Persistence behavior of metamifop and its metabolite in rice ecosystem

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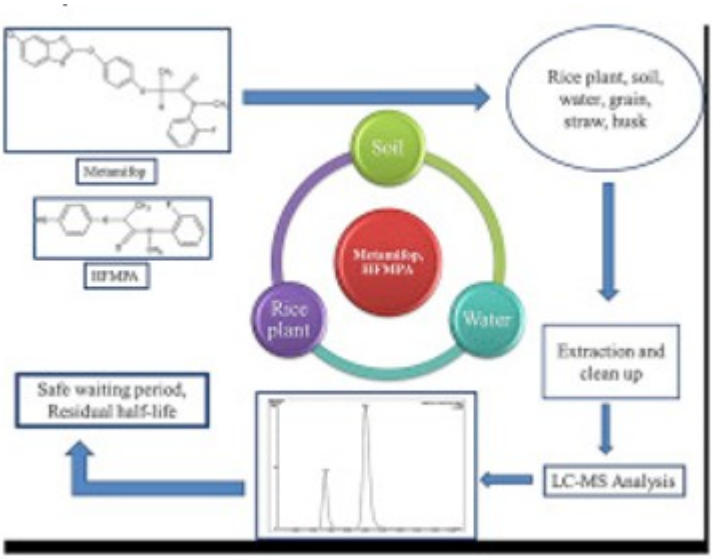
Abstract

A field experiment was conducted to determine the persistence of metamifop in transplanted rice crop for two seasons. Metamifop 10% EC was applied at two doses: 100 g a.i. $ha^{-1}$and 200 g a.i. ha^{-1} at 2–3 leaf stage of *Echinochloa crusgalli*. The residues of metamifop along with its major metabolite, N-(2-fluorophenyl)-2-hydroxy-N-methylpropionamide (HFMPA), were estimated in rice plant, field water and soil using Liquid Chromatography Mass Spectrometry. Limit of detection and limit of quantification of the method for both the compounds were set at 0.003 μg g^{-1} and 0.010 μg g^{-1} respectively. Metamifop showed less persistence in field water and rice plant as compared to soil samples. Presence of HFMPA was recorded in rice plant and soil. Both the compounds were found below level of quantification in harvest samples of straw, grains, husk and soil. A safe waiting period of 52 d was suggested for harvesting of rice when metamifop was applied at 100 g a.i. ha^{-1}(recommended dose).

Graphical abstract



Keywords: Metamifop, HFMPA, Rice, Water, Soil, Persistence

1. Introduction

Demand of food grains in India is rising day by day because of its growing population, which is a matter of concern for country's food security. Rice is the most staple cereal in India which holds 24% share in terms of gross cropped area of the country. The crop has 42% share in cumulative food grain production and 45% share in total cereal production of the country

(Sharma, 2011). However, the average yield of rice (2.2 MT ha^{-1}) in India is quite less in comparison to global average of 2.7 MT ha^{-1}(Sharma, 2011). Among the various production challenges weeds affect the rice yields to the maximum extent (Paul et al., 2014). Crop weed competition in rice can cause yield loss to vary within 40–60% and under unweeded condition the loss may raise up to 96% (Chauhan and Johnson, 2011).

Rice, at its critical stages of growth, suffers heavily from weed infestation which results into yield loss. Populations of grassy weeds are increasing rapidly due to global warming, water shortage and many other factors. This is a huge setback for the policymakers of the country who are trying to achieve the goal of 'Doubling the farmers' income by 2022' (Press Information Bureau, 2016).

Among different weed flora commonly present in the rice field, barn yard grass (*Echinochloa crusgalli*) is the dominant one (Maun and Barrett, 1986) which can cause about 57% reduction in rice yield (Dhaliwal and Arora, 1996). Some other important weed species are *Echinochloa colona*, *Cyperus* spp., *Alternanthera* spp., *Elusine indica*, *Leptochloa chinensis*, *Commelina benghalensis*, *Eclipta alba*, *Fimbristylis miliacea*, *Dactyloctenium aegypticum* etc., which can do considerable damage to rice crop (Sharma, 2011). Weed management using various weed control practices during early period of crop growthprevents yield loss beyond economic threshold level but one of the most conventional weed control method among farmers i.e., hand weeding is almost impractical on today's date. Due to acute crisis of agricultural labor for manual weeding and increasing human labor charges, Indian farmers are getting encouraged in applying herbicide to control these weeds at lesser expense. Several generic herbicidal compounds are being applied in the field, but cannot effectively control barnyard grass as it has some morphological similarities with rice. Herbicidal resistance in weed is also an important factor for making some weedicides inefficient.

Metamifop ((R)-2-[4-(6-chloro-1,3-benzoxazol-2-yloxy) phenoxy]-2′-fluoro-N methyl propionanilide) (Fig. 1a), a new oxygen ester phenoxy-acetic acid group herbicide, can effectively control different annual grassy weeds in rice field, including barnyard grass (Zeng and Jiang, 2004). It is a post-emergence herbicide developed by Dongbu Hannong Chemical Co, Ltd. (Korea Republic) (Xia et al., 2016). The compound is registered in China, Sri Lanka, Japan, Ecuador, Philippines, Vietnam, Cambodia, Malaysia, Indonesia, Colombia and also in the process of registration in India, Russia, Kazakhstan, Brazil, Uzbekistan and Thailand (Agronews, 2017). In Japan, the maximum residue limit (MRL) of metamifop in brown rice is fixed as 0.02 ppm (Metamifop MRL, 2017). The compound has low toxicity to mammals (acute oral LD_{50} > 2000 mg kg^{-1}) but moderate to honeybee (oral acute 48 h LD_{50}– 100 µg bee^{-1}), earthworm (acute 14 day LC_{50}– 1000 mg kg^{-1}), fish (acute 96 h LC_{50} - 0.307 mg L^{-1}) and aquatic invertebrates (acute 48 h EC_{50}- 0.288 mg L^{-1}) (Lewis et al., 2016). The enzyme acetyl-CoA carboxylase,

responsible for lipid biosynthesis in grass, is inhibited by the use of metamifop which leads to chlorosis and ultimately death of the plant (Lewis et al., 2016). According to Adhikary (2016), metamifop applied at 2–3 leaf stage of weeds, effectively controlled grassy weeds in rice field and herbicidal resistance did not develop in weeds as well. In another study, it was found that metamifop 10% EC (Emulsifiable Concentrate) at 100 g a.i. ha^{-1} showed excellent control on grassy weeds and produced higher yields in direct seeded rice (Nithya et al., 2011). A major metabolite of metamifop, N-(2-fluorophenyl)-2-hydroxy-N-methylpropionamide (HFMPA), which was also considered to be first degradation product of the herbicide (Moon et al., 2010), (Fig. 1b), was found in both soil and grains of paddy (Janaki and Chinnusamy, 2012). In an experiment, ^{14}C-metamifop was applied to chemically reduced anaerobic soil at a rate of 0.10 ppm, equivalent to approximately field dosage rate of 100 g of active ingredient per hectare. This study confirmed that use of a chemical reducing agent like sodium sulfide could shorten the pre-incubation time of the anaerobic soil metabolism (Chang et al., 2005).

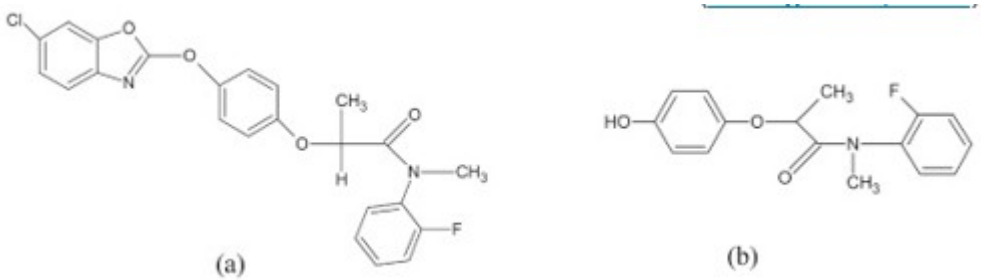


Fig. 1. Structure of metamifop (a) and HFMPA (b).

It is now very much clear that pesticides may persist in the environment and can be toxic to humans if consumed through food, drinks or by any other means. Hence, to evaluate their bio-magnification potential in food chain, persistence of metamifop and its major metabolite, HPFMA, needs to be determined in different components of rice growing environment. Limited information is available on residual fate of metamifop along with its metabolite, HFMPA, in transplanted rice at different locations of India. Thus, the present experiment was conducted to determine the dissipation kinetics of metamifop in transplanted rice over two consecutive seasons. Location of this study was selected as West Bengal which is the largest rice producing state of India, dominated by transplanted rice (Adhikari et al., 2011). The residues were estimated using Liquid Chromatography Mass Spectrometry (LC-MS) instrument which can produce more confirmatory results as compared to conventional chromatographic instruments. This study would also help to work out the crucial interval period between metamifop application and harvest of rice for safe consumption of the crop.

2. Materials and methods

2.1. Chemicals

Analytical standard of metamifop (99.5% purity), HFMPA (99.0% purity) and metamifop 10% EC formulation was supplied by M/s FMC India Pvt. Limited. All solvents and reagents used in the experiment were of analytical grade. Standard stock solutions (100 mg L^{-1}) of metamifop and HFMPA (both individual and mixture) were prepared by dissolving 100 mg of both these compounds in 1000 mL acetonitrile. As and when required, working standard solutions of both these compounds were made through serial dilution of the stock solution.

2.2. Instrument

Waters LC-MS System (2695 Separation Module), attached with Micromass – Quattro Micro API mass unit equipped with Mass Lynx software, was used in the experiment for analysis. Waters Symmetry C_{18} (5 µm, 2.1 × 100 mm) chromatograph column was used for the separation of analytes.

2.3. Field experiment

An experiment was conducted at Kalyani, West Bengal (altitude 11 m, latitude 22.99°N, longitude 88.43°E) over two consecutive kharif seasons to investigate the residual fate of metamifop and HFMPA in rice plant (variety MTU 7029), field water (standing water in the field) and soil as well as extent of residues in plant, grain, husk and field soil at harvest. Soil of experimental plot was sandy loam with average pH of 6.85 and contained high organic carbon (0.96%). Average rainfall received during experiment was 728.10 mm in season I and 853.70 mm in season II. The experiment was laid out in Randomized Block Design (RBD) with plot size of 30 m^2. Metamifop 10% EC was applied at 100 g a.i. ha^{-1} (recommended dose) and 200 g a.i. ha^{-1} (double the recommended dose) at 2–3 leaf stage of *Echinochloa crusgalli* in replicated plots. Untreated control plots (only water spray) were also maintained.

2.4. Sampling

Rice plant samples (250 g) from each replicated plot including untreated, were collected at 0 (2 h after spraying), 1, 3, 7, 15, 30 and 60 d after metamifop application. Field water (200 mL) and soil samples (1 kg) were collected at same interval. Straw (250 g), grain (2 kg), husk (100 g) and field soil samples were collected at harvest. All the samples mentioned above were drawn randomly from the field.

2.5. Sample preparation

Samples were processed after collection as early as possible. If not processed immediately, samples (except water) were stored in deep freeze at (−20 ± 2)°C for a minimum period of time.

2.5.1. Plant sample (including straw, grain and husk)

Representative plant sample (50 g) was taken in a homogenizer vessel (Polytron, PT 3100) and homogenized for 4–5 min. After that, 5 g homogenized sample was taken in a 50 mL centrifugetube. A mixture

(20 mL) of acetonitrile and water (8:2, v/v; HPLC grade) was mixed with it. The tube was then kept undisturbed for 2 h. A mixture (2 g) of C_{18} (Bond Elut®) and anhydrous Na_2SO_4(1:1, w/w) was added into the sample. The tube was then placed in a shaker (at 25 °C) and processed for 30 min at 200 rpm speed. The tube was then centrifuged (Avanti J-30I Centrifuge, Beckman Coulter) for 10 min at 5000 rpm speed at 25 °C. Aliquot portion of the sample was collected from the centrifuge tube with the help of a micropipette. The collected fraction was concentrated in a rotary vacuum evaporator at 40 °C and the volume was reconstituted with solvent mixture of acetonitrile and water (9:1, v/v; HPLC grade) added with 5 mM CH_3COONH_4. The sample was then filtered through 0.2 µ membrane filter for final LC-MS analysis.

2.5.2. Water sample

Water sample was partitioned with 100 mL of ethyl acetate in a separatory funnel and organic layer was collected over anhydrous Na_2SO_4. The same process was repeated with 50 mL ethyl acetate twice and the collected organic fractions were combined. This combined fraction was concentrated in rotary vacuum evaporator at 40 °C and the volume was made up with solvent mixture of acetonitrile and water (9:1, v/v; HPLC grade) added with 5 mM CH_3COONH_4. The sample was then filtered through 0.2 µ membrane filter for final LC-MS analysis.

2.5.3. Soil sample

After drying, representative soil sample (10 g) was taken in 50 mL centrifuge tube. A mixture (20 mL) of acetonitrile and water (8:2, v/v; HPLC grade) was added into it. The tube was then kept undisturbed for 2 h. After that, the tube was placed in a shaker (at 25 °C) and shaken for 30 min at 200 rpm speed. Thereafter, the method for processing plant sample from centrifugation step was followed.

2.6. Data analysis

Dissipation of metamifop in rice field followed first order kinetics which can be described as: $C_t=C_0e^{-kt}$ where C_0 represents initial concentration, C_t is the pesticide residual concentration at time $t$and k is the degradation rate constant calculated in days. In first order kinetics, logarithm of pesticide residual concentration is linearly correlated with time and the equation can be written as: $\ln C_t = \ln C_0 - kt$. With this, the half-life value ($t_{1/2}$) of metamifop for each experiment was determined as: $t_{1/2} = \ln 2/k$.

Pre-Harvest Interval (PHI) is defined as the day interval between final pesticide application and harvest of the crop, required for the pesticide residue to get reduced below the Maximum Residue Limit (MRL). It is essential to maintain the PHI for safe consumption of the harvest and this can be obtained as: PHI = [$\ln C_0$ – $\ln MRL$]/k. MRL is expressed in mg kg^{-1}.

3. Results and discussion

3.1. Instrumental detection and linearity

Metamifop and HFMPA, under mentioned instrumental condition, were detected at 2.53 ± 0.10 min and 1.35 ± 0.10 min respectively (Fig. 2). A linear response was observed between different concentrations ranged from 3 to 200 μg L^{-1} of both the analytical standards (x) and detector response (y). This linear regression equation can be represented as: $y=a + bx$. For metamifop, this equation could be expressed as: $y = 140693x + 333.88$, $R^2 = 0.9966$ and for HFMPA, this could be represented as: $y = 45184x + 23.062$, $R^2 = 0.9997$; where R^2 is the correlation coefficient. It was evident from the result that metamifop and HFMPA showed good linearity in respect to detector response (Francotte et al., 1996).

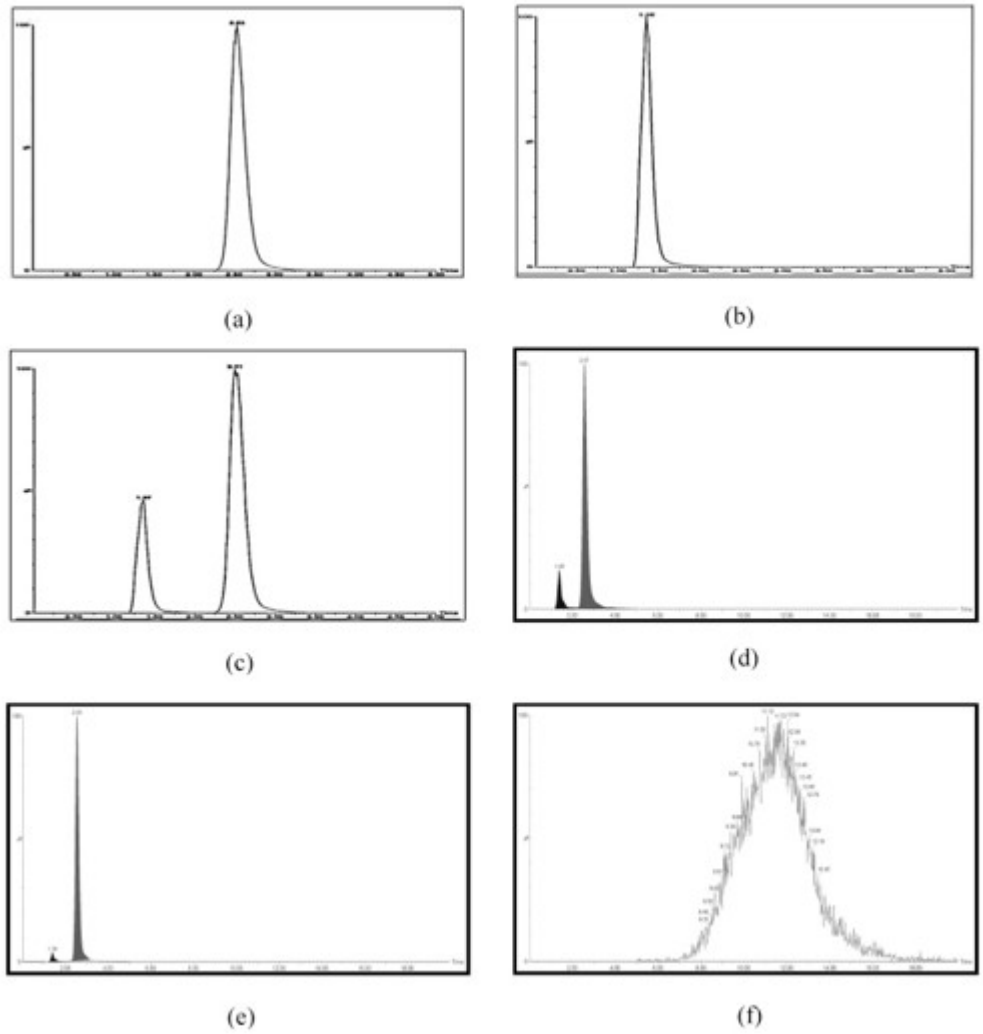


Fig. 2. Chromatogram of analytical standard of metamifop (a), HFMPA (b) and standard mixture of metamifop and HFMPA (c), fortified sample of metamifop and HFMPA (d), field sample of metamifop and HFMPA (e) and blank sample (f) under experimental condition.

3.2. Limit of detection (LOD) and limit of quantification (LOQ)

LOD can be defined as the lowest detectable concentration of analyte in a method. LOC is the lowest analytical concentration that can be measured with acceptable accuracy and precision, under given experimental condition. Francotte et al. (1996)derived these limits in an experiment by the following formulas: LOD = 2 $h_n C_s/h_s$, LOQ = 6 $h_n C_s/h_s$, where C_s represents the amount of analytical standard injected; h_n stands for the largest deviation of detector signal from the mean baseline level, determined at the retention time of the analyte; h_s represents the peak height of the analyte computed from the mean baseline level to the top of the peak. To determine these limits, serial dilution of analytical standard mixture (i.e., metamifop and HFMPA) was done and injected in the instrument. The basis of selection of the peak from the series was that h_s should be 2–10 times larger than the signal-to-noise ratio h_n (Francotte et al., 1996). By following this method, LOD and LOQ were set as 3 μg L^{-1} and 10 μg L^{-1} respectively, for both metamifop and HFMPA.

3.3. Precision

3.3.1. Precision (repeatability)

Precision (repeatability) is used to measure the variability in results in terms of relative standard deviation (RSD) values when repetitive tests are performed on same condition (Cao et al., 2005). In present method, repeatability was determined by adding metamifop and HFMPA in different concentrations to blank samples. The within-batch recoveries and corresponding RSD values for the spiked samples at different levels of 0.01, 0.02, 0.05 and 0.10 mg kg^{-1} are presented in Table 1. Different RSD values corresponding to various substrates spiked with metamifop and HFMPA ranged from 1.25% to 12.96% which confirmed high level of precision in terms of repeatability.

Table 1. Within-batch recoveries and corresponding RSD values of metamifop and HFMPA in different substrates.

Substrate	**Spiking level (mg kg^{-1}/mg L^{-1} (for water))**	**Metamifop**			**HFMPA**		
		Recovery[a](%)	**SD**	**RSD (%)**	**Recovery (%)**	**SD**	**RSD (%)**
Plant	0.01	88.00	0.0004	4.55	94.00	0.0002	2.13

Substrate	Spiking level (mg kg^{-1}/mg	Metamifop			HFMPA		
		Recovery[a](%)	SD	RSD (%)	Recovery (%)	SD	RSD (%)
	0.02	90.33	0.0010	5.38	91.17	0.0012	6.70
	0.05	88.93	0.0029	6.46	87.73	0.0048	10.89
	0.10	85.90	0.0043	5.02	86.17	0.0075	8.65
Water	0.01	87.00	0.0004	4.60	93.00	0.0012	12.40
	0.02	95.00	0.0014	7.42	95.17	0.0022	11.32
	0.05	90.27	0.0059	12.96	86.13	0.0028	6.61
	0.10	93.47	0.0045	4.76	95.60	0.0069	7.19
Soil	0.01	89.67	0.0007	7.91	93.33	0.0008	8.04
	0.02	93.33	0.0008	4.49	94.33	0.0012	6.41
	0.05	86.53	0.0023	5.38	87.07	0.0028	6.44
	0.10	93.37	0.0051	5.41	89.20	0.0017	1.94
Straw	0.01	93.00	0.0006	6.72	85.00	0.0010	11.22
	0.02	87.83	0.0017	9.90	86.50	0.0017	9.66
	0.05	85.07	0.00	3.8	85.80	0.00	9.9

Substrate	Spiking level (mg kg^{-1}/mg	Metamifop			HFMPA		
		Recovery[a](%)	SD	RSD (%)	Recovery (%)	SD	RSD (%)
			16	1		43	5
	0.10	93.67	0.0048	5.17	88.67	0.0053	5.97
Grain	0.01	86.67	0.0010	11.84	86.33	0.0002	2.67
	0.02	93.67	0.0004	2.16	94.17	0.0006	3.24
	0.05	85.40	0.0040	9.27	85.13	0.0025	5.87
	0.10	89.47	0.0020	2.19	86.27	0.0045	5.17
Husk	0.01	86.00	0.0004	4.65	89.33	0.0009	10.16
	0.02	91.33	0.0014	7.47	87.50	0.0005	2.86
	0.05	88.13	0.0026	5.96	83.60	0.0023	5.60
	0.10	92.13	0.0029	3.16	90.90	0.0011	1.25

a. Values are average of three replicates.

3.3.2. Precision (reproducibility)

Precision (reproducibility) denotes the degree of accordance obtained through analyzing same samples under different test conditions such as separate instruments, different analysts and in different laboratories etc. It is also measured by calculating RSD values (Cao et al., 2005). The between-batch recoveries along with corresponding RSD values at same levels of repeatability test are mentioned in Table 2. It was found that RSD values in different substrates spiked with metamifop and HFMPA ranged from 1.21% to

13.43% which are well in agreement with the acceptance limit (Causon, 1997).

Table 2. Between-batch recoveries and corresponding RSD values of metamifop and HFMPA in different substrates.

Substrate	Spiking level (mg kg^{-1}/mg L^{-1} (for water))	Metamifop			HFMPA		
		Recovery[a](%)	SD	RSD (%)	Recovery (%)	SD	RSD (%)
Plant	0.01	88.67	0.0002	2.35	89.67	0.0005	5.03
	0.02	89.67	0.0018	9.82	96.33	0.0010	5.40
	0.05	88.00	0.0024	5.52	85.73	0.0029	6.65
	0.10	93.33	0.0053	5.64	88.10	0.0041	4.68
Water	0.01	89.67	0.0012	12.93	90.67	0.0009	9.38
	0.02	95.33	0.0005	2.36	93.67	0.0011	5.61
	0.05	85.00	0.0050	11.88	87.73	0.0040	9.07
	0.10	90.97	0.0063	6.97	89.57	0.0039	4.30
Soil	0.01	80.33	0.0010	12.09	87.00	0.0005	6.08
	0.02	91.83	0.0008	4.16	87.50	0.0011	6.44

Substrate	Spiking level (mg kg^{-1}/mg	Metamifop			HFMPA		
		Recovery[a](%)	SD	RSD (%)	Recovery (%)	SD	RSD (%)
	0.05	81.47	0.0023	5.69	85.07	0.0022	5.16
	0.10	93.47	0.0050	5.34	88.97	0.0078	8.72
Straw	0.01	92.00	0.0004	4.74	85.33	0.0006	7.53
	0.02	90.33	0.0014	7.64	83.33	0.0011	6.64
	0.05	85.60	0.0031	7.20	81.07	0.0031	7.67
	0.10	86.60	0.0045	5.14	95.63	0.0031	3.28
Grain	0.01	83.67	0.0011	13.22	81.33	0.0009	10.46
	0.02	86.67	0.0010	5.54	94.83	0.0013	6.68
	0.05	84.60	0.0043	10.05	84.53	0.0018	4.37
	0.10	87.13	0.0041	4.75	92.63	0.0046	4.94
Husk	0.01	81.67	0.0011	13.43	90.00	0.0003	2.94
	0.02	89.83	0.0014	7.99	92.67	0.0008	4.49
	0.05	85.73	0.0034	8.03	85.13	0.0010	2.32
	0.10	89.33	0.00	1.2	92.77	0.00	6.1

Substrate	Spiking level (mg kg^{-1}/mg	Metamifop			HFMPA		
		Recovery[a](%)	SD	RSD (%)	Recovery (%)	SD	RSD (%)
			11	1		57	3

a. Values are average of three replicates.

3.4. Accuracy

Accuracy of the test method is the degree of agreement between the absolute value of analyte present in the sample and that recorded during analysis (Francotte et al., 1996). To determine accuracy of the method, recovery experiment was carried out on three replicates of each substrate, spiked at different levels of metamifop and HFMPA (Table 1, Table 2). Each sample was injected three times and mean value was recorded. The average recoveries of metamifop obtained were 89.10% in plant, 90.84% in water, 88.75% in soil, 89.26% in straw, 87.16% in grain and 88.02% in husk. In case of HFMPA, the corresponding values were 89.86% in plant, 89.06% in water, 89.06% in soil, 86.42% in straw, 88.15% in grain and 88.99% in husk. These findings were very much satisfactory and the method was adopted for analysis.

3.5. Persistence of metamifop in plant, water and soil

Residue data of metamifop pertaining to plant, water and soil samples are presented in Table 3. Linear correlation was observed between logarithmically transformed values of metamifop residues and progress of time, which showed that metamifop dissipation in all substrates followed first order kinetics (Fig. 3). Metamifop in rice plant dissipated with progress of time and found below level of quantification (BLOQ) on 7th d for recommended dose (RD) and 10th d for double the recommended dose (DRD) irrespective of seasons. High rainfall as well as faster metabolism in plants may cause quick dissipation of metamifop residues. In case of water samples, metamifop residue was BLOQ on 7th d for RD and 15th d for DRD in both the seasons. Low solubility of metamifop in water (0.687 mg L^{-1}) (Janaki and Chinnusamy, 2012) could be the reason for faster dissipation causing settle down of residues to soil surface. In soil, metamifop was slightly more persistent compared to rice plants as well as field water and dissipated BLOQ on 30th d for both the doses and seasons. Dissipation of metamifop in soil could be attributed to high organic matter content as suggested by Dimou et al. (2004). Half-life values of metamifop in different substrates ranged between 1.91 d and 35.36 d considering both doses and seasons (Fig. 3).

Table 3. Residues of metamifop and HFMPA in different substrates.

Day	Dose	Residue (mg kg^{-1}/mg L^{-1} (for water)) (Mean ± SD)									
		Metamifop						HFMPA			
		Plant		Water		Soil		Plant		Soil	
		Season I	Season II	Season I	Season II	Season I	Season II	Season I	Season II	Season I	Season II
0	RD	0.57 ± 0.030	0.60 ± 0.048	0.19 ± 0.011	0.23 ± 0.048	0.50 ± 0.019	0.53 ± 0.031	BLOQ	BLOQ	BLOQ	BLOQ
	DRD	1.20 ± 0.031	1.29 ± 0.061	0.31 ± 0.030	0.35 ± 0.046	1.01 ± 0.021	1.06 ± 0.020	BLOQ	BLOQ	BLOQ	BLOQ
1	RD	0.30 ± 0.049	0.33 ± 0.031	0.06 ± 0.004	0.08 ± 0.015	0.46 ± 0.020	0.47 ± 0.010	BLOQ	BLOQ	BLOQ	BLOQ
	DRD	0.67 ± 0.040	0.71 ± 0.020	0.14 ± 0.015	0.16 ± 0.033	0.96 ± 0.020	1.00 ± 0.030	BLOQ	BLOQ	BLOQ	BLOQ
3	RD	0.20 ± 0.020	0.18 ± 0.025	0.02 ± 0.003	0.02 ± 0.004	0.39 ± 0.020	0.42 ± 0.009	BLOQ	BLOQ	BLOQ	BLOQ
	DRD	0.45 ± 0.020	0.48 ± 0.019	0.06 ± 0.006	0.06 ± 0.009	0.92 ± 0.011	0.93 ± 0.030	BLOQ	BLOQ	BLOQ	BLOQ
7	RD	BLOQ	BLOQ	BLOQ	BLOQ	0.33 ± 0.029	0.35 ± 0.029	0.02 ± 0.004	0.02 ± 0.004	BLOQ	BLOQ
	DRD	0.15 ± 0.010	0.20 ± 0.010	0.02 ± 0.003	0.02 ± 0.003	0.76 ± 0.020	0.79 ± 0.043	0.04 ± 0.005	0.05 ± 0.009	BLOQ	BLOQ
15	RD	–	–	–	–	0.25 ± 0.020	0.26 ± 0.029	BLOQ	BLOQ	0.23 ± 0.014	0.24 ± 0.030
	DRD	BLOQ	BLOQ	BLOQ	BLOQ	0.50 ± 0.031	0.56 ± 0.019	0.02 ± 0.004	0.02 ± 0.002	0.43 ± 0.046	0.46 ± 0.021
30	RD	–	–	–	–	0.09 ± 0.011	0.10 ± 0.011	–	–	0.16 ± 0.016	0.15 ± 0.012
	DR	–	–	–	–	0.25 ± 0.019	0.27 ± 0.042	BLOQ	BLOQ	0.27 ± 0.036	0.25 ± 0.029

Day	Dose	Residue (mg kg^{-1}/mg L^{-1} (for water)) (Mean ± SD)									
		Metamifop						HFMPA			
		Plant		Water		Soil		Plant		Soil	
		Season I	Season II	Season I	Season II	Season I	Season II	Season I	Season II	Season I	Season II
	D										
60	RD	–	–	–	–	BLOQ	BLOQ	–	–	0.05 ± 0.005	0.05 ± 0.012
	DRD	–	–	–	–	BLOQ	BLOQ	–	–	0.09 ± 0.011	0.10 ± 0.009
90	RD	–	–	–	–	–	–	–	–	BLOQ	BLOQ
	DRD	–	–	–	–	–	–	–	–	BLOQ	BLOQ

RD – recommended dose; DRD – double the recommended dose.

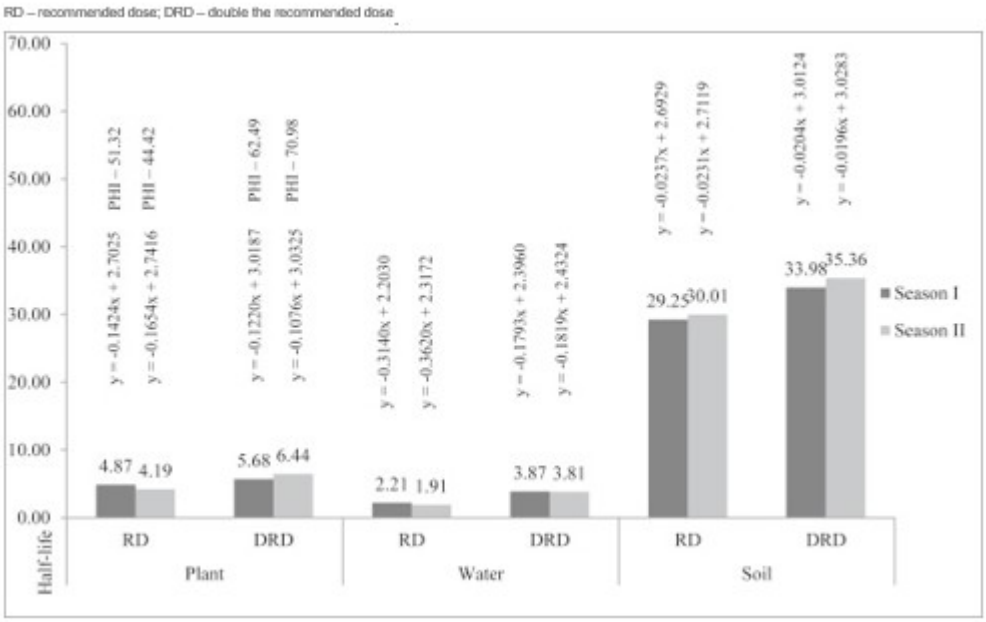


Fig. 3. Regression equation, half-life and PHI values of metamifop in different substrates.

PHI values of metamifop in rice crop had been established considering the default MRL of 0.01 mg kg^{-1} (Regulation (EC), 2005) as the particular data was not available for Indian condition. It ranged between 44.42 d and 70.98 d for rice crop considering both doses and seasons (Fig. 3).

3.6. Estimation of HFMPA residues in plant, water and soil

Presence of HFMPA metabolite in different samples over two seasons are summarized in Table 3. The metabolite HFMPA recorded in rice plant was 0.02 mg kg^{-1} on 3rd d at RD of metamifop regardless of growing seasons. The corresponding values of metamifop in season I and II were 0.04 mg kg^{-1} and 0.05 mg kg^{-1} at DRD respectively. The particular metabolite was BLOQ on 7th d at RD and 15th at DRD of metamifop irrespective of seasons. Initial residual concentration of HFMPA was higher in soil samples as compared to rice plant and even recorded in samples collected at 60^{th} d regardless of doses and seasons. Microbial degradation of metamifop is still considered as the most efficient way compared to physical and chemical processesof soil to reduce its residue levels (Zhang et al., 2014). Soil temperature and pH are two crucial factors that influence metamifop degradation by microbes. The optimal soil pH for metamifop degradation is between 7.0 and 8.0 (Dong et al., 2017). The degradation ability gets reduced above and below this pH range and may result into slower degradation. Moreover, it was found that metamifop was degraded at slow rate in rainy season than winter season due to low soil temperature (Janaki and Chinnusamy, 2012). This entire phenomenon could be attributed to higher concentration of HFMPA in soil at 15th day though it was below level of quantification at 7th day in present study. The metabolite was found BLOQ in water samples throughout the study. This finding was supported by

other experiments in rice where HPFMA residue was detected in rice cultivated soils and grains (Janaki and Chinnusamy, 2012).

3.7. Analysis of harvest samples

Samples of straw, grain, husk and soils at harvest were analyzed, in which both the compounds were found BLOQ. De-Yang et al. (2011) found similar results on harvest residues of metamifop which was below the detection limits. Saha et al. (2016) reported that no residue of metamifop was quantified in harvest samples of rice when applied as mixture with bispyribac sodium.

Untreated control samples of different substrates were analyzed and residues of both metamifop and HFMPA were found BLOQ.

3.8. Conclusion

The present experiment revealed that metamifop is less persistent in different environmental components related to rice cultivation. Findings were highly confirmatory as the method followed was precise and accurate as well as modern sophisticated instrument like LC MS was used in the study. The compound dissipated more quickly in plant and field water than in soil. HFMPA, major metabolite of metamifop, was present in rice plant and soil samples. But, in harvest samples, both the compounds were found below level of quantification. It may be predicted that metamifop would not interact with the following crop in any way. Rice plant can be safely consumed if harvesting would take place after 52 d from metamifop application at recommended dose. As MTU 7029 variety itself is of longer duration (~140 d) (Swarna (MTU 7029), 2011), sufficient time period (more than 100 d) is available between post emergent herbicide application (like metamifop) and crop harvest. On the basis of present findings, it can be concluded that metamifop, under the mentioned experimental condition, may not pose any toxicity threat to rice consumers upon consumption. This experiment can be extensively conducted in future at different locations of varied climates to delineate stronger and conclusive inference.

Acknowledgement

We are very much thankful to the Department of Agricultural Chemicals, Bidhan Chandra Krishi Viswavidyalaya for providing required infrastructure and support.

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