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Residue Levels in Apples and Pears Field-Treated with Two Experimental Chlorothalonil Formulations

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Chlorothalonil is a well-known product largely used in several countries against a broad spectrum of pathogenic fungi which affect economically important crops (1, 2, 3). Chlorothalonil has been recently considered by I.A.R.C. (4). In Italy, Chlorothalonil is included in a list of pesticides presently under revision. A deeper and updated knowledge about its toxicological and environmental properties will improve the evaluation of risks related to the use of that pesticide. In this framework the determination of the residues in crops treated with Chlorothalonil formulations was performed.

As new types of Chlorothalonil formulations become available, it is essential to check both their efficacy and their residue levels after treatment. Two different types of experimental Chlorothalonil formulations have been tested in a field treatment carried out by the Regional Plant Protection Service (Bologna, Italy) on apple and pears cultivations. This paper presents the levels of Chlorothalonil residues in treated apple and pear samples, harvested after several time intervals, under the experimental conditions described below.

MATERIALS AND METHODS

Two different experimental formulations, granules and flowable were utilized. Field treatment, against Botrytis cynerea, was performed on apple cv Stark delicious and pear cv Passa crassana trees, by spraying with

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atomizer at doses of 144 g a.i./hl (granules) and 100 g a.i./hl (flowable). For each formulation, 3 different plots were treated for apples and for pears. Harvest was carried out at different times after treatment (0-7-14-21-28 days), taking 10 ripe fruits from three different trees for each formulation/crop combination.

Frozen apples and pears were sent to the laboratory and maintained at -20°C until analysis. Fruits were cut in half and sampling groups were formed for crops, type of formulation and harvest time. Each sample was analyzed twice.In all, 30 samples were obtained and 60 analysis made for each crop.

Fruits were minced and homogenized by means of a cutter. Then two 100 g aliquots were taken for the analytical procedure performed according to the steps here described (5, 6):

(a) Extraction with 200 ml acetone (RP distilled) in a Waring blender and successive double washing with 50 ml acetone; filtration on Celite 545 (previously kept in oven at 500°C for 4 hours) with buchner under vacuum and measurement of the extract.
(b) Adsorption of the extract (15 ml) on Extrelut-20 Merck (Code No. 11737) column for 10 min, followed by acetone evaporation under nitrogen flow (1 ml/min) for 30 min (7).
(c) Elution of the Extrelut column with 80 ml of petroleum ether 40-60° (RP distilled) and evaporation by Rotovapor; dilution to known volume in benzene (RP distilled).
(d) Gas-chromatographic analysis performed injecting known quantities of the standard solution (0.2 µg/ml Chlorothalonil in benzene, 99.7% purity) and of the sample.

Gas-chromatographic analysis was performed with a Perkin-Elmer 3920/b equipped with an electron capture detector and a glass column (1.80 m length, 4 mm i.d.) packed with QF-1:1.95% - OV-17:1.5% on Chromosorb W HP 100-120 mesh. The operating conditions were as follows:
- Injector temperature: 220°C

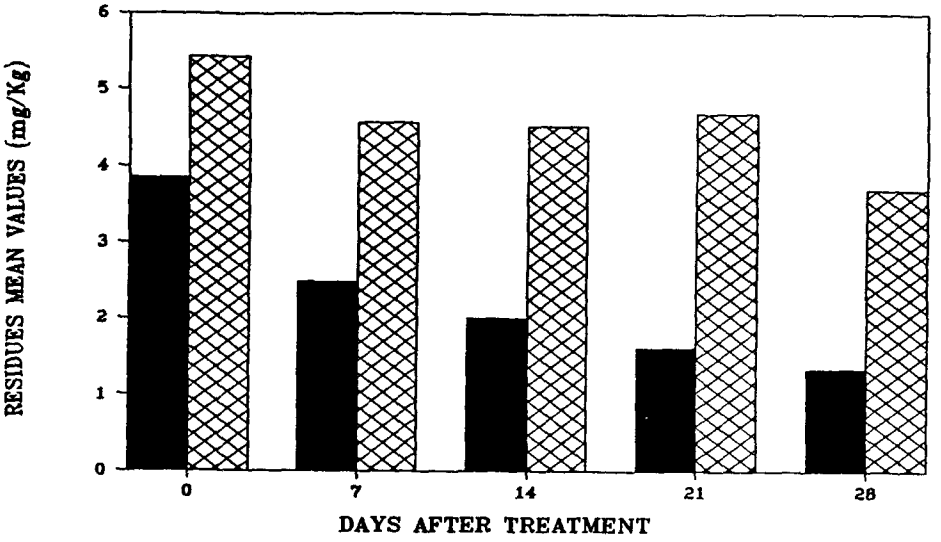

FIGURE 1 – RESIDUES IN PEARS
FLOWABLE GRANULES

- Column temperature: 190°C
- Detector temperature: 300°C (ECD Ni^{63})
- Carrier gas: Argon/methane 5% (8 Kg/cm^2)

Under these conditions, the retention time was 8 minutes approximately and the detector response was stable and reproducible for quantities within the range of 0.2-1 µg. Chlorotalonil-residue values were obtained by systematic gas-chromatographic comparison between known concentrations of the standard solution and unknown concentrations of the sample extract.

Untreated apple and pear samples of the same tested variety did not show any significant interference. Spiked samples yielded over 85% recovery after the addition of 0.2-0.4 ppm.

RESULTS AND DISCUSSION

A total of 120 samples were examined and results are reported in Tables 1 and 2. Reported results are the average of several injections whose single values fell

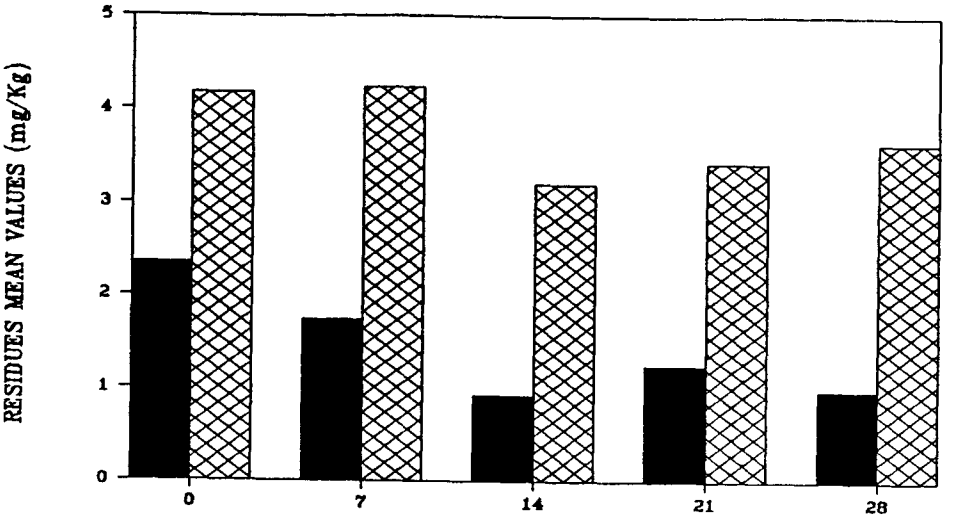

FIGURE 2 - RESIDUES IN APPLES

within the range of experimental error. Figures 1 and 2 show the time/concentration histograms, obtained from the mean values.

The granular formulation leads to higher residue values than the flowable one, for both apples and pears; lower residue levels are found more often in apples than in pears, and more with flowable than with granules. That is probably due to the difference in fruit surface and to the different co-formulating ingredients present in the two formulations.

The overall data indicate that the disappearance rate with time of chlorothalonil residues is quite slow. Apart from toxicological considerations on the residue levels, the results show the influence of the formulation type on the residue levels at harvest. This fact should be considered when legal tolerances are set by governmental authorites.

TABLE 1 - RESIDUES IN PEARS (MG/KG)

	FLOWABLE (100 g a.i./hl) SAMPLES				GRANULES (144 g a.i./hl) SAMPLES			
Days after treatment	1A	1B	1C	MEAN	1A	1B	1C	MEAN
0	4.28 (4.15 - 4.42)	4.01 (3.93 - 4.10)	3.27 (3.25 - 3.30)	3.85 (3.86)	7.31 (7.25 - 7.38)	5.51 (5.40 - 5.63)	3.49 (3.48 - 3.51)	5.43 (5.44)
7	2.77 (2.77 - 2.78)	2.61 (2.57 - 2.65)	2.07 (2.03 - 2.12)	2.48 (2.48)	4.46 (4.37 - 4.56)	4.47 (4.40 - 4.54)	4.75 (4.42 - 5.08)	4.56 (4.56)
14	2.42 (2.41 - 2.44)	2.04 (2.02 - 2.07)	1.56 (1.53 - 1.60)	2.00 (2.01)	5.46 (5.39 - 5.54)	4.01 (3.88 - 4.14)	4.09 (4.04 - 4.14)	4.52 (4.52)
21	1.38 (1.36 - 1.41)	1.66 (1.62 - 1.71)	1.84 (1.80 - 1.88)	1.62 (1.63)	4.31 (4.19 - 4.43)	4.94 (4.92 - 4.97)	4.80 (4.70 - 4.91)	4.68 (4.68)
28	1.31 (1.29 - 1.33)	1.48 (1.44 - 1.52)	1.28 (1.28 - 1.29)	1.35 (1.35)	3.80 (3.73 - 3.88)	3.79 (3.72 - 3.86)	3.49 (3.48 - 3.51)	3.69 (3.69)

TABLE 2 - RESIDUES IN APPLES (MG/KG)

	FLOWABLE (100 g a.i./hl) SAMPLES				GRANULES (144 g a.i./hl) SAMPLES			
Days after treatment	1A	1B	1C	MEAN	1A	1B	1C	MEAN
0	2.2 (2.06 - 2.34)	2.87 (2.80 - 2.94)	1.99 (1.87 - 2.11)	2.35 (2.35)	4.41 (4.35 - 4.48)	4.24 (4.19 - 4.30)	3.90 (3.86 - 3.95)	4.18 (4.18)
7	1.96 (1.47 - 2.45)	1.56 (1.76 - 1.87)	1.67 (1.63 - 1.72)	1.73 (1.82)	4.54 (4.45 - 4.63)	4.24 (4.19 - 4.30)	3.90 (3.86 - 3.95)	4.23 (4.25)
14	0.88 (0.74 - 1.02)	1.26 (1.24 - 1.29)	0.62 (0.60 - 0.63)	0.92 (0.92)	2.82 (2.78 - 2.87)	3.04 (2.98 - 3.11)	3.73 (3.73 - 3.74)	3.20 (3.20)
21	1.01 (0.98 - 1.04)	1.39 (1.36 - 1.43)	1.35 (1.32 - 1.38)	1.25 (1.25)	3.19 (3.15 - 3.23)	4.44 (4.40 - 4.48)	2.64 (2.59 - 2.69)	3.42 (3.42)
28	0.70 (0.69 - 0.72)	0.82 (0.82 - 0.83)	1.43 (1.43 - 1.44)	0.98 (0.99)	3.91 (3.89 - 3.94)	3.75 (3.74 - 3.76)	3.24 (3.23 - 3.25)	3.63 (3.63)

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