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RELEASE OF ^{14}C–BUTACHLOR AND ^{14}C–OXADIAZON FROM CR FORMULATIONS INTO WATER

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ABSTRACT

^{14}C–butachlor and ^{14}C–oxadiazon could be released from four kinds of CR formulations into water respectively, and the release percentage of each herbicide increased with time, which could be expressed by regression equations (very obvious positive relationship). The release percentages of ^{14}C–herbicides from CR formulations were related to herbicide, CR formulation and water type. Total recovery including ^{14}C–released and ^{14}C–left in formulations for each ^{14}C–herbicide was high at the 56th day after treatment. Some of the released ^{14}C–butachlor in water could be hydrolysed although under dark condition. The rate of hydrolysis was influenced by water type and formulations.

Keywords: Release Butachlor Oxadiazon Controlled–release formulation Water

I. INTRODUCTION

It is now well recognized that controlled–release (CR) formulation of herbicides has many advantages over the common formulation[1]. The development of a CR formalation requires, as an initial step, a study of release rate of the active ingredient into the intended environment (e.g. air, water, and/or soil)[1,2]. The information is necessary and is used to manipulate the formulation to modify its release characteristics. The pesticide should be released at an optimum rate to be most effective. The amount of pesticide released into various component (soil, water, plants, fish, etc.) can be determined by periodic analysis of presentative environmental samples. The samples can be analysed using radioanalytical techniques which are more sensitive and faster. Butachlor and oxadiazon are two useful herbicides in rice field. We studied the release of ^{14}C–butachlor and ^{14}C–oxadiazon from CR formulations into water in 1990.

II. MATERIALS AND METHODS

1. Materials

1) CR formulations of ^{14}C–butachlor: BH1 (spec. activity 1.04×10^7 dpm/g; 6.5% a.i.) and BH2 (spec. activity 1.39×10^7 dpm/g; 8.1% a.i.). CR formulations of ^{14}C–oxadiazon:

OA1 and OA2 (spec. activity 4.55×10^7 dpm/g; 4% a.i.). Reference standard butachlor (94%). The compositions of CR formulations of ^{14}C-herbicides are listed in Table 1. All materials described above were supplied by the IAEA, BH and OA formulations were prepared by Dr. Hussain and Dr. Allan respectively.

Table 1

The compositions of CR formulations of two herbicides

CR formulation	a.i.	PVA	POEG	Corncob	Alginate	Kaolin
OA1	Oxadiazon	*	*	*		
OA2	Oxadiazon	*	*	*		
BH1	Butachlor				*	
BH2	Butachlor				*	*

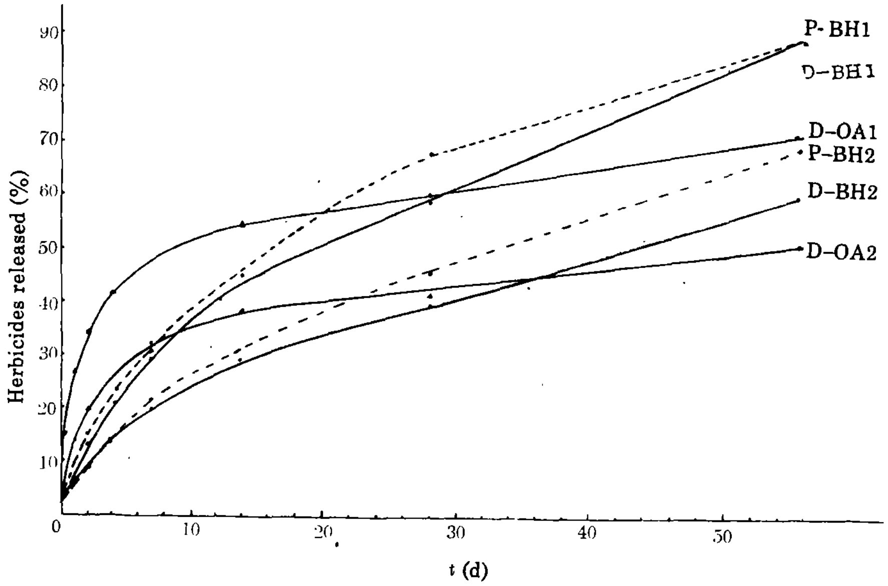

Fig.1 Dynamics of release percentages of each ^{14}C—herbicide from CR formulation into water*

* : Release percentages were expressed in % of the original radioactivity (A_0) which was determined using the combustion of formulations supplied by the IAEA; D = distilled water, P = paddy water

2) Distilled water (pH7); paddy water (pH 7) taken from a local paddy and filtered before use; liquid scintillation cocktail and solvents (analytical reagents).

3) Tightly-capped 1 liter flasks (26); thermometer; glassware including pipettes; graduated cylinders; liquid scintillation vials, etc.

4) Liquid scintillation counter (LSC); Biological oxidizer; HPLC.

2. Methods

1) *Treatment* One liter of distilled water were added into each of 18 clean one-liter flasks respectively. A thermometer through rubber was inserted into the 17th and 18th flasks, their bulbs were extended to center of the flasks. The paddy water

was added into 8 of above flasks (one liter each). In sixteen flasks containing distilled water enough formulation was added to give 16 mg(a.i.) of each formulation in each flask; mean while into each of 8 flasks containing paddy water, enough BH1 and BH2 were added respectively. Each treatment had 4 replicates. All the flasks were wrapped with black paper and kept in two ovens (duplicates of each of the formulations were kept in the same oven) keeping temperature at 26 ± 1°C.

2) Sampling and analysis One ml of distilled water and paddy water were taken and counted by LSC as control. Water samples from each flask were sampled at 2, 4, 8 h, and 1, 2, 4, 7, 14, 28, 56 d. Before taking samples, the contents of each flask were gently stirred with a glass rod for 30 s and allowed to settle for 30 min. Aliquots (10 ml) from the middle of each flask were taken and filtered. Four 1 ml aliquots were counted and the remaining back to the flask. The filter paper was rinsed with 4 ml of fresh distilled water (or paddy water), and the rinsate was added to the flask. The filter paper was analysed for radioactivity by combustion. At the end of 8–week, the entire contents in flasks were filtered and the beads/formulations were saved for later analysis (recorded the weights of filter paper before use). The total volumes of water were recorded and counted (1 ml × 4). The remaining water treated by BH1 and BH2 were extracted with ether, extracts in methanol solution were analysed by HPLC to determine if any degradation had occurred. The flasks were rinsed twice with water (50ml × 2), then acetone, the rinsates were counted respectively.

The filtered beads/formulations were allowed to dry for 2–3 days at room temperature on filter paper. After beads were dried, the total weight and the weight of beads were determined. The beads were extracted with acetone for 24 hour. Extracts were concentrated and counted; the extracted beads were combusted and counted to determine ^{14}C–herbicides remaining in formulations.

Counting, combustion and HPLC analyses: All samples were counted by LSC[3]. The filter paper and extracted beads were combusted for 5 minutes in a Biological Oxidizer using 10 ml absorbed solution (methanol was added into 125 ml of ethanol amine to 1 liter), then 5 ml of cocktail (50 mg POPOP was dissolved in 1 liter toluene, then 5 g of PPO were added and dissolved) were added to count, HPLC (model Waters 490) analysis was conducted with C–18 reverse phase 75 × 3.9 mm, solvent acetonitrile: water = 70%; 30% (V/V), flow rate 1.5 ml/minute and U.V. = 225 nm. The retention time for butachlor was 3.902 minutes.

Ⅲ. RESULTS AND DISCUSSIONS

1. Release of herbicides from CR formulations into water

The dynamics of release of ^{14}C–herbicides from CR formulations into water is shown in Fig.1. It shows that ^{14}C–butachlor and ^{14}C–oxadiazon could be released from

CR formulations into water. The release percentage (Y) of each herbicide increased with time (X), which could be expressed by a regression equation $Y = aX^b$ (Table 2). There were very obvious relationship between Y and X in all treatments.

Table 2

The regression equation of release of each herbicide from CR formulation into water

Treatment*	*a*	*b*	*r*
D–BH1	2.1047	0.6176	0.9960
P–BH1	2.2355	0.6025	0.9937
D–BH2	1.8865	0.5487	0.9982
P–BH2	1.9403	0.5557	0.9972
D–OA1	3.0692	0.3533	0.9701
D–OA2	2.4934	0.4250	0.9784

* D = distilled water, P = paddy water; B = butachlor, O = oxadiazon; H = by Dr. Hussain, A = by Dr. Allan.

The release rates of BH1 and BH2 from CR formulations into paddy water (PW) were higher than that into distilled water (DW) respectively. The release rates of BH1 were higher than that of BH2 from CR formulation into both of PW and DW, and the release rate of OA1 was higher than that of OA2 from CR formulation into DW. These might be related to the compositions of CR formulations of ^{14}C–herbicides. When CR formulations of two herbicides in water were compared, the release percentages of herbicides decreased in order of P–BH1, D–BH1, D–OA1, P–BH2, D–BH2 and D–OA2 at the 56th day after treatment (Fig.1). The results might be resulted from the nature of the CR system used, physical- chemical properties of the pesticide involved, and the mechanism of release involved[1].

2. Total recovery

In the period of study of release rate of ^{14}C–butachlor and ^{14}C–oxadiazon from CR formulations in water, some of ^{14}C–herbicides could be released into water, and among them, some might be hydrolysed[4]; while some of ^{14}C–herbicides still left in formulations. The total recovery of ^{14}C, at the 56th day after treatment by D–BH1, P–BH1, D–BH2, P–BH2, D–OA1 and D–OA2 were 101.5%, 99.22%, 97.20%, 93.75%. 98.90% and 87.91% respectively. It shows that the total recovery of ^{14}C for each of CR formulation is high.

Table 3

The percentage of ^{14}C–butachlor in the released ^{14}C at the 56th day after treatment*

CR formulation*	^{14}C–butachlor/ Total ^{14}C released				Average (%)
D–BH1	53.56	47.91	51.52	53.28	51.59
P–BH1	59.46	62.65	52.61	54.70	57.36
D–BH2	61.68	65.83	72.00	66.27	66.49
P–BH2	85.43	74.43	70.57	62.44	73.22

* According to the calculation of the results analysed with LSC and HPLC.

3. Hydrolysis of ^{14}C–butachlor released in water

At the 56th day after treatment, the percentage of ^{14}C–butachlor in the released ^{14}C is listed in Table 3. The retention time of butachlor in HPLC is 3.902 minutes (Fig.2). The results in Table 3 show that even under dark condition some molecules of ^{14}C–butachlor released into DW or PW have been destroied, which might be resulted from hydrolysis.

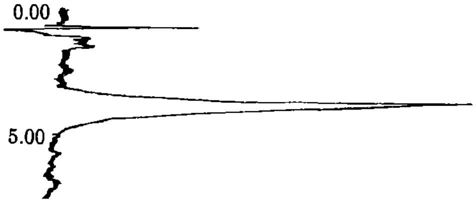

Fig.2 HPLC of butachlor

The rate of hydrolysis of ^{14}C–butachlor in DW is slightly more rapid than that in PW. The hydrolysis and loss of butachlor from BH1 formulation is more rapid than that from BH2 formulation in both of water. The former might be related to water type, and the latter might be related to compositions of CR formulations.

Ⅳ. CONCLUSIONS

^{14}C–butachlor and ^{14}C–oxadiazon could be released into water from two CR formulations. The release percentage (*Y*) of each herbicide increased with time, and could be expressed by a regression equation. There were very obvious positive relationship between *Y* and *X* in all treatments. The release percentage of ^{14}C–herbicides decreased in order of P–BH1, D–BH1, D–OA1, P–BH2, D–BH2 and D–OA2 at the 56th day after treatment. The total recovery of ^{14}C including ^{14}C released and still left in CR formulations for each of CR formulation is high at the 56th day after treatment. Some of ^{14}C- butachlor released in water could be hydrolysed and lost under dark condition.

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