Bull. Environm. Contam. Toxicol. 24,204-210 (1980)

Uptake and Translocation of *o-sec*-Butylphenyl N-Methylcarbamate (BPMC) and O,O-Di*iso*propyl S-Benzyl Phosphorothiolate (IBP) in Rice Plants Applied as Single and Mixed Preparations

Masako Ueji and Jun Kanazawa
National Institute of Agricultural Sciences, Yatabe-Machi, Ibaraki 305, Japan

BPMC is one of carbamate insecticides developed in Japan, and used for the control of insect pests on various crops. Studies on the metabolism of carbamates in plants demonstrated that carbamates were comparatively unstable in plants, and metabolized via oxidation, hydrolysis and conjugation. (OGAWA et al. 1976, 1977; OHKAWA et al. 1974; HILL et al. 1975; ANDRAWES et al. 1971, 1973). In general, metabolic fate of carbamates in plants was different with plant species (POLIZU et al. 1971), enviromental conditions (DHAL et al. 1971), formulations of insecticides (UEJI et al. 1978) and so forth. Recently, the mixed preparations of pesticides have spread owing to the simultaneous control of different pest, intensification of control effects and labor saving for application. BPMC used for the control of rice leaf hoppers has been applied as mixed preparations with organophosphorus insecticides or fungicides. In such a case, it is expected that the metabolic fate of BPMC in plants is different between single and mixed preparations.

This report deals with the uptake and translocation of BPMC in rice plants as single and mixed preparations with IBP, an organophosphorus fungicide developed for the control of rice blast. Furthermore, the uptake and translocation of IBP in rice plants was also examined.

MATERIALS AND METHODS

1) Chemicals

The formulated products used in the experiments were fine granules, which were supplied by Kumiai Chemical Industry Co. Ltd. Single preparation of BPMC contained 3 % of active ingredient and mixed preparation of BPMC and IBP contained 3 % and 17 % of active ingredient, respectively.

2) Crop cultivation

Rice plants (Nihonbare) were grown in 1/200,000 hectare-sized Wagner's pots containing alluvial soil. Before the experiment, fertilizer (8:8:5, N:P:K, 8 g per pot) was added to the soil. At the heading stage, 250 mg of pesticide was applied to the surface of flooded soil, and this amount corresponded to the dosage recommended for the control of rice leaf hoppers in paddy fields. The plants were sampled at the intervals of 1,3,5,8 and 15 days

0007-4861/80/0024-0204 $01.40

after treatment. In order to determine the distribution of BPMC and IBP in plants, plants were separated into roots, leaf sheath and leaf blade, and weighed. At the sampling time, flooded water and soil in a pot were also sampled.

3) Extraction and cleanup

The separated portions of rice plants were finely chopped, and the soils were air dried. About 10 ml of acetone per gram of sample was added to each sample and stood for 24 hrs at room temperature. Then, the mixture was shaken thoroughly for 1 hr, and filtered. Residues were rinsed with 40 ml of acetone, and acetone solution was concentrated under reduced pressure, and after adding 200 ml of 4 % NaCl solution to the concentrate, the mixture was extracted twice with 40 ml of dichloromethane. The flooded water was directly extracted with dichloromethane without the extraction with acetone. The extract was concentrated in vacuo and dissolved in 10 ml of hexane, and the hexane was bisected for analysis of BPMC and IBP. The extracts for analysis of BPMC were cleaned up by passing through a column (1.7 cm x 26.5 cm) packed with 5 g of Florisil (60-100 mesh), and the column was eluted with hexane-acetone (95:5). The first eluate 40 ml was discarded, and the second eluate of 70 ml was collected and concentrated in vacuo. The extracts for analysis of IBP were cleaned up by passing through 8 g of alumina (300 mesh) deactivated by adding 10 % moisture. The column was eluted with 80 ml of hexane-ethylether (85:15), and eluate was concentrated in vacuo.

4) Determination

(1) BPMC

The determination of BPMC was carried out according to the method reported by HOLDEN (1973). BPMC in extracts cleaned up by passing through the Florisil column was hydrolyzed by 0.5 N KOH, and resultant 2-sec-butylphenol was treated with 1-fluoro-2,4-dinitrobenzene to form 2,4-dinitrophenyl 2'-sec-butylphenylether. The reaction mixture was extracted with hexane and concentrated for GLC analysis.

GLC was conducted on a Varian 1200 gas chromatograph equipped with an electron capture detector. The column was 5 ft x 1/8 in. glass column packed with 5 % OV-17 on 60/80 mesh Gas Chrom Q. The temperatures of column, inlet and detector were 170, 220 and 270°C respectively and carrier gas, N_2 was 48 ml per minute. Recoveries on the fortified samples were on the average 91 % at 0.1 ppm level and 97 % at 1.0 ppm level.

(2) IBP

GLC for the determination of IBP was conducted on a Tracor MT-160 equipped with a flame photometric detector in the phosphorus mode. Operating conditions were as follows: 5 ft x 1/6 in. glass column packed with 5 % OV-17 on 60/80 mesh Gas Chrom Q, the temperatures of column, inlet and detector were 175, 215 and 175°C, respectively, and carrier gas, N_2 was 60 ml per minute. Recoveries on the fortified samples were on the average 95 % at 0.1 ppm level and 99 % at 1.0 ppm level.

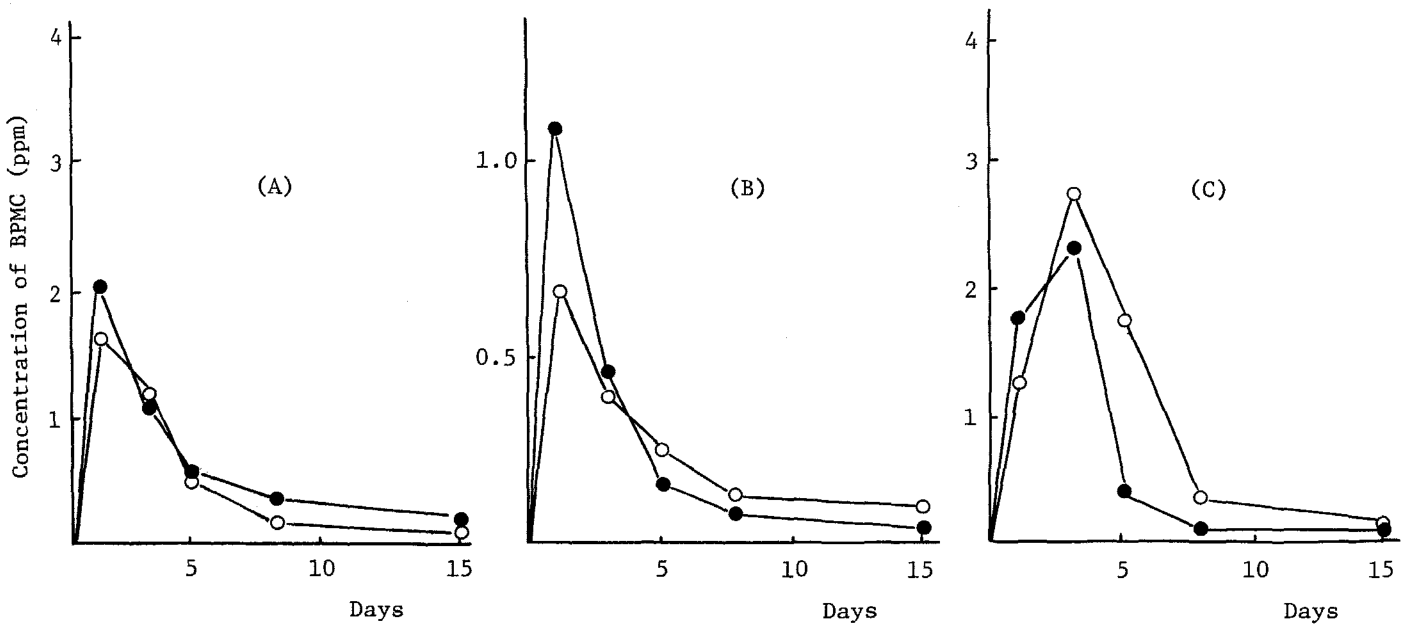

Fig. 1 Concentration of BPMC in roots (A), leaf sheath (B) and leaf blade (C).

●—● single preparation; ○—○ mixed preparation

Determination was conducted in duplication and the results were shown as an average value.

RESULTS AND DISCUSSION

The concentrations of BPMC in roots, leaf sheath and leaf blade were shown in Fig. 1. BPMC was taken up by roots and translocated to upper parts. In roots and leaf sheath, the maximum of BPMC concentration was found one day after treatment, and the concentration of BPMC in leaf blade reached the maximum level 3 days after treatment, and afterwards decreased gradually. This tendency was found in both cases of single and mixed preparations, and no difference of BPMC concentration in each portion of rice plants was found between both preparations. As shown in Fig. 2,

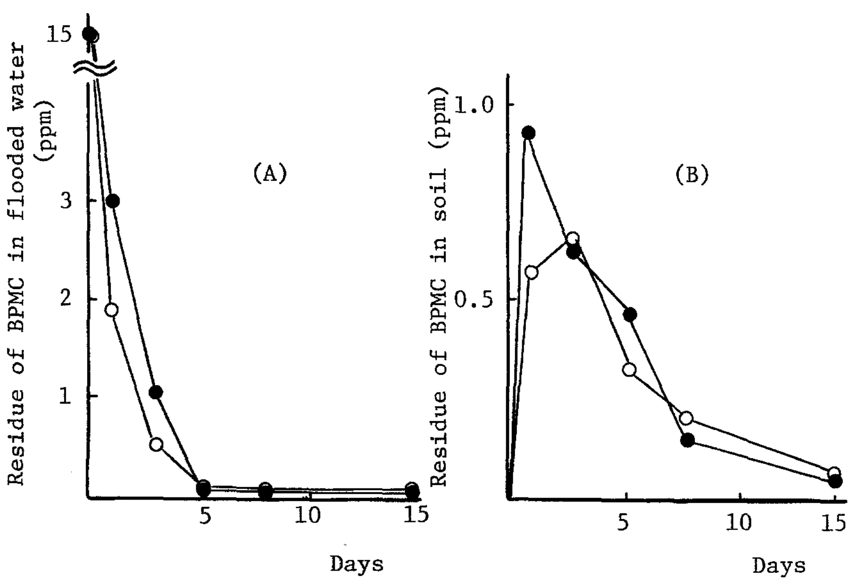

Fig. 2 Residue of BPMC in flooded water (A) and soil (B).
●——● single preparation; ○——○ mixed preparation

the decline of BPMC concentration in rice plants was probably due to the limited uptake derived from the disappearance of BPMC in flooded water and soil in addition to the degradation of BPMC absorbed in plants. OGAWA et al. (1976) found that when the roots of rice plants were dipped in aqueous solution of BPMC, BPMC was absorbed and translocated to an upper part, but most of BPMC was rapidly lost by evaporation.

The uptake and translocation of IBP in rice plants are shown in fig. 3. The maximum concentration of IBP treated with mixed preparation was found 3 days after treatment in roots and leaf sheath and 5 days after treatment in leaf blade. The decrease of IBP absorbed in plants was considerably slow as compared with that of BPMC, and in each portion of rice plants IBP concentration was about ten times higher than BPMC concentration 15 days

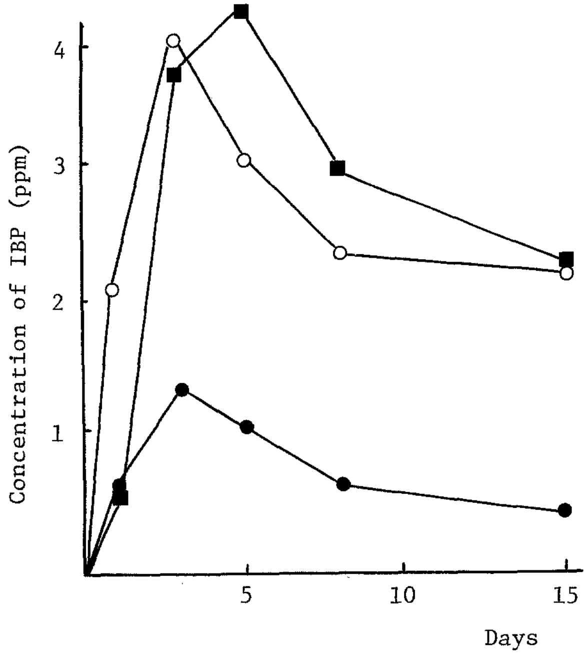

Fig. 3 Concentration of IBP in roots (○——○), leaf sheath (●——●) and leaf blade (■——■).

after treatment. KANAZAWA et al. (1976) found that residue level of IBP in dried straw of rice plants was 35 ppm 45 days after treatment, and considered that this high residue level may be due to high content of active ingredient of IBP in the IBP formulation and the high stability in rice plants.

The uptake ratio of BPMC and IBP in rice plants to the application dosage was shown in Fig. 4. The contents of BPMC and IBP in formulated products were 3 and 17 %, respectively, but the uptake ratio of BPMC in rice plants was higher than that of IBP. Namely, the maximum uptake of BPMC to the dosage was 9.5 and 8.3 % in the single and mixed preparation, respectively, and that of IBP was only 2.3 %. It is possible, therefore, that the high residue level of IBP in rice plants kept for the long time after treatment was not only due to the high content of IBP but also the high stability in plants.

Summary

When BPMC was applied as single or mixed preparation with IBP to rice plants, BPMC absorbed through roots and translocated to upper portions. The uptake and dissipation of BPMC in rice plants were not different between both preparations. The disappearance of BPMC in plant was rapid and residue level of BPMC

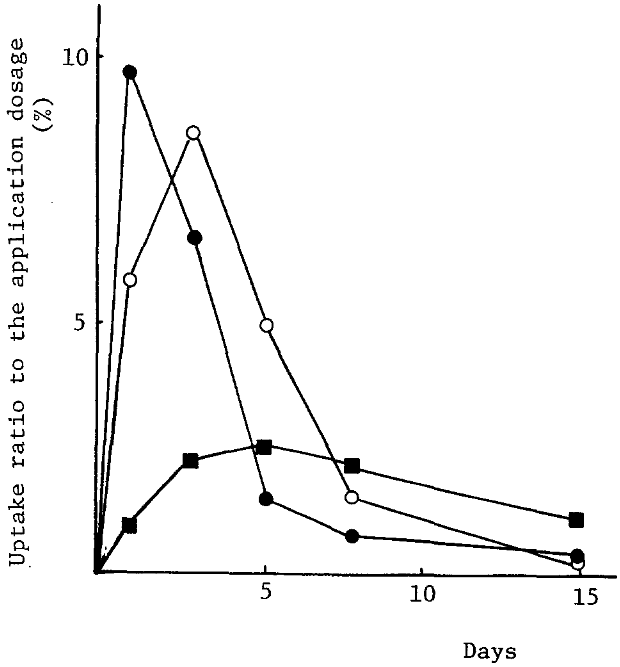

Fig. 4 Uptake ratio of BPMC and IBP in rice plants to the application dosage.

●——● BPMC in single preparation
○——○ BPMC] in mixed preparation
■——■ IBP

was below 0.2 ppm 15 days after treatment. On the other hand, the concentration of IBP applied as mixed preparation decreased slowly as compared with that of BPMC. The persistence of IBP in rice plants was considerably long, and it may be due to the high stability in plants.

ACKNOWLEDGEMENT

We acknowledge greatly to Kumiai Chemical Industry Co. Ltd. for supplying the chemicals and Dr. C. Tomizawa, National Institute of Agricultural Sciences, for a critical reading of the manuscript.

REFERENCES

ANDRAWES, N.R., W.P. BAGLEY and R.A. HERRETT: J. Agr. Food Chem. 19, 731 (1971).

ANDRAWES, N.R., R.R. ROMINE and W.P. BAGLEY: J. Agr. Food Chem. 21, 370 (1973).

DHAL, P. and R. LAL: J. Assoc. Offic. Anal. Chem. 54, 1095 (1971).

HILL, J.E. and R.I. KRIEGER: J. Agr. Food Chem. 23, 1125 (1975).

HOLDEN, E.R.: J. Assoc. Offic. Anal. Chem. 56, 713 (1973).

KANAZAWA, J., M. UEJI, T. MASUDA, H. IIZUKA, A. OTAKE and S. KAMANO: Bull. Natl. Agric. Sci. Ser.C, No.30, p.65,(1976).

OGAWA, K., M. TSUDA, F. YAMAUCHI, I. YAMAGUCHI and T. MISATO: J. Pesticide Sci. 1, 219 (1976).

OGAWA, K., M. TSUDA, F. YAMAUCHI, I. YAMAGUCHI and T. MISATO: J. Pesticide Sci. 2, 51 (1977).

OHKAWA, H., R. YOSHIHARA, T. KOHARA and J. MIYAMOTO: Agric. Biol. Chem. 38, 1035 (1974).

POLIZU, A., H. GREGER and A.V. ALEXANDER: Qual. Plant. Mater. Veg. 20, 215 (1971).

UEJI, M. and J. KANAZAWA: J. Pesticide Sci. 3, 371 (1978).