Detection of Pesticide Residues in Organic and Conventional Fruits and Vegetables Available in Ireland Using Gas Chromatography/Tandem Mass Spectrometry (GC-MS/MS) and Liquid Chromatography/Tandem Mass Spectrometry (LC-MS/MS) Detection

Rachel Tobin^{1*}, Tony Walsh², Jim Garvey² and Tracey Larkin¹

¹Department of Applied Science/Shannon Applied Biotechnology Centre, Limerick Institute of Technology, Ireland

²Department of Agriculture, Food and Marine Pesticide Regulation and Control Division, Backweston Laboratory Campus, Ireland

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***Corresponding author:** Rachel Tobin, Department of Applied Science/Shannon Applied Biotechnology Centre, Limerick Institute of Technology, Moylish Park, Limerick, Ireland, E-mail: Rachel.Tobin@lit.ie

Abstract

Irish organic consumers believe that organic foods are a healthier choice due to the lack of synthetic pesticides used in organic agricultural practices; however, few scientific studies have shown that organic samples are void of any pesticide residues. Nine different fruit and vegetable types of organic and conventional origin were sampled from large supermarkets. Analysis for 465 pesticide residues was carried out using GC-MS/MS and LC-MS/MS analysis. Of the 27 organic samples tested, 15 contained one or more detected pesticide residues, with one of these being above the limit of quantification (LOQ) for the method, imazalil in organic onion, 11.13 ng/g. Of the conventional samples 17 of the 27 samples contained one or more residues. Twelve of the residues detected in conventional samples were above the LOQ with concentrations ranging from 9.84 to 154.10 ng/g. A similar number of organic (15) and conventional (17) samples tested positive for detectable residues, however the number of residues detected was higher in conventional (43) than in organic (29), and the concentration of these residues were higher. It is concluded that it cannot be said that organic fruits and vegetables are void of pesticides based on the results of this study.

Keywords: Organic; Fruits; Vegetables; Pesticides; GCMS; LCMS

Introduction

Pesticides are chemical, biocidal products that are used for the control of organisms that effect plant, human or animal health, in particular when the organisms cause damage to natural or manufactured products e.g. food crops. Pesticides fall in to three main categories; fungicides, herbicides and insecticides, based on their target action [1]. Most pesticides are toxic to humans on some level and the World Health Organisation (WHO) has classified these effects from Ia- Extremely hazardous to U- Unlikely to present acute hazard based on the LD₅₀ (lethal dose required to kill 50% of a test animal population) for the rat mg/Kg body weight [2].

Organic agricultural practices are distinguishable from non-organic or conventional practices mainly by their non-use of soluble minerals for soil fertilization and pesticides for plant protection and growth. The use of such substances is strictly prohibited under organic certification standards. The Codex Alimentarius- Organically Produced Foods document (2007) outlines a small number of substances approved for use in organic agriculture, some of these include;

- Manure, slurry and urine for soil fertilization and conditioning.
- Rotenone, neem, tobacco, copper hydroxide, copper oxychloride, and sulphur for plant pest and disease control [3].

The rejection of synthetic chemicals is one of the main drivers of choice when people choose to buy organically produced foods [4]. And in particular in Ireland, 68 % of respondents to an An Bord Bia survey stated 'Free from chemicals and therefore healthier' when asked what they believe is the main benefit of eating organic foods [5].

Reports suggest that despite the ban on the use of synthetic pesticides in organic farming, organic food products can still contain pesticide residues. Soil, rain, and ground water can all carry these substances to crops growing on organic farms. Environmental conditions such as trees, hedgerows, and nearby conventional farms can all influence the presence of pesticides in organic food products. It is also suggested that the presence of lower levels of pesticides in organic products is not necessarily an advantage as far as food safety is concerned due to the strict control of pesticide levels in conventional produce [6,7]. The study by Gonzalez M, et al. [6] evaluated the levels of lipophilic organochlorine pesticide (e.g. dichlorodiphenyltrichloroethane (DDT), Aldrin, heptachlor) residues in leafy vegetables from

organic and conventional farms in Argentina. The study found detectable residues in both organic and conventional samples but reported that all levels were below those allowed by the Codex Alimentarius. The study also found that the levels found in organic samples were lower than those found in the conventional samples.

A recent study carried out in Spain using a multi-residue analysis with simultaneous extraction analysed for 90 pesticides, bio-pesticides and mycotoxins (toxins produced by fungi) in organic cereals, cucumbers and wines. The study found pesticide/bio-pesticide residues (nicotine, epoxiconazole and piperonyl butoxide) in 6 of the 13 cucumber samples. The levels of these compounds ranged from 10.4 to 47.0 $\mu\text{g kg}^{-1}$ [8]. A Portuguese study analysed organic strawberry farms for 14 organochlorine pesticides over two consecutive years (2009-2010). The study found two pesticides, lindane and β -endosulfan, over the accepted Maximum Residual Limits (MRL's). The researchers also found other pesticides residues below the MRL's (aldrin, o, p'-DDT and methoxychlor) and noted that levels decreased from 2009 to 2010 [9].

Few studies have shown that organic samples are free from pesticide residues, however most do show that fewer residues are found, and at lower levels, when compared to conventional samples. But is this a clear advantage of organic products if the levels found in conventional products are also low in terms of food safety? MRL's are placed on all pesticides used in agriculture and these are strictly controlled by the European Union (active substances), and also at a state level (pesticide products). The United Kingdom Pesticides Residue Committee (2007) measured 220 organic samples in 2006 and found no MRL violations, whereas 1.8% of the 3342 conventional samples tested were in violation of the limits [10]. In these cases where there is a higher chance, albeit a small chance, of consuming products that contain pesticide residues above the MRL, organic products are more appealing. Organic samples are perceived by many consumers as being 'free' from chemicals, should consumers be aware that this is not always the case? Does 'no added chemicals' necessarily mean no chemicals will be present in the case of fruits and vegetables? To date, there are no published studies that have compared the levels of pesticides in organic and conventional fruits and vegetables on the Irish market.

Experimental-Instrumentation

Liquid Chromatography/Tandem Mass Spectrometry

An Agilent 6490 LC-Triple Quadrupole (QQQ) in MS/MS mode was used for the analysis of 319 pesticide residues. Separation was carried out through an Agilent Poroshell C18 2.7 μm 21 x 150mm column using a gradient mobile phase system of 5 mmol ammonium formate in ultra pure water (A) and 5 mmol ammonium formate in methanol (B). The flow rate was 0.4 ml/min and separation was carried out in 20 minutes as follows; 0.8 min, 40% B; 3.5 min, 40% B; 5.0 min, 60% B; 6.0 min, 60% B; 12 min, 65% B; 17 min, 100% B; 20 min, 100% B.

MS/MS detection was carried out in both positive and negative electron ionization (EI) modes depending on the

residues included in the method (2 separate sets of standards were prepared). The source parameters for detection were as follows: capillary voltage 3.5 kV (positive) and 2.5 kV (negative); nozzle voltage, 300 V (positive), 0 V (negative); desolvation gas (nitrogen) temperature, 120°C and flow rate 20 ml/min; sheath gas temperature, 350°C and flow rate 12 ml/min; and the nebulizer pressure was 35 psi. Data processing was carried out using Agilent Mass Hunter Quantitative software.

Gas Chromatography/Tandem Mass Spectrometry

GC-MS/MS analysis of 146 pesticide residues was carried out using an Agilent 7000 Triple Quadrupole (QQQ) system. The GC was operated in pulsed splitless mode at a flow rate of 3 ml/min and the column was an Agilent HP-5MS 5 % Phenyl Methyl Silox (30 m x 250 μm x 0.25 μm). The oven temperature program was: 70°C held for 2 mins, 25°C/min to 150°C for 0 min, the 3°C / min to 200°C for 0 min, then 8°C/min to 280°C for 10 min. The MS/MS section was operated in a positive ionization mode and all other MS parameters were the same as for the LC/MS/MS. Data processing was also carried out using Agilent Mass Hunter Quantitative software.

Confirmation by Tandem Mass Spectrometry: The minimum requirements for the confirmation of a given pesticide were a) a retention time (RT) match with an offset of less than 0.03 min with respect to a standard from the same run. And b) a second transition ion peak (at the same RT) with a ratio relative to the parent ion peak within the qualifying range; >50 % ratio with 10% tolerance, 30-50 % with 20 % tolerance, 10-30 % with 30 % tolerance, and < 10 % with 50 % tolerance.

Quantification by Tandem Mass Spectrometry: Quantification of a given pesticide was calculated from a 5 point calibration curve in duplicate with a minimum r_2 value of 0.95 for LC-MS/MS and 0.98 for GC-MS/MS. The range of quantification for the GC-MS/MS was 10 to 250 ng/ml, and the range for the LC-MS/MS was 0.5 to 12.5 ng/ml. Pesticides positively detected but present below the LOQ for the method are reported as trace.

Sampling

Nine different fruits and vegetables popular to the Irish market were selected for the study namely; apple, banana, broccoli, carrot, cherry tomato, onion, orange, potato and vine tomato. The sampling plan was constructed using survey data of Irish consumers on organic food purchasing habits where a large majority of survey takers stated that they visit large supermarkets for their organic produce along with general purchases [11]. Therefore samples were sourced mainly from large supermarkets from March to September 2011. All samples were purchased no more than 24 hours before preparation.

Sample Preparation: All samples in batches were washed, inedible parts removed (peeled if necessary) and chopped into small cubes. The cubes were mixed and approximately 300 g representative sample was blended using a Hitachi BLN1 household blender until a uniform paste was achieved (duration depended on the nature of the sample). After blending, 100 g of the sample was accurately weighed into a 200 ml freeze drying

Table 1: The results of the analysis of 465 pesticide residues in organic and conventional samples including country of origin, pesticide name, mode of action, retention time and concentration. Org = Organic, Conv = Conventional.

Sample	Country of Origin	Compound	Type of pesticide	RT	Conc ng/g	Analysis	MRL ng/g
apple 1 org	N.Zealand	thiabendazole	fungicide	4.95	trace	LCMS	5000.00
apple 2 org	Chile	clear					
apple 3 org	N.Zealand	clear					
apple 4 conv	N.Zealand	clear					
apple 5 conv	N.Zealand	myclobutanil	fungicide	9.59	trace	LCMS	500.00
		fluazinam	fungicide	15.77	trace	LCMS	300.00
apple 6 conv	Chile	thiabendazole	fungicide	4.95	trace	LCMS	5000.00
		chlorantraniliprole	insecticide	7.67	trace	LCMS	500.00
		methoxyfenozide	insecticide	9.34	trace	LCMS	2000.00
		pyriproxifen	insecticide	16.12	trace	LCMS	200.00
		diphenylamine	growth regulator/ protection in cold storage	10.48	20.79	GCMS	5000.00 not approved
banana 1 org	Dominican Rep.	fenpyroximate	insecticide	16.74	trace	LCMS	50.00
		clofentezine	insecticide	14.10	trace	LCMS	2000.00
		pirimiphos-ethyl	insecticide	15.91	trace	LCMS	No toxicological info. Default MRL 10.00
		ethion	insecticide	16.07	trace	LCMS	10.00 (Not approved)
		pyriproxifen	insecticide	16.12	trace	LCMS	200.00
		propargite	insecticide	16.53	trace	LCMS	10.00
banana 2 org	Dominican Rep.	clear					
banana 3 org	Peru	clear					
banana 4 conv	Belize	clear					
banana 5 conv	Costa Rica	thiabendazole	fungicide	4.94	trace	LCMS	5000.00
		azoxystrobin	fungicide	8.25	trace	LCMS	2000.00
banana 6 conv	None Stated	azoxystrobin	fungicide	8.25	trace	LCMS	2000.00
broccoli 1 org	Holland	metamitron	herbicide	2.95	trace	LCMS	100.00
		thiabendazole	fungicide	4.49	trace	LCMS	5000.00
broccoli 2 org	Holland	metamitron	herbicide	2.95	trace	LCMS	100.00
		thiabendazole	fungicide	4.50	trace	LCMS	5000.00
		dodine	fungicide	14.1	trace	LCMS	200.00
broccoli 3 org	Holland	metamitron	herbicide	2.94	trace	LCMS	100.00
		thiabendazole	fungicide	4.49	trace	LCMS	5000.00
		spinosyn A	insecticide	16.88	trace	LCMS	2000.00
		spinosyn D	insecticide	17.22	trace	LCMS	2000.00
broccoli 4 conv	U.K	metamitron	herbicide	2.94	trace	LCMS	100.00
		thiabendazole	fungicide	4.49	trace	LCMS	5000.00
broccoli 5 conv	Ireland	metamitron	herbicide	2.94	trace	LCMS	100.00
		thiabendazole	fungicide	4.49	trace	LCMS	5000.00
broccoli 6 conv	Ireland	metamitron	herbicide	2.94	trace	LCMS	100.00
		thiabendazole	fungicide	4.48	trace	LCMS	5000.00
		imazalil	fungicide	11.76	trace	LCMS	50.00
carrot 1 org	Scotland	thiabendazole	fungicide	4.50	trace	LCMS	50.00
carrot 2 org	Scotland	thiabendazole	fungicide	4.51	trace	LCMS	50.00
carrot 3 org	Ireland	thiabendazole	fungicide	4.49	trace	LCMS	50.00
carrot 4 conv	Ireland	thiabendazole	fungicide	4.49	trace	LCMS	50.00
carrot 5 conv	Ireland	thiabendazole	fungicide	4.50	trace	LCMS	50.00
carrot 6 conv	Spain	thiabendazole	fungicide	4.49	trace	LCMS	50.00

		linuron	herbicide	7.71	75.27	LCMS	200.00
		imazalil	fungicide	11.77	trace	LCMS	
cherry T 1 org	Spain	clear			trace		
cherry T 2 org	Holland	clear					
cherry T 3 org	Italy	clear					
cherry T 4 conv	Ireland	propamocarb	fungicide	1.97	trace	LCMS	10,000.00
		cyprodinil	fungicide	11.72	68.17	LCMS	1000.00
		fludioxonil	fungicide	8.19	31.95	LCMS	1000.00
cherry T 5 conv	Ireland	clear					
cherry T 6 conv	Holland	clear					
onion 1 org	Holland	imazalil	fungicide	11.78	11.13	LCMS	50.00
onion 2 org	Holland	clear					
onion 3 org	Argentina	clear					
onion 4 conv	Holland	clear					
onion 5 conv	U.K.	clear					
onion 6 conv	Argentina	clear					
orange 1 org	S. Africa	thiabendazole	fungicide	4.52	trace	LCMS	5000.00
orange 2 org	S. Africa	thiabendazole	fungicide	4.53	trace	LCMS	5000.00
orange 3 org	S. Africa	thiabendazole	fungicide	4.52	trace	LCMS	5000.00
		imazalil	fungicide	11.82	trace	LCMS	5000.00
orange 4 conv	S. Africa	thiabendazole	fungicide	4.52	trace	LCMS	5000.00
		imazalil	fungicide	11.81	18.87	LCMS	5000.00
orange 5 conv	S. Africa	imidacloprid	insecticide	2.55	trace	LCMS	1000.00
		carbendazim	fungicide	3.50	trace	LCMS	200.00
		thiabendazole	fungicide	4.53	trace	LCMS	5000.00
		pyrimethanil	fungicide	7.88	trace	LCMS	10,000.00
		imazalil	fungicide	11.83	trace	LCMS	5000.00
orange 6 conv	S. Africa	imidacloprid	insecticide	2.55	trace	LCMS	1000.00
		carbendazim	fungicide	3.50	trace	LCMS	200.00
		thiabendazole	fungicide	4.52	31.60	LCMS	5000.00
		pyrimethanil	fungicide	7.88	trace	LCMS	10,000.00
		imazalil	fungicide	11.84	63.24	LCMS	5000.00
potato 1 org	Israel	pencycuron	fungicide	14.25	trace	LCMS	100.00
		3-chloroaniline	herbicide	5.48	trace	GCMS	Not listed
		chlorpropham	herbicide	11.05	trace	GCMS	10,00.00
potato 2 org	Israel	clear					
potato 3 org	Israel	clear					
potato 4 conv	Ireland	pencycuron	fungicide	14.24	trace	LCMS	100.00
potato 5 conv	Ireland	clear					
potato 6 conv	N. Ireland	clear					
vine T 1 org	Holland	clear					
vine T 2 org	Italy	chlorpyrifos	insecticide	15.96	trace	LCMS	500.00
vine T 3 org	Holland	iprodione	fungicide	28.44	trace	GCMS	5000.00
vine T 4 conv	Ireland	clear					
vine T 5 conv	Ireland	propamocarb	fungicide	1.98	9.84	LCMS	10,000.00
		cyprodinil	fungicide	11.71	trace	LCMS	1000.00
		chlorothalonil	fungicide	14.82	98.29	GCMS	2000.00
vine T 6 conv	Ireland	propamocarb	fungicide	1.99	11.70	LCMS	10,000.00
		fludioxonil	fungicide	8.18	14.51	LCMS	1000.00
		cyprodinil	fungicide	11.71	trace	LCMS	1000.00
		chlorothalonil	fungicide	14.82	154.07	GCMS	2000.00

Note: Bolded compounds are those measured to be in the quantifiable range of the particular method used.

container, the sample was shell frozen in a Lab Conco Shell Freezer at -42°C and stored at -80°C. Samples were then freeze-dried using a Thermo Heto PowerDry LL300 freeze dryer, the duration of which was also dependent on the nature of the sample. When fully dried, the samples were weighed, ground to a fine powder using a mortar and pestle and stored in sterile plastic tubes at -20°C in the dark. It is important to note for the purpose of this study that, apart from cooking, all samples were prepared as if being consumed before the drying process. Therefore pesticide residues detected should represent those present in the food eaten by a consumer and not simply on a whole sample.

Sample Extraction: Samples were extracted using a Mini Luke multi-residue solvent extraction according to The Ministry of Public Health, Welfare and Sport, Analytical Methods for Pesticide Analysis, 6th Edition (1996) [12]. In summary, 1.5 g of dried sample was added to 30 ml of acetone, dichloromethane and petroleum ether (90 ml total) and homogenised using an Ultra Turrax IKA digital homogeniser. 60 ml of this mixture was evaporated to near dryness (volume circa. 2 ml) using a Büchi Rotavapor R-205 and reconstituted in 10 ml of ethyl acetate, this gave each extract a concentration of 1 g/ml. The samples were then filtered through 0.2 µm syringe filters and transferred to amber vials. Samples for analysis by LC-MS/MS were diluted 1:20

before transfer to vials by adding 0.5 ml of the filtered sample in ethyl acetate to a volumetric flask and making up to 10 ml with methanol. This dilution was accounted for at the data acquisition.

Results and Discussion

The results of the analysis of 465 pesticide residues using GC/MS/MS and LC/MS/MS are shown in Table 1. In total, 54 samples were included in the study, 27 of these were organic, and 27 were conventional.

Of the 27 organic samples, 15 contained one or more pesticide residues. Cherry tomatoes were the only group of the organic samples that were clear from any pesticide residue. One of pesticide residues detected was present at a quantifiable level (>0.5 ng/g), imazalil (Figure 1) found in an organic onion sample was measured to have a concentration of 11.13 ng/g, but was below the MRL at 50 ng/g. A total of 29 residues were found across the organic samples.

Of the 27 conventional samples tested, 17 contained one or more residues. Twelve of the pesticides identified were present above the LOQ. These were; diphenylamine (Figure 2) found in apple (20.78 ng/g); linuron found in carrot (75.27 ng/g); fludioxonil and cyprodinil found in the same cherry tomato sample (68.17 and 31.95 ng/g respectively); imazalil in orange

Figure 1: Imazalil peak at detection step in organic onion sample 1 (diluted by a factor of 20), compared to peak from screener mix prepared at concentration of lowest calibration standard (bottom peak) and other organic samples analysed in the same batch.

Figure 2: Diphenylamine peak at quantification step detected in apple 6 (conventional) by gas chromatography/tandem mass spectrometry with standard curve.

(peel removed) (18.87 ng/g); thiabendazole and imazalil in a second orange sample (31.60 and 63.24 ng/g); propamocarb (9.84 and 11.70 ng/g) and chlorothalonil (98.29 and 154.07 ng/g) in two of the vine tomato samples and fludioxonil in another vine tomato sample (14.51 ng/g). In total, 43 residues were found in the 27 conventional sample batches.

The sample with the largest amount of detectable residues, six, was an organic banana sample, and this refers to the pulp of the banana only. This result shows that pesticide residues are not a food surface issue that can be rinsed off before eating. Residues can be found within a fruit and uptake from soil is possible even when organically grown. Broccoli and oranges both contained the most detectable residues as food groups. Across the 6 samples in each group, 16 residues were detected in broccoli and oranges. This may show that more pesticides are applied to these foods in agriculture, or that the uptake of pesticides is significant/the surface of the food is more conducive to holding residues.

The MRL is cited for each pesticide quantified in the method in Table 2. Each limit is specific for the food type and is cited from the current EU Pesticides database updated on the 02/05/2013 under the Regulation (EC) No. 1107/2009. None of the pesticides quantified were above the MRL's [13].

In terms of food safety this study cannot show that organic products are a safer choice in terms of human health compared to their conventional counterparts. In agreement with the review by Tobin R, et al. [14], it is not correct to promote organic foods on the basis that the chemicals found in conventional agriculture (and as proven in this study, in organic) present a serious health risk at the levels commonly found in the food we eat. It is also noted in the review of the Irish organic food market that consumers may choose organic products not for food safety, but because the non-use of pesticides supports animal welfare, biodiversity

Table 2: A summary of the results.

	Organic (n=27)	Conventional (n=27)
No. of samples containing detectable residues	15	17
No. of total residues (>LOQ)	29 (1)	43 (13)
Concentration range of residues quantified	11.13 ng/g	9.84-154.07 ng/g

and soil health [14]. Studies have also noted the prevalence of other contaminants, in particular natural contaminants such as mycotoxins and pathogenic bacteria in organic foods and these should be taken in to consideration in any comparison of the safety of these two types of food propagation [4,7]. Pussemier L, et al. [7] states that natural toxicants need to be better identified in organic production and studies by Oliveira M, et al. [15] and Weißner et al. [16] have measured higher levels, albeit safe levels, of pathogenic bacteria in organic foods [7,15,16].

Conclusion

A similar number of organic (15) and conventional (17) samples tested positive for detectable residues, however the number of residues detected was higher in conventional (43) than in organic (29), and the concentration of these residues were significantly higher. This result is in agreement with the previous study by Gonzalez M, et al. [6]. Table 2 summarises the results of the study.

The study concludes that both organic and conventional fruits and vegetables purchased from Irish supermarkets may contain pesticide residues and it cannot be said that organic products are void of these compounds because they are not physically applied in organic agricultural practices. However the level of exposure to these compounds from organic products may be significantly

lower. But does this form a particular advantage from a health perspective given that none of the pesticides measured were above, or close to the MRL's applied under EU regulation? And hence are organic fruits and vegetables truly distinguishable from conventional products in terms of the presence of pesticides when comparing the final food product?

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