TOXAPHENE IN SOIL FROM AN AGRICULTURAL AREA IN NORTHWEST MEXICO

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Introduction

Toxaphene is a complex mixture of chlorinated camphenes, due to its bicycle heptane or norbornane skeleton, up to a total of 16640 chlorinated bornanes congeners are theoretically possible from chlorination; however, due to steric considerations and manufacturing conditions, the technical product consist almost entirely of hexa- to decachlorobornanes which comprise about 10770 compounds (Vetter, 1999). Toxaphene was introduced as an insecticide in 1947 and became one of the most widely used organochlorine pesticides in the United States and in the world during the 1970s. It has a broad spectrum of pesticidal activity and was used mainly on cotton, but also was sprayed extensively on soybeans, peanuts, tobacco, vegetables, turf, and many other crops (Saleh, 1991).

In the United States, the bulk of toxaphene usage was in the southern part of the United States accounting for 81.7% of the total consumption. Toxaphene was also used in Mexico and Central America region. In Mexico, toxaphene usage took place from early 1950s until its ban in 1993. Total consumption in Mexico was estimated as 68 kt, with peak application of 3 kt in 1974. Use in 1981 was 1.8 kt, and it declined to zero in 1995 (Li, 2001).

Due to availability of water from Colorado River, Mexicali Valley (MV) is one of the most important agricultural areas in Northern Mexico. Mexicali valley has a highly technified agricultural practice with approximately 210,993 ha of agricultural lands under irrigation. Due to its closeness to the international border with the United States, MV showed an extensive exchange of technology with the agricultural area of Imperial Valley, in Southern California, including the acquisition of different agrochemical products as pesticides. Thus, in order to enhance productivity and accomplish the agricultural prototype of the "green revolution" established in the agricultural areas of Northern Mexico, large amount of pesticides were used in MV, being organochlorine pesticides as DDT and Toxaphene the most important pesticides used since late 1940s to early 1970s (Moreno-Mena, 2005).

Several studies have reported that volatilization of toxaphene from soils residues is a major and continuing source of emissions to the atmosphere (Bidleman and Leone, 2004; Li et al., 2001; Ma et al., 2005a; McLeod et al., 2002). Alegría et al (2008) have reported revolatilization of residues from local or regional soils as the main source of toxaphene to the atmosphere in Southern Mexico. Hence, in this work we details results of toxaphene in soil and sediment samples of MV, in order to set a baseline for further studies.

Materials and methods

During March 2008, 27 soil samples were collected in the agricultural valley of Mexicali, Baja California, Northwest Mexico (Fig. 1). All sampling sites were located in public areas (i.e. field games, public parks, and schools) of communities spread all over the valley and all of them surrounded by agricultural lands. This sampling design considered the higher exposure risk to the local population, and considering the low disturbance of the ground (no tillage) in comparison to that in the agricultural areas where tilling, flooding, and burning practices occurs. Soil samples were composite of 3 individual samples collected by hand at the upper 0-15 cm depth. Individual samples were pooled and subsampled into glass containers (~500 g) and stored by refrigeration until the laboratory, where they were frozen to -20°C until analyzed. In addition, 3 sediment samples were collected from drain channels within the agricultural area. Sediment samples were collected using a Petite Ponar stainless steel drag (0.1 m^3), collecting the upper 0-10 cm of surficial sediment into glass containers with a metal spoon. Sediment samples storage was the same as that followed for soils samples.

Prior to analysis, frozen samples were thawed and freeze-dried, pulverized and sieved through a 1-mm stainless steel mesh before the analysis. The extraction method was that proposed by Zeng and Vista (1997). Briefly, 40 g of sample was surrogate spiked and soxhlet extracted for 24 h with dichloromethane. The organic extracts were concentrated, solvent-exchanged to hexane, and concentrated to ~1 ml.

Cleanup of sample extracts were done on a 1-cm i.d. glass column packed from bottom to top with 12 cm high of silica and then 6 cm high of alumina (both 3% deactivated with water HPLC). Extracts were applied in ~1ml of hexane and eluted in two fractions: fraction one (F1) with 15 mL of hexane to eliminate non-polar interferences such as hidrocarbons; and fraction two (F2) containing OC compounds with 40 ml of hexane/dichloromethane (70/30 v/v). After cleanup procedure, fractions F2 were concentrated by rotary evaporation to ~1 ml, solvent exchange to hexane and blowed down with a gentle stream of nitrogen. Prior to GC analysis, the volumes were adjusted to 1 ml with isooctane and a mixture of internal standards was added.

Total toxaphene was quantified as the sum of 7-Cl, 8-Cl and 9-Cl homologs by GC-ECNI-MS on an Agilent 7890A GC - Agilent 5975C MSD, using a DB-5MS (30 m, 0.25 mm i.d., 25 µm film thickness) column, and Helium as carrier gas at a flow of 0.6 ml/min and methane as reagent gas at a flow of 40%. Sample volumes of 2 µl were injected splitless. Inlet was at 250°C and the oven temperature was programed as follow: 90°C for 1 min, then, 20°C/min to 160°C for 0 min, then 1.5°C/min to 225°C for 0 min, and then 20°C/min to 270°C for 10 min. Ion source and quadrupole temperatures were 150°C. Detector was operated in the ion monitoring mode to enhance sensitivity. Ions monitored were: 343/345 *m/z* for 7-Cl; 379/381 *m/z* for 8-Cl and 413/415 *m/z* for 9-Cl. Quantification of total toxaphene was done using a standard of technical toxaphene obtained from Dr. Ehrenstorfer analytical standards (Germany). Total toxaphene results were based on the areas of all sample peaks that matched those in the standard.

Finally, passive air samplers (PAS) were deployed at one station close to soil sampling station MV19, in the north part of the valley, from March 2011 to May 2012. Samples were collected every three to four months during about 430 m^3 air was sampled. Duplicate PAS was deployed for OC pesticides analysis. However, for toxaphene analysis both extracts were mixed and analyzed together. Depuration compounds (DC) were used to determine sampling rate (m^3/d). The procedure for deriving sampling rate using DCs was that described by Shoeib and Harner (2002).

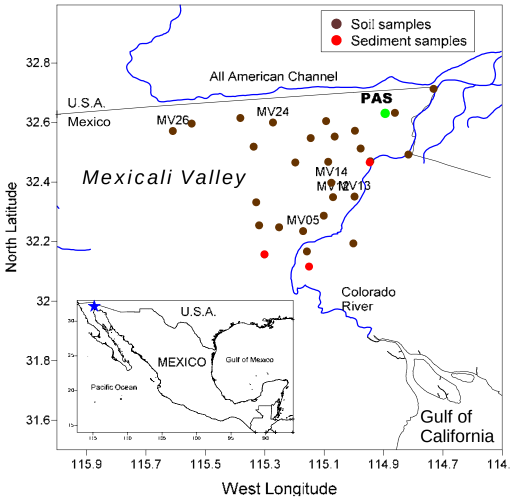

Figure 1. Soil and sediment sampling locations in Mexicali Valley. Passive air sampler in green color

Results and discussion

Toxaphene concentration level in soil and sediment samples area summarized in Table 1. For soil and sediment samples, ΣTOX varied in the range of 0.4 – 1651.0 ng/g, and 6.7 – 19.7 ng/g respectively. Median value for soils was 17.9 ng/g, and 13.3 ng/g for sediments. Due to the wide range of concentration of toxaphene in samples of MV, no significant difference between soil and sediment concentration were found. In general, ΣTOX results in MV were lower than those reported for agricultural soils of Texas, Georgia and South Carolina, where toxaphene residues where reported in the range of 3.3 – 2500 ng/g (Harner et al., 1999; Bidleman et al., 2004), excepting those result in sampling site VM13, where maximum concentration of 1651 ng/g was observed (Figure 2). Despite this maximum result, MV showed overall a relative homogenous surficial distribution pattern with median concentration of 17.9 ng/g and 5spots with relative high concentration of ΣTOX in VM05, VM12, VM14, VM24 and VM26 sites. It is noteworthy that this area is featured for location of several small rural villages where domestic use of toxaphene for termite and ants control might be the principal origin, as well as that originated from pest control in cotton crops.

ΣTOX composition of 7-Cl, 8-Cl and 9-Cl congeners in soil and sediment samples, were similar to that in technical standard. 7-Cl congener in soil and sediment samples account 28 – 62% of ΣTOX, while 8-Cl and 9-Cl account 19-52% and 7-31% respectively. Although congener composition of ΣTOX do not suggest degradation processes, a more detailed analysis of specific congeners is required in order to evaluate depletion patterns of those congeners and establish degradation processes in MV samples.

Table 1. Toxaphene concentration in soil and sediment samples (ng/g), and passive air samples (pg/m^3) from Mexicali Valley. Range concentration of Cl-7, Cl-8, and Cl-9 homologs.

		7-Cl	**8-Cl**	**9-Cl**	**TOX**
Soils (27)	Mean±SD	57.4±105.9	82.1±175.0	29.3±67.2	168.8±346.5
	Median	8.2	7.9	3.6	17.9
	Range	0.2-477.8	0.1-839.3	0.1-333.9	0.4-1651.0
Sediments (3)	Mean±SD	6.9±3.4	3.8±2.6	2.5±1.0	13.3±6.5
	Median	8.3	2.5	2.5	13.3
	Range	3.0-9.3	2.1-6.9	1.6-3.5	6.7-19.7
PAS (3)	Mean±SD	585.5±923.5	0.5±0.9	0.4±0.7	1547.3±1470.3
	Median	97.3	0.08	0.04	220.8
	Range	8.5-1650.6	0.01-1.5	0.01-1.2	23.6-4397.5

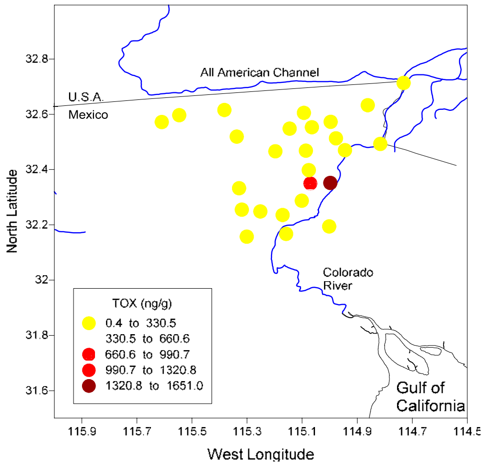

Figure 2. Surficial distribution of ΣTOX in soil samples of Mexicali Valley.

For passive air sampling monitoring, the annual mean sampling rate at all the cycle was in the range of 2 to 5.5 m^3/d with an overall mean of 4.0±1.8 m^3/d. This results were similar to those of Gouin et al (2005) who reported 3.1 m^3/d for samplers deployed in eastern Canada, and 3.9±2 m^3/d for the global atmospheric passive sampling study (Pozo et al., 2006) The ΣTOX in PAS of this study were in the range of 23.6 to 4397.5 pg/m^3. The median value for the annual cycle was of 220.8 pg/m^3 with a highest concentration of 4397.5 pg/m^3 in summer of 2011 (Figure 3) and a lowest concentration on spring season of 2012. This pattern was similar to that reported by Wong et al (2009) where large differences in seasonal concentration of some pesticides for the same region were found.

As mention before, several studies have reported re-volatilization of residues from local soils as a major source of toxaphene to the atmosphere. Wong et al. (2009) have reported air concentration of ΣTOX of 689 pg/m^3 in an air sampling station located in the north area of MV. According to depletion pattern observed in some individual congeners (P63), they also observed the typical soil emission signature reported for other soils in the southern U.S.

Despite the extensive use of pesticides in MV, at this time there are just a few reports about toxaphene concentration level in different matrices such as soils, sediments, water, and air. Considering physiographical features of MV and concentration levels in soil and sediment samples, this valley is of concern as potential source of toxaphene to remote areas

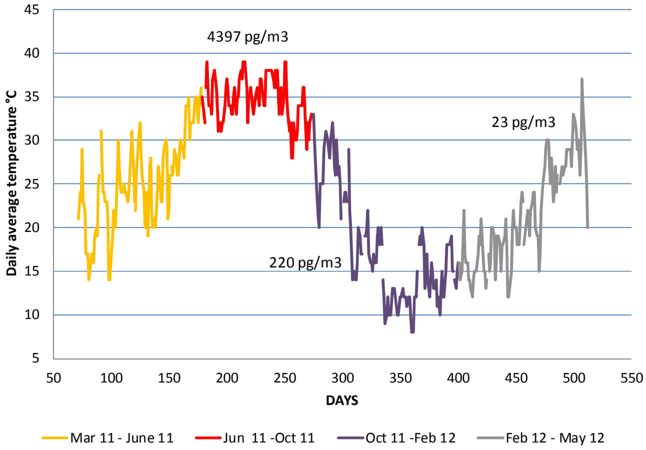

Figure 3. ΣTOX in passive air sampling during march 2011 to may 2012 in MV.

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References

1. Alegría H.A., Wong F., Jantunen L.M.M., Bidleman T.F. et al. (2008); *Atmos Envir.*42: 8810 – 8818.
2. Bidleman T.F., Leone A.D., Falconer R.L., Harner T., Jantunen L.M.M. Wiberg K., Loo B. 2003. ACS Books, American Chemical Society, Washington, DC.
3. Bidleman T.F., Leone A.D. (2004); *Environ Poolut.* 128: 49 – 57.
4. Gouin T. Harner T, Blanchard P, Mackay D. (2005); Environ Sci Technol. 39: 9115 – 9122.
5. Harner T., Wideman J.L., Jantunen L.M.M., Bidleman T.F., Parkahurst W.J. (1999); *Environ Pollut.* 106: 323 – 332.
6. Li Y.F. (2001); *J Geophys Res.* 106: 17919 – 17927.
7. Ma J., Venkatesh S., Li Y.-F. (2005); *Environ Sci Technol*. 39: 8123 – 8131.
8. McLeod M., Woodfine D., Brimacombe J., Toose L., Mackay D. (2002); *Environ Toxicol Chem*. 21: 1628 – 1637.
9. Moreno-Mena J.A. and López-Limón M.G. (2005); *Estudios Fronterizos*. 6: 119 – 153.
10. Pozo K., Harner T., Wania F., Muir D.C.G., Jones K.C., Barrie L.A. (2006); *Environ Sci Technol*. 40: 4867 – 4873.
11. Saleh M.A. (1991); Rev Environ Cont Toxicol 118:1-85
12. Shoeib M. and Harner T. (2002); *Environ Sci Technol*. 36:4142 – 4151.
13. Vetter W. and Oehme M. (1999); Springer, Berling Heidelberg New York, pp 237 – 287.
14. Wong F., Alegria H.A., Bidleman T.F., et al. (2009); *Environ Sci Technol*. 43: 704 – 710.
15. Zeng, E.Y. and Vista, C.L. (1997); *Environ Toxicol and Chem* 16: 179 – 188.