Disappearance of Thiamethoxam Used on Date Fruits Under Local Conditions of the Kuwait State

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ABSTRACT: Different type of pesticides including thiamethoxam, is widespread against the common pests (insects) in the state of Kuwait. Therefore, the present work aimed to determine the degradation behavior of the thiamethoxam residues on and in date fruits after application on date palm trees at fruiting stage. Two varieties of dates (i.e. Khelas and Burhi) from five farms located in three areas (i.e. Al Wafrah, Ahmadi and Abdali) were treated with thiamethoxam at the recommended rates. Representative samples of the treated fruits were taken randomly at one hour (zero time), 1,3,7,10,15,21,30,48 and 60 days after application for residue analysis. Thiamethoxam residues was determined by GC equipped with ECD. The obtained results revealed that the date fruits variety had an important role in the initial deposits of tested pesticides. Based on the initial deposit, dates of variety Khelas retained higher level of thiamethoxam, than Burhi variety i.e. (4.44,4.81 and 5.01 mg/kg) for Khelas, respectively, whereas they were (4.25,4.53 and 4.64 mg/kg) for variety Burhi, respectively. The range of half- life time (t 0.5) of thiamethoxam, on and in dates palm varieties Khelas and Burhi gave (2.8 - 3.5 and 3.1 - 3.5 days), respectively. All detected residues after 21-30 days were lower than the MRL's of thiamethoxam (0.01 mg /kg). Undetectable thiamethoxam residues was recorded on and in the two varieties of date fruits at the stage of Roteb and Tamir. Such date fruit samples were taken at 48 and 60 days after treatment (at harvest time).

Keywords: Residues; thiamethoxam; dates palm fruits, Kuwait.

1. INTRODUCTION

The use of pesticides in controlling date palm pests in the state of Kuwait is recommended in many cases. The potential risk of the residues of such pesticides to date consumers with health effects could be expected especially with the high consumption of dates especially in Gulf countries. So, more attention was given toward health risks due to pesticide residues. Generally, the information about the levels of pesticide residues in date products is very rare, and the situation calls for the need of more accurate programs for monitoring and detecting the minimum concentrations of pesticide residues before marketing dates to confirm the safety of this important product. Recently, few studies in some Arab countries focused on determination of pesticide residues on and in dates such as **Abdallah *et al*, 2018**, **El-Saied and Al-Doseari, 2010**, **Kamel *et al*, (2007), Suloiman and Osman 2005 & 2003** in the KSA**, Mfarrej *et al*, 2017, Al- Sumarrie and Abo Akela, 2011** in UAE, **Hussain *et al*, 2015** and **Farag *et al*, 2011** in Egypt, **Khan *et al***, 2001 in Sultanate of Oman.

Therefore, the present study aimed to determine the initial deposits and dissipation of thiamethoxam residues on and in date fruits collected from three different locations in Kuwait state. Also, to determine the dissipation rate, half-life values (RL_{50}) and pre-harvest interval (PHI) for the thiamethoxam.

2. MATERIALS AND METHODS

The disappearance study of thiamethoxam, residues on and in date fruits after application on date palm trees at fruiting stage under local conditions of Kuwait State was carried out as follows:

2.1. Pesticides used:

The tested pesticide was thiamethoxam (Tiomex 25% WG), supplied from Sundat (s) PTE. ITD Co. Singapore and applied at the rate of 7 gm/100 L water, for Aphids and Red palm weevil (RPW).

2.2. Experimental farms:

Two varieties (i.e.Khelas and Burhi) of date palm trees were applied by thiamethoxam in five farms (i.e. Casa, Faisal Al - Damak, Alsuhhadaa, Sfaran and Al Waha) located in three areas namely Al Wafra (north country), Al Ahmadi (middle of the country) and Al Abdali (south country) (Fig.1).

2.3. Design of experiment:

The date palm trees used in the present study were about 15 years old. The date palm trees received the normal agronomic practices throughout the experimental period. Every ten randomized date palm trees of. Khelas and Burhi were treated with one of the experimental formulations (i.e. thiamethoxam) on summer 2016. Inside the experimental area (50 m^2) 10 tree of every variety were left without treatment as untreated check and for recovery purposes. A spray motor with long hand equipped one nozzle was used for applying the tested pesticides. Random samples from 10 palm trees at the four corners and middle sections of the area were chosen to collect about 300 g date fruits from each varieties of palm tree. Representative samples of yellow fruits, roteb and tamir were taken at random one hour after application, 1, 3,7,10,15, 21, 30, 48 and 60 days after treatment for thiamethoxam residue analysis. Sub sampling was done where three representative samples of 100 g of treated dates were taken. Subsamples

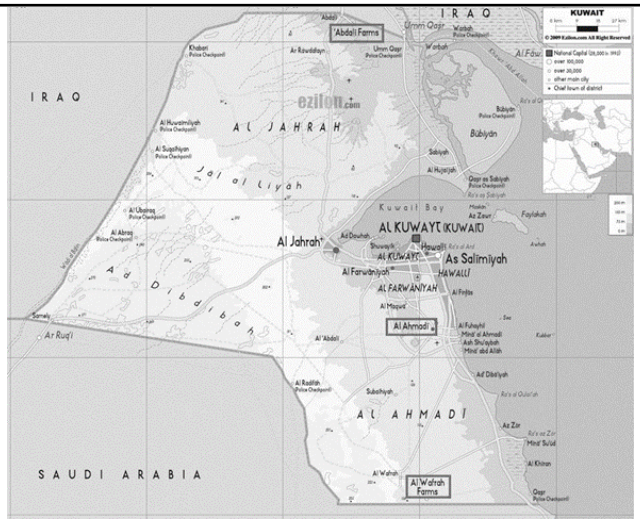

Fig. (1) Map of Kuwait, show the three areas of investigation (Al Abdali, Al Ahmadi and Al Wafra)

were kept in clean polyethethylene bags and stored at -20 °C in a deep freezer until the time of residue analysis. A control treatment was also collected for analysis as the same of the treated fruits.

2.4. Residue analysis:

Analyses of tested pesticides were carried out in the Central Agricultural Pesticide Laboratory, (CAPL), and ARC, Cairo, Egypt.

2.5. Extraction and clean-up of pesticides residues:

Extraction and clean-up of thiamethoxam residues was done by using a modified QuEChERS method (**Paya *et al*, 2007**). A sample of 10 g of date flesh was extracted with 10 ml of acetonitrile (acidified with 1% acetic acid) in 50 ml falcon screw cap tubes.Tubes were vortexed for 1 min.Then 1 g of sodium chloride and 4 g of magnesium sulfate anhydrous were added. Samples were vortexed for10 min and then centrifuged for 10 min at 4000 rpm and 4 ºC. Aliquots of 1 ml of the supernatant were transferred into 15 ml centrifuge tubes for clean up by dispersive solid-phase extraction with primary secondary amine (PSA; 25 mg), graphite carbon black (GCB; 10 mg), and $MgSO_4$ (150 mg). The tubes were vortexed for 10 min and then centrifuged as mentioned before. The supernatant was filtered through 0.22 ml PTFE filter (Millipore, USA) into a 1.5 ml amber HPLC glass vial, and kept at -20ºC until analysis of CPM and IMD. For FIP, 1 ml of the supernatant after centrifugation was dried at 35–40 ºC under a gentle current of nitrogen and the residue was redissolved in 2 ml of toluene. Then samples were filtered in the PTFE filters as mentioned above.

2.6. Determination of active ingredient Thiamethoxam by GLC:

Residues were determined by an Agilent series 6890N gas chromatography (GC), equipped with electron capture detector (ECD). The column was PAS-5, (30 m x 0.25 mm x 0.25 µm film thicknesses) and the injection port temperature was 290 0C, initial temperature 200 ^{0}C for 2 min, 5 min, up to 270 ^{0}C and the detector temperature 300 ^{0}C. The carrier gas was nitrogen at a flow rate of 3 ml/min. Retention time: 5.9 min..

2.7. Standards and recovery experiment:

Standard pesticides were purchased from Chem Service (West Chester, PA, USA). Trifluoroacetic anhydride (TFA) and 1-methylimidazole were purchased from Sigma chemical company (St. Louis, MO, USA). All solvents were of HPLC grade. Chemicals and reagents were of analytical grade. Analytical standards were prepared from a stock solution of 1000 µg/ml. Dilutions were carried out to obtain three levels of concentration containing 50,100 and 250 ng of Thiamethoxam. The standards were then dried under a stream of nitrogen and the reagents were added as described previously and injected to the GC system from which a calibration curve was constructed. Concentration levels for the calibration of Thiophanate-methyl were 1, 0.2, and 0.02 µg/ml and those for Bifenzate were 1, 0.5, and 0.1 µg/ml.

Recovery studies were carried out by spiking 3 replicates of untreated date samples (control) with 50, 100, and 50 µg/kg of Thiamethoxam, Samples were analyzed using their prescribed procedure and mean values of the three replicates were calculated. Recovery percentages were satisfactory for the three pesticides and ranged from 92% to 101%. The minimum detection limits of Thiamethoxam, was 0.005, 0.001, and 0.003 mg/kg, respectively.

2.8. Statistical analysis:

All obtained data were subjected to statistical analysis and graphically illustrated according to **Timme and Frehse, 1980** .The half-lives ($t_{0.5}$) and tenth-lives)$t_{1/10}$) were calculated mathematically according to **Moye *et al*, 1987** from the following equation:

$T_{(1/2)}$ =Ln 2/k ,$t_{(1/10)}$= Ln 10/k ,k_0/1) = t_x). Ln a/bx, k_0 :is the degradation rate constant at the intervals in an hour, k: is the mean of k_0 ,a: the residue level at the initial time (zero time), bx: is the residue level at the successive intervals in an hour.

3. RESULTS & DISCUSSION

3.1. Degradation of thiamethoxam residues on and in date fruits:

3.1.1.Residues of thiamethoxam:

Data in Table (1) and Fig (2) Showed the initial deposits of thiamethoxam determined one hour after application on and in date fruits of Khelas and Burhi varieties collected from five farms (Casa, Faisal Al – Damak, Al Shuhadaa, Sfran Farm and Al Waha Farm) recording 4.44, 4.25, 4.81, 4.53, 5.01 and 4.64 mg/kg), respectively.

These amounts rapidly decomposed after 24 hours from treatment to reach 3.32, 3.05, 3.26, 3.6, 3.9 and 3.32 mg/kg, respectively. Following that period, thiamethoxam residues on and in date fruits of Khelas variety collected from Casa Farm, Al Shuhadaa Farm and Sfran Farm were decreased to (2.76, 1.63, 0.75, 0.31 and 0.09 mg/kg), (2.1, 1.25, 0.76,0.26 and 0.05 mg/kg) and (3.9, 2.84, 1.78, 0.91, 0.49 and 0.12 mg/kg) at 3, 7, 10,15 and 21 days after application, respectively. While thiamethoxam residues on and in Burhi fruits collected form Faisal Al - Damak Farm, Al Shuhadaa Farm, El-waha Farm) decreased gradually to (2.27, 1.44, 0.89, 0.26 and 0.08 mg/kg), (2.65, 1.65, 0.61, 0.25 and 0.05 mg/kg) and (2.77, 0.611.64, 0.85, 0.35 and 0.13 mg/kg), at the same intervals periods, respectively.

Samples of Khelas and Burhi dates (Roteb and Tamir), taken 30, 48, 60 days after treatment (at harvest time) contained no detectable amounts of thiamethoxam.

Fig. (2) illustrated that, the residue half-life ranged from 2.8 to 3.5 and 3.1 to 3.5 days on and in Khelas and Burhi varieties, respectively. All of the detected residues were lower than MRL (0.01 mg/kg) at the harvest time. On the other hand, the obtained range of pre-harvest intervals (PHI's) was 25-28 days after application on khelas and or Burhi varieties.

Reviewing the obtained results, it could be proved that, the residues of the tested pesticides not detected at the harvest time. Dates of Khelas variety retained the higher level of thiamethoxam, thiophanate methyl and bifenzate deposit than Burhi variety. The corresponding data were (4.44,4.81 and 5.01 mg/kg), (2.72, 3.79 and 5.1 mg/kg) and (1.1,1.15 and 1.3 mg/kg), respectively, while dates of Burhi variety retained levels of (4.25,4.53 and 4.64 mg/kg), (2.47, 3.54 and 4.48 mg/kg) and (0.84,0.87 and 0.91 mg/kg), respectively. Such data demonstrate the effect of the treated surface on the initial pesticidal deposit and hence confirm that the type of variety had an important role on the initial deposits of pesticides after treatment.

The obtained results also showed that the initial deposits of thiamethoxam in dates of two tested varieties Khelas and Burhi were higher than that recorded in thiophanate methyl and bifenzate. Undetectable thiamethoxam, thiophanate methyl and bifenzate residues were recorded on and in Khelas and Burhi varieties dates (Roteb and Tamir), taken 48 and 60 days after treatment (at harvest), respectively.

The disappearance of pesticides from date palms as well as other plants may occur initially according the law of first order kinetics, but it is usually a two or more-step reaction with an initial phase that has been termed dissipation and slower phase called persistence. The first phase is probably due to volatilization, adsorption or translocation and the second to chemical, photochemical and microbial degradation.

The obtained results are in agreement with those obtained by **Khan *et. al* (2001), *Al*-Rehiayani and Osman (2005), kamel *et. al*. (2006), AbdRabou *et al.* (2015), El-Tokhy and Amer (2017) and Abbassy *et al.* (2017).** Other pesticide residues and degradation behavior in date palm fruits were determined by different researchers such as dimethoate **(Khan et al, 2001),** dicofol **(Al-Rehiayani and Osman, 2006),**

Table (1): Degradation pattern of thiamethoxam on and in Khelas and Burhi varieties after application at the rate of 7g /100L water under field conditions in certain farms located in different areas in Kuwait, during summer season 2016.

Times after application	Levels of Residues (mg/Kg)					
	El-alwafra area		Al Ahmadi area		El-Abdali area	
	Casa Farm	Faisal Al - Damak Farm	Al Shuhadaa Farm	Al Shuhadaa Farm	Sfran Farm	El-waha Farm
	V. Khelas	V. Burhi	V. Khelas	V. Burhi	V. Khelas	V. Burhi
Zero time	4.44	4.25	4.81	4.53	5.01	4.64
1 day	3.32	3.05	3.26	3.60	3.90	3.23
3days	2.76	2.27	2.10	2.65	2.84	2.77
7 days	1.63	1.44	1.25	1.65	1.78	1.64
10 days	0.75	0.89	0.76	0.61	0.91	0.85
15 days	0.31	0.26	0.26	0.25	0.49	0.35
21 days	0.09	0.08	0.05	0.05	0.12	0.13
30 days	ND	ND	ND	ND	ND	ND
48 days*	ND	ND	ND	ND	ND	ND
60 days (harvest)**	ND	ND	ND	ND	ND	ND
t0.5(days)	3.2	3.1	2.8	3.1	3.5	3.5
MRL			0.01			
PHI(days)	26	26	25	25	28	28

* :(Roteb) ** :(Tamir)

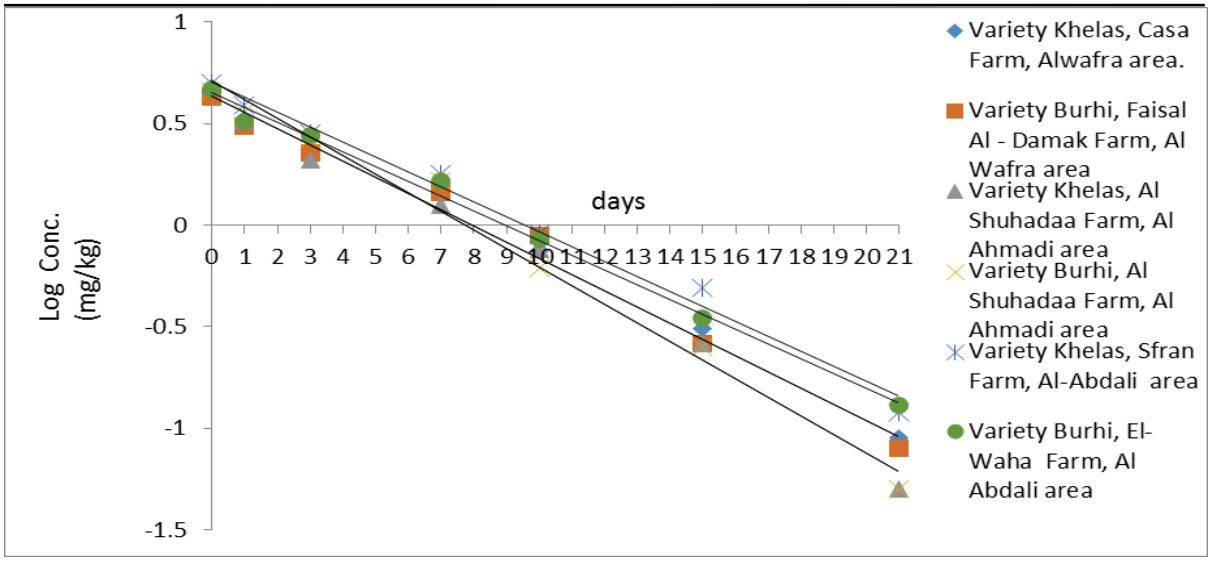

Fig (2) Dissipation lines of thiamethoxam under field conditions on and in Khelas and Burhi varieties after application in five farms located in different areas in Kuwait during summer season 2016.

abamectin, flufenxuron and amitraz **(Kamel *et al*, 2007), chlorpyrifos, diazinon and fipronil (AbdRabou *et al*, 2015),** chlorpyrifos **(El-Tokhy and Amer, 2017)** and chlorpyrifos-methyl **(Abbassy *et al*, 2017).**

The results obtained proved the importance of detecting the residue levels of pesticides in sample of dates before being marketed. Also, monitoring pesticide residues in dates helps to assess the potential risk of pesticides to consumers.

REFERENCES

Abbassy, M.A., Y.M.M. Salim, M.S. Shawir and A.M.K. Nassar (2017). Disappearance and hazard quotient of chlorpyrifos-methyl, fipronil, and imidacloprid insecticides from dates. Journal of Consumer Protection and Food Safety, 1-8.

Abdallah,O.I. S.S. Alamer and A.M. Alrasheed (2018). Monitoring pesticide residues in dates marketed in Al-Qassim, Saudi Arabia using a QuEChERS methodology and liquid chromatography–tandem mass spectrometry. Biomedical Chromatography. 2018; **32**:e4199. Avilable at: wileyonlinelibrary.com/journal/bmc, https://doi.org/10.1002/bmc.4199

AbdRabou. E.H., S.F. Elsharabasy and W.L. Abouamer (2015). Estimation of insecticide residue in date palm fruits after controlling the red palm weevil. Int. J. Food Nutr. Sci. 4 (5): 27–31.

Adnan I. Al Samarrie, A.I., and A. Abo Akela (2011). Distribution of injected pesticides in date palm trees. Agriculture and Biology Journal of North America. Avilable at: Science-Huβ, http://www.scihub.org/ABJNA

Al-Rehiayani S., and K.A. Osman (2005). Fate of preharvest-prayed dicofol in date fruits: Residue analysis by HPLC. Agric Mar Sci 10: 21-26. 7.

EL-Saeid, M.H. and S. A. AL-Dosari (2010). Monitoring of pesticide residues in Riyadh dates by SFE, MSE, SFC, and GC techniques. Arabian Journal of Chemistry, 3, 179–186.

El-Tokhy and Amer .(2017) Residues of Chlorpyrifos Insecticide in Date Fruits after Controlling of Red Palm Weevil in New Valley, Egypt. *J. Plant Prot. and Path., Mansoura Univ., Vol.8 (9), 459 – 465, 2017.*

Farag, R.S., M.S. Abdel Latif, A.E. Abd El-Gawad and S.M. Dogheim (2011). Monitoring of pesticide residues in some Egyptian herbs, fruits and Vegetables. International Food Research Journal 18: 659-665.

Hussain, A.E., S. F. Elsharabasy and W.L. Abouamer (2015). Estimation of insecticide residue in date palm fruits after controlling the red palm weevil. International Journal of Food and Nutritional Sciences, Vol.4, Iss.5, Oct-Dec, 2015.

Kamel, A., S. Al-Dosary, S. Ibrahim and M.A. Ahmed (2007). Degradation of the acaricides abamectin, flufenoxuron and amitraz on Saudi Arabian dates. Food Chem 100:1590–1593.

Khan, A.J., K.M. Azam and S.A. Razvi (2001). Pesticide residues analysis of date palm fruits by gas chromatography mass spectrophotometry. In: Proc Second International Conference on Date Palms, Al-Ain, UAE, March 25–27, 211–215, Available at: https://www.pubhort.org/datepalm/datepalm2/datepalm2_27.pdf

Mfarrej, M.F., K. Al-Darmaki, A. Al-Dhanhani and E. Afach (2017). Determination of Pesticide Residues on Date Palm in the UAE. International Journal of Applied Engineering Research, Volume 12, Number 16: 6012-6021.

Moye, H. A.; M. H. Malagodi; J. Yoh; G. L. Leibee; C. C. Ku and P. G. Wislocki (1987). Residues of avermectin B1a rotational crop and soils following soil treatment with (^{14}C)

avermectin B1a.J. Agric. Food chem., 35:859-864.

Paya, H., A. Taghizadeh, H. Janmohammadi and G.A. Moghadam (2007). Nutrient digestibility and gas production of some tropical feeds used in ruminant diets estimated by the in vivo and in vitro gas production techniques. Amer J Anim Vet. Sci. 2:108–113.

Suleiman, A., and K.A.Osman (2005). Fate of pre-harvest sprayed dicofol in date fruits: residue analysis by HPLC-UV. Agric. Mar. Sci. 10, 21–26.

Suloiman, A., and K.A.Osman (2003). Residue levels of pre-harvest sprayed amitraz in date fruits (2003). J. Pestic. Control Environ. Sci. 11 (1), 1–12.

Timme, G. and H. Fisher (1980). Statistical interpretation and graphic representation of the degradationed behaviour of pesticide residues. Pflanzenschutz Nachrichten Bayer, 33(1):47-60.

اختفاء مبيد ثيموثوكسام على التمور تحت الظروف المحلية بدولة الكويت

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الملخص العربي

يوصى باستخدام المبيدات التقليدية لمكافحة آفات نخيل التمر بدولة الكويت، وينتشر استخدام أنواع مختلفة منها بما في ذلك مبيد ثيموثوكسام، تجاه الآفات الشائعة (حشرية)، ولذا فإن الهدف من هذه الدراسة هو تقدير سلوك الهدم والتدهور لمتبقيات المبيد ثيموثوكسام على الثمار بعد التطبيق على النخيل في مرحلة الإثمار. تم معاملة صنفين من التمور هما الخلاص والبرحى في خمس مزارع موجودة في ثلاث مناطق بشمال ووسط وجنوب الكويت (هي العبدلي، الأحمدي، الوفرة) بالمبيد المختبرة، وذلك بالمعدلات الموصي بها. أخذت عينات ممثلة من الثمار المعاملة عشوائيا بعد ساعة واحدة، 1، 3، 7، 10، 15، 21، 30، 48، 60 يوما من التطبيق لتحليل المتبقيات. أوضحت النتائج المتحصل عليها تأثير الدور الهام للصنف على كمية الراسب الأولي، وبناء على هذه القيمة الأخيرة وجد أن صنف الخلاص قد أحتفظ بمستوى أعلى من رواسب المبيدات عنها من صنف البرحى، وذلك لكل من الثيموثوكسام حيث بلغت (4,44، 4,81، 5,01 ملليجم/كجم)، على الترتيب لصنف الخلاص، بينما بلغت (4,25، 4,53، 4,64 ملليجم/كجم) على الترتيب لصنف البرحى. وتراوحت قيم فترة نصف العمر لكل من الثيموثوكسام على وفى أصناف التمور الخلاص والبرحى (2.8 – 3.5- 3.1 – 3.5 يوم)، على الترتيب. وبالنسبة للحدود القصوى المسموح بها (MRL's) لمبيد ثيموثوكسام (0.01 mg/kg)، فقد دلت النتائج على انخفاض مستويات المتبقيات عنها بعد 21- 30 يوما بعد المعاملة، ولم يمكن الكشف عن متبقيات المبيد في كل من صنفي الخلاص والبرحى (رطب وتمر) بعد 48، 60 يوم من المعاملة (وقت الحصاد).