PESTICIDE RESIDUES AND METAL CONTENTS IN FLUE-CURED TOBACCO LEAF, ONTARIO, 1986-88

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Between 1986 and 1988, 30 Ontario farms growing flue-cured tobacco (*Nicotiana tabacum* L.) were surveyed for their annual pesticide applications, and their cured tobacco crops were sampled for analysis of pesticide residues and toxic metals. The use surveys showed that applications of synthetic pyrethroids for cutworm control increased while those with chlorpyrifos decreased from an earlier survey. Acephate was the most widely used insecticide for foliar insects and was followed by deltamethrin and permethrin. Analysis of cured tobacco leaf revealed no detectable synthetic pyrethroid insecticide residues. Diphenamid residues appeared in cured leaf where it had been applied for weed control, however the residue was mainly the N-methyl metabolite, N-methyl 2,2-diphenylacetamide. Minor residues of several organochlorine insecticides were still to be found in cured leaf 10 to 20 years after their use had been terminated. Organophosphorus insecticide residues were absent or at trace levels in cured leaf except for acephate. Acephate residues were found where the insecticide had been used; however, these residues were present primarily as the methamidophos metabolite and were found at all stalk positions with the higher levels in sand leaves.

Additional key words: *Nicotiana tabacum* L., insecticides, herbicides, nematicides, fungicides.

INTRODUCTION

The spectrum of pesticides used in the production of flue-cured tobacco (*Nicotiana tabacum* L.) in Ontario has been in constant flux over the last two decades as the result of changes in registration status due to health and environmental concerns and/or the appearance of pest resistance. Organochlorine insecticides were predominately used in the 1960s, and the organophosphorus insecticides were predominately used in the 1970s (3,4,8,9). During the 1980s the synthetic pyrethroids became the most commonly used group of insecticides (6,7). Specific insecticides in use have also been changing. In 1973, leptophos, chlorpyrifos, and endosulfan were the major insecticides **(Table 1)**. By 1978, *Bacillus thuringiensis* Berliner was a major insecticide and leptophos had been removed from the marketplace because of a health hazard. By 1983, acephate, cypermethrin, and permethrin were major insecticides, and later deltamethrin became the most popular pyrethroid. The use patterns of fungicide and herbicide have changed less frequently than insecticides.

Monitoring of insecticide residues in flue-cured tobacco leaf and soils commenced in 1970 and results to 1978 were reported by Frank et al. (3,4). In 1976, monitoring and surveillance were changed from a general survey of the cured tobacco sold on the auction floors to a survey of 34 selected farms, distributed across the tobacco-growing belt. This made it possible to obtain specific data on the identity and quantity of pesticides used on each farm and to correlate use patterns and residues. At the same time, the analysis for herbicides and fungicides were added. In this paper, we report the results of the farm samplings collected and analyzed between 1986 and 1988.

MATERIALS AND METHODS

Field Work

Between 1986 and 1988, 27 to 30 farms remained in the survey and each of the three years were monitored for pesticide use and residues in flue-cured tobacco leaf. Samples of the cured leaf were analyzed for certain heavy metals (Cd, Ni, and Pb) of concern to the buyers and manufacturers. All farms were located in the prime growing regions of the Lake Erie and Lake Ontario watersheds. Records kept by growers on the use of insecticides, fungicides, and herbicides were obtained at the time of an annual visitation to

Table 1. Use of pesticides in tobacco production in Ontario taken from four surveys (1973-1988)[a].

Pesticides	Areas Treated 1973	1978	1983	1988
	ha			
Area Grown	43,000	43,000	40,500	24,300
diphenamid	0	4,680	6,450	1,970
glyphosate	0	1,030	620	450
naproamide	0	0	230	2,280
pebulate	2,820	1,290	710	430
sethoxydim	0	0	0	50
trifluralin	0	20	110	0
acephate	0	2,910	19,500	5,100
azinphosmethyl	0	110	0	300
B.t.	5,100	7,630	3,440	2,590
carbaryl	5,370	1,100	0	360
chlorpyrifos	11,150	16,900	9,580	1,780
cypermethrin	0	0	7,500	1,650
deltamethrin	0	0	3,870	7,420
diazinon	7,750	1,170	1,390	630
endosulfan	8,210	2,360	540	100
leptophos	10,490	170	0	0
lindane	3,660	750	1,340	0
malathion	365	0	390	0
methomyl	0	5,820	0	0
oxydemeton methyl	0	10,700	6,170	0
permethrin	0	1,900	7,480	5,920
pirimicarb	0	980	130	1,250
trichlorfon	1,290	16,300	1,710	620
benomyl	0	0	230	370
captan	0	0	0	230
metalaxyl	0	0	1,990	0
1,2-D + 1,3-D	25,510	25,590	32,600	16,300
Used	Total Active Ingredient			
	kg			
Herbicides	14,700	16,400	17,800	7,400
Insecticides	132,900	85,300	39,900	21,200
Fungicides	3,260	3,300	1,070	30
Nematocides	1,661,000	1,156,600	1,610,000	766,800

[a] *Roller (8,9), Magee (6), and Moxley (7)*

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each grower who had been cooperating in the program since 1976. Cured leaf samples were collected from each farm during the month of September. Three samples were taken from each leaf stalk position: namely, sand, cutter, and tip. Samples were returned to the Agriculture Canada's Research Station at Delhi where they were dried and ground to give a subsample of 250-300 g each and delivered in November of each year to the Agricultural Laboratory Services Branch, Ontario Ministry of Agriculture and Food, for the analyses of pesticide residues and toxic metal contents.

Analytical Procedure

Residues of organochlorine and organophosphorus insecticides and metals in leaf were determined as described by Frank et al. (3,4). Detection limits for organochlorine compounds were improved over those in previous surveys and the general level was 5 ppb. Synthetic pyrethroid insecticide analysis was included using the method of analysis as described by Braun and Stanek (2). Trichlorfon and oxydemeton-methyl analyses were carried out only on samples from those farms which had indicated their use. The procedure for trichlorfon was identical to that for other organophosphorus insecticides with the exception that the gas chromatographic determination was carried out at 125 degrees C. Oxydemeton-methyl was determined according to the procedure described by Thornton et al. (11) whereby residues were converted to the respective sulfone prior to determination. Recoveries of trichlorfon and oxydemeton-methyl from fortified samples averaged 87% and 84%, respectively.

Residues of diphenamid and its metabolites were determined in accordance with the method described by Sirons et al. (10). For metal analyses, tobacco (1 g) was digested by boiling gently for 5 hr with a maintained volume of 10 ml concentrated nitric acid, adding 20 ml water, and heating just below boiling for an additional 2 hr. The sample was then filtered and adjusted to 100 ml final volume with water. Determinations of Cd, Ni, and Pb were made by atomic absorption spectroscopy with a Perkin Elmer model 2380 equipped with background connection. Recovery of metals varied from 98% to 102% from tobacco leaves.

RESULTS AND DISCUSSION

Pesticide Use Surveys

Information collected on the 27 to 30 farms between 1986 and 1988 is compiled in **Table 2.** The findings were compared with the official provincial-wide surveys conducted on pesticide use on Ontario farms in 1988 and discussed in the introduction **(Table 1).**

From 1973 to 1988, the hectarage in tobacco production declined by 43%, from 43,000 to 24,300 ha (1). At the same time, the amount of pesticides used in tobacco production declined; in the case of herbicides, insecticides, and nematicides, the decline in use was 50, 84, and 54% respectively. The pattern of pesticide use on the 27 to 30 surveyed farms reflected the same trends found in the pesticide use survey for the whole tobacco industry. In 1988, the organophosphorus insecticide, acephate, and the synthetic pyrethroids, deltamethrin, and permethrin, were the major compounds used in the control of insects.

Residues in Tobacco Leaf

The organochlorine insecticides, DDT, dieldrin and endrin, not used since the early 1970s, are still residual in tobacco soil and continue to be taken up into tobacco leaf tissues. Residues in the cured tobacco leaf are presented in **Table 3.** The use of endosulfan has been phased out and is reflected in the absence of detectable residues in cured leaf by 1988. Chlordane has not been applied to soil for several years; however, in 1988 some residues were identified because of methodologies being used that lowered the detection limits. Residues in previous studies had been below the detection limits. Dieldrin residues in tobacco leaf appeared to decline between 1986 and 1988 while t-DDT appeared to increase. The latter is considered to be an anomaly.

Table 2. Pesticides used on 27-30 farms[a] surveyed and sampled, 1986-88.

Pest and Pesticide	Number of Farms		
	1986	1987	1988
Total Farms	29	30	27
Soil Insects			
lindane	5	3	3
Cutworm			
acephate	4	5	6
chlorpyrifos	1	1	2
cypermethrin	8	7	4
deltamethrin	8	11	9
permethrin	8	6	5
Hornworms			
acephate	25	27	24
B.t.	3	3	3
trichlorfon	1	0	1
Aphids			
acephate	25	19	22
dimethoate	2	0	0
oxydemeton methyl	1	3	0
pirimicarb	0	5	2
Weeds			
diphenamid	8	6	4
glyphosate	1	0	0
napropamide	0	0	3
pebulate	1	1	1
sethoxydim	1	0	0
Nematodes[b]			
1,3-D	3	4	2
1,3-D + MIS	10	11	6
1,3-D + chloropicrin	8	8	8
1,3-D + MIS + chloropicrin	5	6	10
metamsodium	1	1	1

[a] Originally 34 farms enrolled in the program in 1976.
[b] 1,3-D - 1,3 dichloropropene, MIS - methylisothiocyanate

p,p′, and o,p′ DDT as a percent of the total DDT residue appeared to decline while the residue of o,p′, and p,p′ DDE increased; as expected. The decrease of parent material and increase of metabolite were, however, smaller than the year to year variations in total DDT residues found in the cured leaf **(Table 4).** These fluctuations are discussed later. No residues of endrin were found in tobacco leaf.

Twenty-seven to 34 selected farms have been monitored over the past 12 years (1976-1988) and the analyses of cured tobacco leaf for the years 1976-1980 and 1981-1985 have been reported previously (4,5). Regression analyses were performed on the pesticide residue data collected over the 12-year period for t-DDT, dieldrin, and toxic metals and the calculations appear in **Table 5.** While the regression analyses were significant, the correlation coefficient was acceptable for t-DDT but not for dieldrin. In spite of the fact that aldrin has not been available for use since 1969, residues of its metabolite dieldrin have fluctuated and tended to increase until 1983. Since 1983, residues have declined. On the other hand, t-DDT residues have declined over the 12-year period. In some years, residues have appeared to be abnormally higher or abnormally lower than expected; however, a downward trend can be observed over the whole period.

Residue concentrations of the currently used pesticides appear in **Table 6.** Residues of five of the 10 insecticides

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Table 3. Organochlorine insecticide residues in cured tobacco leaf derived from residues in soils from past uses.

Insecticide (Year of last use)	Priming	Residue in dried flue-cured tobacco								
		1986			1987			1988		
		Mean ± SD		Detectable Residues	Mean ± SD		Detectable Residues	Mean ± SD		Detectable Residues
Farms (No)		29			30			27		
		---- ug/kg ----		%	---- ug/kg ----		%	---- ug/kg ----		%
t-DDT (1971)	P1	777	278	100	539	282	100	959	475	100
	P3	257	119	100	255	121	100	291	128	100
	P5	111	44	100	133	60	100	161	24	100
Dieldrin (1969)	P1	67	32	100	39	32	87	18	11	96
	P3	25	17	100	23	40	93	8	4	85
	P5	10	4	93	8	6	73	7	4	85
Endrin (1972)	P1	<5	—	0	<5	—	0	<5[a]	—	0
	P3	<5	—	0	<5	—	0	<5	—	0
	P5	<5	—	0	<5	—	0	<5	—	0
t-Endosulfan (1978)	P1	15	11	90	7	7	50	<5[a]	—	4
	P3	7	5	72	7	20	27	<5	—	0
	P5	<5	—	31	<5	—	13	<5	—	0
Heptachlor epoxide (1969)	P1	10	16	41	4	6	33	9	5	74
	P3	3	3	21	3	2	13	3	1	0
	P5	2	2	7	1	1	0	1	1	4
Chlordane (1978)	P1	<5	—	0	<5	—	3	5	6	11
	P3	<5	—	0	<5	—	0	2	2	7
	P5	<5	—	0	<5	—	0	1	1	4

[a] Limits of detection in the case of endosulfan residues of each component could be measured to 5 ug/kg.

Table 4. t-DDT residues and composition in cured tobacco leaf.

Residue	1986			1987			1988		
	P1	P3	P5	P1	P3	P5	P1	P3	P5
	---------- ug/kg ----------								
t-DDT	777	257	111	539	255	133	949	291	161
	---------- % ----------								
o,p'-DDE	NA[a]	NA	NA	NA	NA	NA	2.4	1.5	5.3
p,p'-DDE	49.7	50.5	55.4	52.3	56.8	53.8	56.8	60.2	55.2
p,p'-TDE	0.7	2.1	1.1	0.3	0.2	0.2	0.6	0.8	0.7
o,p'-DDT	14.0	14.2	15.2	14.2	12.2	12.4	13.6	14.0	14.9
p,p'-DDT	35.6	33.2	28.3	33.2	30.8	33.6	26.6	23.5	23.9

[a] NA - not analyzed

Table 5. Regression analyses of t-DDT, dieldrin, and toxic metals in cured tobacco leaf analyzed between 1976 and 1988 from the surveyed farms.

	Regression Equation (Log Y)	F	Correlation Coefficient	Half life Disappearance	Rate loss per year
			%	years	%
t-DDT	2.951 - 0.031x	29.5 ***	78.6	9.7	7.2
dieldrin	1.765 - 0.036x	7.5 ***	48.3	8.5	8.2
Cd	0.473 - 0.019x	3.5 ns	46.6	(16.1)	–
Ni	0.463 - 0.046x	10.7 *	78.0	6.5	–
Pb	0.470 - 0.050x	481.0 ***	99.3	6.0	11.6

*P = 0.05; *** P = 0.005; ns – not significant

used appeared in cured leaf. Residues of lindane came from soil treatments at planting time. Cypermethrin, dimethoate, pirimicarb, and acephate residues came from foliar application. Acephate residues were present primarily as the methamidophos metabolite, and residue levels were similar over the three years. In spite of the use of deltamethrin and permethrin, no residues were identified on cured leaf.

Diphenamid was used at planting time and resulted in residues of the parent material and its major metabolite, N-methyl 2,2-diphenylacetamide, being present in the cured tobacco leaf **(Table 7).** No residues of 2,2-diphenylacetamide were found to the limit of detection.

Metal concentrations in tobacco leaf appear in **Table 8.** The data for Cd, Ni, and Pb concentrations in the cured tobacco leaf were subjected to regression analysis for the 12-year period, 1976-1988 **(Table 6).** The regression analyses was not significant for the decline in Cd.

Table 6. Residue concentrations of insecticides currently used in the production of cured tobacco leaf, 1986-88.

Insecticide	Priming	1986 Farms Using	1986 Detectable Residues	1986 Mean ± SD		1987 Farms Using	1987 Detectable Residues	1987 Mean ± SD		1988 Farms Using	1988 Detectable Residues	1988 Mean ± SD	
		No.	No.	-- mg/kg --		No.	No.	-- mg/kg --		No.	No.	-- mg/kg --	
lindane	P1	5	4	7	4	3	3	13	—	3	3	43	8
	P2		3	6	2		1	14	—		2	15	—
	P3		2	6	5		0	—			1	6	—
acephate	P1	13	13	55	83	17	17	44	44	22	22	53	37
(methaminophos)	P3		2	29	15		6	14	12		6	39	22
	P5		1	70	—		10	<5	—		3	11	2
cypermethrin	P1	1	1	33	24	1	0	<5	—	0	0	<5	—
	P3		1	24	—		0	<5	—		0	<5	—
	P5		0	<5	—		1	47			0	<5	—
dimethoate	P1	2	2	77	—	0	0	<5	—	0	0	<5	—
	P3		1	110	—		0	<5	—		0	<5	—
	P5		1	10	—		0	<5	—		0	<5	—
pirimicarb	P1	0	0	—		0	0	—		1	1	20	
	P3		0	—			0	—			0	<5	
	P5		0	—			0	—			0	<5	

Table 7. Diphenamid residues in dried flue cured tobacco leaf, 1986-88.

Year	Number Samples	Priming	Diphenamid	N-methyl 2,2-diphenylacetamide	Total ± SD[a] residue	
			mg/kg			
1986	8	1	0.22	1.27	1.49	1.87
		3	0.07	0.21	0.28	0.21
		5	0.05	0.11	0.16	0.05
1987	6	1	0.07	0.14	0.21	0.19
		3	0.05	0.14	0.21	0.19
		5	0.04	0.13	0.17	0.12
1988	4	1	0.06	0.09	0.15	0.07
	3	3	0.03	0.05	0.08	0.07
		5	0.04	0.05	0.09	0.08

[a] No residues of 2,2-diphenylacetamide identified to a limit of 0.01 mg/kg.

Table 8. Concentration of cadmium, nickel, and lead in cured tobacco leaf, 1989.

Primings	Concentration in leaf Cd Mean ± SD		Ni Mean ± SD		Pb Mean ± SD	
	mg/kg					
P1	3.3	1.1	0.7	0.5	1.4	0.8
P3	1.8	0.3	0.7	0.3	0.4	0.2
P5	1.7	0.4	1.1	0.3	0.4	0.2

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