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INTRODUCTION

PERVEMAC II is a cooperative research and development project granted by the European Union, which was built on the results of the previous project, PERVEMAC, which developed an unprecedented and extensive program of pesticide and mycotoxin residue monitoring in fruits, vegetables and cereals consumed in the Macaronesian archipelagos. PERVEMAC II continues the monitoring program two more years, from July 2017 through June 2019. Sampling of vegetal products is being carried out taking into account the pattern of annual vegetal consumption in each region, and the number of samples per year was decided on the basis of the number of inhabitants in each region: one vegetal sample per 2500 inhabitants and year for Cape Verde. In the present effort we show the results for the first stage, six months (July through December 2017), of the monitoring program developed in Cape Verde, reaching a total of 103 samples for the first semester of sampling, corresponding to 22 different commodities: tomato (27 samples) has been the most sampled product in 2017, paying special attention due to the new pests reaching this crop in Cape Verde; carrots (8), cabbages (10), pepper, orange, apple (6 each), papaya, cucumber (5 each), banana (4) were the most sampled ones, adding 26 more samples for 14 additional commodities. The origin of the 103 samples is mostly from local agriculture, 78 samples, adding 25 samples for imported items: apple (6), citrus fruits (8), kiwi (2), pear (2), watermelon (1), plum (1), grapes (3), pepper (1) and carrot (1). For imported products the 92% has been fruits (23/25).

EXPERIMENTAL

The analysis of pesticides has been carried out using Quechers (AOAC method, acetate buffered) followed by GCMSMS and LCMSMS determination (MRM), addressing 95 and 57 different pesticides respectively. The dithiocarbamate residues were analyzed using the single residue method (SRM) based upon carbon disulfide determination.

RESULTS AND DISCUSSION

The pesticide residues results show clear differences between local vs imported products, with a significant lower content of pesticide residues in the local products regarding the import products. In Cape Verde the import of plant food is mainly fruit (23/25 92%), however, the consumption of fruits is balanced local/imported, finding great differences among those fruits produced locally: banana, papaya, mango and those imported: apple, pear, orange, kiwi, watermelon. In Cape Verde we also find other fruits produced locally in small quantities: strawberry, orange. For vegetables the case scenario is different, the vegetables mainly consumed are from local origin. The origin of imported fruits is mainly Europe, finding some cases where it is not possible to identify origin.

A total of 117 pesticide residues have been detected in the 103 samples of fruits and vegetables analyzed in this work, with a ratio of 1,14 residues per sample. If we distinguish between local agriculture and import, we find 35 pesticide residues for 78 samples of local origin and 82 pesticide residues for 25 imported samples, with a ratio of 0,45 and 3,28 residues per sample, respectively: imported fruits and vegetables have 7,3 times more pesticide residues than local ones.

MRL violations have been found in 5 different samples: cucumber (*chlorpyrifos + dimethoate + omethoate*) tomato (2 samples, with *chlorpyrifos* both) from local origin and lemon (*oxamyl*) watermelon (*dimethoate + omethoate*) imported. All the MRL violations found correspond to traditionally broadly known pesticides.

Dithiocarbamates: CS₂ method

- 4 g homogenized sample + HCl + SnCl₂·2H₂O + 4 mL iso-octane. 1:1 (w/v)
- Sonication (10 min), Heating (90°C, 90 min), cooling (room temperature, 30 min), sonication (5 min) and Cooling (4°C, 60 min).
- Injection of a 1 µL aliquot of the organic layer into the GC system.

GC-PFPD

- Instrument:** Varian 3800 and a Varian 8400 autosampler.
- Column:** Varian CP Sil-5 CB for sulfur (30 m x 0.32 mm, 4 µm).
- Injection:** Varian 1079 PTV, 220°C.
- Column Oven:** 45°C held for 2 min, 40°C/min ramp to 281°C for 2.1 min. Total time: 12 min.
- Detection:** PFPD (sulphur optical filter), 200°C.

LC-MS/MS

- Instrument:** Varian 320 MS QQQ, 2 Varian 212-LC pumps and a Varian 410 autosampler (10 µL loop).
- Column:** ACE 3 C₁₈-AR (100 x 2.1 mm, 3 µm), 40 °C
- Mobile phases:** 5 mM ammonium formate / 0.2% formic acid (A). Methanol : Mobile phase A, 90:10, v/v (B).
- ESI-MS detection:** Ion spray voltage 5000 V, source and desolvation temperatures, 42°C and 200°C, nebulizing and drying pressures (N₂), 65 psi and 35 psi.

GC-MS/MS

- Instrument:** Varian 3800 coupled to a Varian 4000 Ion Trap MS/MS and a Varian 8400 autosampler.
- Column:** SGE BPX-5, 30 m x 0.25 mm, 0.25 µm. 70°C held for 3.5 min, 25°C/min ramp to 180°C for 10 min, 4°C/min ramp to 300°C for 10 min. Total time: 57.90 min.
- Injection:** Varian 1079 PTV. 70°C held for 3.5 min, 100°C/min ramp to 300°C for 10 min. Total time: 12.80 min.
- Detection:** Transfer-line, manifold and trap temperatures, 280°C, 50°C and 220°C.

Table 1. List of pesticides analyzed

Pesticide analytes	LQ	Analytical Method
Abamectin	0.01	LCMSMS
Acetamiprid	0.01	GCMSMS
Acrinathrin	0.02	GCMSMS
Azoxystrobin	0.01	LCMSMS
Benalaxyl	0.01	GCMSMS
Bifenthrin	0.01	GCMSMS
Bitertanol	0.01	LCMSMS
Boscalid	0.01	GCMSMS
Bromopropylate	0.01	GCMSMS
Bromconazole	0.01	GCMSMS
Bupirimate	0.01	GCMSMS
Buprofezin	0.01	GCMSMS
Cadusafos	0.01	GCMSMS
Carbaryl	0.01	LCMSMS
Carbendazim	0.01	GCMSMS
Carbofuran	0.01	LCMSMS
Carbofuran 3-OH	0.01	LCMSMS
Chlorpyrifos	0.01	GCMSMS
Chlorpyrifos-methyl	0.01	GCMSMS
Cyfluthrin	0.01	GCMSMS
Chlortal-dimethyl	0.01	GCMSMS
Cimoxanilo	0.01	LCMSMS
Clofentezine	0.01	LCMSMS
Clorantprilprole	0.01	LCMSMS
Clorfenapyr	0.01	GCMSMS
Chlorfenvinphos	0.01	GCMSMS
Cypermethrin	0.01	GCMSMS
Cyproconazole	0.01	GCMSMS
Cyprodinil	0.01	GCMSMS
Deltamethrin	0.02	GCMSMS
Diazinon	0.01	GCMSMS
Dicloran	0.01	GCMSMS
Diethofencarb	0.01	GCMSMS
Difenoconazole	0.01	GCMSMS
Diflubenzuron	0.01	LCMSMS
Diffufenican	0.01	GCMSMS
Dimethomorph	0.01	LCMSMS
Dimethoate	0.01	GCMSMS
Dinocap	0.01	LCMSMS
Dithiocarbamates	0.05	SRM
Endosulfan sulphate	0.01	GCMSMS
Endosulfan- (alpha)	0.01	GCMSMS
Endosulfan- (beta)	0.01	GCMSMS
Epoxiconazole	0.01	LCMSMS
Ethion	0.01	GCMSMS
Ethofumesate	0.01	GCMSMS
Etofenprox	0.01	GCMSMS
Ethoprophos	0.01	GCMSMS
Etoazole	0.01	GCMSMS
Famoxadone	0.01	LCMSMS
Fenamidphos	0.01	GCMSMS
Fenarimol	0.01	GCMSMS
Fenbuconazole	0.01	GCMSMS
Fenbutatin oxide	0.01	LCMSMS
Fenhexamid	0.01	LCMSMS
Fenitrothion	0.01	GCMSMS
Fenoxycarb	0.01	LCMSMS
Fenpropathrin	0.01	GCMSMS
Fenpyroximate	0.01	LCMSMS
Fenthion	0.01	GCMSMS
Fenvalerate (Esfenvalerate)	0.01	GCMSMS
Fipronil	0.01	GCMSMS
Flubendiamide	0.01	LCMSMS
Flucythrinate	0.01	GCMSMS
Fludioxonil	0.01	GCMSMS
Flufenoxuron	0.01	LCMSMS
Flusilazole	0.01	LCMSMS
Flutolanil	0.01	LCMSMS
Flutriafol	0.01	LCMSMS
Fonophos	0.01	GCMSMS
Fosthiazate	0.01	GCMSMS
Hexaflumuron	0.01	LCMSMS
Hexythiazox	0.01	LCMSMS
Imazalil	0.01	LCMSMS
Imidacloprid	0.01	LCMSMS
Indoxacarb	0.02	GCMSMS
Iprodione	0.01	GCMSMS
Iprovalicarb	0.01	LCMSMS
Isocarbofos	0.01	GCMSMS
Isofenphos-methyl	0.01	GCMSMS
Kresoxim-methyl	0.01	GCMSMS
lambda-Cyhalothrin	0.01	GCMSMS
Lindane	0.01	GCMSMS
Linuron	0.01	LCMSMS
Lufenuron	0.01	LCMSMS
Malathion	0.01	GCMSMS
Mepanipyrim	0.01	LCMSMS
Metaflumizone	0.01	LCMSMS
Metalaxyl	0.01	GCMSMS
Metconazole	0.01	LCMSMS
Methomyl	0.01	LCMSMS
Methidathion	0.01	GCMSMS
Methoxyfenozida	0.01	LCMSMS
Metrafenone	0.01	GCMSMS
Mevinphos	0.01	GCMSMS
Myclobutanil	0.01	GCMSMS
Nitroimidazole	0.01	LCMSMS
Nuarimol	0.01	GCMSMS
Ofurace	0.01	GCMSMS
Ometoate	0.02	GCMSMS
Oxadixyl	0.01	GCMSMS
Oxamyl	0.01	LCMSMS
Oxyfluorfen	0.01	GCMSMS
Penconazol	0.01	GCMSMS
Pencycuron	0.01	LCMSMS
Pendimethalin	0.01	GCMSMS
Permethrin	0.01	GCMSMS
Phosalone	0.02	GCMSMS
Piridafention	0.01	GCMSMS
Pirimicarb	0.01	GCMSMS
Pirimiphos-ethyl	0.01	GCMSMS
Pirimiphos-methyl	0.01	GCMSMS
Prochloraz	0.01	LCMSMS
Procyridione	0.02	GCMSMS
Propiconazole	0.01	GCMSMS
Propoxur	0.01	LCMSMS
Propylamine	0.01	GCMSMS
Proquinazid	0.01	GCMSMS
Pyraclostrobrina	0.01	LCMSMS
Pyrazofos	0.01	GCMSMS
Pyridaben	0.01	GCMSMS
Pyrimethanil	0.01	GCMSMS
Pyriproxifen	0.01	GCMSMS
Quinalphos	0.01	GCMSMS
Quinometionato	0.01	GCMSMS
Quinoxifen	0.01	GCMSMS
Spinosad	0.01	LCMSMS
Spirodiclofen	0.01	GCMSMS
Spiromesifen	0.01	GCMSMS
Spirotetramat	0.01	LCMSMS
Spiroxamine	0.01	LCMSMS
Tau-fluvalinate	0.01	GCMSMS
Tebuconazole	0.01	GCMSMS
Tebufenozide	0.01	LCMSMS
Tebufenpyrad	0.01	GCMSMS
Teflubenzuron	0.01	LCMSMS
Terbutylazine	0.01	GCMSMS
Tetraclorinfos	0.01	GCMSMS
Tetraconazole	0.01	GCMSMS
Tetradifon	0.01	GCMSMS
Thiabendazol	0.01	LCMSMS
Thiacloprid	0.01	LCMSMS
Thiamethoxam	0.01	LCMSMS
Thiodicarb	0.01	LCMSMS
Thiophanate-methyl	0.01	LCMSMS
Tolclofos-methyl	0.01	GCMSMS
Triadimefop	0.01	GCMSMS
Triadimenol	0.02	GCMSMS
Triazofos	0.01	GCMSMS
Trifloxystrobin	0.01	LCMSMS
Triticonazole	0.01	LCMSMS
Vindozolina	0.01	GCMSMS



Table 2. Results for imported products

	samples	with residues	residues	% samples w/res	residues/sample
Plum	1				
Kiwi	2	1	1	50%	0,50
Lemon	1	1	4	100%	4,00
Tangerine	2	2	6	100%	3,00
Apple	6	6	22	100%	3,67
Orange	5	5	19	100%	3,80
Pear	2	2	6	100%	3,00
Pepper	1				
Watermelon	1	1	3	100%	3,00
Grape	3	3	21	100%	7,00
Carrot	1				
	25	21	82	84%	3,28



Table 3. Results for local products

	samples	with residues	residues	% samples w/res	residues/sample
Zuchini	3	1	1	33%	0,33
Coriander	1				
Strawberry	1				
Lettuce	2				
Lemon	2				
Mango	3				
Orange	1				
Papaya	5				
Cucumber	5	1	3	20%	0,60
Celery	2				
Pepper	5	4	8	80%	1,60
Banana	4				
Cabbage	10	1	1	10%	0,10
Tomato	27	14	21	52%	0,78
Carrot	7	1	1	14%	0,14
	78	22	35	28%	0,45

Table 4. Pesticide identified in the 103 samples analyzed

Pesticides in local samples	Pesticides in imported samples		
Boscalida	Acetamiprid	Espiroxamina	Oxamyl
Cipermetrina	Boscalida	Etofenprox	Penconazol
Clorpirifos	Cipermetrina	Etoaxol	Piraclostrobrina
Cresoxim-metilo	Ciprodinilo	Fempropatrina	Pirimetanil
Deltametrin	Clorantranilprole	Fludioxonil	Piriproxifen
Dimetoato	Clorpirifos	Imazalil	Propiconazol
Dinocap	Difenoconazol	Imidacloprid	Tebuconazol
Ditiocarbamatos	Dimetoato	Iprodiona	Tebufenpirad
Imidacloprid	Dimetomorfo	Lambda-cihalotrina	Tiabendazol
Lambda-cihalotrina	Ditiocarbamatos	Metrafenona	Tiacloprid
Ometoato	Espirodiclofeno	Miclobutanil	Trifloxystrobrina
Tebuconazol	Espirotramat	Ometoato	

Table 5. MRLs violations

Commodity	Pesticide	Value	MRL	ratio	Origin
Cucumber	Chlorpyrifos	0,11	0,01	11	local
	Dimethoate	0,02	0,01	2	local
	Omethoate	0,02	0,01	2	local
Lemon	Oxamyl	0,07	0,01	7	Import
Tomato	Chlorpyrifos	0,02	0,01	2	local
Tomato	Chlorpyrifos	0,03	0,01	3	local
Watermelon	Dimethoate	0,02	0,01	2	Import
	Omethoate	0,02	0,01	2	Import

