



Pesticide residues in fruits and vegetables from the Aegean region, Turkey



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ABSTRACT

The purpose of this study was to investigate pesticide residues in fruits and vegetables from the Aegean region of Turkey. A total of 1423 samples of fresh fruit and vegetables were collected from 2010 to 2012. The samples were analysed to determine the concentrations of 186 pesticide residues. The analyses utilized ultrahigh performance liquid chromatography coupled with tandem mass spectrometry (UPLC/MS/MS) and gas chromatography with an electron capture detector (GC–ECD) confirmed by gas chromatography with mass spectrometry (GC–MS) after a multi-residue extraction procedure (the QuEChERS method). The results were evaluated according to maximum residue limits (MRLs) for each commodity and pesticide by Turkish Regulation. All pomegranate, cauliflower and cabbage samples were pesticides-free. A total of 754 samples contained detectable residues at or below MRLs, and 48 (8.4%) of the fruit samples and 83 (9.8%) of the vegetable samples contained pesticide residues above MRLs. MRL values were most often exceeded in arugula, cucumber, lemon, and grape commodities. All detected pesticides in apricot, carrot, kiwifruit and leek were below the MRLs. Acetamiprid, chlorpyrifos and carbendazim were the most detected pesticide residues.

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1. Introduction

Pesticides are chemical substances applied to crops at various stages of cultivation and during the post-harvest storage of crops. The use of pesticides is intended to prevent the destruction of food crops by controlling agricultural pests or unwanted plants and to improve plant quality (Bakırcı & Hisil, 2011). Pesticide use in commercial agriculture has led to an increase in farm productivity. Despite the wide ranging benefits of using pesticides in agriculture, several incorrect applications can result in high and undesirable levels of the compounds in the produce that reaches consumers. These include inappropriate selection of pesticides used on foodstuffs, over use of pesticides and harvesting the crops before the residues have washed off after application (Chen et al., 2011; Cserháti, Forgács, Deyl, Miksik, & Eckhardt, 2004). Exposure to pesticides can occur via a number of pathways such as indirect (e.g., through food, drinking water, residential and occupational exposure) and direct routes (oral, inhalation and dermal). However, the major concerns are from consumption of pesticide laden food

crops (Boobis et al., 2008). Pesticides have been linked to a wide spectrum of human health hazards, ranging from acute impacts, such as headaches and nausea, to chronic impacts, such as cancer, reproductive harm and endocrine system disruption (Blasco, Font, & Picó, 2006). In addition, incorrect applications of pesticides may cause harm to the environment, increased resistance in the target pest organisms and deleterious effects on non-target organisms. To ensure the safety of food for consumers and to protect consumer health, the monitoring of pesticide residues in food products must be pursued. Therefore, the levels of pesticide residues allowed in foodstuffs are legislatively controlled through setting maximum residue levels (MRLs). These MRLs limit the types and amount of pesticides that can be legally present on foods, as determined by various regulatory bodies which minimize consumer exposure to harmful or unnecessary intake of pesticides worldwide. In addition, MRLs help ensure the proper use of pesticides through authorization and registration (application rates and pre-harvest time intervals) and permit the free circulation of pesticide-treated products (Kvellára, Abrankó, Fodora, & Lehotay, 2010; Knežević & Serdar, 2009).

Many studies have investigated and identified pesticide residues in animals or crop plant products, such as fruit and vegetables, wheat, milk, cheese, butter, eggs, honey, meat and meat products from various countries (Ahmad, Salem, & Estaitieh,

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2010; Bai, Zhou, & Wang, 2006; Blasco et al., 2004; Chen et al., 2011; Darko & Acquaaah, 2008; Hjorth et al., 2011; Knežević & Serdar, 2009; Mallatou, Pappas, Kondyli, & Albanisb, 1997; Osman, Al-Humaid, Al-Rehiyani, & Al-Redha, 2010; Picó, la Farré, Soler, & Barceló, 2007). However, limited information is available regarding pesticide residue contamination in Turkey (Bulut, Akkaya, Gok, & Konuk, 2010; Erdogru, Covaci, & Schepens, 2005; Guler, Cakmak, Dagli, Aktumsek, & Ozparlak, 2010; Yentur, Kalay, & Oktem, 2001). In particular, there is no published literature regarding pesticide residues on fruits and vegetables in Turkey. Fruit and vegetables often contain higher pesticide residue levels compared to other food groups (Chen et al., 2011).

The aim of this study was to investigate the presence of pesticide residues on fruit and vegetables. A total of 1423 samples were collected from the market from 2010–2012. A total of 186 commonly used pesticide active substances were selected. The names of the pesticides and crop samples are listed in Tables 1 and 2. These samples were analysed by UPLC/MS–MS and GC–ECD/GC–MS to determine if they were in compliance with existing regulations limiting the total amount of pesticide residues legally allowed on food crops used for human consumption.

2. Materials and methods

2.1. Chemicals and reagents

All solvents and reagents were of pesticide grade and were dissolved as required for the sample extraction protocol and preparation of mobile phases. Anhydrous magnesium sulphate (MgSO_4), acetonitrile (MeCN), glacial acetic acid (HOAc), anhydrous sodium acetate (NaAc) and a graphitised carbon black (GCB) sorbent were obtained from Merck (Darmstadt, Germany). Methanol and deionised water was purchased from JT Baker (Deventer, Netherlands) and primary secondary amine (PSA) sorbent was from Oxoid (London, England). Pesticide standards were purchased from Dr. Ehrenstorfer (Augsburg, Germany). The purities of all pesticide standards were greater than 98%.

2.2. Preparation of standard solutions

Stock standard solutions were prepared at 1000 mg kg^{-1} by dissolving 10 mg of each compound into 10 ml of solvent. From the individual stock standard solutions, a multi-compound standard solution was prepared with a concentration of 5 mg L^{-1} . The working standard solutions that were used for preparation of the matrix matched standards within a range between 2.5 to $200 \text{ } \mu\text{g L}^{-1}$.

2.3. Fruit and vegetable samples

A total of 1423 samples of different fresh fruits and vegetables were randomly collected from a market in the Aegean region of Turkey from 2010–2012. All samples were taken in accordance with the Turkish regulation (Ministry Of Agriculture & Rural Affairs General Directorate Of Protection & Control, 2006/51). These samples were transported to the test laboratory under cold conditions and kept at $4 \text{ }^\circ\text{C}$. They were analysed within 24 h from their arrival for the presence of pesticide residues following the procedure described below.

2.4. Instruments and apparatus

2.4.1. General instruments

A Heidolph Reax 2000 vortex mixer (Schwabach, Germany), Sartorius CP225D and ED323S–CW analytical balances, and an Eppendorf 5702 centrifuge (Hamburg, Germany) were used.

Additionally, a freezer, pipettes, spatulas, funnels, polypropylene centrifuge tubes, gloves, beakers, filters and vials were needed for the extraction protocol. LC–MS/MS, GC–ECD, and GC–MS were used for the chromatographic analyses.

2.4.2. LC–MS/MS instruments and apparatus

For LC–MS/MS, an ACQUITY TQD tandem quadrupole mass spectrometer (Waters, Manchester, UK) was used. The system was equipped with a quaternary pump, a vacuum degasser and a thermostated autosampler. For the chromatographic separation, a Waters Acquity UPLC BEH C_{18} column ($100 \text{ mm} \times 2.1 \text{ mm}$, $1.7 \text{ } \mu\text{m}$ particle size) was employed. The instrument was operated using an electrospray ionisation source (ESI) in the positive and negative mode. The ESI parameters were: capillary voltage 3.5 kV , extractor voltage 3 V , source temperature $140 \text{ }^\circ\text{C}$, desolvation temperature $450 \text{ }^\circ\text{C}$, cone gas flow 200 L h^{-1} and desolvation gas flow 1050 L h^{-1} (both gases were nitrogen). Collision-induced dissociation was performed using argon as the collision gas at a pressure of $4 \times 10^{-3} \text{ mbar}$ in the collision cell.

Chromatographic analyses were conducted using gradient elution with eluent A composed of methanol (5%) and water with 2 mm ammonium acetate (95%), and eluent B was composed of methanol (95%) and water with 2 mm ammonium acetate (5%). The gradient elution programme started with 100% of eluent A and 100% of eluent B in 10.0 min. This composition was held for an additional 2.5 min before being returned to 100% of eluent A, for a total run time of 15 min. The flow rate of 0.45 ml min^{-1} was used for the separation of analytes. The column temperature was maintained at $50 \text{ }^\circ\text{C}$. A $20\text{-}\mu\text{l}$ volume of the extracted sample was injected.

2.4.3. Gas chromatography instruments and apparatus

The GC analysis was conducted using a GC–electron capture detector (ECD), and the detected pesticides were confirmed by GC–MS. The GC–ECD analyses were performed on a Agilent 6890 N equipped with a split/splitless injector and a 7683B autoinjector (Agilent, Santa Clara, USA). The GC–MS analysis was performed on an Agilent 7890A Turbo MSD 5975C equipped with a PTV Inlet and a 7683B autoinjector (Agilent, Santa Clara, USA). Helium was used as the carrier gas at a flow rate of 1.0 ml/min . Argon was used as the collision gas. Separations were conducted using a HP 5–MS $30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \text{ } \mu\text{l}$ column for GC–ECD and HP 5–MS Ultra Inert $30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \text{ } \mu\text{l}$ column (Agilent, Santa Clara, USA) for the GC–MS. The injection volume was $25 \text{ } \mu\text{l}$, and the injector temperature was held at $280 \text{ }^\circ\text{C}$. Samples were analysed as follows: the temperature programme was set for an initial temperature of $70 \text{ }^\circ\text{C}$ (held for 2 min), increased to $150 \text{ }^\circ\text{C}$ at $25 \text{ }^\circ\text{C/min}$ (held for 1 min), raised to $200 \text{ }^\circ\text{C}$ at $3 \text{ }^\circ\text{C/min}$ (held for 1 min) and, finally, increased to $280 \text{ }^\circ\text{C}$ at $8 \text{ }^\circ\text{C/min}$ (held for 15 min) for the GC–ECD and GC–MS analyses.

2.5. Extraction procedure

All samples that was unwashed and with the peel intact, based on the definition of Turkish regulation (Ministry Of Agriculture & Rural Affairs General Directorate Of Protection & Control, 2009/62), were homogenised using a blender (Waring, DCA, CT, USA) for more than 1 min to obtain thoroughly mixed homogenates. Homogenised samples were analysed according to the QuEChERS procedure (Lehotay, 2007). Briefly, fifteen grammes of homogenised sample was weighed in a 50 ml polypropylene centrifuge tubes. Next, 15 ml of 1% HOAc (10 ml glacial HOAc in a 1 L MeCN solution) were added with 6 g anh. MgSO_4 + 1.5 g anh. NaAc and the tube was closed. The samples were shaken in a vortex for 1 min and centrifuged for 1 min at 1.6 rcf. A 2 ml volume of supernatant was removed to the polypropylene centrifuge tubes

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