Food Control 31 (2013) 108–115

Contents lists available at SciVerse ScienceDirect

Food Control

journal homepage: www.elsevier.com/locate/foodcont

Pesticide residues in fresh-cut vegetables from integrated pest management by ultra performance liquid chromatography coupled to tandem mass spectrometry

M. Arienzo [a,*], D. Cataldo [b], L. Ferrara [b]

[a] Department of Hearth, Resources and Environment, University of Naples Federico II, Largo San Marcellino, 81100, Naples, Italy
[b] Department of Chemical Sciences, University of Naples Federico II, Complesso Universitario Montesantangelo, via Cintia 80100 Naples, Italy

ARTICLE INFO

Article history:
Received 5 July 2012
Received in revised form
10 September 2012
Accepted 18 September 2012

Keywords:
Pesticides
Residue analysis
Fresh-cut vegetables
Integrated pest management

ABSTRACT

A multi residue method based on the modified Quick Easy Cheap Effective Rugged and Safe (QuEChERS) sample preparation method and liquid chromatography coupled to mass spectrometry (LC–MS/MS) was adopted for the analysis of 14 pesticides in 145 vegetable samples from the intensive Sele agricultural plain in south west region of Campania, Italy, tilled by integrated pest management practices and destined to refurnish the Italian fresh cut commercial market. In 51.7% of the samples no residues were found, 41.4% of samples contained pesticide residues at or below the maximum residue level (MRL) and 2.1% of samples contained pesticide residues above MRL. Significant was also the proportion of samples, 4.8%, containing no authorized products due to incorrect agricultural practices. This was the case of Etofenprox and Dimethomorph used at levels above the MRLs. Propamocarb, cyprodinil, and boscalid were the pesticides most frequently found and were detected in 10% of the samples analysed. The application of an index of quality for residues to the analysis of data revealed that most of the analysed samples fall into the category range of excellent-good highlighting the adequacy of the products to the fresh cut market.

1. Introduction

Fresh-cut fruits and vegetables also named as ready-to-use or ready-to-eat represent an important and rapidly expanding food segment, the so called convenience product, of interest for growers, processors, retailers and consumers (http://www.freshcut2011.org/). They have been introduced in Europe at the beginning of the '80s, about ten years after their appearance in U.S. (Agroinnovatech, 2010). In 2000, England and France resulted to be the countries with the higher *turnover* of these products followed by Germany and Italy (Lamikanra, 2002). In recent years, despite the consumer demand for fruits and vegetables decreased in Europe, the fresh-cut industry reported a constant growth in terms of quantity and turnover. Today, the fresh-cut industry is expanding faster than any other segment of the fruit and vegetable market and the fresh-cut segment supplies both the food service industry and retail outlets, expanding to new markets around the world (Dalla Rosa & Rocculi, 2007; Olivas & Barbosa-Cánovas, 2005). In the U.S. packaged salads, cut vegetables and cut fruits comprise more than half, about 35% and 10% of the value of this product segment in the U.S. (Lamikanra, 2002). In Europe, Italy is one of the key players and its level of offer and quality is getting widely recognized. The production of such products is mainly concentrated in the south, especially Campania and Puglia. The Italian market adsorbs about 11,000 tons of the product per year. Recent data (ISMEA, 2011) revealed that sales of ready-to-use vegetables achieved considerable growth during 2008, with volumes rising 16.7 percent and sales up 7.5 percent compared with the previous 12 months.

Fresh-cut products are more perishable than whole produce: although remaining in a fresh state, they are physically altered during processing operations and have living tissues characterized by an accelerated metabolism. These products respond to the demand of the consumer to reduce the meal preparation time as well as the volume of the kitchen waste, but they are at the mean time very fragile because their processing does not result in a biological stabilization and presents, in fact, a *shelf-life* (life duration) limited to few days. The preliminary operations to which these products are subjected cause some mechanical and physiological damages which are responsible of the induction and speeding of the chemical and enzymatic reactions. Thus, in order to obtain fresh-cut fruits and vegetables capable of resisting the operational processing stress and hence of long commercial life is of paramount

* Corresponding author. Tel.: +39 081 674372; fax: +39 081 674090.
E-mail address: michele.arienzo@unina.it (M. Arienzo).

0956-7135/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.foodcont.2012.09.021

importance to process high quality raw products in terms of aspect, physiological condition and integrity of the phonological phase. It is important that these products are obtained through the adoption of integrated pest management practices (IPM) to reduce the dependency from conventional massive use of pesticides or with limited use of selective products with low environmental risk. More in deep, from January 1st of 2014 all the users of pesticides have to apply the general pest defence criteria of the IPM. Recently the EC defined new MRL of the active substances of pesticides, (Commission Regulation EC No 396/2005; Commission Regulation EC No 839/2008; Commission Regulation EC No 128/2009) aiming at a more sustainable use of these chemicals and to replace harmful compounds with environment-safer alternative even non chemical products and to encourage production processes with limited or zero utilization of pesticides.

It is of paramount importance to make sure through appropriate analytical laboratory methodologies that these products do not possess any residue of pesticides exceeding the maximum residual law level, MRL of the Commission Regulation EC No 839/2008. To meet this requirement, a number of methods have been developed for the analysis of pesticide residues in food. Multi residue method development is difficult, due to the fact that compounds of different polarity, solubility and volatility have to be extracted and analysed. Based on the classes of pesticides, several methods using gas chromatography for separation of individual compounds, followed by detection with selective and sensitive detection methods such as electron capture detection (Ismail, Ali, & Habiba, 1993), nitrogen–phosphorus detection (Fenoll, Hellin, Martinez, Miguel, & Flores, 2007) and flame photometric detection (Bolles et al., 1999) have been proposed.

However, the above mentioned detection methods cover a limited range of pesticide analysis and are characterized by the occurrence of false positive and inaccurate quantitation caused by the interferences of unknown compounds that are co-eluting in the same retention time with the analytes. Many of the published methods (Stajnbaher & Zupancic-Kralj, 2003; Albero, Sanchez-Brunete, & Tadeo, 2005) for the pesticide determination in food commodities seem to be complicated while consuming a large volume of solvent and they are very time costly. Therefore, new methods in sample preparation and measurement should be studied and developed. Recently, the QuEChERS sample preparation method has been introduced (Anastassiades, Lehotay, Stajnbaher, & Schenck, 2003; Lehotay, de Kok, Hiemstra, & van Bodegraven, 2005; Nguyen, Lee, Lee, Lee, & Lee, 2007). The original method is based on an acetonitrile extraction/partitioning followed by a cleanup with dispersive SPE. This is a fast and inexpensive method, which provides good recoveries for a large number of pesticides with different physico-chemical properties with a smaller amount of organic solvent consumption, and high sample throughput. Due to these advantages the QuEChERS method has had worldwide acceptance, becoming an official method of the AOAC for pesticide residue analysis in fruits and vegetables (Lehotay, 2007) and also drafted as European Norm (CENT/TC 275, N236, 2006). The method is often coupled with the chromatographic determination by LC–MS and LC–MS/MS using either electrospray ionization (ESI) or atmospheric pressure chemical ionization (APCI) because of its higher sensitivity than that of LC with conventional detectors and their selectivity is improved by the selection of specific ionic fragments (Soler & Pico, 2007; Kmellar et al., 2008).

The aim of our study was to use the QuEchERS sample preparation method plus the LC–MS/MS technique for the simultaneous quantification of 14 pesticides from several classes in fresh-cut fruits and vegetables from the southern province of Salerno, an agricultural area which refurnish two-third of the Italian fresh cut market and where the 80% of crops are produced following the IPM defence principles. The study will verify the eventual exceeding of law MRL limits through a quali-quantitative analysis using an integrated triple quadrupole mass spectrometer which allows the identification and quantification of low molecular weight compounds with a sensitivity of 10–4000 μg kg^{-1}.

2. Material and methods

2.1. Study area

Samples of fresh-cut fruits and vegetables originated from the low land of Sele, an intensive agricultural area placed southern of Salerno, in the Campania region, Fig. 1. The plain of about 500 km^2 is divided into right and left respect to the flow of the Sele River and represents a very fertile area of the Campania region. The plain is delimited to the north by the Meridional chains of Mt Picentini, to the east from the hills of the medium Sele, to the south from chains of the sub-Lucan Appennin and to the west is delimited by the Thyrrenian Sea of the Salerno's Gulf. From the morphological and geological point of view the Sele Plain is a territory of alluvial formation and hence geologically recent, formed by the accumulation of alluvial debris from the surrounding mounts due to the action of various rivers especially the Sele river, creating young, deep and fertile soils. These features make of the Sele Plain the most important and productive lung of the Salerno province. The soils are typically clay loamy and loamy clay, of volcanic origin and the climate is typically Mediterranean with rainy and mild winter and dry summer.

The Sele Low land encompasses a territory of 11 municipalities: Albanella, Altavilla Silentina, Battipaglia, Bellizzi, Campagna, Capaccio, Eboli, Montecorvino Pugliano, Olevano on Tusciano, Pontecagnano, Faiano and Serre, Fig. 1. According to the Agricultural Census survey of 2000, the cultivated surface was of about 35,000 ha of which 14,000 ha fall in the municipalities of Eboli and Capaccio. Tillages are concentrated especially at the right of the Sele river and the main crops are mais, forages, potatoes, vegetables (artichokes, chards, spinach, salad, pepper and tomato), peach, apricots and pears.

2.2. Sampling

145 samples of twelve vegetable species were analysed from October 2010 and April 2011. Vegetables belong to the families of the Asteraceae (3%), *Cichorium intybus* L., of the Brassicaceae (16%), *Brassica rapa var. nipposinica*, and *rosularis* (hereafter identified as other salads), *Brassica juncea var. Rugosa*, *Brassica oleracea* L. *var. Botrytis*, *B. oleracea* L. var. Gongylodes, *Eruca sativa Mill*., Chenopodiaceae (11%), *Beta vulgaris* var. cycla, *Spinacia oleracea*, of Compositae, (16%), *Lactuca sativa, Cicorium endivia latifolium,* of Liliaceae, (2%), *Allium schoenoprasum* L., and of Solanaceae, (1%), *Capsicum annum* L.

2.3. Chemicals

Acetonitrile, HPLC-grade, sodium chloride p.a., and formic acid, 98%, p.a. were purchased from Merck KGaA, Germany. Magnesium sulphate anhydrous p.a., $Na_2HCitrate$ sesquihydrate, $Na_3Citrate$ dihydrate and TPP were purchased from Sigma–AldrichChemie GmbH, Germany, 99%, p.a. Agilent SampliQ QuEChERS AOAC Extraction kits, p/n 5982-5755, and SampliQ QuEChERS AOAC dispersive SPE kits for Pigmented Fruits and Vegetables, p/n 5982-5222 and 5982-5258 were from Agilent Technologies Inc., DE, (USA).