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Monitoring of pesticide residues in tomato marketed in Bogota, Colombia

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ABSTRACT

Worldwide, the presence of pesticide residues in vegetables has been extensively characterized. In Colombia, tomato is among the most consumed horticultural commodities; however, the presence of pesticide residues in tomato has not been determined. Through an extensive sampling in Bogota, we assessed the presence of 24 pesticides in fresh tomatoes. Only one sample containing carbendazim exceeded the Maximum Residue Limit. At least one pesticide was detected in 70.5% of the samples and the most detected were pyrimethanil, carbendazim, dimethomorph and acephate. The results showed that tomato consumption in Bogota does not represent a risk to human health. Nevertheless, a monitoring program must be established to control the contamination of staple foods, such as tomato.

1. Introduction

Up to date many countries have restricted the usage of these pesticides establishing tolerances or maximum residue limits (MRLs) in food (Cho et al., 2009). Nowadays, food monitoring programs for pesticides are carried out worldwide in order to protect consumer health, improve the management of agricultural resources and prevent economic losses. The presence of pesticide residues in vegetables has been extensively characterized in the developed world (Barnat et al., 2010; Claeys et al., 2011; Gambacorta, Faccia, Lambacchia, Di Luccia, & La Notte, 2005; Garrido, Martínez, López, Cortés, & Martínez, 2004; Juraske, Antón, Castells, & Huijbregts, 2007; Knezevic and Serdar, 2009; Omirou, Vryzas, Papadopoulou-Mourkidou, & Economou, 2009). More recently, countries across Asia and Africa started to report the results of local studies (Abou-Arab, 1999; Bempah, Buah-Kwofie, Enimil, Blewu, & Agyei-Martey, 2012; Cengiz, Certel, Karakas, & Gocmen, 2007; Darko and Akoto, 2008; Osman, Al-Humaid, Al-Rehiayani, & Al-Redhaiman, 2010; Osman, Al-Humaid, Al-Rehiayani, & Al-Redhaiman, 2011).

In South America, studies were carried out in Brazil through a well-established monitoring program (Jardim & Caldas, 2012; Penido, Clarete, Rath, & Reyes, 2009). In Colombia, efforts have been made to determine the presence of residues in local markets but lacking representativeness (Castro, Ramos, Estévez, & Rangel, 2004; Gutierrez and Londoño, 2009; Murcia & Stashenko, 2008). Neither of these studies assessed the risk potential to human health.

During the last 30 years pesticide registrations doubled in Colombia, from 186 molecules in 1974 up to 400 active ingredients in 2003 (Cardenas, Silva, & Ortiz, 2010). Despite of legal regulations, the National Public Health Surveillance Program (SIVIGILA) recorded 8016 pesticide poisoning cases in 2010 (Paez et al., 2011). This situation shows the latent risk that pesticides represent for human health in the country. In addition, the diagnosis, surveillance and monitoring of pesticides in food has not been effectively implemented, and there is a strong tendency for farmers to use pesticides excessively (Fierro & Tellez, 1997, pp. 1–48). The country, as part of the Andean Community of Nations, adopted the MRLs proposed by the *Codex Alimentarius*. Periodic monitoring of fresh horticultural products should be a must to guide growers on the judicial use of pesticides and their impact on public health (Berrada et al., 2010).

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Tomato (*Solanum lycopersicum* L.) is among the most consumed horticultural commodities around the world (Dorais, Ehret, & Papadopoulos, 2008). In Colombia, one of the most limiting factors in tomato production is the mismanagement of pest problems due to the improper use of chemical pesticides. During cultivation, pesticides cause direct health issues on the labor involved due to the lack of good agricultural practices implementation. On the other hand, the fresh produce carries excessive pesticide residues, even above MRLs, since growers do not respect the pre-harvest intervals (Bojacá, Arias, Ahumada, Casilimas, & Schrevens, 2013).

Being a local staple food, the presence of residues in fresh tomatoes was assessed by conducting an extensive sampling in Bogota, the sixth largest city in Latin America and Colombia's capital (Skinner, 2004).

2. Materials and methods

2.1. Samples collection

During 2011, 400 samples were randomly taken across Bogota. The number of samples per district was weighted according to the number of inhabitants. Samples collection was carried out following the *Codex Alimentarius* CAC/GL 33 (FAO, 1999, 18 p.), which lays down the sampling and analysis methods for determining recommended pesticide residues for compliance with MRLs.

Each sample consisted of 1 kg of fresh tomatoes purchased in different types of stores such as neighborhood groceries, supermarkets, hypermarkets and open markets. After purchase, the sample was bagged; coded and auxiliary information was registered following the FAO guidelines (FAO, 1999, 18 p.). During transportation, samples were preserved in Styrofoam coolers at 4 °C until processing.

2.2. Pesticide residues analysis

The multiresidue method, developed by Ahumada and Zamudio (2011a), was used to determine the concentration residues of 24 pesticides of the collected samples. The basic characteristics of the pesticides analyzed are presented in Table 1. The extraction procedure followed a modified version of the QuEChERS method (Ahumada & Zamudio, 2011b), and the determination of the pesticides was performed using an ultra performance liquid chromatograph coupled to mass spectrometer.

Table 1
The usage, CAS number, limits of detection (LOD), quantification (LOQ) and recovery percentage of the pesticides analyzed.

Name	Use	CAS No.	LOD (mg kg^{-1})[a]	LOQ (mg kg^{-1})[a]	Recovery (%)
Acephate	Insecticide	30560-19-1	0.01	0.04	91.7
Azoxystrobin	Fungicide	131860-33-8	0.001	0.02	91.3
Benalaxyl	Fungicide	71626-11-4	0.006	0.01	88.3
Carbendazim	Fungicide	10605-21-7	0.003	0.01	106.0
Carbofuran	Insecticide	1563-66-2	0.01	0.02	102.1
Chlorfenapyr	Insecticide	122453-73-0	0.1	0.5	94.9
Cymoxanil	Fungicide	57966-95-7	0.2	0.6	107.1
Difenoconazole	Fungicide	119446-68-3	0.002	0.01	82.8
Dimethoate	Insecticide	60-51-5	0.01	0.02	102.3
Dimethomorph	Fungicide	110488-70-5	0.003	0.01	103.5
Famoxadone	Fungicide	131807-57-3	0.04	0.8	71.3
Hexaconazole	Fungicide	79983-71-4	0.03	0.1	83.9
Imazalil	Fungicide	35554-44-0	0.01	0.04	75.3
Imidacloprid	Insecticide	138261-41-3	0.1	0.3	95.4
Indoxacarb	Insecticide	173584-44-6	0.01	0.02	95.4
Metalaxyl	Fungicide	57837-19-1	0.003	0.01	95.3
Methomyl	Insecticide	16752-77-5	0.01	0.02	105.3
Methoxyfenozide	Insecticide	161050-58-4	0.002	0.03	88.6
Monocrotophos	Insecticide	6923-22-4	0.002	0.04	80.1
Profenofos	Insecticide	41198-08-7	0.1	0.3	80.3
Pyrimethanil	Fungicide	53112-28-0	0.003	0.01	99.4
Spinozad (A + D)	Insecticide	168316-95-8	0.03	0.1	112.3
Tebuconazole	Fungicide	107534-96-3	0.06	0.1	75.7
Thiocyclam	Insecticide	31895-22-4	0.05	0.15	102.4

[a] Values for analytical method developed and validated by Ahumada and Zamudio (2011a).

2.2.1. Reference materials, reagents and solutions

Pesticide reference standards, all >95% purity, were obtained from Dr. Ehrenstorfer GmbH and Chemservice. Stocks were prepared in a concentration around 500 μg mL^{-1}, using methanol as solvent, and were stored in amber glassware under appropriate conditions such as −20 °C and exclusion of moisture and light. All the solvents were HPLC grade supplied by J.T. Baker (Phillisburg, NJ, USA).

2.2.2. Extraction and clean up

A modified version of the QuEChERS method was applied to obtain pesticide extracts. The QuEChERS Restek Q-Sep™ salt kits were used in the extraction process and the Restek dSPE Q-Sep™ adsorbent kits were employed in the clean-up procedure. In a centrifuge tube, 10 g of previously homogenized sample were weighed, 15 ml of solvent were poured into it and then it was manually shaken by one minute. The extraction solvent consisted of acetonitrile and acetic acid 1% (v/v). Thereafter, 6 g of anhydrous $MgSO_4$ and 1 g of sodium acetate were added, and it was shaken again. The tube was centrifuged at 4500 rpm for 5 min and 10 ml of the supernatant (solution A) were measured using a pipette and then transferred to a 15 ml centrifuge tube. In the case of the clean-up procedure, 25 mg of PSA (primary/secondary amine) and 150 mg of anhydrous $MgSO_4$ were added for each extract milliliter of solution A. Afterwards, it was shaken by 30 s and centrifuged by 2 min at 4500 rpm. Finally, the supernatant was filtered through a 0.22 μm PTFE filter (Ahumada & Zamudio, 2011a).

2.2.3. Chromatographic and mass spectrometer conditions

The chromatographic analyses were performed in an ultra-high speed liquid chromatograph Shimadzu Prominence™ coupled to an LCMS-2020 mass selective detector (Maryland, CA, USA). An ABN2ZE Peak Scientific (Billerica, USA) nitrogen generator provided the dryer stream in the ESI source. The chromatograph consisted of an SIL20A UFLC 7673 Shimadzu (Maryland, CA, USA) automatic sampler, a binary high-pressure pump, an online degasification system and an oven to control the column temperature. The analyses were performed with a Shim-pack C18 column (75 mm × 2 mm i.d., 2.1 μm particle size). Mobile phase A consisted of 5 mM ammonium acetate with 0.1% formic acid, while solvent B consisted of 100% acetonitrile.

A built-in DUIS (ESI, APCI) interface was used operating in ESI mode, a drying gas flow of 10·l min^{-1} and a nebulizer gas flow of 1.5·l min^{-1}. The temperatures of the heating block and the desolation line were 200 °C and 250 °C, respectively. The analysis was carried out in both positive and negative modes; the applied voltage at the capillary was 4500 V and −4500 V, respectively. All the analyses were performed in single ion monitoring mode. All samples were analyzed twice following the aforementioned method. The acquisition, control and data processing were performed using the Lab Solutions version 3.5 software. The robustness evaluation of the method followed the Youden's test as described by Ahumada and Zamudio (2011a), using the statistical package PASW STATISTICS 18 included in SPSS. The evaluation results showed the method is robust to changes in the methodology; however, changes in the equipment configuration compromise the performance of the method. The application of the method should follow strict equipment conditions in order to obtain reliable results (Ahumada & Zamudio, 2011a).

After quantification in the laboratory, descriptive statistics were calculated for each pesticide. Then, pesticides concentrations were