Int. J. Environ. Res., 2(1): 71-74, Winter 2008
ISSN: 1735-6865

Dissipation Kinetics of Benthiocarb in Water at Different pH levels under Laboratory Condition

Wasim Aktar, Md.[1*], Paramasivam, M.[1] and Bhattacharyya, A.[2]

[1] Pesticide Residue Laboratory, Department of Agricultural Chemicals, Bidhan Chandra Krishi Viswavidyalaya, Mohanpur-741252, Nadia, West Bengal, India
[2] Export Testing Laboratory, APEDA, Bidhan Chandra Krishi Viswavidyalaya, Mohanpur-741252, Nadia, West Bengal, India

Received 17 May 2007; Revised 20 Oct. 2007; Accepted 5 Nov. 2007

ABSTRACT: Laboratory degradation studies were performed in water at pH 4.0, 7.0 and 9.2 using Benthiocarb (Saturn 50 EC) formulation at the rates of 1.0 (T_1) and 2.0 (T_2) µg/mL. Water samples collected on 0 (2h),3,7,15,30,45,60 and 90 days after treatments were processed for residue analysis of benthiocarb by GC-NPD capillary system. In 60 days, dissipation was 92.82-93.81 % at pH 4.0, 89.12-90.63 % at pH 7.0, and 92.67-93.88 % at pH 9.2 in both treatments showing very little effect of pH on dissipation. The half-life periods observed were 15.13 and 16.01 days at pH 4.0, 17.92 and 18.81 days at pH 7.0 and 11.32 and 12.54 days at pH 9.2 at T_1 and T_2 doses respectively. Dissipation followed a triphasic first order kinetics in water at all the three pH levels.

Key words: Benthiocarb, pH, Dissipation, Kinetics, Herbicide

INTRODUCTION

Benthiocarb (S-4-chlorobenzyl diethyl thiocarbamate) [$C_{12}H_{16}NOSCl$] is a selective herbicide of thiocarbamate group. It is mainly used as a pre or post emergent herbicide in the paddy field (Sharma and Bhunia, 1999). It is applied 3-4 days after transplantation of rice. The compound is absorbed by coleoptiles, mesocotyl, roots and leaves. The compound translocates to the meristem and inhibits protein synthesis (Ishikawa, *et al.*, 1971 and Ishikawa, 1980). As a result, shoot growth of emerging seedlings are inhibited. It is effective as pre emergence to early post emergence herbicide for the control of *Echinochloa*, *Leptochloa*, *Cyperus* sp. and other monocotyledons and annual broad-leaved weeds in direct seeded and transplanted rice at 3-6 kg a.i./ ha (Attalla and Kholosy, 2002). It is non-phytotoxic to rice. Benthiocarb exhibits excellent properties as a mix partner with other herbicides for controlling dicotyledonous weeds like *Galium aparine*, *Chenopadinum alum*, *Setaria* spp., etc. It is a moderately toxic herbicide having LD_{50} (acute oral) 1033 mg/kg for male rates. When used on paddy, the residues of benthiocarb in standing water may harm beneficial flora and fauna in general and fish in particular where pisiculture is practiced in paddy crop (Ishikawa, 1980). Benthiocarb was determined by using gas chromatography coupled with mass spectrometry with programmable temperature vaporizer (Hada, *et al.*, 2000) and capillary gas chromatography equipped with atomic emission detection Stan and Linkerhagner, 1993). As there is no information available on this aspect of benthiocarb, it was thought imperative to investigate dissipation behavior of this herbicide in water at different pH levels.

MATERIALS & METHODS

Analytical grade of Benthiocarb (99.1%) was obtained through the courtesy of M/S PI Industries Ltd. All the solvents like dichloromethane, acetone and ethyl acetate were glass distilled before use. Sodium sulphate was washed repeatedly with distilled acetone and activated at 110 °C for 2 h

---

*Corresponding author: Email-wasim04101981@yahoo.co.in before use. Stock solution (100 µg/mL) was prepared in ethyl acetate and working solution was prepared by diluting it.

The pH of water was adjusted using buffer. Buffer capsules of pH 4.0, 7.0 and 9.2 from E.Merck were used for the purpose of preparing buffer solution. One capsule was required for 100 mL of distilled water to maintain the above mentioned pH. In a series of Winchester bottles (10 L capacity) 6 L distilled water was kept and sixty capsules were added to each of the bottle. The bottles were then left in room temperature for overnight to homogenize the buffer solutions. For carrying out laboratory experiment, water (6 L) of each pH triplicate was spiked; 1.0 (T_1) and 2.0 (T_2) µg a.i/mL with Benthiocarb formulation and was stored in Winchester bottles from July to February 2005-06 under room temperature (15-39.5 ^{o}C). Untreated control was also carried out simultaneously. Samples were drawn periodically on 0 (2 h), 3, 7, 15, 30, 45, 60, and 90 days after treatments and analyzed for benthiocarb residues.

Representative 200 mL water sample was taken in 1 L separating funnel and 5-10g sodium chloride was added to it. It was extracted thrice (100, 50, 50 mL) with dichloromethane by liquid-liquid partitioning. Organic phases were combined, passed through anhydrous sodium sulphate and concentrated on a rotary vacuum evaporator under reduced pressure at 40 ^{0}C followed by a gas manifold evaporator till near dryness. Final solution was made to 1 mL in ethyl acetate and subjected to GC analysis. No clearing was required as no interference peaks were observed during analysis.

The residues of Benthiocarb were analyzed on GC (Agilent Technologies 6890N Network GC system) with nitrogen phosphorous detector (NPD) coupled with Chemito 5000 data processor. The HP-5 capillary column (30m x 0.32mm i.d.) of 0.25 µm film thickness was used. The temperatures were: Oven 210 ^{0}C, Injector 230 ^{0}C, Detector 300 ^{0}C. Flow rate of carrier gas (nitrogen), hydrogen and air were 2, 4 and 60 mL/min, respectively. The retention time, limit of detection (LOD) and limit of quantification (LOQ) were 4.30 min, 0.01 µg/g and 0.05 µg/g, respectively.

RESULTS & DISCUSSION

Average recoveries of benthiocarb from water fortified at 0.25 and 1 µg/mL varied from 90-96% at pH 4.0, 88-98% at pH 7.0 and 88-97% at pH 9.2.

Residues of Benthiocarb in water at different pH levels are presented in table 1. As evident from the data, at pH 4.0, initial residues of 0.97 µg/mL in treatment T_1 dissipated to 0.89 µg/mL in 3 days, 0.32 and 0.06 µg/mL in 30 and 60 days, respectively. Corresponding dissipation were 8.25, 67.01 and 93.81%, respectively. In treatment T_2, initial residues of 1.95 µg/mL dissipated to 1.67, 0.49 and 0.14 µg/mL in 3, 30 and 60 days after application with corresponding dissipation of 14.36, 72.31 and 92.82 %, respectively.

At pH 7.0, initial residues of 0.96 µg/mL in T_1 treatment, dissipated to 0.87, 0.35 and 0.09 µg/mL in 3, 30 and 60 days after treatment with corresponding dissipation of 9.38, 63.54 and 90.63 % respectively, whereas in T_2 initial residues of 1.93 µg/mL dissipated to 1.68, 0.69 and 0.21 µg/mL in 3, 30 and 60 days after treatment showing dissipation of 12.95, 64.25 and 89.12 %, respectively.

At pH 9.2, from treatment T_1 initial residues of 0.98 µg/mL dissipated to 0.78, 0.47 and 0.06 µg/mL in 3, 15 and 45 days after treatment with corresponding dissipation of 20.41, 52.04 and 93.88 %, respectively. In T_2 residues of 1.91 µg/mL on 0 (2 h) day dissipated to 1.53, 1.01 and 0.14 in 3, 15 and 45 days after treatment and corresponding dissipation was 19.89, 47.12 and 92.67 %, respectively.

It is clear that Benthiocarb residues in water dissipated more than 90% in 60 days at pH levels of 4.0, 7.0 and 9.2 in both treatments under laboratory conditions under temperature ranging from 15 to 39.5 °C. The degradation was slow during first 3 days followed by relatively faster degradation from 3rd day onward to 45 days after which it became slow.

Almost identical degradation ranging from 89 to 94 % at all the three pH levels during 60 days study indicate that there was no significant effect of pH on degradation, although dissipation was a little faster at pH 9.2 throughout the studies. Half-life values at pH levels of 4.0, 7.0 and 9.2 varied from 15.13 to 16.01, 17.92 to 18.81 and 11.32 to 12.54 days, respectively (Table 2). At all pH levels degradation was observed to be faster in T_1 than T_2. The slow dissipation at higher rate could attribute to inhibition of microbial activity. The dissipation of Benthiocarb followed a tri-phase first order kinetics.

Table 1. Dissipation of Benthiocarb residues in water at different pH

Time (in days)	Residues (µg/mL) ±SD (% of Dissipation)					
	pH 4.0		pH 7.0		pH 9.2	
	1.0 µg/mL	2.0 µg/mL	1.0 µg/mL	2.0 µg/mL	1.0 µg/mL	2.0 µg/mL
0	0.97±0.09 (-)	1.95±0.01 (-)	0.96±0.03 (-)	1.93±0.07 (-)	0.98±0.06 (-)	1.91±0.02 (-)
3	0.89±0.03 (8.25)	1.67±0.03 (14.36)	0.87±0.06 (9.38)	1.68±0.01 (12.95)	0.78±0.09 (20.41)	1.53±0.11 (19.89)
7	0.73±0.05 (24.74)	1.47±0.09 (24.62)	0.76±0.13 (20.83)	1.51±0.02 (21.76)	0.62±0.01 (36.73)	1.39±0.04 (27.23)
15	0.61±0.01 (37.11)	1.23±0.01 (36.92)	0.63±0.04 (34.38)	1.28±0.05 (33.68)	0.47±0.08 (52.04)	1.01±0.03 (47.12)
30	0.32±0.07 (67.01)	0.49±0.07 (72.31)	0.35±0.08 (63.54)	0.69±0.01 (64.25)	0.16±0.02 (83.67)	0.49±0.06 (74.35)
45	0.14±0.02 (85.57)	0.31±0.05 (84.10)	0.14±0.02 (80.21)	0.38±0.03 (80.31)	0.06±0.07 (93.88)	0.14±0.08 (92.67)
60	0.06±0.05 (93.81)	0.14±0.02 (92.82)	0.09±0.09 (90.63)	0.21±0.02 (89.12)	BDL	BDL
90	BDL	BDL	BDL	BDL	BDL	BDL

Table 2. Regression equation, Correlation Co-efficient and half-life for the dissipation of Benthiocarb in water at different pH

pH	Treatments (µg/mL)	Regression Equation	Correlation co-efficient	Half-life (days)
4.0	1.0	y= 3.028-0.0199x	0.9884	15.13
	2.0	y= 3.3073-0.0188x	0.9934	16.01
7.0	1.0	y= 3.01-0.0168x	0.9918	17.92
	2.0	y= 3.299-0.016x	0.9952	18.81
9.2	1.0	y= 2.999-0.0266x	0.9937	11.32
	2.0	y= 3.3075-0.024x	0.9739	12.54

Similar observations have been reported in degradation of metolachlor in water where dissipation was independent of pH and was subject to photodegradation following pseudo first order kinetics (Liu, *et al.*, 2000). Dissipation of butachlor residues has also been reported (Chang, 1973) following pseudo first order kinetics in river waters. Whereas in another studies (Kumari and Prasad, 2002 and Prasad, 2005), decomposition of trifluralin and metribuzin in water as pH and dose dependent, resulted in faster dissipation under alkaline conditions and at low dose of application. Slightly faster dissipation of benthiocarb at alkaline pH has been observed in our studies also. In one study, it has been shown that Benthiocarb has no residues in paddy field soil as well as water during harvest (Tanigawa and Nishimura, 1999).

CONCLUSION

Considering rapid dissipation of Benthiocarb at the tested doses in water system, its much faster degradation can be expected under field condition. Consumption of paddy grain from Benthiocarb treated field could not be harmful for health as no residues of the herbicide would be found in the harvested plant samples as the dissipation of Benthiocarb would be higher in plant system due to higher enzymatic activity. Hence, the tested doses can be considered safe from the point of view of health hazards, environmental pollution and ground water contamination due to its residual effects.

ACKNOWLEDGEMENT

The authors are grateful to M/s P. I. Industries Ltd., Gurgaon, India for financial assistance and providing analytical standard of Benthiocarb. We are very much thankful to Director of Research, Bidhan Chandra Krishi Viswavidyalaya, Kalyani, and Nadia for conductance of the experiment.

REFERENCES

Sharma, S. K., Bhunia, S. R., (1999).Weed management in transplanted rice (*Oryza sativa)* under Ghaggar flood plains of north-west Rajasthan. Indian J. Agro., **44** (3), 543-547.

Ishikawa, K., Shinohara, R., Yagi, A., Shigematsu, S., Kimura, I., (1971). Identification of S-benzyl N,N-diethylthiocarbamate in paddy field soil applied with benthiocarb herbicide. J. Pest. Sci., **5** (1), 107-109.

Ishikawa, K., (1980). Studies on the fate and behaviour of benthiocarb herbicide on biota and the environment. J. Pest. Sci., **5**(2): 287-293.

Attalla, S. I., Kholosy, A. S., (2002). Effect of weed control treatments on transplanted rice (Oryza sativa L.), Bulletin of Faculty of Agriculture,Cairo University, **53** (4), 531-538.

Hada, M., Takino, M., Yamagami,T., Daishima,S. and Yamaguchi, K., (2000). Trace analysis of pesticide residues in water by high speed narrow-bore capillary gas chromatography-mass spectrometry with programmable temperature vaporizer. J. Chrom. A., **874** (1), 81-90

Stan, H. J. and linkerhagner, M., (1993). capillary gas chromatography - atomic emission detection : a useful instrumental method in pesticide residue analysis of plant food stuffs. *HRC*, J. High Resol. Chrom., **16** (9), 539 - 48.

Liu,Y. J., Lin, C., Yeh, K. J., Lee, A., (2000). Photo degradation of the herbicides butachlor and ronster using natural sun light and di-ethylamine. Bull Environ. Contam. Toxicol., **64** (6), 780-785.

Chang, W.L., 1973. Persistence of rice and cotton herbicides in soils. J. Taiwan Agri. Res., **22** (2), 111-118.

Kumari, B., Prasad, H., 2002. Dissipation kinetics and degradation of metribuzin and trifluralin in water at different pH under laboratory conditions. In 10th. Int. Con. Chem. Crop Protect., Basel, Switzerland, **2**, 19.

Prasad, H., Kumari, B., Rani, D., Kathpal, T. S., (2005). Persistence of metribuzin in water at different pH under laboratory conditions. Pollut. Res., **24** (3), 535-538.

Tanigawa, M. and Nishimura, K., (1999). Change of benthiocarb and simetryn concentration in water and soil in paddy field**.** B. of Nara Agri. Exp. Stat., **30**, 17-22.