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DEGRADATION OF CLETHODIM, FLUAZIFOP-P-BUTYL AND QUIZALOFOP-P-ETHYL UNDER DIFFERENT ENVIRONMENTAL FACTORS

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ABSTRACT

Clethodim, fluazifop-butyl and quizalofop-p-ethyl are selective herbicides which are used for the control of grass weeds in a wide range of broadleaf crops. Degradation by temperature, sunlight, UV-light and pH as environmental factors affecting these herbicides in the present investigation was studied. A sensitive high-performance liquid chromatography (HPLC) procedure was used for the quantitative determination of the tested herbicides.

Results of p-value showed that ethyl acetate was the most proper solvent for extraction. Recovery of fluazifop-butyl and quizalofop-p-ethyl from the water phase was 91.3% and 85.6%, respectively. While methylene chloride gave the highest p-value for clethodim with 89.6% recovery. Fluazifop-p-butyl showed more persistence when exposed to direct sunlight.

Statistically, the half-life time for clethodim, fluazifop-p-butyl and quizalofop-p-ethyl was 3.12, 8.0 and 4.48 hours, respectively after exposing to direct sunlight. Also, the half-life time for clethodim was 12.9, 9.0 and 6.2 days at 50, 60 and 70 °C, respeetively. The corresponding values for quizalofop-p-ethyl were 10.9, 8.5 and 5.9 days. The obtained results showed that fluazifop-p-butyl was more stable to temperature than the other two tested herbicides at the end of

the experiment (12 days).

Fluazifop-p-butyl was more persistent to UV-light than the other tested herbicides. The half-life times for clethodim, fluazifop-p-butyl and quizalofop-p-ethyl as dry thin film were 10.6, 70.4 and 39.8 hours, respectively.

All the tested herbicides were hydrolyzed more rapidly in alkaline media (pH 8.0) than the other tested pH degrees. On the contrary fluazifop-p-butyl showed more persistence to all pH solutions than the other two tested herbicides. The half-life time for clethodim was 4.70, 30.35 and 2.67 at pH 5.0, 7.0 and 8.0, respectively. The corresponding values for quizalofop-p-ethyl were 8.82, 16.63 and 2.0 days. On the other hand, the half-life time for fluazifop-butyl was 34.36 and 2.80 days at pH 5.0 and pH 8.0 respectively.

Key words: *clethodim, environmental factors, fluazifop-butyl, quizalofop-p-ethyl.*

1. INTRODUCTION

Today the distribution of herbicides is over large areas and its deposition is now a common phenomenon (Torstensson, 1994). Residues are found in soil, surface and ground water and sediments (Fielding *et al.*, 1991; Helweg, 1994). Transport through the air and deposition is one of the main sources of contamination of agricultural and non-agricultural areas. Sensitive techniques for the chemical analysis of these substances have been developed. This makes it possible to identify their residues in any part of the environment at lower and lower limits.

Persistence of a chemical is usually a reflection of its resistance to decomposition. Detection limit is very different for different chemicals, and it often takes a very long time to follow up its break down to residues close to the detection limit. The time needed for decomposition to 50% (half-life, D_{50}) and / or to 90% (D_{90}) can be used instead of chemical analysis, and can often show its persistence often given instead. A number of factors may influence persistence time for an environment, and decomposition may be of abiotic and / or biotic nature (Torstensson, 1993).

Herbicides from the aryloxyphenoxyproppanoate group (*e.g.*, diclofop-methyl, fenoxaprop-ethyl, quizalofop-ethyl, fluazifop-p-butyl), and the cyclohexanedione group (*e.g.*, tralkoxydim, sethoxydim, clethodim) normally can be used to control graminaceous weeds in a range of broadleaf crops. Fluazifop-p-butyl and quizalofop-ethyl are rapidly hydrolyzed to acid and translocated in the plants where they conjugate to carbohydrates and lipids (Hendley *et al.*, 1985; and Bewick, 1986). Clethodim is a new selective cyclohexanedione herbicide which is effective against a wide range of annual and perennial grasses and has little or no activity against broadleaf weeds and sedges. It exerts its activity by inhibiting acetyl coenzyme A carboxylase (Rendina and Felts, 1988).

The ultraviolet component of sunlight, which varies in wave length from 240 to 400 nm, is responsible for pesticide photolysis in the environment. Both heat and light might affect the efficiency of pesticides, which are measured by the duration of their residual effect.

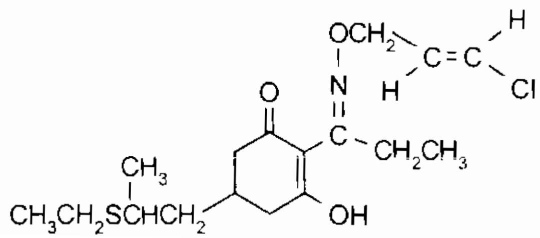
The present study was carried out to investigate the effect of temperature, UV-light (short waves 254 nm) and direct sunlight on stability of clethodim; fluazifop-p-butyl and quizalofop-p-ethyl.

The aims of this study were: 1- to determine the p-value of clethodim; fluazifop-butyl and quizalofop-p-ethyl for different water / organic solvent systems. 2- to investigate the effect of temperature, sunlight and UV-light on persistence of these herbicides. 3- to study the effect of pH and hydrolysis on their persistence.

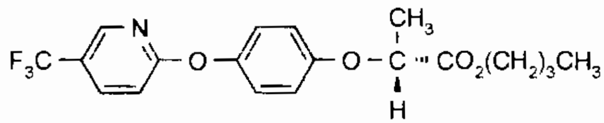
2. MATERIALS AND METHODS

2.1. Herbicides used

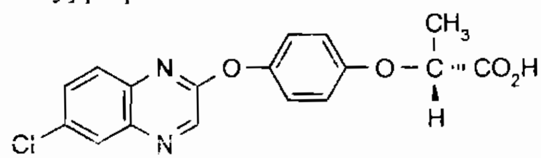
Clethodim (Select): (+)- 2- [(E)- 1- [(E) -3- chloroallyloxyimino] propyl]-5-[2-(ethylthio) propyl]- 3-hydroxycyclohex-2-enone



Fluazifop-p-butyl (Fusilade Super): (R)-2- [4- (5-trifluoromethyl-2-pyridyl] oxy] phenoxy] propionic acid



Quizalofop-p-ethyl (Targa super): (R) –2-[4-(6-chloroquinoxalin – 2-yloxy) phenoxy] propionate



2.2. Determination of p-Value

The p-values were determined by distributing an appropriate amount of solute between equal volumes (10.0 ml) of the two pre-equilibrated immiscible phases of various solvent systems. These systems were water / benzene, chloroform, ethyl acetate, hexane and methylene chloride.

2.3. Thermal Decomposition and Photodegradation

2.3.1. Effect of Sunlight

One ml of the tested herbicides in methanol was spread as uniformly as possible on the surface of uncovered petri dishes (7.0 cm i.d.). The methanol was left to dry at room temperature. The dishes were then exposed to direct sunlight. Dominating temperature was 35–37 °C. Samples were taken at ¼, ½, 1, 2, 4, 8, 12 and 24 hours.

2.3.2. Effect of UV-light

One ml of the tested herbicides was spread on the surface of uncovered petri-dishes (7.0 cm i.d.). After drying at room temperature deposits in petri dishes were exposed to a 254 nm ultraviolet lamp at a distance of 10 cm for 1, 2, 4, 8, 12, 24, 36, 48, 60, 72 and 96 hours.

2.3.3. Effect of Temperature

One ml of the tested herbicides in methanol was placed in a covered test tube. Tubes were placed inta water bath at 50, 60 and 70 °C for 1, 2, 4, 6, 8, 10 and 12 days.

2.4. Hydrolysis Studies in Different pH Solutions

pH values were chosen to provide data on the relative rates of chemical hydrolysis of clethodim, fluazifop-p-butyl and quizalofop-p-ethyl similar to those they may be exposed to in the natural environment. The effect of three different pH values on the hydrolysis of clethodim, fluazifop-p-butyl and quizalofop-p-ethyl was studied.

Aqueous buffers at pH 5.0, 7.0 and 8.0 were prepared using potassium phosphate monobasic and sodium phosphate dibasic. Samples of each buffer (2.0 L) were transferred to 2.5 liter bottles. Herbicide solutions were prepared from analytical grade chemicals.

The herbicides were added to the buffers to yield solutions containing 1.24 clethodim, 2.78 of fluazifop-p-butyl and 0.42 ppm of quizalofop-p-ethyl. After mixing and aseptic removal of triplicate 10 ml zero time samples, the solutions were stored under laboratory conditions in dark. Samples were taken after 1, 3, 6, 12, 18, 24, 30, 36 and 42 days and 25–50 ml of the aqueous solution were extracted three times with 25-50 ml ethyl acetate for both fluazifop-p-butyl and quizalofop-p-ethyl, while dichloromethane was used for extracting clethodim. The extract was dried through anhydrous sodium sulphate, evaporated to dryness on a rotary evaporator under vacuum and analyzed by HPLC.

2.5. Liquid Chromatographic Conditions

A Hewlett Packard HP series 1100, equipped with a degasser G 1322A, Quaternary pump G1311A, thermostatted column compartment G1316A, UV detector G 1314A and Chemstation was used for analysis of clethodim; fluazifop-butyl and quizalofop-p-ethyl. The system was equipped with a stainless steel column (20 cm X 4.6 mm i.d.) packed with ODS-Hypersil 5µm. Fluazifop-butyl and quizalofop-p-ethyl were eluted isocratically with acetonitrile–water (80: 20, v/v), while clethodim was eluted with acetonitrile-buffer (pH 4.6) (10:90 v/v). UV variable wavelength was monitored at 270; 254

and 217 nm for clethodim; fluazifop-butyl and quizalofop-p-ethyl. respectively. A 20 µl injector was used at a flow rate 1.0 ml/min. Under these conditions the retention time (R_t) for clethodim; fluazifop-p-butyl and quizalofop-p-ethyl were 3.486; 4.674 and 4.462, respectively.

3. RESULTS AND DISCUSSION

3.1. p-Value Determination

The p-values of the tested herbicides from water phase are shown in Table (1). The tested solvents showed different p-values. Ethyl acetate gave the highest p-value for hoth fluazifop-butyl and quizalofop-p-ethyl, (91.3% and 85.6% respectively). While methylene chloride gave the highest p-value for clethodim (89.6%). Hexane showed the lowest p-value for clethodim, fluazifop-p-butyl and quizalofop-p-ethyl, (39.1, 58.4 and 50.4%, respectively). These results show that ethyl acetate is the most suitable solvent for the extraction of both fluazifop-p-butyl and quizalofop-p-ethyl, while methylene chloride is more suitable for the extraction of clethodim from aqueous solutions.

Ishimitsu *et al.,* (2001) reported that dichloromethane was successful in extracting clethodim and gave good recovery of clethodim and its oxidation metabolites clethodim sulfoxide and clethodim sulfone. Worobey and Shields (1989) described a new method for the determination of fluazifop-butyl and its metabolite fluazifop acid in soybeans and soybean oil as fluazifop acid. Liquid chromatography with amperometric detection (LC/AD) was used to determine fluazifop acid produced from the metabolism or base hydrolysis of fluazifop-butyl in soybeans and soybean oil.

Table (1): P-values of clethodim; fluazifop-p-butyl and quizalofop-p-ethyl in five immiscible binary solvent systems.

Solvent system	P-value		
	Clethodim	Fluazifop-p- butyl	Quizalofop-p-ethyl
Water / benzene	54.7	79.4	69.3
Water / chloroform	83.7	62.9	53.7
Water / ethyl acetate	76.2	91.3	85.6
Water / hexane	39.1	58.4	50.4
Water / methylene chloride	89.6	88.0	65.8

3.2. Effect of Sunlight, Temperature and UV-light

3.2.1. Effect of Sunlight

Data in Table (2) show that the decomposition percentage of clethodim. fluazifop-p-butyl and quizalofop-p-ethyl after exposure to sunlight had increased gradually. Photodecomposition was positively correlated with the exposure period. The residues of all tested herbicides were greatly deteriorated when exposed to direct sunlight, especially for long periods. Fluazifop-p-butyl was the most persistent chemical. The half-life times of clethodim, fluazifop-p-butyl and quizalofop-p-ethyl were 3.12, 8.0 and 4.48 hours, respectively.

The amounts of clethodim; fluazifop-butyl and quizalofop-p-ethyl decreased from zero to one hour at the rate of 26.8; 12.7 and 15.2% / hour, respectively. The decrease in the amounts of clethodim; fluazifop-butyl and quizalofop-p-ethyl continued after one hour and reached 2.4, 18.5 and 4.1 µg with percent loss 96.8, 86.8 and 90.2%, respectively after 24 hours from exposure to direct sunlight.

Sensitivity to sunlight limits the use of some potential pesticides in agriculture. Classical approaches to overcome this obstacle have involved chemical modifications of the molecular structure of the pesticide or the use of UV-absorbing materials in pesticide formulations. However, both methods suffered serious drawbacks since chemical modification may affect pesticidal activity or biodegradability may introduce ecological problems related to soil and water pollution (Rozen and Margulies, 1991). The radiation energy of sun might be absorbed by a pesticide molecule principally at a given wavelength. The energy might increase the transitional, rotational, vibrational or electronic energy of the molecule. If enough energy was absorbed to interact with the electrons of molecules an electronically excited molecule may result. Based on the above results, it could be stated that sunlight is more effective than UV-light in accelerating the photodecomposition of clethodim, fluazifop-p-butyl and quizalofop-p-ethyl (Table 2).

Table (2): Effect of sunlight on degradation of clethodim, fluazifop-p-butyl and quizalofop-p-ethyl.

Exposure time (hr.)	Amount of tested herbicides (µg) and % loss					
	Clethodim		Fluazifop-p-butyl		Quizalofop-p-ethyl	
	µg	% Loss	µg	% Loss	µg	% Loss
0	76.0	0.0	139.0	0.0	42.0	0.0
¼	73.5	3.3	135.2	2.7	40.1	4.5
½	69.4	8.7	130.4	6.2	38.2	9.0
1	55.6	26.8	121.3	12.7	35.6	15.2
2	43.7	42.5	104.6	24.7	29.5	29.8
4	33.5	55.9	89.2	35.8	22.3	46.9
8	20.6	72.9	69.1	50.3	15.7	62.6
12	10.4	86.3	42.4	69.5	9.4	77.6
24	2.4	96.8	18.5	86.8	4.1	90.2
DT_{50} hours	3.12		8.0		4.48	

3.2.2. Effect of UV-light

It has been demonstrated that UV light exerts chemical changes on a large number of pesticides. Several types of photodecomposition such as hydrolysis, oxidation and isomerization may occur. If similar reactions occur under field conditions. such investigation will be of great importance in environmental contamination, pesticide residues in agricultural products and practical use of pesticides.

Generally, photodecomposition is positively correlated with exposure period. Data in Table (3) show that the decomposition percentages of clethodim, fluazifop-p-butyl and quizalofop-p-ethyl in glass surfaces increased gradually after the exposure to UV-light. The photodecomposition rate of clethodim was more rapid than the other two tested herbicides, while fluazifop-p-butyl was the most persistent one.

Statistically, the half-life of clethodim, fluazifop-p-butyl and quizalofop-p-ethyl as dry thin films were 10.6, 70.4 and 39.8 hours, respectively, and the percentage losses of these three chemicals were 46.2, 6.8 and 12.6%, respectively after 8 hours of exposure to UV-light. While the amount of fluazifop-p-butyl and quizalofop-p-ethyl detected after 60 hours of exposure to UV-light were 78.8 and 13.2 µg with 43.3 and 68.6% loss, respectively, and no detectable amount of clethodim was observed. These results are in general agreement with those obtained by several investigations: (Coupland, 1989; Rick. 1985; and Bridges *et al.*, 1992).

Table (3): Effect of UV-rays on photodecomposition of clethodim, fluazifop-p-butyl and quizalofop-p-ethyl.

Exposure time (hr.)	Amount of tested herbicides (µg) and % of loss					
	Clethodim		Fluazifop-p-butyl		Quizalofop-p-ethyl	
	µg	% Loss	µg	% Loss	µg	% Loss
0	76.0	0.0	139.0	0 0	42.0	0.0
1	68.0	10.5	139.0	0.0	42.0	0.0
2	59.2	22.1	137.3	1.2	40.9	2.6
4	48.8	35.8	130.4	6.2	39.6	5.7
8	40.9	46.2	129.5	6.8	36.6	12.6
12	32.1	57.8	126.5	9.0	33.2	20.9
24	17.4	77.1	119.0	14.4	29.1	30.7
36	10.2	86.6	108.9	21.6	22.4	46.7
48	5.9	92.2	93.2	32.9	---	---
60	1.2	98.4	78.8	43.3	13.2	68.6
72	ND	---	67.5	51.4	9.1	78.3
96	ND	---	48.9	64.8	4.9	88.3
DT_{50} hours	**10.6**		**70.4**		**39.8**	

3.2.3. Effect of Different Temperatures

Data in Table (4) summarize the effect of three different temperature levels (50, 60 and 70 °C) on the stability and degradation of clethodim, fluazifop-p-butyl and quizalofop-p-ethyl. Results indicated that the persistence of the tested herbicides was influenced and positively correlated with temperature and period of exposure. Quizalofop-p-ethyl was degraded more rapidly at different temperatures followed by clethodim, while fluazifop-p-butyl was more persistent than the other two herbicides. The data demonstrated that no thermal decomposition of fluazifop-p-butyl occurred after four days at 50 °C and after two and one day at 60 and 70 °C, respectively. On the other hand, after 12 days of exposure to temperature at 50, 60 and 70 °C, the percentage loss of fluazifop-p-butyl was 11.8, 21.2 and 31.2%, respectively. The percentage loss of clethodim was 4.5, 10.3 and 18.3 % after one day of exposure to mentioned temperatures.

respectively. However, the percentage loss of clethodim reached 47.3, 57.4 and 62.2% after 12 days of exposure to these temperatures, respectively.

Degradation of quizalofop-p-ethyl was more rapid than the other two herbicides. The percentage loss of quizalofop-p-ethyl was 3.57, 10.5 and 17.8% after one day of exposure to temperature at 50, 60 and 70 °C. However, the percentage losses were 57.6, 68.8 and 87.9% after 12 days of exposure to the mentioned temperatures, respectively. Statistically, the half-life time for clethodim was 12.9, 9.0 and 6.2 days at 50, 60 and 70 °C, respectively. The corresponding values for quizalofop-p-ethyl were 10.9, 8.5 and 5.9 days. Nevertheless, fluazifop-p-butyl was more stable than the other two herbicides at the end of the experiment (12 days). Several investigations studied and confirmed the role of temperature in degradation of herbicide residues (Kells *et al.*, 1984 and Coupland, 1989).

3.3. Effect of Different pH Solutions on Hydrolysis

Most pesticides usually contact water either as a spray diluent, or during irrigation of the soil. Hydrolysis can result from the attack of either water or hydroxide ion on the pesticide, and the latter is usually being the more effective reagent. The hydroxide ion concentration is directly related to pH through the ion product of water. Data presented in Table (5) show that the tested pH degree and period of exposure influenced persistence. The three herbicides were hydrolyzed more rapidly in alkaline media (pH 8.0). On the other hand, clethodim was hydrolyzed rapidly in the acidic media (pH 5.0). On the contrary, fluazifop-p-butyl showed more persistence to all pH solutions than the other two tested herbicides. The amount of clethodim decreased from 0 to 6 days at the rate of 10.22, 4.17 and 12.5% / day at pH 5.0, 7.0 and 8.0, respectively. The fast steep decline in the residues of clethodim continued after 18 days to be 85.48, 36.29 and 97.6% with 4.75, 2.02 and 5.42% / day at pH 5.0, 7.0 and 8.0, respectively. Clethodim was not detected after 30 days of exposure to acidic media, and after 24 days of exposure to alkaline media. The half-life time of clethodim was 4.70, 30.35 and 2.67 at pH 5, pH 7 and pH 8, respectively.

Table (4): Effect of different degrees of temperature on the stability of clethodim, fluazifop-p-butyl and quizalofop-p-ethyl.

Exposure time (days)	Amount of tested Herbicides (µg) and percentage loss																	
	Clethodim						Fluazifop-p-butyl						Quizalofop-p-ethyl					
	50 °C		60 °C		70 °C		50 °C		60 °C		70 °C		50 °C		60 °C		70 °C	
	µg	% Loss	µg	% Loss	µg	% Loss	µg	% Loss	µg	% Loss	µg	% Loss	µg	% Loss	µg	% Loss	µg	% Loss
0	152.0	0.0	152.0	0.0	152.0	0.0	139.0	0.0	139.0	0.0	139.0	0.0	42.0	0.0	42.0	0.0	42.0	0.0
1	145.2	4.5	136.4	10.3	124.2	18.3	139.0	0.0	139.0	0.0	139.0	0.0	40.5	3.57	37.6	10.5	34.5	17.8
2	136.4	10.3	121.9	19.8	109.3	28.1	139.0	0.0	139.0	0.0	133.2	4.17	39.2	6.70	33.6	20.0	29.8	29.0
4	122.5	19.4	102.4	32.6	92.8	39.0	139.0	0.0	134.1	3.53	126	9.28	36.4	13.3	30.1	28.3	24.6	41.4
6	114.3	24.8	90.3	40.6	76.5	49.7	136.2	2.01	125.3	9.86	120.2	13.53	31.2	25.7	25.5	39.3	19.4	53.8
8	104.6	31.2	82.0	46.1	52.6	65.4	130.1	6.40	121.4	12.7	112.0	19.42	26.4	37.1	21.2	49.5	13.5	67.9
10	91.3	39.9	71.3	53.1	40.8	73.2	127.5	8.27	117.1	15.76	104.2	25.0	21.9	47.8	16.4	60.9	8.9	78.8
12	80.1	47.3	57.4	62.2	31.6	79.2	122.6	11.8	109.5	21.2	95.6	31.2	17.8	57.6	13.1	68.8	5.1	87.9
DT_{50} days	12.19		9.0		6.2		---		---		---		10.9		8.5		5.9	

Table (5): Effect of different pH values on the stability of clethodim, fluazifop-p-butyl and quizalofop-p-ethyl.

Time (days)	Amount of tested herbicides (ppm) and percentage loss																	
	Clethodim						Fluazifop-p-butyl						Quizalofop-p-ethyl					
	5.0		7.0		8.0		5.0		7.0		8.0		5.0		7.0		8.0	
	ppm	% Loss	ppm	% Loss	ppm	% Loss	ppm	% Loss	ppm	% Loss	ppm	% Loss	ppm	% Loss	ppm	% Loss	ppm	% Loss
0	1.24	0.0	1.24	0.0	1.24	0.0	2.78	0.0	2.78	0.0	2.78	0.0	0.42	0.0	0.42	0.0	0.42	0.0
1	0.98	20.97	1.15	7.26	0.83	33.10	2.69	3.24	2.78	0.0	1.96	29.45	0.38	9.52	0.41	2.38	0.23	45.24
3	0.76	38.71	1.09	12.10	0.52	58.06	2.49	10.43	2.78	0.0	1.22	56.10	0.33	21.43	0.39	7.14	0.14	66.70
6	0.48	61.29	0.93	25.0	0.31	75.0	2.20	20.86	2.70	2.88	0.97	65.10	0.26	38.10	0.35	16.70	0.07	83.30
12	0.30	75.81	0.85	31.45	0.17	86.29	2.04	26.62	2.64	5.03	0.52	81.29	0.15	64.28	0.27	35.70	0.03	92.86
18	0.18	85.48	0.79	36.29	0.03	97.60	1.86	33.10	2.59	6.83	0.21	92.45	0.09	78.57	0.19	54.76	N.D	100
24	0.07	94.35	0.71	42.74	N.D.	100	1.75	37.05	2.48	10.79	0.08	97.1	0.04	90.48	0.11	73.81	N.D.	100
30	N.D	100	0.62	49.19	N.D.	100	1.56	43.90	2.31	16.91	N.D	100	N.D.	100	0.06	85.71	N.D.	100
36	N.D	100	0.54	56.45	N.D.	100	1.32	52.50	2.1	24.50	N.D.	100	N.D.	100	0.01	97.62	N.D.	100
42	N.D.	100	0.41	66.94	N.D.	100	1.02	63.31	1.96	29.50	N.D	100	N.D.	100	N.D	100	N.D.	100
DT_{50} days	4.70		30.35		2.67		34.36		---		2.80		8.82		16.63		2.0	

On the other hand. fluazifop-butyl decreased rapidly in alkaline media (pH 8.0) than the other tested pH degrees. The half-life values of fluazifop-butyl were 34.36 and 2.80 days at pH 5.0 and pH 8.0 , respectively. The amount of quizalofop-p-ethyl decreased from 0 to 12 days with disappearance rate of 5.36, 2.98 and 7.74% / day at pH 5.0. 7.0 and 8.0, respectively. Quizalofop-p-ethyl was not detected after 39 days of exposure to acidic media. and after 18 days of exposure to alkaline media. The half-life time of quizalofop-p-ethyl was 8.82, 16.63 and 2.0 days at pH 5.0, 7.0 and 8.0, respectively.

In general, the previous mentioned results clearly showed that all tested herbicides were hydrolyzed more rapidly in alkaline media (pH 8.0) than the other tested pH degrees. The results also demonstrated that fluazifop-butyl was more persistent to all pH degrees than the other two herbicides. Balinova and Lalova (1992) reported that fluazifop-butyl was hydrolyzed rapidly to the fluazifop acid, and the residues of the metabolite were found to persist much longer in the plant than the active compound.

4. REFERENCES

Balinova A. M. and Lalova M. P. (1992). Translocation. metabolism and residues of fluazifop-butyl in soybean plants. Weed Research Oxford. 32: (2), 143-147.

Bewick D. W. (1986). Pestic. Sci. 17, 349-356.

Bridges D.C., Falb L.N., Smith A.E. and Foy C.L. (1992). Stability and activity of clethodim as influenced by pH, UV light and adjuvant. Adjuvants For Agriculture. 215-223.

Coupland D. (1989). Pre-treatment environmental effects on the uptake, translocation, metabolism and performance of fluazifop-butyl in *Elymus repens*. Weed Research, 29, 289-297.

Fielding M., Barcelo D., Helweg A., Galassi S., Torstensson L., Zoonen P. van Wolter R. and Angeletti F. (1991). Pesticides in ground and drinking water. Water pollution Research. Rep. 27 of the EC Directorate General XII.

Helweg A. (1994). Pesticides in precipitation and surface water. TemaNord 1995: 558.

Hendley P., Dicks J. W., Monaco T. J., Slyfield S. M., Tummon O. J. and Barrett J. C. (1985). Weed Sci. 33, 11- 24.

Ishimitsu S., Kaihara A., Yoshii K., Tsumura Y., Nakamura Y. and Tonogai Y. (2001). Determination of clethodim and its oxidation metabolites in crops by liquid chromatography with confirmation by LC/MS. J. of AOAC International. 84: (4), 1172-1178.

Kells J. J., Meggitt W.F. and Penner D. (1984). Absorption, translocation and activity of fluazifop-butyl as influenced by plant growth stage and environment. Weed Science, 32: (2), 143-149.

Rendina A. R. and Felts J. M. (1988). Cyclohexanedione herbicides are selective and potent inhibitors of acetyl-CoA carboxylase from grasses. Plant Physiol. 86, 983-986.

Rick S.K. (1985). Studies on the timing of application, soil activity and factors affecting soil activity of several selective grass herbicides. Dissertation Abstracts International, 45:7, 1974B.

Rozen H. and Margulies L. (1991). Photostabilization of tetrahydro-2-(nitromethylene)-2H-1-thiazine adsorbed on clays. J. Agric. Food Chem. 39: 1320-1325.

Torstensson L. (1993). Pesticides. In Handbook of Hazardous Materials, pp. 351-365. Academic Press. Inc.

Torstensson L. (1994). Pesticides in precipitation. Consequences for the terrestrial environment. In Pesticides in Precipitation and Surface Water, pp. 84-93.

Worobey B. and Shields J. B. (1989). Determination of fluazifop-butyl and fluazifop acid in soybeans and soybean oil using liquid chromatography with oxidative amperometric detection. J. AOAC. of Anal. Chem. 72: (2), 368-371.

تحلل مركبات الـ clethodim, fluazifop-butyl and quizalofop-p-ethyl تحت ظروف بيئية مختلفة

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ملخــص

تعتبر مركبات الـ clethodim, fluazifop-butyl and quizalofop-p-ethyl من مبيدات الحشائش الاختيارية والتي تستخدم لمكافحة الحشائش النجيلية في العديد من المحاصيل عريضة الاوراق. وقد اجرى هذا البحث لتقدير قيم الـ p-value للمركبات المختبرة لمعرفة أفضل المذيبات التي يمكن استخدامها في الاستخلاص ، بالإضافة إلى دراسة تأثير ثلاث درجات حرارة مختلفة وضوء الشمس والأشعة فوق البنفسجية ودرجات الحموضة المختلفة (وهى عوامل بيئية هامة تؤثر على ثبات المركب عند الاستعمال) على ثبات المركبات المختبرة.

ويمكن تلخيص النتائج المتحصل عليها فيما يلي

يعتبر مذيب الايثايل أسيتيت من أنسب المذيبات المستخدمة لاستخلاص كل من مركبي الـ fluazifop-butyl and quizalofop-p-ethyl من الوسط المائي حيث كانت قيمة الـ p-Value هي ٩١,٣ ، ٥٨,٦ % على الترتيب.بينما اعطى مذيب المتيلين كلوريد أعلى قيمة p-Value لاستخلاص مركب الـclethodim من الوسط المائي حيث كانت ٨٩,٦% .

كانت فترة نصف العمر لمركبات clethodim, fluazifop-butyl and quizalofop-p-ethyl هى ٣,١٢ ، ٨,٠ ، ٤,٤٨ ساعة عند التعرض لضوء الشمس على التوالي. كما أظهرت النتائج أن مركب الـ fluazifop-butyl من أكثر المركبات ثباتا عند التعرض لأشعة الشمس.

كانت فترة نصف العمر لمبيد الـ clethodim عقب تعرضه لدرجات حرارة ٥٠ ، ٦٠ ، ٧٠ م° هي ١٢,٩، ٩,٠، ٦,٢ يوم على الترتيب. بينما كانت فترة نصف العمر لمركب الـ quizalofop-p-ethyl هي ١٠,٩ ، ٨,٥ ، ٥,٩ يوم. وقد أظهرت النتائج أن مبيد الـ fluazifop-butyl كان من أكثر المركبات ثباتا لدرجات الحرارة المختلفة حتى نهاية فترة التجربة وهى ١٢ يوم.

أظهرت النتائج أيضا أن مبيد الـ fluazifop-butyl من أكثر المركبات ثباتا لتاثير الأشعة فوق البنفسجية عن باقي المركبات حيث كانت فترة نصف العمر هي ١٠,٦، ٧٠,٤، ٣٩,٨ ساعة لكل من clethodim, fluazifop-butyl and quizalofop-p-ethyl على الترتيب.

أظهرت الدراسة حدوث تحلل سريع لجميع المركبات المختبرة في الوسط القلوي عنه في باقي الأوساط. بينما كان مركب الـ fluazifop-butyl أكثر ثباتا من باقي المركبات على جميع الأوساط المختبرة. كانت فترة نصف العمر لمركب الـ clethodim ٤,٧، ٣٥، ٣٠، ٢,٦٧ يوم على درجات حموضة ٥ ، ٧ ، ٨ على الترتيب. بينما كانت هذه القيم في حالة مركب quizalofop-p-ethyl ٨,٨٢، ١٢,٣٦، ٢,٠ يوم على الترتيب. كما كانت فترة نصف العمر لمركب الـ fluazifop-butyl ٣٦، ٣٤، ٨، ٢ على درجات حموضة ٥ ، ٨ على الترتيب.