

Residues of hydrocarbon pesticides in plant products and soils in Slovenia

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Abstract

The contamination of plant products in Slovenia with hydrocarbon pesticide residues based on a monitoring performed in the twenty years period of 1973-1992 is discussed. The plant products studied included potato tubers, maize grain, dried hop cones, grapes, fruits (mainly apples and pears) as well as the corresponding soils. Samples were taken at a random irrespective of previous use of pesticides. They are regionally representative. As evident from the tables, the contamination of soils and plant products in the investigated period was very low. The levels detected in the plants were surprisingly low compared to the EU standards.

Key words

Plant products, soils, pesticide residues, Slovenia

Introduction

The use of pesticides is accompanied by some undesirable side effects. Their residues in soil and plants or plant products have attracted much attention. Because the pesticides are mostly biotically very active substances, some anxiety about their residues is understandable, although their contents in soil and especially in plants are extremely low.

In Slovenia, the monitoring of pesticide residues started relatively early, in 1973. The project was carried out in phases of five years. In the 1st year potato tubers, in the 2nd pome fruits, in the 3rd grapes, in the 4th maize kernels in the 5th dried hop cones were sampled and analysed. Because the plant samples were taken on the entire territory of Slovenia, regionally representative and fully randomly, without inquiry about former use of pesticides, we can rightfully suppose that the results presented are really representative averages of the country.

Materials and methods

Samples of soil and plant organs were collected as smaller samples (fruits, grapes, tubers) at one location and then combined into one main sample. The results presented in the tables of this paper are averages from 50 to 180 of such main samples.

The preparation of plant samples and the chemical analyses were performed according to the standard, or in some cases according to somewhat modified standard methods (described in publications from Maček *et al.* for each year). (Anon. 1972, Bhalla *et al.*, 1970, Black, 1965, Frehse, 1970, Gartner, Urek, 1992, Kawanara, Nakamura, 1972, Perkow, 1968, Richard, 1968, Worthing, 1979, Zweig, 1964). All analyses were performed in the Central laboratory of the Agricultural Institute of Slovenia in Ljubljana. (Thanks to: Marko Dorer, Jerca Cencelj, Ph. D., Jona Repe, Andrej Krašnja, Andrej Gartner and Ana Gregorčič, Ph. D., who performed the analyses).

Results and discussion

Potato fields and tubers

In Table 1, the contamination of soil from potato fields and potato tubers with residues of various pesticides is presented (Maček *et al.*, 1974, Maček, Cencelj, 1981a, Maček, Repe, 1984).

Table 1. Contamination of potato field soils and potato tubers with hydrocarbon pesticide residues

Pesticide or metabolite	Year	Results of chemical analyses						
		Soil			Potato tubers			
		% of contaminated samples	Mean content µg/kg	Residues under the detection limit (% of samples)	% of contaminated samples	Mean content mg/kg	Residues under the detection limit (% of samples)	Tolerances of residues mg/kg
gamma-HCH	1973	100.0	33.2		100.0	0.002		1.0
gamma-HCH	1984	100.0	3.0					
Σ DDT	1973	100.0	316.5		100.0	0.002		0.1
Σ DDT	1984			74.0				
DDE	1984	26.0	2.6					
op' - DDT	1984	60.0	17.1	40.0				
pp' - DDT	1984	60.0	11.2	40.0				

It is a generally decreasing trend of the hydrocarbon pesticide residue contents in crops in the examined period. From 1973 till 1984 the contamination of soil with gamma-HCH decreased nearly ten folds. During 1973, all samples of soils and potato tubers were contaminated with gamma-HCH as well as DDT and its metabolites, but the values were almost traces in all (mean content 2 µg/kg).

Orchard soils and fruits

Table 2. Contamination of orchard soils and fruits with hydrocarbon pesticide residues

Pesticide resp. metabolite, fruit and mode of production	Year	Results of chemical analyses						
		Soil			Fruits			
		% of contaminated samples	Mean content µg/kg	Residues under the detection limit (% of samples)	% of contaminated samples	Mean content mg/kg	Residues under the detection limit (% of samples)	Tolerances of residues mg/kg
Σ DDT, (apple, pear)	1975	100.0	13.1		100.0	0.532		0.1
op' - DDT	1985	30.0	1.1	70.0				
Chlorohydrocarbons (soil)	1985	77.0		23.0				
alpha-HCH (apple)	1985	50.0	4.1	50.0			83.4 ¹⁾	
gamma-HCH (apple)	1985	90.0	4.0	10.0	16.6	0.005	16.6	1.0
Endrin (peach, intensive production)	1975			100.0				
Endrin (apple, intensive production)	1975	57.8	84.0	42.2	46.7	0.004	53.3	0.001
Endrin (apple, extensive production)	1975	22.3	28.0	77.7			100.0	0.001
Endrin (pear, intensive production)	1975						100.0	0.001

Notes about residues in traces

1) apple, 16.6% of samples

Table 2 gives the chronology of pome fruits contamination with various hydrocarbon pesticide residues (Maček *et al.*, 1975, Maček, Repe, 1987a, Gartner, Urek, 1992). In the first monitoring years (1975), all of the soil samples in orchards (apples, pears) were contaminated with relatively high content of DDT and its metabolites (mean content 0.532 mg/kg), and in the fruits the tolerances (0.1 ppm) were exceeded considerably. In the same year the analyses of soil samples from intensive and extensive apple production showed minor contaminations with endrin, and all apple samples from extensive orchards and those of pears from intensive orchards showed endrin contents under the detection limit. Half of the apple samples from the intensive orchards showed a content under the detection limit, while the others were contaminated (the mean content being 0.04 mg/kg, which is high above the tolerances). During 1985, soil samples from apple orchards were contaminated with alpha- and gamma-HCH and nearly all apples contained alpha- and gamma-HCH either in traces or below the detection limit.

Vineyard soils and grapes

In Table 3, the contamination of vineyard soils grapes with residues of hydrocarbon pesticides is presented (Maček *et al.*, 1976c, Maček, Repe, 1987b, Gartner, Urek, 1992). During 1986, the majority (60 percent) of the grape samples were contaminated only by traces with op'-DDT. 40 percent of the results were under the detection limit.

Table 3. Contamination of vineyard soils and grapes with hydrocarbon pesticide residues

Pesticide resp. metabolite	Year	Results of chemical analyses							
		Soil			Grapes				
		% of contaminated samples	Mean content µg/kg	Residues in traces (% of samples)	Residues under the detection limit (% of samples)	% of contaminated samples	Mean content mg/kg	Residues under the detection limit (% of samples)	Tolerances of residues mg/kg
alpha-HCH	1976	7.5	1.3	17.0	75.5				
gamma-HCH	1976	19.1	1.1	22.5	58.5				
gamma-HCH	1986			27.0	73.0				
DDE	1976	67.9	8.3	20.7	11.4				
op' - DDT	1976	45.3	8.3	37.7	17.0				
op' - DDT	1986							40.0 ¹⁾	0.1
pp' - DDT	1976	69.8	19.0	18.8	11.4				

Notes about residues in traces

¹⁾ grapes, 60.0% of samples

Hop garden soils and dried hop cones

In Table 4, the contamination of the dried hop cones with residues of various pesticides is presented (Maček *et al.*, 1976b, Maček, Krašnja, 1981b, Maček *et al.*, 1989a). The contamination with gamma-HCH was relatively high during 1975 where 94 percent of samples were contaminated, but to a very low extent with a mean content of 8 µg/kg. In the same year the contamination with DDE was more differentiated. One fourth (28 percent) of the samples was measurably contaminated (mean content recorded 28 µg/kg).

Table 4. Contamination of hop garden soils and dried hop cones with hydrocarbon pesticide residues

Pesticide resp. metabolite	Year	Results of chemical analyses					
		Soil			Dried hop cones		
		% of contaminated samples	Mean content $\mu\text{g}/\text{kg}$	Residues under the detection limit (% of samples)	% of contaminated samples	Mean content mg/kg	Residues under the detection limit (% of samples)
alpha-HCH	1981	100.0	5.5				
alpha-HCH	1987			100.0			
gamma-HCH	1975				93.9	0.008	6.1
gamma-HCH	1981	100.0	10.2				
gamma-HCH	1987	90.0	3.4	10.0			
DDE	1975				28.0	0.028	52.0 ²⁾
DDE	1981	31.7	12.5 ¹⁾				
DDE	1987	25.0	1.6	75.0			
op'-DDT	1987	5.0	0.3	95.0			
pp'-DDT	1987	50.0	6.4	50.0			
Aldrin	1987	100.0	20.7				
Heptachlor	1987			100.0			

Notes about residues in traces

¹⁾ soil, 22.5% of samples

²⁾ cones, 20.0% of samples

Cornfield soils and corn kernels

In Table 5, the contamination of soils from cornfields and maize kernels with residues of hydrocarbon pesticides is presented (Maček, Cencelj, 1978, Maček, Krašnja, 1982, Maček, Repe, 1989b). During 1977, the majority of soil samples was contaminated with low content of DDT and its metabolites, only in some these substances were in traces or under the detection limit. During the period 1983 - 1988, the soil contamination of alpha-HCH diminished from all samples being contaminated either with very low content (mean content of 4,9 $\mu\text{g}/\text{kg}$) or with levels under the detection limit. Also, the soil contamination of gamma-HCH diminished in the same period but not that much. The contamination of soils with op'- and pp'-DDT was relatively unimportant in that period, while contamination with heptachlor and aldrin during 1988 was under the detection limit.

Table 5. Contamination of corn soils and corn kernels with residues of pesticides

Pesticide resp. metabolite	Year	Results of chemical analyses							
		Soil			Residues under the detection limit (% of samples)	Kernels of corn			
		% of contaminated samples	Mean content µg/kg	Residues in traces (% of samples)		% of contaminated samples	Mean content mg/kg	Residues under the detection limit (% of samples)	Tolerances of residues mg/kg
DDT and metabolites	1977	61.4	100.6	5.5	33.1				
alpha-HCH	1983	100.0	4.9						
alpha-HCH	1988				100.0				
gamma-HCH	1983	100.0	6.8						
gamma-HCH	1988	66.6	0.7		32.7				
DDE	1983	20.0	10.1	70.0	10.0				
op'-DDT	1983	5.0	13.0	35.0	60.0				
op'-DDT	1988	44.4	1.4		55.6				
pp'-DDT	1983	15.0	27.0	80.0	5.0				
pp'-DDT	1988	88.9	11.8		11.1				
Heptachlor	1988				100.0				
Aldrin	1988				100.0				

Conclusion

The presented results indicated that the contamination of soils and various plant products with pesticide residues in Slovenia in the period 1973-1992 was relatively scarce (with some minor exceptions). In most cases the contents of residues determined represented only a small part of the tolerances. In some cases clear reduction of residue content in time intervals of some years has been established.

No correlation between soil contamination and the corresponding contamination of plant products from the same fields, orchards and vineyards could be established.

References

1. Anon. (1972) Rückstandsanalytik von Pflanzenschutzmitteln.- Mitteilung VI der Kommission für Pflanzenschutz-Pflanzenbehandlungs- und Vorratsschutzmittel. Deutsche Forschungsgemeinschaft. II. Lieferung, Weinheim/Bergstrasse. (Prometrin, Äpfel, Erde, Kaffee, Karotten, Kartoffeln, Kohl, Lauch, Mais, Wasser, Weinbeeren, Weizen).
2. Bhalla, J., S. Krueger, H. R., Desmukh, O. S. (1970) Estimation of endrin residues in on bhindi fruits by gas chromatography.- Indian Journal of Entomology 32 (3), pp. 180-193 (cit. after Health aspects of Pesticides Abstract Bulletin (HAPAB) (1972), 5 (12), 72-2538).
3. Black, C. E. (eds.) (1965) Methods of Soil Analysis. Part 2, Chemical and Microbiological Properties. No. 9, Madison, Wisconsin, USA.
4. Frehse, H. (1970) Rückstände von Pflanzenschutzmitteln in Nahrung und Umwelt.- In: R. Wegler, (eds.) Chemie der Pflanzenschutz- und Schädlingsbekämpfungsmittel. Bd. 2, Springer Verlag Berlin-Heidelberg-New York, pp. 434-504.
5. Gartner, A., Urek, G. (1992) Ugotavljanje ostankov fitofarmaceutskih pripravkov v kmetijskih tleh in vrtninah (The pesticide residues in agricultural soils and plants). Poročila KIS o strokovnih nalogah za leta 1987-1992, Ljubljana.

6. Kawanara, T., Nakamura, H. (1972) Organochlorine pesticide residues in agricultural products and soil. Part 5, Absorption of some chlorinated hydrocarbon insecticides from soil by eggplant. - *Noyaku Keusasho Hokoku* 11 (10), pp. 51-54 (cit. after HAPAB (1973) 5, 7, pp. 72-1401.
7. Maček, J., Cencelj, J., Dorer, M.; Milharčič, L. (1974) Kontaminacija zemlje iz krompirišč in gomoljev krompirja z rezidui carbarila, diklordifeniltrikloretana in lindana v Sloveniji (The contamination of soils from potato fields and potato tubers with residues of carbaryl, DDT and lindane in Slovenia). *Zbornik Biotech fac Ljubljana*, 23, 57-68.
8. Maček, J., Cencelj, J., Dorer, M. (1976a) Kontaminacija zemlje iz sadovnjakov in plodov jablan ter hrušk z rezidui carbarila in endrina v Sloveniji (The contamination of orchard soils and apple and pear fruits with residues of carbaryl and endrin in Slovenia). *Zbornik Biotech fac Ljubljana*, 225-234.
9. Maček, J., Cencelj, J., Dorer, M. (1976b) Kontaminacija zemlje iz hmeljišč ter storžkov hmelja z rezidui bakra, lindana, diklordifeniltrikloretana in organskih fosfornih estrov v Sloveniji (The contamination of hop garden soils and hop cones with residues of copper, lindane, DDT and organophosphates in Slovenia). *Zbornik Biotech fac Ljubljana*, 28, 61-72.
10. Maček, J., Cencelj, J., Dorer, M. (1976c) Kontaminacija zemlje iz vinogradov ter grozdja z rezidui bakra, DDT, HCH, lindana, captana + folpeta ter difolatana v Sloveniji (The contamination of vineyards soils and grapes with residues of copper, DDT, alpha-HCH, lindane, captan + folpet and difolatan in Slovenia). *Zbornik Biotech fac Ljubljana*, 28, 73-84.
11. Maček, J., Cencelj, J. (1978) Kontaminacija zemlje iz koruzišč ter koruznega zrnja z rezidui triazinov ter njihovih metabolitov v Sloveniji (The contamination of soils from corn fields and corn kernels with residues of triazines and their metabolites in Slovenia). *Zbornik Biotech fac Ljubljana*, 31, 103-111.
12. Maček, J., Cencelj, J. (1981a) Kontaminacija gomoljev krompirja z ostanki insekticidov karbamatov v Sloveniji (The contamination of potato tubers with residues of insecticides carbamates in Slovenia). *Zbornik Biotech fac Ljubljana*, 36, 147-151.
13. Maček, J., Krašnja, A. (1981b) Kontaminacija zemlje iz hmeljišč z ostanki kloriranih ogljikovodikov ter storžkov hmelja z ostanki bakra in ditiokarbamatov v Sloveniji (The contamination of hop garden soils with residues of chlorohydrocarbons and hop cones with residues of copper and dithiocarbamates in Slovenia). *Zbornik Biotech fac Ljubljana*, 37, 313-326.
14. Maček, J., Krašnja, A. (1982) Kontaminacija zemlje iz koruzišč z ostanki triazinov in kloriranih ogljikovodikov ter koruznega zrnja z ostanki triazinov (The contamination of soils from corn fields with residues of triazines and chlorohydrocarbons and corn kernels with residues of triazines). *Zbornik Biotech fac Ljubljana*, 39, 85-94.
15. Maček, J., Repe, J. (1984) Kontaminacija gomoljev krompirja z ostanki insekticidov karbamatov in zemlje iz krompirišč z ostanki kloriranih ogljikovodikov v Sloveniji (The contamination of potato tubers with residues of insecticides carbamates and the soils of potato fields with residues of chlorohydrocarbons in Slovenia). *Zbornik Biotech fac Ljubljana*, 43, 293-298.
16. Maček, J., Repe, J. (1987a) Kontaminacija zemlje z ostanki kloriranih ogljikovodikov in jabolk z ostanki karbarila, ditiokarbamatov v Sloveniji (The contamination of potato tubers with residues of insecticides carbamates of chlorohydrocarbons in Slovenia). *Zbornik Biotech fac Ljubljana*, 47, 181-187.
17. Maček, J., Repe, J. (1987b) Kontaminacija tal iz vinogradov z ostanki kloriranih ogljikovodikov ter grozdja z ostanki ditiokarbamatov, kloriranih ogljikovodikov in bakra v Sloveniji (The contamination of vineyard soils with residues of chlorohydrocarbons and grapes with residues of dithiocarbamates, chlorohydrocarbons and copper in Slovenia). *Zbornik Biotech fac Ljubljana*, 49, 259-266.
18. Maček, J., Repe, J., Gartner, A. (1989a) Kontaminacija tal iz hmeljišč z ostanki kloriranih ogljikovodikov ter hmeljevih storžkov z ostanki bakra v Sloveniji (The contamination of vineyard soils with residues of chlorohydrocarbons and grapes with residues of dithiocarbamates, chlorohydrocarbons and copper in Slovenia). *Zbornik Biotech fac Ljubljana*, 53, 199-204.
19. Maček, J., Repe, J. (1989b) Kontaminacija zemlje iz koruzišč z ostanki triazinov in kloriranih ogljikovodikov ter koruznega zrnja z ostanki triazinov v Sloveniji (The contamination of soils from corn fields with residues of triazines and chlorohydrocarbons and corn kernels with residues of triazines). *Zbornik Biotech fac Ljubljana*, 53, 205-210.
20. Perkow, W. (1968) *Die Insektizide. Chemie, Wirkungsweise und Toxizität.* - Heidelberg, pp. 272.
21. Richard, A. A. (1964) Cleanup method for electron capture determination of endrin in fatty vegetables. - *Journal of the association of the official analytical chemists* 47, 4, pp. 659.
22. Worthing, C. R. (1979) *The pesticide manual.* British Crop Protection Council. 6th edition.
23. Zweig, G. (1964) *Analytical Methods for Pesticides, Plant Growth Regulators and Food Additives.* Academic Press, New York, London.