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Levels of the Herbicide Diquat† in Two Estuarine Molluscs and in the Water and Mud*

Abstract—Soft clams *Mya arenaria* and oysters *Crassostrea virginica* were exposed to 0.35 ppm of the herbicide Diquat during June and July 1967 in Nomini Creek, Virginia, a tributary of the Potomac. No detectable residue was found in oyster meats or in the water. Meats of soft clams, minus the rough integument surrounding the neck, showed no Diquat. The integument, however, contained from 0.00 to 0.05 ppm. Mud samples contained from 1.17 to 7.14 ppm. It was assumed that Diquat was strongly sorbed on clay particles in sediments; residues in clam integuments were due to trapped clay particles.

Introduction

During the past 20 years, herbicides have been used in increasing quantities to control vegetation in fresh-water ponds and lakes. More recently, they are being used for the same purpose in protected coastal marine areas where tidal currents, salinity changes and turbidity may dilute or modify the introduced chemical. Utilization in marine areas is complicated by the presence of edible fish or shellfish which may accumulate the herbicide beyond limits established by state and federal agencies. The possibility of accumulation and effects on growth or mortality has recently received much attention (1-3).

A recently introduced herbicide for terrestrial and aquatic use is Diquat (1,1′-ethylene-2,2′-bipyridylium dibromide), a quaternary ammonium compound. This compound satisfactorily controls aquatic weeds where suspended solids are low (4). Diquat, like other bipyridylium herbicides, is quickly sorbed from solution by clay minerals in soils. Consequently, shortly after introduction to an aqueous environment, it is found strongly sorbed on the surface of suspended clay particles or between lattices (5). The cation sorbed on the surface of the clay particles by ion exchange may become slowly available while that portion sorbed in the interlayer spacing of clays, such as montmorillonite, is more strongly bound (6).

The use of Diquat in marine areas where shellfish are grown made it desirable to evaluate its accumulation in animal tissue and in bottom deposits. Consequently, a field test was designed in which oysters (*Crassostrea virginica*) and soft clams (*Mya arenaria*) were exposed to Diquat.

Area of Test

The tests were conducted at Nomini Creek, a tributary of the Potomac River.[1] Two stations, approximately one mile apart in the upper portion of the creek, were selected on the basis of a past history of dense growth of Water Milfoil *(Myriophyllum spicatum)*. This rooted aquatic plant forms a dense growth in many shallow, protected bays in low-salinity regions of Chesapeake Bay. Water depth at each station was about 4 feet mean low water. At station number 1 the substrate was 88.7% silts and clay, with 11.3% sand; organic matter was 13.8% on a dry weight basis. At station number 2, 78.7% of sediment was in the silt-clay size range, with 21.3% sand; organic matter was 12.7%. Tidal currents in the two areas reached a maximum velocity of about 0.5 knot; salinity varied from about 4.0 to 10.0 parts per thousand (ppt) during the tests.

Methods

Preparation of stations—At each test area a one-acre plot was outlined with four stakes. Forty bushels of oyster shells were planted in a 10 ft² area in the center of each plot to provide a firm substrate for trays and boxes used in the tests.

During April, oysters, 3 to 4 inches long, obtained from the Potomac River, were placed in four wire trays measuring 45″ × 25″ × 8″ with approximately 100 oysters in each tray. Soft clams, 2 or 3 inches long, were obtained from the Potomac and placed in five sediment-filled boxes measuring 18″ × 18″ × 8″ with 18 to 20 clams in each box. Boxes and trays were stored at a dock in shallow water 1,000 feet from station 1. On 25 June, two oyster trays were placed on the shell bottom at station 1 and one was placed at station 2. A single tray was left at the dock. Four boxes containing soft clams were placed in the center of plot 1; one box remained at the dock. Water milfoil covered about 80% of plot 2; coverage on plot 1 was diffuse, but scattered concentrations existed over the entire area.

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† Registered trademark; provided by Chevron Chemical Co.

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Analysis for Diquat was made by the Chevron Chemical Company, Richmond, California. The samples were refluxed in 18 N sulfuric acid to free the Diquat from the sorbed or bound state. After filtration, the extracts were diluted to 1 N strength, then passed through a cation exchange resin which adsorbs Diquat but passes the sulfuric acid and the dissolved constituents of the soil. The Diquat was then eluted with saturated ammonium chloride solution and determined colorimetrically by the sodium dithionite reduction reaction (7). Limit of detection for water and mud is 0.01 ppm and for clams and oysters, 0.02 ppm.

Sampling—Sampling began on 27 June 1967 with the collection of the pre-treatment sample from animals stored at the dock. A single sample consisted of meats from 15 oysters and meats from the entire contents of the soft clam box. Water samples were collected in 1-liter plastic bottles.

Prior to and during the removal of meats from oysters, care was taken to prevent mud adhering to the shells from coming in contact with meats. Shells were scrubbed under flowing water, knives were frequently washed, and, after removal, meats were dipped into freshwater to remove bits of adhering shell or mud. Meats were sealed in plastic bags and iced immediately after opening. Similar techniques were used in obtaining soft clam meats. However, the rough integument surrounding the siphon and extending along the open side of the animal was removed and sealed in a separate bag. After collection, all meats were frozen and shipped to the Chevron Chemical Company for analysis.

On 28 June at 11:00 a.m. after the initial sampling, plot 1 was treated with Diquat at the rate of 2 gallons per acre (0.35 ppm) by representatives of the Chevron Chemical Company and by personnel of the Virginia Institute of Marine Science. Plot 2 received a similar quantity of Diquat on 29 June at 1:00 a.m. Water temperature at station number 2 during treatment was 73°F, salinity was 7.7 ppt, and suspended solids was 36 mg/liter. Temperature, salinity and turbidity at station number 1 were not measured.

Subsequent samples of animals and water for Diquat analysis were taken from both plots at intervals of 9 and 20 hours and at 3, 9, 18 and 36 days in the manner previously outlined. The 2-cm thick samples of substrate were taken at 9, 18 and 36 days. An additional series of ten mud samples was taken on 18 July 1968.

Results

There was no detectable residue of Diquat in water samples, oyster tissue or soft clam meats at any time during the study (Table I). However, low levels of Diquat were present in the integument from around the siphons of clams. Bottom muds contained from 1.17 to 7.14 ppm Diquat, with a mean of 3.96 ppm during the initial 36 days. Approximately one year after treatment, on 18 July 1968, levels in the mud were lower, with means of 4.07 and 1.19 ppm on plots 1 and 2, respectively.

By 4 August 1967, 36 days after treatment, about 70% of the milfoil had been killed on plot 2; on plot 1 the degree of kill was about 40%. During the test, no significant mortality of oysters or soft clams was noted in trays or boxes. The presence of a crystalline style in the digestive diverticula of all animals when opened indicated that both species had been feeding up to the time of collection.

Discussion

Published studies on persistence of Diquat in the marine environment and its effect on animals are lacking. However, limited data are available for freshwater lakes. Four lakes in Wisconsin were treated by Cope (2) with from 1.0 to 3.0 ppm Diquat. Detectable residues persisted from 10 to 48 days, depending on the original concentration and area. After 84 days, residues were not detected. Survival of adult and immature blue gills was not affected but adults had slightly less weight gain than controls. In a series of laboratory studies involving

TABLE I

Time of Sampling and Diquat Residue Expressed as ppm in Clams, Oysters, Water and Mud, Nomini Creek, Virginia, June-July 1967

	Station no.	Time after application						
		9 hrs	20 hrs	3 days	9 days	18 days	36 days	356 days
Water	1		ND*	ND				
	2	ND		ND				
Oyster	1		ND	ND	ND	ND	ND	
	2	ND		ND	ND	ND	ND	
Clam	1		ND	ND	ND	ND		
Clam integument	1		ND**	0.05	0.03	0.02		
Bottom mud	1				3.70	5.20	7.14	4.07***
	2				1.21	1.17	5.36	1.19***

Limits of Detection
Water 0.01 ppm; oyster and clam 0.02 ppm

* None detected.
** Integument not removed from around neck.
*** Mean of five samples.

salt water, 1.0 ppm of Diquat did not influence oyster shell growth after 96 hours (1). Similar studies with shrimp and fish showed no detectable influence on growth or mortality.

The most significant aspect of the present study was the consistent absence of detectable residues of Diquat in oysters and its absence in the edible portion of soft clams. The absence of Diquat residues in water was probably associated with its adsorption by silts or clays in suspension or by bottom muds and with the diluting effects of tidal currents.

The persistence of Diquat in bottom muds is comparable to its presence in soils in terrestrial locations, as outlined by Weber (6). Presence of detectable residues in the rough integument of soft clam siphons was probably associated with soil particles trapped in the folds of the tissue.

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