Pesticide residues in fruits and vegetables from the Macaronesia (PERVEMAC II): Cape Verde, 2018-2019

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ABSTRACT

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 for 30 more months, from July 2017 through December 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 approached on the basis of the number of inhabitants in each region: one vegetal sample per 2500 habitants and year for Cape Verde. In the present effort we show the results for the years 2018 and 2019, 24 months: from January 2018 through December 2019, of the monitoring program developed in Cape Verde, reaching a total of 419 samples for this period, 216 samples in 2018 and 203 samples in 2019. The 81% of the samples (339: 172+167) are from local origin and the 19% are from import (80: 44+36). Paying attention to the origin and nature of the samples, we observe that within the products of local origin 287 (85%) samples are vegetables and 52 (15%) are fruits, while among the products of import 75 samples (94%) are fruits and only 5 samples (6%) are vegetables. Analysis of pesticide residues have been performed on all samples using acetic/acetate Quechers for MRM methods followed by GCMSMS (QQQ) and one SRM for the determination of dithiocarbamate fungicides residues, expressed as carbon disulphide (CS_2). For samples from local origin the pesticide residues found per sample has been more than five times lower than residues in the imported samples. The pesticide residues found in samples of local origin are mostly insecticides, identifying those most relevant ones as a potential hazard for the consumers in Chlorpyrifos, Fenitothrion and Dimethoate + Omethoate. A risk evaluation based upon the EFSA PRIMo (Pesticide Residue Intake Model) has been carried out for the identified hazards.

Dithiocarbamates: CS_2 method

- 4 g homogenized sample + HCl + $SnCl_2 \cdot 2H_2O$ + 4 mL iso-octane. 1:1 (w/v)
- Sonication (10 min), Heating (90ºC, 90 min), cooling (room temperature, 30 min), sonication (5 min) and Cooling (4ºC, 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, 220ºC.
- **Column Oven:** 45ºC held for 2 min, 40ºC/min ramp to 281ºC for 2.1 min. Total time: 12 min.
- **Detection:** PFPD (sulphur optical filter), 200ºC.

GC-MS/MS

- **Instrument:** Agilent 7890BGC couple to Agilent 7000D Triple Quad MS/MS with Agilent autosampler 7693A
- **Column**: 2x HP-5ms, 15 m x 0,25 mm ID, 0,25 µm, coupled with valve for Backflush operation; Colum oven program: 60ºC held for 1.0 min, 40ºC/min to 170ºC follow by 10ºC/min to 310ºC for 3min. Backflush 5 min, 50 psi.
- **Injection**: Agilent ultrainert split/splitless injector; 2 µl injection, 280ºC
- **Detection**: Transfer-line 280ºC, Ion source 280ºC and MS-Quad 150ºC

List of pesticides analyzed

Pesticide analytes	LQ	Pesticide analytes	LQ	Pesticide analytes	LQ
Acrinathrin	0,01	Fenamidone	0,01	Paclobutrazol	0,01
Azoxystrobin	0,01	Fenamiphos	0,01	Parathion-ethyl	0,01
Benalaxyl	0,01	Fenarimol	0,01	Parathion-methyl	0,01
Bifenthrin	0,01	Fenazaquin	0,01	Penconazol	0,01
Bitertanol	0,01	Fenbuconazol	0,01	Pendimethalin	0,01
Boscalid	0,01	Fenitrothion	0,01	Permethrin	0,01
Bromopropylate	0,01	Fenpropathrin	0,01	Phosalone	0,01
Bromuconazole	0,01	Fenpropidin	0,01	Phosmet	0,01
Bupirimate	0,01	Fenpropimorph	0,01	Pirimicarb	0,01
Buprofezin	0,01	Fenthion	0,01	Pirimiphos-ethyl	0,01
Cadusafos	0,01	Fenvalerate+Esfenvalerate	0,01	Pirimiphos-methyl	0,01
Carbaryl	0,01	Fipronil	0,01	Pyridafention	0,01
Carbofuran	0,01	Flucythrinate	0,01	Prochloraz	0,01
Chlorfenapyr	0,01	Fludioxonil	0,01	Procymidone	0,01
Chlorfenvinphos	0,01	Fluopyram	0,01	Profenofos	0,01
Chlorobenzilate	0,01	Fluquinconazole	0,01	Propargite	0,01
Chlorpropham	0,01	Flusilazole	0,01	Propiconazole	0,01
Chlorpyrifos	0,01	Flutolanil	0,01	Propyzamide	0,01
Chlorpyrifos-methyl	0,01	Flutriafol	0,01	Proquinazid	0,01
Chlortal-dimethyl	0,01	Fluvalinate-tau	0,01	Prothiofos	0,01
Cyflufenamid	0,01	Fonofos	0,01	Pyraclostrobina	0,01
Cyfluthrin	0,01	Fosthiazate	0,01	Pyrazofos	0,01
Cypermethrin	0,01	Hexaconazole	0,01	Pyridaben	0,01
Cyproconazole	0,01	Hexythiazox	0,01	Pyrimethanil	0,01
Cyprodinil	0,01	Imazalil	0,01	Pyriproxyfen	0,01
Deltamethrin	0,01	Indoxacarb	0,01	Quinalphos	0,01
Diazinon	0,01	Iprodione	0,01	Quinoxifen	0,01
Dicloran	0,01	Iprovalicarb	0,01	Spirodiclofen	0,01
Dichlorvos	0,01	Isocarbophos	0,01	Spiromesifen	0,01
Diethofencarb	0,01	Isofenphos-methyl	0,01	Spiroxamine	0,01
Difenoconazole	0,01	Isoprothiolane	0,01	Tebuconazole	0,01
Diflufenican	0,01	Kresoxim-methyl	0,01	Tebufenpyrad	0,01
Dimethoate	0,01	Lambda-Cyhalothrin	0,01	Tefluthrin	0,01
Dimethomorph	0,01	Lindane	0,01	Terbuthylazine	0,01
Diniconazole	0,01	Malathion	0,01	Tetraclorvinfos	0,01
Diphenylamine	0,01	Mepanipyrim	0,01	Tetraconazole	0,01
Endosulfan- (alpha)	0,01	Metalaxyl	0,01	Tetradifon	0,01
Endosulfan sulphate	0,01	Methidathion	0,01	Tetramethrin	0,01
Endosulfan-(beta)	0,01	Metrafenone	0,01	Thiabendazol	0,01
EPN	0,01	Mevinphos	0,01	Thiamethoxam	0,01
Epoxiconazole	0,01	Monocrotophos	0,01	Tolclofos-methyl	0,01
Ethion	0,01	Myclobutanil	0,01	Triadimefon	0,01
Ethofumesate	0,01	Nuarimol	0,01	Triazophos	0,01
Ethoprofos	0,01	Ofurace	0,01	Trifloxistrobin	0,01
Etofenprox	0,01	Omethoate	0,01	Trifluralin	0,01
Etoxazole	0,01	Oxadixyl	0,01	Vinclozolina	0,01
Famoxadone	0,01	Oxyfluorfen	0,01	Zoxamide	0,01

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, 0,34 and 3,19 residues/sample respectively: 9,9 times more in import samples than in local samples. The pattern of the presence of pesticide residues in local samples compared to imported ones does not vary between the two years of sampling: 2018 and 2019. A total a 10 different pesticides were found in local samples in 2018 and 11 in 2019 respectively. In the import samples the total of different pesticides found were 28 and 31 respectively in 2018 and 2019. As it is shown in the Table 2 the pesticides residue findings in import samples are 82% fungicides and 18% insecticides. The same pattern is found in the import samples in 2018 with a ratio 80/20. In the other hand, the pesticide residues findings in the local samples show a 68% residues of insecticides and a 32% of fungicide residues. Following the same trend the ratio is the same in 2018.

Taking into account the MRLs established in Regulation 396/2005 in Europe, we did not find significant violations in imported products, while they were detected in local products. A risk assessment has been carried out for the residues found in local samples using the EFSA PRIMo Model, finding several risk cases for chronic intake of vegetables with Chlorpyrifos residues in 2018 and Dimethoate and Ometoate residues in 2018 and 2019. Chlorpyrifos residues were frequently found in 2018 and not in 2019 in local samples. As the differences in Cape Verde's diet are considerable with respect to Europe, we have made a risk estimate based upon the minimum intake need to reach levels of food risk in Cape Verde. Significant risk for Chlorpyrifos in 2018 for acute and chronic ingest and for Dimethoate and Omethoate in 2019 has been identified. Is strongly recommended to avoid this risk to reduce or eliminate the use Dimethoate in Cape Verde Agriculture.

Table 2. Summary of Results

2018	TOTAL	LOCAL	IMPORT
Total samples	216	172	44
Samples with res.	67	29	38
Samples w/o res.	149	143	6
% w/o res.	69%	83%	14%
Total residues	172	51	121
residues/sample	0,80	0,30	2,75

2019	TOTAL	LOCAL	IMPORT
Total samples	203	167	36
Samples with res.	78	45	33
Samples w/o res.	125	122	3
% w/o res.	62%	73%	8%
Total residues	197	63	134
residues/sample	0,97	0,38	3,72

2018+2019	TOTAL	LOCAL	IMPORT
Total samples	419	339	80
Samples with res.	145	74	71
Samples w/o res.	274	265	9
% w/o res.	65%	78%	11%
Total residues	369	114	255
residues/sample	0,88	0,34	3,19

Table 3. Max concentration for each one of the 31 different pesticides found in import products in 2019 monitoring. This Table shows the total number of findings for each pesticide and the producto with max conc.

Product	Pesticide	Highest	Findings
Tangerine	Azoxistrobina	0,54	2
Grape	Boscalida	0,32	10
Apple	Ciflutrin	0,012	1
Pear	Cipermetrina	0,077	1
Tangerine	Clorpirifos	0,010	1
Orange	Clorpirifos-metilo	0,050	2
Pear	Cresoxim-metilo	0,023	3
Orange	Deltametrin	0,080	7
Pear	Difenoconazol	0,016	2
Watermelon	Dimetoato	0,042	1
Pear	Ditiocarbamatos	0,56	8
Orange	Etofenprox	0,22	1
Tangerine	Etoxazol	0,021	1
Grape	Fenhexamida	0,68	1
Orange	Fludioxonilo	0,59	10
Pear	Fluopiram	0,045	5
Tangerine	Imazalil	2,3	15
Pear	Iprodiona	0,040	2
Apple	Lambda-cihalotrina	0,018	2
Grape	Metrafenona	0,024	1
Grape	Miclobutanil	0,045	1
Watermelon	Ometoato	0,041	1
Pear	Piraclostrobina	0,047	8
Tangerine	Piridaben	0,076	1
Pear	Pirimetanil	3,6	10
Pear	Piriproxifen	0,084	4
Tangerine	Propiconazol	0,85	6
Pear	Tebuconazol	0,047	10
Apple	Tetradifon	0,010	1
Apple	Tiabendazol	2,1	9
Pear	Trifloxistrobina	0,042	7

Table 4. List of pestices found in 2019 monitoring in local samples. This table shows the max concentration found, the total number of findings in local samples and the products with the max. Conc. A risk evaluation has been carried out using an estimation of the minimum intake need to reach risk levels.

	Product	Pesticide	Highest	Findings	ARDF (mg/kg bw)	ADI (mg/kg bw x day)	Acute (mg/kg bw)	Chronic (mg/kg bw x day)
2019	Tomato	Cypermethrin	0,078	2	0,2	0,05	154	38
	Pepper	Chlorpyrifos-methyl	0,056	3	0,1	0,01	107	11
	Grape	Kresoxim-methyl	0,085	2	N/A	0,4		282
	Coriander	Deltametrin	0,48	23	0,01	0,01	1,3	1,3
	Zuchini	**Dimethoate**	0,31	7	0,02	0,002	**4**	**0,39**
	Pepper	Ditiocarbamates	0,474	10	0,6	0,05	76	6,3
	Coriander	Fenitrothion	0,020	2	0,013	0,005	39	15
	Zuchini	**Omethoate**	0,067	6	0,002	0,0003	**2**	**0,27**
	Pepper	Tebuconazol	0,61	5	0,03	0,03	3,0	3,0
	Pepper	Tetraconazol	0,11	3	0,05	0,004	27	2,2

Table 5. Risk evaluation carried out using an estimation of the minimum intake need to reach risk levels in adults in Cape Verde

	Product	Pesticide	Highest	Findings	ARDF (mg/kg bw)	ADI (mg/kg bw x day)	Acute (mg/kg bw)	Chronic (mg/kg bw x day)
2018	**Carrot**	**Clorpirifos**	0,56	11	0,005	0,001	**0,5**	**0,11**
	Pepper	Deltametrin	0,21	17	0,01	0,01	2,9	2,86
	Pumpkin	**Dimetoato**	0,16	6	0,02	0,002	7,5	**0,75**
	Cabbage	Fenitrotion	0,12	2	0,013	0,005	6,5	2,50
	Pumpkin	**Ometoato**	0,16	5	0,002	0,0003	**0,8**	**0,11**

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