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Household processing factors of acrinathrin, fipronil, kresoxim-methyl and pyridaben residues in green beans

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ABSTRACT

The influence of household washing and boiling processes on the residue levels of acrinathrin, fipronil, kresoxim-methyl and pyridaben in green beans was studied. The study was conducted on green beans samples collected from an experimental greenhouse during a two weeks period after treatment. Analyses were carried out by QuEChERS extraction method and gas chromatography with electron-capture detection (GC/ECD). Pesticide levels in the unprocessed green beans samples where within the range of 0.1 and 4 mg/kg. The washing processing factors were 0.51 for fipronil, 0.32 for pyridaben, 0.59 for acrinathrin and 0.38 for kresoxim-methyl whereas the boiling factor ranged between 0.50 and 0.72.

1. Introduction

Consumption of fruits and vegetables is important for human health because these foods are primary source of some essential nutrients, including folate, magnesium, dietary fiber and vitamins A, C and K, and contain phytochemicals that may lower risk of chronic disease, like cardiovascular disease, and may be protective against certain types of cancer (DGAC, 2005). However, the yield of any agricultural and horticultural crops can be severely reduced as a result of infestation by pest and diseases, so that, in order to protect crops, plant protection productions are used. Residue of these products can cause negative health effects, being the ingestion of fruits and vegetables the main exposure via for humans (Berreda, Fernándes, Ruiz, Molto, & Font, 2010; Claeys et al., 2011). Hence, it is pertinent to explore strategies to enhance food safety from harmful pesticides for human population.

Maximum Residue Limits (MRLs) encourage food safety by restricting the concentration of a pesticide residue permitted on a commodity and by limiting the commodities on which it is allowed. To evaluate the residue behavior of plant protection products, not only the result of residue test carried out on plant and plant products are necessary but also the results of residue test carried out on processed plant products (processing studies) are important (Commission of the European Communities, 1997). Processing studies, for these plant or plant products that are generally processed before being eaten, allow a more realistic calculation of consumer's dietary intake of the active substance and help to gain acceptance for MRLs at international level.

The processing of food commodities generally implies the transformation of the perishable raw commodity to value added product that has a great shelf life and is closer to being table ready (Chin, 1997). Unit operations normally employed in processing food crops reduce or remove residues of pesticides that are present in them, and each operation has accumulative effect on the reduction of pesticide present (Geisman, Gunther, & Gunther, 1975). The effect of food processing on pesticide residues has been reviewed by researches (Amvrazi, 2011; Holland, Hamilton, Ohlin, & Skidmore, 1994; Kaushik, Satya, & Naik, 2009; Keikothaile, Spanoghe, & Steurbaut, 2010). These effects can be evaluated calculating the processing factors, which are the ratio between residues concentration in the processed commodity and the same in the raw commodity (Bonnechère et al., 2012). A processing factor higher than 1 means an increase in the residue level during processing and a processing factor lower than 1 indicates a decrease.

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The techniques used in the studies focused on commercial or home processing of fruits and vegetables include washing, blanching, peeling, pureeing, cooking, roasting, frying and boiling. Among these, washing is the most common form of processing, because it is the preliminary step in both household and commercial preparation. Loosely held residues of several pesticides are removed with reasonable efficiency by varied types of washing procedures (Street, 1969). Also, cooking is mandatory prior the consumption of some vegetables. Cooking is an act of preparing food for eating by the application of heat. It evolves a wide range of methods, to improve the flavor or digestibility of food. Boiling is the method of cooking food in boiling water. Food suitable for boiling includes vegetables, potatoes, eggs, meat, etc. Boiling treatment has several advantages: it is safe and simple and it is appropriate for large and domestic scale cookery and, also, in the case of green vegetables, maximum color and nutritive value are retained. The main effect of cooking on pesticide residue dissipation includes processes like volatilization, hydrolysis and thermal breakdown during the procedure.

During the last years, a number of papers describing analytical methods and the behavior of acrinathrin, kresoxim-methyl, fipronil and pyridaben residues in fruits and vegetables have been published (Aguilera, Valverde, Camacho, Boulaid, & García-Fuentes, 2012; Bhardwaj, 2012; Malato, Lozano, Mezcua, Agüera, & Fernandez-Alba, 2011; Nougadêre et al., 2012; Sharma, Nagpal, Pakade, & Katnoria, 2012; Valverde, Aguilera, Rodríguez, Boulaid, & Soussi, 2002). The aim of this study was to assess the effect of household processing on the removal of the fungicide kresoxim-methyl, the insecticide fipronil and the acaricides/insecticides acrinathrin and pyridaben in green beans, including washing and boiling procedures. Acrinathrin and pyridaben are authorised in the European Union (EU) for use on green beans, and they are two of the most commonly employed acaricides/insecticides in the cultivation of green beans in the greenhouses of Almería (Spain) to control mites, whitefly or thrips. MRLs established in EU for acrinathrin and pyridaben in green beans are 0.3 mg/kg and 0.5 mg/kg, respectively. In both cases, this MRL is the highest value out of all the EU-MRLs established for these two pesticides in vegetables (see EU-MRLs database at www.eurl-pesticides.eu). Kresoxim-methyl and fipronil are also authorised in EU for use on different vegetable crops but not on green beans. The inclusion of these two pesticides in this study was proposed by green beans farmers supporting this research. Authorized uses and label instructions for the application of these four plant protection products in Spain can be found at the Spanish Ministry of Agriculture website (www.marm.es/es/agricultura/temas/medios-de-produccion/productos-fitosanitarios/registro). Chemical structures of the studied pesticides together with their water solubility and K_{ow} data, and type of activity are included in Table 1 (Tomlin, 2009). In our work, it has been applied a rapid method for analysis of these four pesticides in green beans, using the quick, easy, cheap, rugged and safe (QuEChERS) buffered approach in the sample preparation step, which has been already demonstrated to be suitable for a number of pesticide/vegetable combinations (Kmellar et al., 2008; Lehotay, De Kok, Hiemstra, & Van Bodegraves, 2005; Lehotay, Mastovska, & Lightfield, 2005; Valverde et al., 2010).

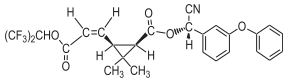
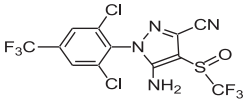
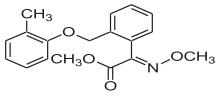
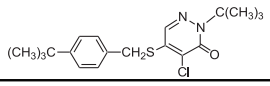
2. Experimental

2.1. Reagents and materials

HPLC grade acetonitrile was supplied by Scharlau (Barcelona, Spain). Acetone, ethyl acetate, cyclohexane and anhydrous sodium sulfate (pesticide residue grade) were obtained from Panreac (Barcelona, Spain). PRS grade anhydrous sodium acetate and acetic acid were also obtained from Panreac. Primary–secondary-amine (PSA) sorbent was supplied by Varian (Harbor City, CA). Certified standards of acrinathrin (98.0% purity), kresoxim-methyl (99.5% purity) and fipronil (98.0% purity) were supplied by Dr. Ehrenstorfer (Augsburg, Germany). Pyridaben (99.6% purity) was obtained from Riedel de Haën (Seelze, Germany). Individual stock standard solutions of acrinathrin, kresoxim-methyl, fipronil and pyridaben were prepared in acetone. Working standard solutions for gas-chromatographic (GC) analysis were prepared by suitable dilution of the stock standard solutions with blank green beans extracts.

The gas chromatograph was a Varian model 3800 (Walnut Creek, CA, USA) equipped with a model 1079 injection port, a model 8200 Cx autosampler, an electron-capture detector (ECD), and a DB-5MS fused-silica capillary GC column (J&W, Folson, CA, USA) of 30 m length, 0.25 mm internal diameter and 0.25 μm film thickness. The chromatographic conditions were as follows: detector temperature, 300 °C; injector temperature, 250 °C; oven temperature program, 1 min at 60 °C, 25 °C/min to 180 °C, 5 °C/min to 260 °C, and hold for 29 min; carrier gas (helium) flow rate, 1.2 mL/min; makeup gas (nitrogen) flow rate, 30 mL/min; injection volume, 1 μL; and splitless time, 0.75 min. The retention times of

Table 1
Chemical structures, water solubility, log K_{ow} and type of activity for acrinathrin, fipronil, kresoxim-methyl and pyridaben (Tomlin, 2009).

Active ingredient	Structure	Water solubility (mg L^{-1})	Log K_{ow}	Type
Acrinathrin		≤0.02 (25 °C)	5.6	Acaricide–insecticide (systemic)
Fipronil		1.9 (pH 5) 2.4 (pH 9) (20 °C)	4.0	Insecticide (systemic)
Kresoxim-methyl		2 (20 °C)	3.4	Fungicide (systemic)
Pyridaben		0.012 (24 °C)	6.37	Acaricide–insecticide (no systemic)