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Pesticide residues in tomato grown in open field

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Abstract

A study was undertaken to evaluate the decline of the residues of benalaxyl, chlorothalonil and methomyl in a variety of processing tomato grown in open field. Tomato plants were subjected to a single chemical treatment, when fruits were close to ripeness, by applying pesticides at the doses recommended by the manufacturers. Fruit samples were periodically taken until the end of the preharvest interval (p.i.). The pesticide residues were extracted using acetone and dichloromethane as solvents and determined by gas (benalaxyl and chlorothalonil) and liquid (methomyl) chromatography. The results obtained showed that all the active ingredients had a degradation of first-order kinetics. The residual concentrations after the p.i. were below the legal limits, nevertheless, the value for benalaxyl seemed to be rather high. This finding indicates the need for careful control of the spraying doses of this fungicide, in particular on varieties of tomato which are used fresh.

Keywords: Benalaxyl; Chlorothalonil; Methomyl; Pesticide residues; Tomato

1. Introduction

During the last decades, the increasing demand of food safety has stimulated research regarding the risk associated with consumption of foodstuffs contaminated by pesticides. It is well known that the level of risk is closely related to the daily intake of contaminated food and that for certain products which are frequently consumed the risk is higher than others (Mestres, 1988).

The tomato is a basic component of the Mediterranean diet and is used almost daily in several European countries, raw, home-cooked or processed as a canned product, juice or paste. A significant oncogenic risk has been associated to this crop by the National Academy of Sciences, which only considers the possibility of contamination by fungicides (Precheur, Bennett, Riedel, Wiese, & Dudek, 1992). In Southern Italy cultivation for the processing industry or for consumption as a fresh product is wide spread and is performed both in open field and in greenhouses. The chemical protection of processing tomatoes is commonly carried out by scheduled treatments, using different kinds of pesticides: benalaxyl, chlorothalonil and methomyl are among those most extensively used in this area. Benalaxyl (methyl-*N*-phenylacetyl-*N*-2,6-xylyl alalinate) is a xylem-systemic fungicide, whereas chlorothalonil (2,4,5,6-tetrachloroisophthalonitrile) is a not-systemic, broad-spectrum fungicide; they are commonly used in conjunction with copper, to increase the spectrum of action and the effectiveness of the treatments. Finally, methomyl (S-methyl-*N*-[(methylcarbamoyl)-oxy]thio- acetimidate) is an insecticide, toxic to insects both through direct contact and by ingestion.

Several reports are available in literature about the detection of residues of such active ingredients (a.i.) in different kinds of vegetable and their derivatives,

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including tomatoes, randomly purchased from local markets (Ahmed & Ismail, 1995; Crisippi, Zini, & Fabbrini, 1993; Delrio et al., 1989; Mattern, Liu, Louis, & Rosen, 1991; Rosso, Giraudi, Gamberini, Baggiani, & Vanni, 2000; Stensvand, 2000). On the other hand, only a few studies have been carried out about the decline kinetics in tomatoes and exclusively on products grown in greenhouses (Cabras, Meloni, Pirisi, & Cabitza, 1985; Gil-Garcia, Martinez-Vidal, Martinez-Galera, Rodriguez-Torreblanca, & Gonzalez, 1997), whereas information on tomatoes grown in open field is lacking.

In view of the importance of this crop and also considering that the EU maximum residue levels (MRL) of the above mentioned pesticides have been recently revised (EU, 2000) further study seems necessary.

The present paper reports the results of an investigation which aims to describe the residual behaviour of the three a.i., applied in open field for the protection of a variety of tomatoes cultivated for processing.

2. Materials and methods

2.1. Experimental design

The investigation was conducted in 2001 at the "Guglielmi" farm, located near Brindisi (Apulia, Southern Italy), on processing tomato, the hybrid RS 862699. The plants were transplanted in open field 15th June in double rows 1.5 m wide, 0.8 m apart in the row, and harvest was performed 15th October. The experiment used a randomized complete block design, with 100 m^2 plots located in separate fields (three replicates) that were subjected to chemical treatment with a mixture of benalaxyl, chlorothalonil and methomyl. The treatment was performed 26th September, when fruits were close to ripeness, by means of a backpack-spraying pump, at 10.00 h A.M. on a sunny and windless day, with a temperature of 24 °C. A separate plot was used to obtain untreated tomatoes for assessing the accuracy of the method developed for residues detection. The formulations of both fungicides contained copper as tetracupric oxychloride. Details about the commercial formulations, the doses employed, the p.i. and the MRL are summarized in Table 1.

2.2. Sample collection

Sampling was made after 1 h, 1, 3, 5, 7, 10, 15 and 20 days from the treatment, by picking a 2 kg sample from each of the replicates. The fruit weight did not increase during the sampling period, therefore the residue decline was not affected by growth dilution. Fruits were randomly sampled from the plants, and the latter were randomly chosen from the block. All samples were put into plastic bags and transported to the laboratory, where they were immediately subjected to analysis.

2.3. Extraction and purification of pesticides

Each whole, unwashed sample was homogenized in a blender (Waring blendor, DCA, CT, USA), and three sub-samples of 25 g were taken and independently submitted to pesticide analyses (three replicates). For this purpose, the sub-sample was transferred to a Serval omni-mixer (Ivan Sorval Inc., Norwalk, CT, USA), to which the internal standards (Metalaxyl 5.2 mg/l and Carbaryl 5.1 mg/l, both in acetone) were added and extracted with 50 ml acetone for 5 min. The sample was then filtered through a Buchner funnel and the solid residue was subjected to a second acetone extraction, then to a third one with 50 ml dichloromethane. The three organic extracts were combined and transferred to a separator funnel for liquid/liquid partitioning with 50 ml petroleum ether. The organic phase was recovered, whereas the vegetable water, to which 2 g of sodium chloride was added, was subjected to two further extractions with 25 ml dichloromethane. The three organic phases obtained were combined, filtered through a bed of anhydrous sodium sulphate to eliminate residual water and reduced to dryness in a rotary evaporator. The dried extract was then dissolved in dichloromethane and cleaned up using a Florisil disposable cartridge (SPE Supelclean, Supelco Inc., Bellefonte, PA, USA), previously activated with 4 ml acetonitrile/dichloromethane (1:4 v/v). The a.i. were recovered by eluting the cartridge with 6 ml of the same solvent mixture. The purified extract was then divided into two parts: one was directly analysed by high performance liquid chromatography (HPLC) for methomyl determination, the other was dried out again to remove acetonitrile, redissolved in 1 ml acetone and analysed by gas-chroma-

Table 1
Details of pesticides and doses used in field trials

Active ingredient	Commercial formulation	Dose (a.i.) (kg/ha)	Pre-harvest interval[a] (days)	MLR (mg/kg)
Benalaxyl	Galben R-4-33 Blu (ISAGRO)	0.20	20 (7)	0.2
Chlorothalonil	Optimist (CHIMIBERG)	0.84	20 (14)	2.0
Methomyl	Lannate 25 (DU PONT)	0.38	10 (10)	0.5

[a] Values for commercial formulations including cupric oxychloride, if present, and for the pure a.i. (in brackets).