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Organochlorine pesticides in residential soils and sediments within two main agricultural areas of northwest Mexico: Concentrations, enantiomer compositions and potential sources

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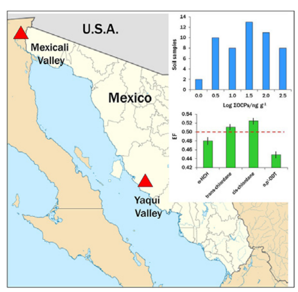
HIGHLIGHTS

- Chlorinated pesticides were measured in soils and sediments in northwest Mexico.
- Profiles of DDTs, hexachlorocyclohexanes and chlordane compounds indicated aged residues.
- Enantioselective microbial degradation was evident for chiral compounds.
- Levels in residential soil were below most regulatory guidance values (RGVs).

GRAPHICAL ABSTRACT



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ABSTRACT

The agricultural Mexicali and Yaqui valleys (MV, YV) in northwest Mexico were heavily treated with organochlorine pesticides in the past. Residential soils and agricultural drain sediments were sampled in 2008–2009 and analyzed for DDTs (*o,p′*- and *p,p′*- isomers of DDE, DDD and DDT); hexachlorocyclohexanes (α-, β-, γ- and δ-HCH) and chlordanes (*trans*-chlordane, *cis*-chlordane, heptachlor and heptachlor *exo*-epoxide). Geometric means (GMs) (ng g^{-1} dry weight) were: MV soils (n = 27) ΣDDT 22, ΣHCH 0.80, ΣCHL 0.88; YV soils (n = 25) ΣDDT 5.0, ΣHCH 0.23, ΣCHL 0.67; MV sediments (n = 3) ΣDDT 5.0, ΣHCH 0.23, ΣCHL 0.53; YV sediments (n = 8) ΣDDT 2.6, ΣHCH 0.12, ΣCHL 0.090. GMs were significantly higher ($p < 0.05$) in MV than YV soils for ΣDDT and ΣHCH, but not for ΣCHL. Comparison to worldwide regulatory guideline values (RGVs) for residential soils showed all compounds below mean or GM RGVs, but above the lowest RGV in some cases. Low *p,p′*-DDT/(*p,p′*-DDT + *p,p′*-DDE) in most soils indicated aged residues. Lack of *p,p′*-DDT metabolism might account for its dominance in a few soils. HCH isomer profiles suggested aged technical HCH in the YV, and technical HCH + lindane in the MV. Heptachlor dominated the ΣCHL, probably from application of technical heptachlor as well as chlordane. Chiral compounds were nonracemic in soils and sediments and indicated enantioselective microbial degradation of (+)α-HCH, (−)*trans*-chlordane, (−)*cis*-chlordane and (+)*o,p′*-DDT. Depletion of (+)*o,p′*-

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DDT in soils may account for similar enantiomer signatures previously reported in air of northwest Mexico.

1. Introduction

Organochlorine pesticides (OCPs) have been used worldwide for over 60 years in temperate, subtropical and tropical countries. Because of their persistence, toxicity and capability of long-range transport, production and use of eight OCPs (aldrin, hexachlorobenzene, chlordane, dieldrin, endrin, heptachlor, mirex, toxaphene) were eliminated globally under the 2001 Stockholm Convention (UNEP, 2016a). Chlordecone and hexachlorocyclohexanes (HCHs) were added to the Convention in 2009 and endosulfan was added in 2013. DDT continues to be available for vector control where approved by the World Health Organization, but is otherwise banned. The use of OCPs was extensive in Mexico since the 1950s, mainly for pest control, agricultural activities, and as vector control for dengue and malaria. González-Farias (2003) estimated that between 1969 and 1979, approximately 9000 tons y^{-1} of OCPs was used in Mexico, of which 7800 tons y^{-1} was produced locally. During this period, the most widely used OCPs were DDT, toxaphene, lindane (γ-HCH), and endrin (González-Farias, 2003; Díaz-Barriga et al., 2003). Li and Macdonald (2005) ranked Mexico in sixth place in the world for DDT usage in agriculture and public health programs. Agricultural use of DDT declined in the 1970s and by 1997 the only approved use of DDT was for vector control (NACEC, 2005), which totaled 69,545 tons between 1957 and 2000 (Pérez-Maldonado et al., 2010). In response to North American Regional Action Plans (NARAPs) of the North American Commission for the Environment Cooperation, Mexico eliminated all use of DDT by 2000 (NACEC, 2005). Chlordane was imported from the U.S. for agriculture and as a termiticide, restricted to termite control after 1997, and all use was prohibited at the end of 1998 (NACEC, 2001, 2003). Lindane was also imported from the U.S. for seed treatment, veterinary and pharmaceutical applications. These uses are being phased out under the lindane NARAP (NACEC, 2013).

The Mexicali Valley (MV) in Baja and the Yaqui Valley (YV) in Sonora are two of the most important agricultural areas in northwest Mexico (Sugunan, 1997). Due to the availability of water from the Yaqui and the Colorado rivers, both valleys have highly technified agricultural practices and well-developed irrigation systems. Agricultural lands under irrigation total 210,993 and 266,673 ha for the MV and YV, respectively. Currently, the YV produces ~2.7 million tons y^{-1} of crops, mainly wheat, corn, safflower, soybean, cotton, tomato, potato, chili, watermelon and zucchini, while MV productivity is ~2.9 million tons y^{-1} of cotton, wheat sorghum, tomato, chili and onions. Although there have been some reports of malaria in the YV, neither valley has been considered a malaria-risk area by the National Institute of Public Health (Betanzos-Reyes, 2011). Large amounts of pesticides have been used historically in both valleys to enhance productivity (Moreno-Mena and López-Limón, 2005; Cantu-Soto et al., 2011). OCPs, organophosphates, pyrethroids, and carbamates were the most applied insecticides. The YV is considered the cradle of the "green revolution" for agriculture (Bejarano Gonzáles, 2002). The largest use of DDT in YV and MV during 50s to late 70s was to accomplish the "green revolution" that is, to increase cropland production (Moreno-Mena and López-Limón, 2005). The main application protocol was air spraying over agricultural lands.

OCP residues in soil contaminate the atmosphere through evaporation from agricultural and urban areas (Bidleman and Leone, 2004; Bidleman et al., 2006; Chakraborty et al., 2015; Kurt-Karakus et al., 2006; Lammel et al., 2011; Tao et al., 2008; Wong et al., 2008, 2010), and soil-air exchange controls background air concentrations (Cabrerizo et al., 2011; Degrendele et al., 2016; Růžičková et al., 2008). OCPs have been found in sediments of remote lakes in Mexico, which suggests atmospheric transport and deposition (Ruiz-Fernández et al., 2014). Lakes, rivers and coastal waters receive OCPs through agricultural drains and transport in rivers and streams (Carvalho et al., 2009; García-de la Parra et al., 2012; García-Hernández et al., 2013; Guan et al., 2009; Lugo-Ibarra et al., 2011; Montes et al., 2012; Pinto et al., 2016).

Recent surveys of DDT residues in soils of Mexico have been conducted in communities where DDT was an issue for human exposure (Díaz-Barriga Martínez et al., 2012; Herrera-Portugal et al., 2005; Martínez-Salinas et al., 2011; Pérez-Maldonado et al., 2010; Torres-Dosal et al., 2012; Yáñez et al., 2002). Other surveys have measured OCPs in agricultural soils of southern and central Mexico (Islas-García et al., 2015; Velasco et al., 2012, 2014; Waliszewski et al., 2004, 2008), and in the Yaqui and Mayo valleys of Sonora (Cantu-Soto et al., 2011; Cejudo et al., 2012; Meza-Montenegro et al., 2013), and one study examined soils across the country in communities, agricultural fields and background sites (Wong et al., 2010).

The objectives of this study were to: a) determine residues of DDT, HCH and chlordane in community soils and sediments of agricultural drainage channels and riverbeds, b) characterize the "chemical profiles" of the residues by determining the proportions of isomers and parent-metabolite combinations for the three OCPs, c) Determine the proportions of enantiomers for chiral OCPs: α-HCH, *trans*-chlordane, *cis*-chlordane and *o,p'*-DDT as an indicator of microbially mediated degradation.

2. Materials and methods

2.1. Soil and sediment sample collection

Soil samples (n = 52) were collected across the MV and YV during March 2008 and August 2009 respectively. Both valleys are located in northwest Mexico, in the states of Baja California and Sonora. The classification order of most soils in the MV is Aridisols (Judkins and Myint, 2012), while Vertisols dominate in the YV (Lobell et al., 2002). Soil samples were from community parks, schoolyards and other public places. A composite was made of three individual subsamples collected from 0 to 10 cm depth using a stainless-steel scoop. Sediment samples (n = 11) were collected from the drainage channels or from the riverbeds of the streams located within the agricultural area of both valleys. These were taken with a Ponar dredge (0.1 m^3) from the upper 0–10 cm. The samples were refrigerated until transport to the laboratory where they were frozen to −20 °C until their analysis. The location of sampling sites is shown in Fig. 1 and site descriptions are given in Supplementary Material (SM-1).