Effects of cleaning procedures on the concentration of pesticide residues on crisp fresh-cut lettuce (cv. Vera)

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Introduction

Consumption of ready-to-eat vegetables has increased due to new trends in diet and lifestyle, thus having an impact on both commercial and domestic environments. Pesticide usage during large-scale production of fruits and vegetables can be problematic as it´s presence, though useful for preventing plagues and diseases, should be closely monitored along the whole process to ensure the safety of the product. Each part of the process needs to be taken into consideration, particularly the post-harvest stages[1,2]. Non-thermic treatments, like ultrasound baths, are being used as an alternative for disinfection which have the potential to lower pesticide residues. Ultrasound in particular is a safe, non-toxic and clean technology that allows for scaling and continuous design, therefore it is already being used at industrial level.[3] On the other hand, there are "domestic" types of cleaning procedures, considered safe and non-toxic, that are not to be forgotten, and also can be attached to industrial scale processes.

Objective

The aim of this work was to test and compare the effectiveness of different cleaning procedures to reduce pesticide residues on crisp fresh-cut lettuce.

Methodology

Field experiment

Incurred samples: Two groups of crisp lettuce were cultivated under controlled conditions for 54 days in a greenhouse with daily watering. Group A consisted of 6 lettuces while group B consisted of 64 plants.

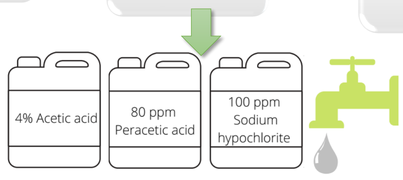
Pesticide application:
Group A: without pesticide application (**control**).
Group B: Pesticide application according to Good Agricultural Practices.[4]

Selected Pesticides: Chlorpyrifos methyl, Pirimicarb, Imidacloprid, Boscalid, Pyraclostrobin.

Treatments

Cut lettuce into ribbons → US treatment at 25, 37, 45 & 80 kHz for 10 and 15 min → Remove excess water and freeze

Separate the leaves from 4 lettuces → Submerge in cleaning solutions for 10 minutes → Wash under running water (20 sec), remove excess water and freeze.



HPLC-MS/MS

Comercial samples

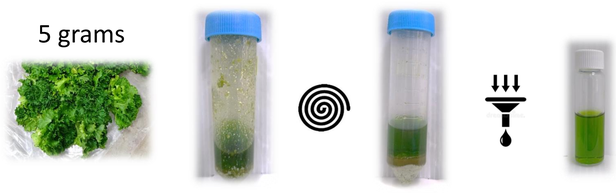
22 commercial lettuces were acquired from different shops in Paysandú to evaluate pesticide residues level by HPLC-MS/MS.

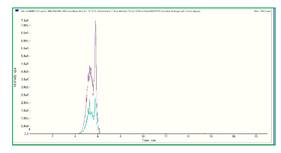
Sample processing

The samples were cut in pieces and then milled with liquid nitrogen and kept frozen until analysis

Pesticide extraction (acetate QuEChERS)

5 grams





Results and Discussion

A QuEChERS method was developed and validated for the analysis of 16 pesticides widely used in lettuce crops

Pesticide	10 µg/kg		25 µg/kg		50 µg/kg	
	RSD	%Rec	RSD	%Rec	RSD	%Rec
Acetamiprid	1	87	3	96	2	98
Boscalid	10	92	9	90	2	108
Carbendazim	--	--	3	82	4	83
Chlorpyrifos	5	112	5	100	3	100
Cyromazine	4	94	1	88	1	85
Chlorpyrifos methyl	--	--	8	92	14	117
Dimethoate	3	97	1	97	1	98
Fluvalinate	20	93	17	96	15	101
Imidacloprid	11	97	4	94	8	94
Iprodione	---	---	---	---	8	91
Methomyl	4	104	2	96	3	96
Pirimicarb	2	101	2	96	1	96
Propamocarb	2	95	2	91	2	90
Pyraclostrobin	--	--	3	117	4	109
Pyrimethanil	7	95	7	96	4	99
Spinosad	2	102	3	100	3	101

Table 1: Standard deviation and recovery percentages for all pesticides.

Most pesticides presented a quantitation limit of 10 µg/kg, except for Carbendazim, Chlorpyrifos Methyl and Pyraclostrobin 25 µg/kg and Iprodione 50 µg/kg.

Matrix effect was low (<20%) for most pesticides, except for Carbendazim, therefore this method can be used without the need of a matrix-matched calibration curve.

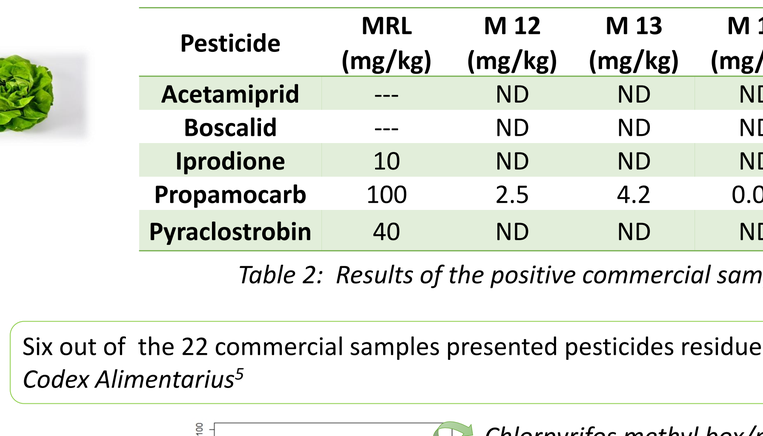
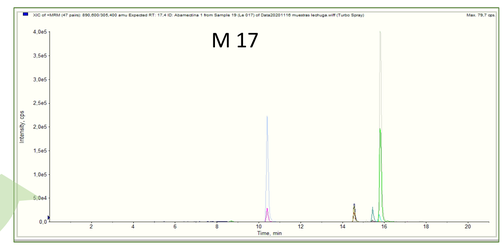


Image 1: Single hierarchical clustering for all processes

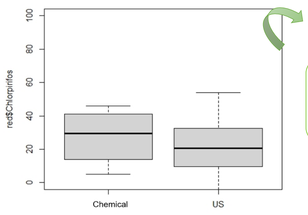
Pesticide	MRL (mg/kg)	M 12 (mg/kg)	M 13 (mg/kg)	M 14 (mg/kg)	M 16 (mg/kg)	M 17 (mg/kg)	M 18 (mg/kg)
Acetamiprid	---	ND	ND	ND	0.12	0.41	ND
Boscalid	---	ND	ND	ND	0.32	0.99	ND
Iprodione	10	ND	ND	ND	0.05	0.13	ND
Propamocarb	100	2.5	4.2	0.03	ND	ND	10
Pyraclostrobin	40	ND	ND	ND	0.125	0.31	ND

Table 2: Results of the positive commercial samples.

Total ion chromatogram obtained through HPLC-MS/MS from a sample.

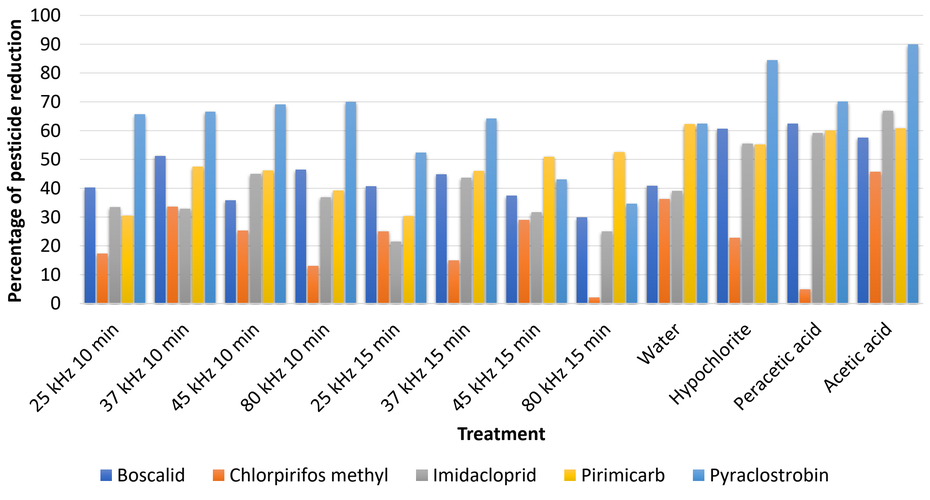


Six out of the 22 commercial samples presented pesticides residues over the LOQ, but all of them were under the MRLs according to de *Codex Alimentarius*[5]



Chlorpyrifos methyl box/plot diagram for domestic and ultrasound treatments.

ANAVA test Pillai-Bartlett with alfa 0.05.
The obtained p/value was 0.28, therefore, no significant differences were found.



Graphic 1: Pesticide residue reduction for each treatment

Conclusions and future work

- A fit for purpose methodology for the determination of pesticides residues in lettuce was developed and validated.
- The applicability of the method was tested in the analysis of 22 commercial samples, where seven showed pesticide residues
- No differences were found between the ultrasound treatments at the selected frequencies and times nor between them and the domestic treatments.
- All treatments managed to reduce pesticide residues, with chlorpyrifos methyl being the most resilient.

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References

(1) Arienzo, M., Cataldo, D., & Ferrara, L. (2013). Pesticide residues in fresh-cut vegetables from integrated pest management by ultra performance liquid chromatography coupled to tandem mass spectrometry. Food Control, 31(1), 108–115.
(2) Sannino, A., Bolzoni, L., & Bandini, M. (2004). Application of liquid chromatography with electrospray tandem mass spectrometry to the determination of a new generation of pesticides in processed fruits and vegetables, Journal of Chromatography A 1036, 161–169.
(3) Khandpur, P., & Gogate, P. R. (2015). Effect of novel ultrasound based processing on the nutrition quality of different fruit and vegetable juices. Ultrasonics Sonochemistry, 27, 125–136.
(4) https://www.laguiasata.com
(5) Codex Alimentarius Commission, Codex Pesticides Residues in Food Online Database, Updated up to and including its 36th Session (July 2013),