Aquatic Macroinvertebrate Response to Field Application of the Combined Herbicides Diquat and Endothall[a]

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Diquat (6,7-dihydrodipyrido(1,2-a:2,1'-c)pyrazinediium dibromide) and endothall (7-oxybicyclo(2,2,1)heptane-2,3-dicarboxylic acid) are widely used to control various species of aquatic weeds. Little attention has been given however, to responses of invertebrate populations to the chemicals. No work has been done concerning the toxicity of a diquat-endothall mixture to invertebrate fish-food organisms. The objective of this study was to evaluate the response of the macroinvertebrate population to the treatment of Chickahominy Reservoir, in Virginia, with a mixture of the herbicides to control egeria (Egeria densa Planchon).

Methods

In July 1973, the 1100-ha, shallow, freshwater impoundment was treated with a surface spray of a 1:1 mixture of diquat and endothall at a rate calculated to yield 0.11 ppm active ingredient diquat and 0.17 ppm active ingredient endothall at a depth of 144 cm (BERRY et al. 1975). Two areas of the reservoir were chosen for ecological monitoring and represent deep (2.5 m) and shallow (1 m) habitats, respectively.

Herbicide levels in the water were determined in samples collected 4, 12, 20, 28, and 40 hours after treatment and on a daily basis thereafter for one month at each study area. Decline rates for diquat was determined by a spectrophotometric assay of triplicate samples and concentrations of endothall were determined in duplicate samples via a gas-liquid chromatographic technique (VAN HORN et al. 1974, VAN HORN 1975).

Macroinvertebrates were collected by allowing colonization of floating artificial substrates consisting of a wood float (15.7 cm x 15.7 cm x 4 cm) from which three strips (2.54 cm x 2.54 cm x 30.5 cm) of 3M Corporation's conservation webbing hung down into the water. This material has been used for inver-

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tebrate sampling (SIMMONS and WINFIELD 1971, PRINS and BLACK 1971, DICKSON and CAIRNS 1972, DANIEL 1972) and resembles the intertwined mats of egeria leaves and stems as invertebrate habitat. Samplers were placed in the areas of dense vegetation 3 months before treatment. In the shallow quadrant, 4 samplers were removed 2 days before treatment and 2 removed on the third and ninth day after treatment. In the deep quadrant, 3 samplers were removed 2 days before treatment, 2 removed on the third, 3 on the ninth, and 2 on the 21st day after treatment. Samplers were collected by rapidly lifting each unit from the water into a standard 30 mesh sieve. The conservation webbing and all organisms trapped in the sieve were fixed in formalin. An Eckman dredge was used to collect samples of egeria near the surface in close proximity to the substrates 2 days before treatment to verify that the invertebrate population on the samplers and on the egeria were similar. The dredge contents were emptied into the sieve and transferred to fixation jars.

Animals were washed from the webbing and plant stems with a mild jet of water; the webbing and plant material was examined with an illuminated magnifier and clinging or encased organisms were collected.

Results and Discussion

Chemical analysis showed that diquat reached a maximum concentration of 0.03 ppm in the deep and 0.73 ppm in the shallow area by 12 hours after treatment. Endothall reached a maximum concentration of 0.08 ppm in the deep area by 24 hours and 3.25 ppm in the shallow area by 4 hours after treatment. Results indicate the occurrence of "hot spots" or areas of uneven chemical distribution. COATS et al. (1964) similarly reported that regions of high herbicide concentrations may appear after treatment. Both herbicides had essentially dissipated 3 days after treatment with only very low levels (less than 0.02 ppm) remaining until the 16th day (VAN HORN et al. 1974).

Chlorosis was apparent in the egeria leaves 2 days after treatment and the plants no longer appeared at the water surface 5 days after treatment. Most of the plants had disappeared from the water column after 14 days, although healthy looking plants could be found on the bottom. Dredging revealed only occasional brown stems and much plant detritus after 22 days (BERRY et al. 1975).

Invertebrate identification revealed 16 taxa inhabiting plant material and 14 taxa inhabiting the artificial substrates (Table 1). Taxa representing major fish food invertebrate species were found in both plant and substrate samples indicating the substrates'usefulness for general monitoring purposes.

TABLE 1
Total Number of Macroinvertebrates from Seven Floating Artificial Substrates and Seven Egeria Samples Collected Before Treatment from Both Shallow and Deep Quadrants. Percent Composition of Each Species of the Population Is Also Given.

Taxon	Plant		Substrate	
	Number	Percent Composition	Number	Percent Composition
Oligochaeta	576	24.4	620	13.3
Hirudinea	24	1.0	85	1.8
Acarina	3	0.1	1	0.0
Amphipoda	97	4.1	179	3.8
Conchostrica	192	8.1	100	2.1
Isopoda	1	0.0	7	0.2
Decapoda	5	0.2	0	0.0
Coleoptera	13	0.6	28	0.6
Diptera	660	27.9	593	12.7
Ephemeroptera	36	1.5	153	3.3
Hemiptera	26	1.1	108	2.3
Lepidoptera	2	0.1	3	0.1
Odonata	48	2.0	88	1.9
Trichoptera	1	0.0	0	0.0
Gastropoda	274	11.6	2667	57.3
Turbellaria	400	16.9	23	0.5
Total Taxa	16		14	
Total Individuals	2358		4655	

Total number of organisms per plant sample was approximately half the total number per substrate sample. This difference is attributed to the greater surface area of the substrate. It was determined that the distribution of taxa in the invertebrate population colonizing the artificial substrate was significantly different (Chi-square test of independence, 2 x 11 Table, a = .05) from that colonizing the plants. Planaria, diptera larvae, clam shrimp, and Oligochaetes were more abundant on the plant samples while molluscs were more numerous on the artificial substrate.

The susceptability of fish food organisms to diquat or endothall alone has been studied to some extent. Diquat concentrations ranging from 0.4 ppm to 3.0 ppm have been found to have no effect on fish food organisms excluding crustacea (MULLISON 1970). Endothall concentrations ranging from 5 to 10 ppm had no toxic effect on pond invertebrates (WALKER 1963). The susceptability of crustaceans to herbicides has been investigated in more detail in laboratory bioassays. The amphipod *Hyallella azeteca* was very susceptable to diquat, with a 96 hr Tl_m of 0.048 ppm (WILSON and BOND 1969). The median immobilization concentration (IC_{50}) for *Daphnia magna* was 7.1 ppm diquat and 46 ppm endothall (CROSBY and TUCKER 1966).

Diversity and taxa found in samples from each study area were equivalent but there were consistently fewer individuals collected per sampler from the shallow than from the deep quadrants. This was perhaps a function of habitat suitability; STRANGE and SCHRECK (unpublished data) found oxygen regimes in the deep quadrant more favorable to habitation than those of the shallower areas. We found that the average number of individuals per substrate were still similar to pretreatment levels following application in both habitats (2-way ANOVA, unequal subclass numbers, a=0.05. Also, the number of taxa remained relatively constant (Table 2). Diquat and endothall concentrations in the deep water never reached toxic concentrations even for amphipods. In the shallow study quadrant, the diquat concentrations exceeded the lethal level for amphipods in "hot spots" but was far below harmful levels for other organisms; endothall was not found in harmful dosages. The herbicide residues observed may have been slightly higher than those actually encountered by the organisms inhabiting the artificial substrates because of variable dispersion patterns of the herbicides. However, egeria in the vicinity of all samplers had died-off by 21 days post-treatment.

TABLE 2

Average Number of Organisms Per Artificial Substrate Collected Before and After Treatment in Both Study Areas.

Taxon	Average Number of Individuals per Sampler							
	Shallow Water Quad.				Deep Water Quad.			
	Days	-2[c]	3[a]	9[b]	-2[a]	3[b]	9[a]	21[b]
Acarina		0.3	1.0	0.5	0.0	1.5	0.0	1.7
Amphipoda		6.3	1.5	9.0	51.3	71.0	39.	56.7
Coleoptera		4.0	5.0	5.0	3.3	22.0	5.0	14.0
Conchostrica		0.8	42.5	39.5	32.3	162.0	147.5	78.7
Diptera		89.0	63.5	337.5	78.7	188.0	216.0	188.3
Ephemeroptera		18.5	3.0	6.5	26.3	52.5	23.0	18.7
Gastropoda		16.5	464.5	301.5	866.1	1065.0	980.0	484.7
Hemiptera		27.0	0.5	0.5	0.0	0.5	0.0	1.0
Hirudinea		4.0	3.0	22.5	23.0	36.0	47.5	12.7
Isopoda		0.0	1.0	4.0	2.0	56.0	12.5	20.0
Lepidoptera		0.3	0.0	0.0	0.7	0.0	0.0	0.0
Odonata		14.3	4.5	6.0	10.3	24.5	21.0	13.3
Oligochaeta		116.0	52.0	133.0	51.3	14.5	32.5	156.7
Turbellaria		1.0	0.0	0.5	5.7	62.5	4.0	9.5
Total Taxa		13	12	13	13	15	11	13
Total Individuals		298	642	866	1151	1756	1528	1056

a/ Average of Triplicate Samples
b/ Average of Replicate Samples
c/ Average of Quadruplicate Samples

In conclusion, the application of diquat and endothall mixture to Chickahominy Reservoir to control egeria did not directly harm invertebrate populations. The artificial substrate employed proved to be an economical and easily constructed means of monitoring macroinvertebrate responses *in situ*. The substrates provided "standard" unoccupied habitats for colonization and attracted fish food organisms normally associated with dense vegetation.

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