Bull. Environ. Contam. Toxicol. (1994) 53:883–887

Environmental Contamination and Toxicology

Dissipation of Pyrazophos Residues in Greenhouse Tomatoes

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Received: 28 October 1993/Accepted: 2 May 1994

Pyrazophos is the common name of an organophosphorus pyrazolopyrimidine, used as a slightly systemic fungicide with protective and curative action for the control of powdery mildews on a wide range of crops and cereals. It is absorbed by foliage and green stems and translocated within the plant (Zweig and Sherma 1978, British Crop Protection Council 1987). In Greece it is used in vegetables, cucurbits, apples, strawberries and cereals to control *Erysiphe* spp., *Sphaerotheca* spp., *Leveillula* spp. and *Oidium* spp. A wide application of pyrazophos in Greece is in greenhouse tomatoes. The recommended preharvest interval for this crop is 21 days. The objective of this study was to obtain data on the persistence and degradation behaviour of pyrazophos in greenhouse tomatoes and to study the influence of accumulation resulting from repeated applications.

MATERIALS AND METHODS

The experiment was conducted in a greenhouse located in Marathon, 42 km from Athens, from September to December 1992. Tomato plants of the Caruso variety were planted in August 1992. The experimental area comprised 6 plots, receiving routine horticultural practices. Each single plot consisted of 12 plants, placed in two rows, spaced 0.8 m from each other. The distance between two consecutive plants on the row was 0.4 m. An aqueous solution of a 29.4 w/v pyrazophos formulation (Afugan^{R} EC, Hoechst) was applied at rates 24g a.i./100L water (recommended dose) and 48g a.i./100L water. The solution was applied with a hand gun airblast sprayer to run off. Four of the experimental plots were receiving the recommended dose and the other two double the recommended dose. Application of pyrazophos formulation was performed on September 25 and repeated, at 10-day intervals, on October 5, 15, 26 and November 5.

Sampling was performed by collecting randomly twelve fruits from each plot, according to FAO/WHO recommendations (1986). Samples were taken 1 hour following last application, in order to allow enough time for the solution to dry. Samples were also taken 1,2,4,7,11,14,21,28 and 35 days after the last application, in order to study the degradation of the fungicide. For evaluating the accumulation effect, due to repeated sprayings, samples were also taken before

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each application. Samples were collected periodically from untreated plants, to be used as a control. The collected fruits were put in polyethylene bags and transferred to the laboratory. The fruits were chopped and blended and the homogenized material was refrigerated in glass jars until analysis.

The samples were analyzed by a general method suitable for organophosphorus compounds (Ministry of Welfare, Netherlands 1988). According to the method, 50 g of homogenized sample are mixed with 50g anhydrous Na_2SO_4 (preheated for 3 hr at 500°C)and 100-mL ethyl acetate. The mixture is blended for 3 min. and the extract filtered. The filtrate is transferred in a sealed flask for gas chromatographic analysis. A Varian aerograph model 3700 gas chromatograph was used, equipped with a nitrogen-phosphorus detector and a 0.95m X 2mm i.d. glass column containing 3% OV-101, Carbowax 20M treated. The injection port temperature was 230°C, the detector 300°C and the column temperature was programmed from 170°C (2 min) to 190°C (1 min) at a rate of 1°C/min. Nitrogen carrier gas flow rate was 30 mL/min. 1-μL of the sample extract was injected and quantification of pyrazophos was performed by measuring the peak height.

RESULTS AND DISCUSSION

The method of analysis that was applied in this work to tomato fruits was very simple and fast, allowing as many as 10 samples to be analysed per day. The response of the detector for pyrazophos was linear in the range 0.1 - 2.5 ng, the regression line been $y = -0.835 + 7.98 x$ ($N = 10$), the standard deviations of the slope and the intercept 0.178 and 0.245 respectively, the standard error 0.418, and the correlation coefficient 0.998. Quantitation of pyrazophos in samples was made by comparing the detector response for the sample to that measured for the calibration standard within the linear range.

The recovery of pyrazophos from tomatoes was determined by spiking control samples with pyrazophos at various concentration levels. Figure 1b shows a gas chromatogram of a fortified tomato sample. The results of the recovery study are presented in Table 1. As seen from this table, average recoveries were from 89 to 102% and relative standard deviations from 2.4 to 9.9%, values within the accepted range for residue determinations (Greve 1984). The method's limit of

Table 1. Mean recoveries* and relative standard deviations (R.S.D.) for pyrazophos in tomatoes, at various fortification levels

Addition mg/kg	Mean Recovery (%)	R.S.D. (%)
0.02	102	8.0
0.05	91	3.5
0.1	90	9.9
0.2	89	4.3
0.5	97	2.4
1	95	4.7
2	91	4.4
5	89	5.4

* Three samples for each fortification level

determination, evaluated as the product of the standard deviation at the lowest validation level with the Student t-value (U.S., E.P.A. 1984), which at 99% confidence level and for 2 degrees of freedom is 6.96, was found to be 0.01 mg/kg. No pyrazophos residues were found in all the control samples analyzed.

Table 2 presents pyrazophos residues found in tomatoes after the last application. As shown from this Table, initial deposits of pyrazophos on tomatoes were 1.89 and 3.58 mg/kg for the recommended and the double application dose respectively. Between days 0 and 4 following application pyrazophos residues remained relatively stable and this may be attributed to the adhesion of pyrazophos on tomatoes, followed by permeation of the pesticide in the fruits. Thereafter residues generally declined slowly related to time. The percentage dissipation of pyrazophos residues 35 days after the last application was 45% and 61% when sprayed at the recommended and the double dose respectively. The conclusion is about the same if a linear dissipation for the residues is assumed. The residue half-lives (Gunther 1969) evaluated with this assumption from the dissipation lines are 36 and 32 days, in the case of the recommended and the double application dose respectively, and it seems that they are independent of the initial deposit and therefore the application dose. Pyrazophos residues 35 days after the last application still remained higher, for both application doses, than the maximum residue limits (MRLs) set by many European countries, which are between 0.1 and 1 mg/kg. No MRLs have been established for this fungicide by the EEC or the FAO/WHO.

Table 2. Pyrazophos residues (mg/kg)* in tomatoes at intervals after the last application

Day	Application dose	
	24g a.i./100L	48g a.i./100L
0	1.89 ± 0.47	3.58 ± 0.39
1	1.91 ± 0.21	3.46 ± 0.19
2	1.97 ± 0.38	3.19 ± 0.40
4	1.87 ± 0.11	3.29 ± 0.12
7	1.39 ± 0.15	2.19 ± 0.52
11	1.63 ± 0.26	2.35 ± 0.24
14	1.28 ± 0.17	1.94 ± 0.28
21	1.05 ± 0.03	2.45 ± 0.18
28	1.35 ± 0.12	2.06 ± 0.32
35	1.04 ± 0.16	1.38 ± 0.39

* Means of duplicate analyses from four replicates (recommended application dose) or two replicates (double dose)

Table 3 presents the effect of repeated applications, at 10-day intervals, on pyrazophos residues in tomatoes. As the results of this Table show, the practice of successive applications of pyrazophos leads to increase of residue levels, even in the case of tomato fruits been at the growing stage, when a dilution effect due to growing exists. It is also seen that 10 days after a single application, the fungicide shows a low residue level, something which is in accordance with the findings of another study using an HPLC method (Cabras et al. 1985).

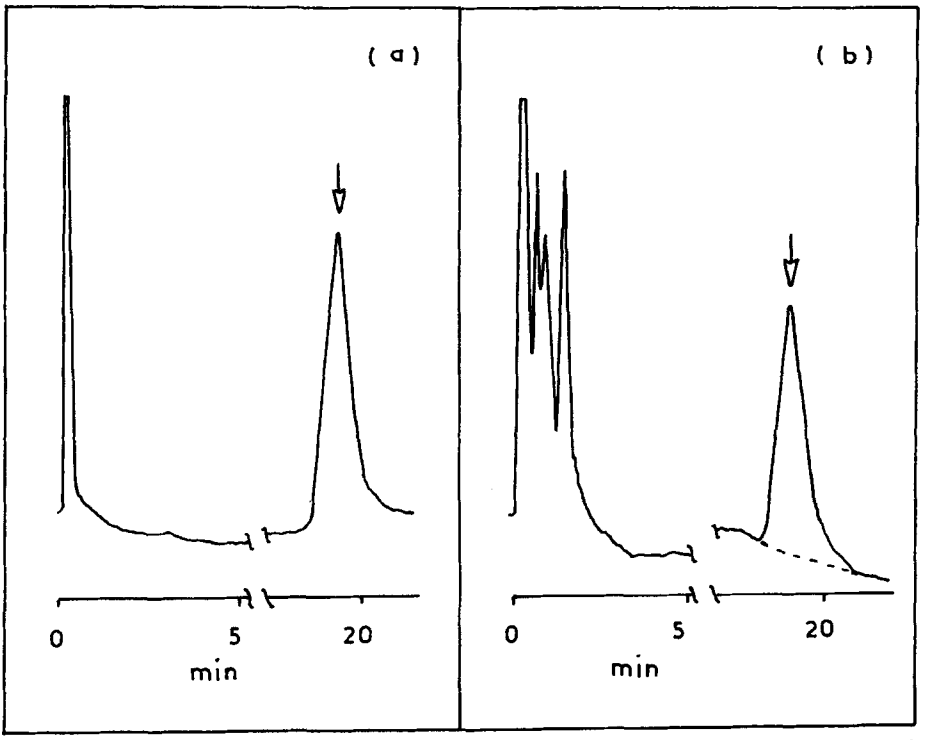

Figure 1. 1μL gas chromatograms of a) 0.5ng pyrazophos reference standard b) Fortified control tomato sample with 0.1 mg/kg pyrazophos. The dotted line is the method blank and pyrazophos is indicated with the arrow.

Table 3. Pyrazophos residues* (mg/kg), 10 days after the last of repeated, at 10-day intervals, application.

No of applications	Crop stage	Application dose	
		24g a.i./100L	48g a.i./100L
1	growing	0.068	0.137
2	growing	0.35	0.71
3	growing	1.10	2.04
4	mature	1.69	2.15
5	mature	1.63	2.35

* The reported values are the means of duplicate analysis

The above results show that pyrazophos has a high persistence on greenhouse tomatoes and should be used with care, avoiding repeated sprayings. As for the recommended in Greece preharvest interval of 21 days, it should either be reconsidered in the case of repeated applications, or alternatively, a restriction of the number of applications should be enforced.

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