

Environmental Studies on Ametryne Herbicide. Photodegradation,
Dehydrogenase Activity, and Phosphorus Mineralization
in Treated Soil.

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ABSTRACT

Photodegradation of ametryne was evaluated by determining the residues after photolysis using gas liquid chromatography. The residue of this compound was degraded as dry film by 62.5% of the tested amount within 18 hr of exposure to sun light. The percent degradation achieved after 45 hr of exposure on soil surface was 67. Ametryne treatments stimulated dehydrogenase activity in clay loam soil. The technical grade gave the highest stimulation, however the dehydrogenase activity as formazan contents were 157.7, 104.4 and 52.0 ppm with ametryne technical grade, ametryne WP formulation and untreated control treatments, respectively. The effect on phosphorus mineralization during the study showed that ametryne technical grade was more effective than WP formulation as inhibitor to this biological process. The mean effect at the end of experiment indicated that ametryne technical grade had an depressing effect while its WP formulation had no effect. The available P_i was 48.95, 54.42, and 56.62 ppm for technical grade, WP formulation and control respectively.

INTRODUCTION

Herbicides are now widely used as pre-and postemergence weed control in Egyptian agriculture. ametryne is one of these herbicides. The residues of these chemicals are being lost in treated soil by the effect of various processes. Photodegradation on soil surface (1) is one of these processes which results in an effect on the persistence of pesticide. In addition chemical structure and soil type also affect this persistence (2,3,4). The effect of pesticide on soil enzymes such as soil dehydrogenase and on phosphorus mineralization are considered among other factors as indicators for the soil biological activity (5, 6).

The present study was carried out to investigate the photodegradation of ametryne on both plates and clay loam soil surface. The study involves also the determination of ametryne effects on the activity of soil dehydrogenase and the production of available phosphorus in clay loam soil.

MATERIALS AND METHODS

Tested Herbicide: Ametryne (Gesapax 80% WP): 2-ethylamino-4-isopropylamino-6-methylthio-s-triazine.

Soil Samples: Clay loam soil was collected from the research Station of Alexandria University at Abis region. Surface soil samples (0-15 cm) of the cultivated soil were airdried and sieved

through a 2. mm (10 mesh) screen. The physical and chemical properties are previously determined (11).

Gas Liquid Chromatography: Shimadzu gas chromatograph equipped with flame photometric detector was used. The chromatographic conditions were: column 2 mx 4 mm id; SE30 packed on chromosorb C temperature (C). column 250 isothermal. injection block 260, detector 280; gas flows (ml/min)-carrier nitrogen 40, hydrogen 0.8, oxygen 1-0; filler 398 nm, specific for sulfur; 10 ul injected equivalent to 25 mg sample; limit of detection 5 ng (0.2 ppm).

Preparation of Soil Layer Plates: One milliliter of herbicide solution was added to 20 grams of sieved soil to give a concentration of 100 ug/gm soil. Distilled water was added to obtain a slurry similar to heavy cream (1). The slurry was spreaded on 20 x 20 cm glass plates and then were allowed to air dry.

Exposure to Sun Light: The soil plates contaminated with ametryne were exposed to sun light through out the day for the intervals of 6, 21, 30, and 45 hr of exposure to sun light. Another experiment involved an exposure of Ametryne as dry film in petri dishes for 1, 3, 12, and 18 hr to sun light using the concentration of 300 ug per each dish was carried out.

Extraction, Clean-Up, and Determination of Ametryne (7):

The soil samples were extracted using methylene chloride at solvent ratio of 5 ml/gm soil. The content was shaken for one hour, and then filtered. The filtrate was evaporated to dryness, dissolved in 5 ml benzene and then subjected to alumina column chromatography (25 gm) for clean up. Ametryne residues were eluted from this column using hexane-di ethylether (150 ml) and the eluents were concentrated and then subjected to gas liquid chromatography.

Effect of Ametryne on Soil dehydrogenase and Phosphorus Mineralization:

Clay loam soil was sampled from a depth of 0-15 cm from the Alex. Agric. Fac. Farm, Kaiaa region that is previously cultivated with sorgham forage and free from pesticides. Air dry soil was crushed, sieved and its some physical and chemical characteristics are previously determined (1) as following: sand: 30%, silt: 32%, clay: 35%, clay loam texture, w.h.c.: 46%, pH 8.6, and CaCO₃: 10.1%. Soil was divided into three sets, one is treated with the aqueous solution of herbicide ametryne WP formulation (2-ethylamino-4-isopropyl-amino-6-methylthio-s-triazine) at the rate of 2 ppm, the second set is treated with 2 ppm of ametryne technical grade in acetone, while the

third one is considered as control treatment. Upon drying, the soil samples were well mixed and then transferred to 250-ml. Erlenmeyer flasks. Soil water content was kept at 60% of w.h.c. and the flasks were closed and incubated in the laboratory and maintained at 24±1°C. Available Pi(8) and dehydrogenase activity (9) as formazan yield were evaluated after 5, 10, 15 and 20 days post-treatment. The results were calculated on air-dry weight basis and statistically analysed according to the split-plot design.

RESULTS AND DISCUSSION

Standardization of Analytical methods:

Gas liquid chromatography using flame photometric detection system (FPD) and SE-30 as a stationary phase was applied with a reasonable chromatographic performance. The GLC response was 2.5 mm/ng and the average of detection limit was 0.20 ppm (Table 1). High recovery (84.2%) of Ametryne residues from clay loam soil was achieved (Table 1), where Me Cl, alumina column and GLC were used for extraction, clean-up and determination of Ametryne respectively. The colourimetric assay of formazan as an indicator to the activity of dehydrogenase was applied. The range of concentration was 10-100 µg in 10 ml acetone (Table 1). Concentration of inorganic Pi was determined colourimetrically. The range of standard inorganic phosphorus was 5 to 50 µg.

Photodegradation of Ametryne:

Table 2 shows the residue amounts of Ametryne left after exposure in petri dishes to sun light at different time intervals as well as the corresponding percent photodegradation. The data indicate that the residue level was 211.5, 200.9, 153.3 and 112.5 ppm after 1, 3, 12 and 18 hr of exposure to sun light respectively. The corresponding % photodegradation was 29.5, 33.1, 48.9 and 62.5. Table 3 shows the Ametryne concentration and % photodegradation when exposed to sun light on soil surface for different time intervals. The concentration of Ametryne on soil surface was 39.5, 34.9, 34.1 and 33.0 ppm after 2, 21, 31 and 45 hr of exposure respectively, the corresponding % photodegradation was 60.5, 65.1, 65.9 and 67.0 respectively. The present results report that the initial photodegradation of Ametryne on soil surface was faster than on petri dish this may be explained on basis that the catalytic effect on soil surface takes a role. The photolysis of Ametryne as triazine herbicide can be supported by results of other investigators atrazine is converted to deethylated- and deisopropylated triazine (10). The present results are also comparable with those obtained for other triazine herbicides. 67% of Atrazine and 68% of prometryne were photodegraded after 96 hr of exposure to sun light (11).

Effect of Ametryne on Phosphorus Mineralization Clay Loam Soil:

Results in Table (4) show that both WP formulation and technical grade of ametryne treatments decreased the production of inorganic available P after 5 and 20 days of treatment indicating that ametryne technical grade was the most effective inhibitor at the 20 th day. However, the mean effects at the end of study showed that ametryne technical grade had an depressing effect (48.95 ppm P) while its WP formulation had no effect. The highest influence of treatments on P_i production appeared at 10 days, while the least action was achieved at the first sampling.

Effect of Ametryne on Soil Dehydrogenase Activity:

The highest effect of treatments on dehydrogenase activity was shown at the second period of sampling, while the lowest action was resulted after 20 days of evaluation (Table 5). It is clear that the ametryne treatments stimulated dehydrogenase activity at the periods of experiment. It is concluded that technical grade appeared to have the highest stimulation where the dehydrogenase activity as formazan contents were 157.73, 104.41, and 52.00 ppm with ametryne technical grade, ametryne WP formulation and control treatments, respectively.

This study indicated that ametryne had influences on soil microbiological processes and may have adverse effects influencing soil fertility. This is in agreement with other reports (11). Also, the results show that the effect of ametryne formulation on soil biology is different with that obtained by its technical grade corroborating the importance of the additives in the formulation of a herbicide to affect the behaviour of the pesticide. This result is agreed with those shown by others (12, 13).

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Table 1. Standardization of Analytical Methods For Ametryne and its Biological Activity

Analytical Parameter	Value Corresponding to Each Parameter
GI ⁵⁰ - Response of ametryne	0.5 mm / ng
GI - Detection limit of ametryne	0.2 ppm
Recovery of ametryne of soil	84.2 %
Concentration range of ametryne	
- 0.0001 to 0.01	0.001 to 0.9
Concentration range of ametryne in soil	0.001 to 0.01

Table 2. Photodegradation of Ametryne Herbicide on Dry Fall in Petri Dish After Different Time Intervals at Exposure to Sun Light

Time (hrs)	Ametryne (ug/dish)	% of Ametryne remaining	% degraded
0	300.0	100.0	0.0
6	200.9	66.9	33.1
12	153.7	51.2	48.9
18	112.5	37.5	62.5

* 300 ug of Ametryne were used for each petri. dish.

Table 3: Photodegradation of Ametryn * Herbicide on Soil Surface at Different Time Intervals of Exposure to Sun Light.

Time of Exposure (hr)	Ametryne residue Found , ppm	% of Ametryne	
		Remained	Degraded
6	39.5	39.5	60.5
21	34.9	34.9	65.1
30	34.1	34.1	65.9
45	33.0	33.0	67.0

The analysis was carried for 10 g soil containing 1000 ug of herbicide (100 ppm).

Table 4: Effect Ametryne WP formulation and its technical grade on available Pi in clay loam soil.

Days	Treatments			Mean
	Ametryne			
	Control	WP formulation technical grade		
	Available Pi; ppm			
5	41.34+1.15 ^a	36.74+0.25 ^b	36.40+1.60 ^b	38.16 ^c
10	64.18+4.19 ^a	66.55+3.06 ^{ab}	61.43+0.53 ^b	64.05 ^a
15	53.54+1.55 ^a	52.47+0.94 ^b	42.74+2.22 ^b	49.58 ^b
20	67.43+1.56 ^a	61.90+1.82 ^b	55.21+1.57 ^c	61.51 ^a
	L.S.D. = 2.9510 (at 0.05)			L.S.D. = 6.3573
Mean	56.62 ^a	54.42 ^a	48.95 ^b	
	L.S.D = 3.1786 (at 0.05)			

Table 5: Effect Ametryne WP formulation and its technical grade on dehydrogenase activity in clay loam soil.

Days	Treatments			Mean
	Ametryne			
	Control	WP formulation	Technical grade	
	Available F ; ppm			
5	57.90+2.44 ^c	82.75+4.20 ^b	133.22+5.97 ^a	169.70 ^b
10	79.77+3.13 ^c	156.04+4.39 ^b	273.29+6.94 ^a	84.26 ^a
15	34.42+2.63 ^c	98.37+7.48 ^b	119.99+4.82 ^a	84.26 ^{bc}
20	35.91+2.06 ^c	82.49+1.62 ^b	104.40+6.33 ^a	74.27 ^c
	L.S.D. = 12.5755 (at 0.05)			L.S.D. = 16.3084
Mean	52.00 ^c	104.91 ^b	157.73 ^a	
	L.S.D = 8.1542 (at 0.05)			

ملخص عربي
 "دراسات بيئية على مبيد الحفائف أمترين"
 التحطيم الضوئي ونشاط انزيم ديهيدروجيناز
 ومعدنة الفوسفور في التجربة المعاملة

تم تقييم التحطيم الضوئي لمبيد أمترين بتقدير متبقيات بعد التحطيم الضوئي ، باستخدام التحليل الكروماتوجرافي بالغاز . ولقد تحطمت متبقيات هذا المبيد بمقدار ٦٢.٥ ٪ خلال ٨١ ساعة من التعرض للضوء على هيئة - فيلم جاف في طباق بخرى بينما تحطم ٦٧ ٪ من متبقياته عندما عرض للشمس لمدة ٤٥ ساعة على سطح التجربة الطبيعية أظهرت معاملات الامترين زيادة في نشاط انزيم الديهيدروجيناز في التجربة الطبيعية وكانت الزيادة في حالة المادة النقية من المبيد الملامس في حالة المبيد المجز على صورة مسحوق قابل للبلل . كانت قيم الفوازان الدانه على نشاط الانزيم هي ١٥٧٧ ، ١٠٤٤ ، ٢٥ جزء في المليون المقابلة للمعاملات المادة النقية للامترين ، المسحوق القابل للبلل للامترين ، الكونترول على التوالي . أظهرت النتائج ان المادة النقية للامترين أكثر تأثيرا كمنشط لمعدنة الفوسفور في التجربة عن المسحوق القابل للبلل للامترين أثناء التجربة بينما في نهاية الدراسة كانت النتائج تبين ان المادة النقية للامترين ذات تأثير مشيط بهذه العملية الطبيعية بينما المسحوق القابل للبلل لا يوجد بينه وبين الكونترول فروق جوهرية ومنه يمكن ان قيم الفوسفور السطحي في وقت ٤٨٢٥ ، ٥١٣ ، ٢٢٩ جزء في المليون للمادة النقية ، المسحوق القابل للبلل سيمترين تم الفوسفور على التوالي .