

Non-solvent-extractable pesticide residues

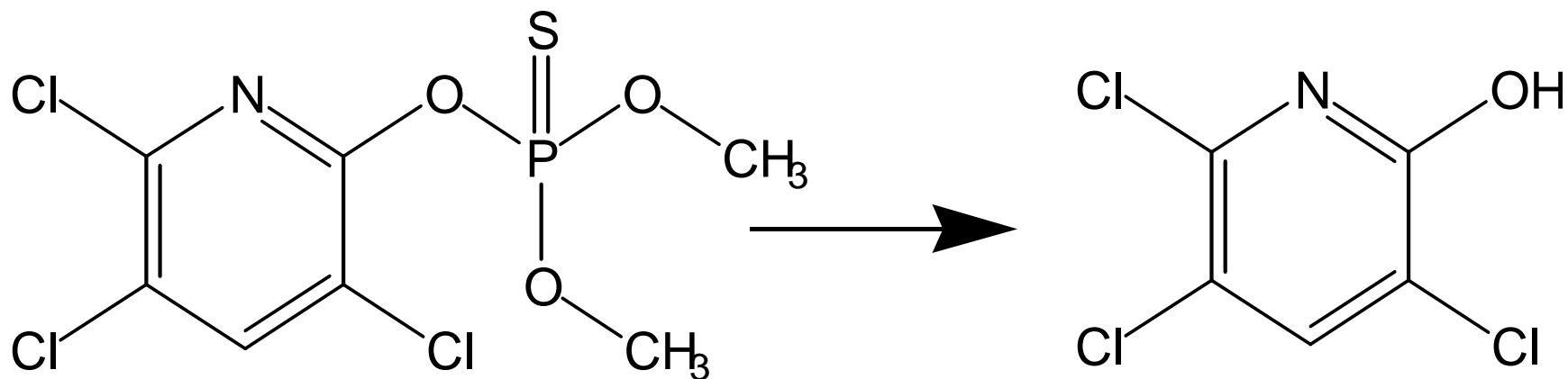


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An investigation of non-solvent-extractable residues of [¹⁴C]chlorpyrifos-methyl in stored wheat



Chlorpyrifos-methyl

3,5,6-trichloropyridin-2-ol

Publication by Wendy A Matthews in Pesticide Science,
Vol 31, Issue 2, p141-149, 1991



Wheat grain treated with ^{14}C -radiolabelled chlorpyrifos-methyl and stored for 5 months

The grain was then extracted with a number of different solvents including methanol and acetonitrile and the extracts were assayed by liquid scintillation counting

Up to 88% of the applied dose was recovered

52% as intact chlorpyrifos-methyl

8% as metabolites

28% remained in the grain tissue



Non-solvent extractable residues (the 28%)

The remaining solvent extracted grain was subjected to both enzymic and chemical solubilisation procedures

- Enzymes (amylase, protease & cellulase) released <2% of radioactivity
- Aqueous salt, alkali and acid solutions released <6% of radioactivity



Non-solvent-extractable residues (28%)

Extracted with varying ratios of methanol/water

<u>MeOH:H₂O</u>	<u>Activity released</u>
0:100	1.7
25:75	32.2
40:60	67.6
50:50	85.9*
70:30	40.4
100:0	0.2

- n = 6, SD 2.6%

[10 g samples with 50 ml (shaken for 24 hr?)]



Composition of the 50:50 Water/MeOH extract

Used TLC to identify components

- No parent chlorpyrifos-methyl was present
- 60% the hydrolytic metabolite
(3,5,6-trichloro-2-pyridinol)
- 26% an unidentified polar compound(s)



Additional Info

- The proportion of non-extractable residues of four OPs was greater in bread and extruded breakfast cereals than in the original grain
- 'Binding' likely to be physical 'encapsulation' or ionic interaction, rather than covalent bonding
- The addition of water should aid extraction by swelling the matrix
- Only organophosphorus compounds studied



Results from FAPAS 2007/8

- Series 9 - Pesticides in cereal-based products – looked at results from the last 6 Rounds
- Mostly lab spiked test materials
- Compared spike values, mean homogeneity values & assigned values



FAPAS Series 19 results

	etrymfos		fenitrothion		malathion		pirimiphos-methyl	
	µg/kg	%	µg/kg	%	µg/kg	%	µg/kg	%
Spike	150	100	150	100	400	100	440	100
Homo	131	87	127	85	456	114	445	101
Ass	136	91	126	84	390	98	431	98

0951 – Maize flour

	chlorpyrifos-methyl		phosphamidon		pirimiphos-methyl	
	µg/kg	%	µg/kg	%	µg/kg	%
Spike	100	100	350	100	300*	100
Homo	90	90	221	63	257	86
Ass	67	67	167	48	263	88

0949 – Oat flour

* incurred residue



FAPAS Series 19 results

	fenitrothion		malathion		deltamethrin	
	µg/kg	%	µg/kg	%	µg/kg	%
Spike	2450	100	2920	100	1180	100
Homo	1777	73	2125	73	792	67
Ass	1541	63	1731	59	886	75

0950 – Wheat flour

	chlorpyrifos		bifenthrin		permethrin	
	µg/kg	%	µg/kg	%	µg/kg	%
Spike	220	100	100	100	180	100
Homo	178	81	84	84	153	85
Ass	164	75	86	86	152	84

0944 – Wheat flour



FAPAS Series 19 results (Corn flakes)

	fenitrothion		phosmet		phosphamidon	
	µg/kg	%	µg/kg	%	µg/kg	%
Spike	80	100	150	100	280	100
Homo	44	55	111	74	189	68
Ass	46	58	109	73	148	53

0946 – Breakfast cereal

	acephate		diazinon		etrimfos	
	µg/kg	%	µg/kg	%	µg/kg	%
Spike	350	100	120	100	200	100
Homo	266	76	71	59	122	61
Ass	167	48	32	26	57	29

0948 – Breakfast cereal



General Conclusions

- May only recover 50-60% of spike value dependent on the pesticide/matrix combination
- The degree of 'binding' increases with time
- Processed cereal products give lower values than cereal grains



Comparative data for 2 methods

- **Method 1 – 1:1 Acetone/methanol extraction**
(25g sample extracted with 100ml of mixed solvent, decanted, and then a second extraction with a further 80ml)
- **Method 2 – 3:1 Ethyl acetate/water extraction**
(Soak 10g of sample in 20ml water for 30mins, then extract with 60ml of ethyl acetate)



Comparison of methods for breakfast cereals

- Seventeen samples of breakfast cereal all containing pirimiphos-methyl were analysed using both methods
- The results were all higher from Method 2
- The ratio of the results were generally between 1.1 and 1.5, but four results were >2

