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DDT and HCH Isomer Levels in Soils, Carrot Root and Carrot Leaf Samples

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Abstract Agricultural cultivation assists organochlorine pesticide migration from contaminated soils to growing plants. This phenomenon is caused by retention processes that modify volatile pesticide exchange between soil, air and plants. The aim of the study was to monitor organochlorine pesticide (HCB, α– and γ-HCH, pp′DDE, op′DDT, pp′DDT) levels and compare these concentrations in soil, carrot roots and carrot leaves. Fifty soil samples, 50 carrot root and 50 carrot leaf samples were taken from the same fields and analyzed by GLC-ECD. The results reveal organochlorine pesticide diffusion from agricultural soils to growing carrot plants and their vapors adsorbtion by leaves. Within the carrot plant, organochlorine pesticides accumulate especially in carrot root peel, 3–7 times more than in root flesh.

Keywords DDT · HCH · Carrots · Soil

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Agriculture activities have modified retention processes of organochlorine pesticides, accelerating volatile pesticide exchange among soil, air and plants (Bro-Rasmussen 1996; Bidleman and Leone 2004). The visual consequence of this phenomenon is the ingress of organochlorine pesticides into growing plants and the persistence of their residues. Organochlorine pesticide residues in the air can exist as gases, or are bound to suspended particles (Jantunen et al. 2000). Furthermore, suspended particles from contaminated soils can be transported by wind and rain to be subsequently captured by growing leaves. The dry deposition of particles suspended in the air onto plant surfaces involves interception, impaction, sedimentation and diffusion processes. Lipophilic organochlorine pesticides that permeate the cuticle, can pass through the epidermis to the leaf interior with relative ease (Reiderer 1990).

Significant differences among plant species have been observed in pesticide absorption as a result of contact with soil particles and vapors (Smith and Jones 2000). The rough or hairy leaf surfaces are more efficient at collecting pesticides through the leaf-air boundary layer. The largest adsorption occurs in broad-leaf species growing close to the ground (Pinder et al. 1991). Organochlorine pesticides, being semivolatile compounds, volatilize from the soil and their concentration in the atmosphere increasing closest to the plant (Simonich and Hites 1994). Direct contact between soil particles and plant surfaces is a significant factor in uptake pathways (Collins et al. 2006). Growing plants can absorb organochlorine pesticide through their roots and adsorb particles from soils.

Organochlorine pesticides such as hexachlorobenzene (HCB), isomers of hexachlorocyclohexanes (HCHs) and isomers of dichlorodiphenyltrichloroethane (DDT) have been applied since 1940s for plant protection and sanitation throughout the world. Their use permitted plant protection,

harvest assurance and the combat of vector-transmitted diseases. Beginning in 1990, DDT use was restricted to sanitary action to combat malaria and since 1999 in Mexico it has been banned. Lindane (γ-HCH) has been permitted in restricted areas in Mexico, but only as a dresser for seed protection. The common characteristic of these pesticides is their persistence in the environment and their bioconcentration in organism lipid compartments.

The aim of this work was to determine the concentrations of persistent organochlorine pesticides (HCB, α, γ-HCH, pp′DDE, op′DDT, pp′DDT) in agricultural soils and carrot plants (roots and leaves), gain evidence about their distribution in soil, roots and leaves and to determine the concentration gradient between the whole root, root peel and root flesh.

Materials and Methods

Before the 2006 harvest, soils and carrot plants (roots with leaves) were randomly sampled from different fields located in the states of Puebla and Mexico in the Mexican Republic. DDT and Lindane had not been applied in these fields for at least 15 years. However, Lindane has been used in some cases as a seed dresser for seed protection against insects during storage prior to sowing.

Sampling sites were randomly selected; fifty soil samples were taken with an Engler stick (5 cm i.d.) to a depth of 10 cm, according to the method for total surface cover. The homogenized sample (approximately 500 g) was stored in a glass jar with a cover and transported to the laboratory. Soil samples were then dried for 2–3 days under laboratory ambient conditions and sifted through a 0.2 mm^2 sieve to obtain homogeneous dried samples that were stored in glass jars at −20°C until analyzed. Fifty carrot plant samples were taken, each one consisting of 20 entire plants pulled from the ground in the same fields where soil samples had also been taken. The plants were wrapped with paper in situ and transported to the laboratory, where the carrot plants were washed in a stream of tap water to remove all soil particles, dried with filter paper and separated into roots and leaves. They were then homogenized with a Hobart homogenizer and stored in glass jars in the freezer at −20°C until analyzed.

Organochlorine pesticide determinations were performed according to previously described methods for soil, carrot root and leaf samples (Waliszewski et al. 2004) using a Varian 3400CX gas chromatograph with an electron capture detector. To evaluate analytical method quality, a fortification study with 10 repetitions at the 1–5 μgkg^{-1} level was performed with the following pesticides: HCB, α-HCH, γ-HCH, pp′DDE, op′DDT and pp′DDT. The results of mean recovery for soil samples went from 92.3% to 97.2%; for carrot roots from 90.6% to 98.1% and for carrot leaf from 92.1% to 98.9%; with a standard deviation of 2.8–8.6, all this indicating an excellent recovery of the organochlorine pesticides studied from fortified samples.

Minitab 12 statistic software was used to evaluate statistically the mean concentration (X), the standard deviation of the mean concentration (SD), standard error of the mean (SEM), median, and the ranges of concentrations for each organochlorine pesticide in soil, carrot root and carrot leaf samples. To determine the quality of population mean concentrations among soils, carrot roots and carrot leaves, paired results were evaluated through two sample t-tests and 95%CI; additionally, a one-way analysis of variance (ANOVA) was carried out, with a post hoc Tukey comparison test ($p \leq 0.05$) on those cases showing significant differences, in order to pinpoint the conditions involved.

Results and Discussion

The samples were analyzed to determine the distribution of organochlorine pesticide residues in soil and carrot plants. The soils and plants had been exposed to environmental pollution, due to the past use of these pesticides for plant protection, as well as in sanitary vector combat action. The principal source of these residues is considered to be their deposit in agricultural soils. They are subsequently adsorbed by the roots and when volatilized, are adsorbed by the leaves of growing plants (Bidleman and Leone 2004). Chemical analyses were carried out to determine soil type as well as its adsorptive metabolic capacity, which plays a predominant role in the retention of organochlorine pesticides (Chen et al. 2007; Luo et al. 2006). The results led to a classification of the soil as sandy with a moderate quantity of organic matter which limited pesticide metabolic capacity.

In soil samples (Table 1), of the organochlorine pesticide determined, the lowest frequency (40%) and mean level (5.3 μgkg^{-1}) corresponded to pp′DDE, the metabolite of insecticide pp′DDT. This result indicates weak metabolic capacity in the monitored soils, resulting in a lower pp′DDE frequency in the monitored area. The α-HCH isomer was detected at 0.7 μgkg^{-1} in 66% of analyzed soil samples. Its origin can be explained by the bioisomerization of Lindane (γ-HCH) from agricultural plant protection activities, especially seed dressing. HCB, considered an industrial pollutant, was detected at 0.8 μgkg^{-1} in 76% of the analyzed soil samples. Insecticide pp′DDT residues (16.1 μgkg^{-1}) and its isomer op′DDT (5.3 μgkg^{-1}) were determined in all analyzed soil samples.

In carrot root samples (Table 2), the lowest frequency (40%) and mean level (5.5 μgkg^{-1}) was for pp′DDE,

Table 1 Frequency (%), mean levels and standard deviation (X ± SD), standard errors of means (SEM), median and ranges of organochlorine pesticides concentrations (μgkg^{-1}) in soil ($n = 50$)

Pesticide	Frequency	X ± SD	SEM	Median	Ranges
HCB	76	0.7 ± 0.3	0.1	0.7	0.2–1.5
α-HCH	66	0.8 ± 0.5	0.1	0.7	0.2–2.2
γ-HCH	96	3.1 ± 1.9	0.4	2.6	1.0–7.2
Σ-HCH		3.5 ± 2.4	0.4	2.8	0.7–8.3
pp′DDE	40	5.3 ± 1.5	0.4	5.6	2.0–7.1
op′DDT	100	16.1 ± 6.8	1.2	15.4	4.9–31.0
pp′DDT	100	52.2 ± 19.6	3.6	47.7	22.9–99.2
Σ-DDT		70.5 ± 27.7	5.1	66.5	31.8–136.1

Table 2 Frequency (%), mean levels and standard deviation (X ± SD), standard errors of means (SEM), median, and ranges of organochlorine pesticides concentrations (μgkg^{-1}) in carrot roots ($n = 50$)

Pesticide	Frequency	X ± SD	SEM	Median	Ranges
HCB	76	0.8 ± 0.4	0.1	0.8	0.3–1.8
α-HCH	66	0.9 ± 0.5	0.1	0.8	0.2–2.5
γ-HCH	100	3.3 ± 2.2	0.4	2.9	0.9–7.6
Σ-HCH		3.9 ± 2.7	0.5	3.2	1.0–9.0
pp′DDE	40	5.5 ± 1.3	0.4	5.6	2.9–7.2
op′DDT	100	17.2 ± 7.5	1.4	16.3	5.8–33.2
pp′DDT	100	52.1 ± 20.4	3.7	45.7	22.6–108.3
Σ-DDT		71.0 ± 28.9	5.3	64.3	32.6–45.3

followed by α-HCH (66% and 0.9 μgkg^{-1}) and HCB (76% and 0.8 μgkg^{-1}). All carrot root samples analyzed revealed Lindane at 3.3 μgkg^{-1}, op′DDT at 17.2 μgkg^{-1} and pp′DDT at 52.1 μgkg^{-1}. Thus, carrot roots absorb lipophilic organochlorine pesticides from the soils and this accumulates in their vegetal tissues, depending on their concentrations in the soil.

Analyzed carrot leaves (Table 3) showed the same frequency of organochlorine pesticides as carrot root samples, but with varying mean levels: HCB 0.8 μgkg^{-1}, α-HCH 0.9 μgkg^{-1}, Lindane 3.9 μgkg^{-1}, pp′DDE 8.2 μgkg^{-1}, op′DDT 22.0 μgkg^{-1} and pp′DDT 67.1 μgkg^{-1}.

The lipophilic organochlorine pesticides can be taken up by plant roots through soil water phases as passive or diffuse processes and adsorbed as vapors. The uptake consists of balancing concentrations between the aqueous parts of the plant roots and the surrounding concentrations and sorption into root lipids and walls (Simonich and Hites 1994). These routes include penetration of organochlorine pesticides into the roots and the subsequent translocation through xylem (Schroll et al. 1994), direct vapor adsorption on leaves (Trapp and Matthies 1997) and direct deposition onto plant surfaces, either wet or dry. The uptake increases

Table 3 Frequency (%), mean levels and standard deviation (X ± SD), standard errors of means (SEM), median, and ranges of organochlorine pesticides concentrations (μgkg^{-1}) in carrot leaves ($n = 50$)

Pesticide	Frequency	*X* ± SD	SEM	Median	Ranges
HCB	90	0.8 ± 0.3	0.1	0.8	0.2–1.5
α-HCH	66	0.9 ± 0.5	0.1	0.7	0.2–2.6
γ-HCH	100	3.9 ± 2.3	0.4	2.4	0.9–6.9
Σ-HCH		3.6 ± 2.4	0.4	3.4	0.9–8.6
pp′DDE	40	8.2 ± 1.2	0.3	8.2	6.3–9.9
op′DDT	100	22.0 ± 11.0	2.0	19.4	5.8–33.2
pp′DDT	100	67.1 ± 26.9	4.9	60.6	24.8–48.3
Σ-DDT		92.4 ± 38.3	7.0	80.5	39.5–96.4

when lipophilic properties of organochlorine compound increase and are influenced by chemical composition, especially the plant lipid content (Schwab et al. 1998; Wild and Jones 1992).

Gaseous uptake from ambient air has been demonstrated to be the main uptake pathway into plant foliage for a variety of pesticides. The organic vapor bioconcentration inside leaves reveals relationships between different leaf/air bioconcentration factors (Kamp and McLachlan 1997). Since lipophilic pesticides tend to partition to leaf lipids, differences in the lipid content of plant foliage would seem the most reasonable explanation for this behavior. For foliar uptake models, the leaf lipid content represents the most sensitive plant characteristic for the uptake of lipophilic pesticides (Muller et al. 1994). Variability in extractable lipid contents could explain the interspecies variability in leaf/air bioconcentration factors for a different of semivolatile pesticides, where gaseous uptake was the dominant uptake process. Moreover, evaluating interspecies variability in leaf/air bioconcentration factors needs to be considered not only for lipid quantity but also for lipid quality presented in the plant (Kamp and McLachlan 1997; Bohme et al. 1999).

The distribution of organochlorine pesticide residues in the three compartments; soil, carrot root, and carrot leaves indicate that the mean HCB level in the soil increased from soil to carrot roots and leaves in the order of 0.7–0.8 μgkg^{-1} ($p > 0.05$; ns). In general, HCB levels in the study were low and only 3 times higher than the HCB detection limit of 0.2 μgkg^{-1}. The same behavior was presented in the α-HCH isomer, revealing 0.8 μgkg^{-1} in soil and 0.9 μgkg^{-1} in carrot root and carrot leaf samples. The lack of significant differences ($p > 0.05$) in its concentrations among the three compartments is due to the low levels that circulate in the soil and air, leading to low contamination in growing plants. The Lindane (γ-HCH) insecticide level increased from 3.1 μgkg^{-1} in soil, to 3.3 μgkg^{-1} in roots and to 3.9 μgkg^{-1} in carrot leaves. The non-significant

differences ($p > 0.05$) observed between mean concentrations of Lindane signified the presence of its residues in cultivated soils, its absorption across the root lipid bilayer, its route through transmembrane channels in growing roots and the uniform redistribution of these residues within the plant (Mattina et al. 2000, 2007).

Among the DDTs, the limited size of these residues was seen in pp′DDE: 5.3 μgkg^{-1} in soil, 5.5 μgkg^{-1} in carrot root and 8.2 μgkg^{-1} in carrot leaf samples. The significant differences ($p < 0.05$) observed in pp′DDE concentrations between soil-leaf and root-leaf samples verify the adsorption and volatilization processes from soil to roots and leaves as being significant in the crossover of pesticide residues in the agricultural environment. The op′DDT isomer showed levels of 16.1 μgkg^{-1} in soil, 17.2 μgkg^{-1} in carrot root, and 22.0 μgkg^{-1} in carrot leaf samples. Lipophilic carrot roots absorb lipophilic op′DDT pesticide from the soil and distribute it in roots and leaves. The higher levels ($p < 0.05$) observed in leaves stem, originates from the additional adhesion processes of volatilized op′DDT vapors and contaminated soil particles adsorbed by growing plant leaves. The highest concentrations for all analyzed organochlorine pesticides were found for insecticide pp′DDT, increasing from 52.2 μgkg^{-1} in soil and 52.1 μgkg^{-1} in carrot roots, to 67.1 μgkg^{-1} in carrot leaves. The significant ($p < 0.05$) increase of concentrations from soil and carrot roots to leaves is due to the movement of organochlorine pesticides from contaminated soil to lipophilic roots, a special copartition of absorbed pp′DDT in the whole plant and the cuticular composition of carrot leaves, which favor lipophilic adsorption of circulating air-volatilized pp′DDT. Total DDT levels (pp′DDE + op′DDT + pp′DDT = Σ-DDT) were influenced by high pp′DDT insecticide levels: 70.5 μgkg^{-1} in soils, 71.0 μgkg^{-1} in carrot root, and 92.4 μgkg^{-1} in carrot leaves, the latter being significantly higher ($p < 0.05$) compared to soil and root samples.

To identify quality and aging of the contamination source, the relationship of pp′DDT to its metabolite pp′DDE were calculated. The relationship for all environmental compartments was high: 9.85 for soil, 9.47 for carrot roots and 8.18 for carrot leaves, indicating the latent presence and domination of insecticide pp′DDT in the agricultural environment, its permanent crossover from the soil to the growing plants and adsorption of volatilized residues by leaves growing near the soil.

To determine if the organochlorine pesticides accumulate in edible parts of carrot roots, one sample of carrot roots was taken and the roots were peeled according to the common treatment carried out for human consumption (Table 4). Organochlorine pesticide residues are taken up by carrot roots from soil and subsequently translocated throughout plant tissue with specific bioaccumulation. Due to the lipophility of all organochlorine pesticides and the specific carrot root lipid content, the highest residue levels were detected in peel. Calculating the concentration factor, the pesticide concentrations, peels versus whole carrot roots were 3.1–7.0 times higher in the peel and compared peels versus peeled roots were 21–35 times higher, a result that agrees with those previously obtained by Trapp (2002).

Table 4 Comparison of mean organochlorine pesticide concentrations (μgkg^{-1}) in whole carrot roots, peeled carrot roots and carrot root peel

Pesticide	Whole carrot roots	Peeled carrot roots	Peel	Concentration factor	
				Peels versus Peeled roots	Peels versus Whole roots
HCB	0.8	0.1	3.2	4.0	32
α-HCH	0.7	0.1	2.2	3.1	22
γ-HCH	3.9	1.1	22.9	5.7	21
Σ-HCH	4.6	1.2	25.1	5.5	21
pp′DDE	5.8	1.6	38.8	6.7	24
op′DDT	16.9	3.4	118.3	7.0	35
pp′DDT	54.2	13.2	330.6	6.1	25
Σ-DDT	70.5	18.2	487.7	6.9	27

The conclusion of this monitoring study is that carrot plants grow in agriculture soils that contain organochlorine pesticide residues. These residues are mobilized via a soil-to-plant pathway. Contamination of carrots occurs through absorption from contaminated soil processes and thereafter by the distribution within the plant tissues by an ascendant circulation system. Additional contamination comes from the adsorption of volatilized pesticide vapors and contaminated soil particles. Thus, soil and vegetation are reservoirs of organochlorine pesticide contamination that constitute vectors through which these pesticides may enter the human food chain (Davidson et al. 2003). These results indicate that growing plants can contain organochlorine pesticide residues and their concentrations depend on the specific biochemical composition of the plant and its bioaccumulation efficacy.

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