Bull Environ Contam Toxicol (2012) 88:358–361
DOI 10.1007/s00128-011-0503-9

Pesticide Residues in Tomatoes from Greenhouses in Souss Massa Valley, Morocco

R. Salghi · G. Luis · C. Rubio · A. Hormatallah · L. Bazzi · A. J. Gutiérrez · A. Hardisson

Received: 3 August 2011 / Accepted: 16 December 2011 / Published online: 1 January 2012

Abstract Eight pesticide residues in tomato samples collected in the area of Souss Massa Valley (Southern Morocco) were analyzed. The detected residue levels ranged from 0.001 to 0.400 mg kg^{-1} for dicofol, from 0.003 to 0.170 mg kg^{-1} for procymidone, from 0.001 to 0.250 mg kg^{-1} for chlorothalonil, from 0.050 to 0.500 mg kg^{-1} for bifenthrin, from 0.001 to 0.010 mg kg^{-1} for λ-cyhalothrin, from 0.001 to 0.300 mg kg^{-1} for cypermethrin, from 0.010 to 1 mg kg^{-1} for deltamethrin and from 0.003 to 1.123 mg kg^{-1} for endosulfan. European MRL for endosulfan in tomatoes set in 0.500 mg kg^{-1}, was exceeded in 8 samples, and MRL for deltamethrin set in 0.300 mg kg^{-1} for tomatoes was exceeded in 2 samples.

Keywords Morocco · Tomatoes · Pesticide residues · Maximum residue limits (MRL)

R. Salghi
Laboratory Engineering Process Engineering Energy and Environment, National School of Applied Sciences, PO Box: 1136/S, Agadir, Morocco

G. Luis · C. Rubio · A. J. Gutiérrez (✉) · A. Hardisson
Area of Toxicology of University of La Laguna, 38071 La Laguna, Tenerife, Spain
e-mail: ajguti@ull.es; ajgutitox@gmail.com

A. Hormatallah
Department of Plant Protection, Laboratory of Pesticides, Agricultural and Veterinary Institute Hassan II, Agadir Horticultural Complex, BP: 18/S, Agadir, Morocco

L. Bazzi
Team Chemistry Applied Physics, Faculty of Science, BP: 28/S, Agadir, Morocco

In recent decades, farming areas have been developed in Morocco, and greenhouses dedicated to intensive cultivation have been established. The Moroccan agricultural sector occupies a total area of 76,000 ha, and the Souss Massa valley is the major region for vegetable production, exporting 85%–90% of its total production, principally to the European Union market (AACUE 2007). Morocco produces over 3 million tons of fresh tomatoes annually, and approximately 1.3 million are exported, mainly to the European Union, USA and Canada (AACUE 2007; Gambacorta et al. 2005).

Intensive cultivation technologies result in high infestation of tomato crops by some pests and diseases, causing major losses of quality fruits (Ravelo-Pérez et al. 2008), pesticides are widely used to control them (Araoud et al. 2007; Cengiz et al. 2007; Zawiyah et al. 2007). The chemical protection of tomatoes is commonly carried out by scheduled treatments that use different kinds of pesticides (Gambacorta et al. 2005). This constant use of pesticides increases the possibility of finding multiple residues of these compounds in the resulting tomatoes, beyond prescribed legal limits, creating a significant risk to human health (Cengiz et al. 2007; Zawiyah et al. 2007).

Pesticide residues in foods must fall below the Maximum residue limits (MRLs) established by every country (Araoud et al. 2007; Columé et al. 2001; Osman et al. 2010; Zawiyah et al. 2007). In Europe, Regulation (EC) No. 396/2005 modified by Regulations (EC) No. 839/2008 and No. 459/2010 of the European Parliament and Council, respectively, set the MRL of pesticides in plant and animal products. Table 1 shows the MRL established by the European Union for each one of the analyzed pesticides.

Monitoring the pesticide residues in tomatoes is part of every quality evaluation and the determination of pesticide residues in vegetables has as its main objective the

Table 1 Pesticides analyzed in this study and MRL for each, as set by the EU

Pesticide	MRL (mg kg^{-1})
Bifenthrin	0.20
Chlorothalonil	2.00
Cypermethrin	0.50
Deltamethrin	0.30
Dicofol	1.00
Endosulfan	0.50
λ-Cyhalothrin	0.10
Procymidone	0.02

MRL maximum residue limit

prevention of any possible risk to human health (Kurz et al. 2008; Mukherjee 2003; Osman et al. 2010). Therefore, our main objectives were (1) to determine the presence of pesticide residues: three organochlorine pesticides (chlorothalonil, dicofol and endosulfan), four pyrethroids (bifenthrin, deltamethrin, cypermethrin and λ-cyhalothrin) and one dicarboximide (procymidone) in tomatoes grown under greenhouse conditions from Souss-Massa (Morocco) using a multiresidue method GC-ECD and (2) to ensure that the pesticide residues levels in tomatoes do not exceed the MRLs established by European Union.

Materials and Methods

A total of 120 tomato samples, cultivated under greenhouse conditions in the region of Souss-Massa (Southern of Morocco) and destined for exportation, were analyzed. All samples had been treated with pesticides. Samples were harvested between May 2009 and June 2010.

20 exporting growers from 10 packinghouses were randomly selected for this study. Each sample corresponds to an exporting grower. Tomato samples were collected in a proportional and representative way in accordance with quantities exported by each exporting grower. Each sample was put in sterile polyethylene bag, transported to the laboratory and stored in the cold room at 4°C until the analysis.

A representative sample (200 g) was blended using a food processor and mixed thoroughly (El-Mouden et al. 2009; Zawiyah et al. 2007). A homogenized subsample (50 g) was weighed and then mixed with 150 mL of acetone prior to extraction (El-Mouden et al. 2009). The mixture was blended for 2 h and the extract was filtered. After filtration, the acetone extract was partitioned with saturated sodium chloride solution (30 mL) and dichloromethane (70 mL) using a separating funnel. The filtrate, corresponding to dichloromethane fraction, was evaporated under vacuum using a rotary evaporator at 40°C. The extract was transferred to the FLORISIL clean-up column and pesticides were eluted with a mixture of diethyl ether/*n*-hexane (6:4, v/v). Pesticide residues were analyzed by gas chromatography (El-Mouden et al. 2009). Eight pesticides (insecticides and fungicides): three organochlorines, four pyrethroids and one dicarboximide, were analyzed.

A Hewlett–Packard 6890 Gas Chromatograph (Palo Alto, CA, USA), equipped with an ECD detector (electron capture detector) at 300°C was employed. The gas chromatograph was also equipped with a Hewlett-Packard 6890 autosampler (Palo Alto, CA, USA) and a capillary column of 25 m × 0.32 mm i.d. × 0.52 μm film thickness, of 5% phenyl-methyl polisiloxane HP-5. The injection temperature was 250°C and the temperature program was established as follows: 80°C for 0.10 min and 80–180°C min^{-1}. The carrier gas flow was He at 2.6 mL min^{-1}; anode gas: detector gas flow was N_2 at 10 mL min^{-1} and the make up was N_2 at 60 mL min^{-1}.

To evaluate the efficiency of the analytical procedures a recovery assay was employed. The method was validated by determining the limits of quantification (LOQ), recovery percentages and coefficient of variation. Analytical standards of chlorothalonil, dicofol, procymidone, endosulfan, λ-cyhalothrin, cypermethrin, deltamethrin and bifenthrin (over 99% pure) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Each standard was dissolved in acetone (50 mL) to obtain stock solutions of

Table 2 Average recoveries and coefficient of variation percentages for pesticides subjected for analysis

Compound	N	Spiking level/LOQ (mg kg^{-1})	Regression equation	R^2	Average recovery (%)	CV (%)
Bifenthrine	53	0.0009	A = 11,329 C − 0.5	0.9999	97	1.90
Chlorothalonil	48	0.0015	A = 10,189 C − 5	0.9998	90	5.50
Cypermethrine	44	0.001	A = 5,632.9 C + 0.15	0.9997	97	3.50
Deltamethrine	56	0.002	A = 4,946.9 C − 0.249	0.9979	96	12.5
Dicofol	16	0.007	A = 1,672.9 C − 4.5	0.9902	87	6.30
Endosulfan	56	0.002	A = 7,667.4 C + 0.001	0.9999	93	7.10
λ-Cyhalothrin	47	0.004	A = 5,337.1 C + 0.140	0.9995	95	1.26
Procymidone	60	0.002	A = 3,062.9 C − 10	0.9999	96	4.50

R^2 regression coefficient

Table 3 Pesticide residues in tomato samples (mg kg^{-1}) from Souss-Massa (Morocco)

Sample	Dico	Proc	Chlo	Bife	Endo	λ-Cyh	Delt	Cype
1	0.01	0.006	0.1	0.500	0.009	0.01	0.02	0.009
2	0.10	0.01	0.2	≤LOQ	1.123	≤LOQ	0.22	0.02
3	0.02	0.10	0.15	0.002	0.08	0.005	0.02	0.02
4	≤LOQ	0.15	0.12	0.004	1.00	0.006	0.01	0.04
5	0.002	0.17	0.17	0.301	1.02	0.01	0.25	0.30
6	0.12	0.01	0.25	0.102	1.01	0.01	0.02	0.06
7	0.010	0.008	0.14	0.103	0.009	≤LOQ	0.02	0.07
8	0.130	0.007	0.12	0.012	1.120	≤LOQ	0.02	0.04
9	0.01	0.02	1.00	0.001	0.003	≤LOQ	0.02	0.04
10	0.009	0.04	≤LOQ	0.130	1.150	0.016	0.02	0.05
11	0.008	0.003	0.002	0.012	1.200	0.015	0.02	0.03
12	0.4	0.01	≤LOQ	0.009	1.120	0.006	0.01	0.02
13	0.15	0.004	0.30	0.008	0.03	0.01	0.01	0.02
14	0.12	0.003	0.12	0.412	0.03	0.01	0.01	0.09
15	0.003	0.01	0.003	0.150	0.4	≤LOQ	0.018	0.01
16	≤LOQ	0.01	0.20	0.012	0.05	≤LOQ	0.01	0.009
17	0.05	0.004	0.102	0.004	0.04	≤LOQ	0.02	0.07
18	0.03	0.012	0.123	0.003	0.05	0.009	0.30	0.08
19	0.05	0.11	0.002	0.011	0.04	0.008	1.00	0.002
20	0.06	0.12	≤LOQ	0.042	0.03	0.01	0.003	≤LOQ

Dico dicofol, *Proc* procymidone, *Chlo* chlorothalonil, *Bife* bifenthrin, *Endo* endosulfan, *Delt* deltamethrin, *λ-cyh* λ-cyhalothrin, *Cype* cypermethrin, *LOQ* limit of quantification

Table 4 Pesticide residues in tomato samples (mean or range expressed in mg kg^{-1})

Country	Compound found	Mean or range (mg kg^{-1})	Reference
Spain	Procymidone	0.53–0.55	Columé et al. (2001)
Egypt	Chlorothalonil	0.26	Dogheim et al. (2002)
	Cypermethrin	0.22	
	Dicofol	0.26	
India	Endosulfan	0.21	Mukherjee (2003)
	Cyhalothrin	ND	
Spain	Cypermethrin	0.012	Chavarri et al. (2004)
	Deltamethrin	ND	
Malaysia	Cypermethrin	0.29	Zawiyah et al. (2007)
France	Chlorothalonil	0.04–0.85	Guillet et al. (2009)
	Procymidone	0.003–0.09	
Morocco	Cypermethrin	0.04–0.79	El-Mouden et al. (2009)
	Deltamethrin	0.01–0.05	
	Dicofol	0.01–1.06	
	Endosulfan	0.01–0.40	
Saudi Arabia	Dicofol	0.05	Osman et al. (2010)

ND not detected

approximately 200 mg L^{-1}, which were stored light protected at 4°C until further use. The freshly working standard solutions were obtained by dilutions with n-hexane. Using the HP5 column the detector response for the pesticides tested was linear in the range of the concentrations studied (0.001–1 mg kg^{-1}).

Table 2 shows the recovery percentages of pesticides in tomatoes and includes the regression equation showing the relationship between the signal of the detector (A, peak area) and the concentration of the pesticide in tomatoes (C, expressed as mg kg^{-1}). In all cases, regression coefficients (R^2) resulted to be higher than 0.99. Recoveries were found from 87% to 97%. The quantification limits for all pesticides were between 0.0009 and 0.007 mg kg^{-1} and coefficient of variation were between 1.26% and 12.5%.

Results and Discussion

Eight pesticide residues were detected in all samples analyzed: three organochlorine pesticides (dicofol, chlorothalonil and endosulfan), four pyrethroids (bifenthrin, deltamethrin, λ-cyhalothrin, and cypermethrin) and one dicarboximide (procymidone). Pesticide residues found in tomato samples produced in Souss-Massa (Morocco) are shown in Table 3.

The detected residue levels ranged from 0.001 to 0.4 mg kg^{-1} for dicofol, from 0.003 to 0.17 mg kg^{-1} for procymidone, from 0.001 to 0.25 mg kg^{-1} for chlorothalonil, from 0.050 to 0.50 mg kg^{-1} for bifenthrin, from 0.001 to 0.010 mg kg^{-1} for λ-cyhalothrin, from 0.001 to 0.30 mg kg^{-1} for cypermethrin, from 0.010 to 1 mg kg^{-1} for deltamethrin and from 0.003 to 1.123 mg kg^{-1} for endosulfan. Endosulfan is the pesticide that shows the highest residue levels in tomatoes while λ-cyhalothrin was the pesticide with the lowest residues.

The MRLs established by EU legislation (Table 1) for endosulfan and deltamethrin were exceeded in 8 and 2 samples, respectively. This study reveals that out of 20 samples, eight samples were found to have a residue value of 1–1.20 mg kg^{-1} of endosulfan and two of 0.30–1 mg kg^{-1} of deltamethrin.

Comparing our results with those found for tomatoes grown in other locations (Columé et al. 2001; Dogheim et al. 2002; El-Mouden et al. 2009; Guillet et al. 2009; Mukherjee 2003; Osman et al. 2010; Zawiyah et al. 2007) it is observed that pesticide residues in tomatoes from Souss-Massa (Morocco) present similar values as those found in tomatoes from Egypt, India and Malaysia. Table 4 shows a summary of the pesticide residues in tomato samples for different countries. In existing literature, there are few studies analyzing more than one pesticide in tomatoes. Only the studies about the tomatoes commercialized in Egypt, France and Morocco detected more than one pesticide residue (Dogheim et al. 2002; El-Mouden et al. 2009; Guillet et al. 2009).

Tomatoes cultivated under greenhouse conditions are highly sensitive to pests and need frequent pesticide treatments, leading to higher residues in the final products. The massive use of endosulfan and deltamethrin pesticides in the production of greenhouse tomatoes needs to be controlled and reduced and these pesticides should be subject to stricter customs control and management in Europe.

References

AACUE (2007) Acuerdo de Asociación entre Centroamérica y la UE. Available at: http://www.aacue.go.cr/comercio/sectoriales/documentos/Tomates. Accessed 15 June 2011

Araoud M, Douki W, Rhim A, Najjar MF, Gazzah N (2007) Multiresidue analysis of pesticides in fruits and vegetables by gas chromatography–mass spectrometry. J Environ Sci Health B 42(2):179–187

Cengiz MF, Certel M, Karakas B, Göcmen H (2007) Residue contents of captan and procymidone applied on tomatoes grown on greenhouses and their reduction by duration of a pre-harvest interval and post-harvest culinary applications. Food Chem 100:1611–1619

Chavarri MJ, Herrera A, Ariño A (2004) Pesticide residues in field-sprayed and processed fruits and vegetables. J Sci Food Agric 84:1253–1259

Columé A, Cárdenas S, Gallego M, Valcárcel M (2001) Semiautomatic multiresidue gas chromatographic method for the screening of vegetables for 25 organochlorine and pyrethroid pesticides. Anal Chim Acta 436:153–162

Dogheim SM, El-Marsafy AM, Salama EY, Gadalla SA, Nabil YM (2002) Monitoring of pesticide residues in Egyptian fruits, vegetables during 1997. Food Addit Contam 19(11):1015–1027

El-Mouden OID, Zougagh M, Lemerhyeratte A, Salgui R, Bazzi L, Hormatallah A, Chakir A, Ríos A (2009) In house pesticide residue monitoring of tomatoes from Souss-Massa (Morocco) and pesticide residue levels in tomatoes grown in a greenhouse after multiple applications of dicofol and difenoconazole. Ital J Food Sci 21(4):517–528

Gambacorta G, Faccia M, Lamacchia C, Di Luccia A, La Notte E (2005) Pesticide residues in tomato grown in open field. Food Control 16:629–632

Guillet V, Fave C, Montury M (2009) Microwave/SPME method to quantify pesticide residues in tomato fruits. J Environ Sci Health B 44:415–422

Kurz MHS, Goncalves FF, Adaime MB, da Costa IFD, Primel EG, Zanella R (2008) A gas chromatographic method for the determination of the fungicide chlorothalonil in tomatoes and cucumbers and its application to dissipation studies in experimental greenhouses. J Braz Chem Soc 19(6):1129–1135

Mukherjee I (2003) Pesticides residues in vegetables in and around Delhi. Environ Monit Assess 86:265–271

Osman KA, Al-Humaid AM, Al-Rehiayani SM, Al-Redhaiman KN (2010) Monitoring of pesticide residues in vegetables marketed in Al-Qassim region, Saudi Arabia. Ecotoxicol Environ Saf 73:1433–1439

Ravelo-Pérez LM, Hernández-Borges J, Borges-Miquel TM, Rodríguez-Delgado MA (2008) Pesticide analysis in tomatoes by solid-phase microextraction and micellar electrokinetic chromatography. J Chromatogr A 1185(1):151–154

Regulation (EC) No. 396/2005 of the European Parliament and of the Council of 23 February 2005 on maximum residue levels of pesticides in or on food and feed of plant and animal origin and Amending Council Directive 91/414/EEC with EEA relevance

Regulation (EC) No. 839/2008 of the Commission on 31 July 2008 amending Regulation (EC) No. 396/2005 of the European Parliament and the Council as regards Annexes II, III and IV relating to boundaries maximum residue levels for pesticides in or on the surface of certain products

Regulation (EC) No. 459/2010 of the Commission on May 27, 2010 by amending Annexes II, III and IV of Regulation (EC) No. 396/2005 of the European Parliament and the Council as regards MLRs for certain pesticides in certain products

Zawiyah S, Che Man YB, Nazimah SAH, Chin CK, Tsukamoto I, Hamanyza AH, Norhaizan I (2007) Determination of organochlorine and pyrethroid pesticides in fruit and vegetables using SAX/PSA clean-up column. Food Chem 102(1):98–103