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PHOTOSTABILITY, SPRAY SOLUTION pH, AND INTERACTION OF EMAMECTIN BENZOATE, PROFENFOS AND SPINOSAD OR THEIR BINARY MIXTURES AGAINST THE LARVAE OF THE COTTON LEAFWORM, *SPODOPTERA LITTORALIS* (BOISD.) (LEPIDOPTERA: NOCTUIDAE)

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ABSTRACT

Photostability, spray solution pH, and interaction of profenfos, emamectin benzoate, and spinosad or their binary mixtures against larvae of the cotton leafworm, *Spodoptera littoralis* were evaluated. Laboratory bioassays of larval mortality on field-treated castor bean leaves showed that residual efficacy of emamectin benzoate, spinosad and profenfos exhibited high level of activity against the 2nd and 4th instar larvae *of S. littoralis* at 16, 18 and 22 days after application. Studies were conducted in the laboratory to investigate how the addition of insecticides to different samples of Nile River water would affect the pH of spray mixtures. The pH values of five Nile River water samples were alkaline; as they were significantly different and ranged from 7.8 to 8.2 while pH of tap water was 7.4. Results showed that the spray solutions remained alkaline following addition of the three tested insecticides. Mortality percentages of the 4th instar larvae of *S. littoralis* significantly decreased when profenfos diluted in alkaline phosphate buffer (pH 8 or more). Also, diluting emamectin benzoate and spinosad in phosphate buffer (pH 4 to 9) indicated that the optimal pH of spray solutions was ranged between 6 and

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7. When emamectin benzoate, spinosad and profenfos tested alone against the 4th instar larvae of *S. littoralis*, the calculated LC_{50} values were 0.712, 20.02 and 253 ppm, respectively, 24 hr post-treatment. Such value was decreased to 0.353, 16.25 and 231.5 ppm, respectively, 48 hr post-treatment. Present results indicated that there was an antagonistic effect of profenfos when mixed either with emamectin benzoate or spinosad. While there was an additive effect of the binary mixture of emamectin benzoate with spinosad.

Key words: Photostability, spray pH, profenfos, emamectin benzoate, spinosad, *Spodoptera littoralis*.

INTRODUCTION

The Egyptian cotton leafworm, *Spodoptera littoralis*, is one of the most important polyphagous pests, widely distributed in the Mediterranean region, North and East Africa, Asia and Europe (Quero *et al.*, 2002).

The insecticide market has been dominated by the organophosphate (OP), carbamate, and pyrethroid classes of insecticides (Argentine *et al.*, 2002). Selecron® or profenfos is a broad spectrum OP insecticide/acaricide used to control insect pests and mites in crops (Mbogho, 2008). Avermectins, a group of chemicals produced by soil-inhibiting *Streptomycete* bacteria, have demonstrated high toxicities to a number of insects, mites and nematode pests (Putter *et al.*, 1981). Abamectin is a fermentation product composed of two avermectins derived from the soil bacterium *Streptomyces avermitilis* and emamectin benzoate (Proclaim®) is an analog of abamectin, produced by the same fermentation system as abamectin (Ware and Whitacre, 2004). Spinosyns are among the newest classes of insecticides, represented by spinosad (Success®, Tracer Naturalyte®) and Spinosad is a fermentation metabolite of the actinomycete, *Saccharopolyspora spinosa*, a soil-inhibiting microorganism (Thompson *et al.*, 1999). However, Spinosad

is known to exert exceptional activity on several caterpillar species, including *S. littoralis*. Due to the selective action of spinosad on target pests and its negligible effect on predatory insects and mites, it seems to be valuable for IPM programmes (Van Leeuwen *et al.*, 2006).

In recent decades, many reports on the photodegradation of organic substances appeared on relative journals (Yu *et al.*, 2008). Little information is available on the photodegradation of many of the new pesticides. Therefore, the present work aimed to evaluate the photostability of some selected insecticides under field conditions. Many factors can affect the performance of a pesticide, i.e the pH of the water used in foliar sprays. The present study is planned to evaluate the insecticide performance at different final pH spray solutions. The laboratory bioassay was performed to assess the interaction between profenfos, emamectin benzoate, and spinosad and to determine the feasibility of using their mixtures for control of *S. littoralis*.

MATERIAL AND METHODS

1- *Spodoptera littoralis*:

The stock culture of the Egyptian cotton leafworm, *S. littoralis*, was maintained for several years under the laboratory conditions of 25 ± 2.0 °C, 75.0 ± 5.0% R.H., and LD 16:8. Larvae were fed on castor bean leaves and adults were fed on 10 % sucrose solution. The 2nd and 4th instar larvae (24 hrs-old) were used in the experiments.

2-Tested insecticides:

Selecron 72 % EC (the commercial formulation of profenfos) is produced by Syngenta Co., with a recommended rate of 750 Cm^3/ 400 L. Proclaim 5% SG (the commercial formulation of emamectin benzoate) supplied by Syngenta Co., with a recommended rate of 60 gm/ 400 L. and Tracer 24% SG (the commercial formulation of spinosad) is produced by AgroSciences Co., with a recommended rate of 120 gm/ 400 L.

3- Photostability test:

For the determination of the residual activity of profenfos, emamectin benzoate and spinosad, castor bean leaves were sprayed in the open field with the recommended field rate (RFR) and half-recommended field rate (HRFR) of each tested insecticide. Castor bean leaves were collected from sprayed plant trees at 0, 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, and 22 days following the spray application. Ten 2nd and/or 4th instar larvae of *S. littoralis* were fed for 24 hrs on castor leaves treated with both RFR and HRFR of each tested insecticide. Each insecticide treatment was replicated four times. Control larvae were fed for 24 hrs on castor leaves sprayed in the open field with tap water. Mortality counts were observed and recorded at 24 hrs posttreatment. Percentages of mortality were corrected, when needed, according to Abbott formula (Abbott, 1925). Sun light density average was 32,600 lx.

4-Effect of Insecticides on Spray solution pH:

Water samples were collected from five sources of Nile River at El-Beheira Governorate as well as Tap water and tested on the same day as collected. Nile River surface water samples were collected from two locations of Rashid branch (Kom-Shoraik village about 50 Km south of Damanhour city and Rashid city), two locations of El-Mahmodia canal (Kom-Shoraik village and Khorshid, Alex.), and one location of El-Nobareia canal (El-Bostan region) (about 45 Km east of Damanhour city). Water samples were taken in June 2007 from the Nile River. A single grab water sample was collected in 2 L. glass bottle. The sample was collected from share at a depth of 10-20 cm below the water surface. The pH value for each water sample was measured before and ½ hr after the addition of each tested insecticide at concentrations of a final spray solution of RFR and HRFR. Values of pH averages (three replicates) were estimated by measuring a 100 ml sample of each dilution with a high accuracy electrochemistry test pen (pH PAL, *ti* Trans instruments, TI99-13154, UAS). Because the average of pH values deviated by a maximum of 0.2 pH unit for any treatment, statistical analysis was not conducted.

5-Effect of spray solution pH on insecticide efficacy:

To investigate the influence of spray solution pH on the efficacy of the three tested insecticides against cotton leafworm, a series of phosphate buffer (0.1 M) at pH values of 4, 5, 7, 8, and 9 were prepared. Each tested insecticide at RFR was diluted in the phosphate buffers of different pH values. Castor leaves were dipped for 15 second in each and left to dry at room temperature. Four replicates of ten 4th instar larvae of *S. littoralis* were fed for 24 hrs on the treated castor leaves of each tested insecticide as well as phosphate buffer as a blank. Each treatment was replicated four times. Mortality counts were observed and recorded at 24 hr post-treatment.

6- Insecticide mixture Interactions:

Assessing whether chemicals (insecticides) in a mixture act in isolation (resulting in additive effect) or whether components interact to produce either antagonistic or synergistic toxicity. Concentrations of individual chemicals were normalized to their respective median lethal concentrations (LC_{50}) and collectively fit to a linear regression to determine whether toxicologic responses to binary mixtures were additive, antagonistic, or synergistic.

These studies were identical to the leaf dip bioassay method outlined above. Larvae were fed for 24 hrs on castor leaves treated with each tested insecticide alone or with a binary mixture of two tested insecticides at different concentrations with three replicates for each. Control larvae were fed for 24 hr on castor leaves dipped for 15 second in tap water. Mortality counts were observed, recorded at 24, 48, and 72 hr post-treatment and corrected as mentioned above. LC_{50} in ppm was estimated for each tested insecticide, alone or in combination, according to the method of Finney (1971). To evaluate the effect of different binary mixtures of the three tested insecticides, the following equation was used to calculate the cotoxicity factor:

$$\text{Cotoxicity factor} = \frac{\text{observed \% mortality} - \text{expected \% mortality}}{\text{expected \% mortality}} \times 100$$

(Mansour *et al.*, 1966).

Data were statistically analyzed to obtain the analysis of variance (ANOVA) and least significant differences (L.S.Ds) by the method of Steel and Torrie (1984) according to which the data were transformed, when desired, using square root and angular transformation.

RESULTS AND DISCUSSION

1- Insecticide photostability:

Table (1) shows that emamectin benzoate and spinosad exhibited high level of activity against *S. littoralis* larvae for 16 and 18 days after treatment (DAT). Profenfos exhibited high level of activity against *S. littoralis* larvae for 22 days. All of the three tested insecticides were effective in killing *S. littoralis* larvae when applied at RFR and HRFR.

It is observed that after 8 days of insecticide application, profenfos either at RFR (1.875 ml/liter) or at HRFR (0.9325 ml/liter) resulted in 100% and 85% mortality percentages for the 2nd instar larvae of *S. littoralis*, respectively. The corresponding mortality percentages were decreased to 22.5% and 5%, 20 DAT. RFR and HRFR of profenfos, 8 DAT, resulted in 95 and 80 % mortality percentages in the 4th instar larvae, respectively. The corresponding mortality percentages were decreased to 27.5% and 15%, 20 DAT. At RFR profenfos remained toxic up to 22 DAT (7.5 and 12.5% mortality) against the 2nd and 4th instar larvae of *S. littoralis*, respectively. However, under sunlight (simulated) conditions, the rate of photodegradation of chlorpyrifos was rapid on a soil surface but comparatively slow on glass and leaf surfaces (Walia *et al.*, 1988). In another work, Walia *et al.* (2006) observed that, as compared to dark conditions, iodofenphos on soil, glass and leaf surface was accelerated under illuminated conditions. Helliwell and Stevens (2000) found that alphacypermethrin provided >99% control of Chironominae for 19 days after application at all rates evaluated, whilst the chlorpyrifos standard gave 97% control over the same period.

Table (1): Residual activity of profenfos, emamectin benzoate and spinosad against 2nd and 4th instar larvae of *Spodoptera littoralis* fed on field-treated castor plant leaves with the recommended- and half recommended-field rates (RFR and HRFR).

Insect larval instar	Insecticide	Rate	Mortality, % Day after treatment											L.S.D 0.05	Half time (day)
			0	2	4	6	8	10	12	14	16	18	20	22		
2nd	Profenfos	1.875 ml/L	100±0.0	100±0.0	100±0.0	100±0.0	100±0.0	92.5±2.04	92.5±2.9	80.0±3.5	75.0±4.1	47.5±2.9	22.5±2.9	7.5±2.9	4.213	17.8
		0.9375 ml/L	95.0±5.8	95.0±2.0	90.0±2.0	90.0±4.8	85.0±4.1	75.0±4.08	57.5±2.9	52.5±5.4	37.5±2.9	25.0±4.1	5.0±2.0	0.0	8.001	14.2
	E. benzoate	0.15 gm/L	100±0.0	100±0.0	100±0.0	100±0.0	100±0.0	85.0±4.1	82.5±2.0	37.5±2.9	17.5±2.9	0.0	0.0	0.0	3.160	12.8
		0.075 gm/L	100±0.0	100±0.0	100±0.0	100±0.0	90.0±4.1	72.5±2.9	32.5±2.9	17.5±2.0	0.0	0.0	0.0	0.0	3.714	10.5
	Spinosad	0.3 gm/L	87.5±2.9	87.5±2.9	85.0±4.1	85.0±5.8	82.5±5.0	72.5±2.9	67.5±4.8	42.5±5.0	32.5±2.0	15.0±2.0	0.0	0.0	5.529	15.3
		0.15 gm/L	82.5±2.0	82.5±5.8	80.0±4.1	80.0±3.5	75.0±4.1	60.0±4.1	55.0±4.1	35.0±5.8	12.5±2.0	0.0	0.0	0.0	6.183	12.5
	Control	-	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0		
4th	Profenfos	1.875 ml/L	100±0.0	100±0.0	100±0.0	100±0.0	95.0±4.1	100±0.0	90.0±4.1	82.5±2.9	80.0±4.1	67.5±2.0	27.5±2.0	12.5±2.0	4.524	18.8
		0.9375 ml/L	90.0±4.1	90.0±4.1	85.0±5.8	85.0±4.1	80.0±4.1	67.5±2.0	62.5±2.9	60.0±4.1	42.5±5.0	27.5±2.9	15.0±3.5	2.5±0.0	5.855	15.2
	E. benzoate	0.15 gm/L	100±0.0	95.0±4.1	95.0±5.8	92.5±2.9	85.0±4.1	72.5±2.9	55.0±4.1	32.5±5.0	15.0±4.1	0.0	0.0	0.0	5.756	10.3
		0.075 gm/L	90.0±4.1	90.0±4.1	87.5±2.9	85.0±4.1	77.5±2.9	67.5±2.9	42.5±5.0	20.0±4.1	0.0	0.0	0.0	0.0	5.573	9.3
	Spinosad	0.3 gm/L	82.5±5.0	82.5±2.9	77.5±3.5	75.0±3.5	75.0±4.1	72.5±2.9	62.5±2.9	37.5±2.9	17.5±2.0	5.0±2.0	0.0	0.0	4.753	11.4
		0.15 gm/L	80.0±4.1	80.0±2.0	77.5±2.0	77.5±2.0	67.5±5.0	67.5±2.9	42.5±2.9	25.0±5.8	0.0	0.0	0.0	0.0	5.473	13.1
	Control	-	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0		

Data indicated also that the bioinsecticide, emamectin benzoate, applied at RFR and HRFR resulted in 100% and 90% mortality for the 2nd instar larvae of *S. littoralis* and 85% and 77.5% mortality for the 4th instar, 8 DAT. Also, 85 and 72.5 % mortalities were achieved for the 2nd instar larvae of *S. littoralis* up to 10 DAT, at RFR and HRFR, respectively. On the day 14 post-treatment, 37.5 and 17.5 % mortality were achieved. At RFR, emamectin benzoate remained toxic up to 16 DAT and caused 17.5 and 15% mortalities against the 2nd and 4th instar larvae, respectively. On day 16, no mortality was recorded for the 2nd and 4th instar larvae at HRFR.

Results indicated also that spinosad applied at RFR or HRFR resulted in 82.5% and 75% mortality for 2nd instar larvae and 75% and 67.5% mortality for 4th instar larvae of *S. littoralis*, respectively, 8 DAT. Also, 72.5 and 60 % mortality were achieved for the 2nd instar larvae of *S. littoralis* up to 10 DAT, at RFR and HRFR, respectively. On the day 14 post-treatment, 42.5 and 35 % mortality were achieved for 2nd instar larvae. With RFR, Spinosad remained toxic up to 16 DAT (32.5 and 17.5% mortality) against the 2nd and 4th instar larvae, respectively. On the day 18 posttreatment, no mortality was recorded using HRFR. In this study 10 days of exposure in June/July was enough for significant reduction in the residual mortality of emamectin benzoate and spinosad. Table (1) shows also the calculated half time values for each tested insecticide. Such values of profenfos were 17.8 and 18.8 days for the 2nd and 4th instar larvae, respectively. The half time values of emamectin benzoate were12.8 and 10.3 days for the 2nd and 4th instar larvae, respectively. Among spinosad, the half time values were 15.3 and 11.4 10.3 days for the 2nd and 4th instar larvae, respectively.

However, avermectins (e.g., abamectin) are very susceptible to photodegradation (MacConnell *et al.* 1989). Numerous photodegradates have subsequently been identified for both abamectin (Crouch *et al.*, 1991) and emamectin benzoate (Proclaim®) (Feely *et al.*, 1992). For these reasons, field use rates of between 8.4 and 16.8 g ai/ha are recommended for the compound (Anonymous 1995). MacConnell *et al.* (1989) showed that there were marked differences in the half-life of

abamectin on Petri dishes and on leaves in light and dark environments and prolonged stability in the dark resulted in greater penetrability into leaves and improved efficacy at controlling mites. Emamectin benzoate is being developed as a broad spectrum lepidoptericide on a wide variety of horticultural crops (Dybas, 1988). Emamectin benzoate is very compatible with IPM. Rapid photodegradation of both abamectin and emamectin benzoate occurs on the leaf surface (Ware and Whitacre, 2004). However, excellent efficacy was found for up to 14-21 days after application under glasshouse and simulated field conditions when emamectin benzoate was applied at the proposed field rate (Jansson *et al.*, 1996).

Present results indicated that spinosad remained toxic up to 18 DAT. However, residues of spinosad present on plant surfaces dissipate at a moderate-to-rapid rate, primarily due to sunlight photolysis. Dissipation half-lives of 2 to 16 days have been observed for residues on leaf and fruit surfaces, with the rate dependent on the amount of sunlight received and degree of shading (Saunders and Brett, 1997). The application of both, full and reduced doses of spinosad resulted in very high efficacy against Colorado potato beetle larvae, with residual activity between 10 and 20 days (Barčić *et al.*, 2006). Spinosad can stay available for uptake over a long period, providing long-lasting control (Van Leeuwen *et al.*, 2006).

Spinosad toxicity in tomato plants grown in rockwool was highly persistent, in clear contrast to foliar applications, where spinosad is readily dissipated from the plant surface by photolysis (Kollman, 2002). Spinosad is partly taken up by leaf tissue and this enhances its effectiveness over time (Saunders and Brett 1997). The spinosyns bind readily to organic matter on leaf surfaces since photodegradation of spinosad residues occurs readily on plants, thus tolerances on crops are not of great concern (Dow Agrosciences, 1998).

In general, present data showed that all tested insecticides were comparable in their residual efficacy in controlling *S. littoralis* under field conditions when applied at the proposed field use rate. At the lower rate, profenfos was consistently the most effective insecticide

followed by emamectin benzoate and spinosad, although data trends suggest that emamectin benzoate was the most effective insecticide at controlling this pest and it seems to photodegrade rapidly.

2-Effect of Insecticides on Spray solution pH:

Effects of profenfos, emamectin benzoate, and spinosad at RFR or HRFR on spray solution pH values of the water samples as well as tap water are presented in Table (2).

The pH for the five water samples prior to addition of insecticides was alkaline; as they were significantly different and ranged from 7.8 to 8.2 while pH of tap water was 7.4. Slight changes in pH values were recorded after the addition of the tested compounds. In general, pH values remained alkaline after ½ hr of the addition of the insecticides. A slight decrease in pH values were observed as a result of insecticide addition since it decreased by about 0.1-0.2. Literature indicated that water may became acidic after additions of several compounds (Dimethoate, MSR, Orthene, Malathion), or may not changed so much for others (Diazinon), and actually became more alkaline after addition of others as Lorsban (Palumbo *et al.*, 2001).

The rates of spinosad applied for controlling pests by foliar application on different crops range from 50 to 300 g ha^{-1} (Thompson *et al.*, 2000). However, Palumbo *et al.* (2001) found no significant changes in pH levels after the addition of spinosad, regardless of the buffer concentration. However, reports from Dow Agrosciences have suggested that the performance of Success® (Spinosad) is thought to be altered when mixed and sprayed under moderately acidic (pH < 6) conditions (Saunders and Brett, 1997).

Water pH can affect a pesticides chemical breakdown (hydrolysis) in spray solution. It has been documented that certain insecticides degrade or undergo hydrolysis faster in water with a high pH (Boerboom, 1995). Hock (1995) indicated that if the water supply is alkaline, especially if the pH is 8 or greater, and the applied pesticide is sensitive to hydrolysis, it should lower the pH of the water in the spray tank. However, it has been shown that in many areas of El-Beheira Governorate water supplies have sufficient natural alkalinities to cause

hydrolysis of certain pesticides. This means that a pesticide may begin to break down as soon as it is added to the tank. In practical terms, according to Boerboom (1995), this means that the degree of pest control may be somewhat less than desirable, or even nonexistent, because certain amount of the active ingredient may be decomposed to an inactive form before it reaches the plant and the pest. These results should serve as a useful guideline as water pH levels from different sources may change when considering the use of insecticide. However, prior to mixing spray solution it is a good to check the pH of the water before and after mixing pesticides.

3-Effect of Spray solution pH on insecticide Efficacy:

Table (3) and Fig. (1) clearly show that acidic spray solutions reduced the residual efficacy of the three tested insecticides against cotton leafworm. This phenomenon was more pronounced with the bioinsecticides emamectin benzoate and spinosad than the OP insecticide profenfos. Spinosad mortality percentage was decreased from 87.5 % at pH 6 to 45 and 52.5 % at pH 4 and 5, respectively. However, acidic pH conditions also had a significant impact on the residual mortality from 100% (pH 6 or 7) to 57.5% (pH 4) of *S. littoralis* larvae treated with emamectin benzoate. Spinosad or emamectin benzoate was apparently affected by lower pH. Palumbo *et al.* (2001) found that mortality of beet armyworm did not differ significantly between the untreated check and the two spinosad rates sprayed in acidic solutions. Larvae exposed to acidic spray solutions fed significantly more than those feeding on leaves treated with non-acidic sprays. Residual efficacy of the RFR of profenfos was slightly affected by lower pH. It is observed that only 20 and 15 % reduction in efficacy from 92.5 % at pH 6 to 72.5 and 77.5 % mortality at pH 4 and 5, respectively. Mortality percentages of *S. littoralis* larvae did not differ between the three tested insecticides sprayed in acidic solutions (pH 6 and 7).

Table (2): Influence of Profenfos, Emamectin benzoate and Spinosad on pH levels of aqueous spray concentrations before (Pre-test), and at ½ hour following addition of insecticides to water collected from different locations of Nile River.

Insecticide	RFR* and HRFR	Water pH value												Pre-test Mean±S.E.
		Rashid branch				El-Mahmodia canal				El-Nobareia canal		Tap water		
		Kom-Shoraik		Rashid city		Kom-Shoraik		Khorshid						
		Pre-test	1/2 hr	Pre-test	1/2 hr	Pre-test	1/2 hr	Pre-test	1/2 hr	Pre-test	1/2 hr	Pre-test	1/2 hr	
Profenfos	1.875 ml	7.8	7.7	7.9	7.8	8.2	8.1	8.0	7.8	8.2	8.1	7.4	7.3	7.92±0.3
	0.9375 ml	7.8	7.7	7.9	7.8	8.2	8.1	8.0	7.9	8.2	8.1	7.4	7.3	7.92±0.3
E. benzoate	0.15 gm	7.8	7.6	7.9	7.7	8.2	8.0	8.0	7.8	8.2	8.0	7.4	7.2	7.92±0.3
	0.075 gm	7.8	7.6	7.9	7.8	8.2	8.0	8.0	7.9	8.2	8.0	7.4	7.2	7.92±0.3
Spinosad	0.30 gm	7.8	7.7	7.9	7.8	8.2	8.0	8.0	7.9	8.2	8.1	7.4	7.3	7.92±0.3
	0.15 gm	7.8	7.7	7.9	7.8	8.2	8.1	8.0	7.9	8.2	8.1	7.4	7.3	7.92±0.3
Meam±S.E		7.8±0.0[d]		7.9±0.0[c]		8.2±0.0[a]		8.0±0.0[b]		8.2±0.0[a]		7.4±0.0[e]		

RFR*; Recommended field rate. HRFR; Half recommended field rate (/1 liter water).

Table (3): Toxicity of profenfos, emamectin benzoate and spinosad,, dissolved at the recommended field rate in different pH spray solutions of 100 mM of phosphate buffer (PB) against 4th instar larvae of *S. littoralis*.

Insecticide	RFR* (ppm)	Mortality, % pH spray (Phosphate buffer)						L.S.D.$_{0.05}$
		4	5	6	7	8	9	
Profenfos	1350	72.5±2.04	77.5±2.89	92.5±3.53	90.0±4.08	42.5±3.34	25.0±2.89	4.106
E. benzoate	7.5	57.5±2.04	67.5±5.40	100.0±0.0	100.0±0.0	62.5±2.04	57.5±2.89	4.952
Spinosad	72	45.0±3.54	52.5±2.04	87.5±2.89	82.5±4.08	70.0±2.04	55.0±2.04	5.325
PB	—	5.0±2.04	7.5±2.04	5.0±2.04	2.5±0.0	2.5±2.04	5.0±2.04	
L.S.D.$_{0.05}$		4.847	4.972	3.852	3.516	4.684	5.884	

Means within column followed by the same letter(s) are statistically equaled according to L.S.D.0.05 value.
RFR*; Recommended field rate.

Dow AgroSciences has reported problems with the residual efficacy of spinosad at pH levels below 6. The reasons for this breakdown in residual centers around how spinosad is formulated. Palumbo *et al.* (2001) explained that Success, like Tracer, is formulated as a suspension concentrate made up of suspended granules, each granule containing many spinosad monomers. When Success is mixed in spray solutions at a pH above 6, the Success granules remain intact, thus protecting it from UV degradation. However, at pH < 6, the granules break down, exposing the spinosad monomers to rapid degradation. In the present study, at pH of 7, 8, and 9, residual efficacies of spinosad were 82.5, 70, and 55 % mortality for 4^{th} instar larvae. Residual efficacy of emamectin benzoate recorded 100, 62.5, and 57.5 % mortality at pH of 7, 8, and 9, respectively. Palumbo *et al.* (2001) showed that acidic spray solutions had a negative impact on the residual efficacy of Success against beet armyworm and cabbage looper.

In contrast, Fig. (1) showed that alkaline spray solutions reduced the residual efficacy of profenfos against *S. littoralis*. Mortality percentage was decreased from 92.5 % at pH 6 to 90.0, 42.5 and 25% at pH 7, 8, and 9, respectively. However, many pesticides, particularly the OP insecticides, undergo a chemical reaction in the presence of alkaline materials which destroys their effectiveness. This reaction is called alkaline hydrolysis and occurs when the pesticide is mixed with alkaline water. The more alkaline the water, the more rapid the breakdown of the pesticides (Hock, 1995 and Cloyd, 2000). According to Cloyd (2000), it is very important to double check a spray solution's pH before application. Spray solutions for most pesticides should have a pH close to neutral (pH = 7). If the pH is higher, it may reduce the efficacy of the product. On the other hand, some products become phytotoxic if the spray solution pH is too low (Pasian, 2004 and Yates, 2004).

Resistance to various insecticides has caused to re-evaluate pest management programs for maximum effectiveness of the active ingredients. Each pesticide application needs to be made under conditions that will yield maximum activity. An area that deserves more attention is the effect of water quality on efficacy of many pesticides

(Yates, 2004). However, it has been documented that spray solution with high pH or high mineral content can reduce pesticide performance by causing rapid breakdown in the spray tank or limiting uptake into the plant. Several commercial products are marketed to adjust the pH of spray solution, in part to protect pesticides from rapid hydrolysis. Addition of a buffering agent to the spray preparation is an easy and economical way to guarantee maximum results from pesticide applications (Hock, 1995 and Fishel and Ferrell, 2007). However, insecticides and miticides are more susceptible to alkaline hydrolysis than fungicides and herbicides. Many insecticides and miticides degrade under alkaline conditions. For example, malathion, kelthane, dylox, and turcam are very sensitive, degenerating within a few hours after being diluted in alkaline water. In general, the carbamate and OP chemical classes are more susceptible than chlorinated hydrocarbons or pyrethroids. Other pest-control materials can be affected by high pHs. The pH value above 8 can reduce the efficacy of the *Bacillus thuringiensis* (B.t.) toxin and the insect-growth regulator azadirachtin (Hock, 1995, and Cloyd, 2000).

Present results indicated that there are water sources in El-Beheira Governorate that have pH values between 7.8 and 8.2. According to Fishel and Ferrell (2007) one factor that influences the pH of open water is the amount of resident plant life. In these systems, there are high concentrations of carbonate in the water. The pH of the water may rise in poorly buffered systems because carbonate leads to increases in pH. Therefore, if some water canals at El-Beheira Governorate have high levels of healthy aquatic plants, it is possible for pH to reach a measurement of 8 or more. However, determining the pH of the spray mix water and adding an acidifier, a type of pesticide spray mix adjuvant, if necessary, is inexpensive compared to the cost of losing a pesticide's effectiveness (Fishel and Ferrell, 2007). Finally, present results point out that for protection of the pesticides from rapid hydrolysis, adjustment the pH of spray solution must be taking into considerations before these types of products are used.

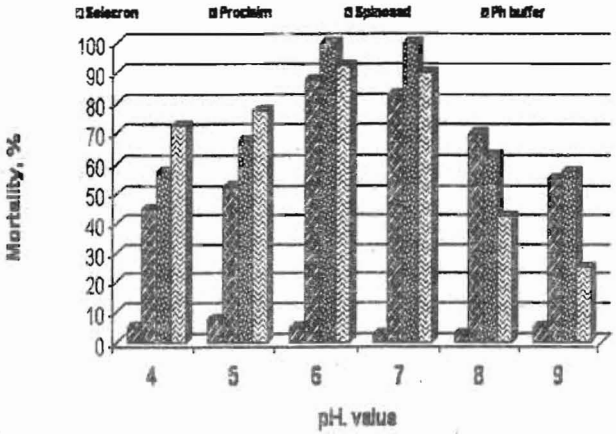

Fig. (1): Percent mortality of the 4th instar larvae of *S. littoralis* treated with profenfos, emamectin benzoate and spinosad insecticides diluted at the recommended field rates in different pH spray solutions of 100 mM phosphate buffer.

4- The interaction of insecticide mixtures:

Table (4) shows comparison of LC_{50} and slope values of emamectin benzoate, profenfos and spinosad, tested alone against 4th instar larvae of *S. littoralis*. The LC_{50} value calculated for emamectin benzoate was 0.712 ppm, 24 hr post-treatment. Such value was decreased to 0.353 ppm, 48 hr post-treatment. The LC_{50} values calculated for profenfos were 253 and 231.5 ppm, 24 and 48 hrs post-treatment, respectively. The LC_{50} values calculated for spinosad were 20.02 and 16.25 ppm, 24 and 48 hrs post-treatment, respectively.

Table (4): Comparison of LC_{50} and Slope values of Emamectin benzoate, Profenfos and Spinosad, tested alone against 4th instar larvae of *S. littoralis*.

Insecticide	DAT*	Regression equation	LC_{50}	Fiducial limit		Slope
				Lower	Upper	
Emamectin benzoate	24	Y=0.298 + 2.015 X	0.712	0.618	0.811	2.015
	48	Y=0.980 + 2.169 X	0.353	0.293	0.414	2.169
	72	Y=1.176 + 2.041 X	0.265	0.208	0.325	2.041
Profenfos	24	Y=-4.760 + 1.981X	252.956	217.668	293.829	1.981
	48	Y=-5.630 + 2.381 X	231.534	202.383	264.784	2.381
	72	Y=-5.630 + 2.381 X	231.534	202.383	264.784	2.381
Spinosad	24	Y=-3.123 + 2.399 X	20.019	17.908	22.368	2.399
	48	Y=-2.695 + 2.226 X	16.246	14.303	18.436	2.226
	72	Y=-2.713 + 2.252 X	16.026	14.116	18.176	2.252

DAT*; Day after treatment (hrs).

Table (5) represents the comparison of mortality percentages of binary mixtures at two different concentrations of emamectin benzoate, profenfos and spinosad against 4th instar larvae of *S. littoralis* and their cotoxicity factors.

The expected mortality for the mixture of two insecticides was the sum of the expected mortalities of each of the dosages used in the combination. Cotoxicity factor (CF) calculated for the mixture of profenfos and spinosad, 24 hr post-treatment, was –43.7. While CF value calculated for the mixture of emamectin benzoate and profenfos, 24 hr post-treatment was –45.2 (Table, 5). According to Mansour *et al.* (1965) cotoxicity factor with a negative value means an antagonistic effect of profenfos either with emamectin benzoate or spinosad. The value of cotoxicity factor calculated for the mixture of emamectin benzoate and spinosad, 24 hr post-treatment, was +10. However, the cotoxicity factor with the positive value meant an additive effect of emamectin benzoate with spinosad.

Results of Ahmad (2004) indicated that ethion produced a good potentiation with deltamethrin, cypermethrin, alphacypermethrin, and zetacypermethrin, on putatively resistant field populations of the cotton bollworm, *Helicoverpa armigera* (Lepidoptera), whereas profenfos,

chlorpyrifos, quinalphos, and triazophos exhibited an antagonism with deltamethrin as well as cypermethrins. The combined application of spinosad and abamectin is recommended by Ismail *et al.* (2007) against life stages of the two-spotted spider mite, *Tetranychus urticae* Koch (Acari: Tetranychidae). However, applications of combinations of insecticides in reduced doses (spinosad with B.t., neem and pyrethrin) are suitable in IPM in potato against Colorado potato beetle, ***Leptinotarsa decemlineata,*** larvae (Barčić *et al.*, 2006).

Table (5): Comparison of mortality percentages of binary mixtures of Emamectin benzoate, Profenfos and Spinosad at two different sublethal concentrations (LC_{25} and LC_{10}) against 4th instar larvae of *S. littoralis* and their cotoxicity factors.

Insecticides		Concentration (ppm)	Mortality, % Time after treatment (hr)		CF**	
			24	48	24	48
E. benz.* + Prof*	LC_{25}	0.50 + 225.00	40.00	66.67	- 45.20	- 31.80
	LC_{10}	0.25 + 90.00	06.67	30.00	- 85.10	-35.60
E. benz. + Spin.*	LC_{25}	0.50 + 12.00	76.67	90.00	+10.00	- 00.19
	LC_{10}	0.25 + 6.00	40.00	86.67	+33.30	+40.00
Prof. + Spin.	LC_{25}	225.00 + 12.00	43.33	56.67	- 43.70	- 31.30
	LC_{10}	90.00 + 6.00	26.67	30.00	- 27.00	00.00

* E. benz.; Emamectin benzoate, Prof.; Profenfos, Spin.; Spinosad.

** CF: Cotoxicity factor.

In conclusion, the results of this study gave highlight on some properties of emamectin benzoate and spinosad, as bioinsecticides, compared with the conventional insecticide, profenfos, and its possible application for the control of *S. littoralis*. However, an in-depth study is necessary to gather more data on systemic properties, in combination with an evaluation in the field.

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الملخص العربى

الثبات الضوئى، الأس الهيدروجينى لمحلول الرش، و تداخل كل من ايمامكتين بنزوات وبروفينفوس و سبينوساد ومخاليطها المزدوجة ضد يرقات دودة ورق القطن الكبرى *Spodoptera littoralis*

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تم دراسة الثبات الضوئى، الأس الهيدروجينى لمحلول الرش، وتداخل كل من ايمامكتين بنزوات و بروفينفوس و سبينوساد ومخاليطها المزدوجة ضد يرقات دودة ورق القطن الكبرى *Spodoptera littoralis*. أظهرت نتائج التقييم الحيوى المعملى للنسب المئوية للموت فى اليرقات المرباة على أوراق نبات الخروع المعامل حقليا أن تأثير المتبقى لمبيد ايمامكتين بنزوات و بروفينفوس و سبينوساد أظهر مستويات عالية من النشاط الأبادى ضد يرقات دودة ورق القطن الكبرى *S. littoralis* لمدة 16و 18 و 22 يوما بعد تطبيق المبيد، على الترتيب. تم دراسة تأثير أضافة تلك المبيدات الى عينات من مياة النيل والتى جمعت من أماكن مختلفة من محافظة البحيرة على تركيز الأس الهيدروجينى لمحاليل الرش. أختلفت معنويا قيم تركيز الأس الهيدروجينى لخمس عينات من مياة النيل والتى جمعت من أماكن مختلفة من محافظة البحيرة قلويا وتراوحت فى المدى من 7.8 الى 8.2 بينما كان تركيز الأس الهيدروجينى لعينات من مياة الصنبور 7.4. أظهرت النتائج أن تركيز الأس الهيدروجينى لعينات مياة النيل ظل قلويا حتى بعد أضافة أى من المبيدات الثلاثة المختبرة عند التركيز الحقلى ونصف الحقلى على السواء. أظهرت النتائج أيضا أن النسب المئوية للموت فى اليرقات أنخفضت معنويا عندما تم أذابة المبيد الفوسفورى بروفينفوس فى محلول فوسفات منظم تركيز الأس الهيدروجينى لة 8 أو أكثر. كما أن أذابة المبيد الحيوى ايمامكتين بنزوات و سبينوساد فى محلول فوسفات منظم تركيز الأس الهيدروجينى لة تراوح بين 4 و 9 يشير الى أن تركيز الأس الهيدروجينى الأمثل يتراوح بين 6 و 7. تشير النتائج الى أن قيم التركيز القاتل لـ 50 % من يرقات العمر الرابع لحشرة دودة ورق القطن الكبرى *S. littoralis* كانت 0.712 و 20.02 و 253 جزء فى المليون لكل من مبيد ايمامكتين بنزوات و سبينوساد و بروفينفوس، على الترتيب، وذلك بعد 24 ساعة من المعاملة. ولقد أنخفضت تلك القيم وذلك بعد 48 ساعة من المعاملة لتصبح 0.353 و 16.25 و 231.5 جزء فى المليون. تشير النتائج أيضا الى أن خلط مبيد بروفينفوس سواء مع مبيد ايمامكتين بنزوات أو مبيد مع سبينوساد قد أحدث تأثيرا تضاديا antagonistic effect، بينما عندما تم خلط مبيد ايمامكتين بنزوات مع مبيد سبينوساد أحدث تأثيرا أضافيا additive effect وذلك بناءا على قياس قيم معامل السمية المشتركة.