



## Target vs non-target analysis to determine pesticide residues in fruits from Saudi Arabia and influence in potential risk associated with exposure



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### ABSTRACT

The occurrence of pesticide residues in fruits was determined by a target method for 62 analytes and a wide scope screening method against a database of 500 pesticides. Limits of quantification (LOQs) were from 0.5 to 6.3  $\mu\text{g kg}^{-1}$  for the target method and from 0.5 to 119  $\mu\text{g kg}^{-1}$  for the non-target. Thirty samples: dates, apples, oranges, tangerines, lemons and grapefruits were selected because their high consumption, except lemons and grapefruits that were to cover all citrus fruits. Using the target method, 15 compounds (mostly insecticides and fungicides) out of 62 pesticides (organophosphorus, carbamates, pyrethroids, chloroacetanilides, triazines, triazoles, imidazoles, etc.) were detected. Residues were in 100% of the samples, 80% contained at or below maximum residue limits (MRLs), and 20% above. Non-target method identified several additional pesticides (cypronil, fludioxonil, boscalid and pyraclostrobin in apples). The highest acute risk were for acrinathrin, chlorpyrifos and imazalil with estimated short-term intake (ESTI) > 100% acute reference dose (ARfD), followed by imidacloprid and thiabendazole with ESTI  $\geq$  70% ARfD. The higher chronic risk were for ethion and fluvalinate with estimated daily intakes (EDIs) of 8.8 and 1.5% of the admissible daily intake (ADI), respectively.

### 1. Introduction

Pesticide-residue determination in food is relevant for the protection of human health since it is the first step to establish potential intake (Alves et al., 2017). More than 1000 substances active against pests are used worldwide. Although, pesticides are extensively regulated through maximum residues limits (MRLs), the consumer is lifelong exposed to low amounts of hundreds of different pesticides. Recent examples on pesticide risk assessment, including cumulative and probabilistic approaches, remark the importance among other many uncertainties of accurate analytical data on the amount and variety of pesticide residues that could be present in the sample. Otherwise, the risk due to pesticide intake could be under or overestimated (Boon et al., 2015; Jensen et al., 2013, 2015; Kennedy et al., 2015a; Verbeke et al., 2015).

However, systematic pesticide residue determination is an ongoing topic of research in food and chemical toxicology because until recently was almost impossible to ensure that all the pesticide residues present were identified due to the large number of possible compounds and to the analytical schemes used to determine pesticides and/or their degradation products based on target multiresidue methods (Anacleto et al., 2017; Ewence et al., 2015; Kennedy et al., 2015b; Picó and

Barceló, 2015; Pous et al., 2001). By definition these methods are able to determine a more or less large range of compounds using gas chromatography (GC) or liquid chromatography (LC) coupled to mass spectrometry (MS) but with the limitation that pesticides or transformation products not included in the predefined list of analytical standards are not be detected, even though they are present in the sample (Masiá et al., 2014; Masia et al., 2016; Pirsheh et al., 2017; Trevisan et al., 2017; Uclés et al., 2017). This makes almost impossible to map the entire pesticide profile of the sample. Many multi-residue analytical methods have been developed, in particular, using LC coupled with a triple quadrupole mass spectrometer (QqQ) in selected reaction monitoring (SRM) because, for most of pesticides, is more sensitive than GC (Ghoniem et al., 2017; González-Curbelo et al., 2017; Petrarca et al., 2017; Stachniuk et al., 2017; Zhang et al., 2017).

Recent developments in high-resolution mass spectrometry (HRMS) coupled to LC (LC-HRMS) have open new possibilities for the analysis of pesticide residues without having any “a priori” list of standards available. (Masiá et al., 2014; Masia et al., 2016; Pérez-Ortega et al., 2017). For cost, time and practical reasons, data obtained using non-targeted acquisition is usually evaluated using a database or library of typically several hundreds of pesticides (Picó and Barceló, 2008).

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**Abbreviations**

ADI	admissible daily intake
ARfD	acute reference dose
C18	octadecylsilica
CE	collision energy
DP2	declustering potential two
dSPE	dispersive solid-phase extraction
EC	European Commission
EDI	estimated daily intake
EFSA	European Food Safety Authority
ESTI	estimated short-term intake
FAO	Food and agriculture organization
GC	gas chromatography
HRMS	high resolution mass spectrometry
IDA	information dependent acquisition
UESTI	international estimation of short-term intake
IRD	ion release delay
IRW	ion release width

LC	liquid chromatography
LC-HRMS	liquid chromatography high resolution mass spectrometry
LOD	limit of detection
LOQ	limit of quantification
MRL	máximum residue limit
MS	mass spectrometry
MS/MS	tandem mass spectrometry
PSA	primary secondary amine
QqQ	triple quadrupole
QqTOF	quadrupole time-of-flight
RSD	relative standard deviation
SRM	selected reaction monitoring
UHPLC-MS/MS	ultra-high pressure liquid chromatography tandem mass spectrometry
UHPLC-QqQ-MS/MS	ultra-high pressure liquid chromatography triple quadrupole tandem mass spectrometry
UHPLC-QqTOF-MS/MS	ultra-high pressure liquid chromatography quadrupole time-of-flight tandem mass spectrometry

Although the interrogation of the data is performed against the list of compounds included in the database or the library, retrospective evaluation is always possible as data for all compounds that have given sufficient detector response have been acquired (Farre et al., 2014; Picó et al., 2010; SANTE, 2015). The disadvantage of these instruments is that they are less sensitive than the QqQ. However, last generation instruments increased specificity and sensitivity to achieve appropriate threshold for trace level determination and are increasingly applied as routine instrument to determine pesticide residues (Masia et al., 2016; Picó and Barceló, 2008).

The purpose of this study was to evaluate pesticide residue levels in fruits from Saudi Arabia in relation to admissible daily intake (ADIs) and Acute Reference Doses (ARfDs) derived from toxicological studies and MRLs according to the European Food Safety Authority (EFSA), Food Agriculture Organization (FAO) and World Health Organization (WHO) guidelines (EFSA/FAO/WHO, 2011). The influence on these results of the analytical protocol was established by comparing the results obtained by a target method for 62 active substances (listed and classified in Table 1) and based on LC-QqQ-tandem MS (MS/MS) to those obtained by a “wide scope screening method” based on LC-HRMS [using a quadrupole time-of-flight (QqTOF)]. The latter identify pesticides against a database of more than 500 pesticides and transformation products including the 62 of the target method (Table S1). In this way, more accurately and realistic estimation of the pesticide residue exposure will be achieved. Furthermore, there is little information on the pesticide residues level on fruits and vegetables produced or marketed in Saudi Arabia. To our knowledge, this is the first time that LC couple to different mass analyzers is used to determine these residues in fruits from this area. Only a small number of works are related to determination of certain-pesticides in vegetables (Osman et al., 2010, 2011). Saudi Arabia is importing 80 percent of its food requirements from foreign countries while the remaining 20 percent of foods are locally produced according to the World Bank (2017). Pesticides and other agro-chemical products market in Saudi Arabia grows 3.1% in 2014 due to increased arable land of crops. Insecticides’ consumption reached 3171 tons of active ingredients in 2014. Then, a proper risk assessment of pesticide residue intake through the diet is crucial to avoid health problems.

## 2. Materials and methods

### 2.1. Pesticide standards and pesticide database

Pesticide standards at high purity (98–99.9%) were acquired from

Sigma-Aldrich (Steinheim, Germany) and were listed in Table 1. Individual standard solutions were prepared in methanol at a concentration of 1000 mg L<sup>-1</sup>. The working standard solutions were prepared by mixing the appropriate amounts of individual standard solutions to a final concentration of 0.5 mg L<sup>-1</sup> in a 10 mL volumetric flask, and make up the solution to the mark with methanol. All solutions were stored in 10 mL vials at 4 °C in the dark.

Furthermore, a database that includes 500 active ingredients (Table S1) with information on accurate mass, retention time, isotopical pattern and MS/MS spectrum (for some pesticides) was used to identify pesticides present in the sample and not covered in the target method. Those pesticides that are not in the MS/MS library were searched in the Metlin database to ensure MS/MS match (The Scripps Research Institute, 2017). When possible the analytical standard was acquired to unequivocally identify and to quantify the pesticide.

**Table 1**  
Pesticides covered by the target multi-residue method using LC-QqQ-MS/MS.

Action	Active substances
Insecticides	<p><b>-Organophosphorus:</b> azinphos-ethyl, azinphos-methyl, chlorpyrifos, chlorfenvinphos, coumaphos, diazinon, dichlofenthion, dimethoate, ethion, etofenprox, fenitrothion, fenthion, fenthion-sulfoxide, fenthion-sulfone, malathion, omethoate, parathion-ethyl, parathion-methyl</p> <p><b>-Carbamates:</b> carbofuran, carbofuran-3-hydroxy, methiocarb</p> <p><b>-Neonicotinoids:</b> acetamiprid, chlothianidin, imidacloprid, thiametoxan</p> <p><b>-Pyrethroids:</b> acrinathrin, bifentrin, flumethrin, fluvalinate</p> <p><b>-Other:</b> buprofezin, 2,4-dimethylanilin (DMA)<sup>a</sup>, N-2,4-Dimethylphenyl formamide (DMF)<sup>a</sup>, N-2,4-Dimethylphenyl-N'-methylformamidine (DMPF)<sup>a</sup>, hexythiazox, pyriproxyfen, spinosad A</p>
Herbicides	<p><b>-Chloroacetanilide:</b> Alachlor, acetochlor, metholachlor</p> <p><b>-Thiocarbamate:</b> molinate,</p> <p><b>-Triazines:</b> atrazine, atrazine-deisopropyl, atrazine-deethyl, propazine, simazine, terbuthylazine, terbuthylazine-deethyl, terbuthylazine-2-hydroxy, terbutryn, terbumeton, terbumeton-deethyl</p> <p><b>-Ureas:</b> isoproturon</p> <p><b>-Other:</b> propanil</p>
Fungicides	<p><b>-Benzimidazole:</b> Carbendazim</p> <p><b>-Imidazole:</b> imazalil, prochloraz, thiabendazole</p> <p><b>-Triazole:</b> tebuconazole</p> <p><b>-Chlorophenyl:</b> tolclorfen-methyl</p>

<sup>a</sup> Metabolites of the amitraz.

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