Toxicity Of Sulfuric Acid To Aquatic Plants And Organisms[1]

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ABSTRACT

The toxicity of sulfuric acid to largemouth bass (*Micropterus salmoides* Lacépède), mosquitofish (*Gambusia affinis* Baird and Girard), scuds (*Hyallela azteca*), freshwater shrimp (*Palaemontes* sp.), midges (*Chironomondae*), snails (*Planorbidae*), and hydrilla (*Hydrilla verticillata* Royle), naiad (*Najah guadulupensis* (Springle) Magnus), vallisneria (*Vallisneria americana* Mich.), and *Chara* (Chara sp.) was determined by static tests in 3.8 liter bioassay jars and 57 liter aquariums. Aqueous solutions of sulfuric acid at pH 3 were not toxic to hydrilla but were extremely toxic to all faunal groups tested.

INTRODUCTION

Prior research indicates that the chronic effects of decreasing pH usually result in detrimental changes in aquatic systems. These changes are manifested by reduced fish and invertebrate reproduction, shifts toward less desirable fish and invertebrate populations, and anaerobic conditions. (1, 2, 5, 6, 9, 11). McKee and Wolf (7) reported that pH of 6.7 to 8.6 with an extreme range of 6.3 to 9.0 is necessary to support a good mixed fauna in aquatic ecosystems.

Hydrilla has been reported to grow over a wide range of pH. Within a hydrilla mat, the pH fluctuates naturally from 7.2 to 10.2 during a 24 hour period (13). Haller reported that the optimum pH for hydrilla growth was between 5.6 and 6.2 and that pH of 3 may kill hydrilla (4). Like other strong acids, sulfuric acid disassociates almost completely in water to release sulfate and hydrogen ions. Although an increase in sulfate ions is associated with the placement of sulfuric acid in water, the toxicity of sulfuric acid to aquatic life apparently is a function of the resulting pH.

This research was conducted to evaluate the Hyde Hydronic method (U.S. Patent #3,463,628, August 26, 1969) of

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using commercial concentrated sulfuric acid to control hydrilla (8). The study was designed to determine the effects of sulfuric acid on hydrilla and other aquatic plants, and on groups of selected aquatic fauna.

METHODS AND MATERIALS

Bioassay jars (3.8 liter) were used to determine pH toxicity. In separate tests, 90 individuals of each species were evaluated at the following densities: Largemouth bass (50-60 mm), 3 per jar; mosquitofish (45-55 mm), 3 per jar; scuds, 10 per jar; freshwater shrimp, 5 per jar; midges, 10 per jar; and aquatic snails, 10 per jar.

Three treatments were randomly assigned to the jars; (1) control, pH 8.3; (2) pH 5 (27 ppm H_2SO_4); and (3) pH 3 (80 ppm H_2SO_4).

Observations were made as recommended by the Environmental Protection Agency (3). The invertebrates were examined hourly for the first 8 hours and then at 24 and 48 hours. The fish were observed hourly for the first 8 hours and then at 24, 48, 72, and 96 hours.

The effect of pH 3.5 on hydrilla was evaluated using 20 3.8 liter bioassay jars in which four 15 cm apical sections per jar of the species were planted. After the plants became established the pH was lowered to 3.5 in 10 jars by stirring in concentrated sulfuric acid drop by drop. The pH was monitored hourly after the desired pH was reached for the first day, and twice a day for the remainder of the experiment. Ten similar jars served as controls.

Rooted submersed macrophyte communities consisting of hydrilla, naiad, vallisneria, and chara were established in ten 57 liter aquariums. Crushed limestone was added to five aquariums after the communities had become established. The acid treatment was randomly assigned to eight acquariums. Four of the aquariums treated with acid had slanted bottoms and four had flat bottoms. This compared acid pooling versus acid lying uniformly over the bottom. The aquariums were not aerated since this would cause a mixing throughout the aquarium and would not result in the desired acid sheet across the hydrosoil. The pH in the test aquariums was lowered to 3.0 by 280 ppm H_2SO_4.

RESULTS AND DISCUSSION

In general, the effects of sulfuric acid on most faunal groups tested were rapid. All organisms except the midges and mosquitofish were killed at a pH of 3 within 24 hours (Figure 1). Snails were very susceptible to pH change. Immediately after treatment the affected snails attempted to retract their exposed body parts and then explosively exuded a red liquid within two minutes after application. Thereafter no further activity was observed nor could be elicited. All snails were dead in the pH 3 test by the 24 hour observation. At pH 5, mortality was severe for the first two hours, but leveled off thereafter (Figure 1). No control organisms were lost during the entire testing period.

Scud and shrimp were also very susceptible to pH change. Death followed a brief period of erratic swimming, loss of equilibrium, and then abrupt cessation of all activity. Within minutes, body tissue and the exoskeleton underwent color changes from translucent to an opaque white and reddish-orange respectively. All scud were dead in the pH 3 jars within 6 hours. Mortality in the pH 5 test was slow but continuous over the first 24 hours. No mortality was observed threafter (Figure 1). All organisms survived in the control jars. All fresh water shrimp were dead by the two hour observation at pH 3. Mortality was 25% by the four hour observation at pH 5. No shrimp were lost after this observation (Figure 1).

Midges were the most tolerant of the invertebrates to the acid. After 24 hours there was little difference between pH treatments, or between treatments and controls (Figure 1). Since as many midges were lost in the control jars as in the pH 5 jars after 48 hours, the test on this organism was inconclusive. However, it does illustrate that the midges were very tolerant to pH changes.

Largemouth bass were very tolerant to sulfuric acid at pH 5; however, all were dead after 24 hours in the pH 3 jars (Figure 1). A slight difference was noted between controls and pH 5.

Overall, mosquitofish were more tolerant to the pH changes than largemouth bass (Figure 1). Mortality at pH 3 was 60% by 8 hours and 80% by 24 hours. After the 24 hour observation, very few were lost. At pH 5 about 20 % mortality was recorded in 4 hours and few died after this.

Based on our results it was concluded that the effects of concentrated sulfuric acid for hydrilla control by the Hydronic method would be immediate and lethal to most aquatic fauna, especially to the less mobile groups. However, since vegetation tends to buffer H_2SO_4, the effects on animal life in natural, heavily vegetated habitats could be less than that indicated in the bioassay tests.

The results in the aquatic plant jar tests were quite different from the faunal jar tests. Buffering of the acid solution by the plants was detected six hours following treatment (Figure 2). The plants were not noticeably effected by sulfuric acid as there were no visible differences between the treated and untreated plants.

The pH was buffered quickly in aquariums containing limestone (Figure 3). The pH rapidly climbed in these aquariums after the initial treatment while the pH remained low in the aquariums with just a sand substrate. It took 13 days before the pH in the latter aquariums was as high as those with the limestone 4 days after treatment (Figure 3).

In the aquarium tests, aquatic plant control was found to be erratic, temporary, and usually confined to the portions of the plants in direct contact with the acid layer along the bottom. The plants were severely burned about 2 inches from the bottom in test aquariums with the maximum effect noted 4 days after treatment. The aquariums became anaerobic 5 days following treatment and were then aerated to alleviate the problem. Variation was extreme depending on the density of the plants in each aquarium. In the aquariums with heavy plant growth, only the bottom of the plants were burned. In aquariums with moderate to light plant density, all plants were killed. There was no evidence that the aquariums with dense aquatic populations had been treated with sulfuric acid within 14 days following treatment. The plants quickly buffered the acid as in the jar tests so that lowering of the pH was not effec-

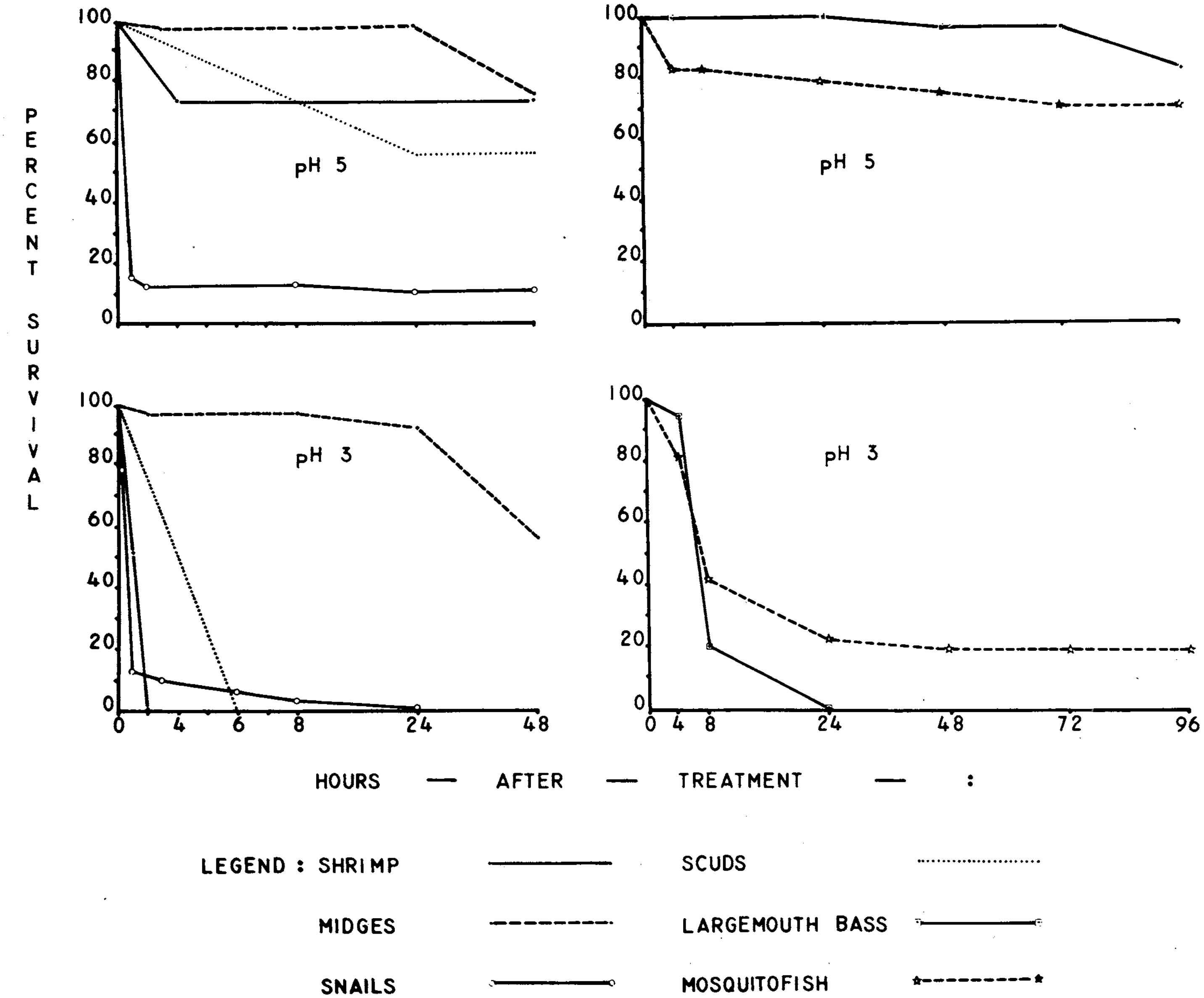

Figure 1. Comparison of percent survival over time at pH 5 and 3 on shrimp, midges, snails, scud, largemouth bass, and mosquitofish.

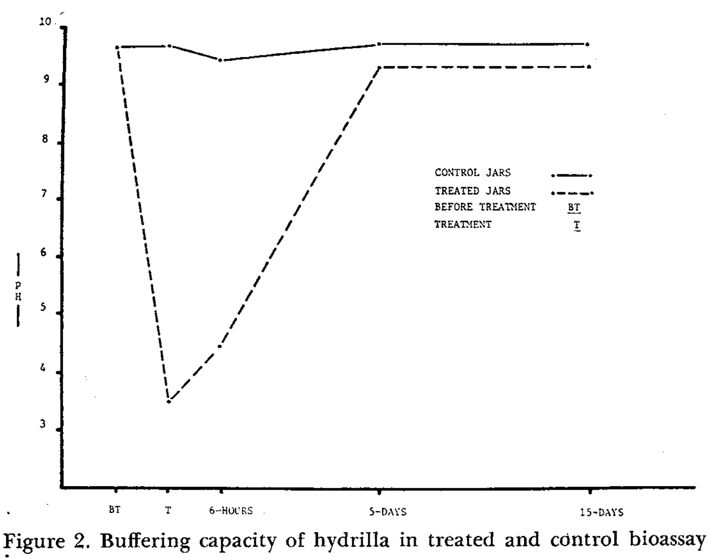

Figure 2. Buffering capacity of hydrilla in treated and control bioassay jars.

tive. In all aquariums, except one with moderate plant density, regrowth occurred within 21 days. Vallisneria seemed least effected since it was the first plant to exhibit regrowth. However, regrowth of chara, hydrilla, and naiad was noted one day after vallisneria. Hydrilla had again become dominant by 36 days following the treatment.

There was no apparent difference between the slanted and flat aquariums. At the time acid was applied, the sulfuric acid was observed flowing over the bottom in the slanted aquariums. Mixing did not seem complete since the acid pooled at the lower end. However, there was not a significant difference in pH readings between the slanted and flat aquariums after 1 day. Factors other than toxicity and environmental effects must be considered when evaluating a candidate herbicide. According to the Herbicide Hand book of the Weed Science Society of America (11) the following major properties make a compound desirable as a herbicide: (1) kills (controls) or reduces target plant species to acceptable levels at low concentrations; (2) wide margin of

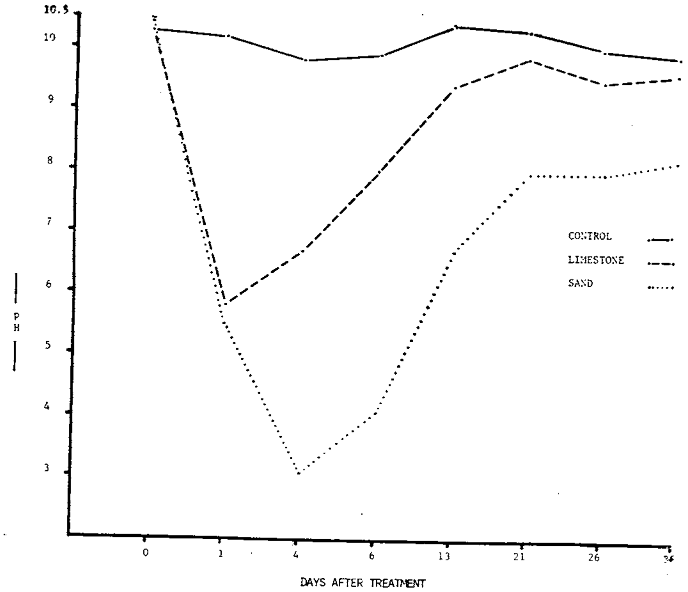

Figure 3. Comparison of sand and limestone substrates as buffering agents in aquarium tests.

safety between phytocidal concentrations and those required to kill nontarget organisms; (3) safety to applicator, public, and the environment; and (4) reasonably predictable results at recommended rates.

Based on our tests results and literature reviewed, it was concluded that field applications of concentrated sulfuric acid would be more detrimental to aquatic fauna than hydrilla, be hazardous to the applicator and public under field conditions, require high dosages to kill the target species and would produce erratic, unpredictable results. Environmental restrictions are now far more stringent, and few sites meet the requirements outlined earlier by Phillippy (10).

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