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Volatilization of Benthiocarb Herbicide from the Aqueous Solution and Soil*

Kanji ISHIKAWA,** Yasuo NAKAMURA** and Shozo KUWATSUKA

Laboratory of Soil Science, Faculty of Agriculture, Nagoya University,
Chikusa-ku, Nagoya 464, Japan

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Volatilization of benthiocarb herbicide (*S*–4–chlorobenzyl *N,N*–dietylthiocarbamate) from its aqueous solution and from soil was studied in the laboratory. Exposure of the aqueous solution of ^{14}C-benthiocarb to sunlight resulted in a remarkable decrease in radioactivity, which was approximately proportional to the decrease in the amount of water by evaporation. The presence of soil in the aqueous solution, however, largely depressed the radioactivity loss. Volatilization of benthiocarb from unflooded soil was much less than from flooded soil. More than half of the radioactive substances volatilized from the aqueous solution exposed to the sun was composed of parent benthiocarb itself, while the rest consisted of volatile photodegradation products such as 4–chlorobenzaldehyde, formed under the experimental conditions used in this study.

In the previous paper,[1] it was reported that benthiocarb herbicide (*S*–4–chlorobenzyl *N,N*–diethylthiocarbamate, Saturn®) was degraded by irradiation with ultraviolet light or sunlight. It was degraded more rapidly than seven other common pesticides when they were irradiated with ultraviolet light. The loss of radioactivity from the aqueous solution exposed to sunlight was roughly proportional to the amount of evaporated water. The decrease was presumed to be due to the volatilization of benthiocarb itself and/or its degradation products. Some thiocarbamate herbicides were reported to be fairly volatile,[2–6] and their volatilization from the soil surface was largely affected by the moisture content of the soil. On the other hand, it is generally recommended that benthiocarb herbicide is applied to paddy fields within the period from a few days before to 3 weeks after transplanting rice seedlings. The volatilization as well as the photodegradation process seems a very important factor to consider in studying the dissipation of the herbicide in fields. In this paper, the volatilization of benthiocarb from its aqueous solution or from flooded and unflooded soils upon exposure to sunlight and the identification of the volatilized substances are reported.

MATERIALS AND METHODS

1. *Radioactive Benthiocarb and Reference Compounds*

Two kinds of radioactive benthiocarb labelled at two different positions in the molecule were used. One was labelled with carbon–14 at the benzene-ring,[7] and the other was labelled at the benzyl-methylene carbon.[8] These radioactive samples were purified by thin layer chromatography. Their specific radioactivities were 3.21 and 7.15 mCi/mmole, respectively. The radioactive purity of both samples was 99.9%. In many cases, radioactive benthiocarb was diluted with unlabelled benthiocarb prior to using the chemical.

2. *Authentic Compounds*

The compounds were described in the previ-

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* Studies on the Metabolism of Benthiocarb. Part VI. See reference[1]

** Visiting researchers from Life Science Research Institute, Kumiai Chemical Industry Co., Ltd., Kikugawa-cho, Shizuoka-ken, 439, Japan (present address) ous paper.[1]

3. *Soil Sample*

A soil sample was taken from furrow slices of a paddy field at the Paddy Field Experimental Farm, Aichi-ken Agricultural Research Center in an unplanted period in winter. The soil was crushed and passed through a 2 mm sieve. The main physico-chemical properties of the soil sample were as follows: kaolinic clay mineral; sandy clay loam; clay content 23.1%; pH (H_2O) 5.83; total carbon 1.93%; C.E.C. 13.6 me/ 100 g; maximum water holding capacity 53.5%. The other properties were reported previously.[7]

4. *Thin Layer Chromatography and Measurement of Radioactivity*

The procedures used were described in the previous paper.[1]

5. *Loss of Radioactivity by Volatilization*

^{14}C-Benthiocarb labelled at the benzylmethylene carbon was used only in this experiment. A 150 ml aliquot of a 10 ppm ^{14}C-benthiocarb solution (2.00×10^7 dpm) was placed in each of two Petri dishes (12 cm i.d.). One was covered with a quartz glass plate and the other was left uncovered. Both dishes were exposed to the sun for 2 days, but at night both were covered with a glass plate and placed in a dark room at 20°C. Every 2 hrs the dishes were weighed to measure the amount of the solution left, and a small aliquot of each solution was pipetted into a counting vial to measure the radioactivity, using a liquid scintillation spectrometer.[1]

6. *Effect of Soil on Volatility*

For each 50 g (based on dry weight) of the soil sample was mixed with 100 ml of water in a beaker. The beaker was allowed to stand at room temperature for 20 days. ^{14}C-Benthiocarb (26.5×10^4 dpm) mixed with the unlabelled chemical in a small amount of acetone was added to the surface water of each beaker to make the final concentration of the aqueous solution 10 ppm before exposure to the sun. For the control test, glass beads, instead of soil, were placed in a beaker up to the same depth as the soil layer. The beakers were placed under sunlight, and the radioactivity in each beaker was measured every 2 hrs. The flooded surface water was taken out by decantation to determine the radioactivity. The residual soil was transferred into a 300 ml centrifuge-tube, and 14 g of potassium carbonate and 100 ml of benzene were added. The tube was capped air-tight, shaken for 1 hr, and then centrifuged for 10 min at 3,000 rpm. The liquid phase was transferred into a separatory funnel, and an aliquot of each layer of benzene and water was radioassayed. The soil residue in the tube was stirred and a portion of the soil was oxidized with sulfuric acid- potassium dichromate.[9] The $^{14}CO_2$ evolved was trapped in 10 ml of an alkali scintillator (5 g of PPO and 0.3 g of POPOP in one liter of monoethanol amin-methylcellosolve-toluene (1 : 3 : 6) solution)[10] and radioassayed. The radioactivity in the soil layer was expressed as the sum of the radioactivities in the benzene and water extracts and in the soil residue. An aliquot of the surface water in the beaker for control, in which glass beads were placed, was also radioassayed.

7. *Soil Treatments*

^{14}C-Benthiocarb solution was prepared by dissolving ^{14}C-benthiocarb in water together with a Saturn® emulsifiable concentrated formulation which contained 50% of benthiocarb as the active ingredient. The effect of applying benthiocarb in the following ways were examined: a) The reference solution: 100 ml of water and 10.5 ml of ^{14}C-benthiocarb (1.1 mg, 26.7×10^4 dpm) solution were mixed in a 200 ml beaker, and glass beads were placed in the beaker up to the same depth as the soil in b). b) Adding into the surface water of flooded soil: 100 g of the soil sample and 100 ml of water were mixed together in a 200 ml beaker, and allowed to stand at room temperature for one week. The ^{14}C-benthiocarb solution (10.5 ml) was added dropwise on the surface water. c) Spraying on the soil surface under upland conditions: Water was added to 100 g of the soil sample to adjust the moisture content to 60% of the maximum water holding capacity. The sample was mixed well, allowed to stand at room temperature for one week, and the moisture content was readjusted by adding water. The ^{14}C–benthiocarb solution (10.5 ml) was sprayed uniformly on the soil surface. d) Incorporating into the soil under upland conditions: The soil was treated in the same way as c). After spraying the ^{14}C–benthiocarb solution, the soil was mixed well.

Each beaker was placed in a separate dessicator (15 cm i.d.) in which another small beaker containing 10 ml of liquid paraffin was placed to trap the vaporized lipophillic materials. The dessicators were closed tightly and exposed to the sun. After the designated periods, the liquid paraffin was mixed and an aliquot was pipetted into a counting vial for radioactive determination.

8. Identification of Volatile Compounds

In order to trap and identify the vaporized materials, an apparatus was set up as shown in Fig. 1. The apparatus consisted of three flasks A, B and C, a condenser E, a salted ice bath D, and connecting glass tubes to allow the passage of air and/or volatilized materials. Three hundred ml of the ^{14}C–benthiocarb solution (10 ppm, 59.2×10^6 ppm) was placed in flask A (one liter). This flask was made of colorless Pyrex Code 7740 glass, which transmits visible and partly ultraviolet light of wavelength longer than 280 nm. The flask was then exposed to sunlight. Volatilized materials in the flask were introduced to the condenser E by pumping air through inlet F at the rate of about 840 ml/min using an air-pump. A large portion of the volatilized materials condensed in the condenser cooled with flowing water and was collected in flask B. Residual volatile materials untrapped in E were trapped in *n*–propyl alcohol in flask C. Flasks B and C were cooled with salted ice in the bath D. All glass parts of the apparatus except flask A were covered with aluminum foil. As a control for light, a brown glass flask which intercepts ultraviolet and most of the visible light, was set up in place of flask A. One more system was set up, using a colorless Pyrex glass flask but without employing an air-pump, as a control for photodegradation. These three systems were placed under sunlight at the same time. The conditions are shown in the foot note of Table 3. Six, 12, and 30 hrs later an aliquot of the parent solution in flask A and all of the water trapped in flask B were extracted with ether. Small aliquots of the ether layer and residual water were radioassayed. The ether extracts were dried with anhydrous sodium sulfate, concentrated, and chromatographed on silicagel plates. The *n*–propyl alcohol in flask C was also radioassayed and chromatographed.

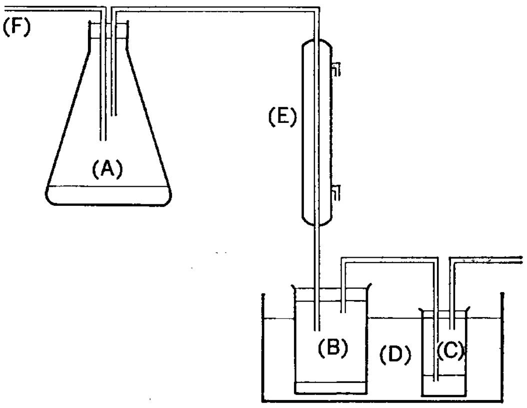

Fig. 1 Test equipment for the investigation of volatilized compounds.

Flask A, containing the benthiocarb solution, was exposed to sunlight. Air was supplied through the inlet F. Volatilized substances were cooled by passing through the condenser E. The condensates were collected in flask B and trapped in *n*–propyl alcohol in flask C. Vessel D contained salted ice to cool the trapped substances. All parts except flask A were covered with aluminum foil to intercept light.

RESULTS

Figure 2 shows the changes in the amount of water and radioactivity in the vessels covered or not covered with a quartz glass plate, when the aqueous solution of ^{14}C–benthiocarb was exposed to sunlight during the period of 12 hrs of daytime for 2 days. The skies were clear during the daytime of the experimental period and the solutions were surely exposed to strong sunlight ranging from 60,000 to 120,000 lux. The amounts of water evaporated were almost in direct proportion to the exposure time. The quartz glass plate cover on the vessel containing the ^{14}C–benthiocarb solution kept the water loss below 10% during the experiment, while the absence of the cover glass allowed more than 80% of the water to evaporate during the same period. The radioactivity decreased in proportion to the exposure time. The difference in the radioactivity levels of covered

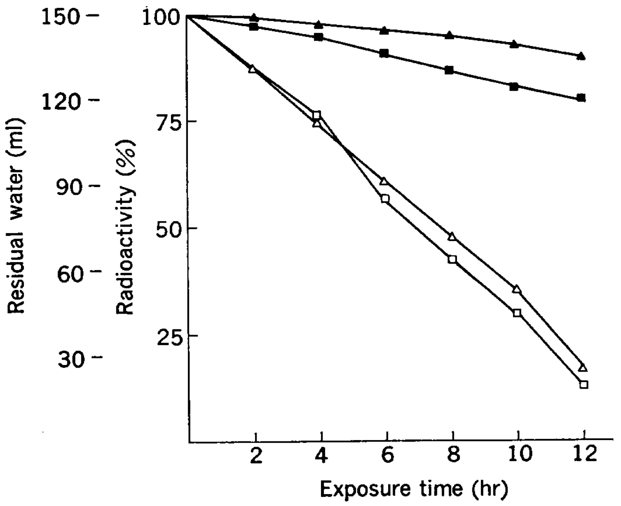

Fig. 2 Residual amounts of benthiocarb solution and radioactivity under exposure to sunlight.

▲ Residual water with a quartz glass plate,
△ Residual water without a quartz glass plate,
■ Radioactivity with a quartz glass plate,
□ Radioactivity without a quartz glass plate.

and uncovered solutions became larger as time elapsed. However, the radioactivity per unit volume of the solutions in the two vessels were similar to each other. Moreover, a large part of the radioactivity in the solutions was attributed to parent ^{14}C–bentiocarb.[1]

The effect of the presence of soil in the solution on the volatilization of radioactive compounds was investigated. Table 1 shows the amounts of water evaporated and residual radioactivity, when ^{14}C–benthiocarb added to the surface water in a beaker containing either soil or glass beads was exposed to the sun. The surface water of the flooded soil system evaporated a little more slowly than that of the control system. The radioactivity present in the whole flooded soil system decreased more slowly compared to the control system, indicating that the soil retarded the volatilization of radioactive compounds. The radioactivity in the surface water of the soil system, however, decreased quite rapidly with time, and it reached less than one-third of the applied amount within 6 hrs. A large portion of the radioactivity lost from the flooded water was found to be absorbed by the soil.

Table 2 shows the volatilization of radioactive substances from upland and flooded soils treated with ^{14}C–benthiocarb. The radioactivity trapped in liquid paraffin is given in terms of percent of the applied radioactivity. The radioactivity detected in liquid paraffin gradually increased with time. The amount of trapped radioactivity decreased in the order: reference water solution>radioactivity applied into the surface water of flooded soil>radioactivity sprayed on the surface of upland soil>radioactivity incorporated into upland soil. As the trapped radioactivity may be proportional to the amounts volatilized, the order described above may also show the order of volatility rates, i.e., ^{14}C–benthiocarb volatilized more rapidly from the reference water solution than from the surface water of the flooded soil system. Moreover, the amounts of ^{14}C–benthiocarb volatilized from both upland soil systems were very small, even when it was applied on the soil surface, compared with the amount volatilized from the flooded soil system. This was due to the adsorption of ^{14}C–benthiocarb on soil particles. Thus, the volatilization process was retarded according to the degree of adsorption. The rate of volatilization was least when the radioactive material was incorporated

Table 1 Effect of soil on the volatility of benthiocarb in aqueous solution.

	Exposure time (hr)			
	0	2	4	6
(Reference solution)				
Amount of water evaporated (ml)	0.0	11.5	23.5	33.5
Total radioactivity (×10^4 dpm)	26.7	24.0	22.3	20.6
(Flooded soil)				
Amount of water evaporated (ml)	0.0	4.5	18.5	30.5
Total radioactivity (×10^4 dpm)	26.7	25.9	25.1	24.8
Surface water	26.7	18.3	14.3	8.0
Soil residue	0.0	7.6	10.8	16.8

Table 2 Volatility of benthiocarb under various soil conditions.*

Method of adding ^{14}C–benthiocarb	Trapped radioactivity (%)						
	hrs			days			
Exposure time	2	4	6	1	2	3	7
Reference solution	0.2	0.5	0.8	1.5	4.0	5.5	10.4
Added to surface water of flooded soil	0.3	0.8	0.9	1.9	2.8	4.1	6.5
Sprayed on upland soil	0.2	0.3	0.3	0.7	0.8	1.2	1.7
Incorporated into upland soil	0.1>	0.1>	0.1	0.2	0.1	0.2	0.2

* Values are expressed in terms of percent of the applied radioactivity.

into upland soil.

Figure 3 shows the changes in the amounts of radioactivity detected in flasks A, B and C of the apparatus given in Fig. 1. The radioactivity in flask A decreased in both colorless and brown flasks as time elapsed. A portion of the volatilized substances was cooled and collected in flask B, while other portions were trapped in *n*–propyl alcohol in flask C. The radioactivities in both flasks B and C gradually increased, as shown in Fig. 3. Differences were observed somewhat between the behavior or radioactive substances in the colorless flask and those in the brown flask which cut off ultraviolet rays of sunlight, especially during the first 12 hrs of the test. The radioactivity trapped in the *n*–propyl alcohol from the colorless flask was markedly larger than that from the brown flask within the first 12 hrs. The total radioactivity gradually decreased, reaching 92.7% of the original amount in the colorless flask and 94.3% in the brown flask after 30 hrs. The color of the flask or the presence of sunlight did not affect the decrease very much, but the substances volatilized seemed to be somewhat different under different conditions. The substances volatilized from the colorless flask appeared to be a little more volatile than those from the dark brown flask.

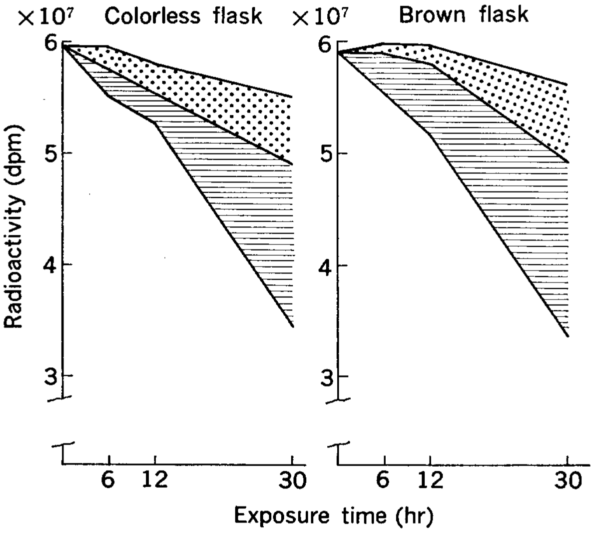

Fig. 3 Radioactivity found in the cold water (▤) and *n*-propyl alcohol (░) traps and remaining in the original solution (□) using the set-up in Fig. 1.

The identification of trapped volatile radioactive substances was carried out by thin layer chromatography. Benthiocarb, 4–chlorobenzaldehyde and several other spots were detected on the silicagel plates. Their amounts are shown in Table 3. A large portion of the radioactive substances trapped in flasks B and C as well as those remaining in flask A was found to consist of parent benthiocarb, while 4–chlorobenzaldehyde and other photo-degradation products were present in lesser quantities. These findings showed that parent benthiocarb accounted for a large amont of the volatilized substances, confirming the suggestion given above. 4–Chlorobenzaldehyde was not found or was present only in small amount in the residual water (flask A) or in the trapped fractions (flasks B and C). In the case of the control test for photodegradation in which air was not passed through the apparatus, the aldehyde was detected in an amount corresponding to 3.5% of the added radioactivity. However, the quantitative determination of 4–chlorobenzaldehyde by thin layer chromatography is very difficult because of its high

Table 3 Amounts of radioactive substances volatilized from and remaining in the aqueous solution of ^{14}C–benthiocarb exposed to the sun.*

	Radioactivity, %				
	Remaining in water (flask A)	Volatilized radioactivity trapped in			Total (A+B+C)
		Water (flask B)	*n*–Propyl alcohol (flask C)	Total (B+C)	
Colorless flask					
(Water, ml)	(246)	(54.4)			
Ether fraction	57.4	24.8	9.5	34.3	91.7
Benthiocarb	34.3	13.2	6.9	20.1	54.4
4–Chlorobenzaldehyde	0	0	0.9	0.9	0.9
Others	2.5	0.3	0.2	0.5	3.0
Loss**	20.6	11.3	1.5	12.8	33.4
Water fraction	1.0	0	—	0	1.0
Total	58.4	24.8	9.5	34.3	92.7
Brown flask					
(Water, ml)	(240)	(61.2)			
Ether fraction	56.8	26.0	11.5	37.5	94.3
Benthiocarb	47.1	21.6	10.6	32.2	79.3
4–Chlorobenzaldehyde	0	0	0.2	0.2	0.2
Others	0.2	0.3	0.2	0.5	0.7
Loss**	9.5	4.1	0.5	4.6	14.1
Water fraction	0	0	—	0	0
Total	56.8	26.0	11.5	37.5	94.3
Colorless flask without air-flow					
(Water, ml)	(300)				
Ether fraction	98.8				98.8
Benthiocarb	70.3				70.3
4–Chlorobenzaldehyde	3.5				3.5
Others	11.0				11.0
Loss**	14.0				14.0
Water fraction	1.2				1.2
Total	100				100

* Three hundred ml of the aqueous solution of ^{14}C–benthiocarb (10 ppm, 59.2×10^6 dpm) were placed in each flask and exposed to the sun for 5 days (12 hrs/day) under 40,000 to 120,000 lux.

** Loss means the loss of radioactivity during the determination process.

volatility. A large portion of the aldehyde is lost during the concentration of the extract solution and during the chromatographic process.[1] Therefore, the amount of "loss" given in Table 3 includes a large amount of 4–chlorobenzaldehyde. From the values given in Table 3, the volatilized benthiocarb accounted for 59% (20.1/34.3) of the total volatilized radioactivity even in the colorless flask, and 87% (32.2/37.5) in the brown flask.

The total amount of 4–chlorobenzaldehyde plus the percentage loss in the volatilized fraction was 39% [(0.5+12.8)/34.3] of the total volatilized radioactivity in the colorless flask and 13% [(0.2+0.4)/37.5] in the brown flask. These data indicate that when the aqueous solution of ^{14}C–benthiocarb was exposed to sunlight under the given experimental conditions, about 60% of the volatilized radioactivity was composed of benthiocarb itself, and that the rest was composed of volatile photodegradation products, a large part of which was presumed to be 4–chlorobenzaldehyde.

DISCUSSION

Generally speaking, volatilization is one of the important processes related to the dissipation of pesticides from the fields.[11] With respect to benthiocarb herbicide, it is important to clarify its behavior not only in soils but also in the surface water of paddy fields, because it is applied mainly in the surface water of paddy fields within a short period before and after transplanting rice seedlings.

Exposure of the aqueous solution of ^{14}C–benthiocarb to sunlight resulted in the volatilization of radioactive substances accompanied by the evaporation of water. The volatilization of the substances as well as the evaporation of water were remarkably reduced when the glass plate cover was used. Absence of the cover allowed the radioactive substances to evaporate or volatilize freely. Although the amounts of both residual radioactivity and water were remarkably different in covered and in uncovered dishes, the concentration of ^{14}C–benthiocarb in the residual water was nearly equal in both cases. These results indicate that the amounts of evaporated water and volatilized benthiocarb were proportional to each other, i.e., benthiocarb volatilized together with the evaporation of water. Another example of the same type of proportional correlation was observed between the amount of evaporated water and volatilized EPTC when a wet soil containing EPTC was dried.[2] The results of some investigations[2,3,5] indicated that an increase in the moisture content of the soil promoted the volatilization of chemicals from the soil, while dry soil, on the contrary, retained them very much. From another point of view, steam-distillation is representative of such a relationship. Of course, benthiocarb and EPTC were reported to be steam-distilled easily.[12,13]

The presence of soil in the aqueous solution of ^{14}C–benthiocarb largely retarded the volatilization of the herbicide, as shown in Table 1. In the case of flooded soil, ^{14}C–benthiocarb added to the surface water rapidly transferred from the water to the soil phase by adsorption on the soil particles. Nakamura *et al*[14] found that the amount of benthiocarb adsorbed by the soil was proportional to the organic matter content and C.E.C. values of soils. Furthermore, the chenical was found to be desorbed comparatively easily from soils. It is presumed that the equillibrium of benthiocarb distributed between the water phase and the soil phase leaned over the soil phase.

The volatilization of benthiocarb from the unflooded soil was much slower than from the flooded soil. Incorporation into the soil extremely retarded the volatilization process. Such a reduction of vapor loss by incorporation into soils was reported in the case of other thiocarbamate herbicides.[4] It was also reported that the volatilization of thiocarbamate herbicides from the soil surface was closely related to the vapor pressure, i.e., volatility increased with increasing vapor pressure.[6] Of course, the volatilization of pesticides from the soil surface can be affected not only by the vapor pressure, but also by other factors, such as solubility in water, adsorbability on soil, pesticide concentration, soil water, air flow rate, temperature, and diffusion through soil.[15] Using the vapor pressure as a basis, the volatilization of benthiocarb from soil surface is perhaps small, compared with other thiocarbamate herbicides, because the vapor pressure of benthiocarb is much lower than those of the others.[16]

More than half of the radioactivity volatilized from the aqueous solution of ^{14}C–benthiocarb, when air was passed through the set-up, was attributed to parent benthiocarb itself, and the rest to photodegradation products, such as 4–chlorobenzaldehyde which was a major photodegradation product.[1] The formation of 4–chlorobenzaldehyde from benthiocarb under the sun may cause the loss of a fair amount of the radioactivity from water because the aldehyde is highly volatile compared with benthiocarb and other degradation products.

Considering the results described above, the volatilization of benthiocarb from water is closely correlated with the evaporation of water. The amount of benthiocarb volatilized from the aqueous solution is large, but the presence of soil in the solution largely supresses the volatilization process by adsorption of the chemical on soil particles. The adsorption process is presumed to play an important role in reducing the volatilization of the herbicide from surface water particularly in paddy fields. The dissipation of benthiocarb in paddy fields was investigated by Ishikawa *et al.*17) Though they did not determine the amount of benthiocarb volatilized from the paddy fields, they presumed that the amount was small based on the results obtained with regards to its distribution in the soil layer and the surface water, and its dissipation process in both layers and in rice plants.

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要約

室内試験により，除草剤ベンチオカーブの水溶液および土壌からの揮散について研究した．^{14}C-ベンチオカーブ水溶液に太陽光を照射すると，水溶液中の放射能は水分の蒸発量に比例して減少した．水溶液中に土壌を添加すると，ベンチオカーブは速やかに土壌層へ吸着移行し，放射能の揮散は顕著に抑えられた．非湛水土壌の表面に散布したベンチオカーブの揮散は湛水土壌からの消失に比べると，はるかに少なかった．太陽光照射時に水溶液から揮散する放射性物質の半分以上はベンチオカーブ自身であり，残りは，生成した *p*-クロルベンズアルデヒドなどの揮発性の光分解生成物として揮散した．

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