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Organochlorine Pesticide Residues in Leek *(Allium porrum)* Crops Grown on Untreated Soils from an Agricultural Environment

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Leek (*Allium porrum*) plants from organic farming were harvested at 15, 59, and 210 days after seed germination. Organochlorine pesticide (OCP) levels were quantified by GC-ECD in vegetative tissues (roots and aerial), bulk soil and rhizosphere. Leek plant bioaccumulate OCPs efficiently in their aerial and root tissues and alter the concentration of the soil where they are grown. OCPs distribution pattern of bulk soil was endosulfans > DDTs > dieldrin, while it was endosulfans > HCHs > DDTs in leek tissues. There were statistically significant declines in DDTs, chlordane, dieldrin, and heptachlor in the rhizosphere, indicating that recalcitrant residues of OCPs may be removed from contaminated soil using leek crops under normal growing conditions. The 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 this farm could be the result of atmospheric deposition and/or surface runoff of these pesticides.

KEYWORDS: Organochlorine pesticides; leek (*Allium porrum*); vegetation period; organic production; plant uptake

INTRODUCTION

Persistent organic pollutants (POPs) are a class of compounds characterized by exceedingly long half-lives in the environment, often of an order of years or decades. Included in this group are the organochlorine pesticides (OCPs) such as DDT ([1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane]), chlordane, dieldrin, aldrin, toxaphene, and heptachlor (*1*).

Since the 1950s and 1960s, reports describing uptake by carrots, cabbages, potatoes, cucumbers, spinaches, lettuces, and others crops of heptachlor, lindane, aldrin, chlordane, and DDTs have appeared in the literature (*2*−*5*). In those studies, crops were grown in soils treated with the insecticides up to five and twenty years earlier. For all crops examined, the OCPs concentration was higher in roots, and in several cases, the quantity of contaminants removed from soil has led to speculate about phytoremediation of such recalcitrant compounds from natural soils.

Previous works from this laboratory have shown the occurrence of OCPs in certain crops such as carrots, potatoes, and tomatoes, grown in soils without direct application of these pesticides (*6*), and in agricultural soils, where they have been used during the preceding 20 years (*7*).

The purpose of the present study was to monitor the changes of OCPs through the soil compartment rhizosphere and bulk soil to root and aerial parts during the vegetation period of organic leek production. Such details are ultimately necessary to assess the fate and total risk to human health posed from dietary route.

MATERIALS AND METHODS

Field Plot. Leek (*Allium porrum* of the family *Liliaceae*) 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 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) (*8*). Beginning in October 2000 leek plants were seeded in a portion of the field plot enriched with pine needles. Until the harvest (May 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 and rhizosphere. Bulk soil samples were collected at harvest at a distance of 1 m from vegetation. A single transect was set in the plot, and three equidistant sites were sampled at a depth of 0−15 cm. 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

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Table 1. Length, Weight, Percentage of Total Weight, Humidity, Lipid Content, Total OCPs Concentration (Mean Value ± Standard Deviation) and Absolute Amounts (Burden) of OCPs in Tissues of Leek Plants from Periods 1, 2, and 3

period	N^b	n^c	tissue	length (cm)	weight (g)	% total weight	water %	lipid %	total OCP ng/g dw[d]	OCP burden ng
1 (15 d)[a]	1	7	Σ aerial	7.5	0.032	57.2	87.1	0.5	335.8	10.7
			root		0.024	42.8	72.7	0.2	396.7	9.5
2 (59 d)	3	8	Σ aerial	29.1	0.32	88.9	85.5 ± 1.8	0.4 ± 0.1	224.0 ± 74.1	71.7
			root	5.8	0.04	11.1	72.9 ± 4.6	0.2 ± 0.08	187.7 ± 7.1	7.5
3 (210 d)	3	1	*leaves*	7.8	5.9	25.0	87.5 ± 0.5	0.1 ± 0.08	157.6 ± 10.4	929.8
			stem	46.5	14.8	62.8	88.5 ± 0.8	0.7 ± 0.4	175.8 ± 44.4	2601.8
			Σ aerial	54.3	20.7	87.8	88 ± 0.5	0.4 ± 0.2	160.3 ± 17.0	3318.2
			root	15.73	2.87	12.2	84.5	0.1 ± 0.06	243.2 ± 131.3	698

[a] d = days. [b] N = number of pooles. [c] n = number of individuals in each pool. [d] dw = dry weight; Σ Aerial: leaves + stem.

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 (*9*). Particle size distribution was determined by the pipet method (*10*). Three sizes were estimated: <0.062 mm (clay), 0.2−0.062 mm (silt), and >0.2 (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. Leek plants were harvested at three different time periods: 15 and 60 days after seed germination, periods 1 and 2, respectively. The third one was when edible tissues were at marketable size (210 days, period 3). In period 1, 7 (n) plants were harvested and analyzed as one pool (N). In period 2, 24 plants were harvested and analyzed as 3 pools (N), while for period 3, three plants were harvested, and each one was individually analyzed ($N = 3$, $n = 1$). Root and aerial tissues were separated for all periods, but in period 3, aerial tissues were also fractionated in stem and leaves. The rhizosphere soil was removed from roots with a fine-bristle toothbrush (*2*). 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 (*2*).

Root bioconcentration factors (RBFs) 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 (*11*). The lipid fraction from GPC was evaporated to dryness to calculate the lipid content of leek tissues.

OCPs were analyzed using a Shimadzu GC-17A (Shimadzu Corp., Kyoto, Japan) with 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).

Quantification of the all OCPs was done using an external standard (organochlorine pesticides mixture) US 127 purchased from Ultra Scientific (North Kingstown, RI). The organochlorine compounds included are 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. The detection limits (LODs) for OCP analyses were calculated according to the method of Keith et al. (*12*); they ranged from 0.12 to 0.4 ng/g of dry wt. Duplicate analyses of samples gave results that varied by less than 10%.

Table 2. Moisture Content, Organic Matter Content (OM), Particle Size Distribution and Total OCPs Concentration (Mean ± Standard Deviation) in Bulk Soil and Rhizosphere

soil[a]	depth (cm)	water (%)	OM (%)	particle size distribution (%)[c] clay	silt	sand	total OCPs ng/g dw[b]
BS	0–15	23.5 ± 0.6	8.8	21.2	34.8	44	36.4 ± 1.6
RP_2	0–15	13.2 ± 0.3	4.5	NA	NA	NA	13.7 ± 5.5
RP_3	0–15	23.3 ± 1.5	5.5	NA	NA	NA	16.3 ± 2.2

[a] BS = Bulk soil, RP_2 = rhizosphere from period 2 plants, RP_3 = rhizosphere form period 3 plants. [b] dw = dry weight. [c] NA = not analyzed; Particle size distribution of rhizospheres was assumed to be similar to that of the corresponding bulk soil.

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. All OCP concentrations in plants from period 2 and 3 and soil matrix 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. Data for period 1 are the result of a composite of seven plants and are also on a dry weight basis. Student's t test or the Mann−Whitney U test was used to test significant differences between tissues or between soils samples. The significance level was set at $\alpha = 0.05$ (*13*).

RESULTS AND DISCUSSION

Morphometric characteristics, physicochemical properties, OCP concentration and burden in leek tissues during the whole vegetation cycle are shown in **Table 1**.

Roots. The average concentration of OCPs in bulk soil samples from leek crops was 36.4 ± 1.6 ng/g on a dry weight basis (**Table 2**). Despite of the lower lipid content (0.5%) OCPs were found in roots from all three periods showing a great bioconcentration ability of leek roots particularly at the beginning of the life cycle (**Table 1**). Tomato plants of 15 days old, cultivated under the same conditions, accumulated lower levels of OCPs, mainly endosulfan sulfate, than leek plants of 15 days old (*6*). This difference indicates the importance of interspecies variability in plant uptake of OCPs, as was mentioned by Böme et al. (*14*). As was reported by Schroll and Scheunert (*15*), the

Table 3. Concentration of the Main OCPs Found in Soil Fractions, ng/gr on Dry Weight Basis (± Standard Deviation)

compound ng/g dw[a]	K_{ow}[b]	bulk soil	rhizosphere period 2	rhizosphere period 3
α-endosulfan	3.13	0.08 ± 0.07	0.01 ± 0.02	0.04 ± 0.01
β-endosulfan	3.62	0.4 ± 0.14	0.2 ± 0.3	0.2 ± 0.06
endosulfan sulfate	3.66	16.0 ± 0.9	7.1 ± 2.1	11.9 ± 1.8
Σ endosulfan		16.5 ± 0.9	7.3 ± 2.4	12.2 ± 1.8
α-HCH	3.8	0.2 ± 0.08	0.06 ± 0.03	0.04 ± 0.02
β-HCH	3.8	0.4 ± 0.09	0.5 ± 0.1	1.0 ± 0.3
γ-HCH	3.7	1.3 ± 0.7	1.0 ± 0.7	1.0 ± 0.3
δ-HCH	4.1	0.2 ± 0.07	0.4 ± 0.3	0.3 ± 0.02
Σ HCHs		2.3 ± 0.7	2.04 ± 0.9	2.4 ± 0.1
DDT	6.2	3.6 ± 0.6	0.6 ± 0.4	0.6 ± 0.2
DDE	5.7	3.5 ± 0.6	1.0 ± 0.6	0.4 ± 0.02
Σ DDTs		7.12 ± 0.5	1.6 ± 0.8	1 ± 0.2
α-chlordane	6	1.68 ± 0.4	0.3 ± 0.2	0.04 ± 0.04
γ-chlordane	6	1.27 ± 0.12	0.7 ± 0.4	0.2 ± 0.1
Σ chlordane		3 ± 0.5	1.03 ± 0.6	0.3 ± 0.1
dieldrin	5.2	5 ± 0.74	0.6 ± 0.03	0.1 ± 0.02
heptachlor	5.3	0.07 ± 0.01	0.2 ± 0.3	0.2 ± 0.06
heptachlor epoxide	4.2	2.54 ± 0.44	0.9 ± 0.5	0.1 ± 0.05
Σ heptachlor		2.6 ± 0.4	1.1± 0.8	0.3± 0.05

[a] dw = dry weight. [b] K_{ow} = octanol/water partition coefficient.

increase in plant material would be responsible of the decrease in OCPs levels in roots from periods 2 and 3. This can be supported by the significantly different pesticide levels between bulk soil and rhizospheres from periods 2 and 3 (Student's *t*, $p = 0.002$ and $p = 0.0002$, respectively). These data could indicate the potential for the phytoremediation of pesticide residues by leek plants. Variations in burdens from root tissues were related with variations in relative percentage to total weight (**Table 1**).

OCPs distribution pattern of bulk soil was endosulfans > DDTs > dieldrin (**Table 3**), while in roots it was endosulfans > DDTs > HCHs in period 1 and endosulfans > HCHs > DDTs for periods 2 and 3 (**Figure 1**). Pine needles are known by their ability to accumulate atmospheric pollutants (*16*). So, the enrichment of bulk soil when plants were seeded could explain the high levels of OCPs with a $K_{ow} > 5$, such as DDTs, dieldrin, chlordane, and heptachlor, in bulk soil and roots from period 1. From **Figure 1**, it is also obvious that endosulfans represent about 80% of total OCPs found in root tissues during the whole vegetation cycle.

Technical endosulfan is a mixture of two isomers, that is, α- and β-endosulfan, in the 7:3 ratio. Endosulfan is of great concern, because of its persistence and extreme toxicity to fish and aquatic invertebrates (*17*). As a consequence of its extensive usage endosulfan residues are commonly found in the environment. Endosulfan is hydrolyzed in water to nontoxic diol, but in soil it is degraded to the highly toxic endosulfan sulfate. β-Endosulfan and endosulfan sulfate are known to persist and adsorb preferentially to the soil particles being their half -lives ~76 and 100 days, respectively (*18*−*20*). Thus, endosulfan is found to disappear from soil moderately rapid, with little carryover from one season to the next. Although a great increase in root material was observed from period 2 to period 3, there were no significant differences in the total endosulfan levels (**Table 1**, **Figure 1**). This result shows the continuous uptake of this pollutant from soil by leek roots as well as the occurrence of endosulfans in the soils as a consequence of its usage in the surrounding areas. Moreover, our results showed that endosulfan sulfate levels were 40−200-fold greater than parent compounds (α- and β-endosulfan) in bulk soil samples and 60−300-fold greater in leek roots (**Tables 3** and **4**). The major pathways for endosulfan movements from the surrounding farms to the

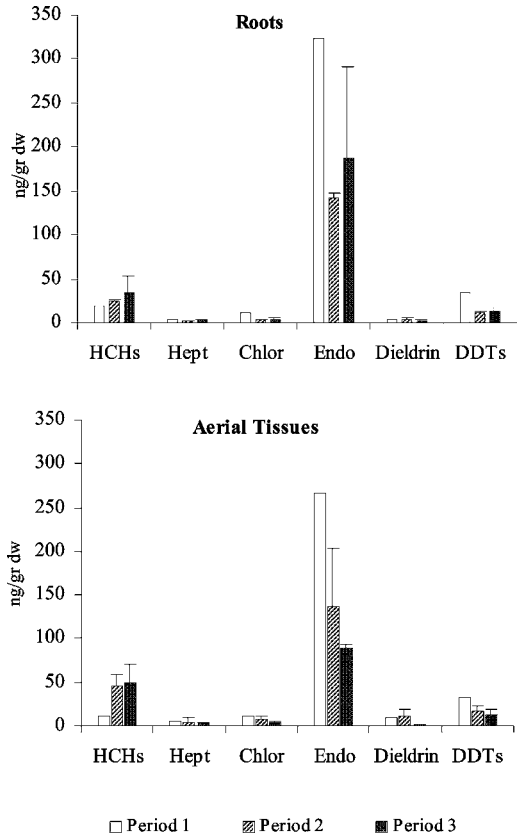

Figure 1. Concentration (mean value, ng/gr on dry weight basis) of OCPs groups in roots and aerial tissues of leek plants from periods 1, 2, and 3. HCHs, α- + β- + γ- and δ- hexachlorocyclohexanes; Hept, heptachlor + epoxide derivative; Chlor, α- + γ- chlordanes; Endo, α- and β- endosulfans + sulfate derivative; DDTs, DDT + DDE. Error bars indicate standard deviation.

organic farm could be via runoff or drift, and to a lesser extent by volatilization (*20*). It is known that endosulfan sulfate is exclusively formed through biological oxidation in plant tissues and by soil microorganisms (*21*) or colembolla (*22*). Therefore, endosulfan sulfate residues found in all samples analyzed could be a product of in situ biotransformation in the organic farm.

There are two formulations of HCH on the international market, pure lindane (γ-HCH = 94−99%) and the technical grade, which is an isomeric mixture in the proportions 60−70% α-, 5−12% β-, 10−12% γ-, and 6−10% δ- (although all isomers are toxic, only lindane is insecticidal) (*23*−*24*). Analysis of bulk soil and rhizospheres showed no differences in the total HCHs levels (**Table 3**). However, a decrease in α-isomer levels was observed in both rhizospheres (Student's *t*, $p = 0.02$ and $p = 0.013$ for periods 2 and 3, respectively) while the β-isomer showed an inverse behavior. Once HCHs are in the soil, soil associated microbes degrade them, or they volatilize to the atmosphere (*23*). Thus, the β-isomer is the most persistent with respect to microbial degradation and has the lowest volatility, while the α- isomer is the more volatile and rapidly degraded. The α-/γ- HCH ratio showed a drop throughout the life cycle that could indicate an input of pure lindane into leek roots (**Table 4**). Because no differences were detected in soil matrix, one possible explanation is that the γ- isomer could be being mobilized from aerial tissues to roots.

The results showed that the concentrations of DDT and DDE in the rhizosphere of leek crops were significantly lower than

Table 4. Concentration of Endosulfans (α-, β-, and Sulfate), HCHs (α-, β-, γ-, and δ- Isomers), and DDTs (DDT and DDE) in Leek Tissues, ng/gr on Dry Weight Basis (± Standard Deviation)

Period[a]	Tissue[b]	α-Endosulfan	β-Endosulfan	Endosulfan sulfate	α-HCH	β-HCH	γ-HCH	δ-HCH	DDT	DDE
1 (15 d)	Aerial	0.4	1.1	264.4	1.1	8.0	D.L.	2.9	24.5	7.6
	Root	0.7	1.4	321.9	1.2	10.3	2.5	4.3	26.4	8.3
2 (59 d)	Aerial	D.L.[c]	D.L.	137.8 ± 65.0	2.4 ± 2.1	18.7 ± 4.3	15.4 ± 2.8	9.3 ± 5.1	10.1 ± 6.7	7.6 ± 1.6
	Root	0.1 ± 0.1	0.4 ± 0.7	141.0 ± 5.9	0.7 ± 0.1	6.0 ± 0.7	13.1 ± 2.1	5.1 ± 0.5	6.3 ± 2.1	5.6 ± 2.5
3 (210 d)	Aerial	0.4 ± 0.3	1.2 ± 0.5	88.1 ± 2.8	3.2 ± 3.1	11.6 ± 5.6	10.0 ± 2.4	24.1 ± 11.9	10.0 ± 6.8	2.8 ± 0.4
	Leaves	0.2 ± 0.3	1.0 ± 0.9	94.3 ± 5.1	3.2 ± 3.2	11.0 ± 5.5	9.7 ± 4.7	13.3 ± 9.2	11.9 ± 8.3	3.3 ± 0.9
	Stem	0.9 ± 1.5	1.4 ± 1.2	80.8 ± 10.7	3.1 ± 2.8	12.9 ± 6.7	10.5 ± 2.3	51.7 ± 32.0	5.4 ± 3.2	1.7 ± 1.5
	Root	D.L.	1.0 ± 0.3	185.4 ± 105.0	1.9 ± 1.4	6.4 ± 4.7	16.8 ± 8.9	8.2 ± 4.5	6.5 ± 2.6	6.6 ± 2.1

[a] d = days. [b] Aerial tissues = stem + leaves. [c] D.L. = detection limit.

bulk soil levels (**Table 3**). This decrease was related with the bioaccumulation of these pollutants in root tissues (**Table 4**). The DDE/DDT ratio of ~1 found in bulk soil was also observed in roots from periods 2 and 3. These results indicate the equilibrium reached by leek roots at ripening stages. In addition, it has been reported that certain enzymes present in root exudates may directly degrade certain soil contaminants (*2*, *25*). Thus, the DDE/DDT ratio of >1 found in the rhizosphere could be due to microbial activity or direct enzyme induced biodegradation. Moreover, the observed drop relative to bulk soil could be the result of a plant assisted mobilization to root tissues.

Chlordane, dieldrin, and heptachlor levels in root tissues were < 5 ng/g, dry weight basis (except for γ- chlordane in period 1, <10 ng/g, data not shown). Chlordane levels in rhizospheres 2 and 3 were significantly lower than those in the bulk soil (Student's *t*, $p = 0.013$ and $p = 0.00093$, respectively). Rhizospheres and roots showed a component ratio (α/γ isomers) of ~0.2, while it was 1.3 in the bulk soil. Similar results between rhizosphere and bulk soil were found in zucchini plants (*26*). At this point, we can only speculate if the change in the α/γ ratio is due to differential transport efficiencies or variations in the kinetics of metabolism of the components within rhizosphere or root tissues.

Heptachlor and heptachlor epoxide were found in roots from all analyzed periods, but the ratio parental/metabolite was >1 in period 1 and ~1 in periods 2 and 3 (data not shown). The levels of the epoxide derivative would suggest substantial contaminant metabolism within roots. However, heptachlor epoxide levels in rhizospheres were significantly lesser than in the bulk soil (Studen's t $p < 0.05$) indicating that heptachlor epoxide uptake within root tissues is enhanced by its physicochemical characteristics. As was observed for chlordane, heptachlor, and DDT, dieldrin levels in the rhizosphere from periods 2 and 3 showed a decline relative to the bulk soil levels (Student's *t*, $p = 0.000006$ and $p = 0.000005$, respectively) (**Table 3**). These results indicate the uptake of OCPs from soil by leek roots.

Differences in the root bioconcentration factors (RBFs) among OCPs throughout the vegetation period were found (**Table 5**). Endosulfans and DDTs RBFs decreased from period 1 to 3, while α-, γ-, and δ-HCH isomers showed an increase in their RBF. These results are in good agreement with the enrichment in HCHs observed in leek roots and rhizosphere from periods 2 and 3 (**Figure 1**, **Table 3**). Although the RBF was reported to be positively related to the logarithm of the K_{ow}, in our results as well as in previous reports, DDT was not in line with this correlation (*27*).

Aerial Tissues. Most of the OCPs absorbed by leek plants were found in aerial tissues of periods 2 (95.6%) and 3 (83.6%), whereas an equal proportion was found among tissues from the first period (**Table 1**). Residues in stem account for about 73% of the total amount of OCPs found in aerial tissues of plants from period 3. These results indicate the relevance of aerial tissues in OCPs uptake by leek plants during their growth.

Table 5. RBF of the Main OCPs Calculated as Pesticide Concentration in the Plant Dry Mass Divided by Pesticide Concentration in the Soil Dry Mass for Leek Roots at the Beginning, Middle, and End of the Vegetation Period

	period		
compound	1	2	3
α-endosulfan	9.1	0.9	*a*
β-endosulfan	3.9	1.2	2.8
endo-sulfate	20.1	8.8	11.6
α-HCH	5	2.9	8.0
β-HCH	23	13.2	14.2
γ-HCH	1.8	9.7	12.4
δ-HCH	18.6	22.1	35.6
DDT	7.6	1.8	1.9
DDE	2.3	1.6	1.8
α-chlordane	1.1	0.2	0.5
γ-chlordane	7.6	2.1	2.8
dieldrin	0.7	0.8	0.6
heptachlor	53.4	6.1	17.8
hepta-epoxide	0.4	0.5	0.8

[a] α- endosulfan was not detected in leek roots.

OCPs levels in aerial tissues decreased during leek life cycle, while an increase was observed in root tissues from periods 2 and 3; however, these differences were not statistically significant (**Table 1**). As in root tissues, a dilution by growth would be responsible of the lower concentration in period 3. Despite the higher values found in stem from period 3, no significant differences were observed between total OCPs levels in the tissue and leaves. Under the field conditions reported here for leek crops as well as in previous reports for tomato crops growing on untreated soils (*6*), OCPs levels were similar between subterranean plant parts (root) and aboveground plan parts (stem or leaves) at mature stages. This observation was not consistent with previously published data in which plants were cultivated in treated soils (*2*, *5*, *26*). Thus, in the organically treated soils, the air-to-plant route would be as important as the soil-to-plant route in both species.

OCPs distribution pattern in aerial tissues throughout the life cycle was endosulfans > DDTs > HCHs for period 1, and like in root tissues, it was endosulfans > HCHs > DDTs for periods 2 and 3 (**Figure 1**). Endosulfan levels decreased throughout periods, with this difference being statistically significant between periods 2 and 3 (Mann−Whitney, $p = 0.049$). Endosulfans account for 80% of the total OCPs in period 1; however, this percentage decreased to 56 in period 3, leading to an increase in the proportion of HCHs (**Figure 1**). Following the three periods, HCHs percentage from total OCPs levels in aerial tissues abruptly climbs to 30% at the end of the cycle.

These differences were lower in roots than in aerial tissues, probably as a consequence of either roots reaching the equilibrium faster than aerial tissues or a lower endosulfans availability for aerial tissues at the end of the summer season.

Endosulfan levels in aerial tissues from period 3 were significantly less than those in root tissues (Mann−Whitney, $p = 0.049$). Endosulfan sulfate residues were ~200 times greater than the α- and β- isomers (**Table 4**) in periods 1 and 2, whereas in period 3, they were ~80 times greater. Similar ratios between metabolite and parent compounds were found for endosulfans in tomato tissues grown in the organic farm (*6*). The similar endosulfan sulfate levels observed between aerial and root tissues of leek plants in the first two periods suggest the mobilization within tissues of the residues facilitated by the lower K_{ow} (3.66) (**Table 4**). However, the difference observed between both tissues in the period 3 supports the previously mentioned hypothesis that lower availability of endosulfans in the atmosphere of the organic farm is occurring. Moreover, temperature and pH of the soil could also influence the ability of leek plants to accumulate OCPs.

All HCH isomers were present in aerial tissues of leek plants throughout the life cycle, suggesting the use of technical mixture in the surrounding area. The α-/γ-HCH ratio can be used as diagnostic of HCH sources. Inputs of γ-HCH (lindane) decrease the ratio found in air and vegetation containing a background of technical HCH (α-/γ- = 4−6) (*28*). Thus, the low α-/γ- HCH ratio found in all samples may reflect recent inputs of lindane to the atmosphere of the studied area.

The most common DDT forms in the environment are *p,p′*-DDT, its isomer *o,p'*-DDT present in the technical product, and its degradation product *p,p′*-DDE, although in some cases other degradation products, such us DDDs, can be present at significant levels in the atmosphere (*29*). In this work, a DDE/DDT ratio of <1 was found in all samples (**Table 4**). It is known that high DDT concentrations are measured when an intensive use of DDT is still present or took place in the recent past (*29*). Thus, our results could indicate a recent input of DDT, although the use of this insecticide has been banned in Argentina since 1990 (*30*), but it is still permitted in Brazil for endemic disease vector control (*31*). So, DDT could be arriving from lower latitudes as a consequence of the process known as "global distillation" (*1*).

Dieldrin, hepatchlor, and chlordane levels in aerial tissues were <10 ng/g on dry weight basis (data not shown) and no differences were found throughout periods for the two last pesticides, while a marked decrease in dieldrin concentration was present in period 3. Moreover, it is known that chlordane is readily translocated throughout plant tissues despite the minimal water solubility and that certain crops bioaccumulate chlordane more efficiently than others (*5*). So, from the data here reported, it could be suggested that leek plants mobilize this pesticide within their tissues.

The present report is the first comprehensive study of the uptake of OCPs residues throughout leek tissues during a vegetation period. Thus, the results indicate that aerial and root tissues of leek plants bioaccumulate OCPs efficiently. Therefore, when crop residues are reincorporated into soil, the subsequent soil OCP values may reflect contributions from decomposed plant material rather than changes either within soil or via the atmospheric deposition into soil. Moreover, leek plants alter the concentration of the soil where they are grown. The high levels of pesticide metabolites found in all tissues suggest the ability of leek plants to metabolize parent compounds. The data indicate that certain plants such as leek may efficiently accumulate residues of persistent organic pollutants in their tissues, suggesting phytoremediation as a possible treatment strategy. However, the amounts of OCPs accumulated in plant parts analyzed are probably not worth for phytoremediation, so alternative plants with similar characteristics need to be found.

Despite most OCPs analyzed have been banned, they are still present in significant levels in leek plants from the organic farm. However, the OCPs levels found in the edible tissue were below the maximum residue limits (MRL) considered by the Codigo Alimentario Argentino (CAA, 32) and the *Codex Alimentarius* (33). Finally, as was previously mentioned in the Materials and Methods, the farm where the study was carried out is included in an important agricultural belt, and it is surrounded by conventional farms. Despite the organic farming management, the results obtained in this work verify the contamination from adjacent conventional fields. Consequently, the products of this farm can only be sold in the conventional market.

ABREVIATIONS USED

OCPs, Organochlorine Pesticides; POPs, Persistent Organic Pollutants; DDTs, the 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, the sum of α-, β-, γ- and δ- hexachlorocyclohexanes; OM, Organic Matter; GPC, Gel Permeation Chromatography; K_{ow}, *n*-octanol/water partition coefficient; RBF, Root Bioconcentration Factor; CAA, Codigo Alimentario Argentino; (MRL), Maximum Residue Limits

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