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Occurrence and Distribution of Organochlorine Pesticides (OCPs) in Tomato (*Lycopersicon esculentum*) Crops from Organic Production

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Organochlorine pesticides (OCPs) were quantified by GC-ECD in tomato (*Lycopersicon esculentum*) during a vegetation period. Plants were harvested at 15, 60, and 151 days after seed germination. Leaves, stem, roots, and fruit (peel and flesh) were analyzed separately. The results showed that tomato plants were able to accumulate OCPs from soils, and a trend to reach the equilibrium among tissues at mature stages was also observed. Endosulfans comprised the main OCP group, probably due to its spray during summer months in the surrounding areas. Banned pesticides such as DDTs, heptachlor, and dieldrin were found. OCPs levels in the fruit were below the maximum residues limits (MRL) considered by the *Codex Alimentarius*. DDE/DDT and α-/γ-HCH ratios of <1 would indicate recent inputs of DDT and lindane in the environment. The occurrence of OCPs in the study farm, where agrochemicals have never been used, is a result of atmospheric deposition of those pesticides.

KEYWORDS: Organochlorine pesticides; tomato (*Lycopersicon esculentum*); vegetation period; organic production; plant uptake

INTRODUCTION

Organochlorine pesticides (OCPs) such as DDT ([1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane]), chlordane, dieldrin, and heptachlor are included in the group of persistent organic pollutants (POPs). They are a class of compounds of particular concern in the environment due to their recalcitrance in natural solids, global transport, distribution, and toxicity (*1*). POPs have been linked to carcinogenicity and endocrine disruption in mammals, and concerns over toxicity are exacerbated by pollutant hydrophobicity, which results in bioaccumulation in fatty tissues and biomagnification through food chains (*2*). Consumption of plants or plant products such as vegetables, fruits, and grains forms a major part of the food consumption of human beings and cattle. Given that vegetation is the link among the atmosphere, soil, and human food supply, contamination of plants will have a great influence on the total daily intake of a substance (*3*). Thus, it is important to understand those processes by which pollutants enter into this environmental compartment. Plants may accumulate OCPs via different pathways, namely (1) adsorption to the root surface, (2) root uptake and transport to the shoot, (3) absorption of soil volatilized OCPs by aerial plant parts, (4) foliage and fruits contamination by soil particles, and (5) deposition of airborne OCPs (*4*). When trying to predict concentrations in plant tissues, one will be confronted with several problems related to the variety of plant species and the heterogeneity in this group with regard to physiology, rooting depth, leaf area, growth period, and so on (*5*, *6*).

For several years, this laboratory has investigated the environmental fate of OCPs in the Los Padres Lake watershed (Buenos Aires province, Argentina), which is characterized primarily by rural and small-case farming land use. We have reported high OCPs levels in agricultural soils where these pollutants have been used during the preceding 20 years. Moreover, pesticides such as DDT, lindane (γ-hexachlorocyclohexane), and heptachlor were detected in potatoes and carrots grown in those soils (*7*, *8*). Therefore, the aim of the present work was to study the occurrence and distribution of OCPs during the vegetation period of organic tomatoes growing on a farm situated in the Los Padres Lake watershed. Tomato was selected for this study because it is widely distributed throughout the study area and due to the economic importance of its crop.

MATERIALS AND METHODS

Field Plot. Tomato (*Lycopersicon esculentum* of the family Solanaceae) plants were growing in the southeastern region of Buenos Aires province, Argentina (37° 55′−38° 02′ S; 57° 34′− 57° 33′ W) in a local farm where agrochemicals have never been used. The growing location is situated in the Los Padres Lake watershed, and it is included

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Table 1. Moisture Content, Organic Matter Content (OM), Particle Size Distribution, and Total Organochlorine Pesticides (OCPs) Concentration (Mean ± Standard Deviation) in Bulk Soil and Rhizosphere[a]

				particle size distribution (%)			
soil	depth (cm)	water (%)	OM (%)	clay	silt	sand	total OCPs (ng/g of dw)
PA	0–15	23.5 ± 0.6	8.8	21.2	34.8	44	36.4 ± 1.6
PB	0–15	21.7 ± 0.8	5.1	21.6	35.6	42.8	20.3 ± 15.5
RP_2	0–15	18.2 ± 1.6	5.3	NA	NA	NA	6.2 ± 3.6
RP_3	0–30	23.4 ± 1	5.9	NA	NA	NA	12.7 ± 1.2

[a] PA, plot A; PB, plot B; RP2, rhizosphere from period 2 plants; RP3, rhizosphere from period 3 plants; dw, dry weight; NA, not analyzed; rhizosphere particle size distribution was assumed to be similar to those of the corresponding bulk soil (plot B).

in an important agricultural belt in the northwestern area of the body of water. The annual average temperature was 13.5 °C, the minimum mean in July was 7 °C, and the average high in January was 19.2 °C. The soil is described as typical Argiudoll (Centeno Series) (*9*). Beginning in October 2000 tomatoes were seeded in a portion of the field plot (A) enriched with pine needles and transplanted in November to another plot (B), without aggregates, until the harvest (March 2001). The plots were weeded and watered as necessary.

Soil Matrix. Two operationally defined soil samples differing in proximity to plant roots were collected. Bulk soil samples were collected at harvest at a distance of 1 m from vegetation. A single transect was set in each plot, and three equidistant sites were sampled. One depth was selected in plot A (0−15 cm), and two (0−15 and 15−30 cm) were selected for plot B. The rhizosphere soil was defined as the soil that did not fall off the roots at harvest. Soil samples were frozen and stored at −20 °C until required for analysis. Moisture, organic matter (OM), and texture (clay, silt, and sand content) were determined in different soil subsamples. Water content was determined by constant-weight drying in an oven at 110 °C. Total organic matter was determined by wet oxidation using the Walkley−Black method (*10*). Particle size distribution was determined by the pipet method (*11*); three sizes were estimated: <0.002 mm (clay), 0.002−0.062 mm (silt), and >0.062 (sand). In the case of the rhizosphere particle size content, it was assumed to be similar to that of the corresponding bulk soil.

Vegetation Matrix. Tomato plants were harvested at three different time periods: 15 and 60 days after seed germination, periods 1 and 2, respectively. The third period was when edible tissues were at marketable size (151 days, period 3). Three plants were harvested in each period, and each plant was analyzed individually. Root, stem, leaves, and fruits (peel and flesh) were separated. The rhizosphere soil was removed from roots with a fine-bristle toothbrush (*12*). Tissue samples were frozen and stored at −20 °C until required for analysis. Water content was determined by constant-weight drying in an oven at 60 °C (*12*).

Root bioconcentration factors (RBF) were calculated as the mean concentration in root tissues divided by the mean concentration in bulk soil, both expressed on a dry weight basis.

Analytical Methods. Samples were homogenized using a blender jar. Subsamples (of approximately 5 and 2 g for soils and plant tissues, respectively) were ground in a mortar with anhydrous sodium sulfate and extracted with a 50:50 mixture of hexane and methylene chloride in a Soxhlet (Melville, NJ) apparatus for 4 h. Extracts were concentrated under nitrogen to ∼3 mL. Lipids were removed from the extracts by gel permeation chromatography (GPC) in Bio Beads S-X3 (200−400 mesh) (Bio-Rad Laboratory, Hercules, CA), and extracts were subfractionated by silica gel chromatography as previously described by Metcalfe and Metcalfe (*13*). The lipid fraction from GPC was evaporated to dryness to calculate the lipid content of tomato tissues.

OCPs were analyzed using a Shimadzu GC-17A (Shimadzu Corp., Kyoto, Japan) with an electron capture detector (ECD) apparatus, equipped with a fused-silica capillary column of 30 m, SPB-5 (0.25 mm i.d., 0.25 μm film thickness, Supelco, Bellefonte, PA). The oven temperature was programmed starting at 100 °C and held for 1 min, followed by increases of 5 °C/min to 150 °C, held for 1 min, then 1.5 °C/min to 240 °C, and then 10 °C/min to 300 °C for 3 min. The injection port was at 275 °C, and the detection was carried out at 300 °C. The carrier gas was ultrahigh-purity helium (1.5 mL/min).

The organochlorine compounds analyzed included α-, β-, γ-, and δ-hexachlorocyclohexanes (HCHs), *p*,*p*′-DDT ([1,1,1-trichloro-2,2-bis-(*p*-chlorophenyl) ethane]) and their degradation products *p*,*p*′-DDE ([2,2-bis(*p*-chlorophenyl)-1,1-dichloroethylene]) and *p*,*p*′-DDD (dichlorodiphenyldichloroethane), heptachlor and its metabolite (heptachlor epoxide), aldrin, dieldrin, α- and γ-chlordane, α- and β-endosulfan, and endosulfan sulfate. Quantification of all OCPs was done using an external standard purchased from Ultra Scientific (North Kingstown, RI). The detection limits (LODs) for OCP analyses were calculated according to the method of Keith et al. (*14*); they ranged from 0.12 to 0.4 ng/g of dry wt. Duplicate analyses of samples gave results that varied by <10%.

Laboratory quality assurance samples were used to estimate the quality of the analytical data. Laboratory quality control included laboratory blanks and surrogate recovery spikes. Results of laboratory blanks indicate that samples were not contaminated due to processing in the laboratory. Therefore, blank corrections were not necessary. The surrogate recovery data were within acceptable levels.

Statistical Analysis. OCP concentrations in vegetation and soil given in this paper are expressed as nanograms per gram on a dry weight basis of the particular matrix and are the arithmetic mean of three individual extractions. A one-way analysis of variance (ANOVA) followed by a Tukey multiple-comparison test was used for pairwise comparisons among tissues throughout the life cycle. Student's *t* test or the Mann−Whitney *U* test was used to test significant differences between tissues in each period or between soils samples. The significance level was set at $\alpha = 0.05$ (*15*).

RESULTS AND DISCUSSION

Soil Compartments. Bulk and rhizosphere soil fractions were collected from field plots of tomato at harvest. OCP sorption onto soil is probably the most important sink for these compounds. This process is influenced by diverse factors such as organic matter content, soil type, and physical−chemical properties of pesticides, that is, vapor pressure, water solubility, and the *n*-octanol−water partition coefficient (K_{ow}), etc. (*16*). The higher organic matter content found in plot A (**Table 1**) could be a consequence of the pine needle enrichment. Moreover, mineral composition was similar in both plots. A positive relationship between organic matter content and total OCP level was observed.

Statistical differences between total OCP concentration of plots A and B were not found, probably due to the high standard deviation of plot B (**Table 1**). Because no difference was found between depths in plot B, only data from the 0−15 cm are reported. Total amounts of pesticides in the rhizospheres of periods 2 and 3 were lower than in the bulk soil (plot B), although the statistical analysis showed significant differences only between rhizosphere 2 and bulk soil (Mann−Whitney $p = 0.0495$). It is likely that three measurements are not sufficient to determine any change between bulk soil and rhizosphere 3 OCP content.

In bulk soil of both plots (A and B) the main OCP groups were endosulfans, HCHs, and DDTs (**Table 2**). Higher OCP

Table 2. Concentrations of the Main Organochlorine Pesticides (OCPs) Found in Soil Fractions (Nanograms per Gram on a Dry Weight Basis ± Standard Deviation)[a]

compound	bulk soil		rhizosphere	
(ng/g of dw)	plot A	plot B	period 2	period 3
α-endosulfan	0.08 ± 0.07	0.07 ± 0.08	0.06 ± 0.04	0.04 ± 0.01
β-endosulfan	0.04 ± 0.14	0.06 ± 0.11	0.02 ± 0.04	0.05 ± 0.04
endosulfan sulfate	16.0 ± 0.9	15.7 ± 14.1	4.9 ± 3.1	9.8 ± 1.3
Σ endosulfan	16.4 ± 0.9	15.9 ± 13	4.9 ± 3.1	9.9 ± 1.3
α-HCH	0.2 ± 0.08	0.1 ± 0.1	0.03 ± 0.01	0.1 ± 0.04
β-HCH	0.4 ± 0.09	0.4 ± 0.4	0.04 ± 0.04	0.1 ± 0.05
γ-HCH	1.3 ± 0.7	1.2 ± 0.4	0.2 ± 0.1	0.5 ± 0.2
δ-HCH	0.2 ± 0.07	1.1 ± 1.3	0.1 ± 0.06	0.2 ± 0.02
Σ HCH	2.3 ± 0.7	2.8 ± 2.1	0.4 ± 0.1	0.9 ± 0.2
DDT	3.6 ± 0.6	0.7 ± 0.5	0.2 ± 0.1	1.1 ± 0.2
DDE	3.5 ± 0.6	0.3 ± 0.06	0.2 ± 0.15	0.4 ± 0.04
Σ DDT	7.1 ± 0.5	1.1 ± 0.5	0.4 ± 0.3	1.1 ± 0.2
Σ chlordane	3 ± 0.5	0.4 ± 0.02	0.2 ± 0.09	0.3 ± 0.02
aldrin + dieldrin	5 ± 0.74	0.1 ± 0.1	0.03 ± 0.01	0.2 ± 0.01
Σ heptachlor	2.6 ± 0.45	0.1 ± 0.04	0.2 ± 0.04	0.3 ± 0.06

[a] Σ endosulfan, α- and β-isomers + the sulfate derivative; Σ HCH, α- + β- + γ-, + δ-hexachlorocyclohexanes; Σ DDT, DDT + DDE; Σ chlordane, α- + γ-isomers; Σ heptachlor, heptachlor + epoxide derivative; plot A, enriched soil where plants from period 1 were grown; plot B, soil where plants from periods 2 and 3 were grown.

levels were found in plot A for DDTs and aldrin + dieldrin (Student's t $p = 0.0001$ and $p = 0.0003$, respectively) and for chlordanes and heptachlor epoxide (Mann−Whitney $p = 0.049$). The waxy surface of pine needles and leaves has the ability to bioaccumulate airborne lipophilic pollutants and may be responsible for the enrichment in those pesticides found in plot A (*17*−*19*).

Technical endosulfan is a mixture of two isomers, that is, α- and β-endosulfan, in a ratio 7:3. Endosulfan is of great concern because of its persistence and extreme toxicity to fish and aquatic invertebrates (*20*). Endosulfan residues are commonly found in the environment as a consequence of their extensive usage. Endosulfan is hydrolyzed in water to nontoxic diol, but in soil it is also degraded to the highly toxic endosulfan sulfate. β-Endosulfan and endosulfan sulfate are known to persist and adsorb in and on soil particles (*20*−*23*). Our results showed that endosulfan sulfate levels were ∼400-fold greater than those of the parent compounds (α- and β-endosulfan) in all soil compartments (**Table 2**). There was no significant difference of the endosulfan sulfate levels between soil fractions, although the bulk soil showed higher amounts than the rhizospheres. This difference was not significant probably due to the great standard deviation of plot B values (CV = 70%). Moreover, α-endosulfan/β-endosulfan ratios were ∼1.

Total HCHs in plots A and B showed no significant differences (Student's t $p = 0.79$) (**Table 2**). γ-HCH (lindane) was the main isomer found in both plots showing an α-/γ-HCH ratio close to 0.1. Ratios of DDE/DDT and α-/γ-HCH are often used as indicators of recent DDT and lindane (γ-HCH) inputs into the environment, low ratios, particularly <1, indicate recent inputs (*24*, *25*). Thus, the hypothesis of recent lindane inputs into the environment could be confirmed. HCH levels in both rhizospheres were lower than in plot B primarily due to a decrease of δ-HCH isomer (Mann−Whitney: period 2, $p = 0.049$; period 3, $p = 0.02$). Also, an increase in α- and β-isomers was observed in rhizospheres from period 3 with respect to period 2 (Student's t $p = 0.035$ and $p = 0.047$, respectively) (**Table 2**). These results could be explained by the fact that tomato plants began to take up and accumulate HCHs in their roots, resulting in a lower concentration of these pesticides in the rhizosphere from period 2. Roots from the third period, when plants reach the equilibrium, were not able to absorb as much of the contaminants, leading to a local increase in the concentration of HCHs within the rhizosphere (**Table 2**).

Data from Table 2 showed that DDE/DDT ratios were ∼1.0 and below 0.5 for plots A and B, respectively. In plot A, DDT, which had been incorporated earlier by pine needles, might be converted to DDE (*17*, *26*). The low ratio found in plot B could mean recent input of DDT in the soil. DDE and DDT levels were lower in rhizosphere from period 2 relative to the amount found in bulk soil (PB) and rhizosphere from period 3. However, these differences were significant only for DDT between rhizospheres (Student's t $p = 0.027$) (**Table 2**). The DDE/DDT ratio in plot B and rhizosphere 3 was ∼0.4, whereas in rhizosphere 2 it was close to 1. Differences between DDE/DDT ratios could be due to the high standard deviation in DDE levels of rhizosphere from period 2 (CV > 70%). However, because several studies have reported enhanced degradation of certain pesticides and other contaminants in the rhizosphere, conversion of DDT to DDE in period 2 should be considered (*12*).

Vegetative Compartments. The total OCP concentration, burden, and lipid levels in tomato tissues from the three periods are shown in **Table 3**. The roots from the first period accumulated the highest OCP levels among all tissues from each period (ANOVA $p = 0.002$). In period 1 OCPs were detected with levels in the order of roots = stem > leaves (Student's t $p = 0.011$ and 0.045, respectively). Statistical analysis indicated no significant differences in tissue concentration for periods 2

Table 3. Length, Weight, Percentage of Total Weight, Moisture and Lipid Content, Total Organochlorine Pesticides (OCPs) Concentration (Mean ± Standard Deviation), and Absolute Amounts (Burden) of OCPs in Tissues of Tomato Plants from Periods 1–3[a]

period	tissue	length (cm)	wt (g)	% total wt	water (%)	lipid (%)	total OCPs ng/g dw	OCP burden (ng)
1 (0–15 days)	leaves	26.87[b]	1.15	42.6	86.3 ± 1.6	0.01 ± 0.006	167.3 ± 25.1	26.7
	stem		1.4	51.8	92.9 ± 0.5	0.006 ± 0.002	322 ± 82.7	26.9
	root	4.83	0.15	5.6	75	0.006 ± 0.003	241.6 ± 22.9	9.1
2 (16–59 days)	leaves	29.3[b]	20.0	59.8	87.2 ± 0.7	0.63 ± 0.07	80.6 ± 66	209.2
	stem		9.4	28.2	90.5 ± 5.1	0.08 ± 0.05	166.1 ± 180.4	116.5
	root	11.4	4.0	12.0	74.9 ± 7.5	0.13 ± 0.1	47.9 ± 15.03	47.3
3 (59–151 days)	leaves	99.5[b]	93.9	10	84.5 ± 5.3	0.7 ± 0.3	61.53 ± 7.8	923.0
	stem		110.7	11.8	83.4 ± 3.5	0.7 ± 0.6	106.5 ± 26.8	1892.7
	root	27.9	31.4	3.3	78.9 ± 2.3	0.12 ± 0.1	95.7 ± 19.6	638.1
	fruit peel	nd	2.7	2.3[c]	66.0 ± 1.7	1.4 ± 1.6	127.8 ± 71.2	124.1
	fruit flesh		114.8	97.7[c]	95.8 ± 0.8	0.6 ±0.3	402 ± 44.6	1659.4

[a] dw, dry weight. [b] Aerial tissues = leaves + stem. [c] Percent relative to total fruit weight of 117.5 g. nd, not determined.

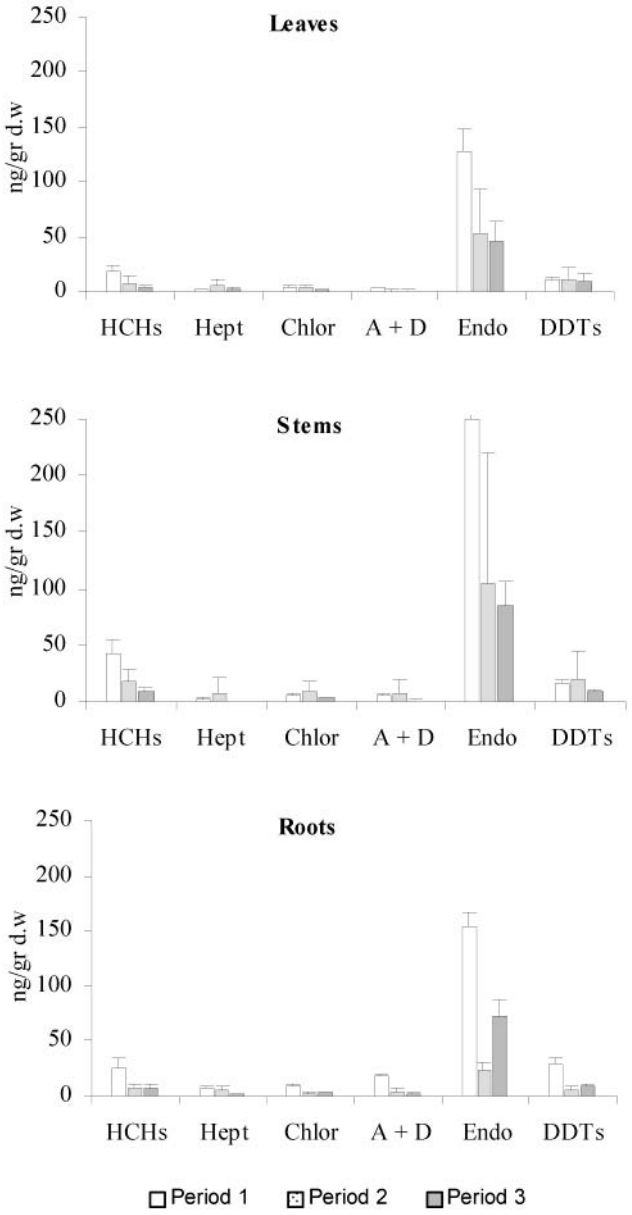

Figure 1. Concentration (mean value, ng/g on a dry wt basis) of organochlorine pesticide (OCPs) groups in the vegetative tissues of tomatoes from periods 1 (grown in plot A) and 2 and 3 (grown in plot B). HCHs, α- + β- + γ-, + δ-hexachlorocyclohexanes; Hept, heptachlor + epoxide derivative; Chlor, α- + γ-chlordanes; A+D, aldrin + dieldrin; Endo, α- and β-endosulfans + sulfate derivative; DDTs, DDT + DDE. Error bars indicate standard deviation.

and 3, showing the equilibrium reached by tomato plants in the mature state. Plant roots have typically been found to contain larger amounts of soil-derived pesticides relative to other plant tissues (*12*, *27*, *28*). Growth-dilution effect and transplant of tomato plants from plot A to plot B would be responsible for the lower OCP levels in roots from periods 2 and 3 (ANOVA $p = 0.002$) (**Table 3**).

Schroll and Scheunert (*29*) found that the bioconcentration factors (concentration in the plant dry mass divided by those in soil dry mass) for hexachlorobenzene in shoots decreased with the age of the plants in lysimeter experiments by the growing of the plant material. Despite the surface area increase of tomato plants from periods 2 and 3 (**Table 3**), we have noted that there was no significant difference in total leaves OCP concentration (ANOVA $p = 0.74$). However, the absolute amounts (burden)

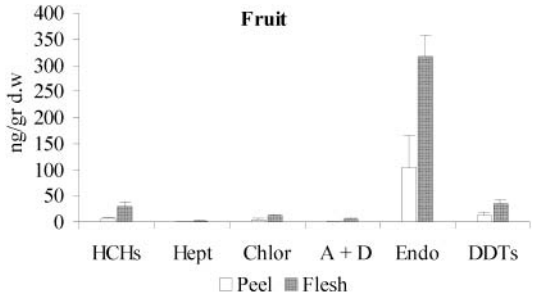

Figure 2. Concentration (mean value, ng/g on a dry wt basis) of organochlorine pesticide groups (OCPs) in tomato fruits (peel and flesh) from period 3. HCHs, α- + β- + γ-, + δ-hexachlorocyclohexanes; Hept, heptachlor + epoxide derivative; Chlor, α- + γ-chlordane; A+D, aldrin + dieldrin; Endo, α- and β-endosulfans + sulfate derivative; DDTs, DDT + DDE. Error bars indicate standard deviation.

of OCPs in each tissue increased continuously throughout the life cycle (**Table 3**), supporting the results of older studies (*29*). It is assumed that foliage contamination from OCPs depends on the concentration in the atmosphere (*30*). Our data suggest the relevance of the atmospheric route in the organic pollutant uptake by tomato plants.

Differences observed among OCPs concentration in tissues of tomato plants from all periods were not related to the lipid content, although lipid composition remains unknown (**Table 3**).

Endosulfans, HCHs, and DDTs were the main OCP groups in roots and aerial parts during the whole life cycle (**Figure 1**). The tomato root profile in period 1 resembles those of soil (plot A) (**Table 2**). Plants growing in soil containing substantial amounts of endosulfans, DDTs, HCHs, dieldrin, and chlordane (plot A) contained higher amounts of these compounds in roots than those plants growing in plot B (periods 2 and 3) (ANOVA, Tukey test $p < 0.05$).

Distribution of endosulfan throughout tissues in period 1 were (**Figure 1**) stem >roots > leaves (Student's *t*, Mann−Whitney $p < 0.05$), and endosulfan concentration in leaves from period 1 were significantly higher than those from periods 2 and 3 (ANOVA $p < 0.05$) (**Figure 1**). HCHs and DDTs distributions in tissues from period 1 were stem > leaves = roots and roots > leaves = stem, respectively (Student's t $p < 0.05$). HCH levels in stem from period 1 were higher than in periods 2 and 3 (ANOVA, Tukey test $p < 0.05$). Differences in the HCHs and DDTs distribution patterns among tissues could be related to the different K_{ow} values of both groups. Thus, HCHs with a lower value ($K_{ow} < 4$) would be able to translocate from roots to aerial tissues (*4*), leading to a higher accumulation in the stem, whereas DDTs with a higher one ($K_{ow} > 6$) would mainly accumulate in root tissues.

Tomato fruits did contain OCPs not only in their outer peel but also in the inner flesh tissues, which may indicate absorption rather than adsorption (**Table 3**). The presence of total OCPs in fruit flesh 3-fold greater than those observed in fruit peel (Student's t $p = 0.008$) was of particular interest. This result could be a consequence of either continuous uptake by aerial tissues (fruit peel, leaves, and stem) of airborne OCPs, followed by translocation via phloem throughout the plant and accumulation in fruit flesh or removal of pesticides from peel by weather influences such as photodegradation and volatilization (*4*).

The distribution pattern of OCPs in fruit (peel and flesh) was similar to that in other tissues (**Figure 2**). In fruit flesh all OCP groups were found at higher levels relative to the amounts in fruit peel (Student's t $p < 0.05$).

Table 4. Endosulfans/HCHs/DDTs Ratios in Tomato Tissue and Soil Fractions[a]

	period		
tissue/soil	1	2	3
leaves	1:0.2:0.07	1:0.2:0.2	1:0.1:0.1
stem	1:0.1:0.09	1:0.2:0.2	1:0.1:0.1
root	1:0.2:0.2	1:0.3:0.2	1:0.1:0.1
fruit peel			1:0.06:0.01
fruit flesh			1:0.1:0.1
bulk soil PA	1:0.1:0.4		
bulk soil P B		1:0.2:0.1	1:0.2:0.1
rhizosphere	NA	1:0.1:0.1	1:0.1:0.1

[a] Endosulfans, α- and β-isomers + sulfate derivative; HCHs, α- + β- + γ-, + δ-isomers; DDTs, DDT + DDE; PA, plot A; PB, plot B; NA, not analyzed.

Endosulfan is one of the few organochlorine insecticides still in use; it is primarily used on summer crops such as tomatoes in the agricultural belt in the northwestern area of Los Padres Lake. Thus, endosulfan levels in aerial tissues of tomato could represent the potential emission source of atmospheric volatilization and transport of this group after its application in surrounding areas. Because significant amounts of endosulfans were found in soils (**Table 2**), root uptake followed by translocation to aerial tissues should also be considered. Research has reported that drift from aerial agricultural spraying can produce lethal concentrations in fish in shallow exposed water bodies 200 m away from the target spray area (*31*). In Los Padres Lake, it is also common during summer months for a massive "fish kill" to occur. One possible explanation could be that lethal concentration inputs of endosulfans applied in the surrounding area reach the body of water.

In the present study, detectable amounts of chlordane as well as other pesticides with $K_{ow} > 4$ were found in aerial tissues of tomato (**Figures 1** and **2**). However, Mattina et al. (*27*) suggested from their studies that chlordane was not translocated from root to edible aerial tissues in tomato. Therefore, these pollutants could have been taken up from atmospheric matrix by tomato plants.

HCH decreased in leaves, stems, and roots throughout the investigated periods (ANOVA $p < 0.05$), whereas they increased in fruit flesh (**Figures 1** and **2**). This result could be a consequence of the ability of HCH to be translocated within plant tissues and accumulated in growth organs such as fruits.

Endosulfans/HCHs/DDTs ratios in tomato tissue and soil fractions are shown in **Table 4**. In aerial tissues the endosulfans/DDT ratio increases throughout periods, reaching the endosulfans/HCHs values in period 3. In roots, these OCPs groups were at the same ratio during the whole cycle. The difference between tissues could be explained by the high levels of HCHs and DDTs found in the soil from period 1 (plot A). At the end of the vegetation cycle (period 3) an increase in the use of endosulfans as well as the equilibrium reached by tomato plants could be responsible for the observed ratios in leaves, stem, roots, and fruit flesh (**Table 4**). Differences found in the endosulfans/HCHs/DDTs ratio for fruit peel could be due to a minor exposition time of tomato fruits with respect to the other tissues. Many researchers have used plant pollutant concentration to qualitatively indicate atmospheric contamination level. Most of these attempts were successful because vegetation integrates contamination over time (*32*). Therefore, the ratio found for fruit peel could indicate OCPs atmospheric contamination in the study area (**Table 4**).

Strong evidence exists that some organic pollutants are degraded in the atmosphere, and it is important to investigate a possible degradation at the plant surface (*32*). **Table 5** shows the metabolite and isomer levels for the three main OCP groups in tomato tissues. Endosulfan sulfate levels in leaves, stem, and roots decreased throughout the life cycle (ANOVA $p < 0.05$). Stem levels were higher than those from other tissues, probably as a consequence of endosulfan mobility facilitated by its lower *n*-octanol/water coefficient ($K_{ow} < 4$). Moreover, the surface area increment would be relevant in OCP uptake by leaf tissues. Simonich and Hites (*32*) and Standley and Sweeney (*33*) found oxidation of α- and β-endosulfan to endosulfan sulfate at the plant surface and in leaves and bark, respectively. Because endosulfan sulfate concentrations in leaves from the third period (**Table 5**) were lower than those found in roots (Student's t $p = 0.037$) and stems (Student's t $p = 0.037$), α- and β-endosulfans may have entered the tomato plants from the atmosphere and been metabolized in leaves followed by translocation by the phloem.

Roots and rhizosphere showed a high endosulfan sulfate/α-endosulfan ratio in the third period and a low ratio in the second one (**Table 5**). These results suggest the release of endosulfan sulfate from plant roots to the rhizosphere, together with photosynthesis products such as organic acids, carbohydrates, proteins, and lipids (*28*). Besides, α- and β- endosulfan transformation to endosulfan sulfate within the rhizosphere should be considered.

β-Endosulfan levels in peel were higher than in fruit flesh (Student's t $p = 0.17$) (**Table 5**). However, an inverse relationship was found for endosulfan sulfate (Student's t $p = 0.003$). This result could be explained by either translocation of endosulfan sulfate from other tissues or an in situ metabolism in fruit flesh.

Table 5. Concentration of Endosulfans (α- and β-Endosulfan and Endosulfan Sulfate), HCHs (α-, β-, γ-, + δ-Isomers), and DDTs (DDT and DDE) in Tomato Tissues (Nanograms per Gram on a Dry Weight Basis ± Standard Deviation)

period	tissue	α-endosulfan	β-endosulfan	endosulfan sulfate	α-HCH	β-HCH	γ-HCH	δ-HCH	DDT	DDE
1 (0–15 days)	leaves	1 ± 0.3	1.1 ± 0.4	126.5 ± 18.5	1.2 ± 0.7	4.2 ± 2.1	9.9 ± 6.5	2.4 ± 2.1	8.9 ± 0.4	2.8 ± 1.5
	stem	1.2 ± 0.4	1.1 ± 0.9	246.9 ± 66	1.7 ± 0.8	8.9 ± 4.1	27.5 ± 7.1	4.7 ± 3.1	9.4 ± 0.7	7.4 ± 2.3
	root	0.8 ± 0.3	2 ± 2.2	151.6 ± 10	1.9 ± 0.8	3.7 ± 1.3	16.2 ± 8	3.7 ± 0.3	19.2 ± 6.2	9.1 ± 2.3
2 (16–59 days)	leaves	1.5 ± 2.6	2.9 ± 1.9	48.2 ± 36.1	0.8 ± 0.5	2.2 ± 1.9	4 ± 4	1.1 ± 0.8	8.24 ± 9.8	2.2 ± 2
	stem	0.9 ± 0.9	3.2 ± 3.8	99.7 ± 110.3	1.1 ± 1.4	4.2 ± 0.6	9.4 ± 7.8	3.6 ± 1.3	10.5 ± 14	8.6 ± 10.7
	root	1.3 ± 1.1	0.9 ± 0.5	21.1 ± 6	0.4 ± 0.1	1.1 ± 0.7	4.7 ± 1.6	0.8 ± 0.7	2.5 ± 1.7	23.2 ± 6
3 (60–151 days)	leaves	3.5 ± 4.7	3.3 ± 2	38.2 ± 12.1	0.6 ± 0.5	1.6 ± 0.3	0.9 ± 0.3	1.2 ± 1.4	2.3 ± 2	6 ± 7.5
	stem	0.9 ± 0.3	1.6 ± 0.4	82.1 ± 21.6	1.3 ± 0.4	2.1 ± 0.5	4.6 ± 2.1	1.6 ± 0.5	6.8 ± 0.7	1.8 ± 0.4
	root	0.3 ± 0.1	0.9 ± 0.3	71.4 ± 14.4	1.3 ± 0.1	1.2 ± 0.9	3.9 ± 2.5	1.7 ± 0.6	7.3 ± 1.2	2.4 ± 0.5
	fruit peel	12.3 ± 2.1	10.8 ± 4.4	80.6 ± 54.9	1.4 ± 0.7	1.5 ± 1	2.1 ± 0.9	1.4 ± 0.9	8.8 ± 6.6	3.2 ± 0.5
	fruit flesh	4.5 ± 2.7	6.6 ± 2.8	305.5 ± 35.2	7.4 ± 2.8	5.4 ± 4.3	14.4 ± 1.3	2.3 ± 0.7	29.2 ± 3.7	6.4 ± 3.6

Table 6. Root Bioconcentration Factors (RBF) of the Main Organochlorine Pesticides (Pesticide Concentration in the Plant Dry Mass Divided by Pesticide Concentration in the Soil Dry Mass) for Tomato Roots at the Beginning, Middle, and End of the Vegetation Period[a]

	period		
compound	1	2	3
α-endosulfan	10	18.6	4.3
β-endosulfan	50	15	15
endosulfan sulfate	9.2	1.3	4.5
α-HCH	9.5	4	13
β-HCH	9.2	2.7	3
γ-HCH	12.3.	3.9	3.2
δ-HCH	18.5	0.7	1.5
DDT	2.6	N.C	N.C
DDE	5.3	N.C	N.C

[a] NC, not calculated because DDT levels in plot B were significantly lower than in plot A.

Uptake from soil by plant roots is the predominant pathway of accumulation for organic compounds that have high water solubility and low K_{ow} values such as endosulfans. The higher levels of these pollutants found in roots from period 1 show that they were incorporated efficiently from soil (**Table 5**). The translocation of endosulfans within tomato tissues could be an explanation for the similar concentration found in leaves, stems, and roots from period 3.

The α-/γ-HCH ratio calculated from the results outlined in **Table 5** showed that it was below 0.2 in all tissues from the first two periods, whereas in the third period the ratios were higher, reaching values of ∼1 in leaves and fruit peel. Our results indicate that recent inputs of lindane into the environment had probably occurred at the beginning of the vegetation period. Decreasing lindane inputs into the atmosphere appear to be the driving force leading to the increase of the α-/γ-HCH ratios (*34*). It is known that pure lindane is applied as an insecticide on potato crops during spring (corresponding with the beginning of the tomato life cycle) in the southeastern region of Buenos Aires province (*35*).

However, care should be taken when vegetation concentration ratios are interpreted to determine "recent" emission of pollutants (like the ratio of DDT to DDE) because degradation may be enhanced on the surface of vegetation (*32*). Our results showed that DDE/DDT ratios were about or below one in all analyzed samples (**Table 5**).

The RBF was reported to be positively related to the logarithm of the K_{ow} (*36*). However, in our results as well as in previous reports DDT was not in line with this correlation (*37*). Most of the OCPs analyzed showed a higher RBF in period 1 followed by a decrease in periods 2 and 3. This decrease was caused by the growing of the plant material. However, an increase of RBF was observed for α-endosulfan in period 2 and for endosulfan sulfate in period 3 (**Table 6**) . This fact could be related to a biotransformation process within root plants (*22*, *38*).

The findings in this paper are significant as they indicate that tomato plants are able to accumulate OCPs from soils. However, those pesticides with $K_{ow} > 4$ could not be translocated to aerial tissues by this species. Besides, more research is necessary to exactly differentiate the uptake of chemicals by roots and aerial tissues in this species. Moreover, the DDE/DDT and α-endosulfan/β-endosulfan/endosulfan sulfate ratios found in all tissues suggest the ability of tomato plants to metabolize parent compounds.

In summary, the study demonstrates that although OCPs have never been applied on the farm, they are all present in the soil environment and tomato tissues. Wind dispersion, surface runoff, and volatilization and subsequent redeposition by precipitation of pesticides applied in the surrounding areas contribute to pollution of a "nontarget" areas such as the organic farm. Residues of banned pesticides such as DDT, heptachlor, and dieldrin were detected in tomato plants. However, the OCP levels found in the fruit (edible tissue) were significantly below the maximum residue limits (MRL) considered by the Codigo Alimentario Argentino (CAA; *39*) and the *Codex Alimentarius* (*40*).

ABBREVIATIONS USED

OCPs, organochlorine pesticides; POPs, persistent organic pollutants; DDTs, sum of *p,p′*-DDT and its degradation products *p,p′*-DDE and *p,p′*-DDD; *p,p′*-DDT, 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane; *p,p′*-DDE, 2,2-bis(*p*-chlorophenyl)-1,1-dichloroethylene; *p,p′*-DDD, dichlorodiphenyldichloroethane; HCHs, sum of α-, β-, γ-, and δ-hexachlorocyclohexanes; OM, organic matter; GPC, gel permeation chromatography; ANOVA, analysis of variance; K_{ow}, *n*-octanol/water partition coefficient; CV, coefficient of variability; RBF, root bioconcentration factor; CAA, Codigo Alimentario Argentino.

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