POLLUTION FROM MINES IN THE "NEW LEAD BELT" OF SOUTH EASTERN MISSOURI

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In the south eastern part of Missouri, the Clark National Forest straddles the Ozark Plateau and contains the headwaters of some of the most beautiful rivers in the state. This scenic part of Missouri annually attracts large numbers of people to enjoy the recreational benefits of the cool springs and clear rivers. However, in 1955, rich mineral deposits were discovered in this area and by 1962 a rich lead-zinc ore belt was found to extend for approximately thirty-six miles almost due south from Viburnum, Missouri, through Iron and Reynolds Counties. The name given this new ore district was the Viburnum Trend or the "New Lead Belt".

Most of the lead ore was found to occur in the upper part of the Cambrian Bonneterre Formation, mostly a dolomite, at depths ranging from 700 to 1,200 feet (Mineral and Water Resources of Missouri, 1967). Galena was the principal ore mineral with lesser quantities of sphalerite and chalcopyrite.

The state of Missouri is the leading producer of lead in the United States and had an annual production of 152,649 short tons in 1967 and 210,800 short tons of lead metal in 1968. The significance of the new lead discovery is reflected by the U. S. Bureau of Mines Mineral Industry Survey Report (Aruendale, 1968) that the New Lead Belt alone will have the capacity for mining, concentrating and smelting an annual capacity of 350,000 tons of lead metal. The expansion of existing facilities and development of new mines will place international significance on the area since it will make south eastern Missouri the leading lead-producing district in the world. The mining development is located approximately seventy miles south east of Rolla, Missouri (Figure 1). A major portion of the lead-bearing property was within the Clark National Forest and the land must be leased from the U. S. Government in order to develop the lead reserves.

The streams in the mining district are in the Black River Basin where forests and farms make up the rolling Ozark landscape. Meager agricultural use and sparse population have helped to keep the streams of this basin relatively unpolluted. Except for the cleared areas around the mines and scattered farms, the country is densely covered with oak and shortleaf pine. The climate of the area is moderate with mild winters and humid summers. Annual precipitation is from 40-44 inches. According to the 1960 census, Iron County had a population of 8,041 and Reynolds County a population of 5,161.

Together with the natural enthusiasm for the forthcoming industrialization, a general concern for the future of the local streams has developed. The experience of other areas has demonstrated that pollution by lead and other heavy metals may have serious consequences upon the ecology and water quality of streams receiving mining wastes. In addition, milling and flotation operations would contribute other chemicals, some of which may have unknown toxic properties.

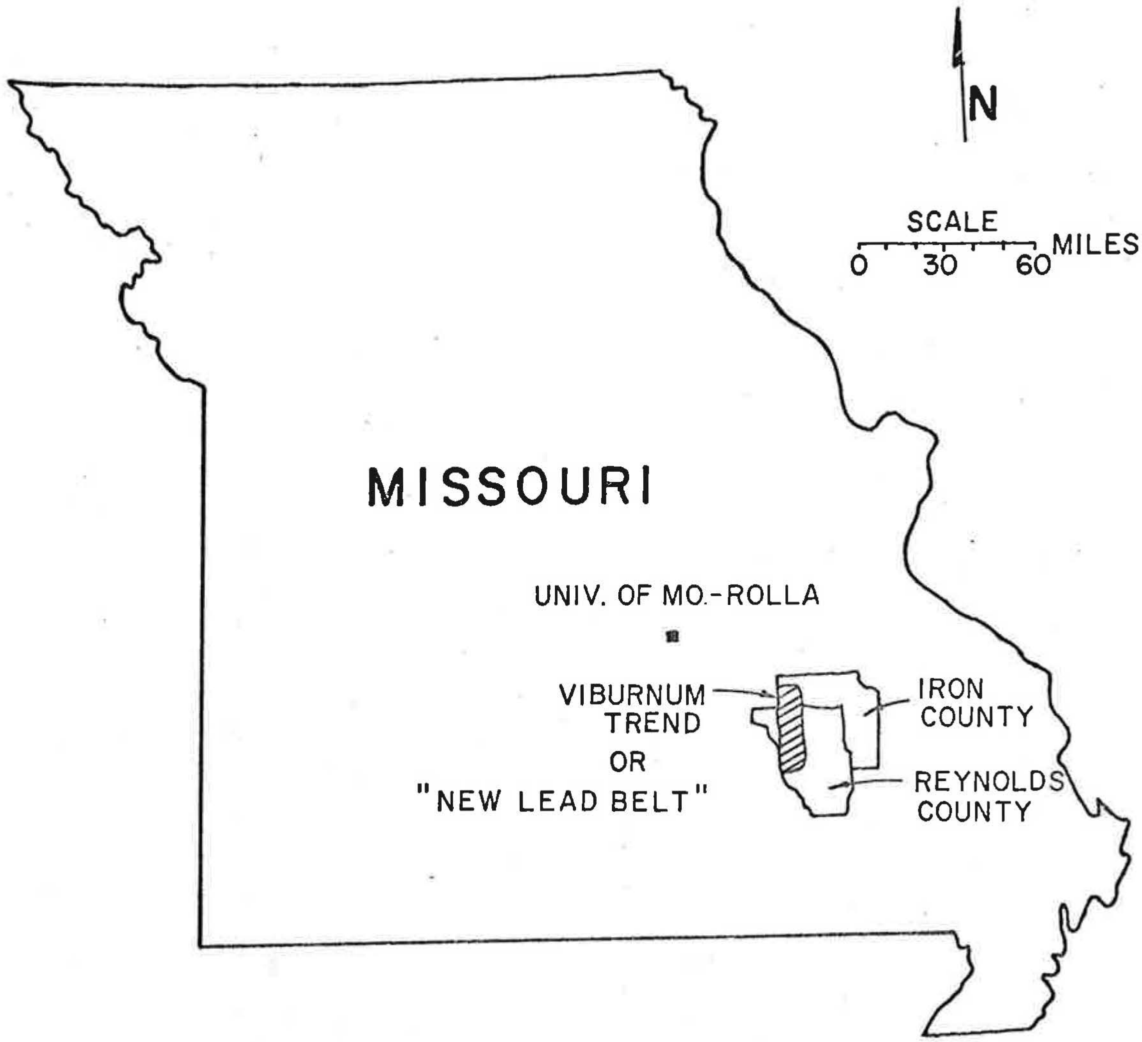


FIGURE 1.

GENERAL LOCATION OF THE "NEW LEAD BELT" IN IRON AND REYNOLDS COUNTIES, MO.

Since the Bonneterre Formation is also a good aquifer, extensive pumping (5,000-7,000 gpm) is necessary in order to keep most mines in the "New Lead Belt" operational. The mining companies in this area have also decided to treat their effluents by holding the tailings in retention ponds before discharging them into the streams. This, however, does not prevent certain reagents from reaching the streams, thus presenting a potential hazard. One of the very important problems now facing the mining industry is the practice of good water pollution abatement programs.

The unusual topography of the mining area channels the mining wastewaters from each mine into separate stream tributaries. Other streams flowing into the area from the eastern edge of the same drainage basin are unaffected by the new mining development. This unusual drainage pattern has been most advantageous in establishing a series of sampling stations on stream tributaries below mines in the "New Lead Belt". Additional sites may also be added with the future construction of additional mines. Control sites have also been established on unpolluted streams that will not be affected by population increases or industrial development. The selected sites separate pollution effects from individual mines and also permits the sampling of cumulative effects in the larger streams. The unique drainage pattern, location of mines and sampling sites is shown in Figure 2.

In order to evaluate the pollution of stream waters, the natural background concentrations of the investigated

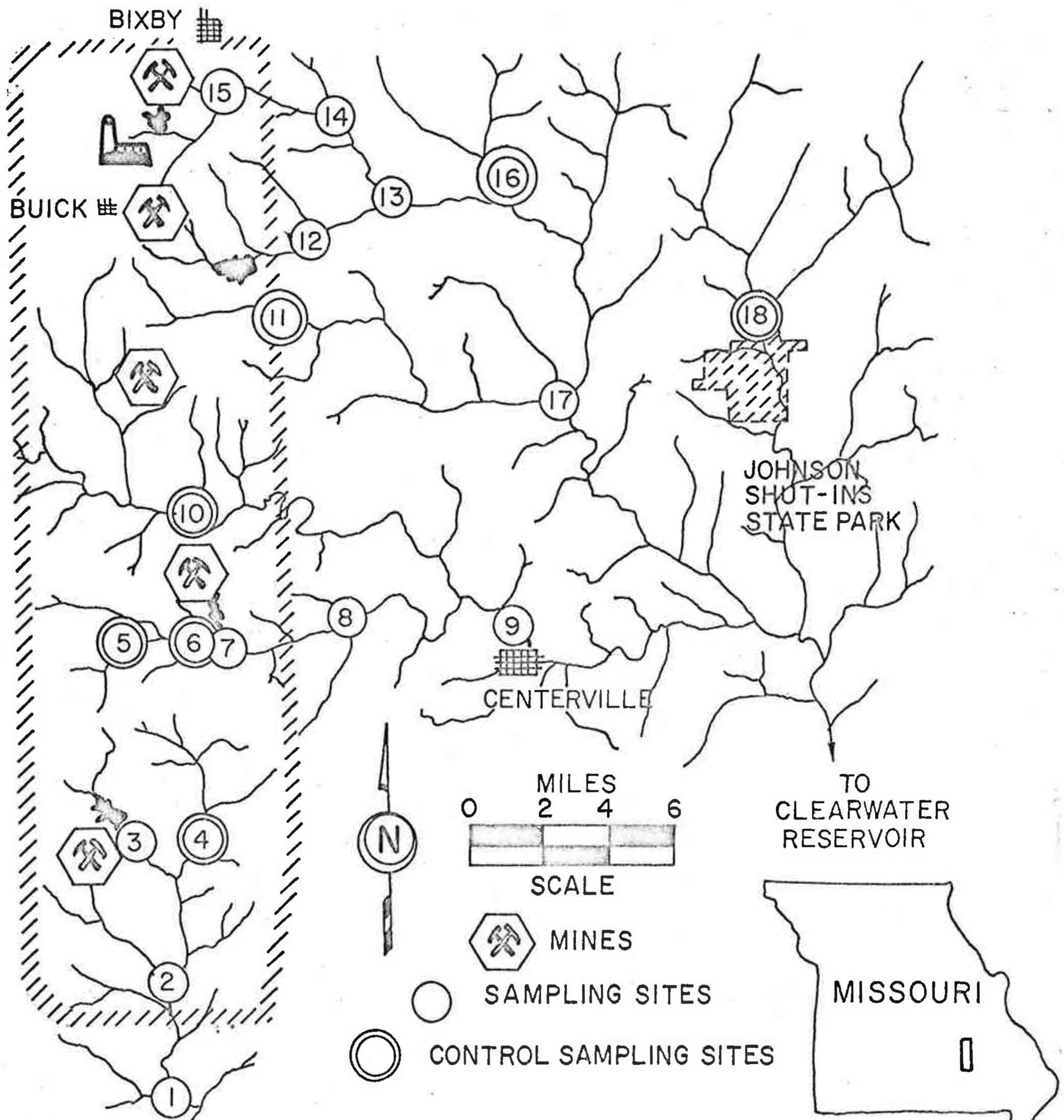


FIGURE 2.

LOCATION OF SAMPLING STATIONS IN THE "NEW LEAD BELT" OF S.E. MO.

constituents should be known. Because of heavy industrialization and density of population, natural background conditions rarely exist today in critical areas. Old measurements are usually either non-existent or unreliable, and only recently have analytical procedures been sufficiently improved for accurate analysis. The necessary collection of much irreplaceable background data has been carried out in the "New Lead Belt" and baselines established for the pollution surveys of streams (Wixson and Bolter, 1969).

Major lead companies developing mines and mills in the "New Lead Belt" have rendered valuable assistance in preliminary and continued research by allowing on-site visitations, meetings with key personnel and making available pertinent information most vital to this study. All companies have expressed the desire to prevent stream pollution and develop good pollution abatement programs.

In the "New Lead Belt" the first mill started production in 1967 with four mines and mills now in various stages of production and one new mine now under construction. One plant (Fletcher Mine, St. Joseph Lead Company) has greatly assisted by providing samples and amounts of reagents used at their facility for separating and concentrating the lead, zinc, and copper by the flotation process. This has allowed the development of research techniques for specific compounds or decomposition products which may cause pollution problems in receiving streams. The small area being polluted at the present times serves as an indicator of future environmental changes that may occur with the development of additional mines. Milling reagents used by different mining companies may vary but the effects on the water quality and stream biota will be similar.

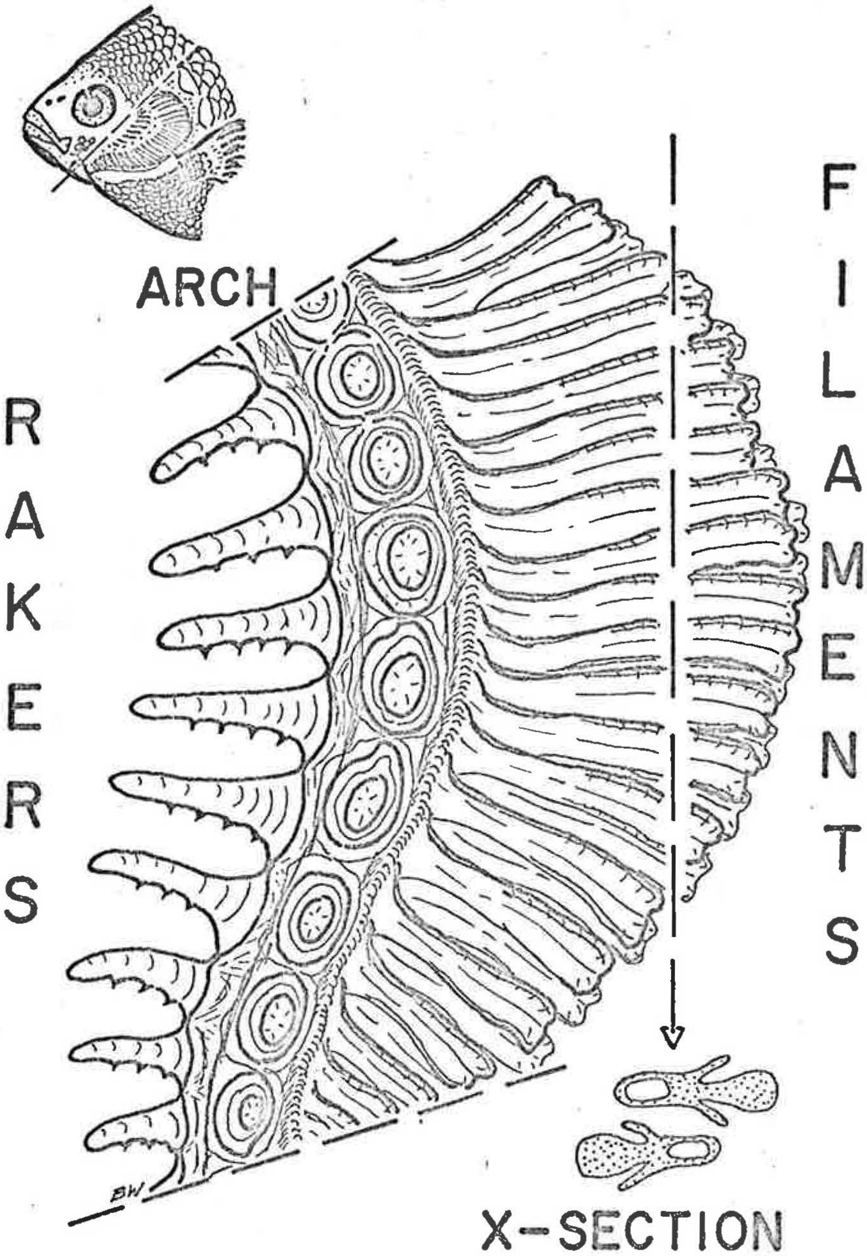
METHODS

Copper, lead and zinc were determined by analysis with a Perkin-Elmer model 303 atomic absorption spectrophotometer. All three elements were present at concentrations below instrumental detection limits using standard methods. It was therefore necessary to develop methods of analysis with sufficient sensitivity to detect low concentrations of heavy metals.

At the present time copper is determined by a combination of solvent extraction using the APDC/MIBK method and atomic absorption. Lead and zinc are determined directly using the newly developed "sampling boat" technique. These methods permit detection of the three elements at concentrations below 0.5 ppb (parts per billion). Water was collected at several selected stations in the "New Lead Belt". At the sample sites, the water pH and temperature were determined. Upon returning to the laboratory, the samples were immediately filtered through a 0.45 micron millipore filter and then stored in a refrigerator. Analysis was carried out as soon as possible thereafter.

Field and laboratory studies were also conducted with varying concentrations of heavy metals found in mining wastewaters to determine the TLm (median tolerance limit) and toxic concentrations for bluegill sunfish Lepomis macrochirus which are representative fish in the streams of the area. The Missouri Department of Conservation, Division of Fisheries, assisted the study by furnishing the necessary bluegill sunfish for laboratory static bioassays. Bee Fork Creek, one of the first streams to receive tailings from the new lead mining operations was selected for intensive study. Results from field measurements and laboratory toxicity studies were then combined to determine the effects of separate and mixed metals of lead, zinc and copper (Handler, 1969). The mode of the action of the metals was investigated through post-mortem examination of the experimental fish. Gills were removed (Figure 3) from controls and test fish exposed to heavy metals, treated and embedded in parafin. Gill tissue sections, five microns in thickness, were then prepared with a JUNG model 1130 microtome. Slide mounted gill sections were then stained with a method outlined by Glick (1958) and modified by Quinn (1968) to make the heavy metals obvious in the tissue. A Bausch & Lomb PB-252 microscope with polaroid camera attachment was then used to take color photomicrographs to compare the effects of lead and copper.

Prior studies have shown that wastewaters from mining environments may cause pH changes, dissolved oxygen deficiencies or other changes in water quality that may be harmful to aquatic life. With this in mind, certain important chemical parameters were measured and evaluated. Calcium, magnesium, and total water hardness was determined in order to charac-



SIDE VIEW
LEPOMIS MACROCHIRUS
GILL

FIGURE 3.

terize the major constituents of the stream water. The pH of the stream water was of interest since it strongly affects precipitation and absorption of heavy metals in solution as well as aquatic life. A portable pH meter was used to determine hydrogen ion concentration and a Precision Scientific galvanic cell oxygen analyzer was employed to determine water temperature and dissolved oxygen. A field portable water analyzer (Delta Scientific model 260) was used to determine fluorides in the field. Water and biotic grab samples obtained at the same time were bottled and returned to the laboratory for the following determinations: turbidity with a Hach model 1860 laboratory turbidimeter; total alkalinity by titration with 0.02 N H_2SO_4 to the phenolphthalein end point; and water hardness as determined by the EDTA titrametric method (Standard Methods, 1965).

Biological samples were collected at the sampling sites along with water quality samples. Biological evaluations pertinent to the research area included studies of the effects of mining pollution on bacteria, algae and fish. Since bacteria play an important role as decomposers in stream environments, Standard Plate Counts at 20° C were made to enumerate the numbers of bacterial colonies and compare population differences between unpolluted and polluted streams. Filamentous algae were collected and returned to the laboratory for identification, following the key by Palmer (1962), and further study. Nonfilamentous algae were collected with the water samples and counted by means of the transparent millipore filter technique (McNabb, 1960). Confirmatory photomicrographs were taken for comparison of both types of algae in polluted and unpolluted streams. Representative fish from the study area were collected with seines or dip-nets and identified following the key presented by Pflieger (1966) for the Fishes of Missouri.

RESULTS AND DISCUSSION

Heavy metal studies indicated that the range of values for copper, lead and zinc were from 1-20 ppb (parts per billion). The most frequently occurring values for all 3 elements were from 4-6 ppb. This parameter was used as the normal unpolluted background value for the three heavy metals.

Figure 4 shows the distribution of copper results from all nonpolluted stations. The distribution curves for lead and zinc are similar. The value of this parameter is in the interpretation of the histograms to determine contamination. The short term contamination effect in local areas is evidenced by values higher than, and distinct from, the most frequently occurring concentration range. This type of contamination has been demonstrated below Fletcher Mine where contaminated concentrations are, on the average, two-three times higher than background values (Figure 5). Contamination of long term effects would be evidenced in subsequent studies by a shifting of the most frequently occurring concentration range to higher values.

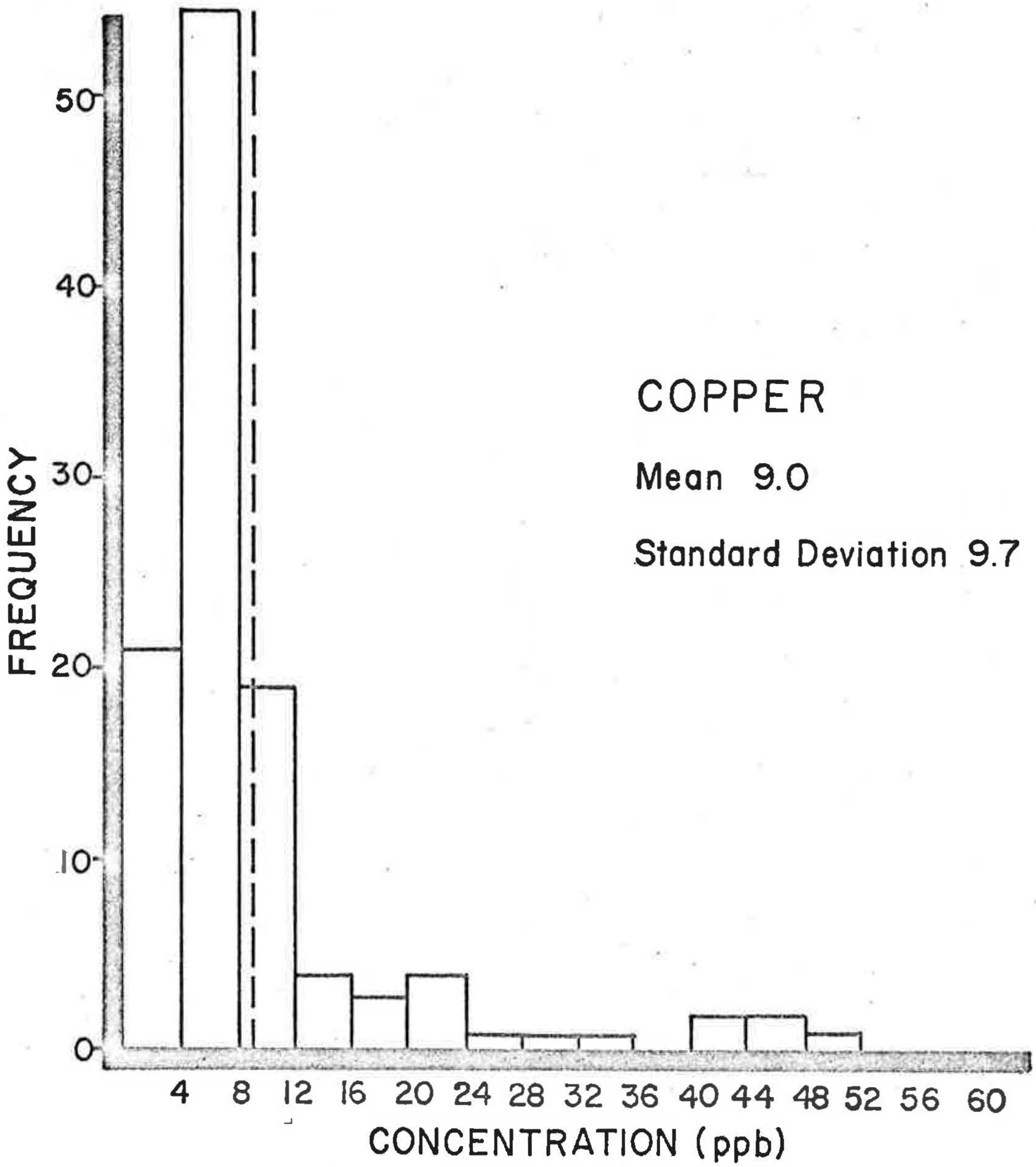


FIGURE 4. DISTRIBUTION OF COPPER RESULTS FROM ALL NON-POLLUTED STATIONS

Sampling Station	Six (Control)	Seven	Eight	Nine
		- Below Mine Discharge -		
Lead	5.8	15.3	9.1	6.2
Zinc	7.3	15.9	14.1	6.1
Copper	6.4	17.4	7.4	7.0

Figure 5. Heavy Metal Analysis (in parts per billion) for Bee Fork.

Toxicity studies indicated that the slightly basic water conditions (pH 7.8-8.2) of mine wastewater in the "New Lead Belt" would precipitate the heavy metals into existing settling ponds at concentrations now contained in the tailings discharges. Lead, zinc, and copper were found to precipitate rapidly in slightly basic (pH 7.4-8.2) water but to remain in solution in slighly acidic (pH 6.0) water. The heavy metals remaining in solution under laboratory conditions, were found to penetrate the gill tissue and destroy the membrane capability for oxygen transfer (Wixson and Handler, 1969). Copper was found to be the most toxic heavy metal studied. The concentrations of heavy metals now present in the tailing discharges were not found to approach the limits of acute toxicity to fish or to present other stream pollution problems under present water quality conditions. However, more long term studies need to be carried out to determine cumulative effects.

No significant changes in water quality were found for dissolved oxygen, alkalinity, hardness or stream temperature, however, ongoing studies have indicated that mine wastewaters may be detected by a higher fluoride concentration (1 ppm) than normally found in surface stream waters (0.15 ppm). The distribution of data on pH of stream waters in the "New Lead Belt" is shown in Figure 6.

At the Fletcher mine, underground water is pumped out at a rate of 5,000 to 7,000 gpm. Part of this water (1,600 gpm) is used for the milling flotation process where several reagents

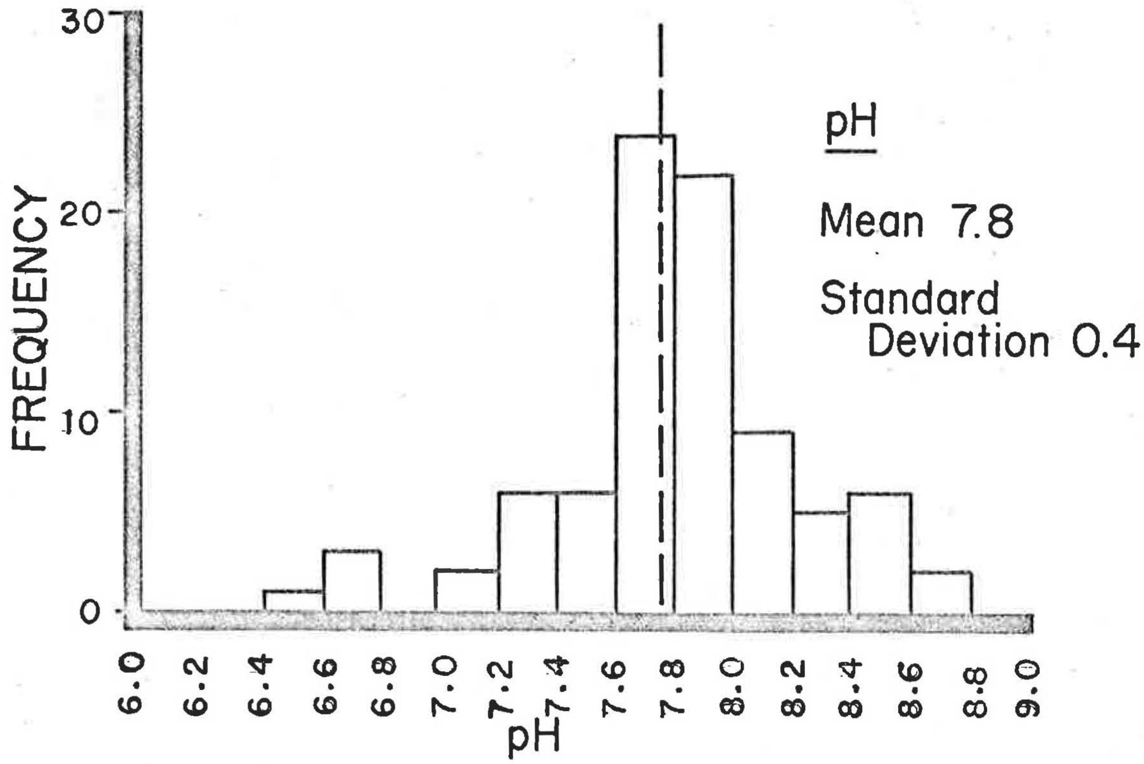


FIGURE 6. DISTRIBUTION OF pH DATA OF STREAM WATERS IN THE NEW LEAD BELT

are added. The automated flotation mill is controlled by a computer which continuously receives analytical information from an X-ray monitoring unit. The flotation reagents used comprise a series of compounds as listed in Table 1. The flotation effluents are then channeled, together with the rest of the underground water, into three settling ponds in series. Figure 7 illustrates the flow-diagram of the mine water and tailings of Fletcher plant. The total area of the three settling ponds is approximately 50 acres and the tailings flow into Bee Fork Stream via West Fork Hollow. All three settling ponds discharge over the top of a spillway arrangement. The mine water discharge from the settling ponds is approximately three times the volume of the receiving stream.

A monomolecular surface film composed of flotation reagents was found to exist in the settling ponds. This film was not detained in the settling ponds long enough for sufficient biological decomposition but moved rapidly across the surface of all three ponds. This surface film of flotation reagents was found to contribute to the stream pollution problem by contributing to the growth of bacteria and undesirable mats of blue-green algae Oscillatoria in streams receiving the settling pond effluent (Figure 8). Present studies have indicated that gram negative streptococci bacteria are able to metabolize the Xanthates for growth (Figure 9). This relationship between the organic flotation reagents, bacteria, and blue-green algae seem to have caused the growth of large algal mats in the stream bottoms. Standard Plate Counts at

343, SODIUM ISOPROPYL XANTHATE
Z-200, DIETHYL DITHIOCARBAMATE
FROTHER 71, MIXED ALCOHOLS
ZINC SULFATE, $ZnSO_4$
SODIUM CYANIDE, NaCN
COPPER SULPHATE, $CuSO_4 \cdot 5H_2O$
SODIUM DICHROMATE, $Na_2Cr_2O_7 \cdot 2H_2O$

Table 1. List of Reagents used in the Lead-Zinc Flotation Process (Courtesy of St. Joseph Lead Company).

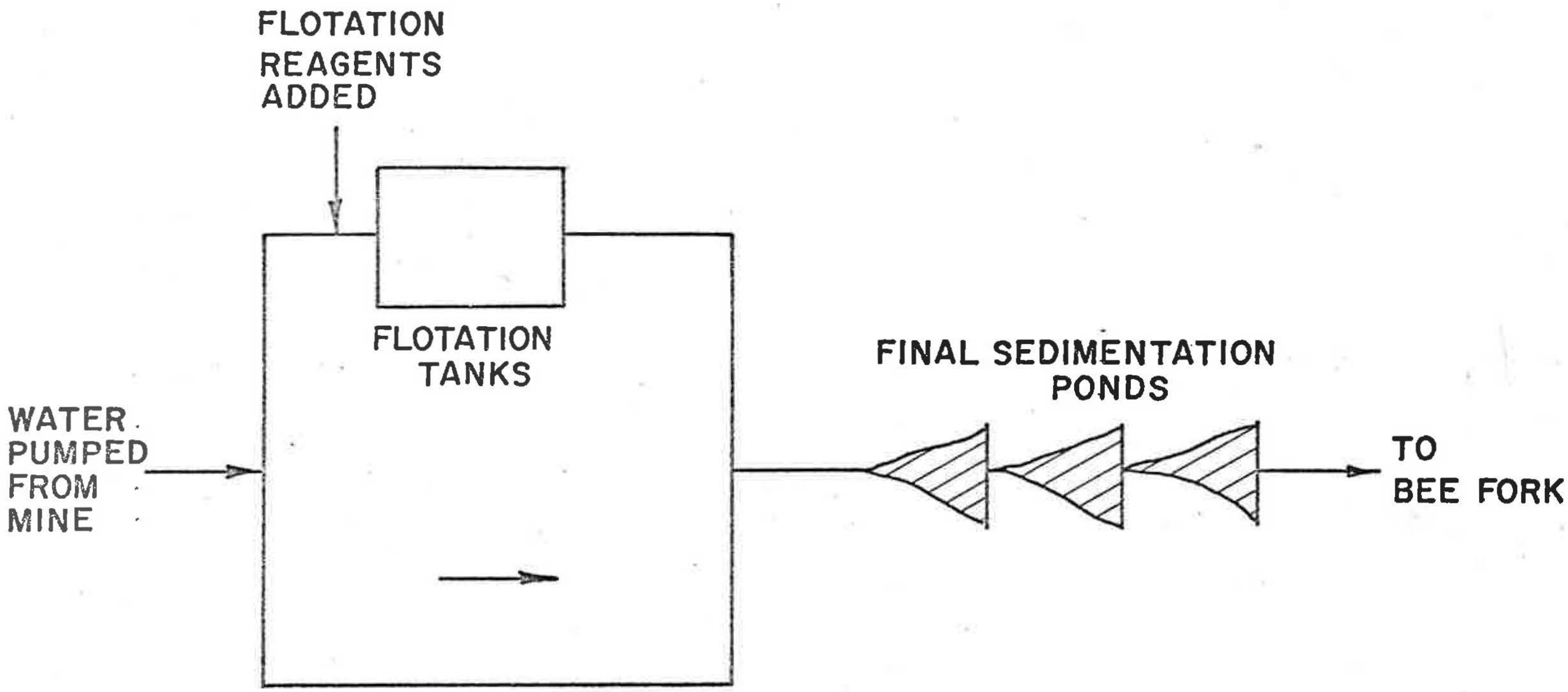


FIGURE 7. FLOW DIAGRAM OF MINE WATER AT FLETCHER PLANT

Figure 8. Undesirable growths of bacteria and blue-green <u>Oscillatoria</u> mats in a stream receiving lead-zinc milling wastewater.

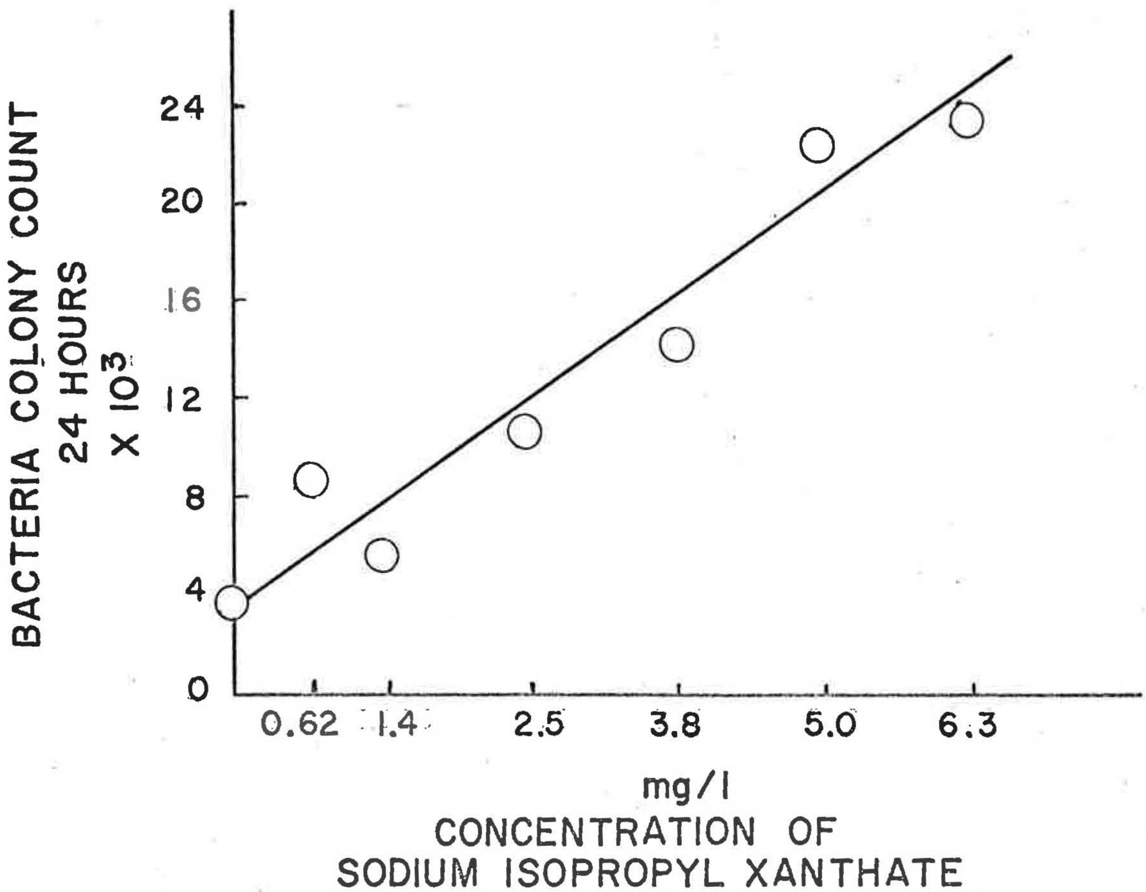


FIGURE 9. GROWTH OF BACTERIA USING SODIUM ISOPROPYL XANTHATE AS FOOD SOURCE

20°C incidated a two fold increase in the bacterial growth in milling wastewater discharges as compared with unpolluted background values. The assimilation of similar alcohol monolayers as a food source by bacteria in water has been pointed out by prior investigators (Ludzack and Ettinger, 1957) (Chang, et. al., 1962) (Wixson and Davis, 1968).

Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) determinations, useful evaluations in most pollution surveys, were found not to be applicable in this study. Other methods of analyzing the surface film of flotation reagents are now being developed. Other investigators (Mat'yakubova, Kuzovlev and Toropov, 1968) measured the surface tension of water to determine the presence of mining flotation reagents in river pollution.

Bottom sampling methods for quantitative evaluation of benthic or stream phytoplankton populations, were found to be meaningless in the "New Lead Belt" since these stream populations were usually unreliable due to the scouring action and destructive shifting of the loose gravel stream bottoms during frequent storm runoff. Other investigators (Clifford, 1966) have noted this destructive rainfall action and pointed out that the use of benthic organisms for water pollution surveys are not valid for the gravel bottom stream conditions found in south eastern Missouri. Microscopic examination of water samples revealed the presence of many diatoms composed primarily of the genus *Stauroneis*. Diatom populations were visibly larger in

Oscillatoria mats found in polluted streams. Further work is needed in order to use diatoms as biolgical indicators of pollution.

It is anticipated that additional wastewaters from expansion of existing milling operations will be discharged into the "New Lead Belt" streams during the coming year along with increased amounts of subsurface waters from mines. The evaluations of which organic or inorganic compounds affects the water quality and ecological systems, will contribute much valuable information toward protecting other streams and rivers from future lead-zinc mining pollution. This knowledge may also contribute to the substitution of flotation reagents, more efficient wastewater treatment of tailings and the development of better pollution abatement programs.

Based on the information gathered through this research, the following recommendations are presented for future stream pollution abatement in the "New Lead Belt" of south eastern Missouri: (1) separation of mine discharge water from milling and flotation process wastewater; (2) utilization of necessary settling ponds in mine discharge water to precipitate ore particles brought to the surface by pumping; (3) increased detention time for flotation process effluent for adequate biological and physical decomposition of reagents; (4) baffeling or below surface discharge of flotation treatment effluent to retain surface film of reagents; (5) clearing of trees and heavy underbrush from all settling ponds to remove excess organic matter from water and increase wind aeration process; and (6) continued research to determine improved treatment of flotation and milling wastewaters to remove any potential pollution problems.

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