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Degradation of *o-sec*-Butylphenyl *N*-Methylcarbamate (BPMC) in Soil

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BPMC is one of several carbamate insecticides applied in large quantities in Japan to control planthoppers and leafhoppers on rice plants. When an insecticide is applied in fields, a large part of the insecticide reaches the soil where degradation of the insecticide may take place. Much work has been done with the degradation of insecticides in the soil environment. As for carbamate insecticides, BULL et al. (1970) reported that the degradation of aldicarb was influenced by soil type, pH, moisture content and so forth. LEENHEER and AHLRICHS (1971) studied the adsorption of insecticides upon the surfaces of soil organic matter, and suggested that the adsorption of insecticides tend to increase as water solubility of the insecticides become low. Evidences of participation of soil microorganism(s) in the degradation of carbamate insecticides in soils have been suggested by BOLLAG and LIU (1971,1972 a,b), SUZUKI and TAKEDA (1976 a,b,c,d) and VENKATESWARLU et al. (1977).

Very little work has been done on the persistence of BPMC in soils. The present study deals with the effect of various factors which may influence the degradation of BPMC in soils.

MATERIALS AND METHODS

Test soil

The experiments were conducted with three types of soils selected from typical paddy rice fields in Japan. As shown in Table I, these soils show different characteristics in soil texture, organic matter content, pH, etc. Prior to the experiments, the soils were passed through a 2-mm sieve and kept under the condition of about 30 % relative humidity.

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Table I

Some properties of three soils used

Soil	Organic matter (%)	pH	CEC4) meq/100g	% Composition Sand	Silt	Clay
Saga1)	3.8	5.3	24.2	15	44	40
Tochigi2)	7.9	5.8	38.8	60	32	8
Konosu3)	5.8	5.2	18.7	31	29	40

1) MATSUO et al. (1974); 2) HANYU (1974)
3) CHISAKA and KEARNEY (1970); 4) Cation Exchange Capacity

Chemicals

Technical grade BPMC was supplied by Kumiai Chemical Industry Co. Ltd. Its purity was 99.5 % when analyzed by gas liquid chromatography (GLC).

Application of BPMC to the test soils

Fifty grams of each soil were added to Erlenmeyer flasks with distilled water to make 188±2 % of moisture content (Saga 50 ml, Tochigi 51 ml, Konosu 55 ml) and kept in an incubator at 28±1°C. After 1 week, 50 µg of BPMC in 0.1 ml of acetone were added with a microsyringe, and the flask covered with aluminium foil was incubated at 28±1°C. Residual amounts of carbamate in the flasks were estimated at appropriate intervals of days. In order to examine the effect of cations on the adsorption of BPMC in soils, they were added just before the application of the carbamate.

Extraction and cleanup

For extraction of BPMC residues in soil, the content of each flask was vacuum filtered. The aqueous phase in a flask was transferred to a separatory funnel and extracted twice with 30 ml of dichloromethane. The soil was transferred to a 500-ml Erlenmeyer flask and extracted by shaking with 200 ml of acetone for 1 hr and filtered. The acetone solution was concentrated *in vacuo* and extracted twice with 30 ml of dichloromethane. Dichloromethane extracts from the water and soil were combined and concentrated *in vacuo*. In order to examine the soil-bound residues, the soil remaining after extraction with acetone was refluxed with 50 ml of 0.5 N HCl for 15 min. After cooling, 200 ml of acetone was added to the soil and shaken for 1 hr, and filtered. The filtrate was extracted twice with 50 ml of dichloromethane, and concentrated *in vacuo*. The residues of the solvent extracts were dissolved in hexane, and poured onto a column of 5 g of Florisil (60-100 mesh). The column was eluted first with 40 ml of hexane-acetone (95:5), and this fraction was discarded. Then, the second fraction of 70 ml was collected and concentrated *in vacuo*.

Determination

For the determination of BPMC by GLC, o-*sec*-butylphenol released by alkaline hydrolysis of BPMC was converted to its 2,4-dinitrophenyl ether derivative according to HOLDEN's procedure (1973). The concentrate from the second fraction passing through the Florisil column was dissolved in 2 ml of 5 % KOH, and heated at 80°C for 20 min. One hundred ml of distilled water, 10 ml of 5 % borax and 1 ml of a 1 % acetone solution of 2,4-dinitrofluorobenzene were added succesively to the KOH-treated solution. After heating again at 80°C for 20 min., the reaction mixture was extracted twice with 30 ml of hexane, and concentrated for analysis by GLC.

GLC was conducted on a Varian 1200 gas chromatograph equipped with an electron capture detector. Operating conditions were as follows: 5 ft x 1/8 in. glass column packed with 5 % OV-17 on 60/80 mesh Gas Chrom Q, carrier gas, N_2, 48 ml/min. and temperatures of column, inlet and detector, 172, 220 and 270°C, respectively. Recovery was 89—102 % with the fortified soil at the 0.1 to 0.5 ppm level.

RESULTS AND DISCUSSION

Effect of BPMC concentration

Saga soil was used to test the effect of BPMC concentration on degradation. A BPMC acetone solution was added to the soil to make the concentrations of 0.2, 1.0 and 10.0 ppm on the basis of air-dry soil. As shown in Fig.1, the disappearance curve of BPMC in the soil was changed with different concentrations. Forty % of BPMC remained after 10 days and only 5 % was recovered after

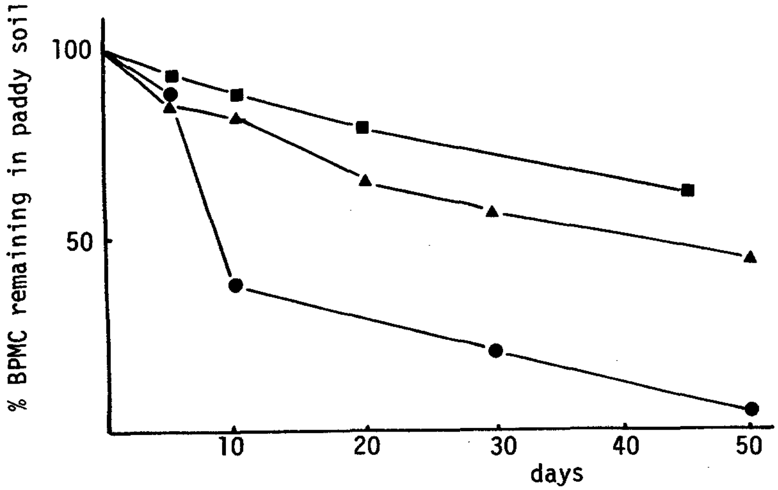

Fig.1. Degradation of BPMC with different concentration in paddy soils. Concentration of added BPMC to soil, ■—■ 0.2 ppm; ▲—▲ 1.0 ppm ; ●—● 10.0ppm

50 days in 10 ppm soil, which 60 % recovery was found after 45 days in 0.2 ppm soil. The persistence of BPMC in the soil was in the following order: 0.2> 1.0>10.0 ppm.

Effect of moisture content

Saga soil was flooded with distilled water to obtain 131, 188 and 275 % of moisture content to the dry soil. As shown in Fig.2, the disappearance of BPMC in the soil was affected by the moisture content. When moisture level was 131 %, recovery of BPMC was the lowest after 60 days and about 25 % of BPMC remained. In the case of 188 and 275 % of moisture content, a similar pattern of the disappearance was found, and about 40 % of BPMC remained after 60 days. OGAWA et al. (1976) studied the degradation of BPMC in soils and found that BPMC disappeared more rapid under upland conditions than flooded conditions.

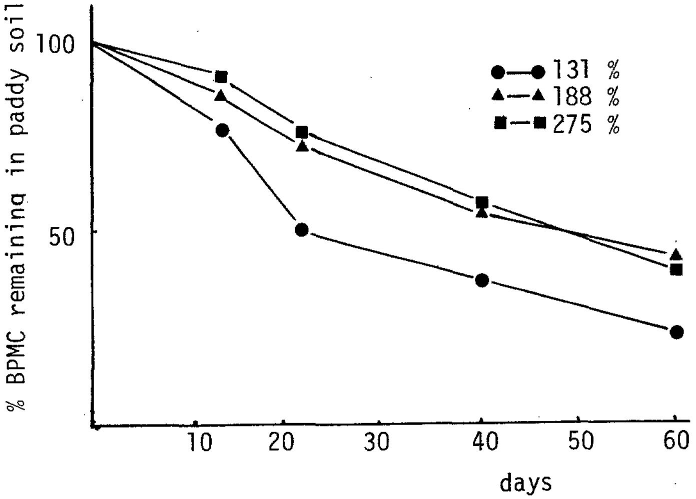

Fig.2. Effect of moisture content on degradation of BPMC in paddy soil.

Effect of sodium azide on the persistence of BPMC in soils

In order to examine the effect of microorganism(s) on the degradation of BPMC in soils, three types of soils were used. To stop the biodegradation of BPMC, 1 ml of a 2 % aqueous sodium azide solution was added to the soils in a group of flasks before the application of BPMC, while the other group of flasks was untreated. The data on the persistence of BPMC and the effect of sodium azide in soils are given in Fig.3. The disappearance of BPMC in soil was different among three soils. In Tochigi soil, only 10 % BPMC remained after 13 days, while in Saga and Konosu soils, considerably high recovery of over

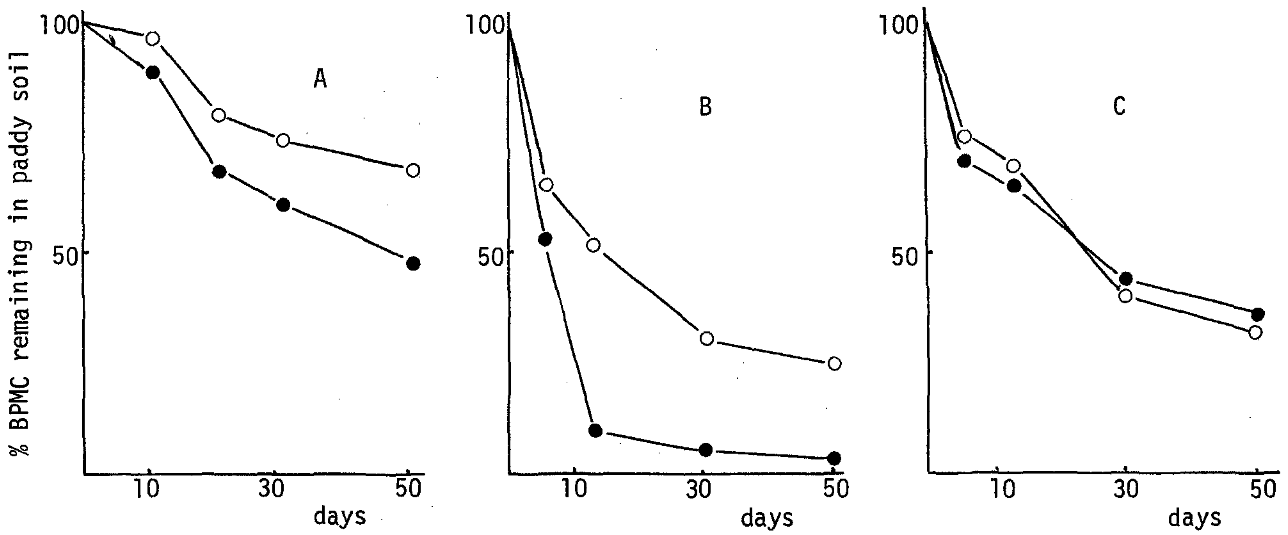

Fig.3. Effect of sodium azide on the degradation of BPMC in paddy soil.
(A) Saga; (B) Tochigi; (C) Konosu; ●—● without sodium azide; ○—○ addition of sodium azide

65 % was found in the same incubation period and about 40 % remained even after 50 days. In the case of addition of sodium azide, the disappearance of BPMC in Saga and Tochigi soils were retarded, suggesting that soil microorganism(s) participated in the degradation of BPMC. In Konosu soil, the effect of sodium azide was not observed, and BPMC disappeared at a similar rate to that without sodium azide. It appeared that the effect of sodium azide on the degradation of BPMC in soils was different with soil types.

KAZANO et al. (1972) found that the amount of carbaryl which was unextractable by organic solvent from soil was proportional to soil organic matter content, and they showed that the amount of carbaryl remaining after extraction with organic solvent was the largest in Tochigi soil. The rapid disappearance of BPMC in Tochigi soil agreed with the high organic matter content.

Soil-bound residues of BPMC

The experiments were conducted at the levels of 50 µg and 500 µg of BPMC per flask which Saga soil was used. In the experiments, the effect of cations was also examined, and 50 or 500 mg of calcium sulfate, magnesium sulfate, ferrous sulfate and aluminum sulfate were added separately to respective flasks. As shown in Table Ⅱ, the bound residues of BPMC in the soil was comparatively low. On the treatment with 50 µg of BPMC, the soil-bound residues reached the maximum of 6.6 % after 20 days. On the treatment with 500 µg of BPMC, the residues reached the maximum of 4.0 % after 10 days, and thereafter disappeared gradually. This slight decline of soil-bound residue in the later stage of experimental period was in accord with the result of GETZIN (1973) who suggested that the bound residues of carbofuran in soils was slowly converted to carbon dioxide.

Table Ⅱ

Soil-bound residues (%) of BPMC in paddy soil.

Days after application	BPMC content at added amounts (µg) 50	500
5	2.4	4.0
10	3.8	3.1
20	6.6	—
30	5.6	1.9
40	4.2	—
50	—	1.4

The effect of cations on the production of soil-bound residues is shown in Fig.4. After 30 days of incubation, the soil-bound residues increased in the soils added with calcium sulfate or magnesium sulfate. Especially, the effect of magnesium sulfate was distinct, and the value was three times as compared with the soil without salts. In the case of addition of ferrous sulfate or aluminum sulfate, the ratio of bound-residue was not changed as compared with the control without salts. GRIM (1968) found that ionic hydration in clay minerals was stronger for magnesium than calcium, and in clay-water system, water was easily carried into the lattice of clay minerals when there were elements such as Mg and Ca ions. It was probable that BPMC itself was also carried into the lattice of the clay minerals with water, and consequently, the soil-bound residues of BPMC increased when Mg and Ca ions were added.

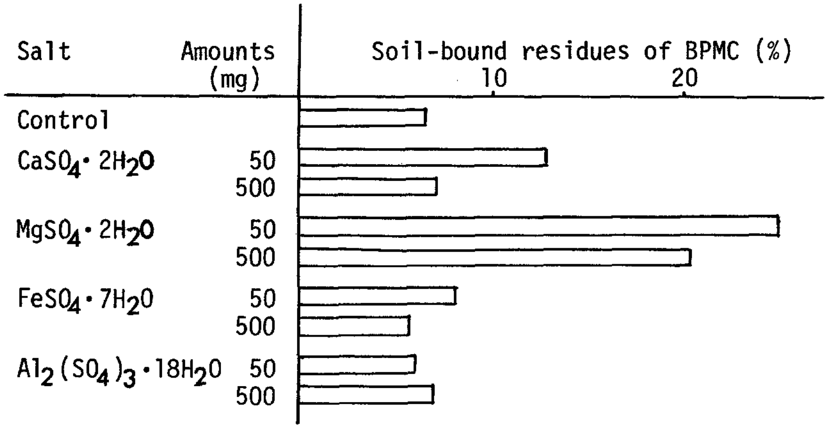

Fig.4. Effect of cations on soil-bound residues of BPMC in paddy soils after 30 days of incubation.

SUMMARY

Disappearance rate of BPMC in paddy soils increased with the increase of BPMC concentration in soils, and in contrast, it declined with higher moisture content. Since the disapperance rate of BPMC in soils was retarded by addition of sodium azide, it was suggested that soil microorganism(s) participated in the degradation of BPMC. On the other hand, it was probable that organic matter content was one of the main factors participating in the disappearance of BPMC. The soil-bound residues of BPMC which were extractable by heating with 0.5 N HCl for 15 min, were relatively low, and their percentages ranged from 2.4 to 6.6 %. The bound-residues were increased by addition of calcium or magnesium sulfate.

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