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Persistence Of Pesticides Applied Pre-Harvest On Citrus Fruits

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ABSTRACT

Pesticides residues analyses from 83 samples pick up from 20 packing-houses in the area of Souss Valley, in the southern part of Morocco, revealed that out of 83 samples only 1 sample was found to have slightly higher residues for chloropyriphos ethyl. All other results showed the presence of pesticides at various levels but within the EU regulation. The compounds frequently found are methidathion, chloropyriphos ethyl, malathion, dimethoate and parathion-methyl respectively at a rate of 43%, 33%, 11%, 7% and 4% of the number of samples. The study on the dissipation of some pesticides in fruits showed that chloropyriphos ethyl is more persistent in the fruit and requires about 80 days from the application date to reach a value of residue equal or lower than authorized RML for the pesticide for EU markets. In contrast, only 7 days from the time of application are necessary for methidathion, malathion and dimethoate to reach the acceptable limit.

KEYWORDS

Pesticide residues;
Citrus;
Persistence.

INTRODUCTION

Moroccan citrus industry is oriented towards export of high quality fresh fruit worldwide. With an average production of about 1.5 million tons per annum from which 50% is exported mainly to European markets. The quality characteristics of best fruit today in the market is determined by the'eye appeal' and internal organoleptic and sanitary characteristics. Nowadays, there is a growing awareness of the consumer regarding pesticides residues in fresh fruits and vegetables. With the tightening regulations of European Union and the USA markets on fruit safety and assurance quality, the trend in many exporting countries during the last 5 to 10 years is to monitor the application of pesticides against the major pests

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of citrus. Morocco with its 75,000 ha of citrus groves is directly concerned with the new legislation and the phytosanitary measures of the importing countries.

The mediterranean climate characterized by mild winter and relatively hot summer with the raining season during spring, autumn and winter is very suitable for the development of many pests and diseases. The major pests that need regular control and application of pesticides include California red scale *Aonidiella auranti* (Mask), citrus thrips, S*cirtothrips citri(Moulton*), citrus leaf miner, medfly (*Ceratitis capitata*), citrus red mite (*Panonychus citri*), aphids, *phythophtora gummosis* and postharvest diseases mainly caused by *Penicillium sp*. To reduce the attack and damages of fruits by insects, careful control is required. Even though, biological approaches and integrated pest management (IPM) strategies are used in many orchards, the application of pesticides remains widely used.

If the pesticides have certainly contributed to the increase in yields and the control of pests and pathogens, pesticides were found to be very harmful for human and the environment. Heavy applications of pesticides led to the development of resistance among various pests, Georghiou[1], natural resources degradation (soil, water, air) and the insidious consequence related to sanitary problems[2]. In fact, different pathological problems such as cancer, sterility, congenital deformations, mental deficiencies, nerves disorders are all found to be related to pesticides residues[3-5].

Insecticides constitute largely the major chemicals used preharvest in citriculture in Morocco as the climate is very suitable for pest growth and development. These compounds belong to the family of organophosphorus or carbamate insecticides with different persistence periods in the fruit. Multiple application of insecticides against medfly, California red scale and others may cause an increase in the pesticides residues in the fruit if precautions are not taken[6].

In 1996, the DGCCRF[7] reported that 6.8% of all samples of fruits and vegetables analyzed annually have higher RML's. Another report from a Cantonal laboratory in Geneva in 2001 found that out of 157 samples of fruits and vegetables, chloropyriphos ethyl and methidathion were found at higher levels[8].

The application of pesticides depend on the nature of the pest and pathogen. In general, in Moroccan orchards several applications of pesticides are needed per year to save the production from heavy damages. For example, medfly may require more than 10 applications per year, SASMA[9]. Despite the heavy application of the pesticides, Moroccan exporters are forced to comply and fulfil the prerequisite conditions imposed by the quality control (EACCE), in term of the respect of RML's for all exporting commodities.

TABLE 1 summarizes some of the pesticides

TABLE 1: Examples of pesticides commonly used on citrus orchards in Morocco

Chemical group	Name	Dosis	Pest
1. Carbamates	Pyrimicarb	50%	Aphids
	Benomyl	50%	Penicillium+
	Thiophanate methyl	70%	Alternaria citri Penicillium
2. Organophosphorus	Dimethoate	40%	Aphids + Medfly
	Oxydementon-methyl	25g/l	Mites + Medfly
	Omethoate	250g/l	Mites
	Cyhesatin	25%	Mites
	Phenthoate	500g/l	Mites
	Malathion	120g/l	Medfly
	Fosthyl-Al	80%	Phythophtora citrophthora
3. Organochlorous	Endosulfan	35%	Mites
	Dicofol	48%	Mites
4. Pyrethrinoids	Delthamethrine	25g/l	Mites + Medfly
	Lambda-cyhalothrine	50g/l	Mites + Medfly
5. Aliphatic Nitrogen	Guazatine	20%	Geothricum candidum

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commonly used on citrus orchards in Morocco[6].

The main objectives of the present study are (i) to investigate the extent of pesticides residues in citrus fruits produced in the area, and (ii) to study the dissipation curves of methidathion, chloropyriphos ethyl, dimethoate and malathion applied preharvest on 'Valencia' orange.

MATERIAL AND METHODS

Determination of pesticides residues in citrus fruits

In order to investigate the presence, frequency and type of pesticides found in fruits of 'Valencia' orange destined for export in the area of Souss Valley. A sample of 83 growers exporters from 20 packinghouses out of the existing 21 in the area, has been randomly selected for this study. Each sample corresponds to a grower-exporter. In large packinghouses, 5 growers are selected and 4 in 17 packinghouses. The dates of collection of samples are between 15/10/01 and 15/06/02. Each sample consisted of 120 fruits. All samples were transported to the laboratory and stored in the cold room at 4°C for further use. From the 120 fruits sample per grower, only a sub-sample of 30 fruits were chosen for analysis of pesticides residues following the method described by DGCCRF[10].

1. Pesticides residues extraction from citrus fruits.

The method used for the extraction of pesticides in the fruit was adopted from Charles et al[11]. For each 50 g of the sample grinded using a food processor apparatus (Type, model blender), add 100 of acetone and stir for 2 hours. The extraction was made respectively in 100 ml and 50 ml of acetone. After filtration, the residues in acetone were partitioned with saturated solution of sodium chloride (30 ml) and 70 ml of dichloromethane in separating funnel. Dichloromethane fraction was collected and the separation process with 70 ml of dichloromethane were combined and dried on anhydrous sodium sulphate. After evaporation on rotary vacuum evaporator at 40°C, the residues were dissolved in 10 ml of an acetone-hexane (1:9) mixture for clean up. For Clean-up, 1 ml of the extract was passed through a florisil column that was conditioned with 5 ml of acetone-hexane (6:4) conditioned 5 ml of hexane. The pesticides residues were eluted by 4 ml of acetone-hexane (6:4) mixture. Samples were analyzed by gas chromatography technique.

2. Gas chromatography determination.

For analyses, a Hewlett–Packard 6890 gas chromatograph equipped with two NPD detectors. The extracts were analysed by GC/NPD under conditions given in the TABLE 2.

Persistence of organophosphorus compounds in the fruits of Valencia orange

As organophosphates are widely used in citrus orchards to control different insects, we have studied the persistence of the following pesticides chloropyriphos ethyl, malathion, dimethoate and methidathion in the fruit of Valencia Orange. Trials were carried out in a commercial orchards in the area of Taroudant, Souss Valley in the Southern part of Morocco. A plot planted with "Valencia" orange in

TABLE 2: The specifications and analytical conditions of GC used in the study

Parameter	Chromatographic conditions
Injection temperature	On column 73 - 250°C at 180°C/min 73°C (0.10 min)
Chromatographic column	HP-5 (5% de copolymère de diphényle- 95% diméthylpolysiloxane) 25 m · 0.32 mm ID. 0.52 µm film thickness.
	HP-1701 (14% copolymére de cyanopropylphényle - 86%dimethylesiloxane) 30 m ·0.32 mm i.d 0.25 µm film thickness
Column temperature	80 -160°C at 25°C/min 160 – 220°C at 10°C/min 220 – 240°C at 10°C/min 80°C (3.00 min) 160°C (2.00 min) 220°C (10.00 min) 240°C (8.80 min)
Detectors temperature	300°C
Gas flows	Carrier gas (He): HP-5 (2.6 ml/min) and HP 1701 (2.2 ml/min). Make-up gas (N2) 10 ml/min Air: 60 ml/min H2: 3 ml/min

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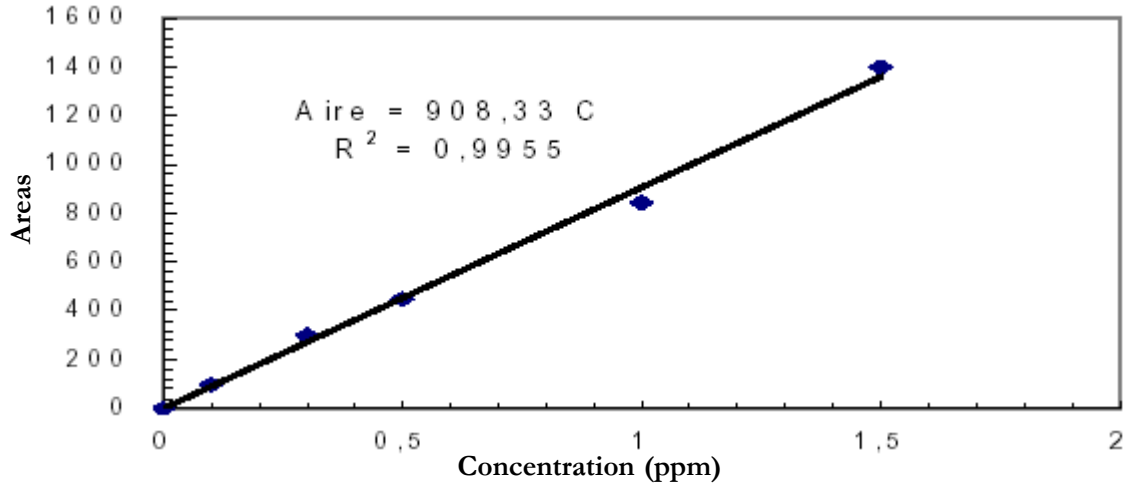

Figure 1: Malathion calibration curve

1972 and grafted on sour orange rootstock at a spacing of 6 x 4 meters leading to a density of about 400 trees/ha. All trees are drip irrigated. The selected trees are apparently healthy with no symptoms of diseases or insects except slight attacks of citrus leafminer. Four compounds methidathion, chloropyriphos ethyl, dimethoate and malathion were used in this study respectively at 8.3 l/ha; 8.3 l/ha; 625 ml/ha and 625 ml/ha. Each pesticide is applied only as a single application on 24/01/2001. The chemical was sprayed on the tree until run-off using a gun sprayer. The total volume applied per tree is about 10 to 15 l. Application was made on three replicates of 4 trees per line and equivalent number of trees are not treated and used as the control.

Fruit sampling

Following pesticide applications, a sample of 20 fruits were harvested randomly at an average of 5 fruits/tree from treated trees at 1 hour; 7; 17; 27; 37; 48; 57; 69; 79; 81 and 127 days after pesticide spray. Harvested fruits were used for the determination of pesticide residues following the same method described above.

RESULTS AND DISCUSSION

The detectors response for the pesticides tested for 2 columns HP170 and HP5 used respectively for pesticide detection and identification showed a very high percent of recovery ranging from 88 to 100% depending on the column and the product. Standard curves for known concentrations were determined for each pesticide ranging from 0.001 to 1ppm. An example of the calibration curve for malathion is shown in figure 1. Similar approach was followed for other pesticides.

Pesticide residues in citrus fruits

From different samples collected in the packing-houses of the Souss, it appears that some chemicals are more persistent than others. The compounds frequently found in the sample are methidation, chloropyriphos ethyl, malathion, dimethoate and parathion methyl respectively at a rate of 43%, 32%,

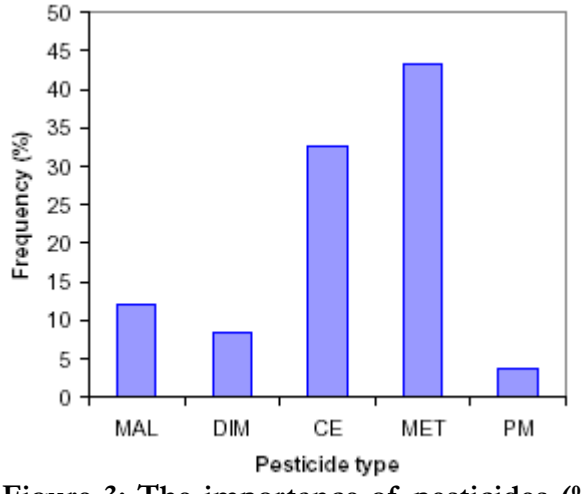

Figure 3: The importance of pesticides (%) found in fruits of Valencia orange fruit.
MAL: Malathion, PM: Paration Methyl, CE: Chloropyriphos Ethyl, DIM: Diméthoate, MET: Methidathion

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12%, 6% and 3.6% as shown in the figure 2.

The residues levels found in fruits ranges for malathion from 0.009 to 0.1; Dimethoate (0.002 to 0.1); Chloropyriphos ethyl (0.02 to 0.36); Methida thion (0.05 to 1.27) and parathion methyl from 0.01 to 0.04 ppm. Most of the values of residues obtained are far below the values imposed by European Union (EU) legislation. Only one sample was found to have a value of 0.36 ppm of chloropyriphos ethyl which is higher than the recommended maximum limit of 0.30 ppm in citrus fruit for most of the EU markets[12].

Another conclusion from these data is that growers seem to comply with the legislation and therefore respect strongly the prerequisite conditions for pesticide use in citrus fruits geared for export.

Pesticide persistence in citrus fruits

Dissipation curves of methidathion, chloropyri phos ethyl, dimethoate and malathion in citrus fruits are illustrated in figure 4. It appears from the same figure that the concentration of the pesticide and its uptake vary considerably from one pesticide to another. The highest residue was obtained at 1 hour from the application for methidathion and the lowest residue level was obtained in fruits treated with dimethoate.

The curves showed a rapid decrease in the pesticide residue during the first two weeks and then a slow reduction afterward. Following the above dissipation curve over the time period, it appears that the acceptable value of the residue limit is attained at about 7 days for methidathion, dimethoate and malathion but it requires about 80 days for Chloropyri phos ethyl. Similar results were reported on methidathion, malathion and dimethoate[13 -15].

However, these values are only valid for the EU markets. In case, the concentration required is lower, thus, the period necessary for the dissipation will increase. Therefore, the application to harvest interval should be longer to avoid unacceptable residues in the fruit.

CONCLUSION

The results drawn under the terms from this work are:

⇒ Pesticides residues analyses from 83 samples pick up from 20 packinghouses in the area of Souss Valley, in the southern part of Morocco, revealed that out of 83 samples only 1 sample was found to have slightly higher residues for chloropyri

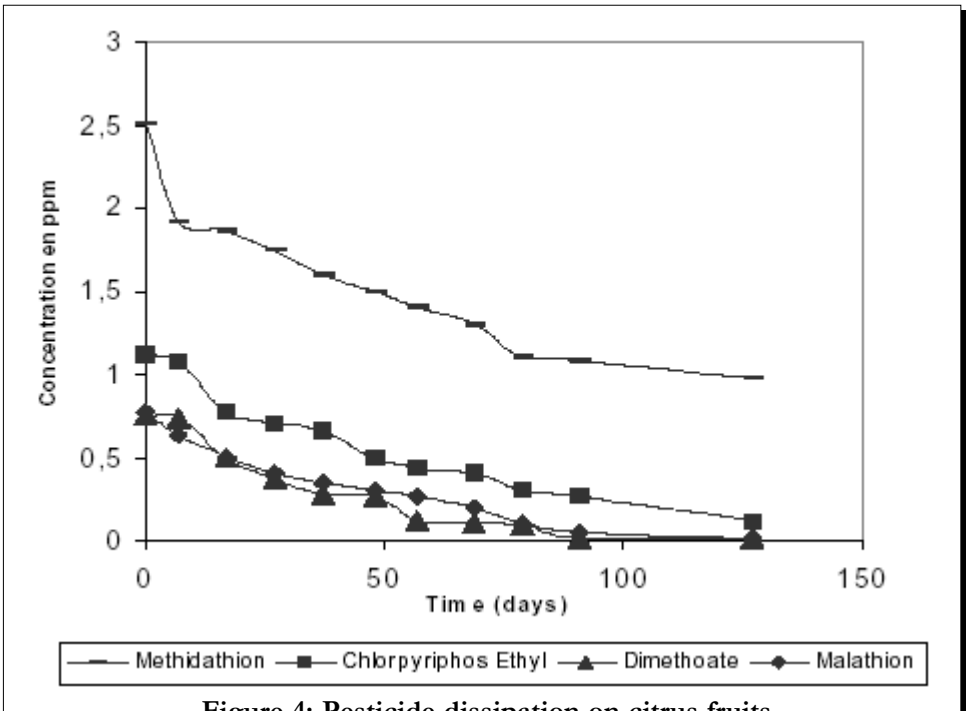

Figure 4: Pesticide dissipation on citrus fruits

phos ethyl.

⇒ The compounds frequently found are methida thion, chloropyriphos ethyl, malathion, dimethoate and parathion-methyl respectively at a rate of 43%, 33%, 11%, 7% and 4% of the number of samples.

⇒ The study on the dissipation of some pesticides in fruits showed that chloropyriphos ethyl is more persistent in the fruit and requires about 80 days from the application date to reach a value of residue equal or lower than authorized RML for the pesticide for EU markets. In contrast, only 7 days from the time of application are necessary for methidathion, malathion and dimethoate to reach the acceptable limit.

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