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Toxicities of Paraquat and Diquat Herbicides to Freshwater Copepods (*Diaptomus* sp. and *Eucyclops* sp.)

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Diquat and paraquat are potent inhibitors of photosynthesis in plants. Both compounds are highly water soluble and are absorbed by weeds (WAY et al. 1971). Levels of these herbicides rapidly decline within 4 to 14 days of treatment (EARNEST 1971). This may occur due to uptake by weeds and adsorption to suspended soil particles or bottom mud (CALDERBANK 1970). Diquat is adsorbed to soil particles by an ion-exchange mechanism (KNIGHT & TOMLINSON 1967).

DAWOOD et al (1965) reported that paraquat was used in Egypt to control aquatic weeds in irrigation canals, drainage ditches and marshes where it caused high mortality of snails, Bulinus truncatus, Biomphalaria alexandria and Lymnaea calliaudi. In New Zealand, treatment of a small river at 2.0 ppm paraquat reduced amphipods to 5% of the pre-treatment level in 30 min exposure (BURNET 1972). There is little information on the toxic effects of these herbicides to freshwater copepods. However, the 48-h LC_{50} and EC_{50} values for cladocerans (Daphnia pulex and Simocephalus serrulatus) to paraquat have been reported earlier (FWPC 1968, SANDERS & COPE 1966). The importance of copepods in the food-chain of an aquatic ecosystem is quite unequivocal which prompted us to do this work.

MATERIALS AND METHODS

Zooplanktonic organisms were collected from a natural lake at Southern University campus by a #20 plankton net. They were acclimatized in 20-gal aquaria for 96 h prior to bioassays. Copepods were separated from other plankton by passing them through a plankton net and concentrating the sample in a 100-mL glass vial. This caused the copepods to aggregate in the upper-half of the vial from where one mL of the sample was pipeted out into 300-mL of test solution in 500-mL finger-bowls. This method excluded most of the non-copepod organisms and resulted in approximately similar number of copepods in each container.

Test solutions were prepared by serially diluting 1% aqueous stock solutions of paraquat and diquat to desired concentrations. Stock solutions were prepared freshly each time. Test and control solutions were aerated continuously. Diquat and paraquat test solutions were made in ranges of 0-14 and 0-100 ppm. Dissolved oxygen and temperature of solutions were measured by a self-stirring electrode type oxygen meter and the pH with a pH meter.

Copepod mortality was recorded after 24 and 48 h by counting dead individuals and subsequently killing alive ones to obtain accurate

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numbers. Animals failing to respond to a pointed glass probe were considered dead. Naupliar stages of copepods were not counted. Average mortality of 3 replications was recorded. The percent composition of cyclopoid and calanoid copepods was determined and they were identified to the genus level. LC_{50} values were calculated by probit analysis using the computer program of DAUM (1972).

RESULTS AND DISCUSSION

Water temperature of the control was 20-22°C, pH 6.5-7.0 and dissolved oxygen 5.2-6.2 ppm. The same parameters for test were 18-22 °C, 6.9-7.0 and 6.2-7.2, respectively. Calanoids (*Diaptomus* sp.) comprised 90% and cyclopoids (*Eucyclops* sp.) 10% of the total.

Percent mortalities of copepods during the 24 and 48-h exposure to diquat and paraquat are given in Table 1 and the LC_{50} values in Table 2. The 24-h exposure LC_{50} values for both herbicides are higher than 48-h. Paraquat was 7 times more toxic than diquat in 24-h exposure and 3.5 times in 48-h. CROSBY & TUCKER (1966) found that diquat was more toxic than paraquat to *Daphnia magna* and reported the IC_{50} values (median immobilization concentration) as 7 and 11 ppm, respectively. These values were however, an expression of toxicity rather than lethality due to these herbicides.

TABLE 1. Percent mortality of freshwater copepods (*Diaptomus* sp. and *Eucyclops* sp.) in various concentrations of diquat and paraquat herbicides exposed for 24 and 48 h.

CONC. (ppm)	24 h N	24 h % Mort	48 h N	48 h % Mort
		DIQUAT		
0	71	0	266	2
5			90	12
10	34	5	665	36
20	66	8	373	57
30	49	26	933	84
50	81	25	507	89
60			97	98
70	78	44		
90	210	55		
100	130	65		
120	145	86		
140	128	100		
		PARAQUAT		
0	354	3	287	5
1	227	19	174	9
3			88	16
5	105	27	129	38
10	153	39	128	42
15	32	44	32	69
20	171	62	82	88
30	38	87	38	100
60	45	91		
80	53	92		
100	66	100		

TABLE 2. Comparative LC_{50} ppm (probit analysis) of paraquat and diquat herbicides for freshwater copepods.

EXPOSURE TIME (h)	HERBICIDE	LC_{50}	LOWER & UPPER LIMIT
24	diquat	74	62 - 86
48	diquat	19	12 - 28
24	paraquat	10	7 - 17
48	paraquat	5.3	3.9 - 8.1

The LC_{50} (48-h) for *Daphnia pulex* to paraquat was reported to be 3.7 ppm (FWPC 1968) and the EC_{50} for *Simocephalus serrulatus* and *D. pulex* as 4.0 and 3.7 ppm, respectively (SANDERS & COPE 1966). The copepods we have tested seem to be slightly more tolerant than the cladocerans. However, such variation in tolerance to different herbicides has also been exhibited by other crustaceans (SANDERS 1970). SANDERS noticed that even different formulations of the same herbicide differed in their toxicities.

The rate of disappearance of paraquat and diquat from water is rather variable and depends upon the movement of water, density of weeds, the presence of mud, suspended silt and sunlight (CALDERBANK & SLADE 1976). It would be improper to make generalizations concerning the adverse effects of these herbicides to copepods. Nevertheless, it should be cautioned that excessive use or inadvertent release of diquat and specially paraquat may cause drastic copepod mortalities in an aquatic ecosystem.

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