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Effect of pH on the Transformation of a New Readymix Formulation of the Herbicides Bispyribac Sodium and Metamifop in Water

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Abstract

A laboratory experiment was conducted to investigate the effect of pH on the persistence and the dissipation of the new readymix formulation of bispyribac sodium and metamifop. The experiment was conducted in water of three different pH viz. 4.0, 7.0 and 9.2. The spiking level of both the compounds in water was 1.0 and 2.0 µg/mL. The residues were extracted by a simple, quick and reliable method and quantified by liquid chromatography tandem mass spectrometry (LC-MS/MS). The method was justified based on the recovery study, which was > 85%. The dissipation of both compounds followed first order kinetics. The half-life values ranged between 19.86–36.29 and 9.92–19.69 days for bispyribac sodium and metamifop, respectively. The pH of water has a prominent effect on degradation of both the compounds. The rate of dissipation of both the compounds was highest in water of acidic pH followed by neutral and alkaline pH.

Keywords

Bispyribac sodium, Metamifop, Water, pH LC-MS/MS

In recent years, the analysis of pesticides in water has attracted attention due to the wide use of such compounds, as well as their environmental impact. Pesticides enter into natural water bodies by spray drift, surface runoff and by leaching from soil (Kookana et al. 1998) and vegetation. Among many other factors, the pH of water plays a major role in the transformation of pesticides in aqueous media (Sarkar et al. 1999). Nowadays the combination products are gaining popularity as plant protection chemical because of their multiple modes of action, synergistic action, etc. The combination product of bispyribac sodium and metamifop is a new introduction in the Indian subcontinent for control wide array weed infestation in different crops. Bispyribac sodium (Fig. 1) is a post-emergent systemic herbicide belonging to pyrimidinylcarboxy class. It inhibits the enzyme, acetolactate synthase (Ding et al. 2009) which is necessary for the growth of plants. The herbicide also inhibits the synthesis of branch chain amino acid viz. valine, leucine, and isoleucine. Bispyribac sodium shows low toxicity to birds, earthworms, bees, aquatic invertebrates and fish. Metamifop (Fig. 1) is also a post-emergent herbicide belonging to an

aryloxyphenoxy propionic acid group which is used to control a wide range of annual grass weeds in different cereal crops including paddy. Persistence of metamifop is moderate in soil under aerobic conditions with the typical half-life of 70 days (IUPAC 2009) with the range of 18–120 days. Solubility of this compound in water is low (0.69 mg/L) and it decomposes before reaching the melting point. Photo degradation of metamifop has already done by (Moon et al. 2010) and they proposed that the homolytic fission of C–O bonds in metamifop occurs in the early stage of photolysis and further reactions with a hydroxyl radical and hydrogen radical forms various metabolites. The reported half-life value of metamifop in rice plant, water, and soil was approximately 3.5–2.2, 1.3–2.3, and 11.7–20.2 days (De-Yang et al. 2011).

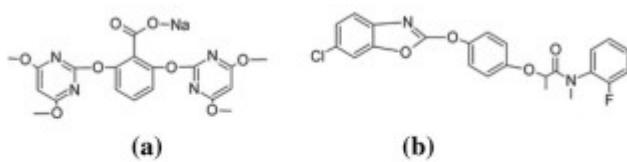


Fig. 1 Chemical structure of bispyribac sodium (a) and metamifop (b)

As the combination product of bispyribac sodium and metamifop (14% SE) is a new introduction in India, there is no information available regarding its fate in aqueous systems. Thus the aim of our study is to find out the effect of pH on the transformation of bispyribac sodium and metamifop in water.

Materials and Methods

Analytical standards of bispyribac sodium (99.71%), metamifop (99.3%) and their formulation (14% SE) were provided by PI industries Ltd., India. High performance liquid chromatography (HPLC) grade ethyl acetate and acetonitrile were procured from RFCL Ltd, India. Sodium chloride, acetic acid and buffer capsule were purchased from Merck India Pvt. Ltd. Distilled water was obtained from the Laboratory distillation unit.

Buffer capsules of pH 4.0, 7.0 and 9.2 were used for preparation of different buffer solutions. One capsule is required for 100 mL of distilled water to maintain the desired pH level. In a series of 250 mL conical flask, 200 mL of distilled water was taken and two buffer capsules were added to each of the conical flask. The conical flasks were shaken manually for 5 min and then left overnight at room temperature for homogeneous mixing. The stock solutions of bispyribac sodium (100 µg/mL) and metamifop (100 µg/mL) were prepared with water from their formulation (14% SE). The composition of the herbicide mixture is 4% bispyribac sodium + 10% metamifop. To prepare a 100 µg/mL solution of bispyribac sodium, 0.25 g formulation was taken and diluted to 100 mL with water, which was a 100 µg/mL stock solution of bispyribac sodium. Similarly to get a 100 µg/mL stock solution of metamifop, we took 0.1 g of formulated product which was diluted to 100 mL with water. The experimental buffer solutions of different pH were spiked individually at two

treatment doses viz. 1.0 µg/mL (T1) and 2.0 µg/mL (T2). The buffer solutions were mixed thoroughly after spiking to get a homogeneous mixture. One set of untreated control blank was simultaneously maintained throughout the experimental period. The experimental flasks were placed in dark at B.O.D incubator and incubated at 28 ± 2 °C. Incubator temperature was maintained by temperature controller. The samples were collected periodically for residue analysis of both bispyribac sodium and metamifop at an interval of 0 (2 h after application), 3, 7, 15, 30, 60, 90 and 120 days after treatment.

Representative 10 mL water sample of bispyribac sodium was taken in a 50 mL polypropylene centrifuge tube and the pH of the water sample was adjusted to 3.0 by adding acetic acid (0.1%). Then 10 mL ethyl acetate was added to the centrifuge tube and the tube was vigorously shaken using a vortex mixture. The tube was then centrifuged at 10,000 rpm for 10 min. The supernatant (4 mL) was collected and concentrated in a nitrogen evaporator at 40 °C. The volume was reconstituted with 4 mL HPLC grade acetonitrile, filtered through a syringe filter and transferred to a 2 mL glass vial for quantification. In case of T₂ dose we have evaporated 4 mL final extract to dryness and the same was reconstituted with 8 mL acetonitrile to make the final concentration within the calibration range.

Representative 10 mL water sample of metamifop was taken in a 50 mL centrifuge tube and 10 mL HPLC grade ethyl acetate + 1 g sodium chloride were added to it. The tubes were then vortexed for 3 min and placed in a roto spin for 30 min at 50 rpm speed. After that the tubes were centrifuged for 10 min at 10,000 rpm. The supernatant (4 mL) was collected, concentrated in a nitrogen evaporator at 40 °C and the volume was reconstituted with 4 mL acetonitrile but in case of T₂ dose the volume was reconstituted with 8 mL acetonitrile. The final extract was filtered through a syringe filter and taken in a 2 mL vial for quantification in liquid chromatography tandem mass spectrometry (LC-MS/MS).

The chromatographic separation of both the analyte was conducted by using LC-MS/MS (Waters, Milford, MA, USA). The separation of analyte was performed by reversed phase Symmetry C18 (5 µm; 2.1 × 100 mm) column (Waters, USA). The binary solvent system was composed of (A) 5 mM ammonium acetate + 0.1% acetic acid in water and (B) 5 mM ammonium acetate + 0.1% acetic acid in methanol. The change of mobile phase composition was: 0.0–2.0 min—95.0% A to 5% A, 2.0–8.0 min 95.0% A, at 10.0 min it was ended with 95% A for bispyribac sodium. In case of metamifop the linear gradient was 0.0–2.0 min—95.0% A to 5% A, 2.0–16.0 min 95.0% A, at 18.0 min it ends with 95% A with a total flow rate of 0.3 mL/min and the injection volume was 20 µL. The positive mode of electrospray ionization was used for the estimation of both the analytes. Optimized ms parameters were as follows capillary voltage: 0.50 kV; source temperature: 120 °C; desolvation temperature: 350 °C; desolvation gas (nitrogen) (L/h): 650; collision gas (argon) (L/h): 30. LC-MS/MS was operated by Mass Lynx software. The ion transitions of bispyribac sodium were 430.87

(protonated parent ion) > 275.00 (used for quantification), 430.87 > 412.84 and 430.87 > 118.83. Protonated parent ion of metamifop was m/z 441.08 and the product ions were m/z 288.23 (used for quantification), m/z 123.07 and m/z 180.38.

Recovery studies were carried out in order to establish the reliability of the analytical method and to know the efficiency of extraction and clean up steps employed in the present study. The recovery experiment was conducted by fortifying bispyribac sodium and metamifop separately into water of different pH (viz. 4.0, 7.0 and 9.2) at 0.02, 0.05 and 0.10 µg/mL level.

The dissipation of the herbicides in water followed the first order reaction kinetics ($C_t = C_0 e^{-kt}$), where C_t represents the concentration of the pesticide residue at the time of t , C_0 represents the initial concentration after application, and k is the dissipation constant and its environmental fate was characterized by the half-life value. The half-life was worked out using the formulae:

$$t_{1/2} = \ln 2 / k.$$

Results and Discussion

The calibration curve was obtained by plotting six calibration point viz. 0.01, 0.02, 0.05, 0.10, 0.50 and 1.0 µg/mL for metamifop and bispyribac sodium separately. The correlation coefficient (R^2) of both the calibration curve was 0.99 which indicated good linearity and reliability. The percentage recovery of both the compounds is shown in (Table [1](#)). The recovery of both the compounds ranged between 87.15% and 96.08% with RSD values \leq 11%. The method was accepted in accordance with SANCO guidelines (SANCO [2013](#)) as the recovery percentage and RSD value was within acceptable range. So the extraction methods adopted are suitable for residue analysis.

Table 1 Recovery of bispyribac sodium and metamifop in water at different pH

Water sample	Spiked level (mg/kg)	Recovery ^a (%) for bispyribac sodium (RSD)	Recovery ^a (%) for metamifop (RSD)
pH 4.0	0.02	90.9 (4.83)	92.7 (10.99)
	0.05	88.48 (6.73)	88.4 (7.05)
	0.10	92.02 (6.37)	93.9 (3.75)
pH 7.0	0.02	87.5 (8.81)	88.9 (5.24)
	0.05	90.48 (4.34)	96.08 (7.97)
	0.10	90.16 (5.55)	90.84 (4.36)
pH 9.2	0.02	92.3 (7.52)	93.6 (2.08)
	0.05	95.2 (1.87)	91.24 (4.43)
	0.10	87.15 (4.55)	89.34 (2.69)

RSD relative standard deviation

^aAverage of five replicates

The dissipation of both bispyribac sodium and metamifop in aqueous system at three different pH levels (viz. 4.0, 7.0 and 9.2) followed first order kinetics, and the persistent nature of the herbicides in water was characterized by their half-life values. The regression equation, half-life and R² value of both the compounds in water is presented in (Table 2).

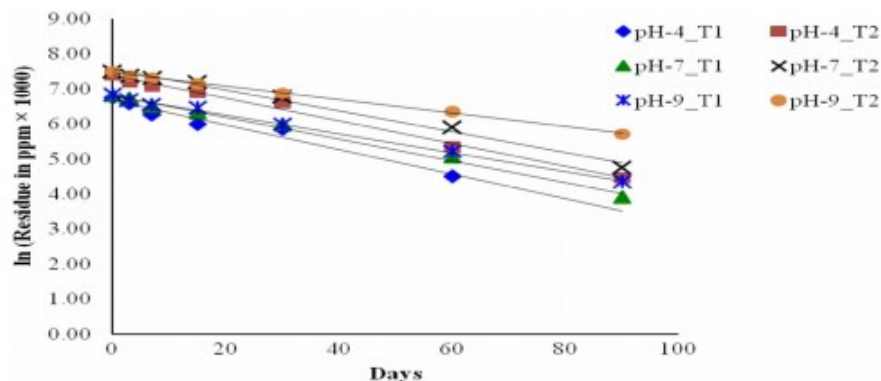
Table 2 Determination coefficient (R²), regression equation, half-life (t_{1/2}) of bispyribac sodium and metamifop at different pH

Name of the sample	Dose	Bispyribac sodium			Metamifop		
		R ²	Regression equation	Half life (t _{1/2})	R ²	Regression equation	Half life (t _{1/2})
pH-4.0	T1	0.9638	y = -0.0349x + 6.6639	19.86	0.9963	y = -0.0699x + 6.7733	9.92
	T2	0.9913	y = -0.0325x + 7.3856	21.33	0.9916	y = -0.0555x + 7.5865	12.49
pH-7.0	T1	0.9934	y = -0.0312x + 6.8175	22.22	0.9766	y = -0.0438x + 6.7883	15.83
	T2	0.9888	y = -0.0296x + 7.5556	23.42	0.9936	y = -0.0396x + 7.6256	17.50
pH-9.2	T1	0.9976	y = -0.0269x + 6.7948	25.77	0.9978	y = -0.0367x + 6.8140	18.89
	T2	0.9978	y = -0.0191x + 7.4594	36.29	0.9799	y = -0.0352x + 7.7250	19.69

The initial concentration of bispyribac sodium in water ranged between 0.86 and 0.92 µg/mL for single dose and 1.66–1.80 µg/mL for double dose. After 7 days of application the range of dissipation of bispyribac sodium was 15.11%–38.76%. The dissipation of the compound was increased to 45.74%–59.30% in 30 days and 67.78%–89.53% in 60 days. More than half of the initial concentration was dissipated within 60 days, irrespective of pH and dose of application. The remaining residue of bispyribac sodium was found 0.09–0.19 µg/mL for single dose and 0.21–0.58 µg/mL for a double dose after 60 days of application (Fig. 2). The residue of bispyribac sodium was found up to 60 days for single dose and 90 days for a double dose at pH 4 whereas at pH 7 and pH 9.2, the herbicide was persisted up to 90 days. The rate of hydrolysis was pH dependent which was reflected by half-life value. The half-life value of pH 4 was shorter than the half-life at pH 9.2. The calculated half-life value for bispyribac sodium ranged between 19.86–21.33, 22.22–23.42 and 25.77–36.29 days for single and double dose at pH 4, pH 7 and pH 9.2

respectively. The highest half-life of the compound was observed in alkaline condition and the low was in acidic solution. According to Australian Pesticides and Veterinary Medicines Authority (APVMA 2011) report, the half-life of bispyribac sodium as an active constituent in a suspension concentrate (SC) formulation was 88 days in sterile solution of pH 5 at 25 °C. In our experiment, the half-life value ranged between 19.86 and 36.29 days, which is much lower than the findings of APVMA.

Fig. 2 Dissipation of bispyribac sodium in water of different pH

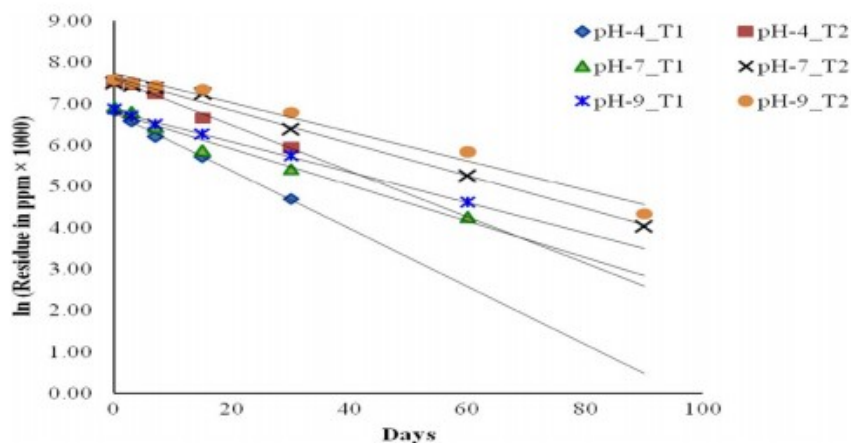


The probable reason for this difference in half-life value is due to the difference in microbial activity since our experimental aqueous solutions were not sterile whereas APVMA conducted the experiment in the sterile condition. Biological effects may accelerate the degradation rate and that results half-life was shortened (Zhang et al. 2010). The temperature also has a significant role in microbial growth and biological reaction (Zavala et al. 2004). Sarkar et al. (1999) showed in their experiment that persistence behavior of the same active constituent was influenced by the formulation type. In our experiment the formulation type was suspo-emulsion (SE) which was different from SC used by the APVMA. Our experimental result indicates that the stability of the compound increases with increasing the pH of water which comply the previous findings. As per USEPA report (USEPA 2001) on environmental fate and ecological risk assessment of bispyribac sodium, the compound is hydrolyzed at pH 5.0 but it is relatively stable at higher pH as hydrolysis do not make a significant contribution to the degradation process at pH 7 and 9. The major metabolic pathway of bispyribac sodium is demethylation and breakage of ether linkage (EFSA 2010). Since, the stability of ether compounds is higher in alkaline pH, the compound shows lower degradation rate at higher pH.

The initial concentration of metamifop was between 0.92 and 1.01 µg/mL for lower dose and 1.81–1.98 µg/mL for double dose. Dissipation of metamifop increased with increment of time and about 11.6%–46.38%, 21.59%–67.03% and 54.64%–88.04% of initial residue of the compound dissipated within 7, 15 and 30 days irrespective of dose of application and pH of water (Fig. 3). Metamifop persisted up to 30 days at pH 4 whereas at pH 7 and 9.2 the compound persisted up to 60 days for single dose and 90 days for double dose. The half-life value of the compound ranged between 9.92–12.49,

15.83–17.50 and 18.89–19.69 days for pH 4, pH 7 and pH 9.2 respectively. Degradation of the pesticide depends not only on the pH of the solution but also on dose (Sarkar et al. 1999). In our experiment, it was found that at lower dose the rate of degradation of the compound was faster than higher dose. Nie et al. (2011) reported that the degradation of AOPP herbicides depends on the chain length of alcohol moiety. Unlike other AOPP herbicides, metamifop bears an aryl amide group instead of ester linkage, which is less susceptible to alkaline hydrolysis. Besides, the presence of a bulky substituent and a methyl group with the amide nitrogen again makes the carbonyl center more protected from alkaline hydrolysis and possibly for this difference metamifop is less hydrolysable at higher pH. Any agrochemical, after application in the field, distributes itself in different compartments of the environment (viz. water, soil, air and biota) and its degradation happens through biotic and abiotic transformation pathways. Moon et al. (2010) showed in their experiment that 10% of metamifop was degraded within 30 min of irradiations ($\lambda = 300$ nm) and > 80% after 4 h of irradiation so photo degradation is one of the important degradation pathways of metamifop. De Yang et al. (2011) reported the half-life of metamifop 1.3–2.3 days in natural rice field water, but in our laboratory study, we got half-life value 9.92–19.69 days. This divergence of half-life may be due to the effect of different experimental condition. There was no control on temperature and sunlight under field condition, but in our laboratory study we conducted the experiment in dark at 28 ± 2 °C. Thus, in this current experiment sunlight has no role in degradation of the herbicide. So the major degradation factors are hydrolysis and microbial degradation, and these are the possible cause for the higher half-life value of metamifop in the laboratory water dissipation study.

Fig. 3 Dissipation of metamifop in water of different pH



The present study highlights the pH dependent dissipation behavior of the new mixture herbicide of bispyribac sodium and metamifop. The pH of water is one of the important factors that affect the degradation of bispyribac sodium and metamifop in water. The result of this current experiment clearly shows that the rate of degradation of both compounds was faster in acidic

condition. The dissipation of both compounds is in the order of acidic water (pH 4) > neutral water (pH 7) > basic water (pH 9.2). This paper describes a simple, quick and reliable method for extraction and quantification of bispyribac sodium and metamifop from water of different pH. It also helps to understand the fate of both compounds in water.

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References

- APVMA, Australian pesticides and veterinary medicines authority (2011) On the evaluation of the new active bispyribac sodium in the product nominee herbicide, Product Number 63233
- DeYang K, Shi LL, Dan ZJ, Wu WZ (2011) Residue and degradation of metamifop in paddy field. *J Ecol Rural Environ* 27:104–107
- Ding G, Li X, Zhang F, Chen J, Huang L, Qiao X (2009) Mechanism-based quantitative structure activity relationships on toxicity of selected herbicides to *Chlorella vulgaris* and *Raphidocelis subcapitata*. *Bull Environ Contam Toxicol*. <https://doi.org/10.1007/s00128-009-9811-8>
- European Food Safety Authority (2010) Conclusion on the peer review of the pesticide risk assessment of the active substance bispyribac (unless otherwise stated all data evaluated refer to the variant bispyribac-sodium). *EFSA J* 8(10):1692. <https://doi.org/10.2903/j.efsa.2010.1692>
- IUPAC (2009) Agrochemical information. <http://agrochemicals.iupac.org>. Accessed 20 Apr 2009
- Kookana RS, Baskaran S, Naidu R (1998) Pesticide fate and behavior in Australian soils in relation to contamination and management of soil and water: a review. *Aust J Soil Res* 36:715–764
- Moon JK, Kim JH, Shibamoto T (2010) Photo degradation pathways and mechanisms of the herbicide metamifop in a water/acetonitrile solution. *J Agric Food Chem* 58:12357–12365
- Nie Z, Hang B, Cai S, Xie X, He J, Li S (2011) Degradation of cyhalofopbutyl (CyB) by *Pseudomonas azotoformans* strain QDZ-1 and cloning of a novel gene encoding CyB-hydrolyzing esterase. *J Agric Food Chem* 59:6040–6046
- SANCO (2013) Guidance document on analytical quality control and validation procedures for pesticide residues analysis in food and feed. European Commission. Document No. SANCO/12571/2013

Sarkar MA, Biswas PK, Roy S, Kole RK, Chowdhury A (1999) Effect of pH and type of formulation on the persistence of Imidacloprid in water. Bull Environ Contam Toxicol 63:604-609

US Environmental Protection Agency (2001) Environmental fate and ecological risk assessment for the registration of bispyribac sodium. Washington DC: Environmental fate and effects division

Zavala MAL, Funamizu N, Takakuwa T (2004) Temperature effect on aerobic biodegradation of feces using sawdust as a matrix. Water Res 38:2406-2416

Zhang CZ, Zhang ZY, Liu XJ, Jiang W, Wu YD (2010) Dissipation and environmental fate of herbicide H-9201 in carrot plantings under field conditions. Food Chem. <https://doi.org/10.1016/j.foodchem.2009.07.036>