

Persistence of benthocarb in soil: influence of ultraviolet and sunlight

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Abstract: Persistence of benthocarb in soil as affected by UV and sunlight exposure was studied. Treated soil was placed in petri-plate, brought to field capacity moisture and then exposed to UV and sunlight. Residues of benthocarb in soil dissipated with half-lives of 2.10, 11.85 and 43.63 days under UV, sunlight and dark condition, respectively. Soil samples kept under dark showed the slowest dissipation. Further, benthocarb residues dissipated quickly under UV light as compared to sunlight. Exposure of thin film of benthocarb confirmed that it is photo labile and dissipated very fast with half-life of 1.16 and 1.77 days following exposure to UV and sunlight, respectively. The study revealed that UV component of sunlight is an important factor for benthocarb dissipation.

Keywords: benthocarb, persistence, soil, sunlight, ultraviolet light

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Introduction

Soil act as a sink for the pesticides used both in agriculture and public health. Even the pesticides applied to crops reach soil by various processes. The presence of pesticides in soil not only affects soil health but also acts as source of contamination to the succeeding crop. Persistence of pesticide in soil is governed by various loss mechanisms like microbial degradation, chemical hydrolysis, photolysis, volatility, leaching, and surface runoff. Laboratory studies are conducted to assess the contribution made by each of the loss mechanisms to the overall dissipation.

It has been observed that pesticides persist longer in laboratory studies as compared to field studies [1-3]. Similarly, the translocated pesticide residues inside plant matrix (following soil application and seed treatment) persist longer as compared to foliar applied surface residues even though biological activity is more inside plant matrix as compared to that in surface.

Benthiocarb [(S-4-Chlorobenzyl diethyl thiocarbamate); S-4-Chlorobenzyl diethyl (thiocarbamate)] is a thiocarbamate group of herbicide, used as a pre/post emergent herbicide in the paddy field [4]. It is applied after 3-4 days of rice transplanting. It is effective against broad leaf weeds of paddy. The compound is absorbed by coleoptile, mesocotyl, roots and leaves. The compound translocates to the meristem and inhibits protein synthesis [5, 6].

Fate and behavior of benthiocarb (thiobencarb) herbicide in biota and the environment [7, 8] and laboratory leaching studies of Oryzalin and diuron [9] have been done. These findings clearly show that light plays an important role in loss of pesticides. It has been reported that degradation of highly persistent DDT in soil was much faster under sunlight as compared to samples kept under dark [10]. Photodegradation studies carried out under natural sunlight or simulated conditions are of great significance in formulating environmental usage and persistence parameters. The effect of light on persistence of benthiocarb has not been reported in literature so far. Therefore, the present experiments were conducted to study the effect of light (UV and sunlight) on persistence of benthiocarb in soil.

Material and Methods

Collection of samples

Soil required for the study was collected from the plough layer (0-15 cm depth) of the University research farm of Bidhan Chandra Krishi Viswavidyalaya, Mohanpur, West

Bengal, India, with no history of pesticide application. It was air-dried in the shade, ground, sieved through a 2-mm mesh screen. The physicochemical properties of the soil (type Entisol) were: pH 7.25, organic carbon 0.42 %, clay 5%, sand 77.5%, silt 17.5%, texture sandy loam and field capacity moisture content 20%.

Application of chemical

Standard stock solution (1000 mg L⁻¹) of analytical grade benthocarb was prepared in ethyl acetate. Lower concentrations were obtained by serially diluting the stock solution with ethyl acetate. Organic solvents like hexane, acetone and ethyl acetate were glass distilled before use. Sodium chloride and sodium sulfate were washed with acetone before use. HPLC grade solvents were procured from Merck India Ltd. These were filtered and distilled prior to use.

Persistence in soil

The treatment of soil with pesticide was carried out in such a way that there was uniform distribution of pesticide without adversely affecting the soil microbial activity. Initially, soil was fortified at 100 mg kg⁻¹ level. Soil (100 g) was taken in a beaker and required quantity of standard stock solution (1000 mg L⁻¹) of benthocarb was added. Additional acetone was added to dip the soil, stirred with glass rod for uniform distribution of pesticide and then left undisturbed till complete evaporation of acetone. The dry soil was again mixed. This fortified soil was diluted with untreated soil in the ratio 1: 9 to get 10 mg kg⁻¹ fortification level. Again the soil was mixed thoroughly. The homogeneity of treated soils was tested by randomly drawing three samples from the treated soil and analyzing them. Since there was not much variation among replicates, the treated soil was considered homogeneous. The treated soil samples (20 g) were transferred and spread uniformly in petri-plates (10 cm id) and brought to the field capacity moisture level by adding 4 mL water. All the petri plates were weighed and divided into three sets. One set of petri-plates was exposed to UV light. Second set was kept in open under sunlight and the third set was kept under dark in incubating chamber at 25±2 °C. Relative humidity inside the incubator was >95%. The water lost was replenished daily by weighing the petri-plates. Samples kept under sunlight and UV light was exposed for 6 h daily. Samples in duplicate from each treatment were drawn at different time intervals and analyzed for benthocarb residues.

Extraction and clean-up of residues

Soil samples collected from different experiments were taken in beaker and enough acetone was added to dip the soil. The samples were stirred with glass rod and kept for 30 min with intermittent shaking. The contents were filtered and soil was transferred back and re-extracted two more times. Acetone extracts were pooled and

concentrated using vacuum rotary evaporator. The concentrated extract was transferred to separatory funnel, diluted with saline solution (200 mL, 10%) and partitioned thrice using ethyl acetate (3 x 30 mL). The ethyl acetate phases were combined and passed through anhydrous sodium sulfate. The extract was evaporated to dryness using rotary evaporator and the residues dissolved in distilled hexane.

Persistence of benthocarb as thin film

To study the stability of benthocarb to UV and sunlight, similar experiment was conducted with thin film of pure compound on glass surface. Standard solution of benthocarb (1 mL, 100 mg L⁻¹) was spread in petri-plates and left undisturbed for evaporation of solvent. The plates were divided into two sets. One set of petri-plates were exposed to UV light and the other was kept in open under sunlight. Samples were exposed to sunlight/UV light for 6 h daily. Samples in duplicate for each treatment were drawn at different time intervals, dissolved in distilled hexane and extract analyzed for benthocarb.

Estimation of residues

Residues of Benthocarb were estimated by Gas Chromatography (GC) Hewlett Packard (USA) model 6890 equipped with Nitrogen Phosphorous detector (NPD) and Chemito 5000 integrator was used. The following GLC parameters were employed, Column (HP-5, 30 m x 0.32mm i.d. (Capillary), 0.25 µm film thickness), Oven, Injection and Detector Temperature were 210, 230 and 300 °C, respectively. Gas Flow Carrier (N₂), Air, and Hydrogen were 2, 60 and 4 mL/min respectively. Under these conditions the retention time of benthocarb was 4.3 min with the minimum detection limit was 0.01 µg mL⁻¹ (2 ng).

Calculation of Residues

The residue content was calculated by using the formula

$$\text{Residue in ppm } (\mu\text{g/g}) = \frac{A_1 \times C \times V_1}{A_2 \times W \times V_2} \times R_f$$

Where,

A₁ = Area of Oryzalin from sample, in chromatogram

A₂ = Area of Oryzalin from standard, in chromatogram

V₁ = Total volume of sample (in mL)

C = Concentration of analytical standard in ppm (µg/mL) x µL injected

W = Weight of the sample (in gm)

V₂ = Injected volume of sample (in µL)

R_f = Recovery factor

Linearity was evaluated by linear regression analysis

The residue data were subjected to regression analysis and the fit of the data to first order kinetics ($C_t = C_0 e^{-Kt}$) was confirmed by testing the statistical significance of correlation coefficient. The half-life values were calculated from dissipation constant calculated from regression analysis.

Results and Discussion

Recoveries of Benthocarb from soil fortified at 0.05 and 0.25 $\mu\text{g g}^{-1}$ and maintained at field capacity moisture regime were 94-98%. Average initial deposits in the soil in different treatments varied from 9.53-9.82 $\mu\text{g g}^{-1}$ (Table 1). The benthocarb residues persisted beyond 30 days in soil kept under dark or exposed to sunlight. However, no residues were detected in soil on 30th day when exposed to UV light. In different treatments 42.06-100% dissipation was recorded in 30 days. Dissipation of residues (Fig. 1) followed first order kinetics ($r > 0.9$) with dissipation half-lives of 2.10-43.63 days in different treatments.

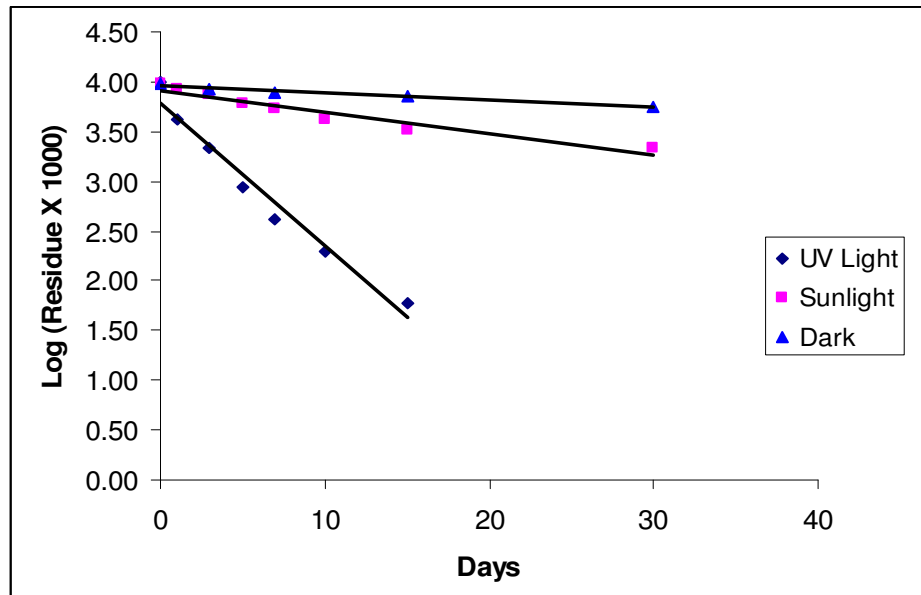


Figure 1. Dissipation of Benthocarb in soil under UV-light, sunlight and dark.

Under UV light, the residues dissipated at a faster rate. More than 50% residues dissipated within first 24 h and around 95.72% in 7 days. Dissipation of benthocarb residues from soil exposed to sunlight was slower than under UV light. Only 14.26%

dissipation was recorded after one day of exposure. Dissipation continued gradually with time and samples collected on 30th day showed overall dissipation of 77.70%. Dissipation from soil samples kept under dark was slowest with only 42.06% loss in 30 days.

The study clearly shows that dissipation is slowest in soil under dark condition ($T_{1/2}$ 43.63 days) as compared to soil exposed to sunlight ($T_{1/2}$ 11.85 days) and UV light ($T_{1/2}$ 2.10 days). The difference in dissipation could be attributed to the effect of UV light, as other processes like chemical and biological degradation is expected to be same due to similar moisture condition. It seems that benthocarb is unstable when exposed to light. The instability of benthocarb to light is further confirmed when its thin film was exposed to sunlight and UV light (Table 2 and Fig. 1) where the half-life values of 3.2 and 1.3 days, respectively, were recorded.

Table 1. Persistence of benthocarb in soil under UV-light, sunlight and dark.

Days	Residues $\mu\text{g g}^{-1}$		
	UV light	Sunlight	Dark
0	9.82	9.67	9.53
1	4.13 (57.94)	8.42 (14.26)	-
3	2.13 (78.31)	7.35 (25.15)	8.42 (14.26)
5	0.87 (91.14)	6.10 (37.88)	-
7	0.42 (95.72)	5.47 (44.30)	7.9 (19.55)
10	0.20 (97.96)	4.13 (57.94)	-
15	0.06 (99.39)	3.27 (66.70)	7.1 (27.70)
30	BDL	2.19 (77.70)	5.69 (42.06)
Regression equation	$y=3.78-0.1432x$	$y=3.93-0.0254x$	$y=3.96-0.0069x$
Correlation coefficient (r)	0.97	0.98	0.97
$T_{1/2}$ (days)	2.10	11.85	43.63

- = samples were not drawn,
BDL=below detectable limit, $<0.01\mu\text{g g}^{-1}$
figure in parentheses denotes % dissipation

Benthocarb, both as thin film or in soil persisted longer under sunlight (mean $T_{1/2}$ 6.81 days) than under UV light (mean $T_{1/2}$ 1.63 days), indicating that UV-component of

light is a major contributing factor for the dissipation. Further, both under sunlight and UV-light, benthocarb persisted longer when embedded in soil than when exposed as thin film. Observed mean half-life of benthocarb in soil was 6.98 days as compared to 1.47 days in thin film. Higher persistence of benthocarb in soil could be due to the adsorption of the pesticide by the various components of the soil like organic carbon, clay, etc. These components present in soil form active sites for the adsorption of the chemicals [11]. Katagi has also reported that photodegradation of pesticides on soil surface is influenced by adsorption to clay minerals or solubilization to humic substances [12].

Table 2. Persistence of Benthocarb as thin film under UV-light and sunlight.

Days	Average amount recovered (μg)	
	UV light	sunlight
0	99.61 (-)	99.57 (-)
1	22.17 (81.56)	81.03 (18.62)
3	7.97 (92.00)	45.73 (54.07)
5	3.95 (94.45)	23.08 (76.82)
7	0.97 (99.03)	4.51 (95.47)
10	BDL	1.73 (98.26)
15	BDL	0.40 (99.60)
30	BDL	BDL
Regression equation	$y=4.79-0.2595x$	$y=5.06-0.1705x$
Correlation coefficient (r)	0.96	0.98
$T_{1/2}$ (days)	1.16	1.77

Data in parentheses denotes % dissipation

Conclusion

It may be concluded that benthocarb is unstable to light especially the UV light. However, the presence of matrix like soil or plant material reduce the effect to some extent. Exposure of thin film of benthocarb confirmed that it is photo labile and

dissipated very fast following exposure to UV and sunlight, respectively. The study revealed that UV component of sunlight is an important factor for benthocarb dissipation. Considering rapid dissipation of benthocarb in laboratory system, its much faster degradation can be expected under natural field condition. For, the natural ecosystem contains a no. of biotic and abiotic factors which facilitates quick degradation of organic compounds excluding Sunlight that contains wave lengths of UV and visible light both specially from dawn to mid day. As a result consumption of food grain from benthocarb 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 benthocarb would be higher in plant system due to higher enzymatic activity. Hence, the tested herbicide can be considered safe from the point of view of health hazards, environmental pollution and ground water contamination.

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