

DISAPPEARANCE OF BOSCALID, PYRACLOSTROBIN, LUFENURON AND LAMBDA-CYHALOTHRIN ON THE EXPORTED GREEN BEANS AND SPRING ONION UNDER EGYPTIAN FIELD CONDITIONS

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Abstract

Dissipation rates and the PHI of boscalid, pyraclostrobin, lufenuron and lambda-cyhalothrin in green beans and spring onion under the Egyptian field conditions were studied. Field trials were carried out at Blue Nile farm (Egypt), one of the biggest exporting farms to Europe. The pesticides were sprayed in the recommended rates of application. Samples were collected in consecutive intervals at 0, 1, 3 and 7 days for green beans and at 0, 1, 3, 7, 10 and 14 days for spring onion.

Analytical methods were developed using Liquid Chromatography Mass Spectrometer LC/ESI-MS to determine pyraclostrobin and lufenuron residues and a GC-NPD method was developed to determine boscalid, and lambda cyhalothrin residues in both crops. The recovery of the investigated pesticides ranged from 73.0% to 104.2% for spring onion and green beans. The calibration curves linearity ranged from 0.02 to 1 mg kg⁻¹ (r^2 ranged from 0.983 to 0.999). The limits of quantitation (LOQs) for tested pesticides were 0.02 mg kg⁻¹ in both crops with Relative Standard Deviation (RSD) of 10.1% in repeatability and 12.3% in reproducibility.

The initial residues after treatment (time 0) in green beans were about 7 times lower than in spring onion. Pyraclostrobin in spring onion was the most degradable pesticides and half-life times ($t_{1/2}$) was 3.1. However, lufenuron in onion was the most stable pesticides ($t_{1/2}$) 9.8 days. The calculated PHIs (waiting period) in green beans were 0 days for boscalid, lambda cyhalothrin and lufenuron and 11 days for pyraclostrobin. In case of spring onion the PHIs were 11, 16, 10 and 28 days for boscalid, pyraclostrobin, lambda cyhalothrin and lufenuron respectively.

Keywords: Pyraclostrobin, boscalid, lufenuron, lambda cyhalothrin, green beans, spring onion, LC-MS, GC-NPD.

INTRODUCTION

Green beans and spring onion crops are one of the most profitable vegetables in Egypt. The export value of green beans and onion reached 9 million USD during 2005 (FAO 2009) and increasing yearly. Europe is the major market for Egyptian green beans and spring onion. Green beans and spring onion are susceptible to infestation by different key pests e.g. gray mold (*Botrytis cinerea*), powdery mildew

(*Phytophthora infestans*), Thrips (*Thrips tabaci*) and cotton leaf worm (*Spodoptera littoralis*). These pests could cause huge losses in the yield, in some cases this may reach a full demolish of hundreds of cultivated acres. Bellis (boscalid, pyraclostrobin), (Tomlin 2006) is the intensively used formulation to control gray mold and powdery mildew. Lambda cyhalothrin and lufenuron are the most frequently used pesticides to control caterpillars and thrips.

Analytical methods have been reported to determine the residues of lufenuron in Grapes (Miliadis et al. 1999) and in coconut (Silva et al 2008), pyraclostrobin in grapes (De Melo Abreu et al 2006). Some of these methods showed low recoveries or not developed with difficult matrices of green beans that contain high quantities of chlorophylls or spring onion which produces many interfering sulphur compounds. However, we developed a rapid and reliable analytical method for each compound to be used in such troublesome matrices.

Dissipation rate and Pre Harvest Interval (PHI) of the tested compounds were not studied in green beans and spring onion under the Egyptian conditions (Egyptian agricultural pesticides committee). In the present work, PHIs were calculated to comply with the MRL set by EU (EU- MRL database), as these crops are cultivated to be exported to EU. The aim of present work is to determine the degradation rates and PHIs of boscalid, pyraclostrobin, lambda cyhalothrin and lufenuron in green beans and spring onion under the Egyptian environmental conditions.

MATERIALS AND METHODS

Field trials

Field trials were carried out at Blue Nile Egypt farms, one of the biggest exporting farms to Europe. The experimental area was divided to plots, 64 square meters each. All agronomic practices were carried out under GLOBALGAP guidelines, to assure the required quality. A random block design was followed, with three replicates for each pesticide. The allocated plots were sprayed by the recommended rates of applications (Bellis 0.8 kg ha⁻¹, Match 0.75 L ha⁻¹, Karate 0.15 L ha⁻¹) using Matabi 20 litter Knapsack Sprayer (Agratech, Rossendale, Lancashire, United Kingdom). The used pesticides formulations were Bellis (25.2% of boscalid and 12.8% of pyraclostrobin), Match (5% of lufenuron) and Karate (9.5 % of lambda-cyhalothrin). Samples were collected at zero time (after 1 hour of application) and at 1, 3, 7 days for green beans and at 0, 1, 3, 7, 10 and 14 days for onion. Untreated samples of each crop were obtained to be used as a blank material. The average, maximum and minimum temperature degrees (25, 32.1 and 17.8 °C), relative humidity (50%), wind speed (16.3 km h⁻¹) and rain volume (0.4 mL) were obtained

from Egyptian meteorological authority during the experiment period. Samples were shipped frozen to Department of Toxicology, Cagliari University, Italy, for analysis.

Chemicals and materials

Methanol HPLC grade (Panreac, Barcelona, Spain), sodium chloride (Riedel-deHaën, Seelze, Germany), sodium sulfate anhydrous, ammonium acetate and formic acid, RS grade (Carlo Erba, Milano, Italy). Membrane filters (0.45 μ m) were purchased from Sigma-Aldrich, (Steinheim, Germany). Analytical standard of pyraclostrobin, boscalid and lufenuron were Obtained from Sigma-Aldrich, (Seelze, Germany) and lambda cyhalothrin from Dr. Ehrenstorfer (Augsburg, Germany). Standard stock solutions (1000 mg L⁻¹) were prepared in acetone for GC analysis and in methanol for LC-MS analysis. Working standard solutions were daily prepared by dilution with untreated green beans and spring onion extracts.

Gas Chromatography Nitrogenous-Phosphorus Detector GC/NPD

An HRGC Mega 5160 (Carlo Erba, Milan, Italy), equipped with Nitrogenous-Phosphorus Detector NPD-40, autosampler AS 550 (Fisons), split-splitless injector, and HP 3396 integrator (Hewlett-Packard, Avondale, PA), was used. The capillary column was an Rtx- XLB (30 m x 0.25 mm x 0.25 μ m, Restek International, Bellefonte, USA). The injector temperature was 240°C and the detector temperature was 300°C. The samples (2 μ L) were injected in the splitless mode (60 s) and, after 60 s, the split ratio was 1:20. The oven temperature was programmed as follows: 80°C (20°C min⁻¹) → 160 °C (50°C min⁻¹) → 250°C (10°C min⁻¹) → 300 °C and then held for 10 min. Helium was the carrier and make-up gas at 110 and 100 kPa, (1.8 mL min⁻¹ and 30 mL min⁻¹), respectively. Hydrogen and air were at 170 and 100 kPa, (25 mL min⁻¹ and 250 mL min⁻¹), respectively. Quantitative determination of boscalid and λ -cyhalothrin was performed by integrating the peak height of the GC-NPD chromatograms. Matrix-matched standards were prepared using untreated green beans and spring onion extracts.

Liquid Chromatography Mass Spectrometer (LC-MS)

Analysis was performed with an HPLC system (Shimadzu, Italy) equipped with an SPD 11 Avp DAD detector, an SIL 11AD vp auto injector and a LC 10AD binary pump coupled on line with a mass spectrometer LCMS-2010 (Shimadzu, Italy). The interface was an electrospray ionization (ESI) source. UV and MS data were acquired and processed using Shimadzu "LCMS solution" software. The injection volume was 20 μ L, and the flow rate was 0.4 mL min⁻¹. The ESI-MS interface was operated in the positive ion-mode for pyraclostrobin and negative ion-mode for lufenuron: ESI source probe 250 °C, CDL 250 °C, block at 200 °C, nitrogen as nebulizer gas at flow of 4.5 mL min⁻¹, probe voltage at 3 kV, scan was 100-600 amu. The SIM mode was used to

monitor the $[M+H]^+$ adducts m/z 388 for pyraclostrobin, and m/z 509 $[M-H]^-$ for lufenuron. Matrix-matched standards were prepared using untreated green beans and spring onion extracts. Chromatographic separation was performed on a 2 x 50 mm, i.d. 3 μ m particle size, C18 Pursuit column (Varian, USA). Mobile phase for pyraclostrobin was methanol and 0.1% aqueous formic acid as follow, starting from 50% methanol to 100% in 6 minutes and kept at 100% for two minutes. The column was equilibrated for 5 minutes at 50% of methanol before injection. For lufenuron, the mobile phase was methanol and 2 mM of ammonium acetate solution, the gradient started from 60% of methanol to 90% in 15 min and re-equilibrated for 5 min. Quantitative determination of pyraclostrobin and lufenuron was realized by integrating the peak area of the LC-MS chromatograms.

Extraction Procedure

Samples (Green beans pods and whole plant of spring onion) were homogenized using a blender (Malavasi, Italy). The samples was extracted according to Garau et al (2002), 5 g aliquot of homogenized beans or onion was weighed into a 40 mL screw-capped tube, 5 g of NaCl and 2.5 g of Na₂SO₄. 10 mL of acetone/petroleum ether (1/1, v/v) for boscalid and lambda cyhalothrin, and 20 mL for pyraclostrobin and lufenuron were added. The tubes were agitated for 15 min in a rotating shaker, the phases were allowed to separate, 1 mL of the organic layer was placed into a vial and subjected to GC injection. For LC, 1 ml of the organic layer was evaporated to dryness under a gentle nitrogen stream and then dissolved in 1 mL of methanol and filtered with a 0.45 μ m membrane filter before LC injection.

Recovery Assay

Untreated green beans and onion samples were spiked with the tested pesticides at three levels (0.1, 0.50, and 1 mg kg⁻¹) and extracted according to the above mentioned procedures. Each recovery experiment was carried out in four replicates.

Standard calibration curves

Matrixes matched calibration standards were prepared, in the concentrations of 0.02, 0.1, 0.5 and 1 mg kg⁻¹. Each concentration was injected under the previous chromatographic mentioned conditions. The peaks area or height was plotted against concentrations and the calibration curve for each fungicide was established.

RESULTS AND DISCUSSION

Analytical Method

Blank samples of green beans and spring onion did not show any interfering peak with the investigated pesticides, so no clean up was required. Linearity of standard curves ranged from 0.02 to 1 mg kg⁻¹ for all compounds (r^2 ranged from 0.983 to 0.999). The recovery for the analyzed pesticides ranged from 73.0% to 104.2% for spring onion and green beans Table 1. Precision and accuracy were determined ($n = 6$) in spring onion and green beans samples, the RSD were 10.1% in repeatability and 12.3% in reproducibility. The limits of quantitation (LOQs) were 0.02 mg kg⁻¹ for all pesticides in both crops

Table 1 - Recovery (% \pm SD) of pesticides in spring onion and green beans ($n = 4$)

Spiked levels (mg/kg)	Pyraclostrobin	Lufenuron	Boscalid	λ -Cyhalothrin
	Spring onion			
0.1	82.3 \pm 9.6	73.0 \pm 5.2	83.0 \pm 8.5	83.6 \pm 8.2
0.5	88.5 \pm 12.1	82.3 \pm 3.7	78.0 \pm 4.2	77.1 \pm 1.4
1.0	89.9 \pm 7.4	78.4 \pm 6.1	84.3 \pm 5.4	98.7 \pm 9.5
Green beans				
0.1	86.1 \pm 8.8	78.2 \pm 2.6	90.1 \pm 11.1	88.8 \pm 9.5
0.5	91.0 \pm 6.3	84.5 \pm 7.3	103.1 \pm 4.7	86.3 \pm 3.3
1.0	92.0 \pm 7.9	82.0 \pm 4.9	104.2 \pm 8.6	89.4 \pm 10.9

Residues Dissipation

The detected residues of the investigated pesticides at the consecutive intervals after treatment are shown in Table 2. Natural logarithms of the obtained residues were plotted against the time intervals and the degradation curves were established. The obtained curves showed pseudo first-order kinetics for all pesticides in spring onion and green beans Table 3.

Table 2 - Residues (mg/kg ± SD) and PHI of the investigated pesticides in green beans and spring onion after treatment

Pesticides	Spring onion		Green beans	
	Days after spraying	mg/kg ± SD (n=3)	Days after spraying	mg/kg ± SD (n=3)
Boscalid	0	1.76 ± 0.21	0	0.28 ± 0.11
	1	0.72 ± 0.03	1	0.24 ± 0.11
	3	0.82 ± 0.08	3	0.21 ± 0.02
	7	0.67 ± 0.22	7	0.11 ± 0.07
	10	0.63 ± 0.03		
	14	0.34 ± 0.09		
	PHI (days)	11		0
	MRL (mg/kg)	0.5		2.0
Pyraclostrobin	0	0.75 ± 0.04	0	0.09 ± 0.02
	1	0.30 ± 0.04	1	0.09 ± 0.00
	3	0.25 ± 0.03	3	0.10 ± 0.00
	7	0.18 ± 0.03	7	0.03 ± 0.01
	10	0.03 ± 0.02		
	14	0.03 ± 0.01		
	PHI (days)	16		11
	MRL (mg/kg)	0.02*		0.02*
Lufenuron	0	0.17 ± 0.06	0	ND
	1	0.12 ± 0.00	1	ND
	3	0.12 ± 0.03	3	ND
	7	0.11 ± 0.01	7	ND
	10	0.06 ± 0.01		
	14	0.06 ± 0.00		
	PHI (days)	28		0
	MRL (mg/kg)	0.02*		0.02*
Lambda-cyhalothrin	0	0.19 ± 0.21	0	0.06 ± 0.01
	1	0.13 ± 0.12	1	0.08 ± 0.00
	3	0.13 ± 0.05	3	0.07 ± 0.03
	7	0.06 ± 0.02	7	0.04 ± 0.01
	10	0.05 ± 0.01		
	14	ND*		
	PHI (days)	10		0
	MRL (mg/kg)	0.05		0.2

ND: not detected. (< LOQ)

* indicates lower limit of analytical determination

Table 3- t_{1/2} values, correlation coefficient (r²) and dissipation rate (k) obtained from the degradation curves of the investigated pesticides in spring onion and green beans.

Pesticides	Spring onion			Green beans		
	(r ²)	K	t _{1/2} (days)	(r ²)	K	t _{1/2} (days)
Boscalid	0.735	0.005	8.5	0.978	0.005	5.3
Pyraclostrobin	0.888	0.009	3.1	0.837	0.006	4.3
Lufenuron	0.805	0.003	9.8	-	-	-
λ-cyhalothrin	0.946	0.005	4.2	0.837	0.003	9.1

Boscalid and Pyraclostrobin

The ratio of boscalid to pyraclostrobin in the used formulation was 2 to1. The initial deposits of boscalid and pyraclostrobin in both crops were consistent with this ratio. The initial deposits of boscalid and pyraclostrobin were 1.76 and 0.75 mg kg⁻¹, in spring onion, respectively, 0.28, and 0.09 mg kg⁻¹ in green beans, respectively. The initial residues of boscalid and pyraclostrobin were about 7 times lower in green beans than in spring onion. This could be attributed to differences in plant morphology of both crops. Green bean leaves cover the pods from receiving most of the spraying solution thus reducing the initial deposit. This is not the case in spring onion which its leaves act as a cup-like structure which collecting most of the spaying solution.

Pyraclostrobin showed fast degradation rate in spring onion and green beans. The Half life time of pyraclostrobin was lower than boscalid in both crops. It showed (3.1 versus 8.5 days) and (4.3 versus 5.3 days) in spring onion and green beans, respectively. In contrast, the published work proved that azoxystrobin, which is belonging to the same group of pyraclostrobin (Strobilurins), showed relatively high persistence in different crops, $t_{1/2}$ = 15.2 days in vine (Cabras et al 1998), 15.2 days in grapes (Cabras and Angioni 2000) and 7.8 days in strawberry (Angioni et al 2004).

For spring onion, boscalid residues (0.34 mg kg⁻¹) were below the MRL (0.5 mg kg⁻¹) after 14 days of treatment, whilst pyraclostrobin residues (0.03 mg kg⁻¹) were still higher than the MRL (0.02 mg kg⁻¹). For green beans, the initial deposit of boscalid (0.28 mg kg⁻¹) were below the MRL (2mg kg⁻¹), whilst for pyraclostrobin residues (0.03 mg kg⁻¹) were also still higher than the MRL (0.02 mg kg⁻¹) after 7 days of treatment. The degradation curves of pyraclostrobin and boscalid were used to calculate PHI (waiting period) in both crops. The calculated PHIs in spring onion were 11 and 16 days for boscalid and pyraclostrobin, respectively. However, No PHI is needed for boscalid in green beans, as the initial deposit is lower than the MRL, while it reached 11 days for pyraclostrobin.

Lufenuron

In spring onion the initial deposit was 0.17 mg kg⁻¹ and showed a slow rate of disappearance (9.8 days) while in green beans, the residues in zero time and also the latter intervals were lower than the LOQ (0.02 mg kg⁻¹). Another portion of zero time green beans sample was extracted and analyzed. The final extract was concentrated to assure the found results. The discrepancy of initial deposits in tested crops is due to the differences in morphological features in both crops as mentioned above. Lufenuron residues (0.06 mg kg⁻¹) were higher than the MRL (0.02 mg kg⁻¹) after 14 days of spraying in spring onion. According to this study the calculated waiting period should be extended to 28 days.

Lambda- cyhalothrin

The initial deposits of λ -cyhalothrin in spring onion was 0.29 mg kg⁻¹ and disappeared with a half-life time of 4.2 days, while in green beans the initial deposit was 0.06 mg kg⁻¹ with a half-life time of 9.1 days. In spring onion the EU MRL is 0.05 mg kg⁻¹, this value was detected after 10 days of treatment. In green beans, the initial deposit was below the EU MRL (0.2 mg kg⁻¹). However, lambda- cyhalothrin showed different behavior in certain crops, $t_{1/2}$ in cauliflower was varied from (2.2-5.2 days) (Sharma and Awasthi 2002), (2.92-2.86 days) in okra Singh et al 2007) and (1.35-2.07 days) in brinjal Ahuja, et al (2006).

CONCLUSION

The investigated pesticides revealed different half lives ranged from 3.1 to 9.8 days. Although all pesticides in both crops were sprayed by the same application rates, the initial deposits were lower in green beans than in onion for all pesticides. This finding is attributed to differences in plant morphology of both crops. The authors recommend extending the PHI of lufenuron in spring onion to be 28 days instead of 14 days. Since boscalid's PHI value is very much lower than pyraclostrobin's in both crops, it is preferable to use both pesticides in separate formulations. As the PHI of lambda cyhalothrin is lower than lufenuron so we recommend using lambda cyhalothrin as a first option to control caterpillars and thrips in green beans and spring onion, respectively, especially, when the investigated crops are near to harvest time.

Still more research is required to obtain full information about the degradation rates and the PHI values of the pesticides used in the exporting farms under the Egyptian environmental conditions.

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اختفاء مبيدات بوسكاليد، بيراكلوستروبين، ليوفينيورون ولامبدا-سيهالوثرين في محاصيل الفاصوليا الخضراء والبصل الأخضر المصدرة تحت ظروف الحقل المصرية

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أجرى هذا البحث بغرض دراسة معدلات إختفاء مبيدات بوسكاليد وبيراكلوستروبين وليوفينيورون ولامبدا-سيهالوثرين في محاصيل الفاصوليا الخضراء والبصل الأخضر المصدرة الى دول الإتحاد الأوروبى، وذلك تحت ظروف الحقل المصرية. تستخدم المبيدات محل الدراسة على نطاق واسع فى المزارع التصديرية بغرض مكافحة العديد من الآفات الرئيسية التى تصيب كلا المحصولين، لاتوجد دراسات سابقة لتحديد معدلات انهيار هذه المبيدات على المحاصيل المختبرة تحت ظروف البيئة المصرية. أجريت للتجارب الحقلية بمنطقة السادات (طريق القاهرة الاسكندرية الصحراوى) بوحدة من مزارع التصدير إلى أوروبا، حيث تم رش المبيدات المختبرة بالمعدلات الموصى بها للتطبيق. جُمعت العينات بعد الرش على فترات متتالية وهى صفر و١ و٣ و٧ أيام للفاصوليا الخضراء وصفر و١ و٣ و٧ و١٠ و١٤ يوما للبصل الأخضر. تم شحن العينات بغرض التحليل إلى كلية الصيدلة جامعة كاليارى- إيطاليا.

تم تطوير طريقة معملية لتحليل متبقيات مبيدات بيراكلوستروبين وليوفينيورون باستخدام جهاز الكروماتوجرافى السائل على الأداء المزود بكاشف مطياف الكتلة، كما تم تطوير طريقة أخرى لتقدير متبقيات مبيد بوسكاليد ولامبدا-سيهالوثرين باستخدام جهاز الكروماتوجرافى الغازى المزود بكاشف النيتروجين والفسفور. تراوحت النسبة المئوية للاسترجاع بين ٧٣٪ إلى ١٠٤,٢٪ فى كلا من المحصولين. كما كان مدى الإستجابة الخطية للمنحنيات القياسية للمبيدات المختبرة فى حدود تركيزات بين ٠,٠٠٢ إلى ١ ملجم/كجم ، وتراوحت قيم معامل الارتباط (r^2) بين ٠,٩٨٣ إلى ٠,٩٩٩. وصلت حدود التقدير لمتبقيات المبيدات المختبرة بطرق التحليل المطورة خلال الدراسة إلى ٠,٠٠٢ ملجم/كجم. بلغت قيم الانحراف المعيارى النسبى لتكرارية طرق التحليل المطورة على المدى القريب ١٠,١% بينما كانت ١٣,٣% لتكرارية طرق التحليل على المدى البعيد، وذلك لكلا المحصولين محل الدراسة.

أظهرت منحنيات الانهيار المتحصل عليها للفقد التدريجى لمتبقيات المبيدات المختبرة فى كلا المحصولين. بلغت فترات نصف العمر لمبيدات بوسكاليد وبيراكلوستروبين وليوفينيورون ولامبدا-سيهالوثرين فى محصول الفاصوليا الخضراء ٥,٣ و٤,٣ و٩,١ يوم بينما كانت ٨,٥ و٣,١ و٩,٨ و٤,٢ يوم فى البصل الأخضر على الترتيب. بالرغم من أن مبيد بيراكلوستروبين فى البصل الأخضر كان أسرع المبيدات المختبرة انهيارا (فترة نصف العمر = ٣,١ يوم) إلا ان كمية المتبقيات التى وجدت بعد ١٤ يوم من الرش كانت ٠,٠٠٣ ملجم/كجم وهى أعلى من الحدود القصوى المسموح بتواجدها على البصل الأخضر (٠,٠٠٢ ملجم/كجم). أظهر مبيد ليوفينيورون ثباتا عاليا فى البصل الأخضر (فترة نصف العمر = ٩,٨ يوم) وبلغت كمية المتبقيات بعد ١٤ يوم من الرش ٠,٠٠٦ ملجم/كجم وهى تمثل ثلاثة أضعاف الحدود القصوى المسموح بتواجدها (٠,٠٠٢ ملجم/كجم)، غير أن سلوك هذه المبيد كان مختلفا تماما فى الفاصوليا الخضراء حيث لم تظهر أى متبقيات فى عينة الصفر بالرغم من الإختبارات التأكيدية التى أجريت للتأكد هذه النتيجة.