

Effect of pH on dissipation kinetics of penoxsulam herbicide in water

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ABSTRACT: Penoxsulam is a new herbicide of Triazolopyrimidine sulfonamide group. In order to explore its persistence in waters of varying pH, dissipation studies of penoxsulam herbicide were conducted in water maintained at three different pH (4, 7 and 9.2) at 1 and 2 $\mu\text{g ml}^{-1}$ fortification levels. Water samples were collected at different time intervals i.e. 0 (2h), 1, 3, 7, 14, 30, 60, 90 days after herbicide application and processed for penoxsulam residues using HPLC. Degradation kinetics of penoxsulam was found to follow first order kinetics which could be better accounted by a monophasic pattern. The calculated half lives ($t_{1/2}$) in water samples of different pH depicted highest stability in acidic pH ($t_{1/2}$ = 69.0 to 77.0 days), followed by neutral ($t_{1/2}$ = 57.75 to 63.0 days) and alkaline pH ($t_{1/2}$ = 33.0 to 34.66 days) irrespective of the dose applied. Penoxsulam degrades rapidly in alkaline water and since it possesses low vapour pressure, its degradation in water is also dependant upon sunlight exposure which causes photolysis of the herbicide.

Key words: Dissipation, first order, half life, kinetics, penoxsulam, pH, water

Penoxsulam, (2-(2,2-difluoroethoxy)-N-(5,8-dimethoxy)-[1,2,4] triazole-[1,5-C] pyrimidine-2-yl)-6-(trifluoromethyl) benzene sulfonamide) is a new post-emergence herbicide of triazolopyrimidine sulfonamide (TSA) chemical class (Fig.1). It has been mainly developed for controlling broad leaf weeds and similar plants in lawns, rice fields and cereal crops and shows best herbicidal activity against many annual and perennial weeds particularly broad-leaved weeds and sedges (Strahan, 2004). Penoxsulam acts as an ALS (acetolactate synthase) inhibitor, an enzyme which is found in plants, fungi and microorganisms and is essential for the biosynthesis of branched-chain amino acids like valine, leucine, and isoleucine (Whitcomb, 1999). The ALS activities in the susceptible plant species are inhibited after penoxsulam absorption, which leads to hindrance in the biosynthesis of branched amino acids ultimately resulting in killing of weeds. However, regular use of this herbicide in rice cultivation can result in a severe impact on the quality of soil and neighbouring natural water resources which constitute unique ecosystems hosting mammals, birds and aquatic organisms. Pesticides generally move from fields to various water reservoirs by runoff or in drainage induced by rain or irrigation (Larson *et al.*, 2010). Penoxsulam is considered toxic to aquatic plants and its presence even at low concentrations in surface water entails an unacceptable risk to them (Sondhia *et al.*, 2016). The low sorption coefficient (0.2-5.1) of the herbicide indicates its high mobility in the environment and high possibility of its transportation from the field to water bodies (Richardson *et al.*, 2008).

TSA herbicides exhibit acidic dissociation constants (pK_s) and thus their water solubility is highly pH dependent. Generally this class of herbicidal compounds are water soluble at basic pH followed by neutral and acidic pH. Jabusch and Tjeerdema (2008) reported that there are major data gaps concerning the ambient fate and distribution of these compounds and it is undetermined to what extent TSA herbicides produce indirect ecological effects on the environment. Herbicides of TSA group are applied in the post emergent form on other crops and can be washed away easily into the aquatic environment.

Water is an essential commodity for life and its contamination by chemical pesticides can be hazardous for all living beings including humans. The mode of degradation of TSA group of herbicides varies with pH and therefore a complete knowledge and environmental fate of these herbicides in different environments is essential for their long term use. Several studies pertaining to the herbicide persistence have been carried out in soils of varying characteristics, crops etc. (Tsochatzis *et al.*, 2010 and Monica *et al.*, 2017) but not in waters of varying pH.

The present study was undertaken with the aim to determine the dissipation and degradation kinetics of penoxsulam in water at different pH under laboratory conditions. The results can then be utilized for further studies in determining the fate of penoxsulam in aquatic system under field conditions and would be useful in predicting the fate of penoxsulam in waters of different regions having variations in pH.

MATERIALS AND METHODS

Chemicals and reagents

The colourless (white crystalline compound) analytical grade penoxsulam (purity 99%) was supplied by Dow Agro Sciences India Pvt. Ltd. Company, Mumbai, India. Organic solvents were obtained from Merck, Spectrochem etc. and were glass distilled before use. Buffer tablets of different pH (4, 7 and 9.2) were procured from Finar Chemicals Ltd, India, and all the other chemicals used during the study were of AR or HPLC grade. Double distilled water was prepared in quartz distillation unit in the laboratory.

Experimental details

The study was conducted to determine the dissipation pattern of penoxsulam herbicide in water maintained at three different pH *viz.* acidic, neutral and alkaline under laboratory conditions. Analytical standard penoxsulam (99% purity) was used for preparing a stock solution of $100\mu\text{g ml}^{-1}$ in acetonitrile (ACN) and thereafter serial dilutions were done with this stock solution.

The pH of water was maintained to 4, 7 and 9.2 in nine conical flasks of 2L each using buffer tablets. One tablet per 100 ml of distilled water was required for maintaining the desired pH. The conical flasks were allowed to stand overnight for homogenous mixing and thereafter fortification with penoxsulam was done at the rate of 1 (T1) and $2\mu\text{g ml}^{-1}$ (T2) in the conical flasks having buffer solutions of different pH. Three conical flasks having solution of different pH (4.7 and 9.2) without herbicide treatment were maintained as control (T3).

Recovery study

The recovery experiment of penoxsulam in water at different pH was performed by fortifying water with technical grade herbicide at two different concentrations *viz.* 0.5 and $1\mu\text{g/ml}$ for method validation.

Extraction and clean up

The extractions of herbicide were carried out after 0 (within two hours), 1, 3, 7, 15, 30, 45, 60 and 90 days of initial treatment of penoxsulam in triplicate. In a 250 ml separating funnel 50ml of herbicide treated buffered water and 50 ml of dichloromethane were partitioned twice with 100 (50 + 50) ml of the solvent. The combined dichloromethane layer was collected and passed through the column packed with anhydrous sodium sulfate. Dichloromethane free of water traces was collected in a round bottom flask (RBF) and evaporated to dryness on the rotary evaporator at 40°C . Finally the herbicide

residues were dissolved in 2ml of acetonitrile. The dissolved residue of the herbicide in ACN was passed through $0.45\mu\text{m}$ millipore membrane filter and subjected to analysis through HPLC. The whole procedure was repeated for herbicide fortified buffer as well as control samples.

HPLC analysis parameters

Ultimate 300 HPLC-Dionex model 322 consisting of RP C18 column ($250 \times 4.6\text{ mm i.d.}$), particle size $5\mu\text{m}$, was used for chromatographic analysis. The mobile phase was 100% ACN at a flow rate of 0.7 ml min^{-1} . Detection of penoxsulam was done at 230 nm wavelength and the R_t of the herbicide under the above conditions was 6 min. The limit of detection (LOD) and limit of quantification (LOQ) as determined on the basis of S/N ratio were 0.005 and $0.018\mu\text{g ml}^{-1}$ respectively.

RESULTS AND DISCUSSION

Recovery of penoxsulam

The recovery data of penoxsulam at three different pH is depicted in Table 1. As evident from the data, the average recoveries of penoxsulam from water fortified at two concentrations 0.5 and $1\mu\text{g ml}^{-1}$ ranged between 82.14 to 87.52% in water of different pH. Higher recovery of penoxsulam from waters maintained at different pH confirmed that the analytical method utilized for herbicide extraction and analysis was satisfactory.

Persistence of penoxsulam in water

The mean persistent herbicide residue and its percent dissipation are depicted in Table 2. The amount of penoxsulam residues after different intervals (1 to 90 d) were calculated taking the value of 0 day as 100%. The initial dissipation of penoxsulam was slow under all the three pH, till 7-15 d, irrespective of the dose applied, but increased thereafter. In comparison with acidic and neutral pH, dissipation of penoxsulam was faster under alkaline pH. As evident from the data penoxsulam

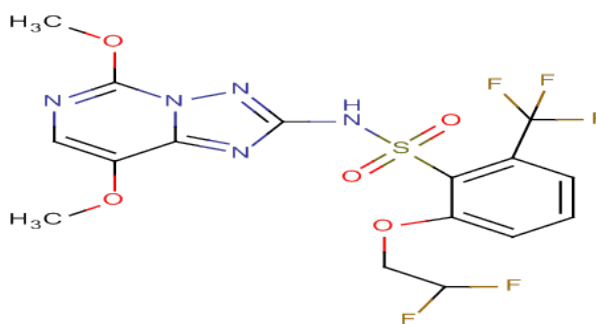


Table 1: Recovery of penoxsulam from fortified water samples of different pH.

Water sample	Recovery%* ± S.D	
Fortification level	0.5 µg/ml	1 µg/ml
pH 4	87.52 ± 3.65	87.41 ± 0.71
pH 7	85.15 ± 3.3	86.96 ± 1.68
pH 9.2	82.14 ± 0.18	82.57 ± 0.11

*Mean of three replicates

persisted up to 60 d under acidic and neutral pH but was below detection limit (0.018 µg ml⁻¹) on 45th d only in case of alkaline water buffer.

Degradation kinetics of penoxsulam

Degradation data of penoxsulam was fitted to first order of kinetic equation

$$C = C_0 e^{-\lambda t}$$

Where **C** is amount of residue of penoxsulam recovered from water at time *t*,

C₀ is amount of residue recovered at *t*=0,

λ is degradation constant and

t is time in days

The computed values of degradation constant (**λ**), half life (*t*_{1/2}), coefficient of determination (*R*²) and regression equation are depicted in Table 3. As is evident from the data, the half life (*t*_{1/2}) of penoxsulam was highest under acidic conditions (77 and 69d) followed by neutral (57.75 and 63d) and lowest under alkaline conditions (33 and

34.66d) at 1 and 2 µg ml⁻¹ fortification rates respectively.

The natural logarithm values of the amount of penoxsulam residue (*C*) recovered at different time intervals were plotted against time as shown in Figure 2a & 2b. The distribution of points in the graph produced single straight lines at all the three pHs and at both the application rates i.e. 1 and 2 µg ml⁻¹ indicating that dissipation of penoxsulam followed first order kinetics. It is evident from the figures that the slope of curve depicting pH 9.2 was most steep and hence the degradation of herbicide in case of alkaline water was fastest in the alkaline pH irrespective of the fortification rate of the herbicide in buffered waters of different pH.

The stability of any pesticide is determined on the basis of its half life in the environment. In case of penoxsulam, stability decreased with increasing pH which is confirmed by the half life data depicted in Table 3. According to the findings of Environmental Protection Agency, USA (2004), the stability of triazolopyrimidine group of compounds is higher in pH 4 and 7 in comparison to pH 9 and the same is also confirmed from the results of the present investigation. Ganguly *et al.* (2016) have also confirmed the lowest stability of diclosulam (triazolopyrimidine herbicide) under alkaline pH in comparison to neutral and acidic pH, irrespective of the dose applied. The phenomenon of penoxsulam herbicide degradation can be attributed to the cleavage of sulfonamide-bridge and opening of the pyrimidine ring. The studies were conducted in the laboratory where there

Table 2: Persistence and dissipation percent of penoxsulam in water at different pH

Days	pH 4		pH 7		pH 9.2	
	1 µg ml ⁻¹	2 µg ml ⁻¹	1 µg ml ⁻¹	2 µg ml ⁻¹	1 µg ml ⁻¹	2 µg ml ⁻¹
0	0.97±0.03(-)	1.87±0.02(-)	0.95±0.02(-)	1.80±0.04(-)	0.94±0.03(-)	1.84±0.03(-)
1	0.94±0.02(3.09%)	1.82±0.02(2.67%)	0.92±0.04(3.15%)	1.77±0.04(1.67%)	0.90±0.02(4.25)	1.74±0.02(4.39%)
3	0.92±0.04(5.15%)	1.77±0.02(5.34%)	0.89±0.02(6.31%)	1.70±0.03(5.56%)	0.84±0.01(10.63%)	1.61±0.04(12.5%)
7	0.86±0.04(11.34%)	1.64±0.02(12.29%)	0.82±0.03(13.68%)	1.57±0.02(12.7%)	0.73±0.03(22.34%)	1.41±0.02(23.36%)
15	0.74±0.02(23.7%)	1.59±0.03(14.97%)	0.78±0.01(17.89%)	1.49±0.01(17.23%)	0.48±0.02(48.93%)	0.91±0.02(50.54%)
30	0.66±0.01(31.95%)	1.08±0.02(42.24%)	0.62±0.02(34.73%)	1.12±0.02(37.78%)	0.24±0.03(74.46%)	0.52±0.03(71.73%)
45	0.52±0.02(46.39%)	0.88±0.01(52.44%)	0.33±0.04(65.26%)	0.78±0.03(56.67%)	0.10±0.02(89.36%)	0.22±0.04(88.04%)
60	0.22±0.04(77.32%)	0.32±0.03(82.8%)	0.14±0.02(85.26%)	0.28±0.01(84.45%)	ND	ND
90	ND	ND	ND	ND	ND	ND

Figures in parentheses denote % dissipation and ND < 0.018 µg/ml

Table 3: Determined values of degradation constant, half life and coefficient of determination of penoxsulam

Computed values	pH 4		pH 7		pH 9	
	1 µg ml ⁻¹	2 µg ml ⁻¹	1 µg ml ⁻¹	2 µg ml ⁻¹	1 µg ml ⁻¹	2 µg ml ⁻¹
Degradation rate constant (λ)	0.009	0.011	0.012	0.011	0.021	0.02
Half life (<i>t</i> _{1/2}) (days)	77	69	57.75	63	33	34.66
Coefficient of determination (<i>R</i> ²)	0.88	0.90	0.91	0.89	0.99	0.99
Regression equation	y = -0.009x + 0.006	y = -0.011x + 0.306	y = -0.012x + 0.019	y = -0.011x + 0.295	y = -0.021x - 0.008	y = -0.02x + 0.271

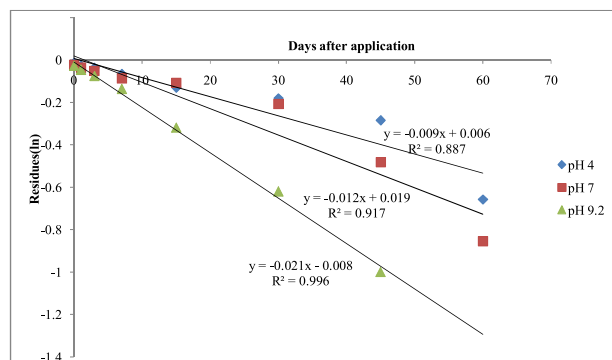


Fig. 2a: Plot between natural logarithm of penoxsulam persistence versus time in days at different pH at $1\mu\text{g ml}^{-1}$

was ample of sunlight and hence photo degradation might have played a role in dissipation and degradation of the herbicide. Penoxsulam possesses low vapour pressure and therefore its degradation through water is highly dependant upon sunlight exposure and thus photolysis seemed to play a major role in its degradation pathway as also reported in the data of United States Environmental Protection agency (USEPA), (2004). Jabusch and Tjeerdma (2006) have also reported that aqueous photodegradation of triazolopyrimidine herbicides proceed via three possible pathways: cleavage of the sulfonamide bridge, stepwise degradation of the triazolopyrimidine system and its substituents and photooxidation of the sulfonyl group and is one of the major routes of degradation of TSA herbicides. Krieger *et al.* (2000), have also reported the photolytic degradation of florasulam (triazolopyrimidine herbicide) on soil and in water indicating that photolytic processes are important contributors to photodegradation of florasulam, a triazolopyrimidine herbicide, in aqueous environments. Penoxsulam, belonging to the same group, seems to have followed a similar pattern of degradation.

Since the herbicide is highly stable in acidic and neutral medium, the monitoring studies of this pesticide in water sources having acidic and neutral nature should be conducted regularly in order to prevent the ill effects of penoxsulam that can be caused on the health of all living beings.

CONCLUSION

It can be concluded from the results obtained in the study that penoxsulam readily dissociates in the alkaline medium in comparison to acidic and neutral and this might also be true for soils having varying pH. However, the results of this study can be further utilized for determining the dissipation of the herbicide in underground water in the fields which gets collected due to leaching process through soils.

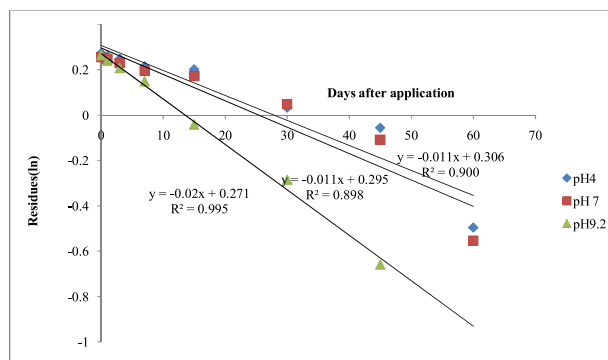


Fig. 2b: Plot between natural logarithm of penoxsulam persistence versus time in days at different pH at $2\mu\text{g ml}^{-1}$

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