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ASSESSMENT OF IMAZAPIC PRESENCE IN SURFACE WATER AND GROUNDWATER IN PADDY FIELD AREA

Anis Zakiah Mazlan[a], Hazilia Hussain[a*], Mohamed Azwan Mohamed Zawawi[b]

[a]Universiti Teknologi MARA, Puncak Alam, Selangor, Malaysia
[b]University Putra Malaysia, Serdang, Selangor, Malaysia

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*Corresponding author
hhazilia@hotmail.com

Abstract

Herbicide is a well-known artificially synthesized substance used in paddy fields as an effective way to increase the quantity and quality of rice production by controlling the weedy rice in the field. In Tanjung Karang area, a new paddy strain was introduced to avoid weedy rice problem which requires farmers to apply herbicide containing imazapic and imazapyr which kills the weedy rice only but does not affect the new paddy strain. However, imazapic has the possibility to cause several health problems and also disrupting aquatic ecosystem. Hence, this research aims to carry out an extraction procedure and detection for imazapic residues in surface water and groundwater to assess its distribution in the study area. In this study, samples were collected from the surface water and groundwater for two consecutive seasons of paddy cultivation. After several clean-up and extraction procedure using solid-phase extraction (SPE) method, the water samples were analyzed using High Performance Liquid Chromatography-UV (HPLC-UV) for the presence of Imazapic residue. In 52.6% of the surface water samples and 51.8% of the groundwater samples, presence of imazapic residues was detected. This is a concern as it may possibly cause harm to the farmers. Results showed significant difference for the level of imazapic concentration detected in surface water during main season and off season (*p*-value=0.005, CI = - 0.39, 0.11). Thus, it can be concluded that the concentration of imazapic residue detected during main season (o.71 ug/ml) was higher compared to the samples collected during off season (0.57 ug/ml).

Keywords: Imazapic, groundwater, paddy field, surface water

1.0 INTRODUCTION

Pesticide is a well-known artificially synthesized substance used in agriculture as an effective way to increase the amount and quality of food production by controlling pests, plague and weeds, all of which can be harmful to crops and reduces productivity [1], [2], [3]. They are also classified into different classes depending on its purpose or target organism, and this includes herbicide, insecticide, fungicide, nematicide, and bactericide [3], [4]. Among all classes of pesticide, herbicide is the one favoured by most agricultural community due to its advantages in high-yield crops by helping the farmers remove crop competing weeds without the need of farm labourers [5]. One such herbicide is Imazapic, a compound that belongs to the imidazolinone family [1], [2], [6], [7], [8], [9], [10]. It is one of various well-known herbicides used by farmers to kill weedy rice in paddy fields [9]. It contains imazapic, and it has been introduced in Malaysia for approximately three years prior to this research [11]. The use of this herbicide was in conjunction with the newly introduced paddy strain by MARDI; the MR220 CL1 and CL2. This new paddy strain is injected with imidazolinone herbicide resistant compound and is therefore known as the new developed non-transgenic herbicide resistant from the previously transgenic resistant crop [8], [11]. However, previous toxicological studies of imazapic compound carried out on animals showed that it may cause eye irritation, anemia, liver damage, increased cholesterol and muscle degeneration [4]. This became a major concern since the herbicide could leach into the aquatic environment through ditches or other paths carrying Imazapic residues. Additionally, Imazapic is persistent in water for up to 39 days. Therefore, apart from disrupting the aquatic ecosystem, contact through water during paddy cultivation routine may be harmful to the farmers [4], [7], [12]. Hence, this research aims to carry out an extraction procedure and detection of imazapic residues in surface water and groundwater to assess its distribution in the study area.

2.0 MATERIAL AND METHOD

This study was carried out in Tanjung Karang Rice Irrigation area, located at 3°25'-3°45' N latitude and 100°58'-101°15' E longitude in Selangor. Rice is grown twice a year, primarily from December to April and July to November. Kampung Sawah Sempadan compartment consists of 1468 lots with total area of approximately 2,300 hectares, divided into 24 blocks (Figure 1) [13], [14]. One paddy plot in Block C of Sawah Sempadan was designated as the specific study area, located at 3°28'17.15"-3°28'21.76" N latitude and 100°13'20.39"-101°13'26.78" E longitude. Surface water and groundwater samples were collected in two consecutive season. First sampling was carried out in July and August 2013 (off season) while the second sampling was in January and February 2014 (main season). One liter each of the surface water was collected in the paddy area inlet, the drain (outlet) and in the drain canal. For the groundwater, one liter samples were collected from the monitoring well that was installed beforehand (Figure 2). The water samples were taken at all the same locations starting from the day before the rice cultivation started (0 day), 1^{st}, 3^{rd}, 5^{th}, 7^{th}, 11^{th}, and 15^{th} day of imazapic containing herbicides application in the paddy fields. The samples were collected using standard sampling method for water sampling [10], [15].

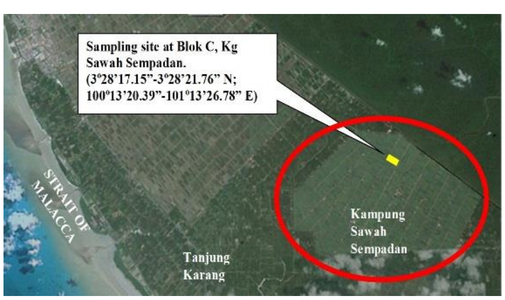

Figure 1 Location of study area at Kampung Sawah Sempadan

All samples were collected directly into the sampling bottles and kept in the chiller under 4°C before extracting using established method [16], [17]. Prior to sample application for the extraction method, the SPE column was conditioned by passing consecutively two times 3 mL DCM, two times 3 mL MeOH, and three times 2 mL purified water acidified (pH 3.0) with acetic acid 1:1 (v/v). After adjusting the pH to 3.0 by adding acetic acid, the samples were well mixed and passed through the SPE tubes at 10 mL min^{-}. The tubes were then eluted with two times of 3 mL DCM before being dried and 4 mL of 2-propanol was then added and allowed to dry until it reaches 1 mL before being injected into HPLC-UV for analytes separation with the injection volume of 20 µL. The analysis of imazapic using HPLC-UV was successfully carried out through optimum parameters; wavelength at 252 nm, 1.2 mL min^{-1} for the flow rate, mobile phase composition mixture of phase A (ACN) and phase B (distilled water; acetic acid, v/v) as mobile phase with elution ratio (45A : 55B) during the analysis time of 3.12 minutes, and with the pH of phase B to be adjusted to pH 3.0 using acetic acid [18].

Figure 2 Monitoring well for groundwater sampling

3.0 RESULTS AND DISCUSSION

3.1 Presence of Imazapic Residues in Surface Water and Groundwater

Results in Table 1 showed that from 116 surface water samples, imazapic compound was detected in 52.6 percent of the samples. However, no significant difference for the number of samples was detected for imazapic concentration between off season and main season. Range of Imazapic concentration detected was 0.3 – 5.12 ug/mL and 0.28 – 6.02 ug/ml for off season and main season respectively. The highest concentration of imazapic was at W5 on the 11^{th} day of off season with 8.75 ug/mL while the highest reading for main season was recorded in sample W1 of the 1^{st} day of sampling time with 6.02 ug/mL. For groundwater samples, only 29 samples were detected with Imazapic from a total of 56 samples (Table 2). Range of Imazapic concentration found is from 0.29 – 16 ug/mL and 0.31-5.84 ug/mL during off season and main season respectively. Based on the results, the percentage of groundwater samples detected with imazapic residue concentration was calculated to be 51.8 percent with the highest reading recorded from sampling point G2 on the 0 day of off season and 3rd day of main season with 16.0 ug/ml and 5.40 ug/ml respectively. Comparison of the percentage of samples detected with imazapic residues between the seasons (off and main season) shows that percentage for off season was slightly higher (57.1 percent) compared to main season (46.4 percent). Although the readings for Imazapic concentration in water samples were not consistent, it can still be detected up until 15th day of sampling. The findings were found to be similar with several studies carried out previously where the concentration of Imazapic were either detected until day 21, day 39 and day 35; or in some studies, it is mentioned that the presence of Imazapic concentration were available in all sampling period [2], [9], [12], [19]. The presence of this compound in water samples could be due to it being one of the compounds that have High Water-Phase-Transport Runoff Potential (HWPTR) and low Sediment-Transport Runoff Potential (LSTRP) [12].

3.2 Comparison of Imazapic Residues in Surface Water during Off and Main Season

An independent t-test showed that there was a significant mean difference in the comparison of imazapic residue concentration in surface water samples during off and main season (*p*-value = 0.005, CI = -0.39, 0.11). The mean recorded for the off season was found to be lower than the mean during the main season with mean value of 0.57 ug/mL and 0.71 ug/mL respectively (Table 3). This can be related to the rain distribution during off season that was lower than the recorded rain distribution data during main season which influenced the high level of imazapic residues presence in surface water. In another study, it stated that the water quality condition could possibly be weather dependent given that it has a potential source of pollution due to land use activities available [20].

Table 3 Comparison of Imazapic residue concentration in surface water between off and main season

Sampling point	Mean (±SD)	df (95% CI)	*p*-value*
Off Season	0.57 (±0.26)	38 (-0.39, 0.11)	0.005
Main Season	0.71 (±0.49)		

*p-value < 0.05

This is because most of the water quality during dry season would stay equally constant with some variations in readings (given that there are no severe exterior disruptions or draught) while during the wet season where the rainfall distribution is maximum, the quality of water at that particular area would potentially become either better or worse depending on the existence of the source of pollution.

3.3 Comparison of Imazapic Residues in Groundwater during Off and Main Season

The data recorded in Table 4 was analyzed using independent Kruskal-Wallis test where it was found that there was no significant difference for mean comparison between concentration of imazapic residues detected in groundwater during off and main season (*p*=0.228). However, based on the evaluation carried out, it was shown that the mean for imazapic residue concentration found in groundwater samples collected during off season are slightly higher (3.17 ug/mL) as compared to concentration found in groundwater samples during main season (1.38 ug/mL). This could be due to the characteristic of Imazapic which has a moderate value of K_{OC}, which is soil organic carbon / water partition coefficient that correlates with its potential of having more mobile organic contaminants into the groundwater [12]. Hence, due to less rain distribution during off season, there is a possibility of less runoff of Imazapic residue from the spraying area, thus more of the residue leaching through the soil into the groundwater sources.

Table 4 Comparison of Imazapic residue concentration in groundwater between off and main season

Samples	Mean (±SD)	Z	*p*-value*
Off season Main season	3.17 (±4.86) 1.38 (±1.87)	-1.27	0.228

*p-value < 0.05

Table 1 Concentration of imazapic residues presence in surface water samples

DATE	CONCENTRATION OF IMAZAPIC FOUND (ug/mL)									
	W1	W2	W3	W4	W5	W6	WP1	WP2	WP3	WP4
					SEASON 1					
0 day	ND	0.30	0.70	ND	ND	ND	NA	NA	NA	NA
1st day	ND	1.60	ND	7.92	ND	2.40	NA	NA	NA	NA
3rd day	0.50	ND	ND	ND	0.30	1.48	NA	NA	NA	NA
5th day	0.39	ND	5.12	3.70	1.20	2.30	ND	3.85	ND	ND
7th day	0.34	ND	ND	ND	ND	ND	0.72	ND	ND	ND
11th day	0.34	0.76	1.03	2.30	8.75	0.65	ND	ND	0.65	0.31
15th day	0.32	0.45	7.03	0.76	1.70	ND	2.10	0.76	ND	ND
					SEASON 2					
0 day	0.79	0.74	ND	ND	ND	0.28	NA	NA	NA	NA
1st day	6.02	ND	ND	ND	ND	2.06	NA	NA	NA	NA
3rd day	ND	0.75	1.37	0.38	ND	2.99	NA	NA	NA	NA
5th day	ND	ND	2.00	ND	ND	0.68	ND	ND	1.70	ND
7th day	0.35	0.38	ND	ND	0.55	5.00	5.40	0.42	ND	ND
11th day	ND	ND	5.14	0.49	0.31	ND	0.65	1.20	0.76	0.80
15th day	0.29	0.34	0.70	ND	ND	ND	4.75	0.96	ND	ND

Table 2 Concentration of imazapic residues presence in groundwater samples

DATE	CONCENTRATION OF IMAZAPIC FOUND (ug/mL)			
	G1	G2	G3	G4
		SEASON 1		
0 day	1.67	16.00	14.00	ND
1st day	ND	0.70	0.30	5.30
3rd day	0.84	0.29	ND	0.28
5th day	1.30	0.33	ND	1.10
7th day	3.60	ND	ND	0.33
11th day	ND	1.03	ND	ND
15th day	ND	ND	ND	3.62
		SEASON 2		
0 day	0.32	ND	4.75	ND
1st day	2.46	ND	ND	ND
3rd day	ND	5.40	ND	ND
5th day	0.58	0.48	ND	0.51
7th day	ND	4.70	ND	ND
11th day	1.20	ND	ND	0.42
15th day	ND	0.61	0.31	0.35

4.0 CONCLUSION

This study demonstrated that imazapic residues can be detected in the surface water and groundwater of this paddy field area. It also showed that the detection of imazapic compound was available until the 15th day of sampling. Nevertheless, the concentration of Imazapic compound detected during main season (0.71 ug/mL) were higher compared to the samples collected in off season (0.57 ug/mL) which can be related to the higher rain distribution during main season that contribute to the leaching of imazapic residues into nearest surface water area through surface runoff carry over. The presence of Imazapic residues in surface water and groundwater sources can lead to several health problems to farmers and people exposed to it as well as effecting the aquatic ecosystem. Therefore, a proper water management control such as adhering to the proper water holding period after the herbicide application is recommended. In addition, the recommended concentration and the frequency of spraying activity should be monitored to avoid any carry over and/or leaching of imazapic residues into the surface water and groundwater sources.

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References

[1] Demoliner, A., S. S. Caldas, F. P. Costa, and F. F. Goncalves. 2010. Development and Validation of a Method using SPE and LC-ESI-MS-MS for the Determination of Multiple Classes of Pesticides and Metabolites in Water Samples. *Journal of Brazillian Chemical Society*. 21(8): 1424-1433. Christine R. 1999. The Eye of the Beholder– Designing for Colour-blind Users. *British Telecommunications Engineering*. 17: 291-295.

[2] Caldas, S. S., R. Zanella, and E. G. Prime. 2011. Herbicides and Environment : Risk Estimate of Water Contamination and Occurrence of Pesticides in the South of Brazil. In Dr Andreas Kortekamp (Ed.). *Herbicides and Environment* 471-493. InTech. [Online]. From: http://www.intechopen.com/books/herbicides-and-environment/risk-estimate-of-water-contamination-and-occurrence-of-pesticide-in-the-south-of-brazil. [Accessed on 12 August 2013].Healy, G., Shafer, S. and Wolff, L. 1992. *Physics Based Vision: Principles and Practice, COLOR*. Boston: Jones and Bartlett.

[3] Mohd Fuad, M. J., A. B. Junaidi, A. Habibah, J. Hamzah, M.E. Toriman, N. Lyndon, A.C. Er, S. Selvadurai, and A. M. Aziman. 2012. The Impact Of Pesticides On Paddy Farmers And Ecosystem. *Advances in Natural and Applied Sciences*. 6(1): 65-70. Poret, S., Jony, R. D. and Gregory, S. 2009. Image Processing for Color Blindness Correction. *IEEE Toronto International Conference*. 1-6.

[4] Nakano, Y., A. Miyazaki, T. Yoshida, and K. Ono. 2004. A Study On Pesticide Runoff From Paddy Fields To A River In Rural Region — 1 : Field Survey Of Pesticide Runoff In The Kozakura. *Water Research*. 38: 3017-3022. Plataniotis, K. N. and Vinetsanopoulos. A. N. 2000. *Color Image Processing and Application.* Berlin: Springer-Verlag.

[5] Colborn, T., and P. Short. 1999. Pesticide Use In The U.S. And Policy Implications: A Focus On Herbicide. *Toxicology and Industrial Health*. 15: 241-276. SeuttgiYmg and Yong Man Ro. 2003. *Visual Contents Adaptation for Color Vision Deficiency*. 1: 453-456.

[6] Krieger R., J. Doull, D. Ecobinchon, D. Gammon, E. Hodgson, L. Reiter, J. Ross. 2001. In Handbook of Pesticide Toxicology-Principles, Volume 2. Chapter 74:Imidazolinone. USA:Academic Press.

[7] Cox, C. 2003. Herbicide Factsheet. *Journal of Pesticide Reform*. 23(3): 10-14.

[8] Alister, C. and M. A. Kogan. 2005. Efficacy Of Imidazolinone Herbicides Applied To Imidazolinone-Resistant Maize And Their Carryover Effect On Rotational Crops. *Crop Protection.* 24: 375-379.

[9] Baumart, J. S. and S. Santos. 2011. The Impact of Herbicides on Benthic Organisms in Flooded Rice Fields in Southern Brazil. In Dr Andreas Kortekamp (Ed.). *Herbicides - Mechanisms and Mode of Action.* 369-382. Croatia:InTech Europe. [Online]. From: http://www.intechopen.com/books/herbicides-and-environment/the-impact-of- herbicides-on-benthic-organisms-in-flooded-ricefields-in-southern-brazil. [Accessed on 12 August 2013].

[10] Geronimo, E. D., V. C. Aparicio, S. Barbaro, R. Portocarrero, S. Jaime, and J. L. Costa. 2014. Chemosphere Presence Of Pesticides In Surface Water From Four Sub-Basins In Argentina. *Chemosphere*. 107: 423–43.Bimber, Oliver, and Ramesh, Raskar. 2005. *Spatial Augmented Reality*. Massachusetts: A K Peters.

[11] Azmi, M., S. Azlan, K. M. Yim, T. V. George, and S. E. Chew. 2012. Control Of Weedy Rice In Direct-Seeded Rice Using The Clearfield Production System In Malaysia. *Pakistan Journal of Weed Science Research*. 18(Special Issue): 49-53.

[12] Zanella, R., M. B. Adaime, S. C. Peixoto, C. A. Friggi, O. D. Prestes, S. L. O. Machado, E. Marchesan, L. A. Avila, and E. G. Primel. 2011. Herbicides Persistence in Rice Paddy Water in Southern Brazil. In Dr Andreas Kortekamp (Ed.). *Herbicides - Mechanisms and Mode of Action.* 369-382. Croatia:InTech Europe. [Online]. From: http://www.intechopen.com/books/herbicides-and-environment/the-impact-of- herbicides-on-benthic-organisms-in-flooded-ricefields-in-southern-brazil. [Accessed on 12 August 2013].

[13] Gholizadeh, A., Mohd Amin Mohd Soom, Mohammad Mehdi Saberioon, and L. Boruvkap. 2013. Visible And Near Infrared Reflectance Spectroscopy To Determine Chemical Properties Of Paddy Soils. *Journal of Food, Agriculture & Environment*. 11(2): 859-866.

[14] Mohd Ekhwan Toriman, M. E., L. Q. Yun, Kamarudin, Mohd Khairul Amri Kamarudin, Nor Azlina Abdul Aziz, Mazlin Mokhtar, Rahmah Elfithri, and K. Bhaktikul, 2014. Applying Seasonal Climate Trends To Agricultural Production In Tanjung Karang, Malaysia. *American Journal of Agricultural and Biological Science*. 9(1): 119-126.

[15] Ohio Environmental Protection Agency. 2013. Surface Water Field Sampling Manual For Water Column Chemistry, Bacteria And Flows. Division of Surface Water. [Online] From: http://www.epa.ohio.gov/Portals/35/documents/SW_SamplingManual.pdf. [Accessed on 10 May 2013].

[16] Ramezani, M., N. Simpson, , D. Oliver, R. Kookana, G. Gill, and C. Preston. 2009. Improved Extraction And Clean-Up Of Imidazolinone Herbicides From Soil Solutions Using Different Solid-Phase Sorbents. *Journal of Chromatography A*. 1216: 5092-5100.

[17] Ismail, B. S., Mehdi Sameni, M. Halimah. 2011. Evaluation of Herbicide Pollution in the Kerian Ricefields of Perak , Malaysia. *World Applied Science Journal.* 15(1): 5-13.

[18] Anis Zakiah Mazlan, Hazilia Hussain, Mohammed Azwan Mohammed Zawawi And Mehdi Sameni. 2015. Analytical Method Development For Imazapic Herbicide Using High Performance Liquid Chromatography. 19(4): 715-721.

[19] Silva, D. R. O. Da, Avila, L. A. De, Agostinetto, D., Dal Magro, T., Oliveira, E. De, Zanella, R., & Noldin, J. A. 2009. Pesticide Monitoring In Surface Water of Rice Production Areas In Southern Brazil. *Ciencia Rural*. 39(9): 2383-2389.

[20] Zaki Zainudin. 2010. Benchmarking River Water Quality In Malaysia. *Jurutera*. (February): 12-15. [Online] From: http://www.myiem.org.my/content/iem_bulletin_2010-185.aspx. [Accessed on 21 July 2014.