

Toxicity of Adjuvants to Bluegill

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Spray additives have been developed in recent years to aid the effectiveness of herbicides. A variety of confusing terms are currently used to define these additives. We will refer to them as adjuvants. Adjuvants encompass a broad range of functional categories including: utility modifier adjuvants, those that function as emulsifiers, dispensants, stabilizing agents and antifoaming agents, spray modifier adjuvants which include stickers, spreaders, thickening agents and foams, and activator adjuvants, which include surfactants, wetting agents, penetrants and oils (McWhorter et al. 1982).

Adjuvants, can either enhance, diminish, or have no effect on the activity of herbicides. Unlike herbicides, most adjuvants are considered to possess no pesticidal properties. For this reason adjuvants are exempt from the rigorous biological testing requirements and pesticide registration laws applied to herbicides or other pesticides. Although several investigations indicate adjuvants, primarily surfactants, are toxic to fish and aquatic invertebrates (Maki 1979, Swedmark et al. 1971, Swisher et al. 1964), the toxicities of the majority of adjuvants to aquatic organisms has not been extensively investigated. Owing to the increased use of aquatic herbicide spray adjuvants, the purpose of this study was to examine the toxicity of several adjuvants, commonly used in conjunction with aquatic herbicides.

METHODS AND MATERIALS

An acute static bioassay was conducted for nine adjuvants using bluegill (Lepomis macrochirus) following the procedures outlined by Standard Methods (A.P.H.A. 1971)³. The fish were provided by the U.S. Fish and Wildlife Service Welaka Fish Hatchery in Welaka, Florida. All fish were held indoors in aeriated 1000 liter circular tanks receiving well water at the Center for Aquatic Weeds in Gainesville, Florida. The fish tested ranged from 1.2 to 2.8 grams and from 40 to 61 mm total length.

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The bioassay for each adjuvant consisted of three replicates of five concentrations and three control replicates (no adjuvants). After a minimum four day acclimation period, ten fish representative of the size range, were placed into each of the eighteen 50 liter tanks containing various concentrations of the adjuvants or control (well water). To determine the acute toxicity of each adjuvant, LD-50's and 95% confidence intervals were calculated for 24 and 96 hours following the prodedures outlined by Litchfield and Wilcoxen (1949) and Standard Methods (A.P.H.A. 1971). Evidence of mortality, defined as no opercular movement, was noted immediately after placing fish into the containers and every 24 hours up to 96 hours when each test was terminated. As the adjuvants Polysar and Herbex made the solution opaque, fish were examined only after 96 hours, at the time when the containers were drained and the experiment was terminated. Temperature of each container was recorded initially and every 24 hours through the end of the experiment using a mercury thermometer.

Changes in alkalinity and pH were examined separately for each surfactant. Fifty liters of water were placed into six containers representing five concentrations and one control. A water sample was collected initially and at the end of 24 and 96 hours from each container. Total alkalinity as calcium carbonate and pH was determined as described in Standard Methods (A.P.H.A. 1971).

RESULTS AND DISCUSSION

The 24-hour LD-50 ranged from 1.9 to 150 mg/1 and the 96-hour LD-50 ranged from 0.96 to 8100 mg/1 (Table 1). Polysar and Herbex⁴, the two spray additives which produced opaque solutions were the least toxic. Their 96-hour LD-50's were 3600 and 8100 mg/1 respectively (Table 1). The LD-50 of the seven other adjuvants were higher during the 96-hour period (Table 1). The three most toxic adjuvants, Spra-Mate, X-77, and Cide-Kick, caused 100% mortality at concentrations of 6.0 mg/1 and greater. Water temperatures were similar for all trials (Table 1).

The results of several other bioassays testing primarily surfactants, are similar to our findings. Lemeke and Mount (1963) reported alkyl benzene sulfonate (ABS) is relatively toxic to bluegill with 24- and 96-hour median tolerance limit (TLm) values of 24.8 mg/l and 21.2 mg/l respectively. Hokanson and

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Table 1. Mean temperatures $^{\circ}$ C (range), 24- and 96-hour LD-50 static bioassay concentrations (mg/1) (\pm 95% C.I.) of nine herbicide spray additives.

	Mean	LD-50	
Adjuvant	Temperature	24 hour	96 hour
Spra-Mate	19.8	1.9	0.96
_	(19.4-19.9)	(1.7-2.2)	(0.7-1.3)
Cide-Kick	19.8	5.4	5.2
	(19.7 - 19.9)	(5.0-6.0)	(4.8-5.6)
X-77	20.0	5.5	5.5
	(19.9-20.1)	(5.1-6.0)	(4.9-6.1)
Formula 403	19.8	54	37
	(19.7-19.9)	(51-58)	(33-42)
IVOD	19.8	62	37
	(19.7-19.9)	(56-69)	(36-39)
Big Sur	20.0	150	112
9	(19.9-20.1)	(122-185)	(97-130)
Nalquatic	19.9	0.0	200
•	(19.8-20.0)		(167-239)
Polysar	19.9		3600
	(19.8-20.0)		(3028-4280)
Herbex	20.0	spirit was seen and and and	8100
	(19.8-20.0)		(6723-9759)

Smith (1971) reported the 24- and 96-hour median tolerance limit (TLm) of linear alkylate sulfonate (LAS) to bluegill was less than 3.5 mg/l.

With the exception of Herbex, which slightly elevated alkalinity and pH, all adjuvants appear to have a minor effect upon alkalinity and pH. The alkalinity and pH values recorded for all adjuvants were well within the tolerable range for this species.

Currently, spray additives are applied according to recommended surface area rates; therefore, final concentrations are dependent upon depth. Based upon our results, the depths required to achieve median lethal concentrations (LD-50) were calculated for each adjuvant (Table 2). These calculations assume additives are mixed thoroughly throughout the water column and remain in solution for 96 hours. Our results indicate the majority of additives (5) would have to be applied at depths of less than 0.2 m, to achieve median lethal concentrations (LD-50) to bluegill. Application of Spra-Mate, the most toxic spray additive, at a depth of 1.5 meter or less, may result in median lethal concentrations toxic to bluegill within 96 hours.

Unlike laboratory conditions where physical, chemical, and biological interactions are minimized, the toxicities of these adjuvants may be affected by external factors in natural

Table 2. Calculated depth at the corresponding 24-hour and 96-hour LD-50 concentrations (mg/1) for each adjuvant.

Depth required 96-hour to achieve lethal LD-50 concentration (m)	0.96 1.5 5.2 0.1 3.7 0.1 112 <0.1 200 <0.1 3600 <0.1 8100 <0.1	
Depth required to achieve lethal concentration (m)	14.0 liters/ha 1.9 0.7 7.0 liters/ha 5.4 0.1 4.7 liters/ha 5.5 <0.1 18.7 liters/ha 54 <0.1 18.7 liters/ha 62 <0.1 4.7 liters/ha 150 0.1 9.3 liters/ha 2.3 liters/ha 2.3 liters/ha 2.3 liters/ha	
24-hour LD-50	1.9 5.4 5.5 54 62 150 0.0 	
Recommended rrate of application		
Adjuvant	Spra-Mate Cide-Kick X-77 Formula 403 IVOD Big Sur Nalquatic Polysar Herbex	

ecosystems. Although our calculations were based upon each adjuvant remaining in solution for 96 hours, it should not be assumed that biological breakdown would lower their toxicity, as biological intermediates could be more toxic. Differences in water chemistry especially alkalinity may also effect spray additive toxicity. Hokanson and Smith (1971) reported toxicities increased (lower LD-50) as water hardness increased.

Our results indicate, with the exception of Spra-Mate, all other spray adjuvants, applied at suggested application rates, would not be toxic to juvenile bluegill. Their effect on other fauna, which may serve as bluegill food, or on other life history stages of this species should be taken into consideration. In addition, just as spray additive-herbicide combinations vary in efficacy spray additive-herbicide toxicity also may vary.

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