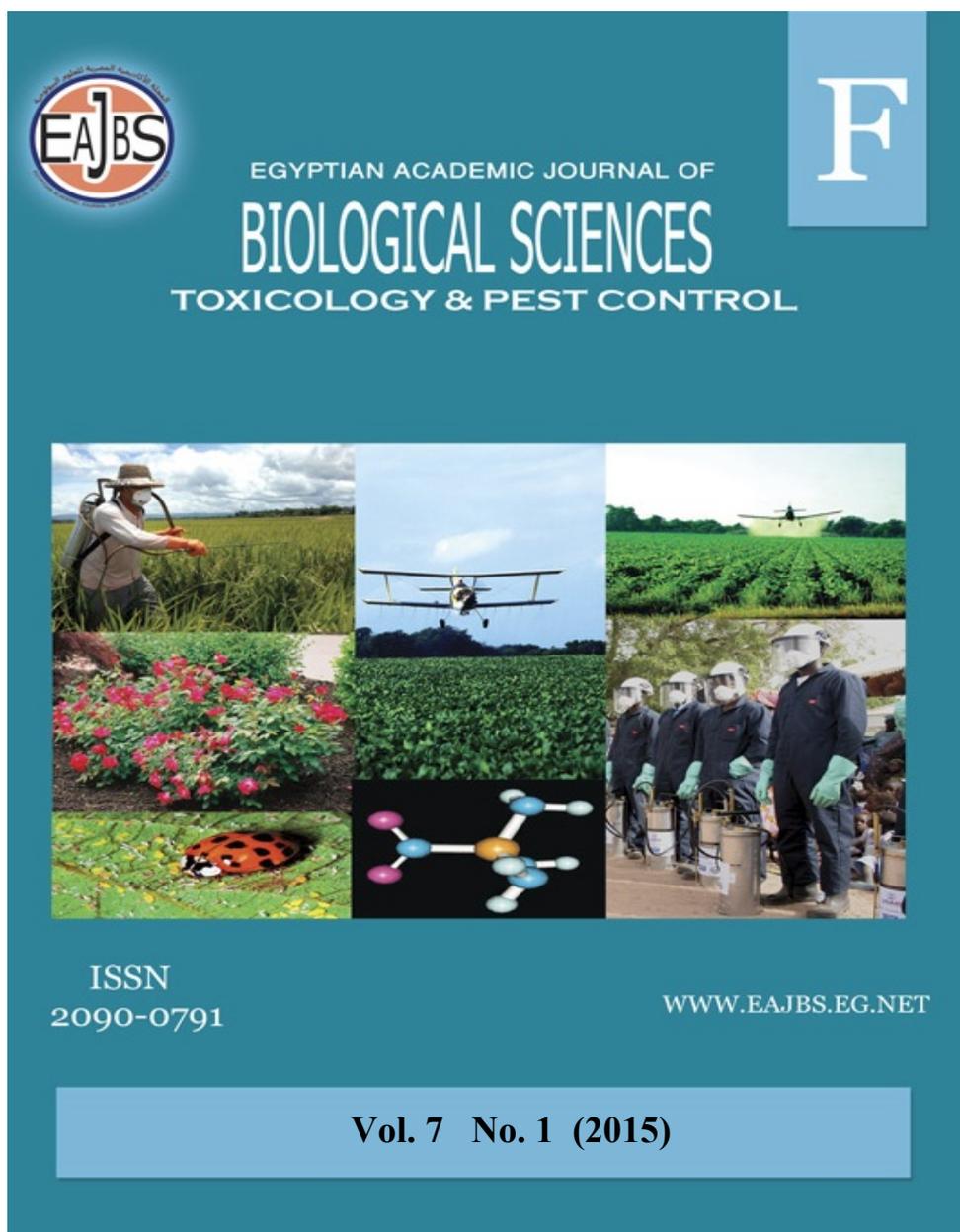


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The effect of water quality on insecticides stability

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ABSTRACT

The present study was aimed to investigate how salinity and pH of water which carries insecticides on their efficacy. Physico-chemical properties [salinity%, TDS mg/L, EC μ s and pH] of four water quality, ie., Nile water (N.W), Agricultural drainage water (Adw), Ground water (G.W, 16m³ deep) and distilled water (d.w) were measured alone and with marshal 20% EC, Sumithion 50% EC and oshin 20% SG. The LC₅₀ values and both initial and residual activities of these insecticides with different kinds of water were also determined under laboratory and field conditions against the cotton aphid, *Aphis gossypii*. The results clearly indicated that both N.W and AdW had high level of salinity and pH, therefore were considered as "Hard" according to standard classification system of Analytical services Litchlab. In addition, all the tested insecticides confirmed lowest toxicity (LC₅₀) and lowest initial and residual effects when these insecticides diluted in both Nile water and agricultural drainage water. These effects could be attributed to such water contains high level of cations (positively charged) such as Ca⁺², Mg⁺², Fe⁺³, Na⁺ and other ions attach to negatively charged insecticide molecules then, render the compound inactive. In addition insecticides particularly organophosphates and carbamates, undergo chemical breakdown in alkaline water (pH>7). So that salinity and pH in spray water can diminish the effectiveness of insecticides. On the other hand, turbidity water has soil particles (clay and silt), these particles can bind with insecticide molecules and harbor microbes that naturally degrade insecticide, and clog Filters and nozzles.

Generally how to keep it from becoming a problem? Please check the water pH before adding any compound. Water should be clean and clear for all pesticide applications. Remember read the pesticide label for recommended pH range.

INTRODUCTION

Water is the most common liquid used to dilute pesticides and deliver them to the target pests. The quality of water carrier can be important factor that should be considered to optimize pest control.

There are three water quality variables that can impact the activity of many pesticides i.e., Acidity & Alkalinity, Salinity and turbidity water (Hall, *et al.*, 1999). Salinity and pH in spray water can diminish the effectiveness of many herbicides, fungicides and insecticides stability (Petroff, 2012). Water salinity, is a concentration of mineral salts i.e., Mg^{+2} , Ca^{+2} , Na^{+} , Fe^{+3} and K^{+} dissolved in water (TDS). Water hardness is usually expressed as ppm or mg/L or grains/ U.S gallon. Water which has 75-150 mg/L is considered "soft", 150-300mg/L is considered "medium hard", >300mg/L is considered "hard" according to standard classification system of Analytical services Litch Lab (Anonymous 2014). Hard water when used as carrier may adversely affect the effectiveness of many herbicides, fungicides and some insecticides (Petroff, 2012).

Water pH, is used to measure the conc. of (H^{+}) and indicates the breakdown of water into (H^{+}) and (OH^{-}). Petroff, 2012, Park & Juang-Hornng, 2014 and Hall, *et al.*, 1999, illustrated that some herbicides like sulfonyl ureas have been known to breakdown in acidic water ($pH < 7$). On the other hand, some insecticides and fungicides have been shown to breakdown in alkaline water ($pH > 7$).

Turbidity water such as streams or ponds generally have significant levels of dissolved solids and organic particles (clay and silt) these particles decrease pesticides activity and can cause equipment wear. Therefore, the present study was conducted to investigate how salinity and pH of carrier water influence insecticides stability.

MATERIALS AND METHODS:

Insects: A colony of the cotton aphid, *Aphis gossypii* were reared under laboratory conditions at $25 \pm 2^{\circ}C$ and $70 \pm 5\%$ R.H. in the laboratory of Sids

Agric. Res. Station, Beni-Sueif Governorate.

Insecticides used: Marshal 20% EC (carbosulfon) 2, 3-dihydro-2,2-dimethylbenzofuran-7-yl(dibutylaminothio) methyl carbamate, produced by Delta Agro. Chem. Co.

- Sumithion 50% EC (Fenitrothion) 0, 0-dimethyl - o - u -nitro-m-tolylphosphorothioate., produced by sumitomo chem. Co. Japan.
- Oshin 20% SG (dinotefuron), (Rs)-1-methyl-z-nitro-3 (tetrahydro- 3-furylmethyl) guanidine (Newnicotinoid), provided by sumitomo. Chem. Co. Japan.

Water Sources: Nile water (N.W), Ground water (G.W, 16m³ deep), Agricultural drainage water (Adw). All water samples were collected from the farm of Naser district, Beni-Sueif Governorate, while distilled water used as standard.

Physico-chemical properties: Salinity %, Total dissolved salt (TDS mg/L), and electric conductivity (μs) of carrier water quality alone and with insecticides were measured using electrical conductance (EC), water pH was also measured by electronic pH-meter at $20^{\circ}C$.

Toxicity response: Mean lethal concentrations (LC_{50} 's) of the candidate insecticides with different carrier water were evaluated against *A.gossypii*. Five aqueous conc. were used by dilution the formulated compounds, Marshal 20% EC, Sumithion 50% EC and Oshin 20% SG with the tested water i.e., N.W, Adw, G.W and dW. Thirty newly emerged adult females of *A. gossypii* pretreatment were treated with serial conc. of each compound using leaf-dipping technique. Five cotton leaf discs were considered as three replicates for each conc. Leaf discs were placed up side down on moistened cotton wool in Petri dishes. Other three replicates were treated with distilled

water as check. All treatments were kept under constant conditions ($25 \pm 2^\circ\text{C}$ and $70 \pm 5\%$ RH). Mortalities were recorded after 24 hr. and corrected using Abbott's formula (1925). The LC_{50} values were estimated by probity analysis (Finney 1971).

Field experiments: Were performed in cotton fields in Sides Agric. Res. Station, Beni-Sueif Governorate during April 2014 cotton season. An area of about $\frac{1}{2}$ feddan was selected and planted with cotton variety Giza 80. This area divided into 39 plots. The tested insecticides, Marshal 20% EC, Sumithion 50% EC and Oshin 20% SG were applied at their recommended rates, $200\text{cm}^3/\text{Fedd.}$, 1L/Fedd. and 50 gm/100L water, respectively diluted with different carrier water using knapsack sprayer under field dilution rate (200 L water/ Fedd). Thirteen treatment including control were examined randomly, and the total number of *A. gossypii* were recorded pre application directly and after 1, 3, 5 and 7 days post spraying. The reduction % in population of *A. gossypii* at different time intervals were calculated using Henderson & Tilton (1955) equation. Initial kill was recorded after 24 hr. post application, while mean residual activity were estimated as mean of % reduction after 3, 5 and 7 days post spraying.

Statistical Methods: Mean lethal concentrations (LC_{50} 's) and reduction % were statistically done (Finney 1971 and Henderson & Tilton 1955) by probit analysis software computer program. Data of residual activity were also subjected to one-way analysis of variance (ANOVA) followed by Duncan multiple range test to determine the significant differences among treatments mean values at 5% probability level.

RESULTS AND DISCUSSION

Effect of carrier water quality on physico-chemical properties of tested insecticidal spray solutions:

The illustrated results in Table (1) summarized the physico-chemical properties of carrier water alone and with tested insecticides. TDS is a useful indicator of water quality and usually expressed as ppm or mg/L. Distilled water was considered "soft", ground water was considered "moderately hard", while both agricultural drainage water and Nil water were considered "Hard water" according to standard classification system of analytical services Lite Lab. (Anonymous 2014). Salinity, TDS, conductivity and pH value were changed remarkably according to the type of water used for dilution the tested insecticides as shown in Table (1).

Table 1: Physico – Chemical properties of candidate insecticides with carrier water quality.

Treatment	Salinity %	TDS* (mg/L)	Conductivity (μS) ^a	Relative Hardness	pH
Nil water (N.W)	0.6	656	1342	Hard	7.9
Agric. Drainage water (Adw)	0.6	617	1268	Hard	7.8
Ground water (G.W)	0.2	219	457	Moderately	7.3
Distilled water (d.W)	0.0	10	20.6	Soft	7.2
Marshal + N.W	0.6	605	1244	Hard	7.52
Marshal + Adw	0.7	644	1316	Hard	7.82
Marshal + G.W	0.2	238	457	Moderately	7.42
Marshal + d.W	0.1	59	120.4	Soft	7.30
Sumithion+N.W	0.6	660	1222	Hard	7.80
Sumithion +Adw	0.6	633	1307	Hard	7.43
Sumithion+G.W	0.2	220	461	moderately	7.27
Sumithion + d.W	0.0	36	12.6	Soft	4.45
Oshin + N.W	0.6	615	1261	Hard	7.9
Oshin + Adw	0.7	665	1357	Hard	7.6
Oshin + G.W	0.2	230	471	Moderately	7.38
Oshin +d.W	0.0	34	72	Soft	7.3

* TDS= Total dissolved salts

^a* μS = $\mu\text{mahos/cm}$

The obtained results indicated that there was a proportional relationship between the salinity of water as TDS mg/L and conductivity, when the conc. of mineral salts ($MgSO_4$, $MgCl_2$, $CaCl_2$, $NaHCO_3$ and KCl) were increase the positively charged cations of spray solution increase, therefore conductivity was increase. Also pH value of the tested insecticides spray solution were changed by the type of carrier water quality. Generally salty water usually alkaline ($pH > 7$) and more resistant to pH change making adjustment with acids more difficult. Salinity > 0.75 ds/m conc. stress sensitive plants and reduce absorption of systemic pesticides through plant roots (Park and Juang-Horng, 2014).

The efficiency of the final insecticidal spray solution in the field is strongly correlated with their physico-chemical characteristics, such as pH, conductivity, surface tension, viscosity and salinity [Furmidage 1962, Abdel-Hafez, 1995 and 2005]. wettability, spreading and field performance of treated leaf surfaces increase by decreasing surface tension of insecticidal spray solutions (Osipow 1964), also retention of the treated plant surface increase by decreasing pH and conductivity (Tawfik & El-Sisi 1987). In

addition, the International organizations FAO and WHO (Anonymous, 2006) outlined the tests and specification that each type of formulation must be pass successfully to achieve target action in the field.

Toxicity response of candidate insecticides with different carrier water quality to *A. gossypii*:

The concentration- mortality regression (LC_{50} 's) for the tested insecticides with different carrier water quality were estimated against the adult female of *A. gossypii*. Data from Table (2) and Figs. (1, 2 and 3) clearly indicated that the LC_{50} values of the tested insecticidal spray solutions with carrier water quality varied due to the intrinsic toxicity of each compound and changed remarkably according to the type of water used for dilution. The toxicity of marshal 20% EC could be arranged according to its ' LC_{50} ' as follows, 1.95, 2.18, 2.94 and 3.57 ppm when diluted in d.W, G.W, Adw and N.W, respectively. Also the LC_{50} values of sumithion 50% EC were arranged in descending order according to its toxicity as follow, 12.71, 16.36, 22.44 and 24.60 ppm, respectively when used d.W, G.W, N.W and Adw as carrier water respectively.

Table 2: Toxicity response of the tested insecticides with different carrier water quality to *A. gossypii*.

Insecticide	Carrier water	LC values (95% FL) ppm					
		LC_{50}	Lower	Upper	LC_{90}	Slop	χ^2
Marshal 20% EC	N.W	3.57	2.891	4.280	23.01	1.584	3.213
	Adw	2.94	2.453	3.436	13.65	2.023	0.887
	G.W	2.18	1.647	2.689	13.52	1.615	0.944
	d.w	1.95	1.508	2.368	9.36	1.879	7.376
Sumithion 50% EC	N.W	22.44	17.322	21.258	128.38	1.692	0.447
	Adw	24.60	18.153	30.958	205.31	1.391	3.044
	G.W	16.36	11.739	20.757	95.56	1.612	4.968
	d.w	12.71	8.598	16.706	77.27	1.635	1.660
Oshin 20% SG	N.W	6.008	4.609	7.422	49.48	1.399	2.500
	Adw	6.012	4.712	7.327	42.41	1.511	2.976
	G.W	4.340	3.353	5.304	23.92	1.729	2.055
	d.w	2.560	1.599	3.473	19.57	1.449	3.294

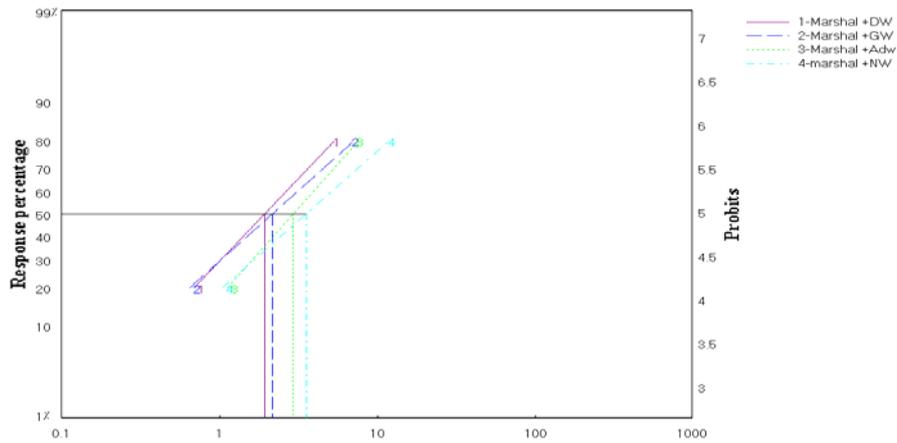


Fig. 1: Toxicity regression lines for Marshal 20% E.C diluted with different carrier water quality

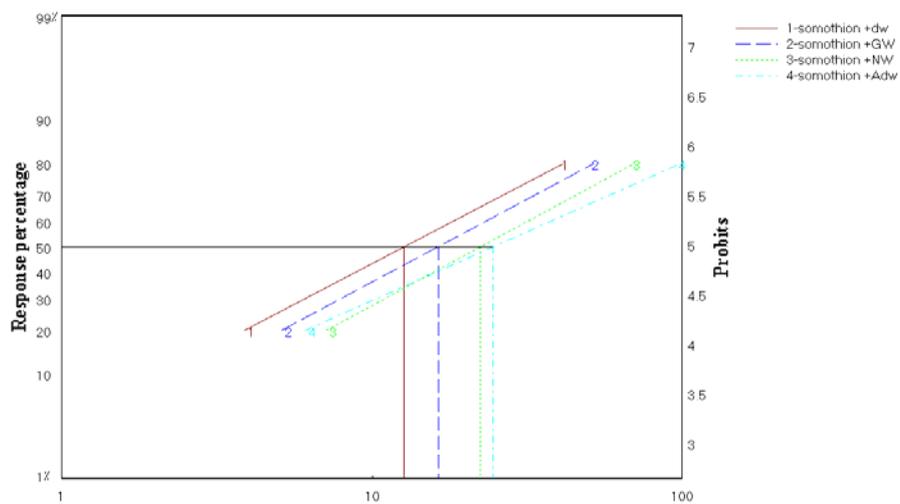


Fig. 2: Toxicity regression lines of Sumition 50%E.C diluted with different carrier water quality against *A.gossypi*

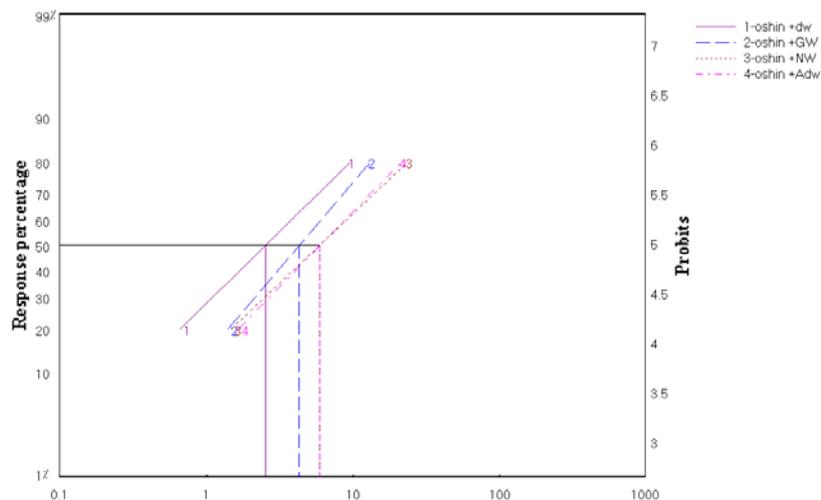


Fig. 3: Toxicity regression lines for Oshin20%S.G diluted with different carrier water quality against *A.gossyii*

Also LC_{50} values of oshin 20% SG were 2.56, 4.34, 6.00 and 6.012 ppm when diluted with d. W, G.W, N.W and Ad. w, respectively (Table 2 and Figs. 1, 2 and

3). It could be concluded that the highest toxicity of the all the tested insecticides were observed when using distilled water "soft" as carrier, followed by ground water "moderately hard". However, the lowest toxicity were recorded when tested compounds diluted in both Nile water and Agricultural drainage water "Hard". These due to both Nile water and agricultural drainage water have high level of salinity and pH compared with ground and distilled water.

Effect of carrier water quality on insecticide stability:

The initial and residual activities of the tested compounds with different carrier water quality were determined against the cotton aphid, *A. gossypii* during April 2014 cotton season under field condition. It is intelligible from data in Table (3) and Figs. (4 and 5), that marshal 20% EC confirmed the highest initial and residual kill (87.55% and 76.75%), respectively when diluted with

distilled water, followed by (86.48% and 71.85%) when diluted in ground water, respectively while, it produced the lowest initial and residual activities when used Nil water as carrier (82.53 and 70.81%), respectively. Also sumithion 50% EC recorded the highest initial and residual effect when diluted in d.W (73.63% and 65.33%), followed, by G.W (72.81% and 63.66 while it gave the lowest initial and residual activity when used N.W (70.06% and 62.68%). Finally oshin 20% SG confirmed the highest reduction % in initial kill after 24 hr post application and residual activity after 7 days when used d.W and G.W as water carrier, it produced (89.92% and 71.68%), and (84.18% and 70.38%), respectively. However it produced the lowest effect in both initial and residual effects when diluted with both Adw (79.30% and 69.72%) as shown in Table (3) and Figs. (4 and 5).

Table 3: Effect of carrier water quality on insecticides stability against *A. gossypii* under field condition.

Treatment		Rate of application	Number of <i>A.gossypii</i> /10 cotton leaves					% Reduction post application (days)				Mean Residual \pm SE
			Pre spraying	Post spraying (days)				Initial kill	% Residual activity			
				1	3	5	7		1	3	5	
Marshal 20% EC	N.W	200 cm ³ /fedd.	205	45.7	48.33	100.3	127.7	82.53	85.2	71.08	56.12	70.81 \pm 6.85 b
	Adw		189.7	39	39	107.7	128.7	83.90	87.09	66.44	52.21	68.58 \pm 8.26 b
	G.W		178	30.7	40	86.7	105	86.48	85.90	71.21	58.45	71.85 \pm 6.47 b
	d.w		190.7	30.3	34.33	71	98.7	87.55	88.71	78.00	63.54	76.75 \pm 5.95 a
Sumithion 50% EC	N.W	1000 cm ³ /fedd.	144	55	62	91.33	97	70.06	72.97	62.52	52.55	62.68 \pm 4.81 d
	Adw		207.7	73.3	107	140.7	148.3	72.34	67.66	59.96	49.71	59.11 \pm 4.24 d
	G.W		213.33	74	86.33	122.7	150.3	72.81	74.60	66.00	50.37	63.66 \pm 5.79 c
	d.w		147.7	49.7	48	93	97.33	73.63	79.60	62.78	53.60	65.33 \pm 6.21 c
Oshin 20%SG	N.W	50gm/ 100 L water	195.3	51	50	116.7	130.7	79.53	83.93	64.68	52.86	67.16 \pm 7.39 c
	Adw		222.3	58.7	66.7	110.3	134.7	79.30	81.17	70.67	57.32	69.72 \pm 5.63 b
	G.W		183.3	37	41	100.6	110.3	84.18	85.96	67.56	57.62	70.38 \pm 6.77 b
	d.w		192	24.7	36.7	98.7	116	89.92	88.00	69.61	57.44	71.68 \pm 7.25 b
Control			178.7	228	284.7	302.33	253.7	-	-	-	-	-
L. S.D at 5 %												4.43

*The values marked with the same letter are not significantly differentiate 5% level according to The L.S.D Level

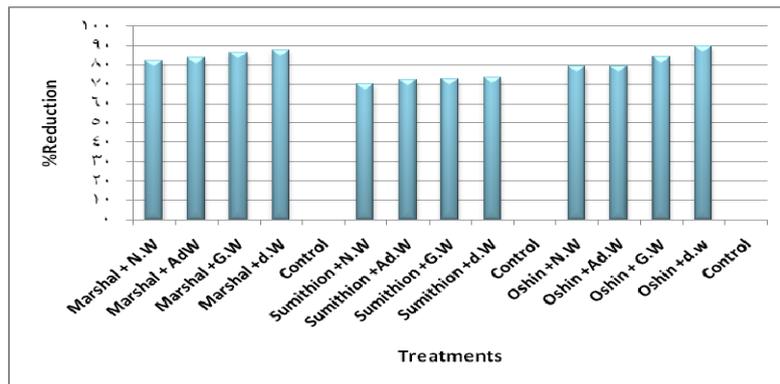


Fig. 4: Initial activity (24 hr.) of the tested insecticides diluted in different carrier water quality against *A. gossypii*

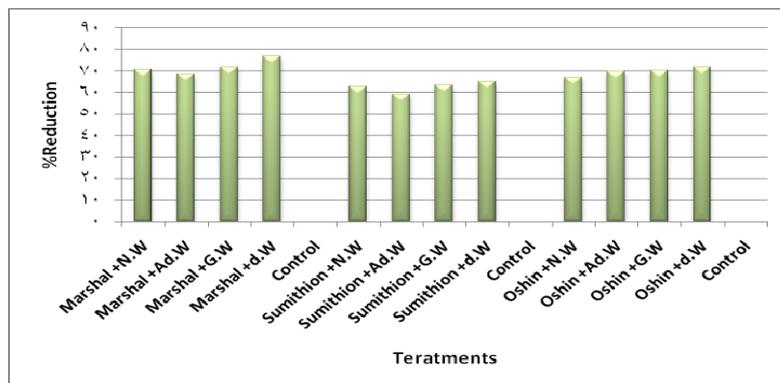


Fig. 5: Residual activity of the tested insecticides diluted in different carrier water quality against *A. gossypii*

In conclusion all the tested insecticides confirmed the highest toxicity in both initial and residual activities after all the time intervals post application (1,3,5 and 7 days) when used distilled water "soft" and ground water "medium hard" as carrier. However produced the lowest effect when diluted in N.W and /or Adw" Hard water".

Variation of these toxicities may be attributed to the change in the physico-chemical properties of the final insecticidal spray solutions, such as salinity and pH as a result of using different type of carrier water. Hard water contain high levels of ions such as Ca^{+2} , Mg^{+2} , Fe^{+3} and other cations (positively charged) attach to negatively charged insecticide molecules, often the association between insecticides and these cations render the insecticide ineffective (Hall *et al.*, 1999). In pervious

studies, Petroff, (2012), illustrated that hard water ions can bind with salts of herbicides and with some surfactants to form an insoluble salt, then fall out of solution decreasing herbicide efficiency (Park & Juang -Horng, 2014). Insecticides, on the other hand can breakdown once mixed with alkaline water, chemical breakdown is termed alkaline hydrolysis and severity and speed in which it occurs is dependent on the pesticides, water alkalinity and temperature. (Nalewja, *et al.*, 1994). Insecticides particularly organophosphates and carbamates are more susceptible to alkaline hydrolysis than other pesticides (park & Juang- Horng, 2014).

Also Petroff (2012) indicated that fungicides such as Bravo and Captan can also inactivate quickly if left in a sprayer tank mixed with alkaline water.

He also pointed that pH 3.5-6.0 satisfactory for most spraying pesticide mixtures, pH 6.1-7.0 adequate for immediate spraying of most pesticides, don't leave the spray mixtures in the tank for over 1 to 2 hours to prevent loss of effectiveness. Also Delorenzo, *et al.* (2009 and 2011) pointed that pesticide toxicity can change with salinity and temperature.

Generally high pH and salinity act together to reduce insecticides stability. On the other hand, turbidity water which has soil particles (clay and silt) can bind with pesticide molecules and harbor microbes that naturally degrade pesticides, and clog filters and nozzles, how to keep it from becoming a problem? Please check the water pH before adding any pesticide and add buffering agents to carrier water whenever necessary. Water should be clean and clear for all pesticide application don't leave the spray mixture in the tank for over 1 to 2hrs to prevent loss of activity. Remember read the pesticide label directions for recommendations and guidance pH range.

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ARABIC SUMMERY

تأثير نوعية الماء الحامل على ثبات المبيدات الحشرية

حنان فاروق السيد عبد الحافظ

معهد بحوث وقاية النباتات - مركز البحوث الزراعية - دقي - جيزة - مصر

هدفت الدراسة الحالية دراسة تأثير كلا من ملوحة الماء ودرجة الأس الهيدروجيني على كفاءة وثبات المبيدات الحشرية. تم قياس الخواص الطبيعية - الكيميائية كنسبة الملوحة ودرجة تركيز الأملاح الذائبة والتوصيل الكهربائي ودرجة الأس الهيدروجيني لأربعة أنواع من المياه، ماء النيل وماء الصرف الزراعي والماء الجوفي (على عمق ١٦م) والماء المقطر. كما تم قياس هذه الخواص لمحاليل المبيدات المرشحة للدراسة كالمرشال ٥٠% EC والسومميثيون ٥٠% EC والأوشين ٢٠% SG عند تخفيفها في أنواع المياه المختلفة. أيضاً تم حساب التركيزات النصفية المميتة (LC₅₀) لمحاليل المبيدات مع جميع أنواع المياه المختبرة. كذلك تم تقدير الإبادة الفورية والأثر الباقي لهذه المبيدات تحت الظروف الحقلية على حشرة من القطن. أظهرت النتائج بوضوح أن كلاً من ماء النيل وماء الصرف الزراعي يحتوى على نسبة عالية من الأملاح الذائبة وسجلت أعلى درجة للأس الهيدروجيني لذا يعتبر كلا من هذه المياه ماء عسر طبقاً للقياسات الدولية لدرجة الملوحة. هذا بالإضافة إلى أن جميع المبيدات المختبرة انخفضت سميتها طبقاً لقيم التركيزات النصفية المميتة، كما انخفضت كلا من الإبادة الفورية والأثر الباقي عندما تم تخفيفها بمياه النيل، ومياه الصرف الزراعي.

ويعزى هذا التأثير إلى أن هذا النوع من المياه يحتوى على تركيزات عالية من الأيونات موجبة الشحنة كأيونات الكالسيوم والمغنسيوم والحديد والصوديوم علاوة على الكاتيونات الأخرى التي بالتالي تنجذب إلى الشحنات السالبة في جزئ المبيد ومن ثم يقل تأثير المبيد وكفاءته الإبادية وثباته. علاوة على أن المبيدات الحشرية خصوصاً الفوسفورية والكريباميت حساسة للتحليل الكيميائي بفعل التحليل المائي في الوسط القلوي ومن جهة أخرى الماء العكر يحتوى على حبيبات عضوية كالطين والسلت والذى ترتبط بجزئ المبيد من جهة ومن جهة أخرى تسد الفلاتر وفتحات آلة الرش هذا بالإضافة إلى التحليل الميكروبي للمبيدات بفعل ميكروبات التربة. وعموماً يمكننا تجنب هذه المشاكل قبل تفاقمها عن طريق استخدام ماء نقي ونظيف في التطبيقات الحقلية للمبيدات وقياس درجة الأس الهيدروجيني لماء التخفيف الحقلية للمبيدات قبل إضافة المبيدات ويمكن إضافة مواد معدلة للحموضة إذا تطلب الأمر ذلك. أخيراً تذكر قراءة الإرشادات على عبوة المبيدات لمعرفة التوصيات الخاصة لدرجة الأس الهيدروجيني لكل مركب.