

Evaluation of Harvest Residues of Cyhalofop-butyl in Paddy Soil

Bipin Kumar · Rajvir Sharma · Shashi Bala Singh

Received: 20 January 2012 / Accepted: 1 June 2012 / Published online: 24 June 2012
© Springer Science+Business Media, LLC 2012

Abstract Cyhalofop-butyl is a recently registered herbicide from the aryloxyphenoxy propionate group in India to control a wide range of grass weed species at various growth stages in rice crop. Field experiment with rice variety Pusa Sugandh 5 was conducted at IARI, New Delhi. Rice crop was sprayed thrice with cyhalofop-butyl at 40, 60 and 80 g ha⁻¹ at the 10, 20 and 30 DAS. Harvest soil samples were extracted and analysed for cyhalofop-butyl and cyhalofop acid residues by HPLC using CH₃OH:H₂O (80:20) mobile phase at a flow rate of 1 mL min⁻¹ at 240 nm wavelength using PDA detector. In harvest soil the residues were below the detectable limits.

Keywords Cyhalofop-butyl · Cyhalofop-acid · HPLC · Residue · Paddy soil

Rice is primary staple food in India and cultivated on about 44 million hectares area, occupying 30 % of the total cultivated area. It is grown under varied agro-climatic conditions under transplanted and wets own to direct seeded rain-fed condition. The assured availability of rice is recognized as an important factor in self-sufficiency of the country's food grain production. However, the release of new genotypes and their wide scale adoption increased greater scope for enhancing rice production in the country.

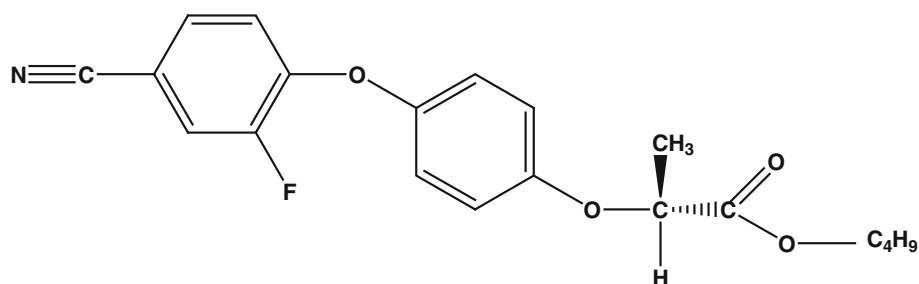
The demand for rice in India is expected to be 140 million tonnes by 2025 (Subramanian et al. 2005).

Rice grain production in India is presently reported to suffer a yearly loss of more than 15 million tonnes due to weeds competition, especially grassy weeds. Moreover some of grassy weeds like *Echinochloa colona*/E. *crusgalli* resemble rice plant during initial stages, and therefore, escape manual removal. To cop up with this situation, alternate herbicide are being used. Cyhalofop-butyl [2-{4-(4-cyano-2-fluorophenoxy) phenoxy} propanoic acid, butyl ester(R)], a recently registered herbicide from the aryloxyphenoxy propionate group (AOPP “fops”) in India, is used at very low rate (40–80 g a.i. ha⁻¹) to control a wide range of grass weed species at various growth stages (Fig. 1). Similar to other AOPP and cyclohexanedione herbicides, the site of action of cyhalofop-butyl is acetyl-coenzyme A carboxylase (ACCase), an enzyme in fatty acid biosynthesis. Plant metabolism studies demonstrate that tolerant rice inactivates the esterase producing a lack of functionality thus reducing the conversion of cyhalofop-butyl to cyhalofop acid, which is the active form of the herbicide. Moreover, it increases the metabolism of the herbicide forming non toxic metabolites much faster than *E. oryzoides* (Ruiz-Santaella et al. 2006).

Antagonism between cyhalofop-butyl and other rice herbicides in barnyardgrass has also been studied (Ottis et al. 2005). The hydrolysis of cyhalofop-butyl was faster in nonsterile than in sterile water (Pinna et al. 2008). Dissolved organic matter reduced the adsorption of cyhalofop-butyl by soil, whereas it increased the adsorption of cyhalofop-acid (Blasioli et al. 2008). The bio efficacy of this herbicide in rice is widely reported but the data on environmental fate is lacking. As no literature is available on the persistence and environmental fate of cyhalofop-butyl herbicide, the present study on evaluation of harvest

B. Kumar · R. Sharma
Division of Agronomy, Indian Agricultural Research Institute,
New Delhi 110012, India

S. B. Singh (✉)
Division of Agricultural Chemicals, Indian Agricultural
Research Institute, New Delhi 110012, India
e-mail: sbs_agch@yahoo.com

Fig. 1 Chemical structure of cyhalofop-butyl**Table 1** Harvest time residues of cyhalofop butyl and acid in paddy soil

Time (Days after third application)	Herbicide remaining ($\mu\text{g g}^{-1}$) \pm SD ^a Dosage at g a.i. ha ⁻¹					
	40		60		80	
	Cyhalofop butyl	Cyhalofop acid	Cyhalofop butyl	Cyhalofop acid	Cyhalofop butyl	Cyhalofop acid
120 days (harvest)	BDL	BDL	BDL	BDL	BDL	BDL

Cyhalofop butyl as acid – BDL ($<0.1 \mu\text{g g}^{-1}$)^a Average of three replicates

residues of cyhalofop-butyl in rice field soil was undertaken (Table 1).

Materials and Methods

Cyhalofop-butyl (97.8 %) was obtained from Dow Agro Chemicals India limited and purity checked by HPLC before use. Formulation of cyhalofop-butyl (Clincher®, 10 % EC) was purchased from local market. The authentic sample of cyhalofop-acid required for the study had a melting point 153–155°C. Standard solutions of cyhalofop-butyl and cyhalofop-acid were made in HPLC grade methanol.

Field experiment pertaining to the residue of cyhalofop-butyl in direct seeded rice were conducted at the Indian Agricultural Research Institute, New Delhi, using randomised block design in the plot of 2×2 m with rice variety Pusa Sugandh 5 sown in 20 cm row to row and seed rate of 100 kg ha^{-1} . Cyhalofop-butyl (10 %EC) was applied at 40, 60 and 80 g ha^{-1} as post emergence spray at 10, 20 and 30 days after sowing. A uniform dose of 120, 60, 60 and $25 \text{ kg N, P}_2\text{O}_5, \text{K}_2\text{O}$ and Zn ha^{-1} was applied in all the treatments in the form of urea, diammonium phosphate, murate of potash and zinc sulphate, respectively at the time of final ploughing. The soil of experimental field was sandy loam in texture and alkaline in nature (pH 7.5).

Soil samples (0–15 cm depth, $\sim 500 \text{ g}$ each) were drawn randomly using a 2.5 cm diameter tube auger from 6 to 7 spot in each plot at the time after harvest. Sample was mixed thoroughly, air dried, grinded and passed through 2 mm sieve. A representative 50 g sample was taken by quartering for

analysis in a 250 mL conical flask and 100 mL of acetone was added. The flask was shaken on horizontal shaker for 30 min and filtered through Whatman no 1 filter paper using Buchner funnel. The extraction was repeated twice (50 mL). The combined filtrate was then concentrated by evaporating the solvent on a rotary vacuum evaporator at 30–40°C to dryness. The residue was diluted with saline water (10 %; 100 mL) and transferred to a 250 mL separating funnel. The aqueous solution was partitioned with dichloromethane ($3 \times 50 \text{ mL}$). The organic layer was passed through anhydrous Na_2SO_4 and the solvent evaporated to dryness on rotary vacuum evaporator. The residues were finally dissolved in methanol for HPLC. Fortified soil samples of cyhalofop-butyl gave more than 80 % recovery as cyhalofop-acid at 0.5 and 1 ppm level.

A reverse phase high performance liquid chromatographic technique was used for quantitative analysis of cyhalofop-butyl and cyhalofop-acid. A Hewlett Packard HPLC instrument (series 1100) connected with rheodyne injection system and a computer (model vectra) was used for analysis. The stationary phase consisted of lichrosphere on RP-18 packed stainless steel column (250 mm \times 4 mm id). Chromatogram was recorded in a window 95 based HP Chemstation programme. Mobile phase was methanol:water (80:20) with flow rate of 1 mL min^{-1} at 240 nm wavelength.

Results and Discussion

Cyhalofop-butyl when injected into HPLC it could be resolved into a sharp peak at 4.43 min at λ_{max} 240 nm. Similarly the cyhalofop acid was also resolved as at sharp

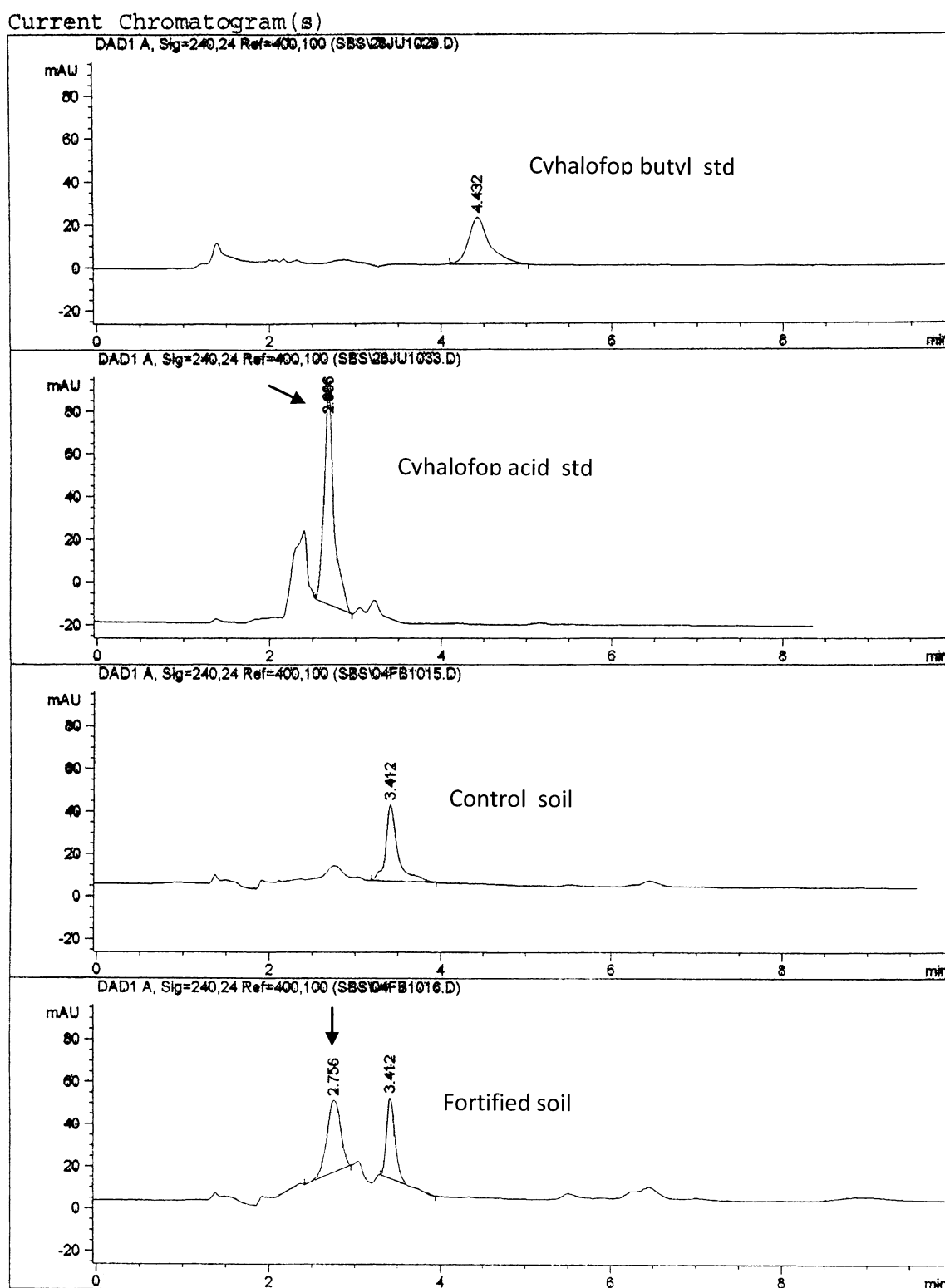


Fig. 2 HPLC chromatogram showing the recovery of cyhalofop butyl in soil as acid

single peak at 2.69 min. Mobile phase best suited for separation was methanol and water in the ratio of 80:20 at flow rate of 1 mL min⁻¹.

Recovery of cyhalofop-butyl was performed at 0.5 and 1 µg g⁻¹ fortification level from soil but due to its rapid conversion to cyhalofop-acid the recovered residue was

always in the form of cyhalofop-acid giving peak at 2.75 min (Fig. 2). Fortified soil samples gave more than 80 % recovery of acid at both the fortification levels. Limit of quantification of cyhalofop-butyl as acid was $0.1 \mu\text{g g}^{-1}$. The harvest soil from each treatment was analysed for cyhalofop-butyl as well as cyhalofop acid residue. No residue of cyhalofop could be detected in harvest soil.

Cyhalofop-butyl rapidly degraded into cyhalofop acid in soil. Even the recovery studies in IARI soil (pH 7.5) indicated that just working up of the experiment within 2 h could not show any recovery of cyhalofop-butyl. Rather cyhalofop acid was the recovered product. The translocated form of cyhalofop-butyl is cyhalofop acid which is also herbicidal in nature. During the period of field experiment maximum temperature was 42.3 and relative humidity was 78 %. The IARI soil was alkaline in pH. Under these experimental field conditions the residues of cyhalofop (ester and acid) were completely lost from harvest soil as they were below detectable levels.

Acknowledgments Bipin Kumar gratefully acknowledges the financial assistance provided by Indian Agricultural Research Institute, New Delhi.

References

- Blasioli S, Braschi I, Pinna MV, Pusino A, Gessa CE (2008) Effect of unsalted dissolved organic matter from composts on persistence, adsorption, and mobility of cyhalofop herbicide in soils. *J Agric Food Chem* 56(11):4102–4111
- Ottis BV, Mattice JD, Talbert RE (2005) Determination of antagonism between cyhalofop-butyl and other rice (*Oryza sativa*) herbicides in barnyardgrass (*Echinochloa crusgalli*). *J Agric Food Chem* 53(10):4064–4068
- Pinna MV, Braschi I, Blasioli S, Gessa CE, Pusino A (2008) Hydrolysis and adsorption of cyhalofop-butyl and cyhalofop-acid on soil colloids. *J Agric Food Chem* 56(13):5273–5277
- Ruiz-Santaella JP, Heredia A, Prado RD (2006) Basis of selectivity of cyhalofop-butyl in *Oryza sativa* L. *Planta* 223(2):191–199
- Subramanian E, Martin JG, Ramasamy S (2005) Effect of weed and nitrogen management on weed control and productivity of wet seeded rice. *Indian J Weed Sci* 37(1&2):61–64