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Industrial Pollution in Coles County, Illinois

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INDUSTRIAL POLLUTION IN
COLES COUNTY, ILLINOIS

(TITLE)

BY

Michael William Conlin

THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF

Master of Science in Zoology

IN THE GRADUATE SCHOOL, EASTERN ILLINOIS UNIVERSITY
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1971
YEAR

I HEREBY RECOMMEND THIS THESIS BE ACCEPTED AS FULFILLING
THIS PART OF THE GRADUATE DEGREE CITED ABOVE

29 July, 1971
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ABSTRACT

The Anaconda American Brass Company at Mattoon, Coles County, Illinois was found to discharge waste containing excessive amounts of copper, hexavalent chromium, sulfates, acids, and alkalies. These wastes were found to enter an agricultural field tile system and to emit at the Shellhammer tile where they entered a small unnamed creek, a large pond along Interstate 57, and Riley Creek.

Tests of the Shellhammer tile and Anaconda American Brass Company effluent were conducted from March, 1970 thru May, 1971. Maximum concentrations determined were as follows: (1) copper -- 15.5 ppm; (2) hexavalent chromium -- 1.5 ppm; (3) pH -- range of 2.3 - 12.4; (4) phosphates -- 8.0 ppm; (5) sulfates -- 1500 ppm. Oil, although not measured chemically, was observed to coat the banks and surface of the receiving waterway on several occasions. The phosphate and oil pollutional sources were not pinpointed in this study.

Natural fish kills (393 dead fish collected) below the tile outfall were found to be associated with excessive copper and chromate levels and/or an extremely acidic pH on one occasion while very alkaline pH levels and/or high sulfate levels seemingly accounted for the three remaining kills.

Results of two practical toxicity bioassays using creek chubs (Semotilus atromaculatus) revealed copper (4.2 - 12.5 ppm) and/or hexavalent chromate (0.85 - 1.45 ppm) to apparently cause 100 percent mortality just below the effluent outfall within 72 hours and 100 percent mortality one-half mile below Shellhammer tile outfall within 48 hours. The second experiment showed copper of 8.5 ppm and/or a pH level of 3.3 to apparently cause 100 percent fish mortality within 24 hours.

Other biota observed to be adversely affected by the tile effluent were algae, crayfish, and muskrats (*Ondatra zibethicus*). Massive amounts of *Ulothrix* were noted to succumb during the periods of heavy copper and chromate pollution in July, 1970. However, *Ulothrix*, *Zygnema*, *Stigeoclonium*, *Microspora*, *Spirogyra*, and *Euglena* survived copper concentrations ranging from 0.10 - 2.50 ppm during the spring of 1971.

INTRODUCTION

Monitoring of industrial effluents presents a myriad of problems. In the past, sources of industrial pollution have often proved difficult to determine due to industries' unwillingness to provide information as to the nature of the waste products. However, by July, 1971 industries are required (under the 1899 Refuse Act) to obtain permits if their outfall line leads into navigable waters or tributaries thereof. For an industrial concern to obtain such a permit will require that its effluent meet present water quality standards prescribed by the Environmental Protection Agency.

Pollutional effects assume many characteristics and a great degree in variation in an aquatic environment (Mackenthun, 1969). The volume and strength of the pollutant as well as the size of the receiving waterway control to a considerable extent the environmental and ecological responses.

Significant information on the character of inflowing wastes is provided by the animals and plants in the receiving waterway (Keup, 1966). A severely toxic substance will eliminate aquatic biota until dilution, dissipation, or volatilization reduces the concentration below the toxic threshhold (Mackenthun, 1969). An in-lab bioassay is often complicated by differences in laboratory and stream or river water constituents such as pH, hardness, dissolved oxygen, and flow rate. Thus a practical toxicity bioassay at the point in question can often yield more information than the literature about the toxicity of a particular effluent.

The main objectives of this study were to monitor a known industrial pollutional source, and to determine its origin and resulting effect on the aquatic community in the receiving waterway.

MATERIALS AND METHODS

This study was conducted from March, 1970 to May, 1971. A total of 10 sampling stations was established but only 7 of these stations were sampled regularly. Figure 1 shows a general map of the study area. Shellhammer tile is located in the NE$\frac{1}{4}$ of T12N-R8E, Lafayette Township, Coles County, Illinois. The primary function of the Shellhammer tile is for agricultural field drainage, but for a number of years now an undetermined number of industries have utilized this drainage system to dispose of certain waste materials.

Water samples were collected (as grab samples) from each station in 1000 ml disposable bottles. The water analyses were conducted on the same day that the samples were collected. Colorimetric analyses were performed utilizing a Hach DR Colorimeter according to methods described in the Hach Colorimeter Methods Manual (Anon., 1967a). Analyses were made for the following: copper (Cu), hexavalent chromium (Cr^{+6}), sulfates (SO_4), ortho phosphates (PO_4), detergents, calcium hardness, total hardness, manganese (Mn), zinc (Zn), iron (Fe), nitrates (NO_3), and nitrites (NO_2). Testing for Mn, Zn, Fe, No_3, and NO_2 was discontinued after May, 1970 as the constituents of prime concern became Cu, Cr, acids, and alkalies. The pH values were determined utilizing a Beckman Zeromatic II pH meter.

Chemical oxygen demands (COD) were determined on several testing days but were not continued due to lack of significant COD.

The Anaconda American Brass Co. was the only known source of copper and chromate draining to the Shellhammer tile area and this industrial concern was contacted and arrangements were made for intensified sampling of their effluent. Methods used by Anaconda American Brass chemists in testing their effluent for Cu and Cr were essentially identical to those colorimetric procedures described above except that in later testing Anaconda allowed their samples to set for some time before testing. Furthermore, the 25 ml to be tested was taken from the top of the sample bottle that had been allowed to settle out. Earlier in the study, split-sample analyses showed a close correlation of results between Anaconda and the author. A 1.0 copper standard solution was tested in various dilutions to further determine accuracy of the colorimetric method used by the author and Anconda. Copper readings were found to be accurate to 0.05 ppm. The minimum detectable hexavalent chromate level was determined to be 0.04 ppm.

Sampling of rinse tanks and effluent at the Anaconda plant was conducted by the author during July and August, 1970. Monitoring of these check points has since been continued on a daily basis by the plant chemist.

Two practical toxicity bioassays were run using creek chubs, Semotilus atromaculatus. Portable wire fish cages containing 10 creek chubs each were placed in Shellhammer tile basin, in I-57 Pond one-half mile below Shellhammer tile outfall, and in Riley Creek upstream from where Shellhammer tile effluent enters (used as a control group). These fish were collected by hand-seine from Cassell Creek, a small stream located 7 miles east of the Shellhammer tile area.

Fish in the tile drainage killed due to toxic effluents were identified according to Eddy (1957) and Hubbs and Lagler (1958).

RESULTS

Copper pollution at Shellhammer tile reached a maximum level of 15.50 ppm on July 21, 1970 (Figure 2). From August 1970 (after installation of anti-pollution equipment) to May 1971, the highest copper determination at the tile was 2.5 ppm. Readings of daily samples taken from a ditch leading from the Anaconda plant show weekly high copper concentrations to vary from 0.15 - 2.50 ppm (Figure 2). The allowable copper concentrations in such effluents is 0.1 ppm (Anon.,1968a).

Weekly high readings of copper in two rinse tanks used by Anaconda for removing excess copper, sulfuric acid, and hydrogen peroxide (prior to August 1970 a chromate cleaner was used rather than hydrogen peroxide) are shown in figure 3. The drag-off of copper in rinse tank #1 can been seen to be much higher than in rinse tank #2. Prior to August 1970 these tanks were dumped daily to a ditch leading from the Anaconda plant. Since that time, these tanks are reportedly never drained and any copper in their effluent supposedly results from overflow of the rinse tanks during dipping operations. Unfortunately, effluent data concerning the rinse tanks and the ditch behind the plant prior to the last week in July 1970 were not available.

Maximum hexavalent chromate levels at Shellhammer tile were also found to occur during July 1970 (Figure 4). The highest chromate reading was 1.5 ppm, while the allowable limit is 0.05 ppm (Anon., 1968a). No chromate was found in the effluent after August of 1970 when the Anaconda plant discontinued use of chromate in their brass dipping procedures.

I-57 Pond copper and chromate levels are shown in figure 5. Pollutional levels of copper and chromate also peaked here during July 1970 with maximum copper and chromate readings of 15.00 and 0.60 ppm respectively. The highest copper level determined in the pond after July 1970 was 0.12 ppm.

Riley Creek (downstream) had a maximum concentration of 0.28 ppm Cu and 0.10 Cr during July 1970, but tests have shown no detectable amounts of these pollutants since that time.

Extreme sulfate and pH readings were often encountered in the Shellhammer tile effluent due to Anaconda'a dumping of waste acid from their deionizer. The maximum sulfate reading occurred in July of 1970 (Figure 6). This pollutional source was found to be a constant problem throughout the course of the study. The sulfate level in I-57 Pond peaked in April 1971 with a reading of 260.0 ppm (Figure 7).

Figure 8 shows the extremely low pH values (2.3 minimum) caused in July 1970 by the dumping of waste acid from the Anaconda plant. Anaconda has neutralized their waste acids before dumping to their ditch since August of 1970. On several occasions "super-neutralization" with caustic soda resulted in extremely high pH levels (12.4 maximum) and fish kills in the Shellhammer tile area (Tables 1 and 2). PH values for the ditch leading from the Anaconda plant are also given in figure 8 for comparative purposes. Peaks in pH in Anaconda's ditch are generally followed by peaks in pH at Shellhammer time (Figure 8) and I-57 Pond (Figure 9). PH values in I-57 Pond ranged from 6.5 - 9.5 during the study period.

Ortho phosphates were found to present occasional problems due to one or more industrial complexes discharging detergents into the watershed. The highest phosphate level determined in Shellhammer tile effluent was 8.0 ppm (Figure 10). Phosphate levels (as shown in figure 10) in I-57 Pond appear within normal ranges. Although Anaconda contends they use no phosphate detergents or cleaners, a sample of their plant effluent on

August 5, 1970 revealed a level of 4.5 ppm alkyl benzene sulfonate (ABS) and/or linear alkylate sulfonate (LAS) detergents. Detergent readings at Shellhammer tile the same day showed a level of 1.25 ppm ABS and/or LAS.

Water hardness determinations shown in figure 11 demonstrate the relative hardness of the effluent and water in the waterway concerned with in this study. Values ranged between 300 - 400 ppm total hardness.

Results of two practical toxicity bioassays using creek chubs are shown in table 1. The toxicity experiment of July 13, 1970 revealed copper and/or hexavalent chromate to be the apparent cause of 100 percent fish mortality one-half mile below Shellhammer tile outfall (I-57 Pond) within 48 hours. The experiment of July 19, 1970 showed copper of 8.5 ppm and/or a pH level of 3.3 to apparently cause 100 percent mortality within 24 hours. Mortality of fish naturally occurring in the creek and I-57 Pond below the tile outfall is shown in table 2. Copper, chromate, and/or an extremely acidic pH was evidently responsible for one of the fish kills while very alkaline pH levels and/or high sulfate levels accounted for the three remaining fish kills. No fish were observed (thru May, 1971) in the Shellhammer tile basin or in the creek leading to I-57 Pond after the large kill of November 24, 1970. The following species were identified following the four fish kills:

Green Sunfish - *Lepomis cyanellus*
Bluegill - *Lepomis macrochirus*
Creek Chubsucker - *Erimyzon oblongus*
Creek Chub - *Semotilus atromaculatus*
Stoneroller - *Campostoma anomalum*
Redfin Shiner - *Notropis umbratilis*
Black Bullhead - *Ictalurus melas*

Dead test and natural fish exposed to copper and chromium effluents were noted to have a rather heavy mucus layer over the gill filaments and body surface. Fish which succumbed to very acidic and alkaline pH levels were noted to have badly ruptured gills as well as heavy strands of mucus extending from the body covering.

Other biota observed to be adversely affected by the tile effluent were algae, crayfish, and muskrats (*Ondatra zibethicus*). Massive amounts of *Ulothrix* were observed in the basin below the tile prior to the start of heavy copper and chromate dumping in July of 1970. Within a week after the increased pollution began, no living algae were observed in the tile area. Algae samples taken during the spring of 1971 showed the following genera to be present in the basin: *Ulothrix*, *Zygnema*, *Stigeoclonium*, *Microspora*, *Spirogyra*, and *Euglena*. *Ulothrix* and *Stigeoclonium* were the only two genera which were present in abundant amounts. The six above mentioned genera of algae survived copper concentrations ranging from 0.10 - 2.50 ppm during the spring of 1971, not to mention oil pollution, and on one occasion a sulfate concentration of 480 ppm. In addition to the algae, dead crayfish and muskrats (2) were observed on several occasions during the pollutional peak of July 1970.

Oil and other petrochemical pollution was noted in the Shellhammer tile effluent during the spring of 1971. No testing of this constituent was conducted due to lack of required instrumentation. There were no immediate detrimental effects of this pollutant on aquatic life observed.

A comparison is made in table 3 of maximum allowable concentrations vs maximum concentrations of pollutants determined in the Shellhammer tile effluent. This table clearly demonstrates the extremeness of the pollutional problems encountered.

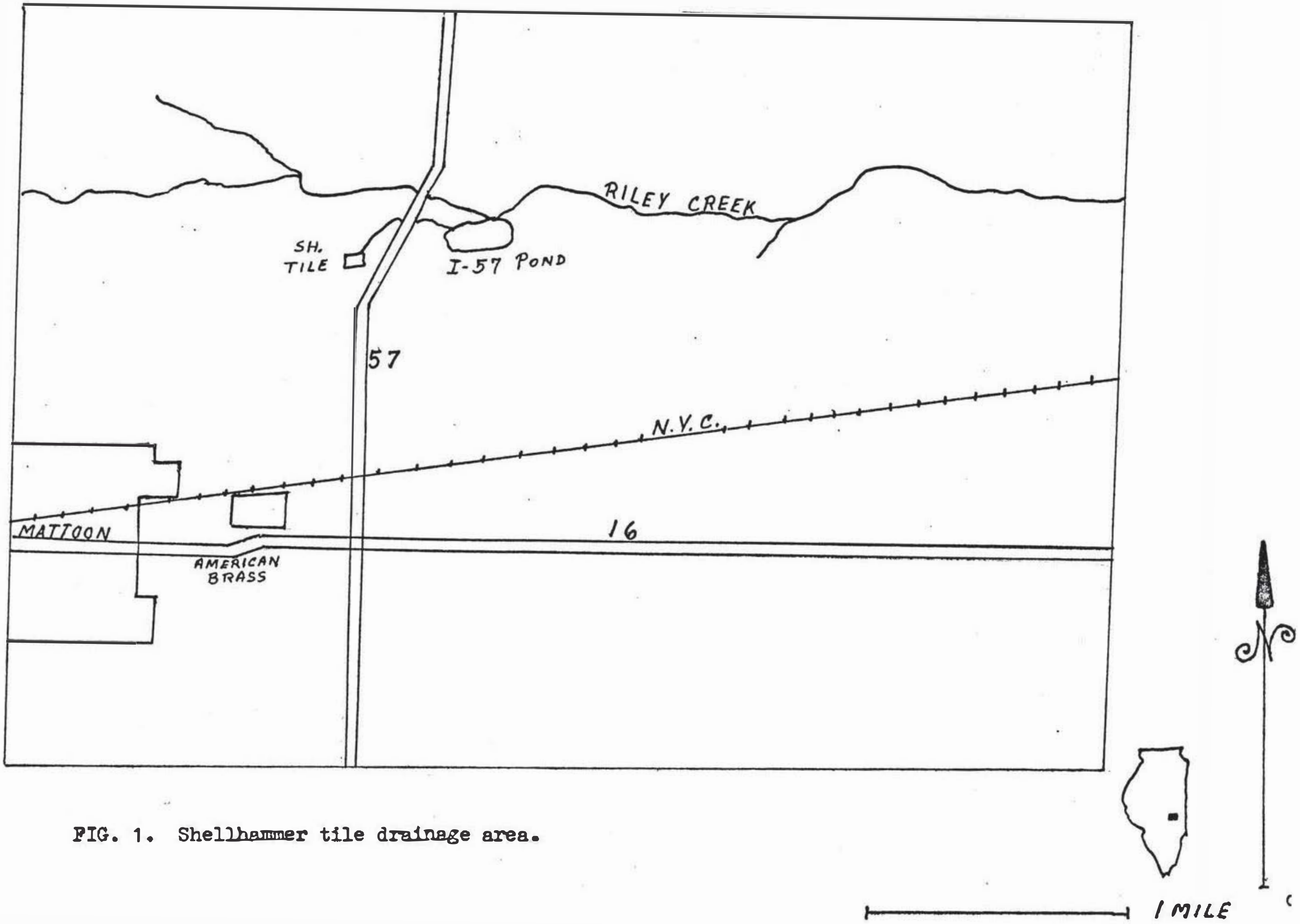

FIG. 1. Shellhammer tile drainage area.

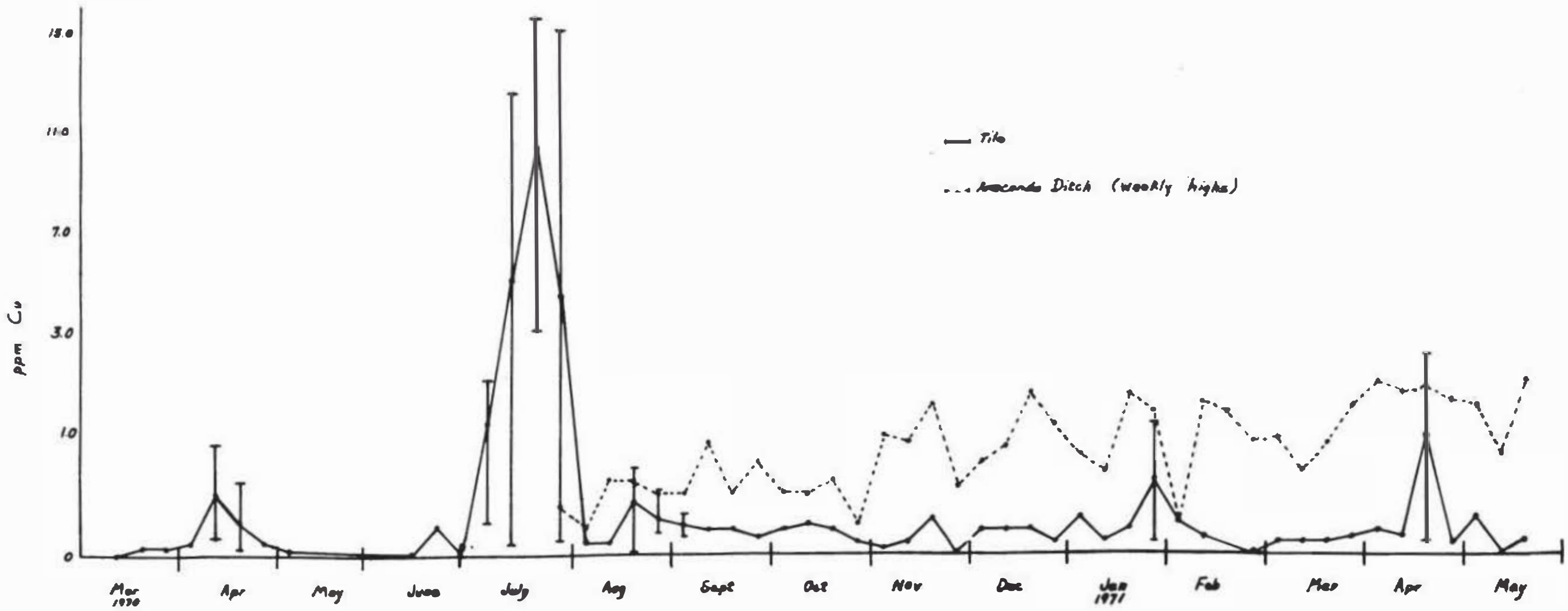

FIG. 2. Copper concentrations determined at Shellhammer tile and Anaconda ditch.

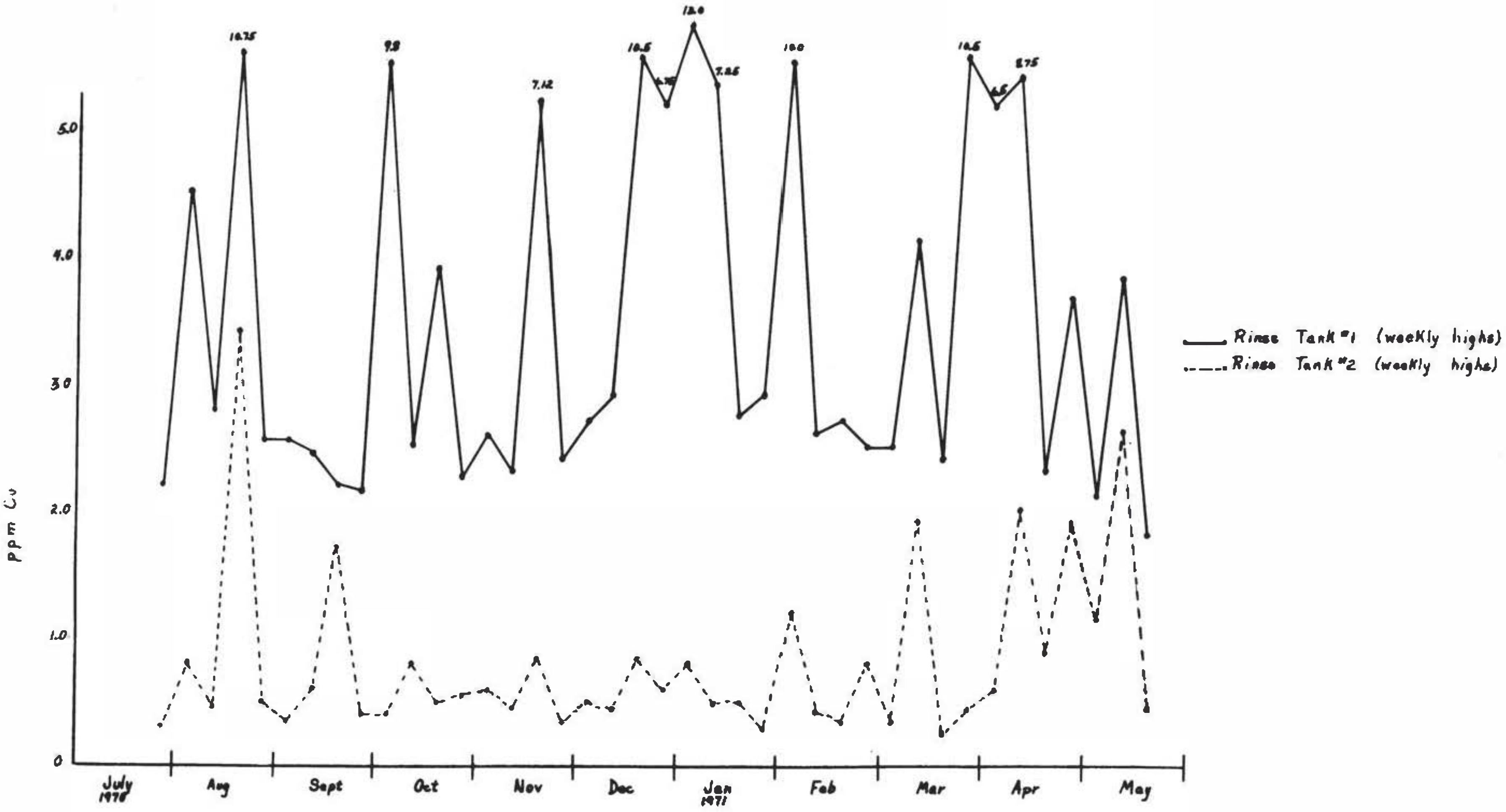

FIG. 3. Copper content of two rinse tanks in Anaconda plant.

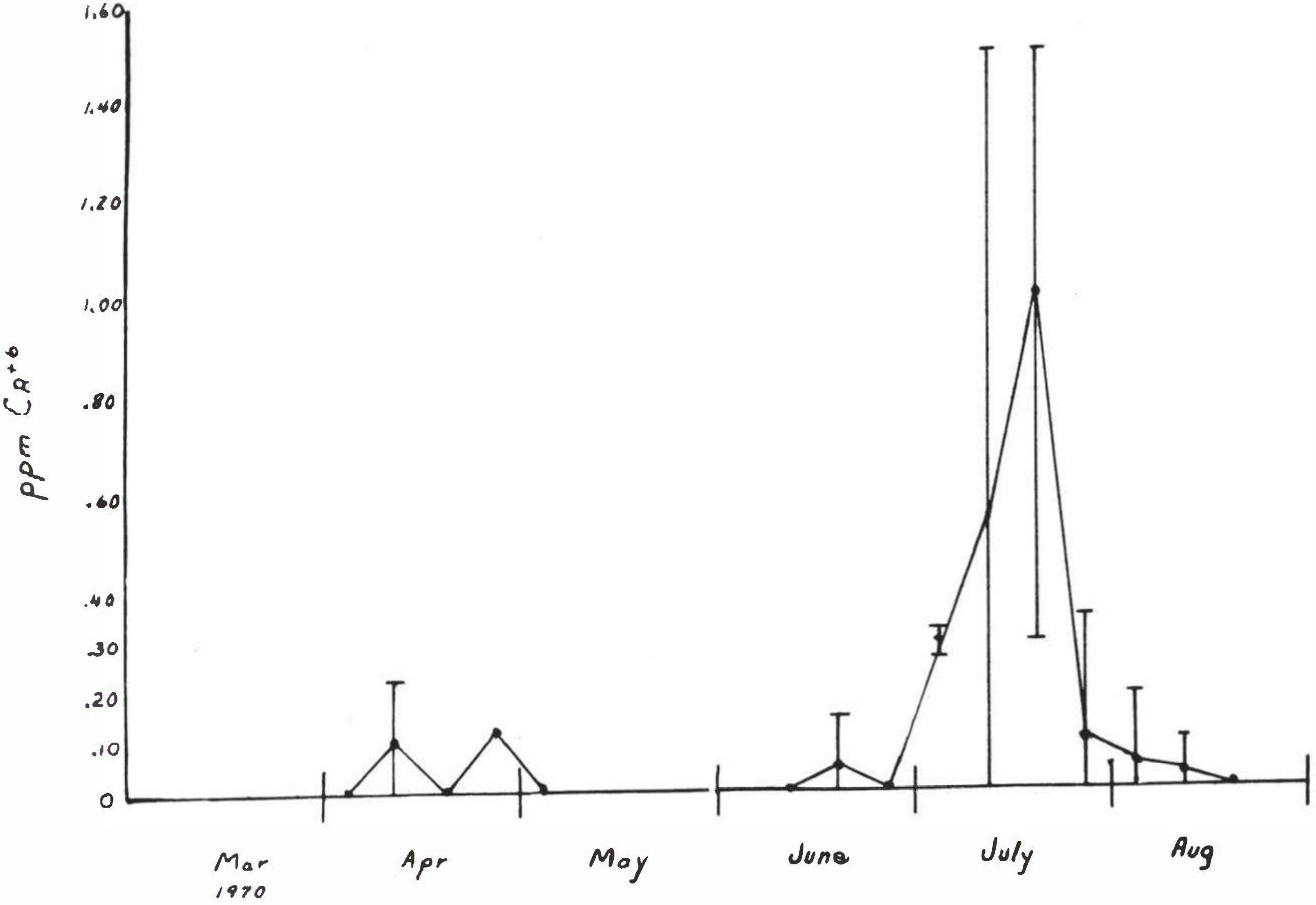

FIG. 4. Hexavalent chromate levels determined at Shellhammer tile.

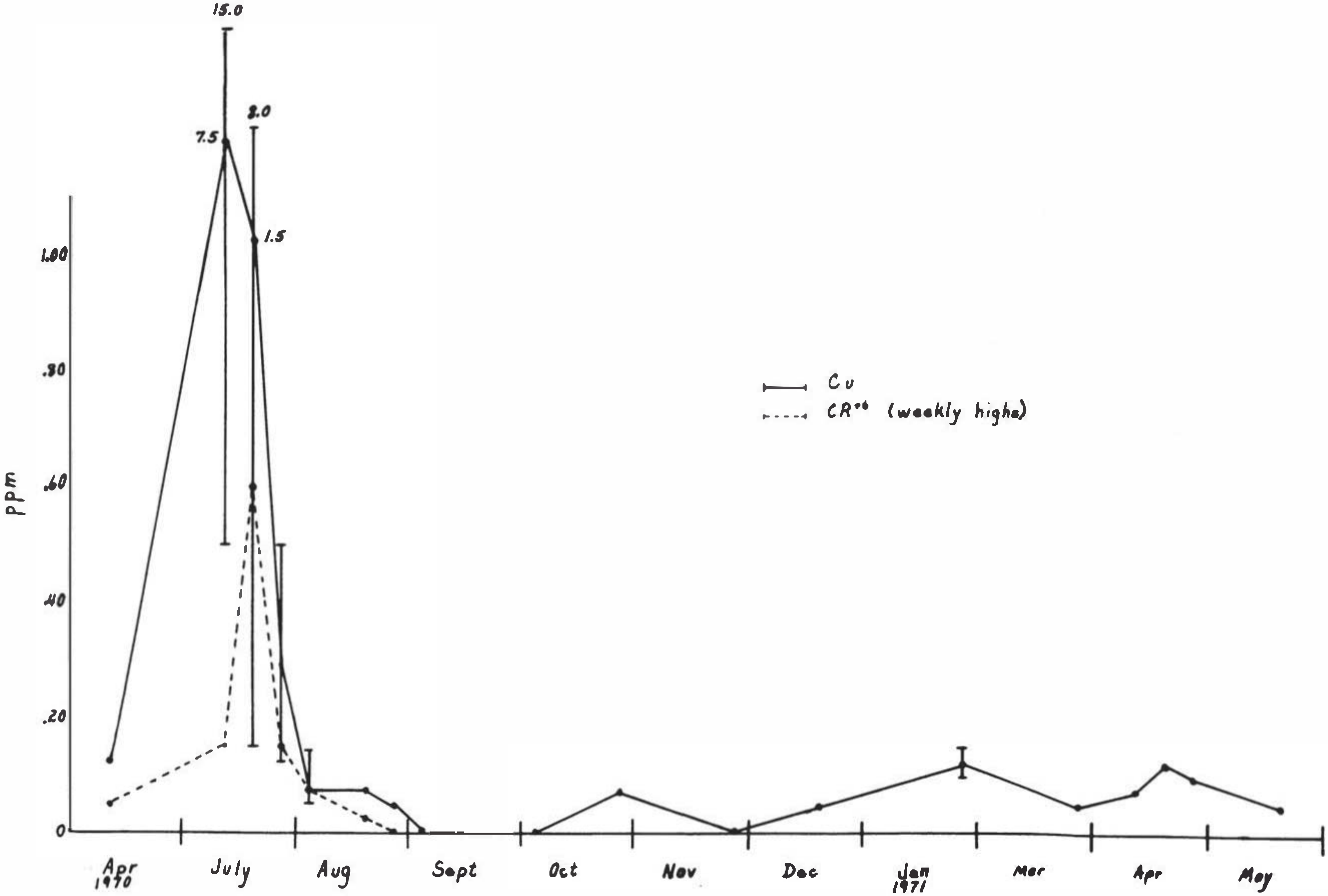

FIG. 5. Copper and hexavalent chromate levels in I-57 Pond.

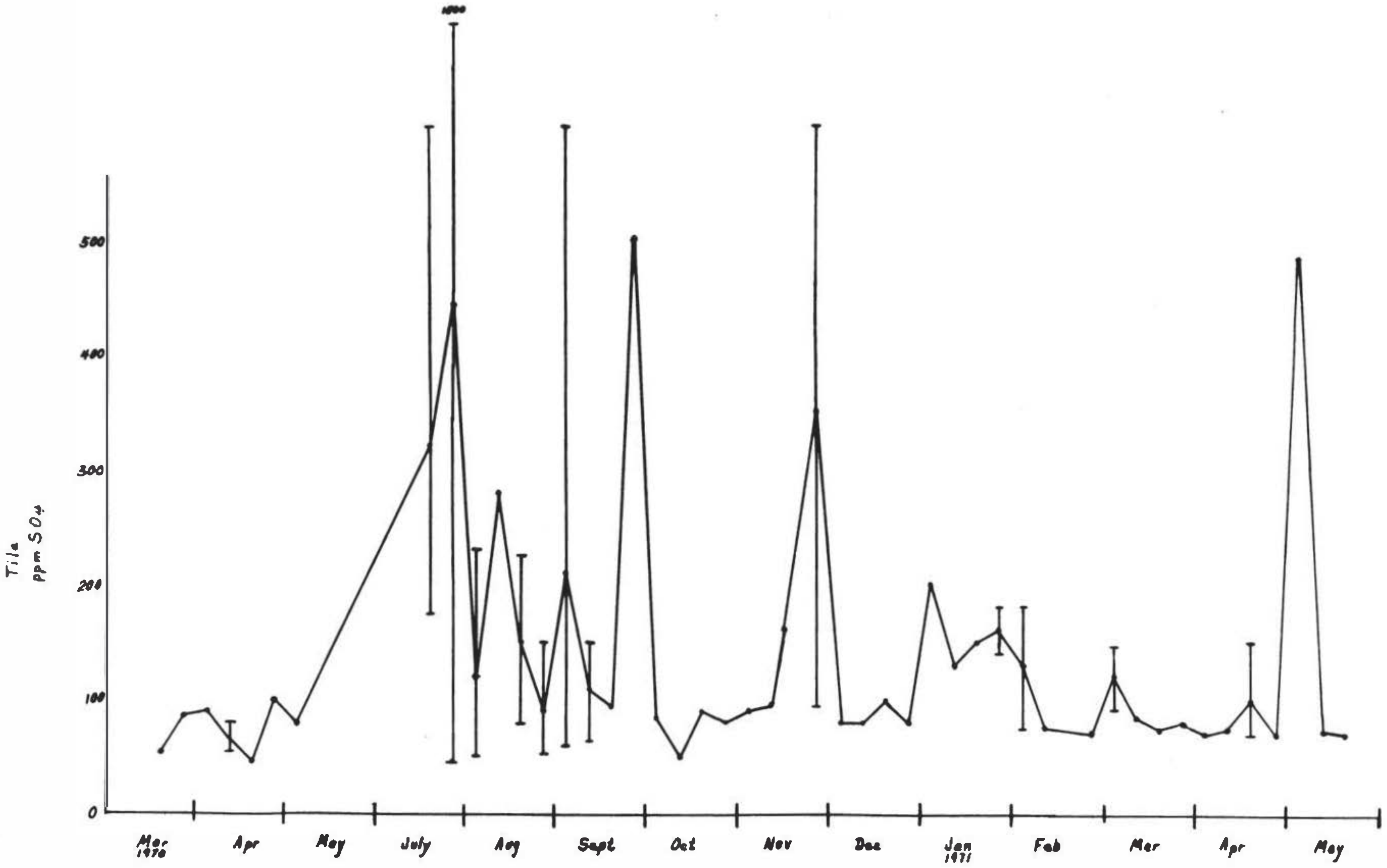

FIG. 6. Sulfate levels of Shellhammer tile effluent.

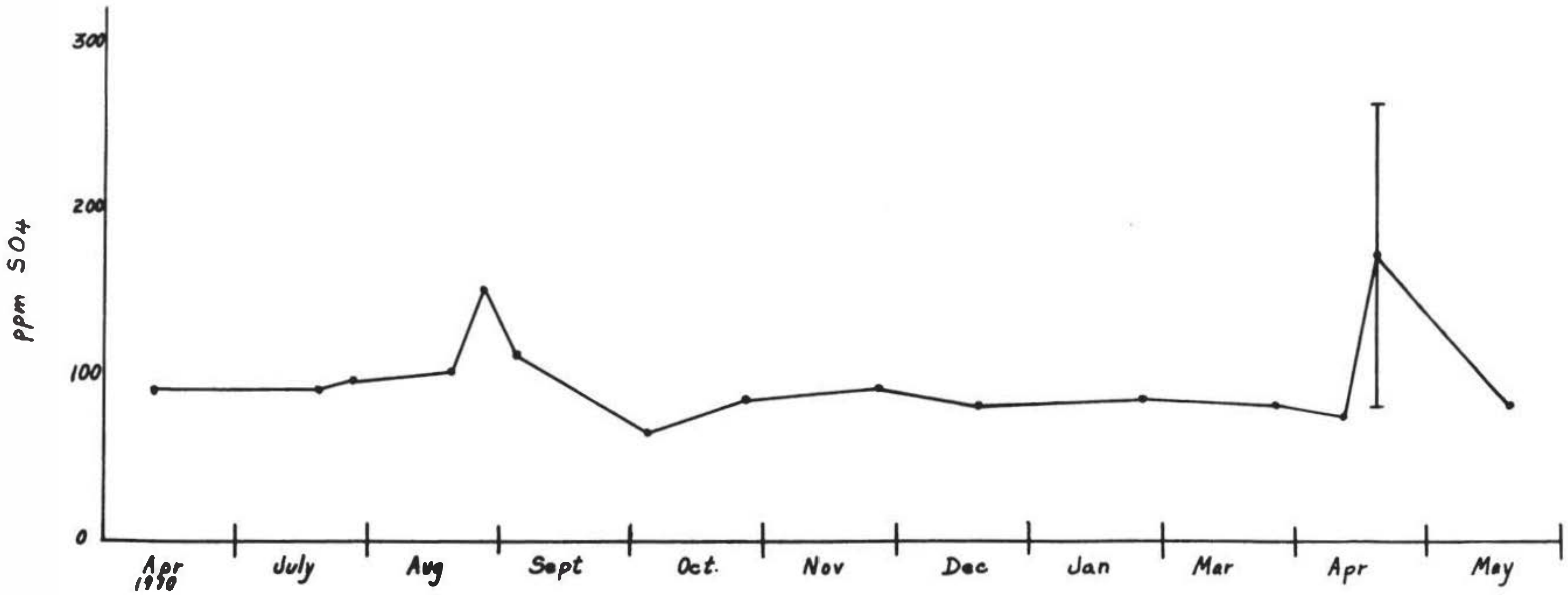

FIG. 7. Sulfate levels in I-57 Pond.

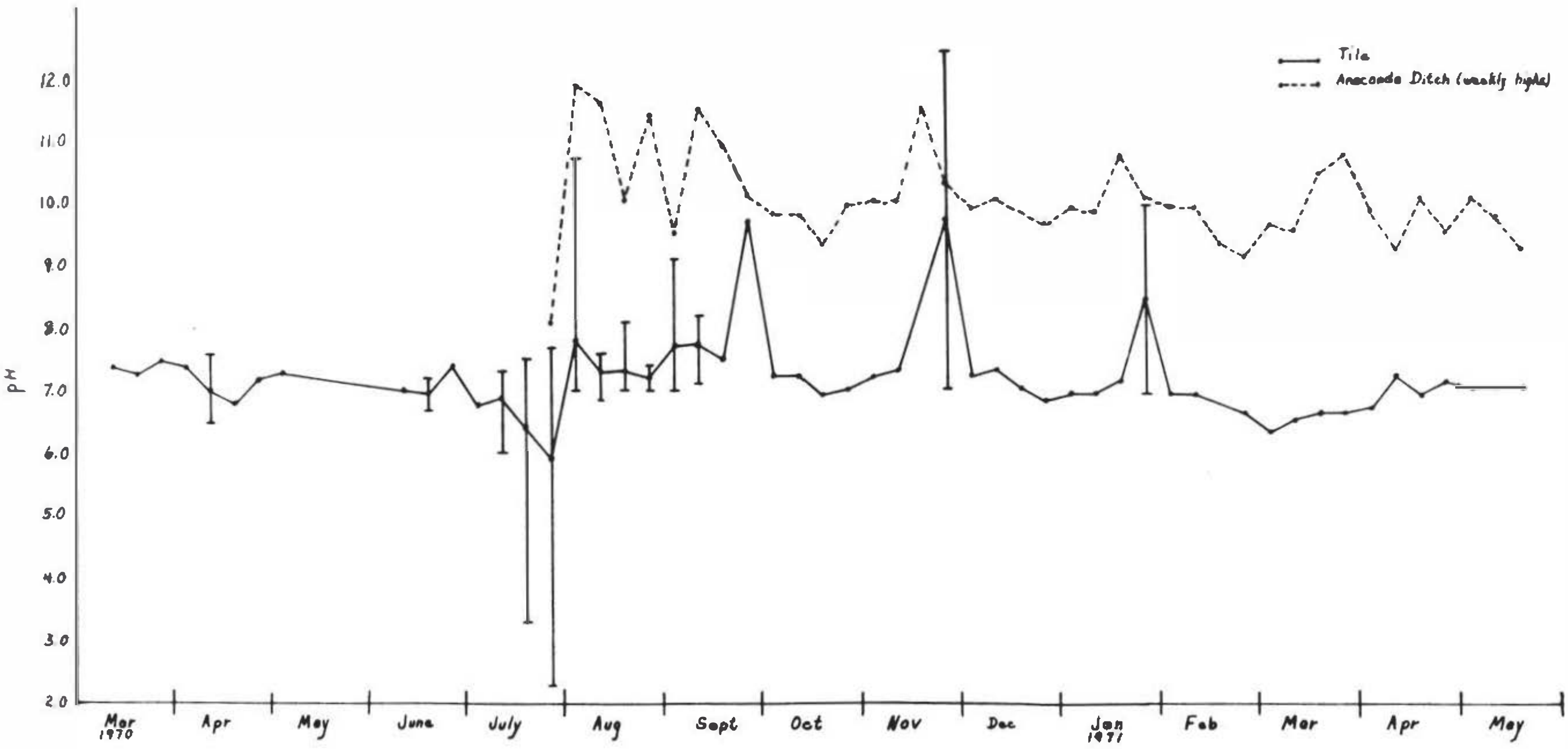

FIG. 8. PH levels of Shellhammer tile and Anaconda ditch.

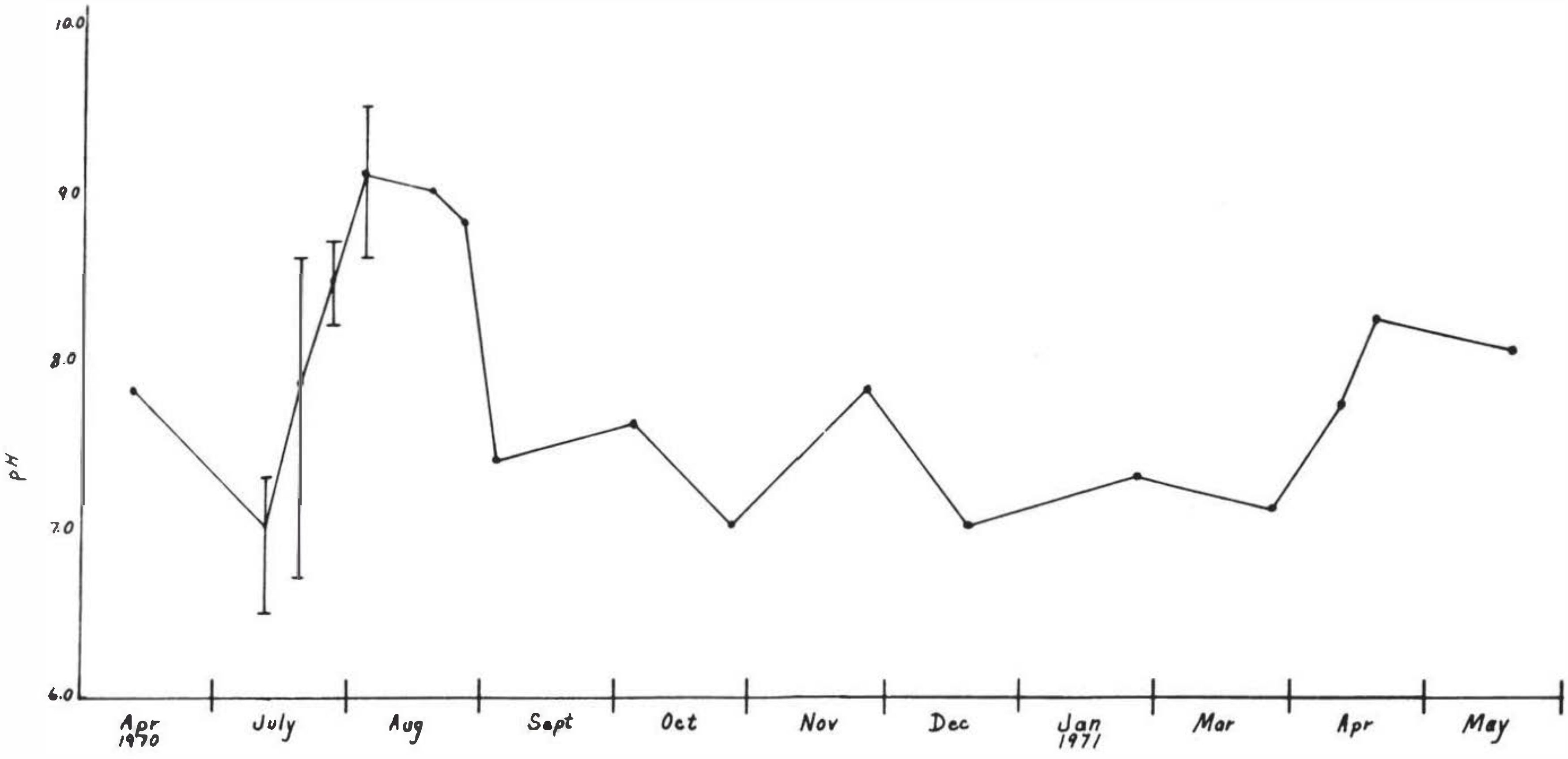

FIG. 9. PH levels in I-57 Pond.

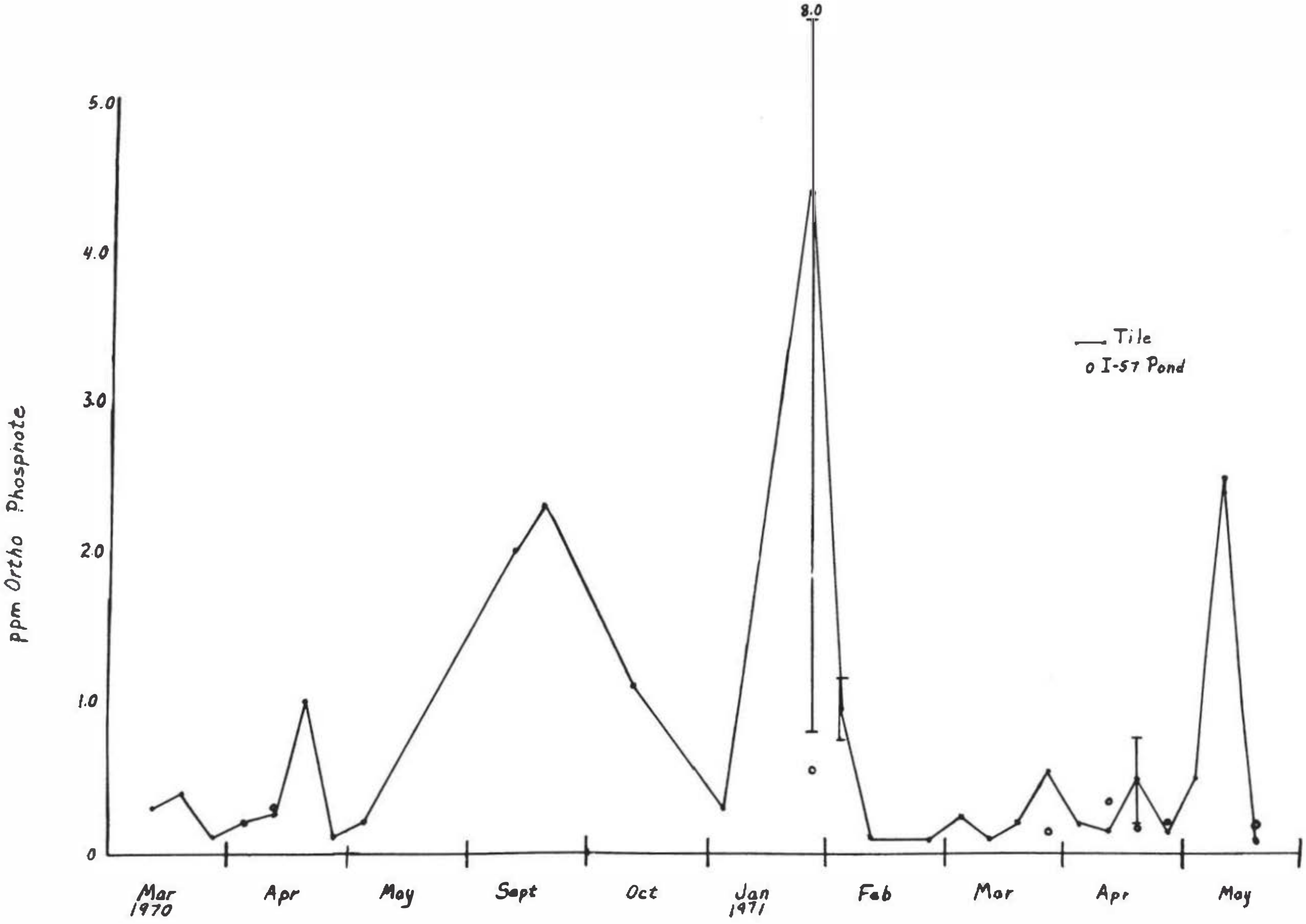

FIG. 10. Ortho phosphate levels occurring in Shellhammer tile and I-57 Pond.

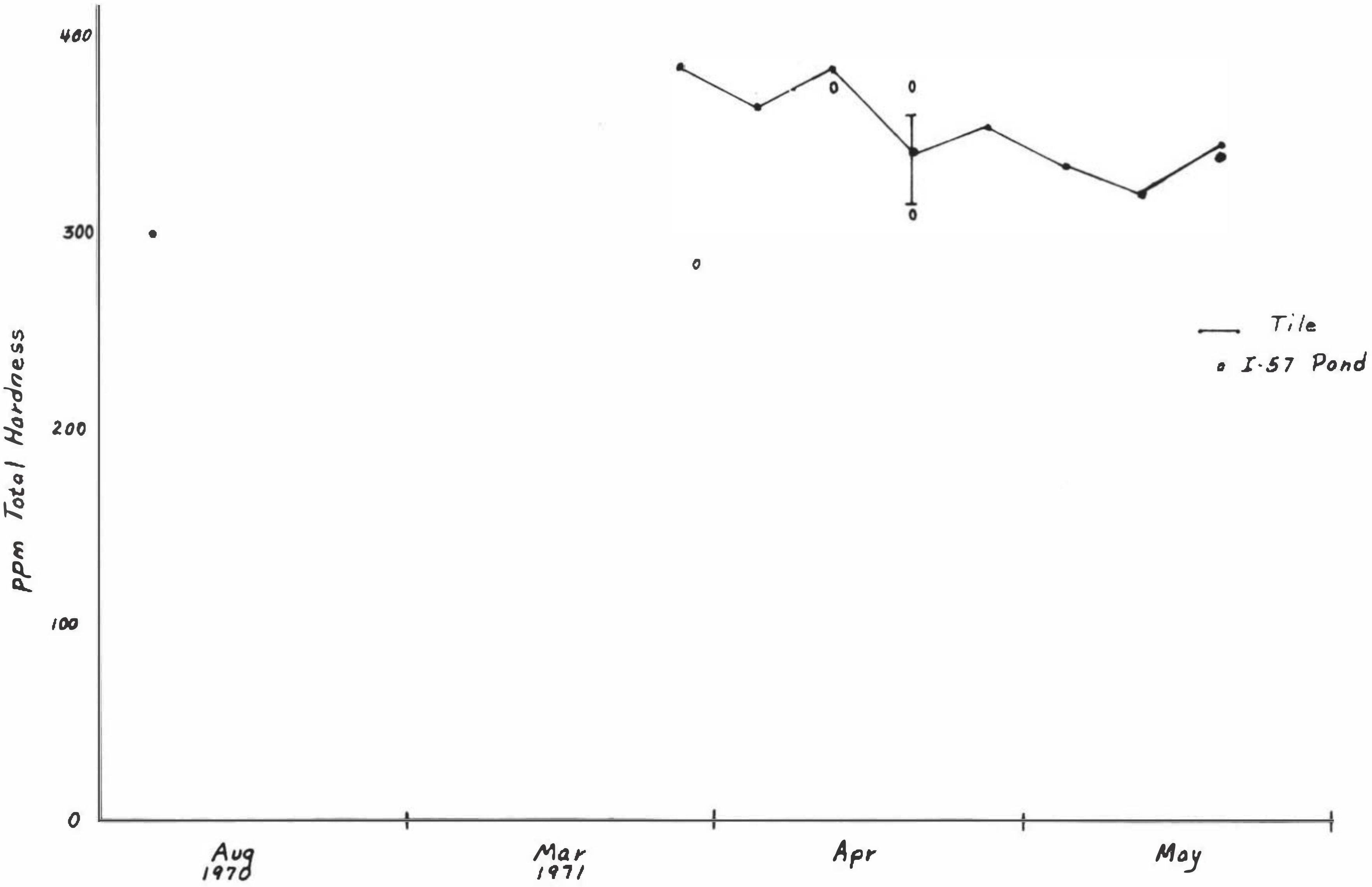

FIG. 11. Total hardness levels in Shellhammer tile and I-57 Pond.

Table 1. Practical Toxicity Bioassay of Anaconda Effluent using Semotilus atromaculatus as the test species.

	Basin				I-57 Pond				Control			
Date	pH	Cu	Cr	M*	pH	Cu	Cr	M*	pH	Cu	Cr	M*
7-13-70	6.0	12.5	1.45	0	7.4	15.00	0.02	0	7.5	0	0	0
24 hrs.	7.0	10.0	0.70	0	7.3	0.50	0.14	80	7.5	0	0	0
48 hrs.	7.4	5.5	0.85	80	6.7	8.00	0.20	100	7.4	0	0	0
72 hrs.	--	4.2	0.85	100	--	--	--	--	--	--	--	0
7-19-70	--	--	--	0					--	--	--	0
24 hrs.	3.3	8.5	0.28	100					7.5	0	0	20

* Mortality (%)

Table 2. Fish kills caused by Anaconda Effluent in 1970.

		Basin and Creek					I-57 Pond			
Date	pH	Cu	Cr	SO_4	Dead Fish	pH	Cu	Cr	SO_4	Dead Fish
7-20-70	3.3	8.5	0.28	600	22	8.4	0.3	0.28	--	-0-
8-5-70	10.7	--	--	50	49	8.6	0.05	0.04	--	-0-
8-7-70	8.7	0.1	-0-	130	12	9.5	0.05	0.04	--	-0-
11-24-70	12.4	0.3	-0-	600	310	7.8	-0-	-0-	90	5

Table 3. Allowable Concentrations of Pollutants vs Maximum Concentrations determined at Shellhammer tile.

Constituent	Maximum Allowable Concentration	Shellhammer tile Maximum Concentration	Specifications
Cu	0.1 ppm	15.5 ppm	Industrial Effluent Criteria
Cr^{+6}	0.05	1.5	Industrial Effluent Criteria
SO_4	200.0	1500.0	Public Drinking Water Criteria
PO_4	4.0	8.4	Public Drinking Water Criteria
Detergents	0.5	1.25	Public Drinking Water Criteria
Oil	Substantially free of visible floating oil	Heavy oil slick	Industrial Effluent Criteria
pH	6.0-10.0 pH	2.3-12.4 pH	Industrial Effluent Criteria

Criteria from Anon., (1967b) and Anon., (1968a)

DISCUSSION

Copper

From the data presented it is clear that the Shellhammer tile area is highly polluted due mainly to effluent resulting from the Anaconda American Brass Company. Further, it is obvious that the biota below the tile has been severely and adversely affected.

Water Quality Criteria (Anon., 1968b) lists copper as being essential for the respiratory pigments in the blood of certain mollusks, crustacea, and annelids. However, in excess this metal is highly toxic to fish, algae, seed plants, and invertebrates. Jones (1938) cites copper as one of the most commonly occurring metallic polluting elements in fresh waters. Levels of copper in surface waters higher than 0.02 ppm are usually attributable to industrial effluents, the use of copper compounds for control of undesirable aquatic organisms and plants or to the corrosive action of water on copper and brass tubing (Anon., 1968b; Kopp and Kroner, 1968).

The copper and chromate effluents considered in this paper resulted from the process used by the Anaconda plant for pickling and polishing their brass hose connections via a dipping process. The hose connections are submerged in a solution of sulfuric acid (pickling tank) to remove oxide scale and other impurities. After pickling, the hose connections are dipped in an adjoining tank containing a chromate cleaner for polishing and brightening purposes. The contents of these two tanks were of no concern as their contents are eventually disposed of thru a chemical disposal company. However, there is a third step in Anaconda's operation which involves rinsing excess chromate and acid from the hose connections. Naturally, copper and chromate are deposited in these two rinse tanks via drag-off. The set procedure (prior to August, 1970) was then to drain these rinse tanks periodically into a small ditch which eventually emits at Shellhammer tile a mile or so away. Wise, et al. (1947) notes that the above process is one commonly used by the copper and brass industry.

Only on 11 of the 100+ sampling dates was the Shellhammer tile effluent found to meet the prescribed copper level of 0.1 ppm. The Anaconda plant has greatly reduced the copper pollution problem in the last year, however, and will soon completely remove all copper from their plant effluent via a copper precipitation process. The speed with which the copper, chromate, and acid pollutants were either reduced or eliminated in the Shellhammer tile drainage system was in no small part due to adverse reports in local newspapers concerning the pollutional problems in July, 1970.

The physiological effects on fish in this study by the copper effluent at Shellhammer tile correlate well with findings by Carpenter (1930), Jones (1935), Ellis (1937), Doudoroff and Katz (1953), and Pickering and Henderson (1964). These authors have attributed the death of fish in solutions of heavy metals chiefly to the coagulation or precipitation of mucus secreted by the gills, or damage to the gill tissues. A chemical reaction takes place between the metallic base and an organic constituent of the mucus secreted by epithelial cells. The resulting product is a colloidal substance which forms a film over the body surface and the gill filaments (Carpenter, 1930). These insoluble metal-protein compounds formed are believed to interfere with respiratory functions of the gills and thus bring about death by suffocation (Carpenter, 1930; Jones, 1935; Ellis, 1937; Doudoroff and Katz, 1953).

On several occasions, small Centrarchids were noted to move away from the copper-chromate pollutant at Shellhammer tile. Avoidance of copper by salmon was studied in the laboratory by Sprague (1964a). His studies demonstrate that salmon avoid water concentrations of copper as low as .004 - .005 ppm. These changes in behavior demonstrates a sublethal stress by pollutants.

Unfortunately, other sublethal effects of the various pollutants were not considered in this study. However, temporary survival of aquatic organisms is meaningless if they fail to reproduce, have poor growth, and exhibit aberrant behavior patterns (Shirer, et al., 1968). Cairns (1966) suggests that alterations of fish breeding behavior may as effectively destroy the species as killing it outright.

Members of the family Salmonidae were found to be severely affected in copper levels of about .050 ppm or more in waters of low hardness by Lloyd and Herbert (1962), Sprague (1964b), and Sprague (1968). The incipient lethal level of .050 ppm Cu for fathead minnows, Pimephales promelas, in softwater (Tarzwell and Henderson, 1960) is similar to resistence levels cited above for the salmon family. Fathead minnows were exposed to copper sulfate in hard water for 11 months by Mount (1968) and he found that 3-7 percent of the 96-hr. TLm value does not affect the growth and reproduction under prolonged, continuous exposure in hard water. Mount's experiments reveal the 96-hr. TLm concentration for these minnows to be .430 ppm Cu.

A representative of the sunfish family, the common bluegill, seems much more resistant to copper than other fish families previously discussed. An incipient lethal level of .210 ppm (in soft water) was found for bluegills by Tarzwell and Henderson (1960). Tests with the bluegill by Pickering and Henderson (1964) show a 96-hr. TLm of 0.66 ppm Cu in soft water and a 96-hr. TLm of 10.2 ppm Cu in hard water.

No direct correlation can be made with the above cited tolerable copper levels since there were always two or more pollutants to consider in the Shellhammer tile effluent. The literature revealed no information on copper-chromate synergism or antagonism, although this is a possibility. Obviously, as shown in tables 1 and 2, and figure 2, copper concentrations were high enough on numerous occasions to cause severe stress and/or death to fish species present. Although no natural fish kills were noted in I-57 Pond, the practical toxicity test of July 13, 1970 demonstrates that copper levels in the pond were high enough on occasion to cause fish mortality.

Hasler (1947) reports (from Churchill, 1946) that the addition of copper to mixed cultures of algae in a Wisconsin lake greatly altered the composition of the population, since the free floating, unicellular plankton algae were all killed by 0.25 ppm Cu (some were killed at 0.08 ppm), while the filamentous forms were inhibited by 0.33 ppm but were not killed at concentrations less than 0.66 ppm. Maloney and Palmer (1956) relate that 0.5 ppm copper as copper sulfate produced 57 percent mortality in seven species of blue-green algae, 35 percent mortality in 17 species of green algae, and 100 percent mortality in six species of diatoms. Although growth may have been inhibited, the following six genera of green algae survived copper concentrations of 0.10 - 2.50 ppm directly below the Shellhammer tile during the spring, 1971: Ulothrix, Zygnema, Stigeoclonium, Microspora, Spirogyra, and Euglena. Massive amounts of Ulothrix died as a result of heavy copper and/or chromate levels during July, 1970. Due to the high levels of both pollutants and the fact that they were mixed together in the tile effluent, it is again impossible to state at what concentration copper and/or chromate became harmful to these algal species.

Chromium

Chromium is present in igneous rocks in nature in minor amounts. The process of weathering results in very little chromium going into solution unless the pH is low (Knoll and Fromm, 1960). Thus, natural chromates are rare and when found in water usually indicate industrial pollution (Kopp and Kroner, 1968). As mentioned earlier, chromium compounds are often present in wastes from many industrial processes relating to the copper and brass industry.

The hexavalent chromium concentration of United States drinking water has been reported to vary between 0.003 and 0.04 ppm with a mean of 0.0032 ppm. Protection of a potable water supply against the intrusion of hexavalent chromium is very necessary due to its carcinogenic potential (Anon., 1965). The limit for hexavalent chromium is 0.05 ppm in both drinking water (Anon., 1967b) and industrial effluents (Anon., 1968a).

The effects of the inorganic salts sodium dichromate and sodium chromate on the internal water balance of the bluegill were studied by Abegg (1950). Sodium dichromate was found to cause an increase in the tissue-fluid content of the musculature as well as causing the precipitation of the mucus covering the body. Fromm and Schiffman (1958) observed that less than 100 ppm Cr invariably caused significant physiological changes in the intestine of the largemouth bass, *Micropterus salmoides*, and death in 80 hours. The above described physiological changes were not directly observed in fish affected by the chromium-copper effluent at Shellhammer tile. As mentioned earlier, sloughing of mucus was observed but this was presumably due to high copper concentrations and/or very acidic pH levels.

According to the literature, the maximum hexavalent chromate levels recorded in the hard waters of Shellhammer tile (1.5 ppm) were not high enough to cause fish mortality. Abegg (1950) worked with the bluegill sunfish and found the 24-hr. TLm for sodium dichromate to be 728 ppm. Cairns and Shirer (1959) found the experimental 96-hr. TLm concentration for dichromate for the bluegill to be 320 ppm in soft water at both 18° and 30° C., 382 ppm in hard water at 18° C. and 369 ppm in hard water at 30° C. Thus, the toxicity of dichromate was affected more by the degree of hardness of the water than by the temperature. In a study done by Pickering and Henderson (1964) the 96-hr. TLm values of potassium dichromate for the bluegill were determined to be 118 ppm Cr in soft water and 133 ppm Cr in hard water.

The above mentioned studies dealing with chromium toxicity vividly demonstrates the need for more standard conditions in bioassays concerning this heavy metal. With so much confusion in the literature, one would be best advised to determine his own 48-or 96-hr. TLm on the effluent in question.

Information in the literature relating to toxic effects of chromium on algae is almost non-existent. Problems associated with determining exact toxic levels of the chromium-copper effluent have been previously discussed.

Acids and Alkalies

It is well known that a pH range of 5.0 - 9.0 is not usually lethal for most freshwater fishes (Mackenthun, 1969). There is no definite pH range within which fish are harmed, but there is a gradual deterioration as the pH values progress either up or down from their normal range. The toxicity of many common pollutants can be dramatically increased by pH changes. PH values in the Shellhammer tile effluent ranged from 2.3 - 12.4 during the study period. The acidic effluent alone or in combination with copper and chromate resulted in several fish kills while a highly alkaline effluent (12.4 pH) in November of 1970 was apparently solely responsible for the death of at least 310 fish.

Ellis (1937) studied experimentally the survival of goldfish, *Carassius auratus*, in natural hard waters acidified to various pH values with eleven mineral and organic acids found in industrial wastes. His data show that mortality was always observed within a few hours when the pH values were 3.4 - 4.0 (or lower), whereas none occurred in four days when the pH values were 4.5 - 4.9 (or higher). Field observations at Shellhammer tile support the conclusions of Ellis.

The use of excessive amounts of caustic soda by Anaconda in neutralization of waste sulfuric acid resulted in extremely high pH levels on several occasions. None of the strong alkalies which are important as industrial wastes (sodium hydroxide, potassium hydroxide, calcium hydroxide) have been clearly shown to be lethal to fully developed fish in natural fresh waters when their concentrations are insufficient to raise pH well above 9.0 (Doudoroff and Katz, 1950). A pH increase from 10.70 to 10.82 (due to sodium hydroxide) was found by King (1943) to cut survival time in half for three species of trout.

One aspect not considered in this study was the suspended solids effect of the sulfuric acid - caustic soda mixture (at or near pH 7.0) on fish in the Shellhammer drainage area. Toxicity of sulfuric acid neutralized with slake lime to channel catfish, _Ictalurus punctatus_, was studied by Sparks, _et al._ (1969) both in the laboratory and in the field. Results of their limited study showed that 10 of 15 channel catfish survived in synthetic waste water for 22-28 days when a suspended solids concentration of 367-509 mg/1 was maintained by moderate aeration. Eleven of 12 catfish survived 22-28 days in synthetic waste from which all setteable solids were removed. Particles in the neutralized mixture were found to mechanically irritate the gills of fish and cause sloughing of mucus from the body and gills.

Perhaps this unexplored factor of high suspended solids was also in part responsible for the degradation observed in the aquatic community below Shellhammer tile.

Oil

Oil is mentioned here due to the severity with which it was emitted from Shellhammer tile for a period of two weeks during April, 1971. Unfortunately no testing of this pollutional constituent was performed due to lack of needed laboratory equipment. However, visual observations mark it as a major pollutional source whose origin was not determined. Possible sources of this pollutant in the Shellhammer tile area are pipe line leaks, gasoline filling stations, bulk stations, chemical transport companies, and industrial waste such as oil, grease, and fats from the lubrication of machinery.

Water Quality Criteria (Anon., 1968b) states that "oil or petrochemicals should not be added in such quantities to the receiving waters that they will -

1. produce a visible color film on the surface;
2. impart an oily odor to the water or an oily or other noxious taste to fish and edible invertebrates;
3. coat the banks and bottoms of the water course or taint any of the associated biota;
4. become effective toxicants according to the criteria recommended in the toxicity section".

Rule 1.03 in Water Quality Standards (Anon., 1967b) lists similar minimum conditions. The petrochemical effluent noted at Shellhammer tile failed to meet any of the above listed requirements. This effluent possibly was responsible for undetected adverse effects on fish and other aquatic life in I-57 Pond as the surface was covered with a scum for several days.

Wiebe (1935) conducted experiments with bass and bream in crude oil and found that death was a result of a film of oil being deposited over the gill filaments. Pickering and Henderson (1966) studied the acute toxicity of several important petrochemicals to fathead minnows, goldfish, and guppies in both soft and hard water.

Films of oil on the surface interfere with the respiration of aquatic insects (Anon., 1968b). Oil may also coat and destroy algae and other plankton and if it settles may coat the bottom, thereby destroying benthic organisms and spawning areas. Even when settled on the bottom, oil continuously yields water-soluble substances that are toxic to aquatic life (Anon., 1968b).

Phosphates and Detergents

Phosphorus is an essential element for aquatic life as well as for all forms of life (Anon., 1968b). Phosphorus as such is a poison and is virtually insoluble in water. However, since it is highly oxidizable it combines in water in oxide form with bases present to form phosphates, which, with nitrates are requirements for making proteins (Coker, 1954).

The major sources of phosphorus entering fresh waters are domestic sewage effluents (including detergents), animal and plant processing wastes, fertilizers and agricultural runoff, and various industrial effluents (Anon., 1968; Bartsch, 1970).

One or more of the industrial complexes draining to the Shellhammer tile area was undoubtedly responsible on several occasions for excessive phosphate levels (8.0 ppm maximum). Although the author received reports to the contrary from farmers living near the drainage tile, phosphates did not appear in this study to constitute a major eutrophication threat to I-57 Pond. Mackenthun (1969) defines eutrophication as " a term meaning enrichment by nutrients through man-created or natural means. Present knowledge indicates that the fertilizing elements most responsible for lake eutrophication are phosphorus and nitrogen". The accelerated process of enrichment results in superabundant growth of algae which upsets the balance in plant and animal life, reduces the aesthetic qualities and economic value of the body of water, and destroys precious water resources (Prescott, 1948; Hasler, 1969; Mackenthun, 1969).

Phosphate detergents undoubtedly contributed to the phosphate levels at Shellhammer tile. On one occasion, a sample taken behind the Anaconda plant revealed a level of 4.5 ppm ABS and/or LAS detergents. Detergents readings the same day at Shellhammer tile showed a level of 1.25 ppm ABS and/or LAS.

Detergents can kill fish and because of their phosphate content they contribute to the cultural eutrophication problem. Pickering (1966) notes that the conversion of the detergent industry of the United States from the use of alkyl benzene sulfonate (ABS) to the more readily biodegradable linear alkylate sulfonate (LAS) has not necessarily reduced this pollutional problem. Even though a detergent may be biodegradable, its pollutional potential is not necessarily less than that of a hard detergent.

Several workers have investigated the toxicity of ABS and/or LAS type detergents to various species of fish. Henderson, et al. (1959) reported that the 96-hr. TLm value of ABS for bluegill in soft water was 5.6 ppm. Thatcher (1966) determined the 96-hr. TLm's of a typical LAS detergent to five species of freshwater fish while Thatcher and Santner (1966) worked with the same five fish species in determining the 96-hr. TLm's of a typical ABS detergent. Results of these two studies show LAS to be two to four times more toxic than ABS.

Sulfates

The waste acid dumped into the Shellhammer tile drainage caused excessive sulfate levels on a number of occasions. Levels of sulfate ranged from 45 - 1500 ppm throughout the course of this study. Although information relating to sulfate toxicity in the literature is almost totally lacking, a discussion of sulfate sources is in order. An abnormally high sulfate level is usually indicative of industrial pollution, as from pulp mills, paper mills, and coal mines (Coker, 1954). In natural waters sulfates are chiefly derived from the oxidation and partial solution of iron pyrites found in igneous rocks. Water Quality Standards (Anon., 1967b) lists 200.0 ppm SO_4 as the maximum allowable concentration in public drinking water supplies.

Although not a final component of chlorophyll, sulfur promotes its formation (Coker, 1954) and therefore contributes to the eutrophication problem. I-57 Pond evidently does not receive enough volume of the high sulfate effluent to cause major problems as no algal bloom was noted during the summer of 1970. However, another possible explanation is that both sulfate and phosphate levels were high enough to cause algal blooms but the copper levels in the pond were high enough to control algal growth.

CONCLUSIONS

The main purpose of this paper was to present the history, causes and effects of an industrial effluent containing sundry contaminates. Besides the obvious degradation of the fauna and flora in the receiving waterway, this study brings to light once again the lack of understanding and/or responsibility of the permissable effluent concentrations and the hazards created when they are exceeded. All too often dependence upon dilution of concentrated baths with other plant wastes and by the receiving waterway has been the only method of waste disposal. This unquestionably was the case in this water quality study. Also, the use of agricultural field drainage systems for the disposal of industrial wastes should be prevented.

LITERATURE REVIEW

Introduction

The literature dealing with toxicity to aquatic life is often confusing and misleading as bioassays are conducted under a variety of conditions. Variables such as the species of fish or alga used in the determinations, temperature, pH, and hardness of the solution used account for a great deal of the confusion (Doudoroff and Katz, 1950: Anon., 1968b).

Kopp and Kroner (1968) note that one must recognize that there are not only acute and chronic toxic levels but also tolerable, favorable, and essential levels of dissolved materials. Different developmental or life stages of the same or different species may vary widely in their tolerance to different materials. Substances in suspension as well as in solution may affect aquatic organisms.

Significant information on the character of inflowing wastes is provided by the animals and plants in the receiving waterway (Keup, 1966). Water quality must permit survival for 24 hours a day for 365 days a year for an organism to perpetuate itself. If the aquatic community is severely affected by a short-term exposure to water of poor quality, some time is needed for them to return to their original populations (Keup, 1966). A severely toxic substance will eliminate aquatic biota until dilution, dissipation, or volatilization reduces the concentration below the toxic threshhold (Mackenthun, 1969). The delay involved in immigration and/or reproduction of individuals to replace those destroyed or driven from an area provides the means for a long-term appraisal of water quality. The biota of a stream or lake is thus a natural monitor of water quality.

The effects of pollution assume many characteristics and a great variation in degree in an aquatic environment (Mackenthun, 1969). The volume and strength of the pollutant as well as the size of the receiving waterway control to a great degree the environmental and ecological responses. Whether an industrial waste of a certain concentration is toxic or not is best determined by biological test at the point in question. A practical toxicity bioassay can yield information about the toxicity of a material in question which is more reliable and pertinent than the literature can provide (Doudoroff and Katz, 1950).

Industrial pollutants considered in this review are heavy metals (copper, chromium), acids, alkalies, oil, and detergents. General information regarding sources and forms of these materials is considered individually and is followed in each case by a discussion of its physiological effects on aquatic life, effects of pH, temperature, and hardness on toxicity, and in the case of the heavy metals, a discussion of synergistic and antagonistic actions.

Water pollution was responsible for the fatality of an estimated 41 million fish in 45 states in 1969 (Anon., 1969). Over 144.6 million fish have been reported killed in more than 4200 separate incidents since the FWPCA began their census-taking in June, 1960. Industrial operations were responsible for 70 percent of the fish killed (28.9 million) in 1969. Of these 28.9 million fish fatalities, metals and chemicals accounted for 43,523 and 921,988 respectively. Data compiled in these annual fish-kill censuses are of great significance as they serve to alert the public and the public officials to the need for stricter control and safeguards to keep our nation's water resources free from dangerous substances (Anon., 1969).

Copper - Sources and Forms

Low levels of copper are commonly found in natural water, generally below 0.02 ppm (Kopp and Kroner, 1968). The copper content of drinking water seldom exceeds 0.6 ppm and levels above 1.0 ppm impart a bitter taste to drinking water. Copper is an essential element to the human body and 2.0 mg has been estimated to be the adult daily requirement (Anon., 1965). Ingesting large oral doses of copper may result in liver damage. The public drinking water limit for copper is 1.0 ppm (Anon., 1967b). Copper is not generally considered a hazard to domestic supplies because copper in concentrations high enough to be dangerous to man renders the water undrinkable as far as taste is concerned (Kopp and Kroner, 1968). Water Quality Criteria (Anon., 1968b) lists copper as being essential for the respiratory pigments in the blood of certain mollusks, crustacea, and annelids. In excess, this heavy metal is highly toxic to fish, algae, seed plants, and invertebrates.

Jones (1938) cites copper as one of the most commonly occurring metallic polluting elements in fresh waters. Levels of copper in surface waters higher than 0.02 ppm are usually attributable to industrial effluents, the use of copper compounds for control of undesirable aquatic organisms and plants or to the corrosive action of water on copper and brass tubing (Anon., 1968b; Kopp and Kroner, 1968). The chloride, nitrate, and sulfate of bivalent copper are highly soluble in water but the carbonate, hydroxide and sulfide are not. Thus, an introduction of cupric ions into waters of pH 7 or above will precipitate as the hydroxide or carbonate and will be removed by absorption and sedimentation (Smith, 1935; Doudoroff and Katz, 1953; Kopp and Kroner, 1968).

A wide range of processes used in the metal finishing and allied industries give rise to toxic metallic and acidic effluents. A few of these processes include degrading, pickling, dipping, etching, brightening, and polishing (Lowe, 1970). These processes are usually followed by rinsing operations to remove excess chemicals from the metallic surface, thus giving rise to effluents. Common constituents of these effluents (Lowe, 1970) are alkalies, acids, solvents, oils, greases, and dissolved metals. These processes are used in the preparation, protection and/or decoration of a variety of metal and non-metallic surfaces. Usually a combination of the above mentioned processes is used for achieving the desired effects (Lowe, 1970).

Wise, _et al_. (1947) note that oxide scale on the surface of copper and/or bronze is quite hard and must be removed. The oxide scale is formed following annealing of copper and brass materials such as wire, tubes, and rods. Oxide scale is removed by pickling (Wise, _et al_., 1947; Rodgers, 1959; Lowe, 1970). Pickling involves the use of acids (commonly sulfuric) to remove scale as well as casting residues and other corrosion products from metal surfaces. Subsequent to pickling, remaining stains are removed in a bright dip solution composed of sulfuric acid and sodium dichromate (Lowe, 1970). The metal is rinsed in tanks after remaining in the pickle and bright dip solution for the required length of time. These rinse waters are usually discharged to drains which subsquently result in the effluent entering a creek, stream, river, or lake (Wise, _et al_., 1947).

During the pickling and bright dipping processes (Wise, _et al_., 1947), the scale and a portion of the base metal are dissolved. After a period of time there is a decrease in sulfuric acid concentration and an increase in the concentration of dissolved metal. These pickling and dipping solutions can be renewed to some extent by addition of more acid and dichromate. When a certain point is reached, however, it becomes necessary to replace the solutions and frequently the acid and dichromate solutions are dumped into drains. The frequency of dumping, of course, depends on the amount of metal pickled and brightened as well as on the length of pickling and dipping and the composition of the metal.

Most effluents from these metal treatment processes are strongly acidic and contain appreciable concentrations of metals. Lowe (1970) lists the following as typical of effluents from pickling procedures used in the copper and brass industry.

Sulfuric acid ---------- 250-300 mg/l
Soluble copper as Cu --- 60-90 mg/l
Soluble zinc as Zn ----- 20-35 mg/l
Suspended solids ------- 10-15 mg/l

Regarding copper effluents, the State Water Commission of Connecticut found that in 1941 the brass and copper industries lost 1500 tons of copper via pickling operations (Wise, *et al.*, 1947). These wastes are extremely injurous in relatively small concentrations. There is often a lack of understanding of the permissable limits of concentrations and the hazards created when they are exceeded. All too often dependence upon dilution of concentrated baths with other plant wastes and by the receiving waterway has been the only method of waste disposal. Many instances of pollution have resulted from the lack of responsibility for control and proper disposal of wastes (Oeming, 1946).

Wise, *et al.* (1947) list four effects of copper and brass industrial effluents upon receiving waterways:

1. Degradation of waters used for public water supplies, for industrial, agricultural, and recreational purposes.

2. Acids and metals in solution are toxic to aquatic life, even in small concentrations in soft water; higher concentrations can be discharged into hard waters without exceeding lethal limits.

3. These wastes affect the natural sequence of processes necessary to bring about self-purification of streams.

4. Suspended solids, either in the wastes or formed by chemical reactions in the receiving waters, blanket the stream bed and destroy aquatic life.

Copper - Physiological Effects

Carpenter (1930) attributed the death of fish in solutions of salts of heavy metals chiefly to the coagulation or precipitation of mucus secreted by the gills, or damage to the gill tissue. Similar observations have been made by Jones (1935), Ellis (1937), Doudoroff and Katz (1953), and Pickering and Henderson (1964). A chemical reaction takes place between the metallic base and an organic constituent of the mucus secreted by epithelial cells. The resulting product is a colloidal substance which forms a film over the body surface and the gill filaments (Carpenter, 1930). These insoluble metal-protein compounds formed are believed to interfere with the respiratory functions of the gills, and thus bring about death by suffocation (Carpenter, 1930; Jones, 1935; Ellis, 1937; Doudoroff and Katz, 1953). Direct damage to gill tissue due to precipitation of protein within the cells has been postulated by Ellis (1937). In toxicity tests of zinc sulfate, zinc nitrate, copper sulfate, copper nitrate, and copper chloride, Jones (1935) noted that when fish were in the various test solutions, they displayed great respiratory distress, the opercular movements were more rapid, but the rate of evolution of carbon dioxide was less than that of controls in tap water. If the fish were removed from the solution a reasonable time prior to death and put in clean water, the mucus film was sloughed off and the fish recovered. Jones went on to demonstrate that toxicity of the heavy metal salts is due mainly to the metallic cation, the toxicity of the anion being relatively small.

The physiological changes brought on by heavy metals is not all external. Ellis (1937) and Doudoroff and Katz (1953) state that the harmful action of some metallic salts which do not coagulate mucus (eg. sodium dichromate) is wholly internal or intracellular, following penetration of the metals into the tissues. In experiments with the winter flounder, Pseudopleuronectes americanus, Baker (1969) found that copper also causes gross internal changes. High and medium levels of copper resulted in necrosis in the kidney, fatty metamorphosis in the liver, destruction of the hemopoetic tissue, and gross changes in the gill architecture. However, histological examinations by Mount (1968) of gill, liver, and kidney of fathead minnows, Pimephales promelas, which had been continuously exposed to copper, showed no detectable histopathology.

Pollutants - Sublethal Effects

Sublethal effects of pollutants are all too often neglected entirely in toxic studies. There is much evidence to show that waste disposal concentrations which merely permit survival of aquatic organisms may not permit them to function properly (Shirer, et al., 1968). Temporary survival of aquatic organisms is meaningless if they fail to reproduce, have poor growth, and exhibit aberrant behavior patterns. Therefore, any changes in activity might well reflect deeper physiological stress (Shirer, et al., 1968). Cairns (1966) suggests that alterations of fish breeding behavior may as effectively destroy the species as killing it outright.

Avoidance of copper by salmon was studied in the laboratory by Sprague (1964a). His studies demonstrate that salmon avoid water concentrations of copper as low as approximately 4-5 ppb. Saunders and Sprague (1967) reported that copper and zinc pollution from a base metal mine caused many adult Atlantic salmon, Salmo salar, which were on their normal upstream spawning migration, to return prematurely downstream through a counting fence during summer and early autumn. This observation of change in behavior documented a sublethal stress caused by pollutants which has seldom been done in the natural environment. Copper-zinc pollution more severe than 0.35 to 0.43 toxic unit seemed to cause avoidance reactions.

Synergism and Antagonism

Synergism is defined as the interaction of two or more effluents so that their collective toxic effect on aquatic organisms is higher than the sum of their individual toxicities (Doudoroff and Katz, 1953). The classic example of synergistic interaction is the one reported by Doudoroff (1952) for copper and zinc. Doudoroff found that although fish could survive for 8 hours in water containing 8 ppm of zinc alone, and for 8 hours in water containing 0.2 ppm of copper alone, most fish died within 8 hours when exposed to a mixed solution containing only 1 ppm of zinc and 0.025 ppm of copper. Sprague (1964) experimented with the toxicity of copper and zinc sulfates to immature Atlantic salmon in soft water. Results of these tests showed that in solutions containing both copper and zinc, fish died twice as fast as would occur if the two metals were simply additive in their lethal action.

A method proposed by Saunders and Sprague (1967) provides a means for predicting toxicity of mixtures of two or more pollutants on the basis of chemical measurements. This system is based on incipient LC50's of the pollutants, or reasonable approximations such as 48- or 96-hr LC50's. The strength of a given toxicant is expressed as a fraction or proportion of its lethal threshhold concentration. The following formula is used in this method:

$$\# \text{ of toxic units} = \frac{\text{actual concentration as measured chemically}}{\text{lethal threshhold concentration}}$$

A value equal to or greater than 1.0 toxic unit is lethal to at least 50 percent of the fish, and values from 0 to 0.99 toxic unit are lethal to less than 50 percent of the fish (Saunders and Sprague, 1967; Sprague, 1970). For a mixture, the number of toxic units may be calculated for each of the component pollutants. Since the strength of each pollutant is expressed in the same units, they may be added together (Sprague, 1970).

The above described method may also be applied to metal cations whose toxicity is counteracted or antogonized by other metal cations in mixed salt solutions. Certain metals which are highly toxic to fish in distilled and soft natural waters have long been known to have a much reduced toxic effect in hard water and in sea water (Doudoroff and Katz, 1953). The relatively low toxicity of heavy metals in highly mineralized water can be due to factors other than cation antagonism, such as the formation of precipitates. Ellis (1937) reported that in solutions prepared with distilled water and containing cupric sulfate, the survival time of goldfish Carassius auratus, averaged 150 minutes in the absence of other salts, 180 minutes in the presence of 5000 ppm of sodium nitrate and 50 ppm of calcium chloride.

In connection with salt antagonism upon copper, Sprague (1968) presents the trisodium salt of nitrilotriacetic acid (NTA) as a promising anti-pollutant to prevent fish kills in case of short-term breakdown of normal pollution controls. Bioassays with copper and zinc, and with these metals plus NTA, were conducted with brook trout, Salvelinus fontinalis, in the laboratory. At 3.3 toxic units of metal, survival was prolonged from 10 to 47 hours if the weight of NTA in solution equalled the weight of metal in solution. At 33 toxic units of metal, a 3.0 times ratio was necessary for survival of most fish and a 4.0 times ratio for complete survival. At 330 toxic units of metal, NTA obviously lengthened survival, but fish died nevertheless. Fish mortality seemed to be related to high pH values (8.7 and 9.3) associated with the strong concentrations of NTA because trout were found to survive even 400 toxic units of metal with five times as much NTA if the pH was lowered with acid.

EDTA (ethylenediamine tetraacetic acid) was also discussed by Sprague (1968). This chelating agent also proved to protect salmonid fish against copper-zinc toxicity. However, six times as much EDTA is required and thus the cost is higher. Sprague mentions that a drawback of NTA is that it is biodegradable in natural waters and the metals would be released back into solution in a few days. In an earlier report by Fitzgerald and Faust (1963), the chelation of copper with citric acid was found to reduce the toxicity of several fishes at least 500-fold.

Copper - Toxicity

Lloyd and Herbert (1962) showed that the copper incipient lethal level is 50 ppb for rainbow trout, *Salmo gairderi*, in soft water (20 mg/1 hardness). The incipient lethal level of copper sulfate to Atlantic salmon was found to be 48 ppb Cu in soft water in studies by Sprague (1968). Further studies by Sprague (1968) showed 50 ppb Cu (in soft water) to be the incipient lethal level to brook trout. Thus it can be seen that members of the family Salmonidae seem to be severely affected in copper levels of about 50 ppb or more in waters of low hardness.

The incipient lethal level of 50 ppb Cu for fathead minnows in softwater (Tarzwell and Henderson, 1960) is similar to resistence levels cited above for the salmon family. Pickering and Henderson (1964) determined 24-, 48-, and 96-hr. TLm values for four species of fish to copper sulfate both in soft and hard water. Their studies showed the 96-hr. TLm value for fathead minnows to range from2 2-25 ppb in soft water and from 114-176 ppb in hard water. Fathead minnows were exposed to copper sulfate in hard water for 11 months by Mount (1968) and he found that 3-7 percent of the 96-hr. TLm value does not affect growth and reproduction under prolonged, continuous exposure in hard water. Mount's experiments reveal the 96-hr. TLm concentration for these minnows to be 430 ppb. However, 95 ppb Cu retarded sexual development and prevented spawning and concentrations as low as 33 ppb Cu were found to inhibit spawning. In a later study dealing with fathead minnows and copper in soft water, Mount (1969) found that under continuous exposure conditions, the maximum acceptable toxicant concentration of copper for the fathead minnow was 13 to 22 percent of the 96-hr. TLm value. Survival, growth, and reproduction were used to evaluate effects. 18.4 ppb was found to reduce survival by 50 percent and prevent spawning.

Another member of the minnow family, the goldfish, was found to die rapidly in 9 ppb Cu (Powers, 1917), but whether his experiments were conducted in hard or soft water was not stated. The 96-hr. TLm for goldfish in soft water was set at 36 ppb Cu by Pickering and Henderson (1964).

A representative of the sunfish family, the common bluegill, Lepomis macrochirus, seems much more resistant to copper than other fish families previously discussed. An incipient lethal level of

210 ppb (in soft water) was found for bluegills by Tarzwell and Henderson (1960). Tests with the bluegill by Pickering and Henderson (1964). show a 96-hr. TLm of 0.66 ppm Cu (660 ppb) in soft water and a 96-hr. TLm of 10.2 ppm Cu in hard water. Cairns and Scheier (1968) and Patrick, _et al_. (1968) list the 96-hr. TLm for this species to be 1.25 ppm in soft water.

The importance of copper sulfate as a fish poison and algicide has resulted in many studies of toxicity in the field. Catt (1934) and Smith (1935) reported on a practicle experiment in the destruction of predatory fish by copper sulfate in Lake Jesse, Nova Scotia. Sufficient copper sulfate was added to give a concentration of 3.06 ppm if the salt was evenly distributed. The waters of Lake Jesse are acidic and Smith (1935) doubts whether the basic copper carbonate would form and precipitate out as it does when added to hard water lakes. Almost all of the fish population (as well as algae and invertebrates) was annihilated. Smith (1935) observed that most of the dead fish were found in shallow water near shore. Deeper waters were searched with a water-glass but very few dead fish were seen on the bottom. This correlated with the fact that very few dead fish were found afloat led Smith to conclude that the fish afflicted by the copper sulfate suffocated due to a precipation of mucus on the gills. Later studies by Smith (1939) showed that a concentration of 3 ppm copper sulfate killed the fish in the acid waters of four Nova Scotian lakes.

The body of information concerning the acute toxicity of various industrial waste components to fish is considerable, but there is relatively little information available concerning the effects of these pollutants on those organisms which serve either directly or indirectly as fish food (Patrick, _et al_., 1968). An early report by

Greenfield (1942) reported *Chlorella vulgaris*, a freshwater unicellular green alga, to be inhibited by 6.4 ppb Cu. Hasler (1947) reports (from Churchill, 1946) that the addition of copper to mixed cultures of algae in a Wisconsin lake greatly altered the composition of the population, since the free floating, unicellular plankton algae were all killed by 0.25 ppm Cu (some were killed at 0.08 ppm), while the filamentous forms were inhibited by 0.33 ppm but were not killed at concentrations less than 0.66 ppm. Maloney and Palmer (1956) relate that 0.5 ppm copper as copper sulfate produced 57 percent mortality in seven species of blue-green algae, 35 percent mortality in 17 species of green algae, and 100 percent mortality in six species of diatoms.

An investigation was made by Crance (1963) on control of the blue-green alga genus *Microcystis* in ponds with copper sulfate. The longest period of time that *Microcystis* remained in a controlled status after an application of 0.05-0.08 ppm of copper sulfate was approximately 25 days. In toxicity tests with *Chlorella pyrenoidosa* using copper sulfate, Hueck and Adema (1968) found a concentration of 1.0 ppm Cu would inhibit development. The diatom *Nitzschia linearis* was determined to have a 120-hr. TLm value of 0.795-0.815 ppm Cu in soft water by Patrick, *et al.* (1968).

Smith (1935) found that the limnetic zooplankton and phytoplankton were completely destroyed in a Nova Scotian lake after application of 3 ppm copper sulfate. *Daphnia pulex*, which was a fairly common constituent of the plankton before copper sulfate application, was entirely absent in later samples. *Daphnia magna* was found to be inhibited at a concentration of 0.056 ppm in laboratory study by Hueck and Adema (1968). However, if *Daphnia magna* were fed with algae cultured in copper-containing media, it was found that a concentration of 0.560 ppm was required for inhibition. Hueck and Adema concluded that poisoning by indirect ingestion of copper is less efficient than poisoning directly by way of dissolved copper.

Hubshman (1967) performed an experiment on the crayfish *Orconectes rusticus* in a moulting stage using copper concentrations in hard water. In 2.5 ppm Cu, all were dead after 15 days. Further, when the adult crayfish were submitted to 1 ppm Cu without interruption, 50 percent died in 15 days. Young crayfish were found to be affected in less than 24 hours while the growth of recently born crayfish was inhibited at a 0.015 ppm concentration. Copper is stated by Hubshman to be cumulative at certain concentrations.

Copper in Bottom Muds

Copper accumulation in bottom muds of Lake Monona, Wisconsin has been reported by Nichols, *et al*. (1946). At the time of the study the lake had a history of extensive copper sulfate treatment (1925-1944). Calculations by Nichols, *et al*. show that if all the applied copper was deposited uniformly over the entire bottom surface of the lake, 1.2 grams of metallic copper would be present for each square foot of area. Testing of bottom muds led to calculations of 260,000 pounds of metallic copper deposited on the bottom compared to 375,000 pounds of metallic copper applied from 1925-1944. Thus, this study demonstrates that the greater portion of copper sulfate was precipitated out in the alkaline hard waters of the lake and remains as a deposite in the bottom mud. The conclusion drawn by Nichols, *et al*. (1946) is that these bottom deposites of copper are of very low solubility under the prevailing pH and hardness and thus contribute very little copper to solution and are of no significance in algae control.

Riley (1939) concluded that at least five factors affect the naturally occurring copper content of lake waters. These factors are:

1. Precipitation which lowers copper content by dilution.
2. Sedimentation - removal from solution by absorption on organic matter.
3. Regeneration from mud.
4. Liberation of copper in summer and autumn from decomposition of littoral vegetation.
5. Liberation of copper in autumn by decomposition of vegetation surrounding lakes

Copper - Conclusions

From their review of the literature, Doudoroff and Katz (1953) conclude that in most natural fresh waters of the United States, copper sulfate concentrations below 0.025 ppm as copper evidently are not rapidly fatal for most of the common fish species. However, concentrations below 1.0 ppm Cu can be quite fatal to fish in many of these waters which are soft. Higher concentrations are tolerated by resistant species in sufficiently hard, alkaline waters.

In most of the natural fresh waters of the United States standards are designed to protect only fish and often permit concentrations that are lethal to other species of the aquatic community (Patrick, et al., 1968). In view of the different tolerance levels to copper among aquatic organisms, modifications of the community structure may occur and these changes in the quality and quantity of the species have a great influence on the survival of other members of the aquatic community. Patrick, et al. (1968) suggest the remedy of running bioassays using at least three components of the food web.

Chromium - Sources and Forms

Chromium is present in igneous rocks in nature in minor amounts. The process of weathering results in very little chromium going into solution unless the pH is low. Chromium may be converted to the hexavalent state under strong oxidizing conditions and occurs as the chromate (CrO_4) anion. Generally speaking, hexavalent chromium exists in water in true solution, regardless of pH or the presence of other ions (Knoll and Fromm, 1960).

Natural chromates are rare and when found in water usually indicate industrial pollution (Kopp and Kroner, 1968). As presented earlier in this review, chromium compounds may be present in wastes from many industrial processes relating to the copper and brass industry. Chromate compounds are also frequently added to cooling water for corrosion control (Anon., 1965). Hexavalent chromium salts are used much more extensively in industry than the more soluble trivalent salts (Kopp and Kroner, 1968).

The hexavalent chromium concentration of United States drinking waters has been reported to vary between 0.003 and 0.04 ppm with a mean of 0.0032 ppm. Protection of a potable water supply against the intrusion of hexavalent chromium is very necessary due to its carcinogenic potential (Anon., 1965). When inhaled, chromium is a known carcinogenic agent; however, it is not known whether ingestion of chromium has the same cancer producing potential. The level of chromate ion that can be tolerated by man is at the present time uncertain (Kopp and Kroner, 1968). The limit for hexavalent chromium in drinking water is 0.05 ppm (Anon., 1967b).

Chromium - Physiological Effects

The effect of the inorganic salts sodium dichromate and sodium chromate on the internal water balance of the bluegill was studied by Abegg (1950). Sodium dichromate was found to cause an increase in the tissue-fluid content of the musculature as well as causing the precipitation of the mucus covering the body. Abegg postulated that the general hydration of the fish placed in solutions of sodium dichromate may be due to the coagulation of the mucus covering the body, changing the permeability of the skin and gills. Sodium chromate proved to have no effect on the water balance of the fish exposed to this solution for 24 hours.

Fromm and Schiffman (1958) observed that less than 100 ppm Cr (using potassium chromate) invariably caused significant physiological changes in the intestine of the largemouth bass, *Micropterus salmoides*, and death in 80 hours. Marked sloughing of mucus from the anus and increasing coughing movements were also noted. No change in the histology of the gills was noted (Fromm and Schiffman, 1958; Schiffman and Fromm, 1959). A decrease in oxygen consumption of 27 percent below normal was noted in fish after 68 hours exposure to 94 ppm Cr (Fromm and Schiffman, 1958).

The major route of entry of hexavalent chromium into rainbow trout is thought by Knoll and Fromm (1960) to be by simple diffusion across the gill membranes. When the trout were exposed to 2.5 ppm hexavalent chromium they accumulated chromium in concentrations exceeding the environment in the spleen, posterior gut, pyloric caeca, stomach, and kidney. Their studies and the later study of Fromm and Stokes (1962) indicate that chromium probably acts internally.

Chromium - Toxicity

The toxicity of chromium varies with the species, temperature, pH, concentration, and synergistic or antagonistic effects (especially with water hardness) (Grindley, 1946).

Thomas (1915) determined that both dichromate and copper salts were much more toxic to killifish, Fundulus heteroclitus, in fresh water than to the same species in salt water. This study seems to show that the salts in sea water are antagonistic to heavy metal toxicity.

Grindley (1946) evaluated the short-term toxicity of potassium chromate and potassium dichromate to yearling rainbow trout in continuously aerated distilled water. When the chromium content of the solutions was 20 ppm the resistance time averaged 60 hours in the chromate solution (75 ppm K_2CrO_4) at pH 6.6 and 72 hours in the dichromate solution (57 ppm $K_2Cr_2O_7$) at pH 5.5. It was concluded that the limiting concentrations below which these salts would not be toxic (in soft water) is slightly below 20 ppm Cr and that at equivalent concentrations of chromium, solutions of potassium dichromate (more acidic) were more toxic than solutions of potassium chromate. Supporting evidence is found in the work of Abegg (1950) with bluegill sunfish. The 24-hr. TLm for sodium chromate (pH 8.1) was 930 ppm (as sodium chromate), while sodium dichromate with a much lower pH (5.9) had a value of 728 ppm.

Schiffman and Fromm (1959) performed experiments on the rainbow trout in hard water using potassium dichromate as the salt. Their results indicate that the 24-hr. TLm concentration is 100 ppm Cr, but exposure of fish to only 20 ppm or even as low as 2 ppm Cr caused significant pathological changes.

The toxicity of chromium wastes from an electroplating plant (diluted with hard water) to members of the family Centrarchidae was studied by Klassen, et al. (1949). In one test, all of ten bluegill sunfish tolerated for more than ten days 83 ppm Cr at 69° F. and pH 8.2.

In their critical review, Doudoroff and Katz (1953) did not accept the explanation of Klassen, et al. (1949) that small variations in temperature could explain the discrepancies. They feel that the observed mortality of fish in some of the experiments was not due solely to chromium.

Cairns and Schierer (1959) found the experimental 96-hr. TLm concentration of dichromate to the bluegill to be 320 ppm in soft water at both 18° and 30° C., 382 ppm in hard water at 18° C. and 369 ppm in hard water at 30° C. Thus, the toxicity of dichromate was affected more by the degree of hardness of the water than by the temperature.

Work by Trama and Benoit (1960) demonstrates that the experimental TLm values concerning the bluegill are quite variable. 96-hr. TLm values were on the order of 110 ppm Cr where hexavalent chromium enters the system as dichromate (or along with acidity equivalent to the dichromate) and about 170 ppm Cr where chromium enters soft water as chromate. Comparison of this study with above studies vividly demonstrates that more standard conditions are needed.

The 96-hr. TLm values of potassium dichromate in soft water varied from 118 ppm Cr for the bluegill to 17.6 ppm Cr for the fathead minnow in a study by Pickering and Henderson (1964). The fathead minnow withstood greater amounts of potassium chromate (in soft water) as the 96-hr. TLm value was 45.6 ppm Cr. The 96-hr. TLm value for fathead minnows in soft water was found to be significantly lower (17.6 ppm Cr) than the value in hard water (27.3 ppm Cr). With the bluegills, however, the 96-hr. TLm value in soft water (118 ppm Cr) and hard water (133 ppm Cr) were not significantly different.

In another study concerning the bluegill Patrick, et al. (1968) determined the 96-hr. TLm value in soft water to be 113 ppm Cr (introduced as potassium dichromate). Fromm and Schiffman (1968) experimentally determined the 48-hr. TLm of potassium chromate for largemouth bass in hard water to be 195 ppm Cr. Fishes exposed to 65 ppm Cr survived for six days.

Information relating to toxic effects of chromium on algae and other members of the aquatic community is almost non-existent. Hervey (1949) found that chromium (introduced as dichromate) in amounts as small as 0.032-0.32 ppm inhibited growth of diatoms. Patrick, *et al*. (1968) arrived at a 120-hr. TLm value (in soft water) of 0.208 ppm Cr for the diatom *Nitzschia linearis* and a 96-hr. TLm value of 17.3 ppm Cr for the fresh-water snail *Physa heterostropha*.

Chromium - Summary

The wide variety of conditions under which the above cited studies were performed makes it difficult to conclude anything with confidence concerning the toxicity of hexavalent chromium. The suggestion is made by Trama and Benoit (1960) that this lack of accord among the workers seems to be a hearty recommendation for the use of standard conditions.

Acids and Alkalies

It is well known that a pH range of 5.0-9.0 is not usually lethal for most freshwater fishes (Mackenthun, 1969). There is no definite pH range within which fish are harmed, but there is a gradual deterioration as the pH values progress either up or down from their normal range. The toxicity of many common pollutants can be dramatically increased by pH changes.

Water Quality Criteria (Anon., 1969b) has the following information concerning pH in the natural environment. In most productive fresh waters, the pH normally falls in the range 6.5-8.5 unless increased by photosynthetic activity. A relatively few aquatic organisms have been found to live at the extreme pH values of 2 and lower, while others can survive at pH 10 and higher. The major buffering system in natural waters is the carbonate system. This system neutralizes acids and bases and thus reduces the fluctuation in pH. The carbonate system also forms an important reservoir of carbon for photosynthesis.

Ellis (1937) studied experimentally the survival of goldfish in natural waters acidified to various pH values with eleven mineral and organic acids found in industrial wastes. His data show that mortality was always observed within a few hours when the pH values were 3.4-4.0 (or lower), whereas none occurred in four days when the pH values were 4.5-4.9 (or higher). The non-lethal limits of pH are narrower for some fish food organisms than they are for fish, however. _Daphnia magna_, for example, did not survive in experimental waters having a pH below 6.0 (Anon., 1968b).

Acids that dissociate to a high degree (sulfuric acid for example) do not appear to be toxic at pH values above 6.0 (Anon., 1968b). At values lower than 6.0 these acids become toxic. Acids that dissociate to a low degree are often toxic at pH values considerably above 6.0. This toxicity at pH levels above 6.0 is due either to the anion or to the compound itself (eg. hydrogen cranide and hydrogen sulfide) (Anon., 1968b).

Toxicity of sulfuric acid neutralized with slake lime to channel catfish, _Ictalurus punctatus_, was studied by Sparks, _et al_. (1969) both in the laboratory and in the field. Results of their laboratory experiments showed that 10 of 15 channel catfish survived in synthetic waste 22-28 days when a suspended solids concentration of 367-509 mg/1 was maintained by moderate aeration. Eleven of 12 catfish survived

22-28 days in synthetic waste from which all settleable solids were removed and 17 of 22 catfish kept in tapwater as controls survived 22-28 days. Red shiners, Notropis lutrensis, red-fin shiners, Notropis umbratilis, green sunfish, Lepomis cyanellus, mosquitofish, Gambusia affinis, and black bullheads, Icatlurus melas, were found to be quite tolerant to the neutralized mixture. Sparks, et al. also found that particles in the neutral mixture mechanically irritate the gills of fish as 6 of 27 fish in the unchanged neutral mixture agitated by one or two air stones had blood clots in their gills, and all the fish in the neutral mixture had strands of mucus extending from their gills. The particles of the neutral mixture caused sloughing of mucus from the body and gills which may have resulted in the impairment of the physiological functions of respiration, osmotic regulation, salt regulation, and excretion.

Temporary high pH levels are often produced in natural waters due to photosynthetic activity of aquatic plants by converting the carbonate to the hydroxide. These high pH levels persist only for a few hours, however, and thus do not produce the harmful effects of continuous high levels due to the presence of strong alkalies (Anon., 1968b).

None of the strong alkalies which are important as industrial wastes (sodium hydroxide, potassium hydroxide, calcium hydroxide) have been clearly shown to be lethal to fully developed fish in natural fresh waters when their concentrations are insufficient to raise the pH well above 9.0 (Doudoroff and Katz, 1950). Support for their conclusion is given in Water Quality Criteris (Anon., 1968b) which states that alkalies that dissociate to a high degree do not appear to be toxic at pH values below 9.0. However, alkaline compounds that dissociate to a low degree are toxic at lower pH values due to either the cation or to the undissociated substance.

A pH increase from 10.70 to 10.82 (due to sodium hydroxide) was found by King (1943) to cut survival time in half for three species of trout (brook, rainbow, and brown, Salmo trutta). Van Horn, et al. (1949) found sodium hydroxide in concentrations as low as 100 ppm to be toxic to minnows.

Oil

Sources of oil pollution are bilge and ballast waters from ships, oil refinery wastes, industrial plant wastes such as oil, grease, and fats from the lubrication of machinery, pipe line leaks, free fatty acids, county drains, gasoline filling stations, and bulk stations (Anon., 1968b).

Water Quality Criteria (Anon., 1968b) states that "oil or petrochemicals should not be added in such quantities to the receiving waters that they will -

1. produce a visible color film on the surface;
2. impart on oily odor to the water or an oily or other noxious taste to fish and edible invertebrates;
3. coat the banks and bottoms of the water course or taint any of the associated biota;
4. become effective toxicants according to the criteria recommended in the toxicity section".

Rule 1.03 in Water Quality Standards (Anon., 1967b) lists similar minimum conditions. The notation is made in Water Quality Criteria (Anon., 1968b) that oil slicks are barely visible at a concentration of about 25 gal./Sq. mile. At 50 gal./Sq. mile an oil film is 30 X 10^{-6} inches thick and is visible as a silvery sheen on the surface.

Wiebe (1935) conducted experiments with base and bream in crude oil and found that death was a result of a film of oil being deposited over the gill filaments. The 96-hr. TLm value of napthenic acid (a petroleum extract used in the manufacture of insecticides, paper, and rubber) has been reported by Cairns (1957) to be 5.6 ppm for the bluegill and 6.1 to 7.5 ppm for the pulmonate snail, *Physa heterostropha*. Pickering and Henderson (1966) studied the acute toxicity of several important petrochemicals to fathead minnows, bluegills, goldfish, and guppies in both soft and hard water.

Oil films on the lower Detroit River were reported by Berry (1951) to be a constant threat to waterfowl by destroying the natural buoyancy and insulation of their feathers. Dramatic losses of water-birds (ducks, geese, coot, swans, grebes, and others) result from the contamination of the plumage by oil from the surface of the water (Anon., 1968b). Hartung (1965) demonstrated inhibition of egg laying and hatching in mallards, *Anas platyrhynchos*, as a result of exposure to oil.

Films of oil on the surface interfere with the respiration of aquatic insects (Anon., 1968b). Oil may also coat and destroy algae and other plankton and if it settles may coat the bottom, thereby destroying benthic organisms and spawning areas. Even when settled on the bottom, oil continuously yields water-soluble substances that are toxic to aquatic life (Anon., 1968b).

Phosphates and Sulfates

Phosphorus is an essential element for aquatic life as well as for all forms of life (Anon., 1968b). Phosphorus as such is a poison and is virtually insoluble in water. However, since it is highly oxidizable it combines in water in oxide form with bases present to form phosphates, which, with nitrates are requirements for making proteins (Coker, 1954). In higher animals, calcium phosphate is a substantial constituent of bones and teeth. Phosphorus also plays an important role in the functioning of nerve and muscle tissue. Animals obtain their phosphorus requirements either directly or indirectly via vegetable foods. The major sources of phosphorus entering fresh waters are domestic sewage effluents (including detergents), animal and plant processing wastes, fertilizers and animal agricultural runoff, and various industrial effluents (Anon., 1968; Bartsch, 1970).

Sulfur is essential for the formation of proteins and is almost always present in natural waters in the amount needed. Sulfates may be present in natural waters in concentrations ranging from a few to several thousand mg/1 (Anon., 1968). In natural waters, sulfates are chiefly derived from the oxidation and partial solution of iron pyrites found in igneous rocks. An abnormally high sulfate level is usually indicative of industrial pollution, as from pulp mills, paper mills, and coal mines (Coker, 1954). Although not a final component of chlorophyll, sulfur promotes its formation (Coker, 1954).

Mackenthun (1969) defines eutrophication as "a term meaning enrichment by nutrients through man-created or natural means. Present knowledge indicates that the fertilizing elements most responsible for lake eutrophication are phosphorus and nitrogen". Young lakes are generally unproductive (low in nutrients) but as the aging process progresses, the water becomes enriched and the lake gets shallower due to accumulated erosion and organic debris. The aging process is often acclerated by domestic and agricultural drainage (Hasler, 1947). The accelerated process of enrichment results in superabundant growth of algae which upsets the balance in plant and animal life, reduces the aesthetic qualities and economic value of the body of water, and destroys precious water resources (Prescott, 1948; Hasler, 1969; Mackenthun, 1969). When algal cells die, the oxygen is depleted and fish kills often result. Rapid decomposition of dense algal scums give rise to foul odors and hydrogen sulfide gas (Mackenthun, 1969). The most troublesome algae in lakes and reservoirs are species of blue-greens (Prescott, 1948) which multiply rapidly and float high in the water.

Hasler (1969) notes that lakes are more susceptible to sewage effluent than are flowing streams because flowing water is not conducive to the growth and attachment of algae and rooted aquatic plants.

Detergents

The use of synthetic detergents (containing surface-active agents or surfactants) for general cleaning purposes often creates frothing of water supplies (Anon., 1965). In their passage through sewage treatment plants, only about 50 percent of the detergents are removed. Detergents are present, therefore, not only in most lowland streams near municipalities but also in drinking water supplies obtained from surface streams (Surber and Thatcher, 1963).

Detergents can kill fish and because of their phosphate content they contribute to the cultural eutrophication problem. Pickering (1966) states that the conversion of the detergent industry of the United States from the use of alkyl benzene sulfonate (ABS) to the more readily biodegradable linear alkylate sulfonate (LAS) has not necessarily reduced this pollutional problem. Even though a detergent may be biodegradable, its pollutional potential is not necessarily less than that of a hard detergent.

A light froth in water is caused by 1 mg/1 ABS surfactant, thus the limiting concentration has been set at 0.5 mg/1 (Anon., 1965), but Water Quality Criteria (Anon., 1968b) gives different recommendations:

1. With continuous exposure, the concentration of ABS (100 percent active) should not exceed 1/7 of the 48-hr. TLm concentration. Concentrations as high as 1 mg/1 may be tolerated infrequently for period not exceeding 24 hours. ABS may increase toxicity

of other materials.

2. The concentration of LAS should not exceed 0.2 mg/1 or 1/7 of the 48-hr. TLm concentration, whichever is lower.

Henderson, *et al.* (1959) reported that the 96-hr. TLm value of ABS for the bluegill in soft water was 5.6 mg/1. Juvenile bluegills were used by Lemke and Mount (1963) in 30-day bioassays to study the toxic effects of ABS. The 30-day TLm ranged between 15.5 and 18.3 ppm of active ingredient. A reduction of growth rate was noted in one test and histological changes in all tests were evident at concentrations one-third of the TLm value. No damage was observed by Henderson, *et al.* in the liver, spleen, kidney, or small intestine, but the epithelial tissues of the gill lamellae were two to three times thicker than normal. There was also pronounced thickening of the cell mass lying between the lamellae.

Thatcher (1966) determined the 96-hr. TLm of a typical LAS detergent to five species of freshwater fish while Thatcher and Santner (1966) worked with the same five fish species in determining the 96-hr. TLm's of a typical ABS detergent. These two studies are compared in the following table:

	LAS	ABS
Emerald Shiners, *Notropis atherinoides*	3.3	7.4
Bluegills, *Lepomis macrochirus*	4.0	8.2
Fathead Minnows, *Pimephales promelas*	4.2	11.3
Common Shiners, *Notropis cornutus*	4.9	17.0
Black Bullheads, *Ictalurus melas*	6.4	22.0

(values in mg/1)

It can been seen that LAS is two to four times more toxic than ABS. Thatcher and Santner (1966) state that this was expected as straight-chain carbon components (comparable to LAS) degrade faster and are more toxic than the slower degrading branched-chain ones (comparable to ABS).

TLm values for eggs of the fathead minnow were determined with both LAS and ABS by Pickering (1966). His studies also show LAS to be more toxic than ABS detergents. LAS was about 2.8 times more toxic than ABS. The 9-day TLm values for the minnow eggs was 2.3 and 6.4 mg/1 for LAS and ABS, respectively. Pickering also found that newly hatched fry are more sensitive to LAS than ABS.

In a study of the chronic toxicity of LAS to the fathead minnow, Pickering and Thatcher (1970) used survival, growth, and reproduction to appraise results. An application factor obtained by dividing the maximum acceptable toxicant concentration by the 96-hr. TLm value was found to be between 0.14 and 0.28 mg/1 LAS. This application factor is proposed by Pickering and Thatcher as a model for estimating maximum acceptable concentrations of LAS for production of other fish species.

Crayfish, Orconectes rusticus, were seriously reduced in number by exposure to 10 ppm ABS over a period of two weeks in hard water, but a snail, Goniobasis sp. was apparently unaffected by this concentration (Surber and Thatcher, 1963).

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