Persistence of Imazapic and Imazapyr in Paddy Soil and Water

Bajrai F.S.M., Ismail B.S., Mardiana-Jansar K. and Omar R.

Abstract— Studies on the persistence of imazapic and imazapyr in a Malaysian soil, namely clay loam and in water, were conducted under greenhouse conditions. The experiment was carried out in clay loam soil of the Sungai Besar paddy plantation area, in Selangor, Malaysia. An analytical method based on an extraction procedure and followed by high-performance liquid chromatographic (HPLC) separation with multi variable detection was optimized and validated for the simultaneous determination of imazapyr and imazapic. Chromatographic separation was carried out with the C8 column. The estimated values of the half-life of imazapyr in water for 75, 150 and 300 g ai/ha following first order kinetics were 22.00, 23.34 and 22.29 days, respectively. Meanwhile for imazapic, the estimated half-life in water for 75, 150 and 300 g ai/ha following first order kinetics were 23.11, 23.74 and 21.59 days, respectively. As for soil, the degradation rates of 26.26, 29.75 and 25.30 days were observed as the estimated half-life values for imazapyr and 38.51, 34.15 and 25.02 days for imazapic for the treatments of 75, 150 and 300 g ai/ha respectively. The rates of degradation of both active ingredients were slower in soil than in water. These results are informative to both farmers and researchers to enable them to keep track on the environmental effects of selected herbicides so that the probability of unwanted ecological effects can be minimized.

Keywords— Imazapic, imazapyr; half-life, persistence; water; soils

I. Introduction

The application of herbicides in the rice cultivation industry is one of the often used methods to control weeds. According to Toriyama [1], herbicides were applied before rice germination to ensure well weed-controlled on the early stages of the rice development because weeds compete and multiply easily in the rice ecosystem. Since weeds can be controlled at the initial stages of their growth, ploughing activities could be reduced and thus moisture and nutrient content in the soil maintained. In fact, herbicides are also capable of controlling weed-like plants that grow in cultivated areas [2]. Effective control of weedy rice and weeds in the early stages of their development prevent weed competition and crop damage in direct seeding crops and therefore increase the production of better quality rice [3-4].

In rice cultivation, weedy rice is one of the biggest challenge that could create negative effect. This statement was also supported by Tewari [5] where weedy rice which has higher bud compete with ordinary rice for nutrients, moisture, and sunlight. This affects the photosynthesis process of rice and thus causes a reduction in the quantity and quality of rice. Chauhan [6] in his research reported that weedy rice can cause yield losses of 50-60% on moderate invasion (15-20 stems m-2) and 70-80% on high invasion (21-30 stems m-2). A study conducted by Moody [7] stated that the invasion of weedy rice in tropical Asian countries is increasing with the increase of direct seeding method; the method thet is most preferred by farmers.

To help reducing the problem of weedy rice in paddy plantation, Clearfield Production System was introduced in early 2000 [8]. According to Azmi et al. [9], Clearfield Production System (CPS) contains the seeds of rice varieties have a gene tolerant to imidazolinone herbicides (OnDuty™). Imidazolinone herbicide consist of imazapic and imazapyr as its active ingredients that can control weedy rice along with other various weeds effectively [9]. According to Senseman et al. [10], the active ingredient of imazapic is often used in the control of annual grassy weeds, grasses that persist during pre and post-germination periods as well as broadleaf weeds, while imazapyr is used to control various types of grasses, broadleaf weeds, woody weed species as well as riparian and aquatic weed species. A summary of the active ingredients' (imazapic & imazapyr) characteristics and chemical properties are presented in Table 1.

TABLE I: Properties of Imazapic & Imazapyr

Parameter	Imazapic	Imazapyr
PAC name	(±)-2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-5-methyl-3-pyridinecarboxylate, 2-(4-iso-propyl-4-methyl-5-oxo-2-imidazolin-2-yl)-5-methylnicotinicacid	2-propanamine, 2-(4,5-dihydro-4-ethyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl)-3-pyridinecarboxylate, 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-nicotinic acid
Chemical formula	Acid: C14,H17,N3,O3 Salt: C14,H20,N4,O3	Acid: C13,H15,N3,O3 Salt : C16,H24,N4,O3
p*K*a	2.0, 3.9, 11.1	1.9, 3.6, 11
Solubility inwater, mg L-1	2200	11272
K_{OC}	137	100 mL g -1
K_{OW}	2.47	1.3
Soil half-life	120 d	90 d

Data quoted from Senseman at al. [10] and Tu et al. [11]

Persistence refers to the soil's ability to hold any kind of pesticides and not allowing them to be transported [12]. In this case, a more stabil herbicides compounds require a longer time to be broken down [13]. The application of imazapic and imazapyr for controlling weedy rice in the Malaysian

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agricultural system may somehow create an environmental effect in both the water and soil media if they have a long persistency. Therefore, it is important to understand the actual behaviour of these compounds in order to determine their potential risk to the environment. The present study was conducted to investigate the contamination levels of herbicide residues in two environmental samples namely water and soil. The water and soil samples were periodically collected and tested to detect the levels of herbicide residues.

II. Materials & Methods

The herbicide that is made up of imazapic and imazapyr as active ingredients was used in the study. Both compounds belong to the imidazolinone chemical group formulated in 150 g ai ha-1 solution. 100 kg of soil was collected from a paddy plantation area in Sungai Besar, Kuala Selangor (GPS coordinates of 3°42'01.9"N 101°00'23.2"E). The soil samples collected from the sampling area were filled into 64 cm3 plastic pots. The factorial arrangement was incorporated into the bock design with four replications. The rates of herbicides spraying used were the recommended dosage (150 g ai ha-1), half the recommended dosage (75 g ai ha-1), double the recommended dosage (300 g ai ha-1) and the control (with no herbicide treatment). The herbicide was applied to the prepared pots on May 2015.

A. *Water sampling*

Water samples (three replications) were collected from the surface area at 0 (day of spraying), 1, 3, 7, 21, 30, 60 and 120 days after treatment.

B. *Soil sampling*

Soil samples (three replications) were collected from the top most soil layer (depth 0 cm to 10 cm) at 0 (day of spraying), 1, 3, 7, 21, 30, 60 and 120 days after treatment. The soil characteristics are summarized in Table 2.

TABLE 2: PHYSICO - CHEMICAL PROPERTIES OF THE CLAY LOAM SOIL

Parameter	**Clay Loam**
pH	4.29
% Organic matter	9.05
CEC (meq/100 g)	5.4618
Sand (%)	32
Silt (%)	37
Clay (%)	32
Exchangeable Al (meq/100g)	0.6

*Data reported are mean values estimated from 3 replicates

C. *Recovery study*

In the recovery study each soil and water sample (5 g) was treated with the combinations of both imazapyr and imazapic. For each pesticide, the soil sample was spiked at one concentration i.e. 1 mg kg-1. The pesticide was then extracted from the soil for determination of the imazapic and imazapyr residue.

D. *Determination of imazapyr and imazapic in the soil and water*

Analyses of the samples of water and soil were carried out using the method proposed by Moser [14] with slight modifications. Soil and water samples were placed separately in 50 mL centrifuge tubes. Extraction was the carried out by initially adding 10 mL of 10 µM ammonium acetate. The mixture was then shaken in a vortex mixer for 30 seconds, then centrifuged for 5 minutes at a speed of 4000 rpm. Then 1.0 mL of the supernatant from each extraction was directly injected into 2 mL vials via 0.2 m nylon filter. Analyses were carried out using a HPLC (Agilent Technology Model 1220 LC equipped with UV detector). The details of conditions used in the study are summarized as in Table 3.

TABLE 3: THE CONDITION OF HPLC-UV FOR RECOVERY STUDY AND SAMPLE ANALYSIS

Column	Agilent ZORBAX Eclipse Plus C8
Length	2.1 x 150 mm
Diameter of the column	5 micron
Column Temperature	25 ± 3^{o}C
Flow rate	0.3 ml/min
Wavelength	300 nm
Injection type	5 µL
Mobile Phase	A : 0.1 % Formic acid, B : Acetonitrile

Data quoted from Senseman at al. [10] and Tu et al. [11]

III. Results and Discussion

The characteristics of the studied soil type, namely clay loam soil are presented in Table 2. The preliminary results of the recovery of imazapic and imazapyr in water and soil are shown in Table 4. The percentage recovery of imazapic and imazapyr obtained at 1 ppm in the clay loam soil was 97.44% and 97.06%, respectively, while in water, the percentage recovery was 100% and 88.24%, respectively.

TABLE 4. RECOVERY STUDY OF IMAZAPIC AND IMAZAPYR IN SOIL AND WATER

Concentration (1 ppm)	**Imazapic**	**Imazapyr**
Soil	97.44 ± 4.44	97.06 ± 2.94
Water	100.00 ± 6.66	88.24 ± 7.64

*Data reported are mean values estimated from 3 replicates

Studies to quantify the degradation rates for imazapic and imazapyr were conducted using the high-performance liquid chromatograph (HPLC). The first-order rate constant "c" was determined from the slope of the linear plot of the natural logarithm of the remaining herbicide concentration [ln(C/C0)] at various sampling intervals, in relation to time. The dissipation time (DT50), i.e. the time taken for the concentration of the pesticide to be reduced to 50% of its initial concentration, was calculated using the equation DT50=ln(2)/k, where k is the absolute value of the slope and the first-order rate constant for the herbicide [15]. Figs. 1 and 2 indicating the pattern of degradation for both imazapic and imazapyr compounds at different concentrations in soil and water medium.

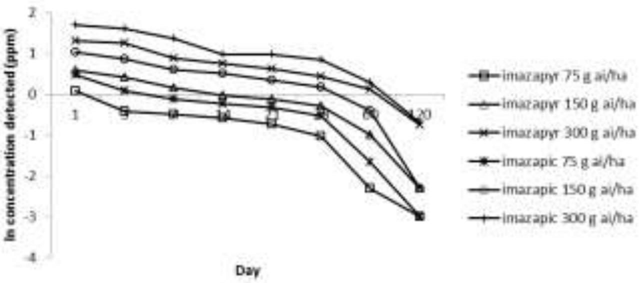

Fig.1. Degradation of imazapic and imazapyr at different concentrations in water samples.

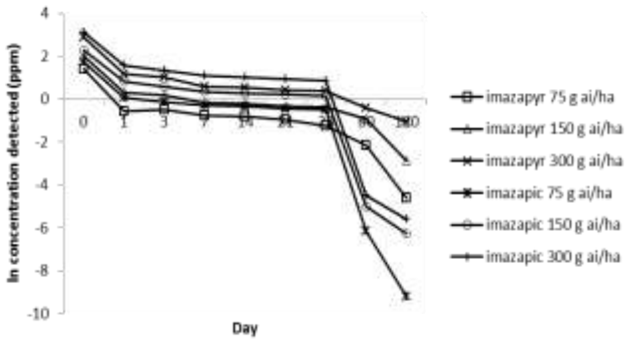

Fig. 2. Degradation of imazapic and imazapyr at different concentrations in soil samples.

The estimated half-life values of imazapyr in water for 75, 150 and 300 g ai/ha following first order kinetics were 22.00 and 23.34 and 22.29 days, respectively. Meanwhile, for imazapic, the estimated half-life values in water for 75, 150 and 300 g ai/ha following first order kinetics were 23.11, 23.74 and 21.59 days, respectively.

TABLE 5. CORRELATION COEFFICIENTS (R2), DEGRADATION RATE COEFFICIENTS (K), AND HALF-LIFE (DAYS) OF IMAZAPIC AND IMAZAPYR AT DIFFERENT CONCENTRATIONS IN WATER SAMPLES

Dose	Imazapic			Imazapyr		
	R^2	k	$t_{1/2}$	R^2	k	$t_{1/2}$
At half the recommended rate (75 g ai/ha)	0.83	0.030	23.11	0.83	0.032	22.00
At the recommended rate (150 g ai/ha)	0.93	0.029	23.74	0.92	0.030	23.34
At double the recommended rate (300 g ai/ha)	0.90	0032	21.59	0.92	0.031	22.29

With references to the soil degradation rates, 26.26, 29.75 and 25.30 days were observed as the estimated half-life values for imazapyr at 75, 150 and 300 g ai/ha, respectively. On the other hand, for imazapic, the estimated half-lives were 38.51, 34.15 and 25.02 days for 75, 150 and 300 g ai/ha, respectively. Based on the above results, the rates of degradation for both active ingredients were slower in soil than in water.

TABLE 6. CORRELATION COEFFICIENTS (R2), DEGRADATION RATE COEFFICIENTS (K), AND HALF-LIFE (DAYS) OF IMAZAPIC AND IMAZAPYR AT DIFFERENT CONCENTRATIONS IN THE SOIL SAMPLES

Dose	Imazapic			Imazapyr		
	R^2	k	$t_{1/2}$	R^2	k	$t_{1/2}$
At half the recommended rate (75 g ai/ha)	0.81	0.018	38.51	0.94	0.025	26.26
At the recommended rate (150 g ai/ha)	0.74	0.020	34.15	0.80	0.023	29.75
At double the recommended rate (300 g ai/ha)	0.82	0.021	25.02	0.78	0.027	25.30

The findings of the present study are consistent with those of a study conducted by Douglas et al (2013) where it was reported that imazapyr breaks down very rapidly via photolysis in water. Imazapic on the other hand is degraded primarily by soil microbial metabolism. However, the degradation of imazapic by sunlight is believed to be minimal when it is applied to terrestrial plants or soil, but it is rapidly degraded by sunlight in aqueous solutions [16]. Imazapyr residues can be relatively persistent in soils (reported soil half-life (t50) = 25-142 days) depending on soil texture, organic matter content, pH levels and environmental factors that promote microbial degradation [10-17].

Many factors affect the persistence of pesticides in the soil environment. Environmental factors, such as temperature, soil moisture, microbial activity, pesticide properties and their characteristics, in particular solubility, have great influence on the persistence and mobility of pesticides [18].

One of the precautions that must be taken into consideration is that the present study was undertaken in the green house, using pots. Therefore, there is the probability that slower degradation in the solution could be due to the fact that no water flowed out of the pots. As for soil degradation, microbial activity usually is the highest in warm, moist, well-aerated soils of neutral pH. The constantly warm temperature in Malaysia and the relatively high organic matter content in the soils could enhance the degradation rate of pesticides in the soil. This finding could be supported by a study conducted by Castillo et al. [19] reported that higher temperatures and sunlight in tropical countries might increase pesticides' degradation rates.

IV. CONCLUSION

The values of the half-life of imazapyr under the conditions of the present study ranged from 22 to 30 days while those of imazapic ranged from 21 to 39 days indicating longer persistence of the latter herbicide in the environment. This study indicated that the potential impact of these herbicides is minimal due to their lower persistency in the paddy environment.

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