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Are Mexican Agricultural Farmlands PCDD/F Soil Reservoirs?

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Abstract Our aim was to identify polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzo-*p*-furans (PCDFs) in agricultural farmland soils in the Northwest of Mexico. We obtained $\approx$50 g of soil in five Yaqui Valley (VY) agricultural fields in the north-western Mexican State of Sonora and in five Culiacán Valley (VC) agricultural fields in the north-western Mexican State of Sinaloa. Fields with minimal tillage, with ferti-irrigation, and those with intensive aerial and manual tillage were included. All soil samples were subjected to the chemical activated luciferase gene expression (CALUX®) test to determine PCDD/F. On average, samples contained 4.2 ± 1.2 PCDD/F ppt TEQ; VY soil samples contained 4.72 ± 1.23 PCDD/F ppt TEQ, while VC soil samples showed 3.6 ± 1.1 PCDD/F ppt TEQ ($p = 0.47$). On considering tillage-type, in agricultural fields catalogued as intensive tillage, PCDD/F concentrations were 4.40 ± 0.43 in agricultural fields catalogued as intensive tillage, while in farmlands of another tillage-type these concentrations were slightly higher (5.53 ± 0.8).

Keywords Dioxins · Furans · Soil reservoirs · Agricultural fields

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Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzo-p-furans (PCDFs) are environmentally detectable chlorinated organic contaminants (Ramamorthy and Ramamorthy 1997); nevertheless, the few existing inventories of the diverse emission sources of these substances have been focused primarily on the site where they form or on the process by which they form. Nonetheless, PCDD and PCDF reservoirs or secondary sources should be more elaborately studied because there are indications that the quantity of PCDD/F deposited in the troposphere is higher than that emitted to the atmosphere; on the other hand, the latter also acts as an emission source (US EPA 2003).

Soils are considered within the most relevant potential PCDD/F reservoirs, and apparently deposit of these substances the atmosphere is the primary way to contaminate soils. However, due to the fact that these are highly liposoluble and scarcely volatile substances there is a greater tendency for them to be deposited in soils than in the air or water (US EPA 2003; Domingo et al. 2001). Once PCDD/Fs are deposited in soils, they are slowly mobilized toward the soils' interior, although they can be remobilized toward the atmosphere by volatilization and particle resuspension or can disappear due to photodegradation. Once incorporated into the soil, PCDD/F can possess a half-life of 10–12 years; on reaching a greater soil depth, the half-life could be 25–100 years (US Department of Health & Human Services 1999). Two factors that additionally contribute to agricultural farmland soils constitute PCDDs/PCDFs reservoirs constitute utilization of sewage sludge and treatment with agrochemicals subjected to previous seasons, above all those with 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) herbicides (Rideout and Teschke 2004; Eljarrat et al. 2003).

Mexico is a country with large extensions of land dedicated to farming during practically the entire year. According to the Mexican National Institute of Statistics, Geography, and Informatics (INEGI 1991), the percentage of soil devoted to agriculture is 15.6% of 1,934,194 km^2, and preliminary numbers for the year 2003 with regard to harvested surface reached 15,575 ha (INEGI 2001). The northeastern bordering Mexican States of Sinaloa and Sonora are traditionally agricultural federative entities that possess 18,913 and 13,435 km^2, respectively, of arable surface. Both States are among the 10 main state extensions for cultivation in Mexico and together comprise a little >10% of Mexican territory for this soil use (SEMARNAT 2002). These circumstances should promote the systematic study of the possible contamination of these farmlands with PCDD/F, and if this is the case, by another similar types of substances.

Materials and Methods

Agricultural farmlands pertaining to the Yaqui Valley in Sonora and the Culiacán Valley in Sinaloa, all localized in the northeast of Mexico, were included. The 10 farmlands selected could have remained without tillage for the past 5 years, or could even had sustained minimal farming, been subjected to ferti-irrigation or to intensive tillage or farming with aerial and/or manual agrochemical treatment, or could possess agrochemical-free field certification with or without a background of application of 2,4-D or 2,4,5-T or other types of herbicides. Similarly, we were not interested in whether the fields had been in recent or former contact with natural, pluvial, or storm drainage. Lands that had functioned previously as fields for unloading or confining toxic-dangerous sewage of any type were excluded from the study, as well as that bordered on industries recognized as potentially producers of PCDD/F emissions.

In each farmland selected, we obtained at least 50 g of soil at a depth of 20–50 cm; these were submitted to drying at 37°C for 6–12 continuous hours. All samples were sent, via air mail in transparent glass bottles that were labeled, coded, and sealed, to the Xenobiotic Detection System, Inc. laboratories in Durham, North Carolina, USA, for PCDD/F identification of the soil-extracted samples. The chemical activated luciferase gene expression (CALUX^{TM}) bioassay applied to all soil samples is based on the bonding of polychlorinated diaromatic hydrocarbons to the intracellular aryl hydrocarbon receptor (Kanematsu et al. 2006).

The samples received at the Xenobiotic Detection System, Inc. laboratories were extracted and cleaned up using a screen sample processing procedure. The screening mode involves the analysis of a single aliquot of the sample. A second aliquot was spiked with a radiolabeled TCDD standard to estimate recovery. According to the results, there was 86% recovery of the spiked sample. Using this mode would indicate whether a sample needed to be further analyzed by either the semi-quantitative mode or by chemical analysis. Sample extracts and standards were applied the genetically engineered cells and induction of luciferase activity quantified. A dioxin-TEQ contamination of the sample was estimated from a least squares best fit using a four variable Hill Equation of induction of luciferase activity from the standard curve of 2,3,7,8-tetrachlorodibenzo-p-dioxin. The response of the sample was analyzed and compared to associated method blanks. Quality control samples were included with each analysis and all of the results for these control samples were within acceptable ranges. PCDD and PCDF quantification was in parts per trillion (ppt) by toxicity equivalencies (TEQ) after inducing these to express luciferase by means of CALUX^{TM}. A percent moisture determination was performed on each of the ten samples. The results were calculated per wet and dry weight basis. In addition, cell viability as a toxicity indicator was determined in all soil samples sent to the laboratory. The limit of detection for these samples is 0.41 ppt. The absolute limit of detection for this method is 0.1 ppt if gets a reading of 1.0 ppt.

Results and Discussion

None of our samples showed microscope-observable toxic cellular effects. All 10 dry samples demonstrated an average PCDD/F concentration of 4.2 ± 1.2 ppt TEQ; samples proceeding from the Yaqui Valley contained 4.72 ± 1.23 ppt TEQ of PCDD/F, while Culiacán Valley samples contained 3.6 ± 1.1 ppt TEQ of PCDD/F. Concentrations found in dry samples collected from farmlands at both locations did not exhibit a statistically significant difference by a Mann–Whitney two sample ranksum test ($p = 0.47$).

Likewise, on considering tillage/farming type in seven of the 10 agricultural farmlands catalogued as intensively farmed PCDD/F concentration was 4.40 ± 0.43, while in fields without this tillage-type and even when we contemplated a field not farmed for at least 5 years, this concentration was slightly more elevated (5.53 ± 0.8) although without significant differences also by a Mann–Whitney two sample ranksum test ($p = 0.10$). PCDD and PCDF concentration between Culiacán Valley and Yaqui Valley agricultural farmlands per wet and dry weight basis do not show statistical differences by a two-sample *t* test ($p = 0.31$ and 0.91 respectively).

The PCDD/F concentration found in the agricultural fields studied herein is higher than that identified in soils of rural areas in the US based on the compilation of diverse studies, i.e., 3.6 pg/g of soil at depths of >5 cm (US EPA 2003). In these areas, previous and intense use of 2,4-D and 2,4,5-T herbicides has been recognized, but it is materially impossible to estimate, a circumstance that can be shared by Mexico (Mannetje et al. 2005; Im et al. 2002; Masunaga et al. 2001).

The agricultural field soils analyzed in this study can be considered as reservoirs and secondary sources of PCDD/F even if these soils had not been subjected to tillage in the past 5 years; nonetheless, according to the Agency for Toxic Substances and Disease Registry (ATDSR) the PCDD/F level is minimally risky and possesses little probability of representing effects on human health (DeRosa et al. 1997). Notwithstanding this, given the fact that these comprise agricultural farmlands it is necessary to promote the performance of studies that are more detailed and that are conducted at more specific sites (Wu et al. 2002).

PCDD/F recirculation from reservoirs identified in soils is a fact that should be taken into account under any circumstance and should be considered an outstanding contributor to the exposure of these compounds in humans due to their recognized effects on health (Huwe 2002). In this respect and although the INEGI cited that only a little >1 million hectares (1.6%) of soil in Mexico is dedicated to agriculture, 10,830,771 individuals participate in the performance of agricultural work and could be susceptible to this particular exposure (Mannetje et al. 2005; Wu et al. 2002).

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