Reductions in Postharvest-Applied Dichlorvos, Chlorpyrifos-methyl, Malathion, Fenitrothion, and Bromide in Rice during Storage and Cooking Processes

Yumiko Nakamura,*,† Yukihiro Sekiguchi,† Shin Hasegawa,‡ Yukari Tsumura,† Yasuhide Tonogai,† and Yoshio Ito†

Division of Food Chemistry, National Institute of Hygienic Sciences, Osaka Branch, 1-1-43 Hoenzaka, Chuo-ku, Osaka 540, Japan, and Food Safety Division, Kobe Center for Quality Control and Consumer Service, 1-4 Onohama-cho, Chuo-ku, Kobe 651, Japan

Residue levels of postharvest-applied dichlorvos (DDVP), chlorpyrifos-methyl, malathion, fenitrothion, and bromide during storage and cooking processes (boiled rice and rice noodle) were investigated for unhulled and brown rice. The concentrations of these organophosphorus pesticides decreased as a function of time; 15.6–28.6% (92 days, unhulled rice) and 0–35.4% (85 days, brown rice) remained at the end of the experimental period. Organophosphorus pesticides remained on the surface. The concentration of bromide decreased for 56 days and then gradually increased to 59.0% in unhulled rice but did not change significantly in brown rice during the experimental period (84 days). Permeation of bromide inside was observed in unhulled rice. Organophosphorus pesticides and bromide could be mostly removed by washing with water followed by steaming. The remains of organophosphorus pesticides were 0–5.6% in boiled rice and 0% in rice noodle. The remains of bromide were 41.2% in boiled rice and 5.1% in rice noodle.

Heavy usage of pesticides including postharvest-applied pesticides has been attracting much attention because pesticide residues in foods may be hazardous to human health. Several studies about the effect of processing and storage on pesticide residues in foods have been conducted (Liska and Stadelman, 1969; Takeda, 1973; Geisman, 1975; Abdel-Kader et al., 1982; Anderegg and Madisen, 1983a,b; Cogburn et al., 1990; Arthur et al., 1991; Lee et al., 1991; Hasegawa et al., 1991a,b; Tsumura-Hasegawa et al., 1992a,b).

Rice is a major part of the diet in Japan and other countries of east and southeast Asia. It is therefore important to study the changes of pesticide residues in rice during storage and processing.

Recently, the Ministry of Health and Welfare in Japan has planned to legislate more than 200 pesticide residue limits by foods in the Food Sanitation Law. Already, 74 pesticides have been legislated.

Dichlorvos (DDVP), chlorpyrifos-methyl, malathion, fenitrothion, and methyl bromide are the pesticides which are permitted for postharvest application for rice in the Unites States and Australia (CFR 40). The tolerances of these pesticides in rice are as follows: DDVP, 0.5 ppm (in processed foods); chlorpyrifos-methyl, 6 ppm; malathion, 8 ppm; fenitrothion, 15 ppm (in Australia); and methyl bromide, 50 ppm. Contrarily, the tolerances for brown rice legislated by the Food Sanitation Law in Japan are as follows: bromide, 50 ppm; malathion, 0.1 ppm; fenitrothion, 0.2 ppm.

In this study, the authors investigated reductions of these five pesticide residues in unhulled and brown rice during the storage and cooking process (boiled rice and rice noodle).

† National Institute of Hygienic Sciences.

‡ Kobe Center for Quality Control and Consumer Service.

MATERIALS AND METHODS

Materials. Pesticide standards, dichlorvos (DDVP), chlorpyrifos-methyl, malathion, and fenitrothion, were purchased from Wako Pure Chemical Industries (Osaka, Japan). Celite 545 was purchased from Wako Pure Chemical Industries. Other reagents were of analytical grade.

Unhulled rice was supplied from Mr. Hasegawa (Gifu Prefecture, Japan). Brown rice was purchased from the retail market in Osaka.

Pesticide emulsions for spray, DDVP (DDVP 50%, Takeda Pharmaceutica, Osaka, Tokyo), Reldan (chlorpyrifos-methyl 25%, Kumiai Chemical Industries, Tokyo, Japan), malathion (malathion 50%, Sankyo, Tokyo, Japan), and sumithion (fenitrothion 50%, Sankyo), were purchased from the Japan Agricultural Corp.

Ashless filter paper, no. 5A and no. 5C was purchased from Advantec Toyo (Tokyo, Japan).

Methods. *(1) Storage of Rice. Four Organophosphorus Pesticides.* A pesticide emulsion mixture was prepared which contained DDVP (0.1 μg), chlorpyrifos-methyl (6 μg), malathion (8 μg), and fenitrothion (15 μg) in 1 mL. This formulation was evenly sprayed over unhulled rice and brown rice (2 kg each) at the concentrations of (DDVP) 0.5 ppm, (chlorpyrifos-methyl) 6 ppm, (malathion) 8 ppm, and (fenitrothion) 15 ppm. The rice was then air-dried and stored at 15 °C in a refrigerator.

Unhulled rice or brown rice (80 g) was taken at the adequate intervals until 91 days (unhulled rice) or 85 days (brown rice) after pesticide application.

(2) Storage of Rice. Methyl Bromide Fumigation. Unhulled rice and brown rice (2 kg each) were fumigated with methyl bromide at 17 g/m^3 for 48 h. The rice was then stored at 15 °C in refrigerator.

Unhulled rice or brown rice (80 g) was taken at adequate intervals until 84 days after methyl bromide fumugation.

(3) Cooking Process. Boiled Rice. Brown rice of day 0 after spraying organophosphorus pesticides and that of day 12 after methyl bromide fumigation were used.

Process 1. Each grain of brown rice (200 g) was polished. *Process 2.* The obtained polished rice (150 g) was washed with 300 mL of water by shaking 3 times for 5 min. *Process 3.* The

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Table I. Recoveries of the Four Organophosphorus Pesticides and Bromide in Unprocessed and Processed Rice[a]

sample	fortified level[b] (ppm)	recoveries (%)				
		DDVP	chlorpyrifos-methyl	malathion	fenitrothion	bromide
chaff	C	98.3	96.3	93.4	97.3	86.7
rice bran	B	83.4	101.0	89.4	88.9	90.0
polished rice	A	73.7	92.6	101.0	103.2	70.0
drainage after washing	A	98.1	92.6	99.1	105.3	90.0
rice powder	A	98.5	95.7	102.1	98.8	90.0
raw rice noodle	A	80.5	90.9	97.9	95.8	80.0
rice noodle	A	89.0	95.2	99.0	104.0	80.0

[a] Data are the averages of three trials. [b] Fortified levels are as follows: A, 0.2 ppm for DDVP, chlorpyrifos-methyl, malathion, and fenitrothion, 5.0 ppm for bromide; B, 1.0 ppm for DDVP, chlorpyrifos-methyl, malathion, and fenitrothion, 5.0 ppm for bromide; C, 1.0 ppm for DDVP, chlorpyrifos-methyl, malathion, and fenitrothion, 10 ppm for bromide.

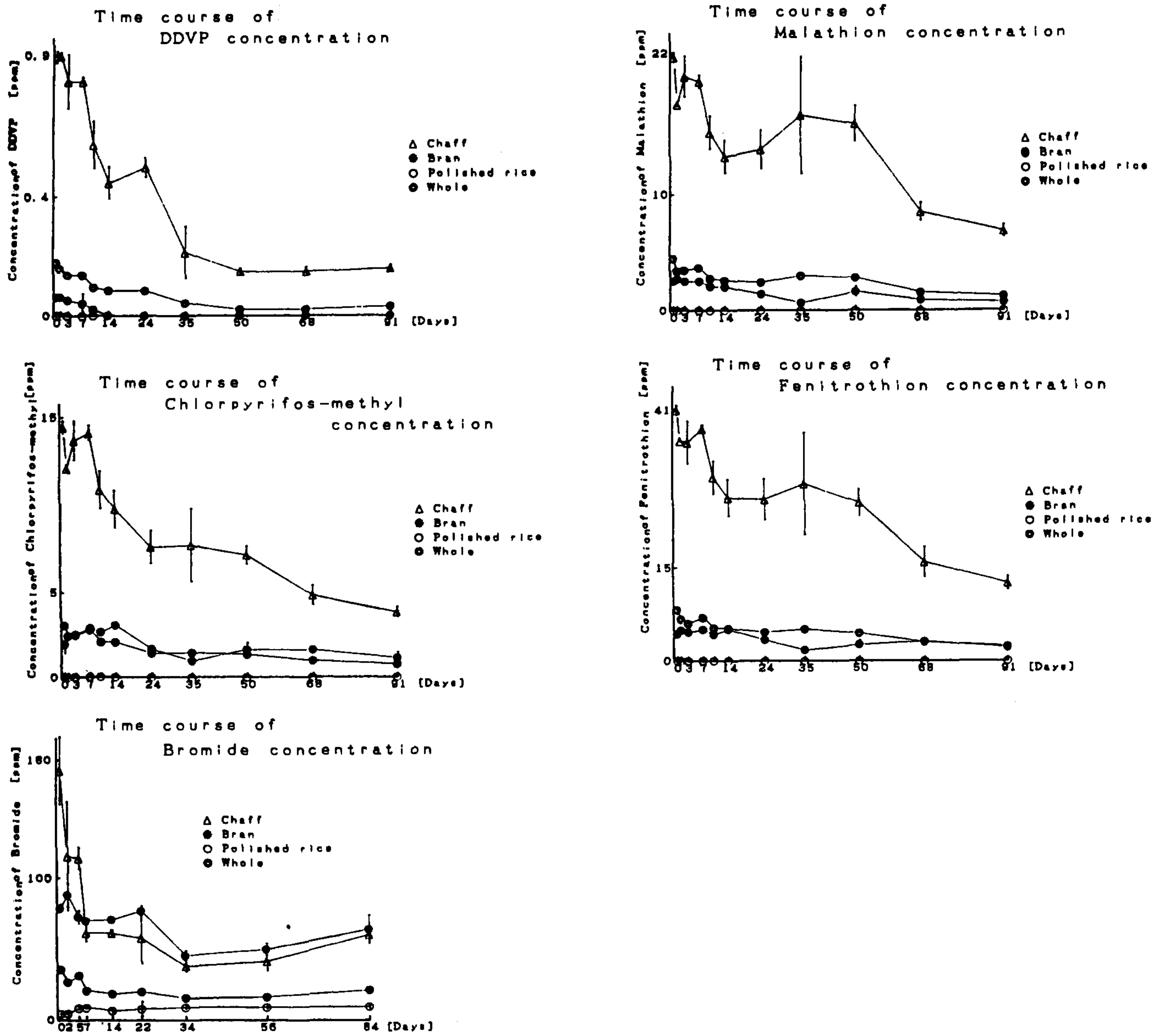

Figure 1. Time courses of the concentrations of the four organophosphorus pesticides and bromide in unhulled rice: (Δ) chaff, (●) bran, (O) polished rice, and (◎) whole.

washed rice (180 g) was air-dried for 1 h. *Process 4.* The dried rice (150 g) was boiled with the appropriate amount of water, yielding the boiled rice (329 g).

(4) *Cooking Process. Rice Noodle.* Brown rice of day 0 after spraying organophosphorus pesticides and that of day 12 after methyl bromide fumigation were used.

Process 1. Each grain of brown rice (200 g) was polished. *Process 2.* The obtained polished rice (150 g) was washed with 300 mL of water 3 times by shaking 5 min each. *Process 3.* The washed rice (180 g) was air-dried for 1 h, and finely milled using a pestle. *Process 4.* The milled rice powder (100 g) was kneaded with 60 mL of water and steamed for 15 min. After cooling, the raw noodle (149 g) was obtained by extrusion molding using a syringe (22G × 1$^1/_4$ in., Termo, Japan). *Process 5.* The raw noodle (149 g) was steamed for 20 min. *Process 6.* The steamed noodle (159 g) was stirred in 300 mL water for 5 min. *Process 7.* Washed noodle was dried for 24 h in an oven (60 °C), yielding rice noodle (65 g).

(5) *Analysis of Four Organophosphorus Pesticides and Bromide.* Unhulled rice was hulled by scrubbing with chopping

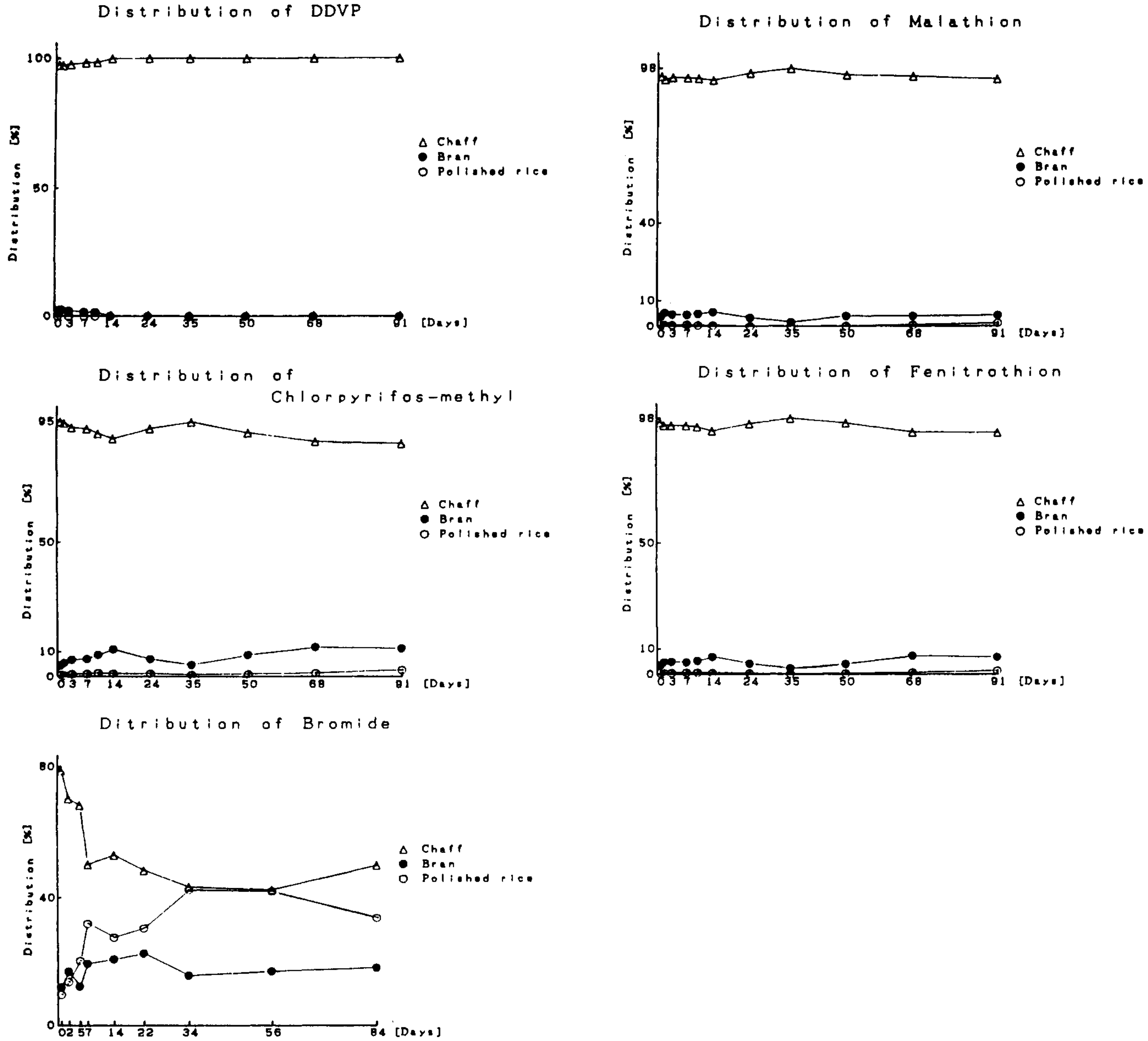

Figure 2. Time courses of the distributions of the four organophosphorus pesticides and bromide in unhulled rice: (Δ) chaff, (●) bran, and (O) polished rice.

boards, yielding brown rice and chaff. Brown rice was polished by a polishing machine KG-15 (Matsushita Electronics, Osaka, Japan), yielding bran and polished rice.

All experiments were performed in triplicate.

Organophosphorus pesticides were analyzed by the coagulation method (Sasaki et al., 1987) followed by extraction with ethyl acetate and FPD-GC determination (Tonogai et al., 1990).

Conditions of FPD-GC were as follows: apparatus, GC 14A (Shimadzu Inc., Kyoto, Japan); column, DB-210 0.25 mm i.d. × 30 m, film thickness 0.25 μm (J&W, Folsom, CA); column temperature, 60 °C (2 min) → (10 °C/min) → 235 °C; inlet and detector temperature, 240 °C; carrier gas, He 1.0 mL/min; make-up gas, N_2; detector, FPD (P mode); injection method, splitless; injection volume, 2 μL.

Bromide was analyzed by the dry ashing procedure under alkaline conditions followed by filtration, derivatization with 3-pentanone, and ECD-GC determination (Mitsuhashi et al., 1987).

The conditions of ECD-GC were as follows: apparatus, G-2800 (Yanaco Inc., Kyoto, Japan); column, CBP1 0.2 mm i.d. × 25 m, film thickness 0.25 μm; column temperature, 80 °C; inlet temperature, 170 °C; detector temperature, 250 °C; carrier gas, N_2 1.0 mL/min; make-up gas, N_2; detector, ECD (^{63}Ni, 10 mCi); injection method, split (split ratio 1:10); injection volume, 2 μL.

(6) *Recovery Test.* Recoveries of the four organophosphorus pesticides and bromide in chaff, bran, polished rice, and the products at each cooking process were tested at the fortification level of 0.2–1.0 ppm for organophosphorus pesticides and 5–10 ppm for bromide.

RESULTS AND DISCUSSION

(1) Recovery Test. Recoveries of the four organophosphorus pesticides and bromide in each part of rice and each cooking process are shown in Table I.

No organophosphorus pesticide was detected from the unhulled or brown rice tested here before pesticide application. The concentrations of bromide in rice before methyl bromide fumigation were 1.04 ± 0.07 ppm (polished rice), 5.08 ± 0.58 ppm (bran), and 12.7 ± 1.2 ppm (chaff) (means ± SD for three trials). The recovery of bromide was calculated by subtraction of the bromide background level in each part of unhulled or brown rice and at each cooking process.

Recovery was 73.7–99.5% for DDVP, 90.9–101.0% for chlorpyrifos-methyl, 89.4–102.1% for malathion, 88.9–105.3% for fenitrothion, and 70.0–90.0% for bromide.

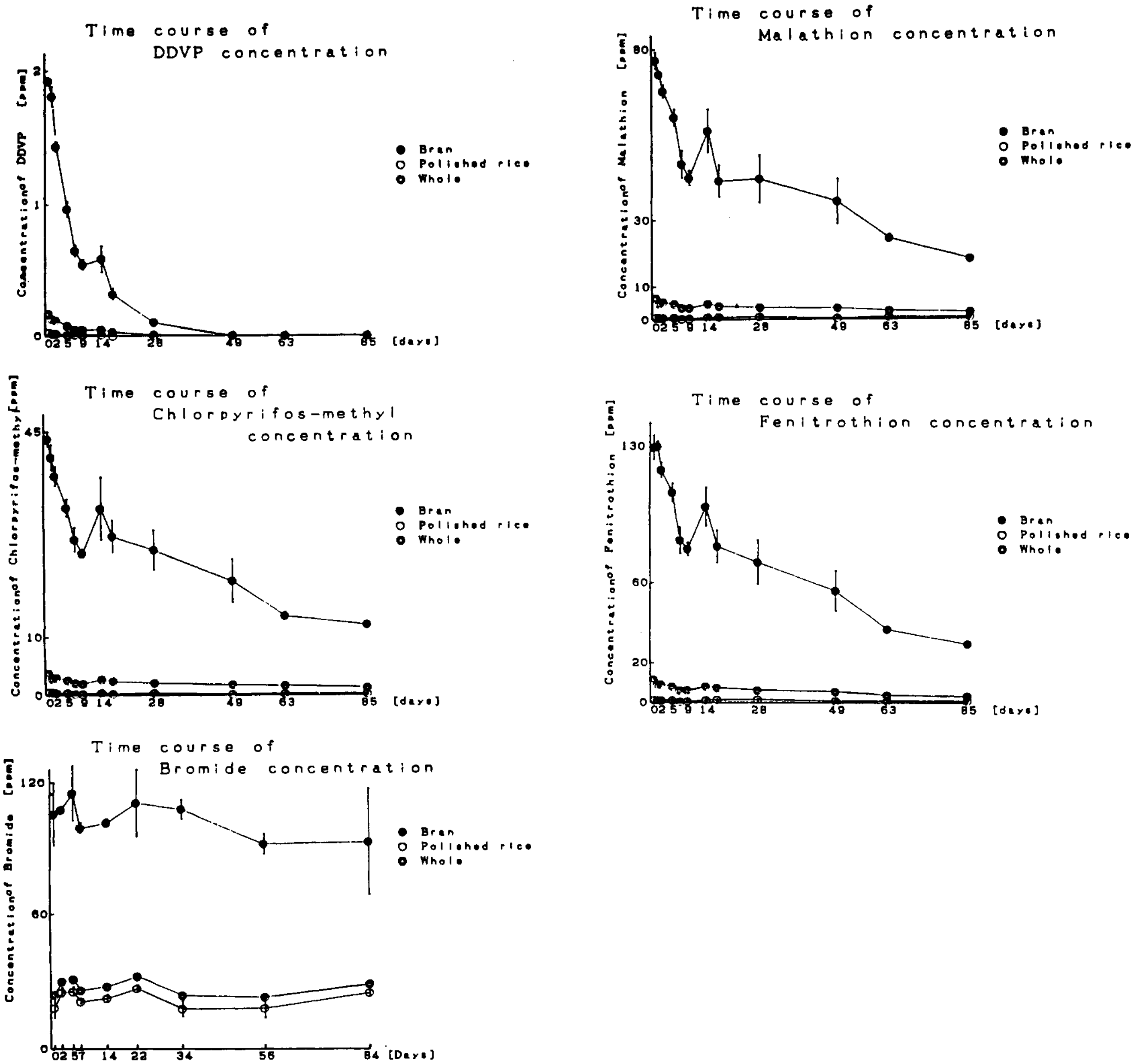

Figure 3. Time courses of the concentrations of the four organophosphorus pesticides and bromide in brown rice: (●) bran, (○) polished rice, and (◎) whole.

It is obvious that the analytical methods described above are applicable for the determinations of the organophosphorus pesticides tested here and bromide.

(2) Time Courses of the Four Organophosphorus Pesticides and Bromide during Storage. The time courses of the concentrations and distribution of four organophosphorus pesticides and bromide in each part of the unhulled and brown rice are shown in Figures 1–4.

The initial concentrations (day 0) of the pesticides and bromide were as follows: (unhulled rice), DDVP, 0.167 ppm; chlorpyrifos-methyl, 3.01 ppm; malathion, 4.48 ppm; fenitrothion, 8.42 ppm; and bromide, 35.3 ppm; and (brown rice) DDVP, 0.171 ppm; chlorpyrifos-methyl, 3.86 ppm; malathion, 6.47 ppm; and bromide, 24.3 ppm.

The concentrations of organophosphorus pesticides and bromide in each part of unhulled and brown rice decreased as a function of time (Figures 1 and 3). The remains of organophosphorus pesticides and bromide at the end of the experimental periods were as follows: (unhulled rice) DDVP, 15.6% (92 days); chlorpyrifos-methyl, 25.3% (92 days); malathion, 27.9% (92 days); fenitrothion, 28.6% (92 days); and bromide, 59.0% (84 days); and (brown rice) DDVP, 0% (49 days); chlorpyrifos-methyl, 35.4% (85 days); malathion, 31.5% (85 days); fenitrothion, 28.4% (85 days); and bromide, 120% (84 days).

The decrease of DDVP was the fastest, and no DDVP was detected in brown rice at 45 days after DDVP application. All of the organophosphorus pesticides were located in the outer side, chaff in unhulled rice and bran in brown rice during the storage periods (Figures 2 and 4). No permeation of the four organophosphorus pesticides inside was observed.

The bromide concentration of the chaff in unhulled rice decreased until 56 days after methyl bromide fumigation and increased gradually thereafter (Figures 1 and 3). The bromide concentrations of the bran in unhulled rice, bran, and polished rice in brown rice did not change significantly during the experimental periods (Figures 1 and 3). Contrarily, the bromide concentration of polished rice in unhulled rice tended to increase (Figure 1). The distribution of bromide in each part was chaff > polished rice > bran in unhulled rice and polished rice > bran in brown

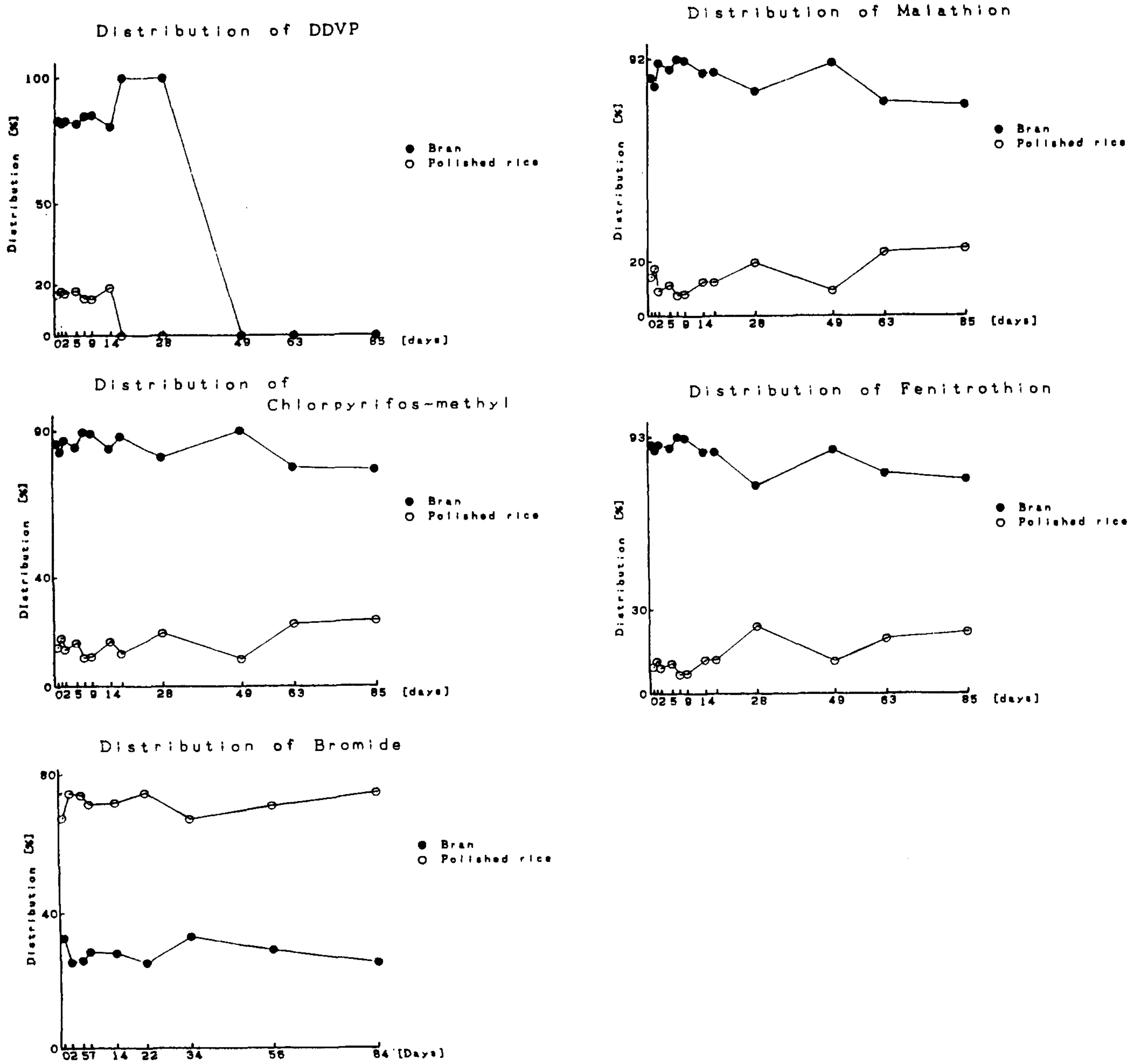

Figure 4. Time courses of the distributions of the four organophosphorus pesticides and bromide in brown rice: (●) bran and (○) polished rice.

rice, as a whole (Figures 2 and 4). Consequently, it was suggested that bromide did permeate inside early after methyl bromide fumigation and might combine with a component of polished rice, such as the carbohydrates.

(3) Time Courses for the Four Organophosphorus Pesticides and Bromide during the Cooking Process. (*1*) *Boiled Rice.* The concentrations of the four organophosphorus pesticides and bromide at each cooking step are shown in Figure 5.

The steps are as follows: *step 1,* polished rice (initial, 100%); *step 2,* drainage after washing the polished rice; *step 3,* washed rice; and *step 4,* boiled rice.

The percentage of organophosphorus pesticides removed by washing with water was 61.8–99.0%. DDVP was removed completely by washing. The remains were almost completely removed by steaming; only 3.7% of chlorpyrifos-methyl and 5.6% of fenitrothion was recovered.

The percentage of bromide removed by washing with water was 49.0%, but 41.2% of bromide still remained

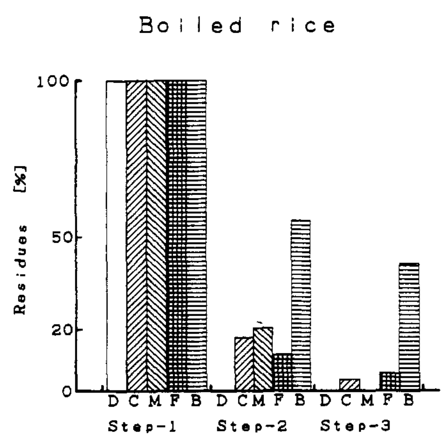

Figure 5. Residues of the four organophosphorus pesticides and bromide in processing (1) boiled rice. Initial concentrations (polished rice) are defined as 100%. Abbreviations: D, DDVP; C, chlorpyrifos-methyl; M, malathion; F, fenitrothion; and B, bromide. The steps are as follows: step 1, polished rice; step 2, washed rice; and step 3, boiled rice.

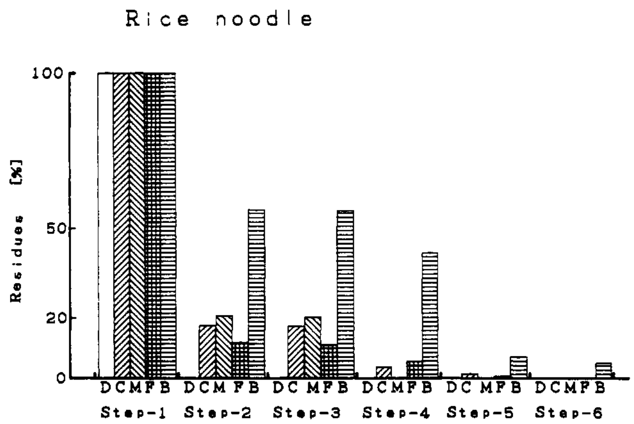

Figure 6. Residues of the four organophosphorus pesticides and bromide in processing (2) rice noodle. Initial concentrations (polished rice) are defined as 100%. Abbreviations: D, DDVP; C, chlorpyrifos-methyl; M, malathion; F, fenitrothion; and B, bromide. The steps are as follows: step 1, polished rice; step 2, washed rice; step 3 rice powder; step 4, raw noodle; step 5, steamed noodle; and step 6, rice noodle.

in the boiled rice. It was suggested that a considerable amount of bromide was combined with a component of polished rice, such as the carbohydrates.

(2) *Rice Noodle.* The concentrations of the four organophosphorus pesticides and bromide at each step are shown in Figure 6.

The steps are as follows: *step 1*, polished rice (initial, 100%); *step 2*, drainage after washing the polished rice; *step 3*, rice powder after washing; *step 4*, raw noodle; *step 5*, steamed noodle; *step 6*, drainage after washing the steamed noodle; and *step 7*, rice noodle.

The percentage of organophosphorous pesticides removed by washing with water was 61.8–99.0%. DDVP was removed completely by washing. The remains were completely removed by steaming twice. The percentage of bromide removed by washing with water was 49.0%, and only 7.2% of bromide remained after steaming twice. The percentage of bromide remained in rice noodle was 5.1% compared to 41.2% that remained in boiled rice. There are two steaming steps in producing rice noodle, so it was suggested that the removal of bromide was more significant in rice noodle than boiled rice.

It was concluded that it is not easy to remove the combined bromide completely, but a large amount of the combined bromide could be removed by the combination of washing with water and steaming.

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