

Levels of Organochlorine Pesticides in Soils and Rye Plant Tissues in a Field Study

STEFAN M. WALISZEWSKI,* OCTAVIO CARVAJAL, ROSA M. INFANZON,
 PATRICIA TRUJILLO, ANGEL A. AGUIRRE, AND MARY MAXWELL

Institute of Forensic Medicine, University of Veracruz, SS Juan Pablo II s/n,
 94290 Boca del Rio, Ver., Mexico

The organochlorine pesticides are lipophilic and persistent and tend to accumulate in soils and growing plants. The contamination of growing plants occurs by adhesion of volatile substances from the air to the plant surface and by the migration of contaminants through xylem in inner ascendant transport. Persistent organochlorine pesticides (HCB, α,γ -HCH, pp'DDE, op'DDT, pp'DDT) levels were determined in soils and rye plants. The aims of the study were the monitoring of organochlorine pesticide concentrations and the comparison of these levels among soil, rye straw, and rye grains. Fifty soil samples and 50 rye plant (50 straw and 50 grains) samples were taken. The GLC-ECD chromatographic results indicated the following contamination levels distributed among soil, straw, and grains: HCB (0.7–1.2–0.7 $\mu\text{g}\cdot\text{kg}^{-1}$), α -HCH (0.6–3.4–1.2 $\mu\text{g}\cdot\text{kg}^{-1}$), γ -HCH (1.8–27.3–4.4 $\mu\text{g}\cdot\text{kg}^{-1}$), Σ -HCH (2.5–30.7–5.6 $\mu\text{g}\cdot\text{kg}^{-1}$), pp'DDE (1.0–7.8–5.5 $\mu\text{g}\cdot\text{kg}^{-1}$), op'DDT (16.1–20.4–17.0 $\mu\text{g}\cdot\text{kg}^{-1}$), pp'DDT (38.0–41.7–49.6 $\mu\text{g}\cdot\text{kg}^{-1}$), and Σ -DDT (54.2–63.2–72.1 $\mu\text{g}\cdot\text{kg}^{-1}$). The study verified the presence of organochlorine pesticides in the Mexican agricultural environment and their migration from soil to the growing rye plants. However, DDT has been banned since 1999 for sanitary reasons, and Lindane is applied only in some cases as a seed dresser. The determined organochlorine pesticide levels in rye plants are low, at residual levels that are below Codex Alimentarius Commission maximum residue limits.

KEYWORDS: Organochlorine pesticides; soil; rye plants

INTRODUCTION

Farm plants participate in the migration of pesticides, which were applied for plant protection. This phenomenon is caused by retention, which modifies volatile substance exchange processes between soil and air (1, 2). One consequence of this process is the introduction of pesticide residues to the forage of ruminants (3–7). The pesticides that are found in the soil and in the vapor phase enter the plants in different ways. These routes include their penetration into the roots and subsequent translocation through xylem (8–12), direct vapor adsorption on the leaves (13–17), and dry or wet direct deposition over plant surfaces. Additionally, the suspended particles that come from contaminated soils are blown by the wind and the rain and are captured later by growing plants. These particles can contribute to the additional contamination that affects great areas of soil (18).

The particle and vapor depositions are phenomena of great importance in the interaction of the atmosphere with plants (16). The pesticide residues in the air can exist as gases or are bound to suspended particles (19). Great efforts were made to model

the transference relationships between the agriculture contaminant vapors and their deposition on the particles in dry and wet conditions (4, 15, 20, 21).

The bibliographic data suggest that the atmospheric deposition of particles can constitute an important supply of organic semivolatile contaminants to the plants and that vapor liberation from soils to the aboveground vegetal surfaces indicates an important reentry of contaminants to the environment (18, 21–23). Cold temperatures promote the deposition and accumulation of organochlorine pesticides. Particularly, the more volatile pesticides, which tend to evaporate in warmer areas, are transported by air currents and deposited in colder areas (2, 24).

Organochlorine pesticides such as hexachlorobenzene (HCB), hexachlorocyclohexanes (HCHs), dichlorodiphenylethane (DDT), dichlorodiphenylethene (DDE) have been applied since the 1940s in plant protection and sanitation throughout the world. Their use permitted the protection of agricultural efforts, assurance of harvest, and combat of vector-transmitted diseases. Beginning in 1990 in Mexico, the use of DDT was restricted only to sanitary efforts, and since 1999 it has been banned. Lindane (γ -HCH) is permitted only as a dresser for seed protection. The common characteristic of these pesticides is their persistence in the environment and bioconcentration in lipidic part of organisms.

* Author to whom correspondence should be addressed [e-mail swal@uv.mx; telephone (229) 912-8741].

The aim of the work was to know the concentrations of persistent organochlorine pesticides (HCB, α , γ -HCH, pp'DDE, op'DDT, pp'DDT) in the soils and in parts of rye plants (straw and grains). The observed contamination of rye plants was originated by their internal transport and external adhesion of particles and vapors. This resulted from their environmental behavior after the past use of these pesticides in plant protection and sanitation.

MATERIALS AND METHODS

During the autumn of 2003, before the harvest, soils and rye plants were sampled from different fields in the states of Puebla and Mexico in the Mexican Republic. In these fields, DDT and Lindane had not been applied as insecticides for at least 10 years. Nevertheless, the insecticide Lindane has been used in some cases as a seed dresser to protect against fungus during storage prior to seeding.

Sampling. Fifty soil samples were taken with an Engler stick (5 cm i.d.) to a depth of 10 cm, according to the method described by Cochran (25) for the total surface cover, taking ~4 kg of soils. In each field, the samples were homogenized to obtain a representative one. Approximately 500 g of the homogenized sample was stored in a glass jar with a cover and taken to the laboratory. The soil samples were then dried for 2–3 days under the laboratory's ambient conditions and sifted through a 0.2 mm² sieve to obtain a homogeneous dried sample that was stored in the glass jar at a temperature of -20 °C until analyzed.

Fifty rye plant samples were obtained by cutting 30 entire plants at 10 cm above the soil surface for one sample, in the same fields where the soil samples were taken. The plants were wrapped in the fields with paper filters and transported to the laboratory. In the laboratory, the rye plants were separated into grains and straw and milled to obtain a uniform powder and representative samples. The milled grain and straw samples were stored in glass jars at -20 °C until analyzed.

Qualitative and Quantitative Organochlorine Pesticide Determination. The determinations of organochlorine pesticides were done by gas chromatography on a Varian 3400CX gas chromatograph with an electron capture detector. The pesticides studied were separated on an SPB-608 320 μ m i.d. and 30 m long capillary column with a temperature program from 193 °C (7 min) to 250 °C at 6 °C/min, holding for 20 min. The carrier gas was nitrogen at 25 cm/min, and 1 μ L was injected in splitless mode. The gas chromatograph–mass spectrometer (Varian model 3800, Saturn 2000 GC-MS-MS) was used to confirm the determination of compounds corresponding to organochlorine pesticide peaks. The confirmation of peaks equivalent to organochlorine pesticides, eluted from the SPB-608 30 m \times 0.32 mm i.d. capillary column, was done by comparing the obtained mass spectra of substances from extracts to those of standard substances, selecting the following specific ions from an ion trap detector (*m/z* values) of HCB. *M*⁺ 282; 249, 214, 142 of HCH isomers. *M*⁺ 288; 254, 219, 181 of pp'DDT and op'DDT. *M*⁺ 352; 235, 199, 165 of pp'DDE. *M*⁺ 318; 246, 210, 176. In the analyzed samples, from the HCH isomers, only the presence of α - and γ -HCH was confirmed in the monitored soil and rye samples.

Analytical Methods. *Soil.* The analysis was done according to the method previously described by Waliszewski and Szymczynski (26). Twenty grams of soil sample was placed into a round-bottom flask of 250 mL, and 50 mL of an acetonitrile/acetic acid/water (30+10+10) mixture was added. The contents were left in darkness for 16 h. Thereafter, the contents were boiled under reflux for 15 min, left to cool, and decanted to a 500 mL separatory funnel. Another 50 mL of extraction mixture was added to the soil sample, and the contents were boiled again for 15 min. The extract was cooled and filtered into the separatory funnel, combining it with the previous one. To the combined extracts was added 300 mL of distilled water, and the contents were mixed. The organochlorine pesticides were extracted three times with 50 mL of hexane each time, and the extracts were combined in another separatory funnel. To remove residues of acetic acid and acetonitrile, the hexane extracts were washed twice with 50 mL of distilled water. Then, the extract was dried by passing it through a sodium sulfate layer

Table 1. Mean and Standard Deviation of Recovery from Fortification Study Made on Soil, Straw, and Grain Blank Samples

pesticide	soil	straw	grain
HCB	98.3 \pm 2.6	91.2 \pm 3.6	93.4 \pm 3.1
α -HCH	99.1 \pm 2.2	94.6 \pm 2.9	95.3 \pm 4.2
γ -HCH	98.9 \pm 1.8	93.8 \pm 4.1	95.1 \pm 4.9
pp'DDE	97.9 \pm 1.9	92.7 \pm 6.5	93.3 \pm 6.1
op'DDT	97.1 \pm 7.1	90.9 \pm 7.1	92.2 \pm 6.5
pp'DDT	94.3 \pm 2.8	94.6 \pm 8.8	95.1 \pm 5.9

to a round-bottom flask. The extract was rotary evaporated to a few milliliters. The concentrated extract was transferred quantitatively to a 10 mL calibrated tube. One milliliter of concentrated sulfuric acid was added, and the contents were vigorously shaken for 1 min and left for 3 min to obtain good phase separation. The hexane extract was passed through the sodium sulfate into a 50 mL round-bottom flask. The sodium sulfate was washed with hexane, and the combined extract and washes were rotary evaporated to a few drops. The concentrate was transferred to a 1 mL volumetric tube and adjusted with hexane to obtain a final volume of 1.0 mL.

Grain and Straw. The analysis was done according to the method previously described by Waliszewski et al. (27). Ten grams of sample was weighed into an Erlenmeyer flask (250 mL), and 150 mL of an acetonitrile/water (65+35) mixture was added. The contents were left in darkness for 16 h. Thereafter, the contents were homogenized in the Ultra-turrax homogenizer for 3 min. The supernatant was decanted into a 1000 mL separatory funnel. The extraction procedure was repeated twice with 100 mL of extraction mixture each time. To the combined extracts in the separatory funnel was added 500 mL of a 5% sodium sulfate water solution, and the contents were mixed. The organochlorine pesticides were extracted three times with 100 mL of hexane each time, and the extract was dried by passing it through a sodium sulfate layer and collected in a round-bottom flask. The combined extracts were rotary evaporated to a few milliliters and quantitatively passed to a 10 mL calibrated tube; the volume was adjusted to 10 mL. One milliliter of concentrated sulfuric acid was added, and the contents were vigorously shaken for 1 min and left for 3 min to obtain good phase separation. The hexane phase was passed through the sodium sulfate into a 50 mL round-bottom flask and rotary evaporated to a few drops. The concentrated extract was transferred to a 1 mL volumetric tube and adjusted with hexane to obtain a final volume of 1.0 mL.

For the cleanup of soil and grains extracts, sulfuric acid was employed, which precipitates organic substances of soil and vegetable origin and hydrolyzes the bound pesticides to the organic matrices (28). The sulfuric acid removes some environmental compounds, such as phthalate esters. Because they are ubiquitous, they propagate in the environment and interfere in the chromatographic determinations, overlapping the peaks of organochlorine pesticides, including HCHs and DDTs (32).

Analytical Quality Study. To evaluate the quality of the analytical methods, a fortification study at the level 1–5 μ g \cdot kg⁻¹ was performed using the following pesticides: HCB, α -HCH, γ -HCH, pp'DDE, op'DDT, and pp'DDT. The standard solution was added to soil, straw, and grain blank samples with contamination levels below the detection limit of 0.2 μ g \cdot kg⁻¹. The obtained results of the mean recoveries and their standard deviations are presented in Table 1. The mean recovery for soil samples oscillated between 94.3 and 99.1%, that for straw between 90.9 and 94.6%, and that for grains from 92.2 to 95.3% with a standard deviation between 1.8 and 8.8%, indicating the excellent recovery of pesticides studied from fortified samples.

Statistical Analyses. The statistical calculations for each organochlorine pesticide determined in the samples of soil, straw, and grains were done for mean (*X*) concentration, standard deviation of the mean (SD), standard error of means (SEM), median, and 95% confidence intervals (95% CI) of the distribution. Moreover, the results were paired according to the sample type (soil, straw, and grain) to express the magnitude of lineal relationships among them, comparing the means

Table 2. Results of Chemical Analyses of Soils from Field Studied

parameter	value	parameter	value
P ₂ O ₅ (mg%)	10.5–14.1	% of carbon	0.63–0.79
K ₂ O (mg%)	7.6–28.7	% of organic matter	1.00–1.41
Mg (mg%)	0.7–0.15	clay (%)	18.1–20.9
KCl (mg%)	3.6–4.0	silt (%)	17.9–22.7
pH	0.60–0.81	sand (%)	53.6–64.7

Table 3. Frequency, Mean Values and Standard Deviations ($X \pm SD$), Standard Errors of Means (SEM), Median, and 95% Confidence Intervals (CI) of Organochlorine Pesticides in Soil

pesticide	frequency, %	$X \pm SD$, $\mu\text{g}\cdot\text{kg}^{-1}$	SEM	median	95% CI	
					lower	upper
HCB	60	0.7 \pm 0.4	0.1	0.6	0.5	0.8
α -HCH	56	0.6 \pm 0.2	0.1	0.7	0.5	0.7
γ -HCH	74	1.8 \pm 0.9	0.1	1.6	1.5	2.1
Σ -HCH		2.5 \pm 3.3	0.5	1.9	1.4	3.5
pp'DDE	12	1.0 \pm 0.2	0.1	1.0	0.8	1.2
op'DDT	100	16.1 \pm 7.6	1.1	14.0	13.9	18.3
pp'DDT	100	38.0 \pm 16.0	2.3	38.0	33.4	42.6
Σ -DDT		54.2 \pm 21.3	3.0	53.0	48.1	60.3

Table 4. Frequency, Mean Values and Standard Deviations ($X \pm SD$), Standard Errors of Means (SEM), Medians, and 95% Confidence Intervals (CI) of Organochlorine Pesticides in Straw

pesticide	frequency, %	$X \pm SD$, $\mu\text{g}\cdot\text{kg}^{-1}$	SEM	median	95% CI	
					lower	upper
HCB	70	1.2 \pm 0.4	0.1	1.2	1.0	1.4
α -HCH	100	3.4 \pm 1.1	0.2	3.6	3.1	3.8
γ -HCH	100	27.3 \pm 8.3	1.1	27.1	24.9	29.6
Σ -HCH		30.7 \pm 9.0	1.3	31.6	28.1	33.3
pp'DDE	100	7.8 \pm 2.2	0.3	8.0	7.2	8.5
op'DDT	100	20.4 \pm 6.9	0.9	20.0	18.4	22.4
pp'DDT	100	41.7 \pm 12.7	1.8	44.0	38.1	45.3
Σ -DDT		63.2 \pm 18.2	2.5	65.0	58.1	68.4

and calculating two-tailed p value and the Pearson correlation coefficients (r). The statistical software Minitab 12 was used.

RESULTS AND DISCUSSION

In the autumn of 2003, 50 soil and 50 rye plant samples, separated into straw and grains, were collected in the states of Puebla and Mexico in the Mexican Republic. The samples were analyzed to determine the organochlorine pesticide levels in the soil and rye plants exposed to the residues. The source of the residues is considered as coming from environmental contamination. Because these pesticides are not more used in Mexico anymore, their origin is thought to be caused from past sprayings done by the Ministry of Health to combat malaria and ectoparasites as well as from agricultural use as a seed dressing. The additional source is from their past use and accumulation in agricultural soils and their posterior volatilization. To classify the soil type, chemical analyses were done. The obtained results of fifty analyzed samples are summarized in **Table 2**. This table shows the physicochemical characteristics of soil samples. On the basis of the results, the soils are classified as sandy soils. These soils have limited microbiological activity, with a low intensity of metabolic processes that reveal adsorptive capacity of environmental contaminants (9, 17).

Tables 3, 4, and **5** show the detailed data of frequencies of determination (%), mean values ($\mu\text{g}\cdot\text{kg}^{-1}$), SD, SEM, median values ($\mu\text{g}\cdot\text{kg}^{-1}$), and 95% CI of organochlorine pesticides (HCB, α -HCH, γ -HCH, Σ -HCH, pp'DDE, op'DDT, pp'DDT,

Table 5. Frequency, Mean Values and Standard Deviations ($X \pm SD$), Standard Errors of Means (SEM), Medians, and 95% Confidence Intervals (CI) of Organochlorine Pesticides in Grains

pesticide	frequency, %	$X \pm SD$, $\mu\text{g}\cdot\text{kg}^{-1}$	SEM	median	95% CI	
					lower	upper
HCB	6	0.7 \pm 0.2	0.1	0.6	0.3	1.1
α -HCH	100	1.2 \pm 0.5	0.1	1.2	1.1	1.3
γ -HCH	100	4.4 \pm 1.9	0.3	4.3	3.8	4.9
Σ -HCH		5.6 \pm 2.3	0.3	5.5	4.9	6.3
pp'DDE	100	5.5 \pm 2.9	0.4	5.0	4.7	6.3
op'DDT	100	16.9 \pm 13.1	1.8	12.5	13.2	20.7
pp'DDT	100	49.6 \pm 27.9	3.9	55.0	41.6	57.5
Σ -DDT		72.1 \pm 41.3	5.8	77.0	60.3	83.8

and Σ -DDT) determined in soil, straw, and grain samples, respectively. In the soil samples, the lower frequency corresponded to pp'DDE, which was 12%, which is the most persistent metabolite of insecticide pp'DDT. The phenomenon can be explained by the small quantities of organic matter, which implies limited microbiological activity of monitored soils with low biochemical activity to pesticide metabolism and volatilization from soil. The α -HCH isomer, which is a bioisomerization product of the insecticide Lindane (γ -HCH), was detected in 56% of analyzed soil samples. In environmental conditions, the insecticide Lindane (γ -HCH), from activity of the microorganisms and sunlight, is transformed to the α -HCH isomer (30). From the analyzed soils, the insecticide Lindane (γ -HCH), which arose from agricultural plant protection activities, such as seed dressing, was determined in 74% of samples. The samples studied contained 60% HCB, which is considered to be a ubiquitous environmental pollutant of industrial origin. However, all of the soils presented residues of op'DDT and pp'DDT in 100% of analyzed samples.

In the rye straw samples, the lower frequency (70%) corresponded to HCB, and all remaining pesticides were present in 100% of analyzed samples. The frequency of the determined pesticides can be explained by the adsorption capacity of vegetal materials that adsorb the volatilized pesticides from contaminated agricultural soils, physicochemical characteristics of these contaminants, the historical use of the soils under agricultural activities, and drift from other regions.

In the monitored rye grains, the lower frequency corresponded to HCB with a value of 6%, and all remaining pesticides showed 100% presence in the analyzed samples. The observed grain contamination can be caused by the equilibrium among tissues during phloem distribution of absorbed compounds with an ascendant flow from the roots and their posterior selective accumulation in the grains (13).

The analyses of organochlorine pesticide distribution among the three compartments, soil, straw, and grains, are summarized in **Table 6**. The higher level of HCB (1.2 $\mu\text{g}\cdot\text{kg}^{-1}$) corresponds to the straw, which diminished to 0.7 $\mu\text{g}\cdot\text{kg}^{-1}$ in soil and grains. The elevated concentrations of straw samples can be justified by a greater adsorption capacity of the straw, continuous uptake by aerial tissues, and extended contact with the pesticide vapors that circulate in the environment. In general, the HCB levels determined in the samples studied were low and only 3–5 times superior to the ones established for HCB detection limit of 0.2 $\mu\text{g}\cdot\text{kg}^{-1}$. The smallest concentration (0.6 $\mu\text{g}\cdot\text{kg}^{-1}$) of α -HCH was determined in soil samples, a level that increased from 1.2 $\mu\text{g}\cdot\text{kg}^{-1}$ in grains to 3.4 $\mu\text{g}\cdot\text{kg}^{-1}$ in straw samples. The higher contamination levels in vegetable materials could be caused by their intense adsorption capacity and conjugation reactions that bind circulating pesticides to different organic structures of plant

Table 6. Comparison of Frequencies and Mean Values and Standard Deviations ($X \pm SD$) of Organochlorine Pesticide Levels among Soil, Straw, and Grain Samples

pesticide	soil		straw		grain	
	frequency, %	$X \pm SD, \mu\text{g}\cdot\text{kg}^{-1}$	frequency, %	$X \pm SD, \mu\text{g}\cdot\text{kg}^{-1}$	frequency, %	$X \pm SD, \mu\text{g}\cdot\text{kg}^{-1}$
HCB	60	0.7 ± 0.4	70	1.2 ± 0.4	6	0.7 ± 0.2
α -HCH	56	0.6 ± 0.2	100	3.4 ± 1.1	100	1.2 ± 0.5
γ -HCH	74	1.8 ± 0.9	100	27.3 ± 8.3	100	4.4 ± 1.9
Σ -HCH		2.5 ± 3.3		30.7 ± 9.0		5.6 ± 2.3
pp'DDE	12	1.0 ± 0.2	100	7.8 ± 2.2	100	5.5 ± 2.9
op'DDT	100	16.1 ± 7.6	100	20.4 ± 7.0	100	16.9 ± 13.1
pp'DDT	100	38.0 ± 16.0	100	41.7 ± 12.7	100	49.6 ± 27.9
Σ -DDT		54.2 ± 21.3		63.2 ± 18.2		72.1 ± 41.3

constituents. The differences between straw and grains are significant, indicating the existence of an inner distribution of α -HCH from soil to the grains through the straw. It also indicates that the straw adsorbs additionally volatilized pesticide vapors that surround the growing plants. The lowest concentration of Lindane (γ -HCH), $1.8 \mu\text{g}\cdot\text{kg}^{-1}$, was determined in soil samples, a level that increased from $4.4 \mu\text{g}\cdot\text{kg}^{-1}$ in the grains to a significant $27.3 \mu\text{g}\cdot\text{kg}^{-1}$ in the straw samples. The observed differences among samples studied indicated that the volatilized pesticide vapors are the principal contamination source of growing plants. The contact surface and its adsorption capacity are the principal factors that influence the contamination rate of growing plants (31–34). Analysis of the HCH total (Σ -HCH = α -HCH + γ -HCH) levels revealed that it follows the tendency of Lindane concentrations. The highest contamination corresponded to the straw samples with $30.7 \mu\text{g}\cdot\text{kg}^{-1}$, which decreased significantly to $5.6 \mu\text{g}\cdot\text{kg}^{-1}$ in grains and to $2.5 \mu\text{g}\cdot\text{kg}^{-1}$ in soils. The tendency of Σ -HCH was produced by Lindane, which dominated as the principal contaminant.

Among DDTs, the smaller level of these residues was determined for pp'DDE, $1.0 \mu\text{g}\cdot\text{kg}^{-1}$, in monitored soils. The level ascended to $5.5 \mu\text{g}\cdot\text{kg}^{-1}$ in grains and to $7.8 \mu\text{g}\cdot\text{kg}^{-1}$ in straw. The observed differences in pp'DDE concentrations among growing rye plants are in agreement with the observations of Waliszewski (13) and Leone et al. (32) about the increase of organochlorine pesticide concentrations from soil to the growing plants. The low level of pp'DDE determined in the soils can be due to limited metabolic processes occurring in the soil studied. These are caused by low quantities of organic matter that do not allow microbiological growth, and their activities retard degradation rates of pp'DDT to pp'DDE (35). The op'DDT follows the tendency of pp'DDE, showing $16.1 \mu\text{g}\cdot\text{kg}^{-1}$ in soil, $16.9 \mu\text{g}\cdot\text{kg}^{-1}$ in grains, and $20.4 \mu\text{g}\cdot\text{kg}^{-1}$ in straw. The deposits of contaminated soil particles adsorbed by the plants are considered to be a principal contamination source for the growing plants in polluted fields. The rye roots absorb the organochlorine pesticides disseminated in the soil, which are then distributed to the plant (13). The straw and grains store the op'DDT caused by the adhesion processes according to the organic matter content and to the inner distribution and ascendant circulation. Finally, the pesticides present the equilibrium reached in the rye plants. The higher contamination of the straw could be caused by an additional source. Perhaps it was constituted by atmospheric transport and deposition on the plant surface and by the adhesion of op'DDT vapors volatilized from contaminated soils.

From the organochlorine pesticides studied, the higher concentration corresponded to the insecticide pp'DDT, which reached $38.0 \mu\text{g}\cdot\text{kg}^{-1}$ in the soils, $41.7 \mu\text{g}\cdot\text{kg}^{-1}$ in the straw, and $49.6 \mu\text{g}\cdot\text{kg}^{-1}$ in the grains. For pp'DDT, the stepwise increase of concentrations from the soil to the grains can be

observed. In general, the pp'DDT concentration distribution from the soil to the grains presented significant differences observed for the other compounds studied. The higher concentration of pp'DDT observed in rye grains can be caused by a special copartition coefficient that favors the grain compartment and its constituents, resulting in its important accumulation in the grains. The DDT total (Σ -DDT) levels were influenced by pp'DDT contents and followed the pp'DDT profile in rye plants, indicating $54.2 \mu\text{g}\cdot\text{kg}^{-1}$ in soils, $63.2 \mu\text{g}\cdot\text{kg}^{-1}$ in straw, and $72.1 \mu\text{g}\cdot\text{kg}^{-1}$ in grains.

To evaluate the intensity of metabolic processes and aged sources of DDT enhanced in the agricultural environment, the pp'DDE/pp'DDT ratio was calculated. The obtained values were 0.026 for the soil, 0.187 for the straw, and 0.111 for the grains, indicating low metabolic activities of the soils studied and significantly higher metabolic activities of rye plants. The ratio pointed out that metabolic reactions may occur in the vegetable and on the vegetation surface. Also, recent sources of DDT in this region cannot be excluded (36). This is because DDT is present in agricultural and urban soils and still volatilizes and drifts to other regions, where it deposits on vegetation surfaces.

Comparing the pesticide residue levels between soil and rye plants, the HCHs evidenced their higher concentration in straw, dominated by Lindane (γ -HCH), whereas the DDTs showed their major concentration in rye grains, dominated by pp'DDT. The observed differences can be explained by the elevated volatility of HCH isomers (vapor pressure of γ -HCH = 5.6 mPa) compared to the pp'DDT (vapor pressure = 0.025 mPa) and their higher adsorption possibilities, copartition coefficients, and inner distribution to the elements of growing plants (17, 23, 37). The distribution of more volatile organochlorine pesticides increased their concentrations at higher altitudes, whereas the less volatile are either unrelated or inversely correlated with altitude (24). The chemical partition between air and plant surfaces influences the storage and distribution in soluble cuticular lipids of the plant. The subsequent chemical exchange between air and vegetation considers the power of volatile constituents, lignins and tannins, which may influence the lipophilic nature of plants.

For each sample group, to determine the statistical significance of differences among organochlorine pesticide levels determined in the samples studied, the results were paired to calculate circumstantial correlation expressed by two-tailed p value and Pearson correlation coefficient (r). The calculated results are provided in Table 7. For HCB the differences between soil and straw means are significant ($p = 0.001$ and $r = 0.065$), signifying bad correlation, whereas the relationship between straw and grain was not significant ($p = 0.395$). For α -HCH, the calculated differences among means were significant ($p = 0.001$) and the correlation coefficients indicated a lack of correlation among soil, straw, and grains and the

Table 7. Results of Comparison Study among Soil, Straw, and Grains of Rye Plant Organochlorine Pesticide Contents [Two-Tailed p Value, Pearson Correlation Coefficient (r), and Mean Differences]

pesticide/ sample	$\mu\text{g kg}^{-1}$		
	two-tailed p value ^a	r	mean difference
HCB			
soil – straw	0.001***	0.065	-0.001
straw – grain	0.395		0.001
α -HCH			
soil – straw	0.001***	-0.356	-0.003
straw – grain	0.001***	0.242	0.002
soil – grain	0.001***	0.005	0.001
γ -HCH			
soil – straw	0.001***	0.069	-0.026
straw – grain	0.001***	0.139	0.023
soil – grain	0.001***	0.321	-0.003
Σ -HCH			
soil – straw	0.001***	-0.440	-0.029
straw – grain	0.001***	0.165	0.025
soil – grain	0.001***	0.017	0.003
pp'DDE			
straw – grain	0.001***	0.052	0.002
op'DDT			
soil – straw	0.006***	-0.002	-0.004
straw – grain	0.136	-0.171	0.003
soil – grain	0.676	0.099	0.001
pp'DDT			
soil – straw	0.204	-0.017	-0.004
straw – grain	0.088	-0.111	-0.008
soil – grain	0.008***	-0.191	-0.012
Σ -DDT			
soil – straw	0.028***	-0.021	-0.009
straw – grain	0.191	-0.123	0.009
soil – grain	0.006***	0.144	-0.018

^a*** indicates significant differences at the 5% level.

individual character of deposition of α -HCH in rye plants. The comparison done for Lindane (γ -HCH), which calculates differences between the mean concentration of the insecticide manifested for the three compartments studied (soil, straw, and grains), contains different quantities of Lindane and the means are different ($p = 0.001$). The Pearson correlation coefficients were low, expressing an absence of correlation among sample groups. The same tendency was revealed for total HCH (Σ -HCH), showing $p = 0.001$ and lower (r) values. A lack of correlation between each sample group of rye grown in the monitored fields was manifested.

The mean DDT concentrations in the samples studied presented different behaviors. For pp'DDE, relationships between only straw and grains were possible to calculate, indicating significant differences, $p = 0.001$, $r = 0.052$, and no correlation. The op'DDT showed a $p = 0.006$ value and differences between mean concentrations for soil and straw comparison and a lack of differences between straw and grain and between soil and grain groups. The calculated Pearson correlation coefficient suggested that the three sample groups are different and that there is no correlation among them. The comparison of mean pp'DDT concentrations revealed only differences between soil and grain sample comparisons ($p = 0.008$), whereas all Pearson correlation coefficients are negative, indicating a lack of correlation among the studied compartments of the agricultural environment. The DDT total (Σ -DDT) showed $p = 0.028$ for soil and straw and $p = 0.006$ for soil and grain comparison and statistical differences between means, and low Pearson correlation coefficients demonstrated no correlation between soil and straw and soil and grain Σ -DDT concentrations. The comparison of straw and grain mean concentrations

indicated $p = 0.191$, and there were no statistical differences among means. It also pointed to a different behavior in the residues, expressed by the negative Pearson correlation coefficient ($r = -0.123$). The data in **Table 7** reveal the absence of uniform transport processes of organochlorine pesticides occurring in field conditions in growing rye plants from the soil to the grains.

In conclusion, the contamination of plants that grow in soils with pesticide residues is caused principally by volatilization and adsorption processes and thereafter by the uniform distribution through the ascendant circulation system. Pesticides can migrate through diverse processes such as volatilization, mobilization with soil particles, and inner ascendant transport in the plant. The pesticides, present in the air, were adsorbed on plant surfaces, whereas, from the soil, they are mobilized during the active inner transport in the rye plants, which permits their specific accumulation according to the equilibrium reached in the grains. Thus, soil and vegetation are reservoirs and indicators for organochlorine pesticide contamination. Moreover, they constitute vectors through which these chemicals may enter terrestrial food chains (24). These conclusions are in accordance with the previous observations of Waliszewski (13) and Leone et al. (32), which indicate that the concentration distribution of organochlorine pesticides varied in growing plants that were grown in contaminated soils. Moreover, their levels depend on the physical–chemical properties of the compound and biochemical constitution of the plant. The study verified organochlorine pesticide presence in the Mexican agriculture environment. The presence of these organochlorine pesticides does not originate from recent plant protection activities because they are banned. The contaminated soils indirectly constitute a pollution source for plant consumers and retard the expected decrease in organochlorine pesticide concentrations in the air.

LITERATURE CITED

- Bro-Rasmussen, F. Contamination by persistent chemicals in food chain and human health. *Sci. Total Environ.* **1996**, *188*, 45–60.
- Bidleman, T. F.; Leone, A. D. Soil-air exchange of organochlorine pesticides in the Southern United States. *Environ. Pollut.* **2004**, *128*, 49–57.
- Simonich, S. L.; Hites, R. A. Importance of vegetation in removing polycyclic aromatic hydrocarbons from the atmosphere. *Nature* **1994**, *370*, 49–51.
- McLachlan, M. S. A simple model to predict the accumulation of PCDD/Fs in agricultural food chain. *Chemosphere* **1997**, *34*, 1263–1276.
- Douben, P. E. T.; Alcock, R. E.; Jones, K. C. Congener specific transfer of PCDD/Fs from air to cow's milk: an evaluation of current modeling approaches. *Environ. Pollut.* **1997**, *95*, 333–344.
- Wagrowski, D. M.; Hites, R. A. Polycyclic aromatic hydrocarbon accumulation in urban, suburban, and rural vegetation. *Environ. Sci. Technol.* **1997**, *31*, 279–282.
- Smith, K. E. C.; Green, M.; Thomas, G. O.; Jones, K. C. Behavior of sewage sludge-derived PAHs on pasture. *Environ. Sci. Technol.* **2001**, *35*, 2141–2150.
- McCrary, J. K.; McFarlane, C.; Gander, L. K. The transport and fate of 2,3,7,8-TCDD in soybean and corn. *Chemosphere* **1990**, *21*, 359–376.
- Wild, S. R.; Jones, K. C. Studies on the polynuclear aromatic hydrocarbon content in carrots (*Daucus carota*). *Chemosphere* **1991**, *23*, 243–251.
- Waliszewski, S. M. Residues of Lindane, HCH isomers and HCB in the soil after Lindane application. *Environ. Pollut.* **1993**, *82*, 289–293.

- (11) Schroll, R.; Bierling, B.; Cao, G.; Dorfler, U.; Lahaniati, M.; Langenbach, T.; Scheunert, I.; Winkler, R. Uptake pathways of organic chemicals from soil by agricultural plants. *Chemosphere* **1994**, *28*, 297–303.
- (12) Nakamura, M.; Suda, R.; Matsueda, T.; Karokawa, Y.; Takada, S.; Fukamachi, K. Uptake of PCDDs and PCDFs by radish plant. *Organohalogen Compd.* **1995**, *24*, 497–500.
- (13) Waliszewski, S. M. HCH isomers and HCB residues in root vegetables after the application of Lindane (γ -HCH) to the soil. *Rev. Int. Contam. Ambient.* **1995**, *11*, 13–19.
- (14) Nerin, C.; Polo, T.; Domeño, C.; Echarri, I. Determination of some organochlorine compounds in the atmosphere. *Int. J. Environ. Anal. Chem.* **1996**, *65*, 83–94.
- (15) Trapp, S.; Matthies, M. Generic one-compartment model for uptake of organic chemicals by foliar vegetation. *Environ. Sci. Technol.* **1997**, *29*, 22333–2338.
- (16) Smith, K. E. C.; Thomas, G. O.; Jones, K. C. Seasonal and species differences in the air-pasture transfer of PAHs. *Environ. Sci. Technol.* **2001**, *35*, 2156–2165.
- (17) Waliszewski, S. M.; Infanzon, R. M. Diferencias en concentración de plaguicidas organoclorados persistentes en suelo, paja y granos de trigo. *Rev. Int. Contam. Ambient.* **2003**, *19*, 5–11.
- (18) Edwards, N. T. Polycyclic aromatic hydrocarbons (PAH's) in the terrestrial environment—a review. *J. Environ. Qual.* **1983**, *12*, 427–441.
- (19) Jantunen, L. M. M.; Bidleman, T. F.; Harner, T.; Parkhurst, W. J. Toxaphene, chlordane, and other organochlorine pesticides in Alabama air. *Environ. Sci. Technol.* **2000**, *34*, 5097–5105.
- (20) Chrostowski, P. C.; Foster, S. A. A methodology for assessing congener-specific partitioning and plant uptake of dioxins and dioxin-like compounds. *Chemosphere* **1996**, *32*, 2285–2304.
- (21) Schweizer, A.; Turgut, C.; Hurler, K. Untersuchung zur Verflüchtigung von Pflanzenschutzmitteln von Pflanzenoberflächen in Abhängigkeit von Temperatur und relativer Luftfeuchte. *Z. Pflanzenkrankh. Pflanzenschutz.* **2000**, *17*, 791–798.
- (22) Waymann, B.; Rüdell, H. Influence of air velocity, application dose, and test area size on the volatilization of lindane. *Int. J. Environ. Anal. Chem.* **1995**, *58*, 371–378.
- (23) Rüdell, H. Volatilization of pesticides from soil and plant surfaces. *Chemosphere* **1997**, *35*, 143–152.
- (24) Davidson, D. A.; Wilkinson, A. C.; Blais, J. M.; Kimpe, L. E.; McDonald, K. M.; Schindler, D. W. Organic cold-trapping of persistent organic pollutants by vegetation in mountains of Western Canada. *Environ. Sci. Technol.* **2003**, *37*, 209–215.
- (25) Cochran, W. G. *Sampling Techniques*; Wiley: New York, pp 28–63.
- (26) Waliszewski, S. M.; Szymczynski, G. A. Inexpensive, precise method for the determination of chlorinated pesticide residues in soil. *J. Chromatogr.* **1985**, *321*, 480–483.
- (27) Waliszewski, S. M.; Szymczynski, G. A.; Rogowska, Z. Rapid and low-cost method for monitoring determination of selected chlorinated pesticides in feed mixtures. *Bull. Environ. Contam. Toxicol.* **1985**, *34*, 518–526.
- (28) Waliszewski, S. M.; Szymczynski, G. A. Determination of selected chlorinated pesticides, bound and free in human semen. *Arch. Environ. Contam. Toxicol.* **1983**, *12*, 577–580.
- (29) Waliszewski, S. M.; Szymczynski, G. A. Determination of phthalate esters in human semen. *Andrologia* **1990**, *22*, 69–73.
- (30) Steinwandter, H. Zum Lindanmetabolismus und Pflanzen. I. Bildung von α -HCH. *Chemosphere* **1976**, *4*, 221–225.
- (31) Walker, K.; Vallero, D. A.; Lewis, R. G. Factors influencing the distribution of Lindane and other hexachlorocyclohexanes in the environment. *Environ. Sci. Technol.* **1999**, *33*, 4373–4378.
- (32) Leone, A. D.; Amato, S.; Falconer, R. L. Emission of chiral organochlorine pesticides from agricultural soils in the cornball region of the U.S. *Environ. Sci. Technol.* **2001**, *35*, 4592–4596.
- (33) Gonzalez, M.; Miglioranza, K. S. B.; Alizpun, J. E.; Moreno, V. J. Occurrence and distribution of organochlorine pesticides (OCPs) in tomato (*Lycopersicon esculentum*) crops from organic production. *J. Agric. Food Chem.* **2003**, *51*, 1353–1359.
- (34) Gonzalez, M.; Miglioranza, K. S. B.; Alizpun, J. E.; Moreno, V. J. Organochlorine pesticides residues in leek (*Allium porrum*) crops grown on untreated soils from an agricultural environment. *J. Agric. Food Chem.* **2003**, *51*, 5024–5029.
- (35) Miglioranza, K. S.; Aizpun de Moreno, J. E.; Moreno, V. J. Dynamics of organochlorine pesticides in soils from southeastern region of Argentina. *Environ. Toxicol. Chem.* **2003**, *22*, 212–217.
- (36) Simonich, S. L.; Hites, R. A. Organic pollutant accumulation in vegetation. *Environ. Sci. Technol.* **1995**, *29*, 2905–2914.
- (37) Tomlin, C. D. S. *The Pesticide Manual*, 12th ed.; British Crop Protection Council: Surrey, U.K., 2000; pp 254–256, 502–504.

Received for review May 21, 2004. Accepted August 30, 2004.

JF040250P