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# EFFECTS OF HYDROGEN SULFIDE ON CHANNEL CATFISH (Ictalurus punctatus)<sup>1</sup>

EDWARD W. BONN Texas Parks and Wildlife Department Denison, Texas

and

BILLY J. FOLLIS Texas Parks and Wildlife Department San Angelo, Texas

## ABSTRACT

The natural production of sulfides is responsible for poor channel catfish production in many acid lakes in Northeast Texas. The TLm of un-ionized hydrogen sulfide for channel catfish fry ranged from 0.8 ppm at pH of 6.8 to 0.53 at pH 7.8. At pH 7.0 the TLm of this gas is 1.0 ppm for fingerling catfish, 1.3 for advanced fingerlings and 1.4 for adult channel catfish. Small fish were also killed quicker when exposed to these concentrations. Maximum concentrations of hydrogen sulfide are produced in the spring. Channel catfish populations can be maintained by continued stocking of adult fish or by raising the pH with agricultural limestone, which in turn lowers the toxic un-ionized hydrogen sulfide.

## INTRODUCTION

Fishery surveys of several lakes in Northeast Texas indicated that very few channel catfish (*Ictalurus punctatus*) were present even after repeated introductions of hatchery fish. When such impoundments were drained or treated with fish toxicants, only a few large catfish were found and in some cases none were recovered. An analysis of the chemical, biological and physical conditions of 53 area lakes indicated that

<sup>&</sup>lt;sup>1</sup> Contribution of Dingell-Johnson Project F-8-R, Texas

most of the poor catfish waters were clear, shallow and acid. Most lakes in East Texas contain large amounts of vegetation in various stages of decomposition.

Adult channel catfish injected with Antuitrin "S" spawned in holding pens in these lakes, but the fry rapidly disappeared. Catfish fry obtained from hatcheries grew well when held in small-mesh screened pens, but continued to disappear. Several fry were found dead or in distress, yet no injury or disease was detected. Since bubbles of hydogen sulfide gas were released whenever the lake bottom was disturbed in the vicinity of the pens, this gas was suspected as the cause of death.

While the effects of hydrogen sulfide have been determined on certain fish and aquatic organisms (Longwell and Pentelow, 1935; Ellis, 1937; Schaut, 1939; Cole, 1941; Jones, 1948; Van Horn, Anderson and Katz, 1949) little published information is available concerning the effects of this gas on channel catfish (McKee and Wolf, 1963). Sinise (1965) mentioned that hydrogen sulfide gas, produced by aerobic bacteria, is harmful to catfish, but gives no tolerance limits.

Much of the literature on the toxicity of hydrogen sulfide to various species of aquatic life is quite conflicting. This is possibly due to the fact that in few of the references is there any specific or even a general pH factor mentioned. Longwell and Pentelow (1935) mentioned a general pH influence on hydrogen sulfide from sewage wastes. Jones (1947) stated that the toxicity of sodium sulfide to trout varied with changes in pH of the solution.

Our preliminary work revealed no correlation between pH alone and survival time. Likewise no correlation was found between total sulfide content and the survival of catfish fry. However, it was observed that pH could make a difference of several times the amount of hydrogen sulfide an individual specimen could withstand. It is known that hydrogen sulfide dissociates primarily according to pH, with temperature and other factors playing a minor role (McKee and Wolf, 1963). In general, the lower the pH, the greater the degree of dissociation.

#### METHODS

#### Laboratory Experiments

In an effort to determine what concentrations of un-ionized hydrogen sulfide are lethal to various sized channel catfish, laboratory tests were conducted with water quality similar to that found in Northeast Texas lakes. Catfish fry and fingerlings were obtained from the State Fish Hatchery at Tyler and from the National Fish Hatchery, Fort Worth, Texas. The fry averaged about 30 mm in standard length and the fingerlings from 80 to 120 mm. All fry and fingerlings were fed a prepared fish food daily while in the holding tank and appeared to be in good condition.

Adult catfish were collected with hoop nets from Lake Texoma and also tested. These fish ranged from 250 to 350 mm standard length. Bluegill (*Lepomis macrochirus*), also used in the tolerance tests, were obtained by seining and were approximately the same size as the fry and fingerling channel catfish.

Ten catfish fry were used with 10 bluegill fry, which were considered as control animals since bluegill are common in acid waters where substantial amounts of hydrogen sulfide are found. The fingerlings were tested with five each of the two species per aquarium, while the adult catfish were tested separately with no control species. The test aquariums were five-gallon wide-mouth jars arranged in a series. Three liters of rainwater were used for each fry test and six liters were needed for testing the fingerlings and adult fish.

Various concentrations of hydrogen sulfide were produced in each jar by adding a calculated amount of concentrated hydrogen sulfide stock solution of 1,000 ppm. This stock was prepared by placing a calculated amount of sodium sulfide in a given volume of distilled water. The stock was kept in a sealed container under refrigeration to reduce the rate of oxidation. The amount of stock placed in each jar was calculated with pH values to produce un-ionized hydrogen sulfide at intervals of 0.1 ppm ranging from 0.2 to 1.0 ppm.

The pH was established and controlled by a buffer using sodium sulfide as the base and citric acid as the acid. This buffer system was determined experimentally by placing equal amounts of equal concentrations of citric acid and sodium sulfide together and measuring the pH. Since a known amount of sodium sulfide was already introduced to obtain a desired amount of un-ionized hydrogen sulfide, the proper amount of acid was calculated and added to give the desired pH. The fish were placed in the jars after the calculations had been made, the chemical added and conditions tested.

The pH was checked with a Hellige comparator and the total sulfide content was tested titrimetrically (Theroux, Eldridge and Mallmann, 1943). The un-ionized hydrogen sulfide was calculated from the dissolved total hydrogen sulfide and the pH of the sample (American Public Health Association *et al.*, 1955).

The air space above the water in the jars was replaced with oxygen and the jars sealed. The units were not aerated because excessive water movement would increase the escape of hydrogen sulfide. The tests were conducted for approximately three hours at  $25^{\circ}$  to  $30^{\circ}$ C. Temperature would not greatly affect the dissociation of hydrogen sulfide unless it was very high or very low. However, it could affect the rate at which the test animals reacted by influencing their metabolic rate.

Fry of channel catfish were tested for susceptibility to total hydrogen sulfide from 1.17 to 10.9 ppm and the pH was varied from 6.8 to 7.8. Tests for fry were repeated as many as eight times for each concentration. The median tolerance limit (TLm) was considered to be reached when half of the test animals died in the prescribed time.

Experiments of the toxic effects of hydrogen sulfide on the larger fish followed much the same lines as discussed for the fry. Since the results of the fry experiments could be used as a guide and fewer specimens of the larger fish were available, testing of these larger fish was not as extensive. Fingerlings and adult catfish were tested at a constant pH of 7.0 for the susceptibility of total hydrogen sulfide from 1.5 to 4.8 ppm. This gave an un-ionized hydrogen sulfide range of 0.5 to 1.6 ppm and tests of 0.1 ppm intervals were repeated at least three times.

#### Field Work

Ten lakes with channel catfish populations ranging from excellent to very poor were chosen for field tests and study. Periodically population samples were taken with gill nets of various size mesh and a ¼-inch mesh bag seine. Water tests were made in conjunction with these collections with special emphasis placed on pH, total sulfides, turbidity and temperature.

After discovering that larger channel catfish are not as sensitive to the effects of hydrogen sulfide, two of the test lakes were stocked with 10 wild adult catfish per acre. These fish were taken with cheese-baited hoop nets from area lakes with good catfish populations and from the draft tubes at Denison Dam, operated by the U. S. Corps of Enigneers. The introduced fish were marked by removing their adipose fin.

Since adult catfish are not readily available for stocking, a method was devised to grow hatchery fish to a size tolerant to the conditions at Lake Ferndale, one of the 10 study sites. The first attempt in May, 1964, failed when 10,000 catfish fry were killed when lake water, used to fill the pond, was suspected of containing a lethal amount of hydrogen sulfide. This gas could not be calculated because field equipment would not accurately measure the pH found to be lower than 6.0.

A second supply of fish was not available until September. Having no feasible method of lowering the hydrogen sulfide, the pH was raised, which in turn lowered the poisonous un-ionized hydrogen sulfide. Four tons of agricultural limestone applied by a commercial spreader changed the pH of the pond water from below 6.0 to 7.9. Two additional applications of crushed limestone were used to maintain a high pH, thus minimizing the dissociation of the total sulfides during the pond experiment. The fish were fed a commercial preparation in amounts adjusted to their increasing size. When received the fingerlings averaged 85 mm total length and were held in the rearing pond until the following summer. At this time they averaged 10 inches total length and were considered large enough to tolerate the lake conditions.

Test pens were used at Lake Ferndale in conjunction with the rearing pond experiment. In these controls, 100 fry were used in May and 10 young adults were tested before the reared fish were released the following summer. These pens were boxes measuring 2 by 2 by 4 feet, covered with fine mesh, fiberglass window screen and anchored to the lake bottom.

#### RESULTS

#### Laboratory Studies

The quantity of total sulfides necessary to produce a TLm of the test catfish varied from 1.82 to approximately 7.0 ppm, depending upon the pH of the water. The number of catfish and bluegill killed out of 10 of each species is given in Table 1. The total sulfides are measured and

TABLE 1.	EFFECT OF TOTAL DISSOLVED SULFIDES AND UN-
	IONIZED HYDROGEN SULFIDE ON CHANNEL CAT-
	FISH AND BLUEGILL FRY. TOTAL AND UN-ION-
	IZED SULFIDES ARE GIVEN IN PPM. RESULTS ARE
	GIVEN IN NUMBERS OF FISH KILLED OUT OF A
	TOTAL OF TEN TEST FISH USED FOR A PERIOD OF
	THREE HOURS.

$\mathbf{p}\mathbf{H}$						
6.8	Total dissolved sulfides	1.17	1.36	1.59	1.82	2.04
	Un-ionized H2S	0.5	0.6	0.7	0.8	0.9
	Channel catfish	0	0	0	5	10
	Bluegill	0	0	0	0	2
7.0	Total dissolved sulfides	1.5	1.8	2.1	2.4	2.7
	Un-ionized H <sub>2</sub> S	0.5	0.6	0.7	0.8	0.9
	Channel catfish	0	1	6	10	10
	Bluegill	0	0	0	0	3
7.2	Total dissolved sulfides	2.1	2.5	2.9	3.3	3.7
	Un-ionized H <sub>2</sub> S	0.5	0.6	0.7	0.8	0.9
	Channel catfish	0	0	10	10	10
	Bluegill	0	1	0	0	1
7.4	Total dissolved sulfides Un-ionized H <sub>2</sub> S Channel catfish Bluegill	2.5 0.4 0 0	2.9 0.5 0 0	3.5 0.6 4 0	4.1 0.7 10 0	$4.7 \\ 0.8 \\ 10 \\ 2$
7.6	Total dissolved sulfides	3.6	4.5	5.4	6.3	7.2
	Un-ionized H <sub>2</sub> S	0.4	0.5	0.6	0.7	0.8
	Channel catfish	0	2	1	10	8
	Bluegill	0	0	0	0	6
7.8	Total dissolved sulfides Un-ionized H₂S Channel catfish Bluegill	$5.5 \\ 0.4 \\ 0 \\ 0$	6.8 0.5 3 0	8.2 0.6 10 0	9.6 0.7 10 0	10.9 0.8 10 0

the un-ionized hydrogen sulfide is calculated from the pH-total dissolved sulfide combination.

Thus the TLm of un-ionized hydrogen sulfide was found to be 0.8 ppm for pH value of 6.8. For pH values of 7.0, 7.2, 7.4, 7.6 and 7.8 the TLm was calculated to be 0.68, 0.65, 0.62, 0.64 and 0.53 ppm, respectively. The pH was difficult to read at 7.6 which probably caused the slightly higher TLm of 0.64 ppm. In this range the phenol red indicator is not as sensitive as the bromothymol blue used in the pH range of 6.2 to 7.6.

Most of the catfish fry died in approximately 10 minutes at the median tolerance limit given above. Bluegill proved to be more tolerant and only a few died at concentrations higher than those where all the catfish were killed. A TLm for bluegill fry was attained only at 0.78 ppm un-ionized hydrogen sulfide at the 7.6 pH.

At a pH of 7.0 the TLm of un-ionized hydrogen sulfide was found to be 1.0 ppm for fingerling channel catfish, 1.3 for advanced fingerlings and 1.4 for adult catfish. The fingerlings died in approximately 20 minutes while the TLm for advanced fingerlings and adults was attained after about 45 minutes.

No TLm was reached for bluegill in the fingerling tests. Only two of these control fish died during the three-hour exposure to un-ionized hydrogen sulfide concentrations as high as 1.6 ppm.

These findings indicate that channel catfish have a greater resistance to this toxic gas with an increase in size or age. When catfish of all sizes were exposed to sub-lethal concentrations of un-ionized hydrogen sulfide, they exhibited nervousness and excessive movement as if attempting to escape the poisonous gas. This occurred when the concentration approached within 0.2 ppm of the TLm for a given pH.

#### Field Tests

During a three-day period water samples were collected at six widely separated locations in Glass Lake, one of the test sites. Table 2 gives the

Station	Water temperature (°F.)	Sample depth (feet)	pH	Total hydrogen sulfide (ppm)	Un-ionized hydrogen sulfide (ppm)
1	87	Surface	7.2	6.82	1.64
1	89	2.5	7.2	5.96	1.43
2	87	Surface	7.2	5.54	1.33
2	88	5	7.1	5.96	1.73
1 2 3 3 4 5 5	88	Surface	7.2	7.25	1.74
3	76	18	6.8	2.13	0.94
4	88	Surface	7.2	2.13	0.51
4	76	24	6.9	5.11	1.99
$\overline{5}$	87	Surface	7.1	4.26	1.24
5	84	18	6.5	3.40	2.07
6	90	Surface	7.3	5.11	1.18
	90	4	7.3	1.28	0.29
ĩ	86	Surface	6.8	2.56	1.13
1	84	3	7.0	3.83	1.26
$\overline{2}$	86	5	7.0	2.98	0.98
$\overline{2}$	84	Surface	6.8	2.98	1.31
ā	86	Surface	7.0	3.40	1.12
3	$\overline{74}$	18	6.6	2.13	1.19
4	88	Surface	7.0	4.26	1.41
6 1 2 2 3 3 4 4 5	84	24	7.0	2.56	0.85
$\hat{5}$	84	Surface	7.0	4.26	1.41
5	80	18	6.4	3.40	2.28

TABLE 2. WATER ANALYSES OF GLASS LAKE, JULY 24-26,1962.

results of these tests with special reference to those factors which influence the un-ionized hydrogen sulfide content. Based on our laboratory findings, 20 of these 22 samples would be lethal to small channel catfish. Only those readings less than 0.6 ppm un-ionized hydrogen sulfide would be harmless to this size fish. Under normal growth conditions for this area, channel catfish would be less than three inches long at this time of the year. Bluegill, which were shown to have a higher tolerance for this gas, are abundant in Glass Lake, while no channel catfish were found. Table 3 is presented to illustrate the influence of pH on the unionized hydrogen sulfide concentration. Using the total sulfide concentration of 6.82 recorded at Glass Lake station 1 and the conversion

TABLE 3.	INFLUENCE OF pH ON UN-IONIZED HYDROGEN
	SULFIDE. CONVERSION FACTORS TAKEN FROM
	PAGE 274 OF STANDARD METHODS FOR THE EX-
	AMINATION OF WATER, SEWAGE AND INDUS-
	TRIAL WASTES.

pН	Conversion Factor	Total Hydrogen Sulfide (ppm)	Un-ionized Hydrogen Sulfide (ppm)
6.0	0.83	6.82	5.66
6.5	0.61	6.82	4.16
7.0	0.33	6.82	2.25
7.2	0.24	6.82	1.64
7.5	0.14	6.82	0.96
7.7	0.091	6.82	0.62
8.0	0.048	6.82	0.33

factors from Standard Methods (American Public Health Association et al., 1955) the un-ionized hydrogen sulfide value could vary from 5.66 ppm at pH 6.0 to as low as 0.327 at pH 8.0. Thus the pH would have to be about 7.7 before the un-ionized hydrogen sulfide would permit small channel catfish to survive in Glass Lake.

Fin-clipped specimens retaken in periodic surveys showed the transplanted adult fish grew rapidly in both Lakes Ferndale and Glass. The condition index for the marked fish in Lake Ferndale was 1.82 in 1964 and 2.00 in 1965. The average condition index for this species in Northeast Texas was 1.89 in 1964. The fish weighed about 0.75 pound each when released in 1962 and grew to an average of 4.38 pounds in 1965. Anglers removed 56.5 per cent of the marked fish from Lake Ferndale by December, 1965. A check of the sexual condition of catfish revealed many had spent gonads, however, repeated collections failed to produce any young channel catfish.

Of the 100 catfish fry placed in a test pen at Lake Ferndale when the first shipment of hatchery fish were received, 86 died within 24 hours. In less than 48 hours, all the test fry in the lake pen were dead. Water tests showed the total hydrogen sulfide to be 0.96 ppm and a pH of less than 6.0. Using the conversion factors in Table 3, this gave an un-ionized concentration of at least 0.797 ppm, which is probably lethal for catfish fry at this pH. While periodic testing showed that the un-ionized gas remained at an injurious level in Lake Ferndale where the pH was low, it did not reach a dangerous concentration in the limed ponds filled with lake water.

Before releasing the young adult catfish the following summer, all 10 test fish survived in Lake Ferndale for longer than a week. Within a month after being released, many of the pond-raised fish were taken by anglers at widespread locations in the lake. By December, creel checks showed they weighed approximately one pound.

#### DISCUSSION

Based on the results of extensive water tests, it is evident that the production of un-ionized hydrogen sulfide is seasonal, but sometimes very erratic. Maximum production can be expected April through June. This is evident in Figure 1 where the un-ionized hydrogen sulfide at Lake Ferndale reached lethal concentrations in the spring of 1964 and 1965.

Werkman and Wilson (1951) believed that while bacteria isolated from cold springs, deep lakes and ocean waters grow from 0° to 30°C., they show optimum growth in the vicinity of 20°C. This corresponds with ZoBell and Conn (1940) who stated that maximum colony counts

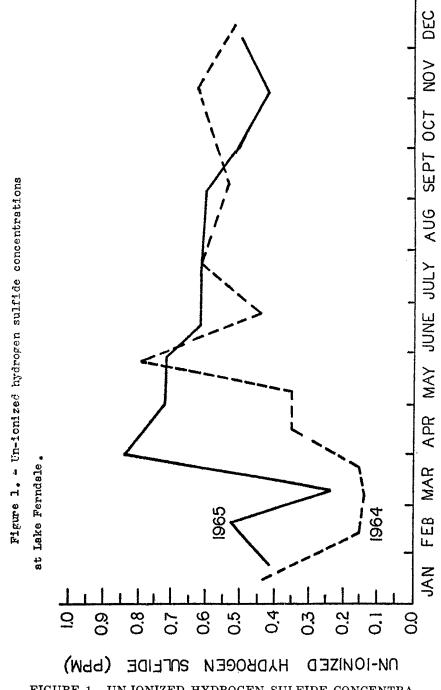


FIGURE 1. UN-IONIZED HYDROGEN SULFIDE CONCENTRA-TIONS AT LAKE FERNDALE.

are incubated with nutrient agar at 18° to 22°C., while few colonies developed from 4° to 12°C. and at 37°C.

Weather conditions and major water level fluctuations, which influence water temperatures and pH values, can alter the time and amount of this toxic gas. In addition the changing limnology of the lake can cause variable concentrations at different locations in each lake.

Another factor brought out by these experiments is the length of time it takes to reach the TLm of the various sized test fish. While the fry were usually dead within 10 minutes the advanced fingerlings and adults did not die for at least 30 minutes when exposed to the median tolerance limit.

The prolonged death of the larger catfish may provide an escape time from an area saturated with hydrogen sulfide if the fish were to come in contact with the gas in their natural habitat. At the same time, smaller catfish, being a bottom dwelling species, may become prey of larger predaceous fish if they leave the protected areas on the lake bottom.

While a temporary population of channel catfish was successfully produced in both Lakes Ferndale and Glass by stocking adult fish, no evidence was found that they replaced themselves. This substantiates our original discovery that channel catfish were scarce or lacking in many lakes that had been stocked with hatchery fish.

If channel catfish are desired in the clear, shallow, acid lakes of Northeast Texas, they should be stocked as larger fish or the water neutralized with agricultural limestone. When the un-ionized hydrogen sulfide is reduced with limestone, channel catfish fingerlings can survive in waters that were previously toxic. They attain good growth and at about 10 inches total length, they have a considerable higher tolerance to the toxic gas found in most of the acid lakes in East Texas.

#### ACKNOWLEDGMENTS

The authors wish to acknowledge the assistance of W. G. McClellan, who served as Assistant Project Leader at the beginning of this study, and T. J. Culpepper and R. G. Hall, who later worked as Summer Assistants in that capacity. Appreciation is also expressed to biology technicians and field assistants of Fisheries Region 3-A for both field and laboratory assistance.

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## INVESTIGATIONS IN THE USE OF ELECTRICITY FOR THINNING OVERCROWDED POPULATIONS OF BLUEGILL<sup>1</sup>

#### SAM L. SPENCER

## Alabama Department of Conservation Game and Fish Division, Fisheries Section Montgomery, Alabama

#### ABSTRACT

A 230-volt, 180-cycle alternating current; a 115-volt, 60-cycle alternating current and a 115-volt direct current were used to attempt to kill intermediate-size bluegill, *Lepomis macrochirus*, Rafinesque, without harming largemouth bass, *Micropterus salmoides* (Lacepede). Bluegill and largemouth bass were placed in screen pens in concrete ponds and exposed to different voltages, electrode types and exposure periods.

No largemouth bass were killed during exposure periods which killed 75 percent of the bluegill.

The 230 volts killed more bluegill than 115 volts A.C. or 115 volts D.C. However, 230 volts A.C. did not kill sufficient percentages of bluegill with short (8-10 second) exposures.

## INTRODUCTION

Fish ponds stocked with a combination of largemouth bass, *Micropterus salmoides* (Lacepede), and bluegill, *Lepomis macrochirus* Rafinesque, may become overpopulated with intermediate-size bluegill which results in poor fishing (Swingle, 1956). The present chemical and mechanical methods used to control excessive numbers of bluegill are costly, time consuming and seldom selective. An electrical method of thinning an overcrowded population of bluegill may have the advantage of being less expensive and possibly more selective than present methods.

This research was undertaken to determine if an electric fish shocker could be used to kill intermediate-size bluegill without harming the largemouth bass.

#### METHODS

This research was conducted in a series of concrete ponds on the Farm Ponds Project of the Auburn University Experiment Station, Auburn, Alabama. Each pond was 24.2 feet long, nine feet wide, and 2.5 feet deep. The test fish were confined to an area three feet long, one foot wide, and 2.5 feet deep by using screens. This confinement allowed all fish to receive an electric shock of approximately equal magnitude.

The water supply for the original experiments was pumped from a nearby stream and filtered through a sand and gravel filter to remove plankton and debris. In later experiments, clear water was obtained from wells.

Bluegill were either seined from a 3.5-acre pond (S-9) or obtained from a State fish hatchery. The largemouth bass were captured by

<sup>&</sup>lt;sup>1</sup>This paper is based on part of a thesis submitted to the Graduate Faculty of Auburn University, Auburn, Alabama, in partial fulfillment of the requirements for the Master of Science Degree in Fisheries Management, March 16, 1963.