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INVESTIGATION OF TRANSLOCATION, DEGRADATION AND DECONTAMINATION OF SOME PESTICIDES IN RELATION TO RESIDUES IN FOODSTUFFS

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This study was designed to establish the extent of translocation, degradation and decontamination of aldrin and lindane in regard to different pedologic characteristics of the soil. The research was conducted at experimental stations with different plant cultures during four years.

It was established that pesticides aldrin and lindane, and their metabolites and stereoisomers, are translocated from the soil into plants. Within the plants, they are translocated from the root toward the leaves and grain.

A certain stereoisomerization of lindane (gamma-HCH) into alpha-HCH was noted, but further experiments are needed to settle uncertainties.

The different soil types at the »Podravina« and »Posavina« stations were also found to have considerable influence on the translocation of pesticides and their degradation.

Many studies on the translocation, degradation, metabolism and isomerization of aldrin and lindane have shown that these phenomena have different manifestations in different soils and plants (1—15).

This paper reports the results of analyses of samples of soils and plants from two different agricultural stations for residues of chlorinated hydrocarbon pesticides.

The soils and plant samples were collected during 1972—1975. The studies of aldrin and lindane translocation and decontamination were carried out on potato and corn in the spring and autumn of 1973, on wheat and carrot in the autumn of 1974, and lastly on carrot only between the spring and autumn 1975. In the preparation of soil, sowing, harvesting or gathering, sample collection and transportation to the laboratories for analysis a maximum difference between the two stations was two days.

The »Podravina« station is near Đurđevac, 100 km north-east of Zagreb. The area belongs to the prevalent Yugoslav soil type of podzol which covers the northwestern and central parts of the country. The experimental station is on a typically sandy soil of the type seen in several areas in Yugoslavia (Deliblatska peščara, Podravski pesci, etc).

The Yugoslav sandy soils are in a temperature zone where other soils give normal harvests. The limiting factor which affects the growth of farm crops on sandy soils is not the climate, but the lack of water and nutrients. Such soils are characterized by greater permeability and better aeration which, it is hypothesized, has influenced pesticide translocation and degradation in comparison with »heavier« soils.

The »Posavina« station is situated at Kruševica, some 40 km east of Slavonski Brod, on the left bank of the Sava river. The soil there is of a more recent alluvial type, azonal by origin, i.e. not showing any specific pedologic development and is characteristically present alongside our biggest rivers Sava, Drava and Danube. When not marshy, oversandy or thin, the alluvial soils are of considerable importance economically i.e. they are generally good, fertile land. According to pedologic analyses of the soil from the experimental stations the »Podravina« station is situated on a highly permeable, clayey, sandy soil, and the »Posavina« station is a sedimented miry clay (Table 1).

SAMPLING AND ANALYSIS

During the preliminary stage 65 sites were investigated twelve of which entered the final selection as possible experimental stations. From these stations on locations in Posavina, Podravina, Međimurje and Istria soil samples were collected and examined for residues of chlorinated hydrocarbon pesticides.

Soil samples were collected using the grid system (10). The samples were taken from a depth of 25 cm and transported in glass bottles to the laboratory where they were examined for residues of aldrin, dieldrin, lindane and other stereoisomers of hexachlorocyclohexane, DDT and its metabolites.

A number of factors such as choice of solvent, type of soil, technique and timing of extraction and cleanup, physico-chemical properties of pesticides and others, may affect the efficiency of pesticide extraction (4). After 24 hours of drying at room temperature soil samples were extracted

Table 1.

Pedologic characteristics of soil samples from the experimental stations

	Đurđevac	Kruševica
1. Mechanical analyses of soil		
2 —0.2 mm (particles) %	20.41	2.61
0.2 —0.05	45.72	11.62
0.05—0.002	17.45	12.58
below 0.002	4.31	29.83
2. Adsorption complex after Kappen		
Y_1 (hydrolytic soil acidity)	9.9	6.0
T-S (nonsaturation of adsorption complex after Kappen)	6.9	8.4
S (sum of base substitution capability after Kappen)	7.2	24.1
T (maximal adsorption complex for bases after Kappen)	13.6	32.5
V (degree of adsorption complex saturation with bases)	51.8	73.0
3. Organic matter (humus) % content	1.0	1.55
4. pH in H_2O	5.61	6.80
pH in n-KCl	4.52	6.83
5. P_2O_5 mg per 100 g of soil	4.30	0.45
K_2O mg per 100 g of soil	8.90	11.50
6. Soil type		
According to US Department of Agriculture classification	clayey and highly permeable	miry clay of medium and poor to medium permeability

in the Soxhlet apparatus with the hexane: acetone (4+1) mixture. All solvents were glass-distilled and free of interfering residues.

Pesticide concentrations in soil samples are presented in Table 2. Each figure is a mean value from three replicates.

All crop samples collected during the experiment were cleaned on the spot to eliminate earth and other impurities, and were transported to the laboratory on the same day. Potato, corn, wheat and carrot samples, after having been minced with a knife, and grated, were homogenized in a Votrex homogenizer with the simultaneous extraction of pesticides with acetonitrile.

After cleaning the extract in a column with 2% water deactivated Florisil and anhydrous sodium sulphate, and after elution, the hexane layer was vaporized and injected into a gas chromatograph.

A Pye Unicam 104 gas chromatograph with 63 Ni electron capture detector was used for analyses. The initial pesticide determination was

Table 2.

The concentration of chlorinated pesticides in soil samples from various sites (μg/kg ± SD)

Station	Pesticide				
	Lindane	Alpha-HCH	Aldrin	Dieldrin	DDT-total
Međimurje					
I	1.5 ± 0.03	2.2 ± 0.04	0.0	0.4 ± 0.04	13.2 ± 0.11
II	1.5 ± 0.03	2.2 ± 0.03	0.0	0.4 ± 0.02	16.3 ± 0.12
III	0.4 ± 0.02	0.0	0.8 ± 0.1	0.4 ± 0.03	10.9 ± 0.09
IV	0.4 ± 0.01	0.0	0.4 ± 0.1	0.7 ± 0.03	5.3 ± 0.10
Istria					
I	10.2 ± 0.19	3.5 ± 0.05	0.0	0.0	2.3 ± 0.07
II	11.4 ± 0.21	3.5 ± 0.06	0.0	0.0	49.1 ± 0.29
III	9.3 ± 0.16	3.5 ± 0.06	0.0	0.0	89.1 ± 0.32
IV	12.3 ± 0.20	3.8 ± 0.07	0.0	0.0	75.6 ± 0.30
Posavina					
I	2.3 ± 0.04	0.5 ± 0.08	0.0	0.1 ± 0.03	0.9 ± 0.07
II	1.0 ± 0.02	0.1 ± 0.01	0.0	0.0	0.6 ± 0.02
Podravina					
I	1.3 ± 0.02	0.3 ± 0.04	0.2 ± 0.03	2.1 ± 0.03	6.9 ± 0.10
II	0.0	0.0	0.0	0.0	2.3 ± 0.05

made on 3% SE-30 glass column, subsequently replaced by a 1.8 m × 4 mm glass column filled with 1.6% OV-17 and 1.95% QF-1 on 100/120 mesh Chromosorb W DMCS at 220 °C. Argon-5% methane was used as a carrier gas at 50 ml/min. The average recovery rate for insecticides from the soil and plant was 87—103 per cent.

RESULTS AND DISCUSSION

The results of chemical analyses for experimental plant cultures are presented in Tables 3, 4, and 5. The values entered are the averages for three stations for the entire period of vegetation. All residue levels in the tables are expressed as μg/kg dry weight and have been corrected for recovery efficiency.

It was demonstrated that the used pesticides underwent degradation in soil due to their own physicochemical properties, pedologic characte-

Table 3.

Average pesticide concentration in 3 samples of potato and corn sampled over the entire growth period (expressed as µg/kg dry weight ± SD)

Sample	Đurđevac (Podravina)				Kruševica (Posavina)			
	lindane	alpha-HCH	aldrin	dieldrin	lindane	alpha-HCH	aldrin	dieldrin
leaves and above ground part of stalk	3.6 ± 0.06	2.0 ± 0.09	2.0 ± 0.10	12.1 ± 0.24	2.3 ± 0.10	0.4 ± 0.12	4.1 ± 0.09	1.9 ± 0.03
mature potato (bulb)	5.7 ± 0.12	0.8 ± 0.08	1.5 ± 0.03	22.8 ± 0.20	17.6 ± 0.16	0.6 ± 0.09	5.2 ± 0.10	31.0 ± 0.36
leaves and stalk	6.0 ± 0.08	0.6 ± 0.07	2.1 ± 0.05	5.3 ± 0.07	3.7 ± 0.07	0.4 ± 0.02	6.7 ± 0.04	4.8 ± 0.13
corn grain	7.5 ± 0.13	1.2 ± 0.06	3.1 ± 0.03	11.0 ± 0.08	13.2 ± 0.28	1.3 ± 0.06	4.0 ± 0.12	6.3 ± 0.18

Table 4.

Average pesticide concentration in 3 samples of wheat and carrot sampled over the entire growth period (expressed as µg/kg dry weight ± SD)

Sample	Đurđevac (Podravina)				Kruševica (Posavina)			
	lindane	alpha-HCH	aldrin	dieldrin	lindane	alpha-HCH	aldrin	dieldrin
leaves and stalk of wheat	19.2 ± 0.17	2.4 ± 0.10	20.4 ± 0.23	18.9 ± 0.19	11.0 ± 0.09	2.1 ± 0.10	212.4 ± 2.3	828.6 ± 7.6
wheat root	148.4 ± 1.00	2.6 ± 0.30	228.3 ± 3.30	569.0 ± 4.8	276.1 ± 3.0	5.1 ± 0.11	834.0 ± 6.0	965.0 ± 6.9
wheat grain	2.2 ± 0.09	0.2 ± 0.02	0.6 ± 0.07	0.0	3.1 ± 0.19	0.3 ± 0.04	23.4 ± 0.97	2.9 ± 0.11
carrot leaves	32.7 ± 0.60	23.1 ± 0.80	6.7 ± 0.18	7.0 ± 0.16	13.8 ± 0.30	9.0 ± 0.17	5.3 ± 0.13	18.0 ± 1.0
carrot root	99.8 ± 1.00	13.7 ± 0.25	40.6 ± 0.90	54.3 ± 1.0	68.3 ± 0.93	6.8 ± 0.33	85.8 ± 0.81	110.0 ± 0.96

Table 5.

Average pesticide concentration in 3 samples of carrot sampled over the entire growth period (expressed as µg/kg dry weight ± SD)

Sample	Đurđevac (Podravina)				Kruševica (Posavina)			
	lindane	alpha-HCH	aldrin	dieldrin	lindane	alpha-HCH	aldrin	dieldrin
carrot leaves[1]	1.6 ± 0.05	2.9 ± 0.10	0.0	0.0	65.2 ± 0.49	32.7 ± 0.28	0.3 ± 0.02	468.2 ± 4.32
carrot root[1]	4.8 ± 0.12	1.2 ± 0.06	1.0 ± 0.05	1.0 ± 0.07	68.3 ± 0.73	12.8 ± 0.33	11.5 ± 0.22	12.4 ± 0.10
carrot leaves[2]	2.7 ± 0.08	4.0 ± 0.09	0.9 ± 0.09	0.0	105.2 ± 1.14	42.4 ± 0.39	0.2 ± 0.03	115.2 ± 1.2
carrot root[2]	3.2 ± 0.07	2.0 ± 0.04	0.5 ± 0.05	0.5 ± 0.03	57.7 ± 0.61	11.4 ± 0.10	30.4 ± 0.28	69.5 ± 0.84
carrot leaves[3]	4.2 ± 0.12	2.5 ± 0.06	0.0	0.0	29.0 ± 0.31	33.1 ± 0.41	5.0 ± 0.07	0.0
carrot root[3]	2.1 ± 0.03	0.4 ± 0.04	0.0	0.0	48.3 ± 0.41	20.0 ± 0.19	40.1 ± 0.37	88.6 ± 0.93
carrot leaves[4]	0.5 ± 0.04	0.2 ± 0.02	0.6 ± 0.03	0.0	52.8 ± 0.51	39.1 ± 0.42	20.7 ± 0.26	605.0 ± 6.97
carrot root[4]	1.7 ± 0.08	1.2 ± 0.05	0.0	0.0	47.2 ± 0.39	18.6 ± 0.17	97.4 ± 0.58	806.1 ± 7.42

Note: plant grown previously 1 potato-wheat; 2 corn-wheat; 3 potato-carrot; 4 corn-carrot ristics of the soil and plant culture types grown on such soil. The values found for aldrin, dieldrin, lindane and alpha-HCH indicate that no contamination of edible plant part was so great as to pose a human health hazard provided that pesticides were applied with care. In fact, in our experiment where the pesticide was used in the recommended amounts no single plant had a pesticide content high enough to come under the ban of our regulations. Of course, concentrations varied depending on the part of the plant which was observed. Pesticide levels were higher in some parts of plant (e.g. root) than in others (e.g. leaves, grain). Pesticide levels also varied according to pedologic characteristics of the soil where the crop was grown (3, 4, 6, 7) and in our investigations this was reflected in the higher levels of lindane in the roots of potato, corn, wheat grain and carrot at »Posavina« station compared with those grown at »Podravina«. The more alkaline soil »Posavina« also had a higher level of lindane than the acid soil. Vaporization of lindane from sandy soil features more readily than in miry clay soils. Pedologic soil features also affected aldrin levels. It was found in higher concentrations in carrot, wheat, corn and potato crops from »Posavina« than in these from »Podravina«. A larger amount of aldrin, dieldrin, lindane and alpha-HCH was contained in the wheat root than in the leaves or mature grain. This was similar to carrot roots in relation to levels of insecticides found. At both stations higher concentrations of applied pesticides and their metabolites were found in the potato, except for lower concentrations of aldrin in the »Podravina« potato than in its young leaves. Our findings show that the first crop of carrots grown in the soil contaminated with pesticides will have a much higher concentration of pesticides than the second and subsequent crops. Apparently, each crop partially »clears« the soil of applied pesticides, their metabolites and stereoisomers.

Our hypothesis on isomerization of lindane into alpha-HCH was built on our finding of several hundred times higher concentrations of alpha-HCH in the soil and plant cultures than could have been introduced into the experiment as an impurity with lindane. It should be mentioned that other hexaclorocyclohexane stereoisomers could not be found despite our search for them.

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Sažetak

TRANSLOKACIJA, DEGRADACIJA I DEKONTAMINACIJA NEKIH PESTICIDA U ODNOSU NA REZIDUE PESTICIDA U PREHRAMBENIM PROIZVODIMA

Ovim se radom htio dokazati stupanj translokacije, degradacije i dekontaminacije aldrina i lindana u odnosu na različite pedološke osebujnosti tla pokusnih postaja na kojima su tijekom četiri godine uzgajane različite biljne kulture.

Dokazano je da se aldrin i lindan, te njihov metabolit, odnosno stereoizomer, translociraju iz tla u biljku, a u samoj biljci od korijena prema listu i zrnju.

Uočena je stereoizomerizacija lindana (gama-HCH) u alfa-HCH, ali bi daljnjim pokusima trebalo ukloniti prisutne dvojbe. Različiti tipovi tla na postajama »Podravina« i »Posavina« također utječu na translokaciju i degradaciju pesticida.

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