are the most important for its high marketing value. Large amounts of pesticides have been used historically in the agricultural areas to enhance productivity [4,5]. OCPs, organophosphates, pyrethroids, and carbamates were the most used insecticides. However, most of the studies on OCPs in Mexico has been made in agricultural soils of southeastern Mexico [6,7], and the central region of Mexico [8]. Recently Sanchez-Osorio et al., reported levels of OCPs in soils and sediments from agricultural areas in the northwest of the country [9].

The aim goal of this work is to make a diagnosis of the OCPs levels in the main five agricultural areas of B.C. and determine how they are compared to the Valley of the Mexicali area and other agricultural valleys in southeastern Mexico. In B.C., as in other parts of the country, agricultural areas are close to settlements and unfortunately the agricultural workers live in precarious conditions and carry out the activity under minimum security conditions. So it is important to determine the exposure risk in the population to these OCPs. We hope that the San Quintin Valley (VSQ) and Maneadero (VM) have the higher OCPs concentration values, due to its longer agricultural tradition and a greater production.

Materials and methods

Soil samples (n = 6 to 8) for five agricultural areas were collected during September 2013 and March 2014. All valleys are located in the Coastal Zone in the northwest of the state of Baja California, Mexico (Fig. 1). Soil samples were a composite of 3 individual soil samples collected using stainless-steel scoops at the upper 0-10 cm depth. All the samples were refrigerated until transport to the laboratory where they were frozen until their analysis. Soil samples were analyzed by accelerated solvent extraction, using n-hexane at a 100 °C, in 2 static cycles of 5 min, and a rinse volume of 60%. Quality controls considered procedure blanks (quartz sand), fortified blanks, and SRM 1944 for organic compounds in sediment (NIST, Gaithersburg, MD, U.S.A.), which were analyzed each batch of 9 samples. Detection limits ranged from 0.03 to 0.37 ng/g d.w. for individual OCPs. Surrogates recoveries were 89 ± 14% for TCmX, and 91 ± 13% for PCB-209. Results for OC pesticides were not corrected for the surrogate recoveries or blanks.

Target compounds were HCH isomers (a-HCH, b-HCH, g-HCH, d-HCH), DDT and its metabolites (o,p- and p,p-isomers of DDE, DDD and DDT), and the chlordane-related compounds cis-chlordane (CC), trans-chlordane (TC), heptachlor, heptachlor epoxide, trans-nonachlor, cis-nonachlor, and metoxychlor, as well as mirex and HCB. OCPs were quantified by an HP 6890 Plus GC with an electron capture detector (GC-ECD) with a DB-XLB column (Agilent, 60 m, 32 mm i.d., 0.25 mm film thickness). OCPs were identified by relative retention time (RRT) compared to those observed in OCP standard. Internal standard was used for analyte quantification.

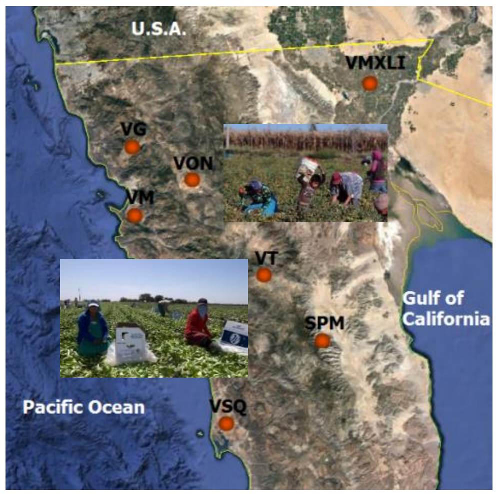

Figure 1. Study areas. Red circles indicate soil sampling sites in San Quintin Valley (VSQ), Trinidad Valley (VT), Maneadero Valley (VM), Ojos Negros Valley (VON), Guadalupe Valley (VG) and San Pedro Martir (SMP-site references).

Results and discussion

Descriptive statistics of OCP concentrations in soils are presented in Table 1. $OCPs_{20}$ (sum of 20 compounds) and DDT_6 (sum of o,p- and p,p-isomers of DDE, DDD) in soils are shown as box and whisker plots in Fig. 2. In general, OCPs concentrations of VM and VSQ (median 32.6 and 18.0 ng/g d.w., respectively) are higher than those found in VG, VON, and VT (median 1.1 to 1.4 ng/g d.w.) due to their extensive agricultural activity. Also, the results of VM and VSQ were similar to those found in the VMXLI by Sanchez-Osorio et al., who reported values of 9.95 ng/g d.w. in soils [9].

For VM, VSQ, VT, and VG, the dominant OCP group was DDTs, except in VON where chlordanes and HCHs were the dominant compounds. The higher median concentrations values of DDT where found in VSQ (16.7 ng/g d.w.) and VM (28.9 ng/g d.w.), with a greater proportion of the p,p-DDE metabolites, which might indicate a non-recent usage of these compounds in these valleys. On average, our DDTs values were lower than those reported in agricultural soils from other states of the country (Puebla, Mexico, San Luis Potosi, Morelos), which ranged from 17 to 83 ng/g d.w. [10,11,12]. However, VM and VSQ showed two sampling sites with 200 ng/g d.w. and ~100 ng/g d.w. respectively. Because of the high population in these areas, it is of concern to evaluate more extensively these areas in order to evaluate the spread of these compound and assess the risk exposure.

The median values of HCHs in the valleys of these study (0.2 to 3.9 ng/g d.w.) are similar to those reported for the VMXLI (0.86 ng/g d.w.) and are lower than those reported by Cantu-Soto et al. [5] in agricultural soils of Sonora (39 ng/g d.w.). Mean values of HCHs in other agricultural soils of Mexico ranged from 3.5 to 58 ng/g d.w. [11,12,13]. Besides, CHLs concentration values in the study areas ranged from B.L.D to 0.46 ng/g d.w. and were similar to those found in VMXLI (0.65 ng/g d.w.) by Sanchez-Osorio et al. [9].

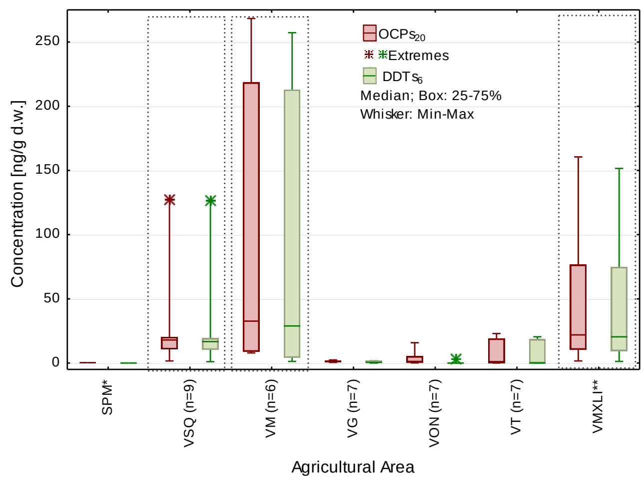

Figure 2. Box and whiskers plot of OCP class sums (ng/g d.w.) in soil samples from Valleys in B.C., Mexico. The top of the box represents the 75th percentile, and the bottom represents the 25th percentile. The horizontal line in the boxes is the median. The whiskers indicate the maximum and minimum values. DDTs (o,p-DDE, o,p-DDD, o,p-DDT, p,p-DDE, p,p-DDD, p,p-DDT. OCPs20 (all compound measured in this study).

Table 1. Organochlorine pesticide residues in soils Valleys in B.C, Mexico, ng/g d.w.

Site	Median	DS	Range		N Pos/total	median	DS	Range		N pos/total
	OCPs		Max	Min		DDTs		Max	Min	
VSQ	15.2	38.6	127.0	1.7	9/9	16.7	16.7	126.4	1.0	9/9
VM	32.6	116.7	268.4	7.9	6/6	28.9	28.9	257.3	1.3	6/6
VG	1.4	0.8	2.4	0.5	7/7	0.5	0.7	1.7	B.D.L	7/7
VON	1.27	5.65	15.82	0.15	7/7	B.D.L.	1.1	3.0	B.D.L.	7/7
VT	1.1	9.8	23.0	B.D.L	7/7	B.D.L.	9.2	20.5	B.D.L.	7/7
VMXLI **	**21.95**	**53.3**	**1.67**	**160.5**	**27/27**	**20.4**	**49.96**	**151.6**	**1.28**	**27/27**
Site	**Median**	**DS**	**Range**		**N pos/total**	**median**	**Ds**	**Range**		**N pos/total**
	HCHs		**Max**	**Min**		**CHLs**		**Max**	**Min**	
VSQ	0.2	0.3	1.0	B.D.L.	9/9	0.15	0.22	0.64	B.D.L.	9/9
VM	3.9	0.5	4.6	3.1	6/6	0.4	0.9	2.4	B.D.L.	6/6
VG	0.3	0.2	0.6	0.2	7/7	B.D.L.	0.2	0.5	B.D.L.	7/7
VON	0.46	0.38	1.18	0.07	7/7	0.46	0.38	1.18	0.07	7/7
VT	0.4	0.3	0.9	B.D.L.	7/7	0.00	0.18	0.49	B.D.L.	7/7
VMXLI**	**0.86**	**2.36**	**8.0**	**0.3**	**27/27**	**0.65**	**2.33**	**8.15**	**0.05**	**27/27**

** Values taken Sanchez-Osorio et al. [9]. number of positive/total samples.

Although the valleys have been extensively used as cropland, there are a lack of information about OCPs concentration levels in the soil. These study shows the presence of ancient OCPs concentrations in the soil of the valleys with highest level in VM and VSQ. These results are important due to the high population that inhabitant in these valleys and the high risk of exposure of the agricultural workers, as it has been reported by Zuñiga-Violante et al. [14] in a study in VSQ, where genotoxic damage in the population have been set due to the exposition to these compounds.

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References

1. Gonzalez-Farias F (2003) Pesticides in the coastal zone of Mexico. In: Klaine SJ, Carvalho FP, Barcelo D, Everaarts J. (Eds.), *Taylor & Francis*, 311-337.
2. Díaz-Barriga F, Borja-Aburto V, Waliszewski SM and Yañez L (2003) DDT in Mexico. In: Fiedler H. (Ed.), *Persistant Organic Pollutants: the Handbook of Environmental Chemistry*, vol. 3. Part O, Springer-Verlag, Berlin, pp. 371-388.
3. Li Y-F and Macdonald RW (2005) *Sci. Total Environ*. **342**, 87-106.
4. Moreno Mena JA and López-Limón, MG (2005) *Estudios fronterizos*, **6**(12), 119-153. Recuperado en 28 de junio de 2017, de http://www.scielo.org.mx/scielo.php?script=sci_arttext&pid=S0187-69612005000200005&lng=es&tlng=es
5. Cantu-Soto EU, Meza-Montenegro MM, Valenzuela-Quintanar AI, Felix-Fuentes A, Grajeda-Cota P, Balderas-Cortes JJ, Osorio-Rosas CL, Acuña-García G and Aguilar-Apodaca MG (2011) *Bull. Environ. Contam. Toxicol.* **87**,556-560.
6. Wong F, Alegria HA, Jantunen LM, Bidleman T F, Figueroa MS, Gold-Bouchot G, Ceja-Moreno V, Waliszewski SM and Infanzon R (2008). *Atmospheric Environment*. **42**: 7737 – 7745.
7. Alegria, H, Bidleman TF and Figueroa MS (2006) *Environmental Pollution*. **140**(3): 483 – 491.
8. Waliszewski, SM, Carvajal O, Infanzon RM, Trujillo P, Aguirre AA and Maxwell M (2004) *J. Agric. Food Chem.* **52**, 7045-7050.
9. Sánchez-Osorio JL, Macías-Zamora JV, Ramírez-Álvarez N and Bidleman TF (2017) *Chemosphere*, **173**, 275-287.
10. Islas-García A, Vega-Loyo L, Aguilar-López R, Xoconostle-Cazares B and Rodríguez-Vásquez R (2015) *J. Environ. Sci. Health Part B* **50**, 99-108.
11. Velasco A, Rodríguez J and Castillo R, Ortíz I (2012*) J. Environ. Sci. Health Part B* **47**, 833-841.
12. Waliszewski SM, Carvajal O, Gómez-Arroyo S, Amador-Muñoz O, Villalobos-Pietrini R, Hayward-Jones PA and Valencia-Quintana R (2008) *Bull. Environ. Contam. Toxicol.* **81**, 343-347.
13. Velasco A, Hernández S, Ramírez M and Ortíz I (2014) *J. Environ. Sci. Health Part B* 49, 498-504.
14. Zúñiga-Violante E et al. (2012) *Revista de Salud Ambiental* [S.l.], **12**(2) 93-101 ISSN 1697-2791. On-line: <http://www.ojs.diffundit.com/index.php/rsa/article/view/328>. Access date: 01 jul. 2017.