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Toxicity of Chlorpyrifos, Fenubucarb, Monocrotophos, and Methyl Parathion to Fish and Frogs After a Simulated Overflow of Paddy Water

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Concern for pesticide contamination of the environment especially the food chain has initiated a lot of researches to assess the extent of this problem. One potential area of contamination is the lake ecosystem and a possible source of pesticide pollution may come from the contaminated rice paddy water drained into irrigation canals. This activity was undertaken to determine the toxicity of pesticides to fish and frogs at various distances from the point of application to the irrigation canals. Data generated may be used to assess the potential of these compounds to contaminate adjacent bodies of water and the food chain as well as provide basis for recommendation for proper water and pesticide management in lowland irrigated rice production.

MATERIALS AND METHODS

A supervised field experiment was conducted in Bo. Bangyas, Calauan, Laguna, Philippines on April 1992. Three formulated insecticides namely methyl parathion (Folidol M501, monocrotophos (Azodrin 202R) and a combination product of fenubucarb and chlorpyrifos (Brodan 31.5 EC) were applied separately in paddy fields of 250 m^2 each at the manufacturers recommended rate, 15 days after transplanting. Paddy water was allowed to overflow to simulate flooding of the paddy after a heavy rainfall 2 hours after application.

Water samples were simultaneously collected at 10, 25. 50 and 100 m distances as soon as the waterhead in the drainage canals reached the 100 m distance away from the paddy. Sampling was repeated at 1, 2. 6. 24 and 48 hours after application. These samples were kept frozen if not analyzed immediately.

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At the same time, fish *(O.mossambicus)* and frogs *(B.marinus)* in screened cages were placed in the drainage canals at designated distances. Mortality of the organisms were noted at 0 (10 min), 1, 2, 6, 24 and 48 hours after overflow after 24 hours exposure.

Insecticide treatment was repeated at 45 days after transplanting and another batch of fish and frogs were exposed to the drained water. Mortality counts were made at the same time intervals after overflow.

Chlorpyrifos, fenubucarb and methyl parathion residues were extracted from water samples (1L) by partitioning twice with 100 ml of 15% dichloromethane in hexanes and once with 100 ml of hexanes. Pooled organic layers were filtered over sodium sulfate and concentrated to approximately 10 ml under reduced pressure. About 10 ml of hexanes was added and the sample was reconcentrated to 5 ml. This step was repeated and finally the sample extract volume was reduced to 2ml under a stream of nitrogen.

Chlorpyrifos, fenubucarb and methyl parathion residues were analyzed using a Hewlett Packard 5840 gas chromatograph equipped with a nitrogen-phosphorus flame ionization detector (NP-FID), glass column (3 ft, 2 mm i.d.) packed with 2% OV-101 on 80./100 mesh Chromosorb W-HP, temperatures (°C): oven, 165; detector, 300; injection port. 250; and gas flows (ml/min of 50, 3 and 30 for air, hydrogen and nitrogen, respectively.

RESULTS AND DISCUSSION

Continuous exposure of fish, *o.* mossambicus, to the flowing drained paddy water containing methyl parathion and monocrotophos, applied separately at 15 or 45 days after transplanting did not result in fish mortality at any distance from the point of application.

The combination of chlorpyrifos and fenubucarb applied 15 days after transplanting resulted in residues in run-off waters that caused 100% fish mortality after 6 hours exposure at 10 m from the point of application. The resulting concentration of insecticide residues ranged from 1.6 x $l0^{-3}$ to 3 x 10^{-4} mg/L chlorpyrifos and 0.065 to 0.01 mg/L fenubucarb residues (Figs. 1 & 2).

However, spraying of rice at 45 days after transplanting, did not result in any fish mortality. This is indicative of the effect of increased plant canopy. It reduces substantial amounts of the spray solution reaching the paddy water, thereby reducing adverse effects on fish.

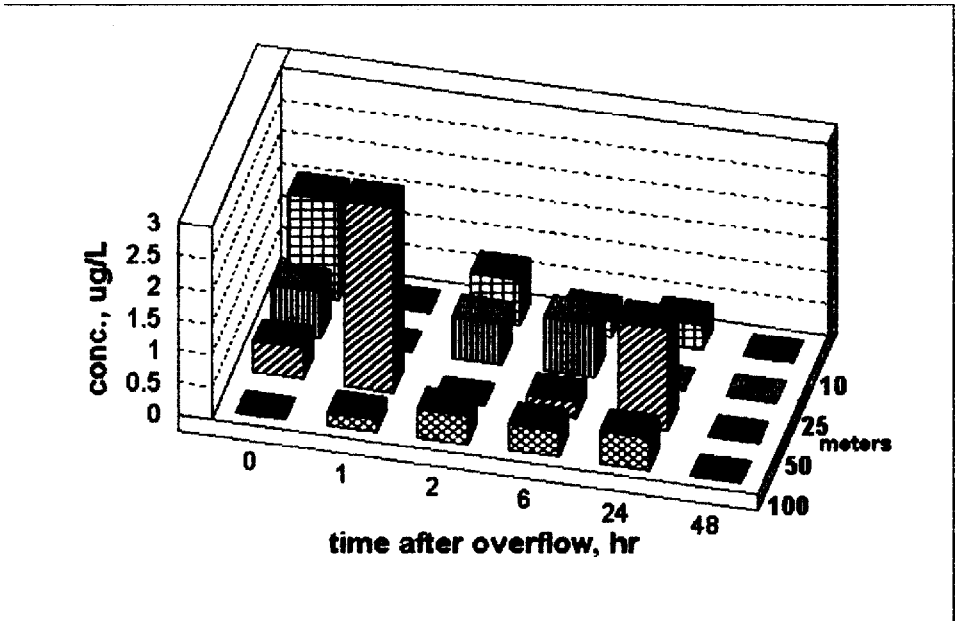

Figure 1. Chlorpyrifos residues in run-off waters where overflow was 2 hours after application at 15 days after transplanting.

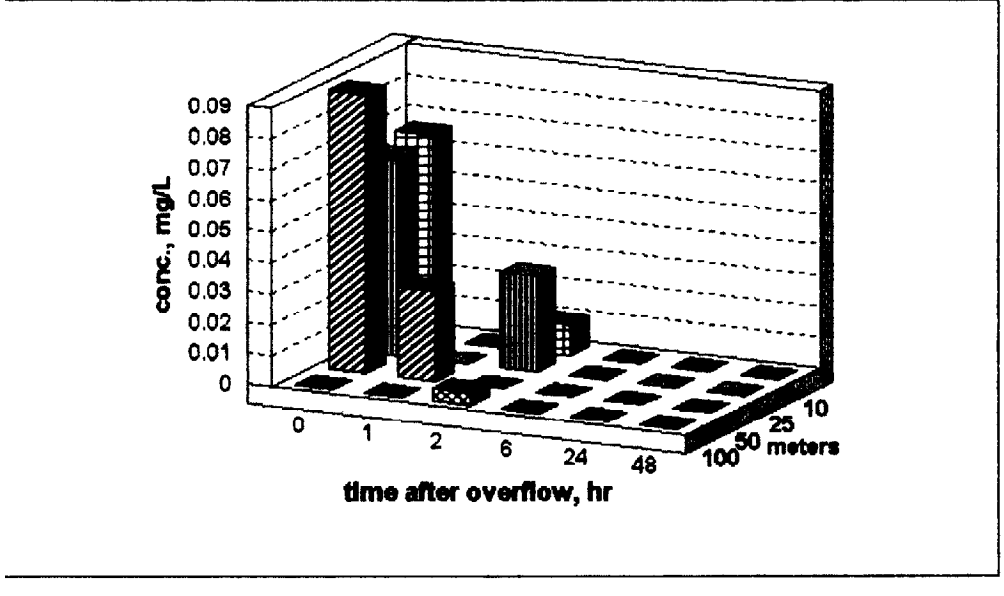

Figure 2. BPMC or fenubucarb residues in run-off waters where overflow was 2 hours after application at 15 days after transplanting.

These results are in close agreement with fish toxicity data generated for chlorpyrifos and a chlorpyrifos: cypermethrin mixture formulation. Fish mortality was substantially reduced when spraying was done at a latter plant stage where the rice plant canopy was extensive (Dupe and Calumpang, 1995).

It is very important that this perspective be maintained as fish toxicity data from the laboratory may be extrapolated to field conditions without taking into consideration the major role that plant canopy plays in the rice paddy ecosystem. The recommended rates of insecticides registered for rice is not the only consideration for extrapolating the impact of insecticides on ricefield vertebrates such as fish. Such an assumption would lead to unrealistic estimates (Cagauan, 1995).

The effect of insecticides on large aquatic organisms varies with the test organism. Frogs were found to be more sensitive than tilapia *(o. mossambicus)* and may serve as a biological indicator for pesticide contamination in waterways.

At 15 DAT, 100% mortality was obtained--for frogs exposed to a combination of EPMC and chlorpyrifos at 25 m and 90% to monocrotophos at 25 m distance from the paddy field immediately and 1 hour after application, respectively. Whereas in the methyl parathion-treated field only 63% mortality in frogs was observed at one hour after overflow of water for the same distance.

More comparative studies for currently recommended pesticides in rice production need to be conducted to assess this initial data.

Recoveries of 87, 89 and 92% were attained for chlorpyrifos, fenubucarb and methyl parathion residues in water, respectively.

Application of chlorpyrifos in the paddy at the rate of 0.32 kg a.i./ha resulted in a maximum concentration of 1.6×10^{-3} mg/L detected at 10 m immediately after overflow. Chlorpyrifos residues were detected in drained paddy water up to 24 hr after treatment

Fenubucarb residues in paddy water were found to be ranging from 0.06 to 0.08 mg/L at 10 to 50 m while residues were below the detection limit at 100 m, immediately after overflow. A sharp drop in residues was observed in samples taken 1 and 2 hr after overflow. A maximum of 0.02 mg/L was detected at 25 m from the paddy. Subsequent samples collected at 6, 24 and 48 hr did not contain residue levels above the detection limit of the

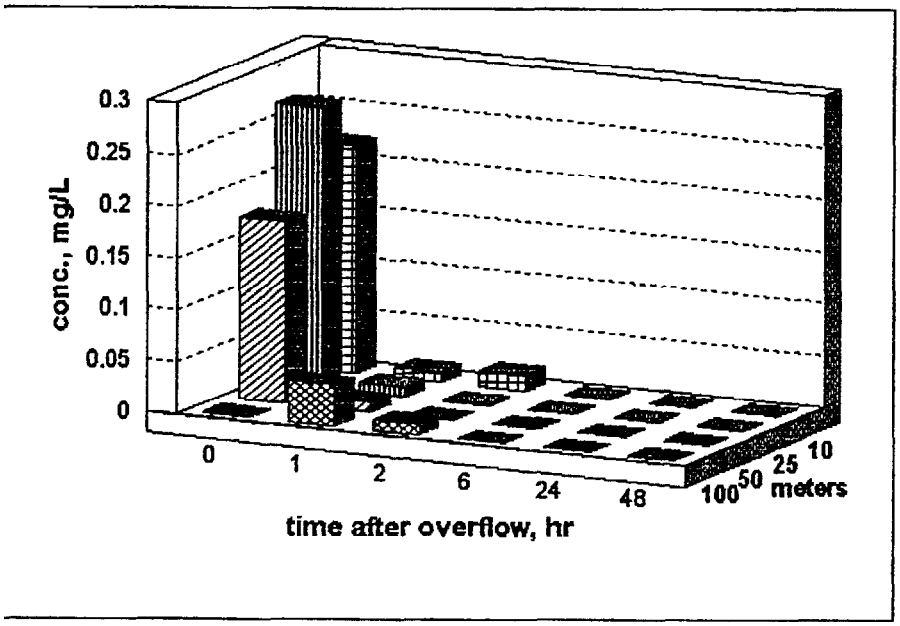

Figure 3. Methyl parathion residues in run-off waters where overflow was 2 hours after application at 15 days after transplanting.

method employed.

Levels of methyl parathion at different distances from the point source and at different time intervals after application and overflow are shown in Fig. 3. Residues detected were found to be 0.2, 0.28, 0.18 mg/L at 10, 25 and 50 m which decreased to 2.3 x 10^{-3} mg/L at 100 m, immediately after overflow.

A general decrease in residue levels with increasing distance was observed immediately after overflow. The decrease in insecticide residues could be due to the adsorption of the residues into the soil matrix and/or organic matter as water flows through the drainage canal. Likewise, a decrease in residues was observed with time at the studied distances. Degradation of the compound, volatilization as well as its continuous adsorption into the soil or suspended particles are possible factors for the observed decrease with time.

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