E-024

FINAL REPORT

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# EFFECTS OF ACID MINE WASTEWATER UPON GRAND LAKE, NEOSHO AND SPRING RIVERS OF NORTHEASTERN OKLAHOMA

AND

# EFFECTS OF GEOLOGICAL FRACTURES AND LINEAMENTS UPON HYDROLOGIC FLOW OF ACID MINE WASTEWATER

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The investigators on this project wish to dedicate their work to the memory of a friend and coworker, David Ritt.

# ABSTACT

This investigation is an attempt to assess the influence of discharging acid mine waters on the surface water quality of Neosho and Spring Rivers, and Grand Lake in northeastern Oklahoma. Concurrently, fracturing effects on bedrock influencing the migration of surface and ground waters was investigated.

Surface water quality was analyzed for calcium, magnesium, iron, zinc, lead, etc., for trend analysis between sites. In addition, alkalinity, pH and specific conductivity were measured and correlations obtained for all parameters. Sediment core analysis was performed for metals loading into the upper end of Grand Lake. Acute toxicity bioassays were performed utilizng the aquatic invertebrates, Daphnia magna and Ceriodaphnia sp. Tar Creek and discharging mine waters were compared to assess changes in physical processes responsible for production of acidity and solublization of large quanities of toxic metals.

The chemical data appeared to correlate with site locale and precipitation events. Changes in water chemistry, while marked in Neosho and Spring Rivers, was less evident in Grand Lake. Grand Lake sediments indicate that deposition of iron and zinc is occuring; reflecting Neosho-Spring River loading. Acute toxicity has not been noted for sediment samples from upper Grand Lake, a result of minimal dissolution of metals at the water-sediment interface. Discharging mine waters are supplying larger quanities of reduced metals into Tar Creek, resulting in even lower surface water pH's.

Orientations of vertical fractures were measured in degrees of azimuth and statistical analyses performed to assess trends. Analyses of orientations indicate major fracturing zones trend northeasterly, with complimentary fracturing occurring northwesterly. Morphology of surface drainage in the area supports the former observations.

# PART I:

# EFFECTS OF ACID MINE WASTEWATER UPON GRAND LAKE, NEOSHO AND SPRING RIVERS OF NORTHEASTERN OKLAHOMA

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# INTRODUCTION

Surfacing mine water from abandoned underground lead and zinc mines, in northern Ottawa County, Oklahoma, has resulted in the areas' placement on the Environmental Protection Agency's list of hazardous sites and available for 'clean-up' with Superfund. The mines are estimated to contain over 76,000 acre-feet of low pH, highly metal-contaminated water (OWRB, 1983). In late 1979, the acidic mine water began surfacing at several points in the Tar Creek drainage basin and in subbasins along Spring River. At the time of this report, Tar Creek is void of life, except for a few aquatic insects and one species of algae capable of tolerating such harsh chemical conditions. Rock Creek, two miles east-southeast of Quapaw is also showing signs of impact from surfacing mine waters.

The overall objective of this investigation was to determine the extent of the impact of acid mine waters upon Neosho and Spring Rivers, and in particular Grand Lake. Grand Lake is a major impoundment, i.e. 1,672,000 acre feet, on the Grand (Neosho) River. The upper-most reach of Grand Lake occurs at the confluence of Neosho and Spring Rivers. The Tar Creek confluence with Neosho River occurs approximately 10 miles upstream. Deterioration of water quality within the Neosho or Spring Rivers could effect Grand Lake resulting in a serious economic impact upon a multimillion dollar recreation and resort industry.

The specific objective of this study, therefore, was to determine the capacity of Grand Lake to neutralize or dilute the acid mine waters without irrevocable damage to the ecology of the impoundment. Previous studies by Governor's Task Force on Tar Creek had determined that Neosho River had sufficient buffer capacity, i.e. alkalinity, to neutralize the acidic Tar Creek waters. Estimates of combined daily lead and zinc loading into upper end of Grand Lake prior to surfacing of mine waters was reported at 359.2 and 6.020 pounds, respectively. The daily loading of lead, zinc and cadmium by Tar Creek into Neosho River is calculated at (lbs/day based on average flow of 8 mgd, 1984) .4, 3227 and 2.7 lbs, respectively. Investigations of heavy metal chemistry and transport in surface waters indicated limited transport of dissolved species in neutral or slightly alkaline water (Stumm and Morgan, 1970, Florence, 1982). This was confirmed for upper end of Grand Lake by Tar Creek Task Force Reports which found relatively low levels of lead and zinc in the water column of upper Grand Lake but much higher levels in sediments. Therefore, a major focus of this study was to determine the critical levels of buffering agent to prevent redissolution of the high levels of lead and zinc from Grand Lake sediments. Normally buffer systems can neutralize acids generated by biological processes; however, anthropogenic activities may increase acidic substances to a level exceeding the buffer capacity of the system. If this occurs, the pH may decline to levels lethal for most biological organisms, i.e. <5 for many species. Thus, the buffer capacity of upper Grand Lake is extremely important for maintaining acceptable water quality to support aquatic life and for recreational activities. The buffer system must not only neutralize acid mine wastes, but also other inputs such as acid rainfall.

A major emphasis of this study thus focuses on the buffer capacity, i.e. acid-base equilibria, of upper Grand Lake to determine if this system has enough "reserve" capcity to neutralize additional pertubations such as acid rain.

# METHODS

Surface water samples were collected from various sites during the course of the study. A 3.2 liter VanDorn water sampler was used for the collection of water samples. All samples for heavy metal analyses were collected midway between sediments and the water surface in polypropylene bottles and acidified to a pH<2. Concurrently, samples were collected and analyzed for pH, alkalinity, specific conductivity, dissolved oxygen, etc., to aid in assessment of the general water quality. All measurements were made directly in the water sampler to minimize changes in water chemistry. Alkalinity samples were collected in polypropylene bottles, filled to overflow to eliminate air spaces, refrigerated, and alkalinity determined electrometrically within six hours. This procedure was compared with phenolphthalein-methylorange and on-site electrometric titrations with no differences noted. In fact, samples containing reduced metals required oxidation with hydrogen peroxide, prohibiting field analysis (ASTM, 1978). Duplicates were compared and all analysis performed according to standardized methods (EPA, 1979).

Sediment cores, 5 cm. X 70 cm., were collected from the upper end of Grand Lake and mouth of Tar Creek with a core sampler with removable PVC tubes. The sampler was a ballcheck single tube core sampler, with PVC core tubes and core catchers to prevent mixing of sediments when the core was withdrawn. The core tubes were packed in ice and frozen until analyzed. Sediment grab samples were also collected from the upper end of Grand Lake, to be used in bioassays with Daphnia magna, Ceriodaphnia sp., and Selenastrum capricornutum, two aquatic invertebrates and a green alga, respectively. Sediments were collected from the upper 6 inches using an standard Ekman dredge. Upon storing in plastic bags, the samples were packed in ice and frozen until analysis was performed.

All sediment sampling was made from a 20 foot barge type boat supplied by the Department of Zoology, Oklahoma State University. The boat is equipped with a 105 horsepower Chrysler engine and a depth chart recorder to permit precise location of sampling sites.

Acute bioassays were performed utilizing *Daphnia magna* and *Ceriodaphnia* sp. Both have been cultured in reconstituted water and maintained on *Selenastrum capricornutum* and yeast, respectively (EPA, 1978 and Mount and Norberg, personal communication). For the *Daphnia* bioassays test solutions contained .1 liter of the reconstituted water, ten replicates of treatments. Grand Lake sediment samples were dried under vacuum and passed through a number 30 sieve. Five grams of sediment was placed in each jar, thoroughly mixed with reconstituted water, and allowed to equilibrate for two days. Ten control solutions were put through the same regime, without Grand Lake sediments. All tests were conducted at 25°C, with a 16:8 hour light:dark cycle. Five neonates, <24 hours old, were placed in each of 10 control and treatment flasks. Additionally, in five treatment and control containers, chironomid larvae were introduced for more effective water-sediment mixing. Any mortality was recorded at 24 hour intervals, for a period of 6 days. *Ceriodaphnia* sp. bioassays were performed as above, without the introduction of chironomid larvae.

Bioassays designed to examine impact on reproduction are in progress. The treatment preparation is as above, with one *Daphnia magna* per container. The young produced are counted and gestation times compared with controls.

# RESULTS AND DISCUSSION

Samples were collected from selected locations on Tar Creek, Neosho River, Spring River and Grand Lake with the corresponding Water Resource Board sites in parentheses (Table 1, Figure 1). The concentration of toxic metals at all sites, excluding Tar Creek sites, fell within the EPA's maximum allowable concentration (MAC) except: For zinc and chromium, sites 10 and 19 (Neosho River), exceeded EPA's MAC, while sites 5 and 13 (Grand Lake) exceeded MAC limits for zinc and chromium, respectively (see Tables 2 and 3).

An intensive effort was made in July, 1983, to collect an extensive set of samples from Grand Lake and the Neosho and Spring Rivers to reflect conditions during low flow, summer conditions (Table 4). All parameters, on the Neosho River, were within acceptable ranges and reflect the minimum of discharge occuring from Tar Creek. All Grand Lake values were within the normal range for surface waters in this area. The clarity of water was strikingly different when comparing site 5 with site 7 on Grand Lake. Large amounts of sediments were transported into Grand Lake (site 5) primarily as a result of the Neosho and Spring Rivers. Elk River was very clear with a slightly lower specific conductance. The zone of mixing of Elk River Arm and Neosho-Spring River Arm of Grand Lake was clearly delimited, sediments settling out quickly once they reached the Elk River confluence.

The analysis performed on August 11, 1983, showed no significant differences other than zinc was slightly elevated below the confluence for Spring and Neosho Rivers. The means for all sites within Grand Lake, Neosho River, and Spring River were calculated and plotted to illustrate general trends (Figure 2-10). Tar Creek sites were excluded because of the high levels of metals. Grand Lake showed slight variation in alkalinity, whereas a high degree of variability was found in Neosho and Spring Rivers (Figure 2). The later may be due to several facts: 1. The inputs of acid mine waste periodically decrease the buffer capacity of the rivers, via the entry of extremely concentrated acidity and reduced metals, which, upon oxidation, produce even more acidity. 2. Low bicarbonate runoff waters mix with the buffered waters of the rivers, resulting in a dilution of the waters and buffers. 3. The rainfall is acid enough during rainfall events as to significantly decrease the normally high alkalinity of the rivers. The USGS monitoring records of flow in the Neosho and Spring Rivers and Tar Creek indicate that large volumes of low pH water may reach the rivers. Rainwater typically has a low alkalinity and a pH of approximately 5.6. The rainfall was measured in July, 1983, and March, 1984, at Twin Bridges State Park, and found to have a pH of 3.60 and 4.05, respectively. This is considered to be acidic and could also decrease the buffering capacity.

It is likely that all three events are occuring, but because this area has large exposed surfaces of carbonates, acidification of river waters is unlikely. Carbonate rocks tend to reduce acidity and buffer the water, i.e. increase alkalinity (Drever, 1982, Krauskopt, 1979). Though Grand Lake is a sink for contaminants transported by the acidified waters, no direct threat of acidification exists, under present conditions, though subtle changes in water chemisty are possible.

There was a positive correlation between rainfall and the pH values for all three groups of sites (Figure 3). The range of pH observed in both rivers is greater than observed for Grand Lake. The low pH values for October and March for the river samples corresponds to a decrease in alkalinity values, whereas the slight fluctuations in pH in Grand Lake indicates adequate buffering capacity for the current inputs of acidic water. Correlation coefficients for several parameters and the relationship between alkalinity and pH are reported (Table 5 and Figure 4).

The observed ranges of calcium and magnesium concentrations in the river systems was much larger then observed at the Grand Lake Stations (Figures 5 and 6). Calcium concentrations correlated very well with alkalinity values suggesting that changes in alkalinity were linked with changes in calcium carbonate dissolution (Table 5).

The loading of iron into the Neosho and Spring Rivers indicate a positive correlation with rainfall events (Figure 7). Large volumes of runoff entering these rivers tend to scour the bottoms of the tributaries and transport the precipitated iron compounds deposited upon oxidation of the acid mine water. Iron, as with lead and zinc, negatively correlates with pH, indicating that higher pH's result in lower soluble iron concentrations (Table 5). The concentration of iron in Grand Lake was not significantly higher than normal, probably due to the transported iron settling out, when contacting these higher pH waters.

The concentration of manganese in Grand Lake was low and fairly constant, whereas the range in concentration within Neosho and Spring rivers was greater (Figure 8). Acid mine drainage has a characteristically higher concentration of manganese then the 'normal' levels found in rivers in this area.

Zinc concentrations ranged more widely in the rivers then did lead concentrations (Figures 9 and 10). The elevated zinc concentrations in mine waters would make suspect, the origin of the zinc in the river waters. Grand Lake mean lead values suggested other sources for the lead in the surface waters. Only one date for Spring river suggested any lead being transported in the water column. Lead's extremely low solubility even in slightly acid waters, indicates it's transport is with particulates. Any lead concentrations detected below Elk River are unlikely to have acid mine water origins. Deposition of iron, lead and zinc into Grand Lake is most likely by sedimentation rather then precipitation. In fact, the Oklahoma Water Resource Board has reported the metals from sediments in the Neosho and Spring Rivers (OWRB, 1983). Tar Creek is contributing to the overall metals loading in the Neosho River while Spring River contributions reflect it's pathway through the many mining fields in the tri-state area. An alarming statistic is from the same OWRB report dealing with plankton metals concentration. Enrichment of metals in plankton as compared to the water concentrations indicate that cadmium, lead and zinc can concentrate in lower food chain organisms (Table 6). The effect of such bioconcentrating of metals is not clearly defined. Whether the filter feeding fish, or the plankton, both or neither, are being stessed is not known. The danger of high levels of metals in the sediments is to benthic organisms and the potential of becoming redissolved into the water column if a pH decrease should occur. A purely physical effect occurs, as seen in Tar Creek, where the benthic organisms are literally buried beneath precipitating metals and sedimenting particulates.

Daphnia magna and Ceriodaphnia sp. acute toxicity bioassays were performed on Grand Lake sediments. No mortality was noted during the course of the experiment, indicating that the sediments were not acutely lethal for either species.

Sediment cores were analyzed from the upper end of Grand Lake (site 5) and the resulting metals concentrations are reported (Figure 11). The total iron concentrations showed no trend whereas zinc tended to decrease with depth. Data on other elements, e.g. lead, cadmium, etc., were unavailable at the time of this report. Analysis on cores from the mouth of Tar Creek are forthcoming.

## TAR CREEK

Tar Creek's surface water quality is dominated by the discharge of acid mine water and runoff from tailings left by the mining operations. The extremely high concentrations of toxic metals is due to the oxidation and dissolution of sulfide compounds, e.g. pyrite, galena,sphalerite, etc. Iron and zinc sulfides are the primary compounds that produce the acidity and resulting metals load in the surfacing mine water. The oxidation pathway for iron sulfide (pyrite) is typical of sulfide oxidations that result in the release of protons (acidity) and dissolved metals (Figure 12). This is primarily for iron and zinc sulfides, lead produces little if any net acidity. Once the pathway of oxidation is initiated, acidity increases along with a corresponding increase in soluble metals. Even in the absence of oxygen a 'backtrigger' reaction may occur in which $Fe_2(SO)_4$ can oxidize the sulfide, and itself be reduced, releasing more ferrous iron to become oxidized, producing acidity, even in the absence of oxygen. Sulfide orebodies several hundred feet deep undergo oxidation, oxygen concentrations being extremely low (Hawley and Shikaze, 1971). In fact, $10^{-60}$ atmospheres oxygen or more are sufficient for pyrite oxidation (Barnes and Romberger, 1968).

The oxidation state of the iron, +2 or +3, controls the change, in part, of the pH from the original value once the water surfaces. If much of the iron is in the reduced (+2) state, contact with surface oxygenated water, results in oxidation of the iron and the pH of the water decreases even furthur. The relationship of pH over time provides just such an example (Figure 13). Surfacing mine water at site 28 generally had a depressed pH as compared to site 26 (Tar Creek). During low flow conditions the pH of Tar Creek water is decreased due to a higher percentage of the flow deriving from acid mine seeps. In fact the pH of Tar Creek water may be lower than the mine seeps due to oxidation of reduced metals. The large amounts of calcium and magnesium in the surfacing mine water (sites 28 and 29, Table 3) suggests that the mine water is reacting with the carbonate bedrock. A water chemistry model is being developed and preliminary results would suggest that large quantities of precipitating metals are not reaching the surface (Curt McCormick, personal communication). This is supported by alternative methods of calculation and chemical analysis' (Table 3 and Figures 14 -16). Calcium and magnesium concentrations reflect the acidity of the environment they are subjected to, and they, like the sulfates, in such acid environments, remain primarily in the aqueous state. A minimum of analysis should be required to estimate the concentation of sulfates, and in turn the amount of iron (and zinc sulfides) oxidized.

Models aid in prediction of chemical patterns from a minimal of chemical data and its application to delineating whether surfacing mine waters might have common origins is being investigated. The formation of acid mine waters in the tri-state area, especially northeastern Oklahoma and southeastern Kansas, must be understood prior to initiating expensive and often ineffective abatement stratagies.

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## TABLE 1

## SITE DESCRIPTION

Site 1 - R23E T24N S5. Located 1/3 mile west (upstream) from the Will Rogers Turnpike bridge on the Neosho River. Above Tar Creek.

Site 2 - R23E T28N S5. Downstream from the Tar Creek confluence on Neosho River. Site is 1/10 mile west (upstream) from the Will Rogers Turnpike bridge.

Site 4 - R24E T28N S30. Located 1/3 mile north (upstream) of Highway 10 bridge on Spring River.

Site 5 - R24E T27N S30. Situated 1/2 mile south of Burlington Northern railroad bridge. This is the upper end of Grand Lake approximately 3/4 mile downstream of the Neosho and Spring River confluence.

Site 6 - R24E T25N S15. Located 1/2 west of Cowskin Bridge (Highway 10) on Elk River (Grand Lake).

Site 7 - R24E T25N S12. Situated at the confluence of Elk River and Grand Lake. Note that this is on Grand Lake and disregards the Grand Lake Water that.is backed-up into the Elk River basin.

Site 10 - R24E T27N S30. Under Highway 60 bridge on the Neosho River.

Site 12 - R24E T25N S14. Located 1.1 miles upstream from Cowskin Bridge (Highway 10) on Elk River.

Site 13 - R22E T25N S26. On Highway 85A Horse Creek Bridge.

Site 14 - R24E T25N S15. Located on Cowskin Bridge (Highway 10).

Site 15 - Grand Lake Dam. Samples collected from east end.

Site 16 - R24E T24N S17. Located on Honey Creek Bridge (Highway 10).

Site 17 - R23E T28N S31. Located approximately 1/6 mile downstream from highway 125 bridge.

Site 18 - R23E T28N S31. Highway 125 bridge over Neosho in Miami, Ok.

Site 19 - R23E T27N S26. Mudeater Bend Bridge over Neosho River.

## TABLE 1, cont.

Site 20 - R24E T27N S19. Highway 60 Bridge and Spring River.

Site 22 - R24E T28N S5. Devil's Promenado Bridge over Spring River.

Site 26 - R23E T28N S30. N.E.O.S.U. and Tar Creek Bridge. (OWRB #20).

Site 27 - R23E T29N S18. Tar Creek and Treece, Ok. (OWRB #7).

Site 28 - R23E T28N S7. Farmers Horse Pasture, Commerce, Ok. (OWRB #14)

Site 29 - R23E T29N S29. OWRB Site #4.

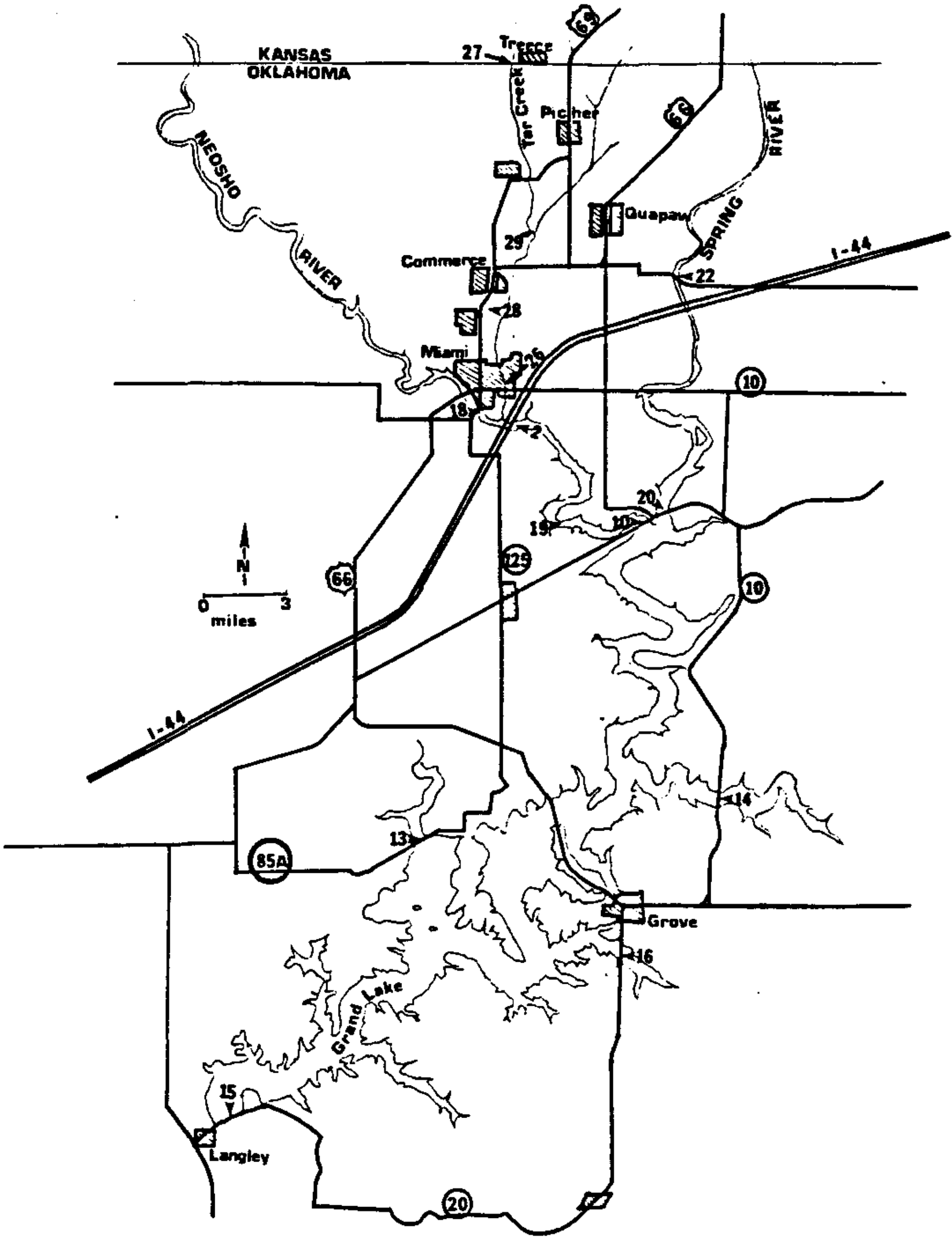

Figure 1. Map of study area with selected sites indicated.

## TABLE 2. SUMMARY OF EPA'S MAXIMUM ALLOWABLE CONCENTRATIONS OF TRACE TOXIC METALS FOR PROTECTION OF AQUATIC LIFE IN RECEIVING WATERS

| Parameter | Maximum Allowable Concentration* (mg/l) |
|---|---|
| Arsenic | 0.44 |
| Cadmium | 0.05 |
| Chromium | 0.021 |
| Copper | 0.043 |
| Lead | 0.400 |
| Nickel | 3.100 |
| Selenium | 0.260 |
| Zinc | 0.570 |
| Mercury | 0.0000017 |

*Calculated for receiving waters with hardness of >200 mg/l (Fed. Reg. 45(231) 79317-79379, Nov. 28, 1980).

# TABLE 3

## RESULT OF ANALYSIS ON TAR CREEK, NEOSHO RIVER, SPRING RIVER AND GRAND LAKE SAMPLES* BY DATE

| | | Ca | Mg | Fe | Pb | Zn | Cu | Cr | Ni | Cd | Mn | Se | Hg | As |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Site 1 | | | | | | | | | | | | | | |
| 08-11-83 | Dis 2.5 m | 44.1 | 10.0 | <0.04 | 0.017 | <0.05 | <0.04 | <0.01 | <0.1 | <0.005 | <0.05 | <0.01 | <0.002 | <0.01 |
| 08-11-83 | Total 2.5 m | 47.0 | 10.0 | 1.24 | 0.012 | 0.08 | <0.04 | <0.01 | <0.1 | <0.005 | <0.05 | 0.01 | <0.002 | <0.01 |
| Site 2 | | | | | | | | | | | | | | |
| 08-11-83 | Dis 2.5 m | 41.1 | 8.6 | <0.04 | 0.020 | 0.05 | <0.04 | <0.01 | <0.1 | <0.005 | <0.05 | <0.01 | <0.002 | <0.01 |
| 08-11-83 | Total 2.5 m | 46.5 | 11.0 | 1.37 | 0.005 | 0.06 | <0.04 | <0.01 | <0.1 | <0.005 | <0.05 | <0.01 | <0.002 | <0.01 |
| Site 4 | | | | | | | | | | | | | | |
| 08-11-83 | Dis 1.0 m | 55.3 | 5.2 | <0.04 | 0.006 | <0.05 | <0.04 | <0.01 | <0.1 | <0.005 | <0.05 | <0.01 | <0.002 | <0.01 |
| 08-11-83 | Dis 3.0 m | 49.2 | 5.1 | <0.04 | 0.008 | <0.05 | <0.04 | <0.01 | <0.1 | <0.005 | <0.05 | <0.01 | <0.002 | <0.01 |
| 08-11-83 | Total 3.0 m | 53.6 | 5.7 | 0.38 | 0.010 | 0.09 | <0.04 | <0.01 | <0.1 | <0.005 | 0.06 | <0.01 | <0.002 | <0.01 |
| 08-11-83 | Dis 6.0 m | 45.0 | 11.6 | <0.04 | 0.008 | 0.47 | <0.04 | <0.01 | <0.1 | <0.005 | 0.11 | <0.01 | <0.002 | <0.01 |
| Site 5 | | | | | | | | | | | | | | |
| 08-11-83 | Dis 6.0 m | 45.9 | 10.6 | <0.04 | 0.016 | 0.33 | <0.04 | <0.01 | <0.1 | <0.005 | 0.12 | <0.01 | <0.002 | <0.01 |
| 08-11-83 | Dis 4.0 m | 31.6 | 5.2 | <0.04 | 0.020 | <0.05 | <0.04 | <0.01 | <0.1 | <0.005 | <0.05 | <0.01 | <0.002 | <0.01 |
| 08-11-83 | Total 6.0 m | 53.5 | 10.6 | 0.42 | 0.018 | 0.68 | <0.04 | <0.01 | <0.1 | <0.005 | 0.15 | 0.01 | <0.002 | <0.01 |
| 08-11-83 | Total 4.0 m | 40.1 | 6.9 | <0.04 | 0.008 | 0.06 | <0.04 | <0.01 | <0.1 | <0.005 | <0.05 | <0.01 | <0.002 | <0.01 |
| Site 7 | | | | | | | | | | | | | | |
| 08-11-83 | Dis | 37.7 | 7.8 | 0.13 | 0.019 | 0.09 | <0.04 | <0.01 | <0.1 | <0.005 | 0.21 | <0.01 | <0.002 | <0.01 |
| 08-11-83 | Total | 47.2 | 7.7 | 0.97 | 0.010 | 0.23 | 0.18 | <0.01 | <0.1 | 0.005 | 0.11 | <0.01 | <0.002 | <0.01 |
| Site 10 | | | | | | | | | | | | | | |
| 10-22-83 | Total | 13.3 | 7.7 | 25.3 | <0.005 | 0.31 | | 0.04 | | <0.005 | 0.61 | | | |
| 03-06-84 | " | 24.8 | 10.4 | 16.80 | <0.005 | 1.35 | | <0.01 | | <0.005 | 0.32 | | | |
| 05-20-84 | " | 51.7 | 11.0 | 1.10 | | <0.01 | <0.04 | | | | 0.12 | | | |

*Graphite furnace elements for 5-20-84 unavailable at time of report. Data for 6-23-84 forthcoming.

TABLE 3, continued

| | | Ca | Mg | Fe | Pb | Zn | Cu | Cr | Ni | Cd | Mn |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Site 13 | | | | | | | | | | | |
| 08-11-83 | Total | 36.1 | 6.1 | 0.09 | <0.005 | <0.05 | <0.04 | 0.03 | <0.1 | <0.005 | <0.05 |
| 08-11-83 | " | 35.7 | 6.4 | <0.04 | <0.005 | <0.05 | <0.04 | 0.02 | <0.1 | <0.005 | <0.05 |
| 10-22-83 | " | 37.4 | 6.7 | 0.30 | <0.005 | <0.01 | | <0.04 | | <0.005 | 0.02 |
| 10-22-83 | " | 38.6 | 6.9 | 0.30 | <0.005 | <0.01 | | <0.04 | | <0.005 | 0.02 |
| 03-06-84 | " | 32.7 | 7.6 | 0.48 | <0.005 | 0.06 | | <0.01 | | <0.005 | 0.05 |
| 05-20-84 | " | 42.4 | 5.3 | 0.61 | | <0.01 | <0.04 | | | | <0.05 |
| 05-20-84 | " | 35.2 | 5.2 | 0.73 | | <0.01 | <0.04 | | | | <0.05 |
| Site 14 | | | | | | | | | | | |
| 08-11-83 | Total | 39.6 | 6.1 | <0.04 | 0.005 | <0.05 | <0.04 | <0.01 | <0.1 | <0.005 | <0.05 |
| 10-22-83 | " | 39.9 | 5.0 | 0.40 | <0.005 | 0.08 | | <0.04 | | <0.005 | 0.02 |
| 03-06-84 | " | 29.5 | 3.2 | 2.20 | <0.005 | 0.08 | | <0.01 | | <0.005 | 0.12 |
| 05-20-84 | " | 44.3 | 3.6 | 0.06 | | <0.01 | <0.04 | | | | <0.05 |
| Site 15 | | | | | | | | | | | |
| 10-22-83 | Total | 38.9 | 6.8 | 0.20 | <0.005 | 0.08 | | <0.04 | | <0.005 | 0.04 |
| 03-06-84 | " | 37.9 | 17.9 | 0.55 | <0.005 | 0.09 | | <0.01 | | <0.005 | 0.06 |
| 05-20-84 | " | 37.4 | 5.4 | 0.38 | | <0.01 | <0.04 | | | | <0.05 |
| Site 16 | | | | | | | | | | | |
| 08-11-83 | Total | 36.2 | 4.8 | 0.07 | <0.005 | <0.05 | <0.04 | <0.01 | <0.1 | <0.005 | 0.13 |
| 10-22-83 | " | 37.8 | 6.6 | 0.40 | <0.005 | 0.17 | | <0.04 | | <0.005 | 0.05 |
| 10-22-83 | " | 38.8 | 6.8 | 0.50 | <0.005 | 0.03 | | <0.04 | | <0.005 | 0.05 |
| 05-20-84 | " | 35.7 | 5.4 | 0.26 | | <0.01 | <0.04 | | | | <0.05 |
| Site 17 | | | | | | | | | | | |
| 08-11-83 | Total | 48.2 | 11.4 | 0.04 | <0.005 | <0.05 | <0.04 | <0.01 | <0.1 | <0.005 | 0.05 |
| 10-22-83 | " | 12.3 | 6.0 | 18.40 | <0.005 | 0.10 | | <0.04 | | <0.005 | 0.34 |
| Site 18 | | | | | | | | | | | |
| 03-06-84 | Total | 23.6 | 11.3 | 12.58 | <0.005 | 0.09 | | <0.01 | | <0.005 | 0.33 |
| 05-20-84 | " | 52.7 | 12.4 | 2.17 | | <0.01 | <0.04 | | | | 0.16 |

TABLE 3, continued

| | Ca | Mg | Fe | Pb | Zn | Cu | Cr | Ni | Cd | Mn |
|---|---|---|---|---|---|---|---|---|---|---|
| Site 19 | | | | | | | | | | |
| 10-22-83 | 13.5 | 8.0 | 27.30 | <0.005 | 0.31 | | 0.05 | | <0.005 | 1.10 |
| 03-06-84 | 22.3 | 8.5 | 18.41 | 0.005 | 1.14 | | <0.01 | | <0.005 | 0.36 |
| 05-20-84 | 51.8 | 12.0 | 1.38 | | <0.01 | <0.040 | | | | 0.11 |
| Site 20 | | | | | | | | | | |
| 10-22-83 | 13.4 | 3.3 | 4.50 | <0.005 | 0.27 | | <0.04 | | <0.005 | 0.12 |
| 03-06-84 | 19.4 | 6.0 | 13.21 | 0.154 | 0.45 | | <0.01 | | <0.005 | 0.47 |
| 05-20-84 | 48.8 | 4.6 | 0.97 | | <0.01 | <0.040 | | | | 0.34 |
| Site 22 | | | | | | | | | | |
| 10-22-83 | 14.3 | 3.2 | 5.50 | <0.005 | 0.28 | | <0.04 | | <0.005 | 0.12 |
| 03-06-84 | 18.4 | 5.6 | 15.61 | 0.029 | 0.54 | | <0.01 | | <0.005 | 0.58 |
| 05-20-84 | 50.9 | 4.6 | 0.24 | | 0.06 | <0.040 | | | | 0.12 |
| Site 26 | | | | | | | | | | |
| 10-22-83 | 1620.0 | 60.0 | 53.90 | <0.005 | 48.30 | | <0.04 | | 0.043 | 1.90 |
| 03-06-84 | 154.4 | 56.4 | 90.80 | <0.005 | 47.37 | | <0.01 | | 0.033 | 1.48 |
| 05-23-84 | 3040.1 | 793.9 | 10.61 | | 62.32 | 0.016 | | | | 2.89 |
| Site 27 | | | | | | | | | | |
| 10-22-83 | 2480.0 | 8.4 | 2.80 | 0.005 | 5.41 | | <0.04 | | 0.027 | 0.12 |
| 03-06-84 | 43.0 | 8.5 | 5.59 | 0.006 | 2.83 | | <0.01 | | <0.005 | 0.18 |
| 05-23-84 | 2615.9 | 124.2 | 0.30 | | 5.86 | 0.022 | | | | 0.33 |
| Site 28 | | | | | | | | | | |
| 10-22-83 | 940.0 | 1350.0 | 533.00 | <0.005 | 73.30 | | <0.04 | | <0.005 | 4.62 |
| 03-06-84 | 195.6 | 145.7 | 487.19 | <0.005 | 1.01 | | <0.01 | | <0.005 | 4.37 |
| 05-23-84 | 1646.3 | 1414.0 | 455.51 | | 47.17 | 0.020 | | | | 4.32 |
| Site 29 | | | | | | | | | | |
| 10-22-83 | 1420.0 | 1600.0 | 433.00 | <0.005 | 217.50 | | <0.04 | | 0.104 | 7.32 |
| 03-06-84 | 174.6 | 238.8 | 396.93 | 0.008 | 235.33 | | <0.01 | | 0.055 | 5.16 |
| 05-23-84 | 3747.1 | 2569.4 | 338.35 | | 178.77 | 0.021 | | | | 5.16 |

# TABLE 4

## General Water Quality Measurments for July-August, 1983

### Site 1

| | Depth meters | Temperature °C | Dissolved Oxygen mg/L | pH SU | Sp. Cond. umhos/cm |
|---|---|---|---|---|---|
| 15 July | 0 | 28.0 | 7.0 | 7.4 | 350 |
| | 1 | 27.5 | 7.1 | | 350 |
| | 2 | 27.5 | 7.0 | | 355 |
| | 3 | 27.0 | 6.6 | | 358 |
| | 4 | 27.0 | 6.4 | | 360 |
| | 5 | 27.0 | 5.7 | | 360 |
| | 6 | 27.0 | 5.8 | | 380 |
| 20 July | 0 | 29.8 | 7.9 | | 365 |
| | 1 | 29.3 | 6.5 | | 370 |
| | 2 | 29.3 | 6.5 | | 375 |
| | 3 | 28.9 | 5.9 | | 380 |
| | 4 | 28.0 | 5.3 | | |
| | 5 | 27.0 | 1.5 | | |
| 1 August | 0 | 30.9 | 5.7 | | 431 |
| | 1 | 30.2 | 5.3 | | 431 |
| | 2 | 30.3 | 5.2 | | 432 |
| | 3 | 30.2 | 3.9 | | 438 |

### Site 2

| | Depth meters | Temperature °C | Dissolved Oxygen mg/L | pH | Specific Conductance umhos/cm |
|---|---|---|---|---|---|
| 15 July | 0 | 29.0 | 6.5 | 7.2 | 360 |
| | 1 | 27.8 | 6.1 | | 365 |
| | 2 | 27.8 | 5.9 | | 368 |
| | 3 | 27.5 | 5.7 | | 375 |
| | 4 | 27.5 | 5.7 | | 380 |
| | 4.3 | 27.5 | 0.8 | | 1000 |
| 20 July | 0 | 31.0 | 8.5 | | 380 |
| | 1 | 29.9 | 6.8 | | 380 |
| | 2 | 29.5 | 6.2 | 6.8 | 382 |
| | 3 | 29.0 | 5.6 | | 392 |
| | 4 | 28.0 | 4.3 | | 850 |
| | 4.3 | 27.5 | 0.8 | | 1080 |
| 1 August | 0 | 31.2 | 5.5 | | 441 |
| | 1 | 30.9 | 4.9 | | 441 |
| | 2 | 30.7 | 4.6 | | 447 |
| | 3 | 30.3 | 4.1 | | 482 |

## Site 4

| | Depth meters | Temperature °C | Dissolved Oxygen mg/L | pH SU | Specific Conductance umhos/cm |
|---|---|---|---|---|---|
| July 17 | 0 | 26.5 | 6.7 | 7.0 | 360 |
| | 1 | 26.2 | 6.2 | | 363 |
| | 2 | 26.0 | 6.2 | 6.9 | 370 |
| | 3 | 26.0 | 5.6 | | 370 |
| July 27 | 0 | 30.1 | 5.4 | | 393 |
| | 1 | 30.1 | 5.2 | | 400 |
| | 2 | 30.1 | 5.3 | | 403 |

## Site 5

| | Depth meters | Temperature °C | Dissolved Oxygen mg/L | pH SU | Specific Conductance umhos/cm |
|---|---|---|---|---|---|
| July 20 | 0 | 32.0 | 10.5 | 6.7 | 355 |
| | 1 | 31.0 | 9.4 | | 355 |
| | 2 | 29.5 | 7.6 | | 370 |
| | 3 | 28.2 | 5.3 | | 378 |
| | 4 | 28.2 | 5.1 | | 398 |
| | 5 | 27.7 | 4.3 | | 402 |
| | 6 | 27.3 | 3.0 | 6.6 | 400 |
| | >6 | 27.2 | 3.4 | | 421 |
| July 27 | 0 | 31.2 | 7.9 | | 380 |
| | 1 | 31.0 | 7.2 | | 382 |
| | 2 | 30.6 | 6.6 | | 380 |
| | 3 | 30.2 | 4.8 | | 395 |
| | 4 | 29.8 | 3.0 | | 398 |
| | 5 | 28.8 | 1.2 | | 404 |
| July 29 | 0 | 33.0 | 8.3 | | 390 |
| | 1 | 32.0 | 6.6 | | 390 |
| | 2 | 31.5 | 6.1 | | 388 |
| | 3 | 31.2 | 5.8 | 7.3 | 385 |
| | 4 | 31.0 | 3.5 | | 412 |
| | 5 | 30.1 | 2.0 | | 430 |
| | 6 | 29.7 | 1.1 | | 445 |

## Site 6

| | Depth meters | Temperature °C | Dissolved Oxygen mg/L | pH SU | Specific Conductance umhos/cm |
|---|---|---|---|---|---|
| July 20 | 0 | 31.5 | 12.6 | 7.2 | 270 |
| | 1 | 31.0 | 12.5 | | 270 |
| | 2 | 31.0 | 12.6 | | 272 |
| | 3 | 31.0 | 12.8 | | 278 |
| | 4 | 29.0 | 5.9 | | 290 |
| | 5 | 28.5 | 2.0 | | 300 |
| | 6 | 28.2 | 2.5 | | 350 |

## Site 7

| | Depth meters | Temperature °C | Dissolved Oxygen mg/1 | pH SU | Specific Conductance umhos/cm |
|---|---|---|---|---|---|
| | 0 | 31.0 | 10.7 | | 320 |
| | 1 | 30.8 | 10.0 | | 325 |
| July 20 | 2 | 30.5 | 10.0 | | 327 |
| | 3 | 30.0 | 7.5 | | 329 |
| | 4 | 29.0 | 6.4 | | 329 |
| | 5 | 28.9 | 6.0 | | 330 |
| | 6 | 27.9 | 1.7 | 6.9 | 325 |
| | 7 | 27.3 | 1.3 | | 332 |
| | 8 | 27.2 | 1.0 | | 330 |
| | >8 | 27.1 | 0.8 | | 465 |
| | 0 | 30.9 | 6.4 | | 312 |
| | 1 | 30.7 | 6.3 | | 320 |
| July 29 | 2 | 30.5 | 6.0 | | 322 |
| | 3 | 30.3 | 5.8 | | 325 |
| | 4 | 30.1 | 5.6 | 7.3 | 325 |
| | 5 | 30.1 | 5.8 | | 327 |
| | 6 | 30.0 | 5.1 | | 330 |
| | 7 | 29.7 | 2.7 | | 324 |
| | 8 | 29.0 | 1.0 | | 338 |

## Site 10

| | Depth meters | Temperature °C | Dissolved Oxygen mg/L | pH SU | Conductance umhos/cm |
|---|---|---|---|---|---|
| | 0 | 29.0 | 6.6 | 7.0 | 360 |
| | 1 | 29.0 | 6.2 | | 360 |
| July 15 | 2 | 28.3 | 5.5 | | 360 |
| | 3 | 28.0 | 5.4 | | 360 |
| | 4 | 28.0 | 5.4 | | 360 |
| | 5 | 28.0 | 5.1 | | 360 |
| | 6 | 28.0 | 5.2 | | 362 |
| | 7 | 28.0 | 5.2 | | 365 |
| | >7 | 28.0 | 0.6 | | 370 |

## Site 12

| | Depth meters | Temperature °C | Dissolved Oxygen mg/L | pH SU | Specific Conductance umhos/cm |
|---|---|---|---|---|---|
| | 0 | 32.0 | 8.2 | | 259 |
| | 1 | 31.0 | 6.3 | | 261 |
| July 29 | 2 | 31.0 | 5.4 | | 263 |
| | 3 | 30.6 | 4.4 | 6.8 | 267 |
| | 4 | 30.0 | 2.7 | | 278 |
| | 5 | 29.3 | 1.1 | | 293 |
| | 6 | 28.5 | 0.9 | | 420 |

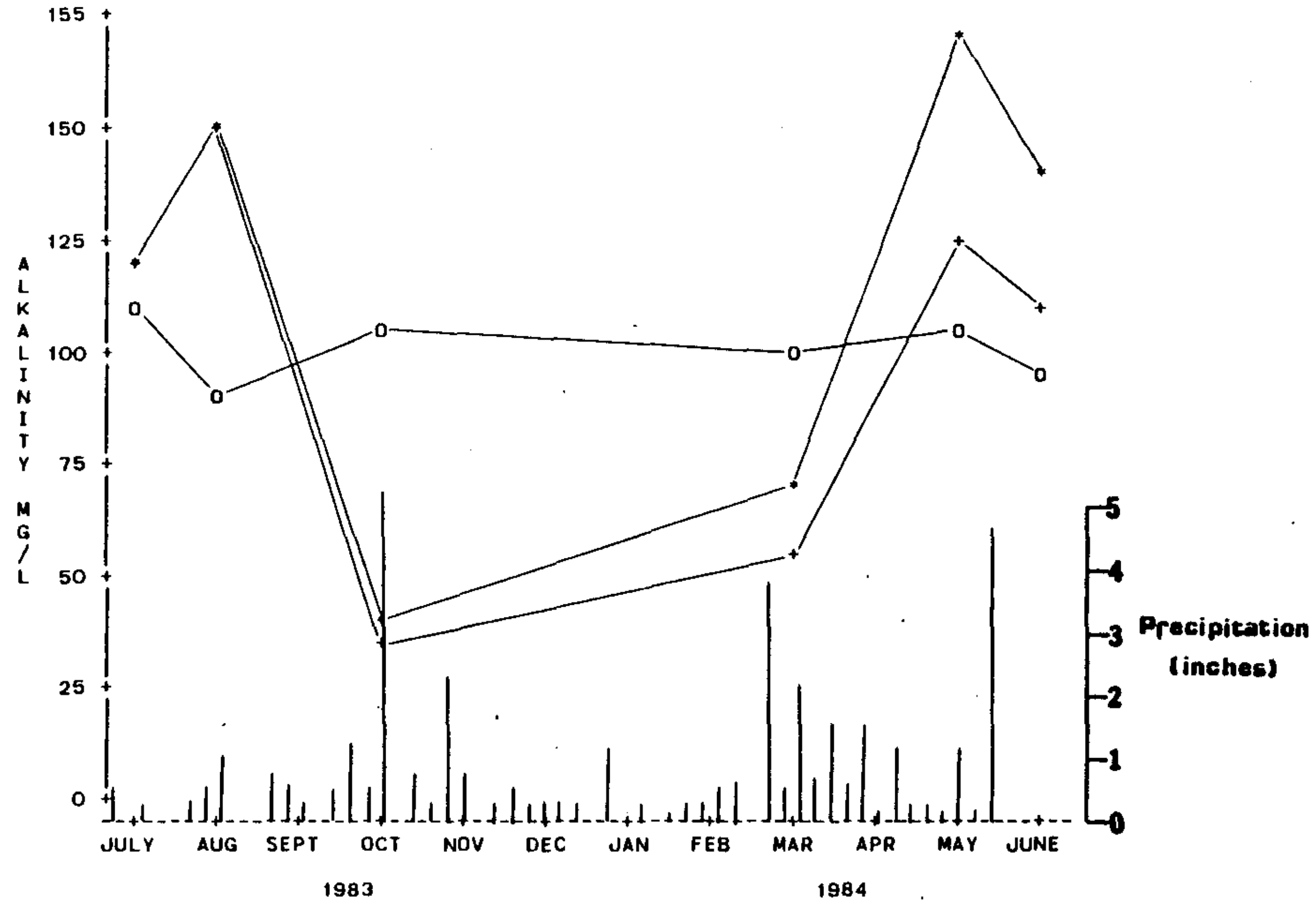

Figure 2. Plot of mean alkalinity (as CaCo3) values over time. Grand Lake sites (0), Neosho River sites (*) and Spring River sites are shown.

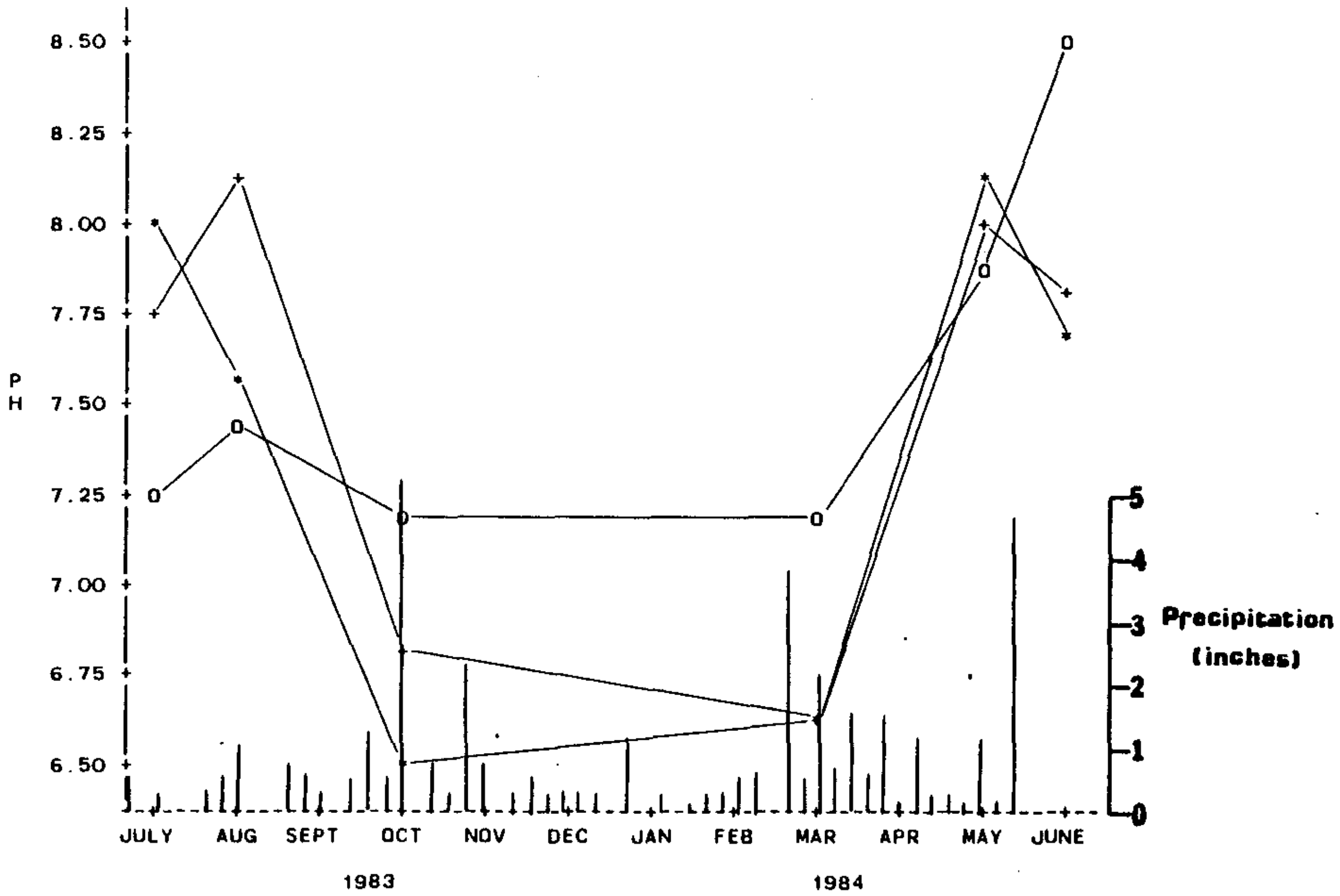

Figure 3. Plot of mean pH values over time. Grand Lake sites (0), Neosho River sites (*) and Spring River sites (+) are shown.

## TABLE 5

## CORRELATION COEFFICIENTS FOR ALL DATA
n=number of observations

| | PARAMETER | | | | | | |
|---|---|---|---|---|---|---|---|
| | ALK | CA | MG | MN | FE | PB | ZN |
| PH | 0.59 | 0.72 | 0.065 | -0.48 | -0.66 | -0.20 | -0.61 |
| n= | 60 | 32 | 32 | 32 | 32 | 23 | 32 |
| ALK | | 0.84 | 0.34 | -0.47 | -0.62 | -0.22 | -0.52 |
| n= | | 31 | 31 | 31 | 31 | 23 | 31 |
| CA | | | 0.48 | 0.45 | 0.25 | -0.08 | 0.49 |
| n= | | | 61 | 61 | 61 | 52 | 61 |
| MG | | | | 0.83 | 0.31 | -0.08 | 0.60 |
| n= | | | | 61 | 61 | 52 | 61 |
| MN | | | | | 0.73 | -0.06 | 0.63 |
| n= | | | | | 61 | 52 | 61 |
| FE | | | | | | -0.04 | 0.65 |
| n= | | | | | | 52 | 61 |
| PB | | | | | | | -0.09 |
| n= | | | | | | | 52 |

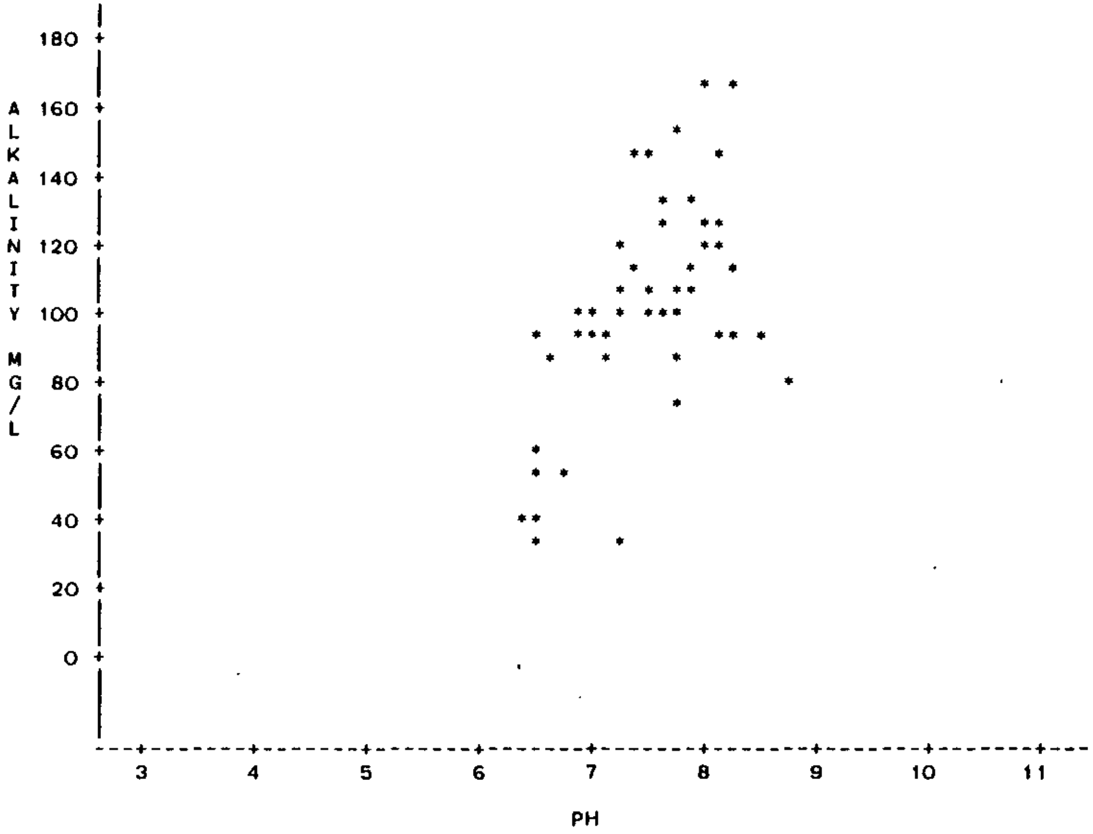

Figure 4. Plot of alkalinity (mg/L as CaCO3) and pH.

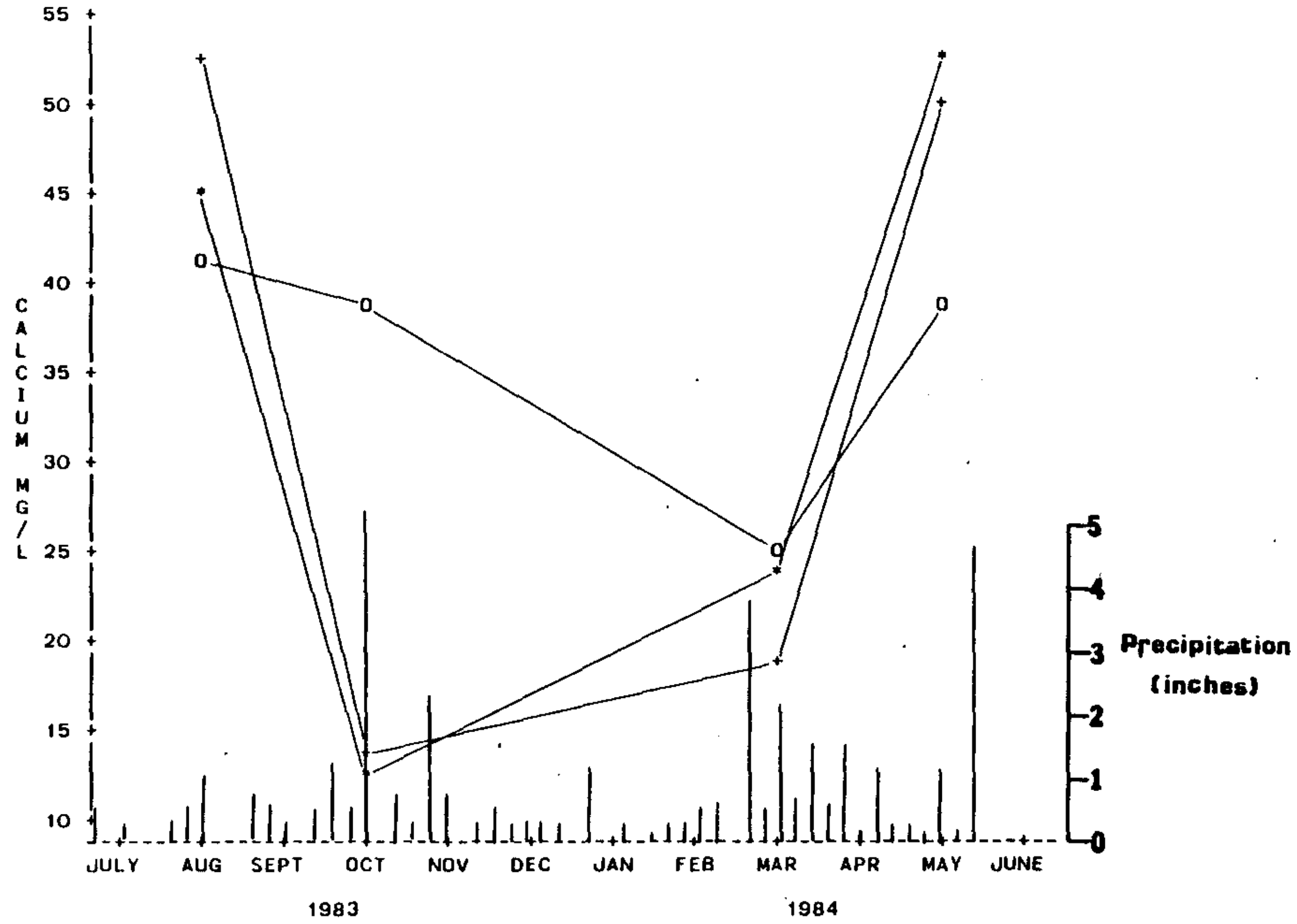

Figure 5. Plot of mean calcium values over time. Grand Lake sites (0), Neosho River sites (*) and Spring River sites (+) are shown.

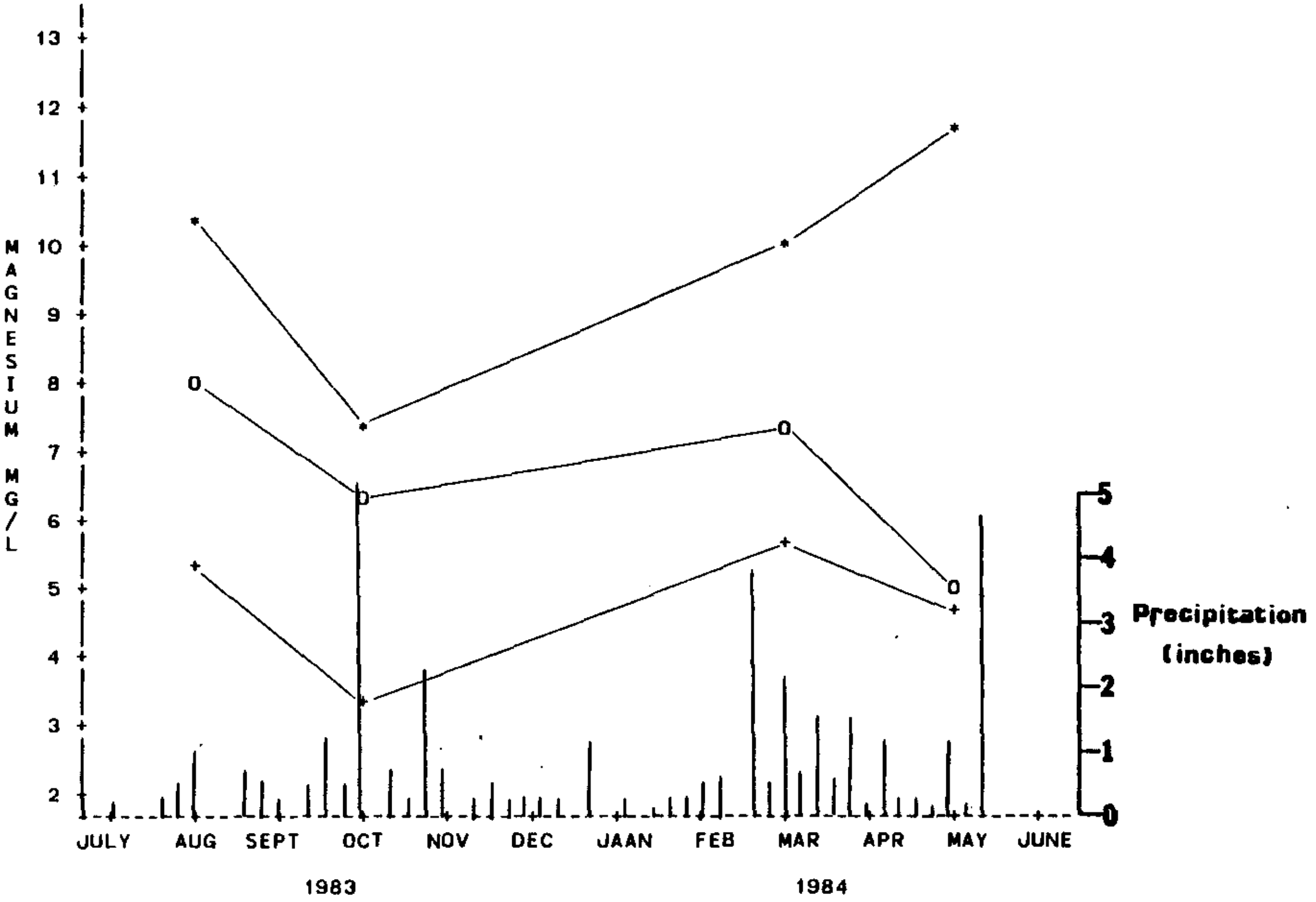

Figure 6. Plot of mean magnesium values over time. Grand Lake sites (O), Neosho River sites (*) and Spring River sites (+) are shown.

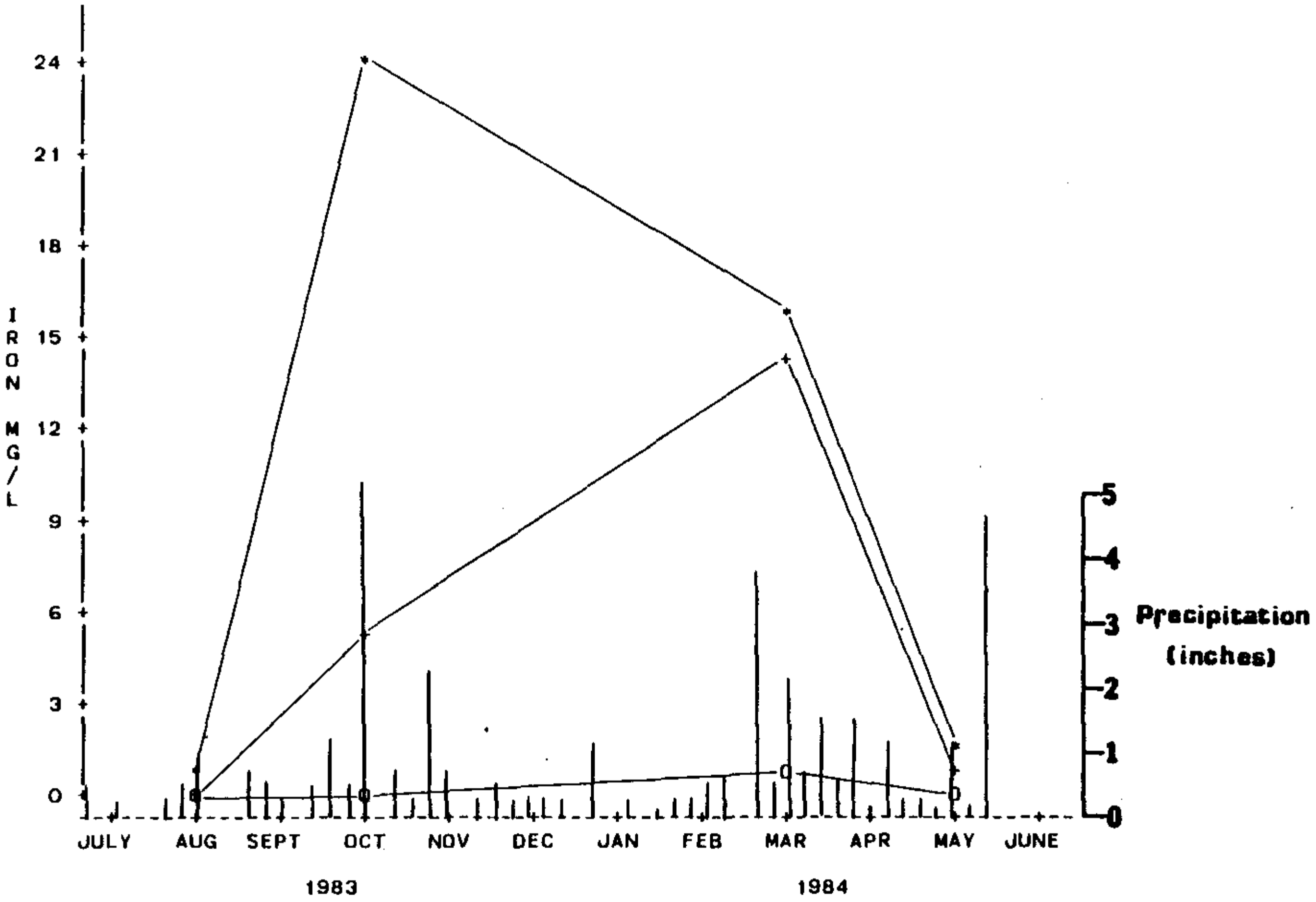

Figure 7. Plot of mean iron values over time. Grand Lake sites (O), Neosho River sites (*) and Spring River sites (+) are shown.

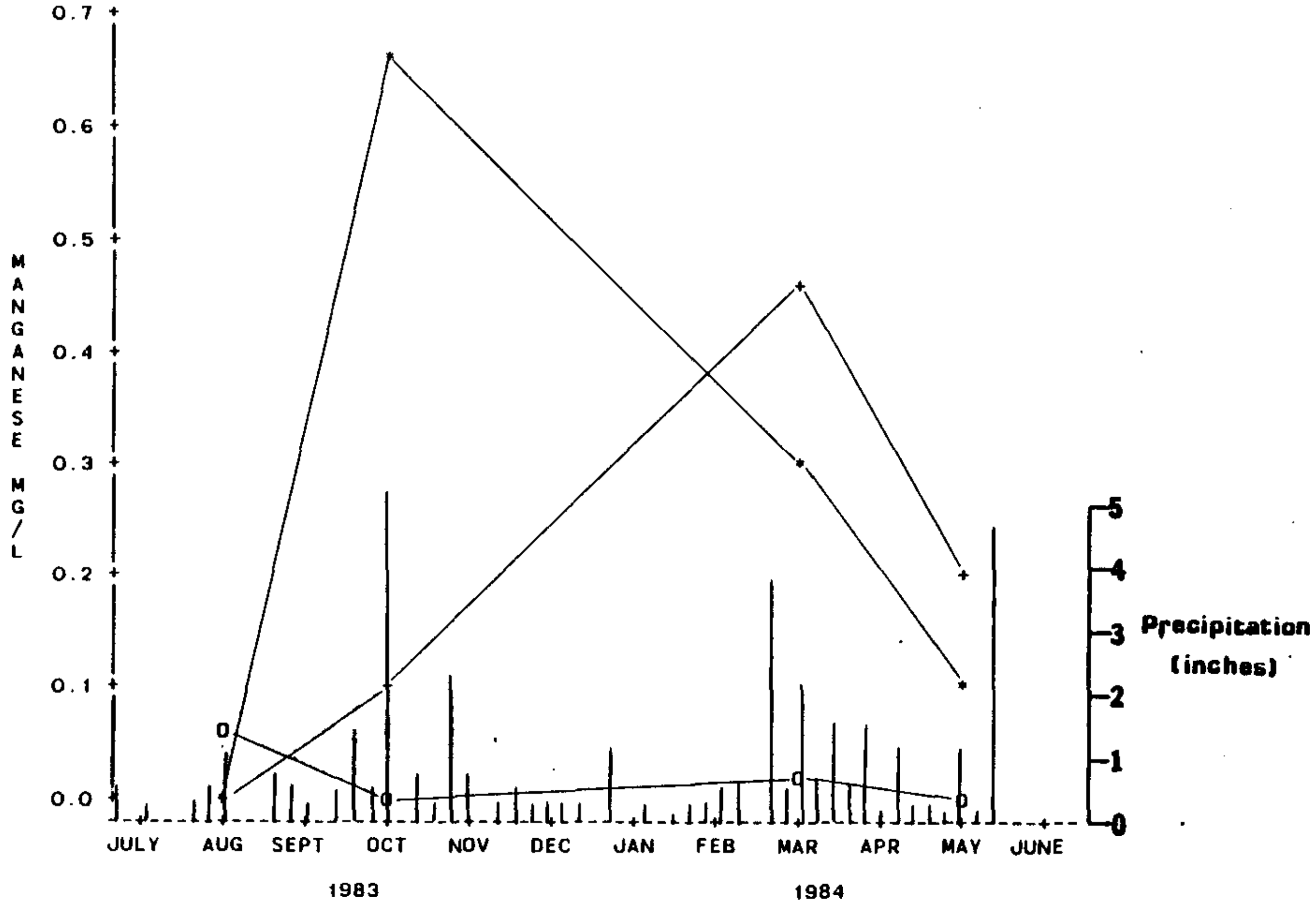

Figure 8. Plot of mean manganese values over time. Grand Lake sites (0), Neosho River sites (*) and Spring River sites (+) are shown.

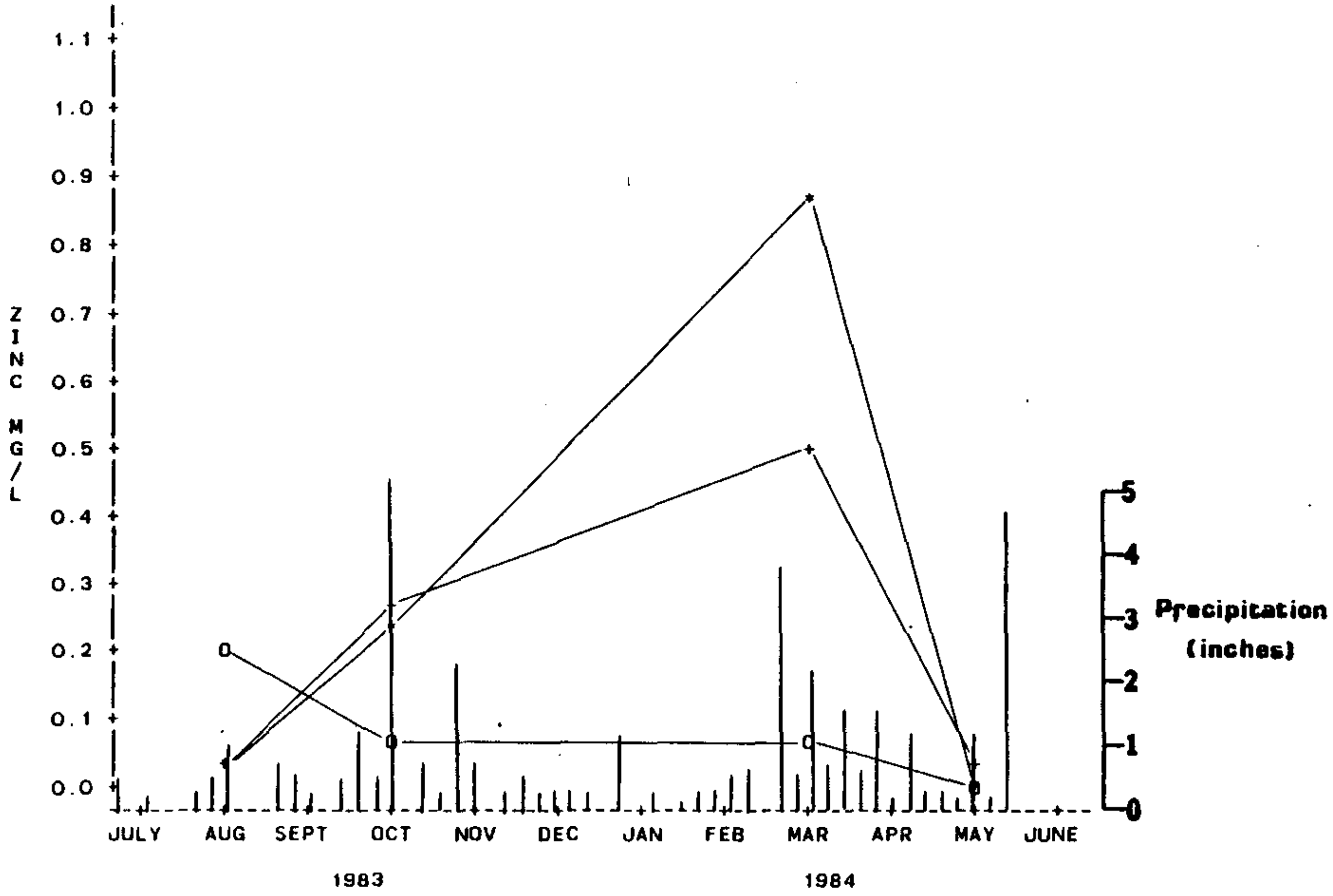

Figure 9. Plot of mean zinc values over time. Grand Lake sites (0), Neosho River sites (*) and Spring River sites (+) are shown.

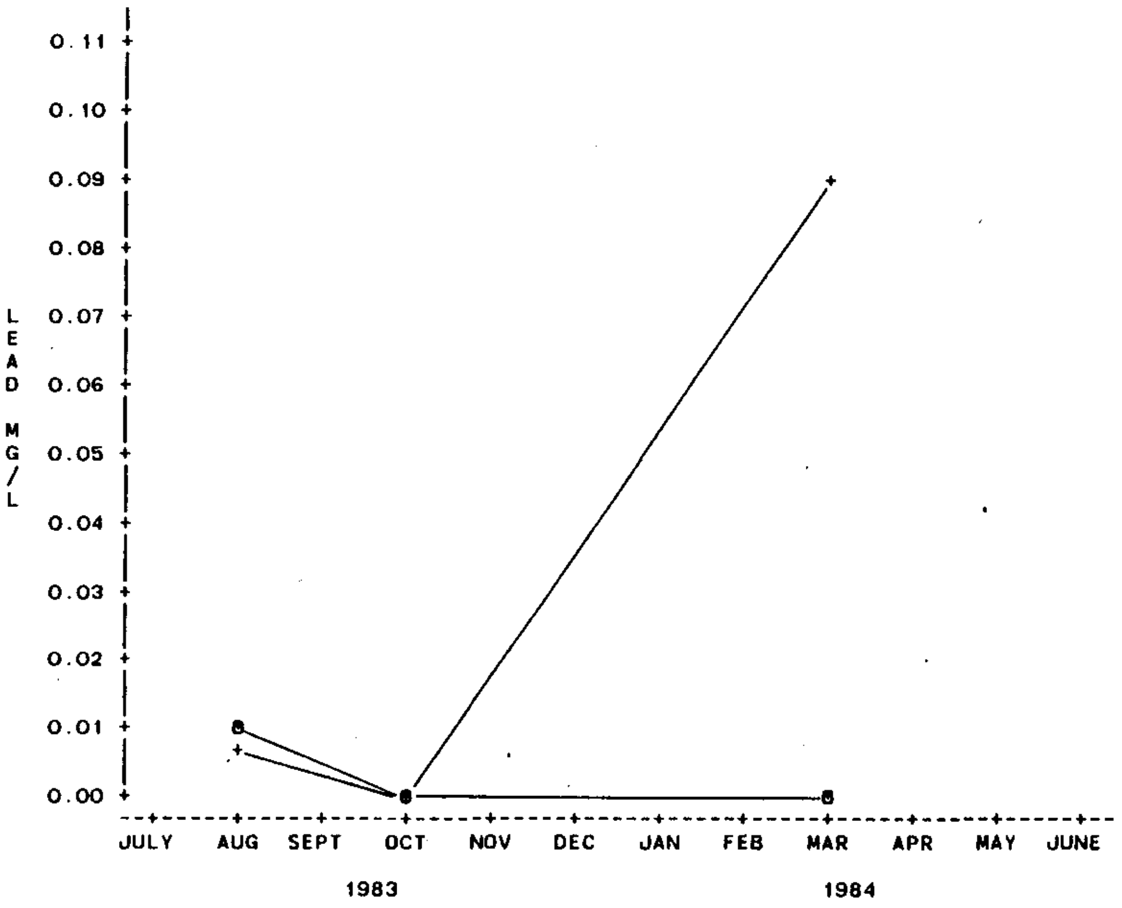

Figure 10. Plot of mean lead values over time. Grand Lake sites (O), Neosho River sites (*) and Spring River sites (+) are shown.

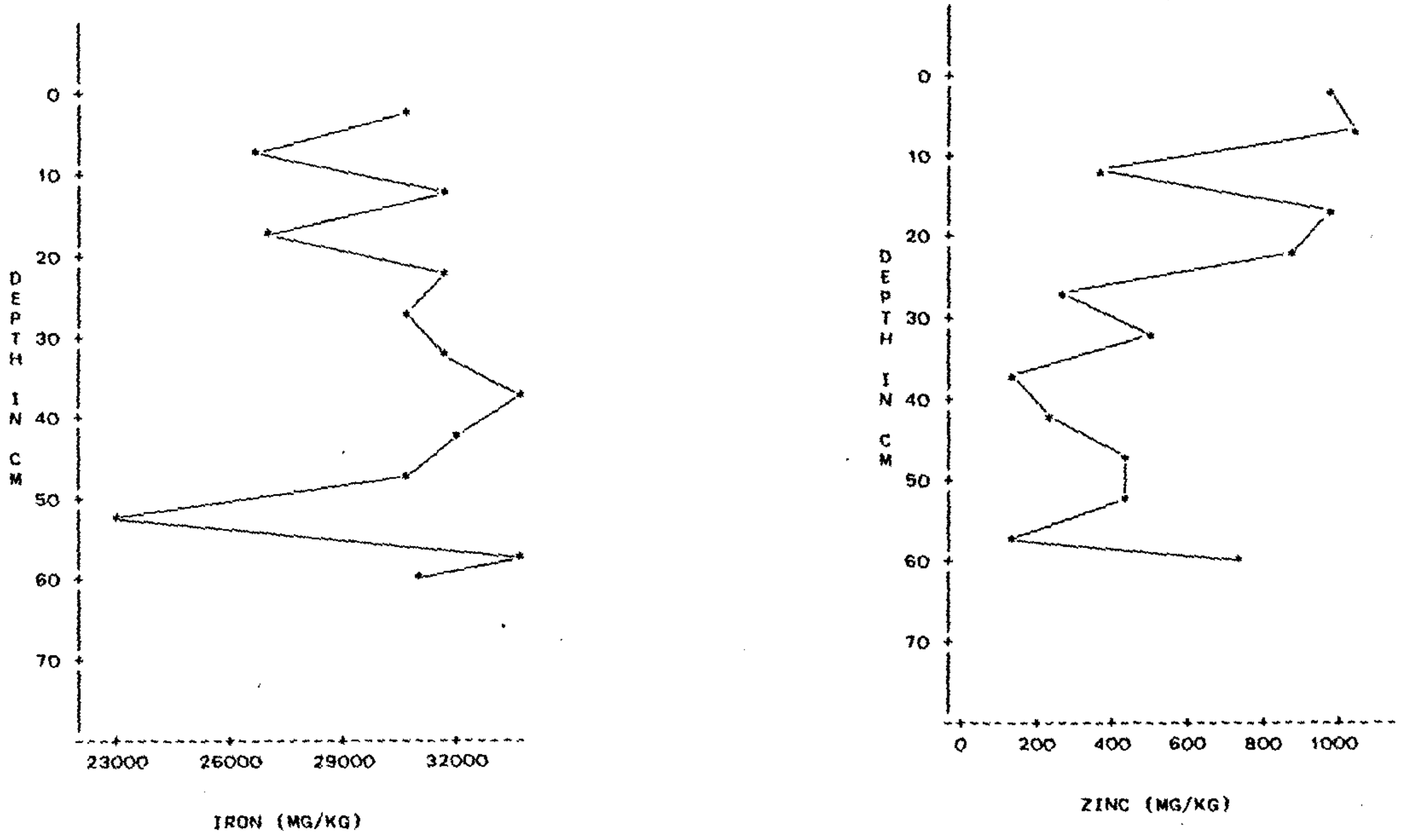

Figure 11. Plot of iron (mg/kg) and zinc (mg/Kg) from core sample by depth.

## TABLE 6

## HEAVY METAL CONCENTRATIONS IN PLANKTON IN THE NEOSHO AND SPRING RIVERS, AND CORRESPONDING ENRICHMENT FACTORS IN PARENTHESES.

| STATION | METAL CONCENTRATION (MG/KG or PPM) IN PLANKTON | | |
|---|---|---|---|
| | CADMIUM | LEAD | ZINC |
| NEOSHO ABOVE TAR CREEK (22A) | 2.96 (1096) | 2.0 (200) | 33.0 (68) |
| NEOSHO BELOW TAR CREEK (22B) | 17.40 (8286) | 115.6 (11,560) | 91.7 (282) |
| NEOSHO PRIOR TO SPRING RIVER | 20.92 | 120.9 | 84.2 |
| SPRING RIVER PRIOR TO NEOSHO RIVER (24) | 446.06 (446,060) | 481.3 (17,826) | 274.6 (1154) |
| UPPER END OF GRAND LAKE (26) | 78.96 | 41.4 | 192.9 |

FROM AGGUS, L.R., VOGELE, L.E., RAINWATER, W.C., AND D.I. MORAIS. 1983 EFFECTS OF ACID MINE DRAINAGES FROM TAR CREEK ON FISHES AND BENTHIC MACROINVERTABRATES IN GRAND LAKE, OKLAHOMA. PREPARED FOR THE TAR CREEK ENVIRONMENTAL EFFECTS SUBCOMMITTEE.

$$\text{ENRICHMENT FACTOR} = \frac{[\text{METALS PHYTOPLANKTON}]}{[\text{METALS IN WATER}]}$$

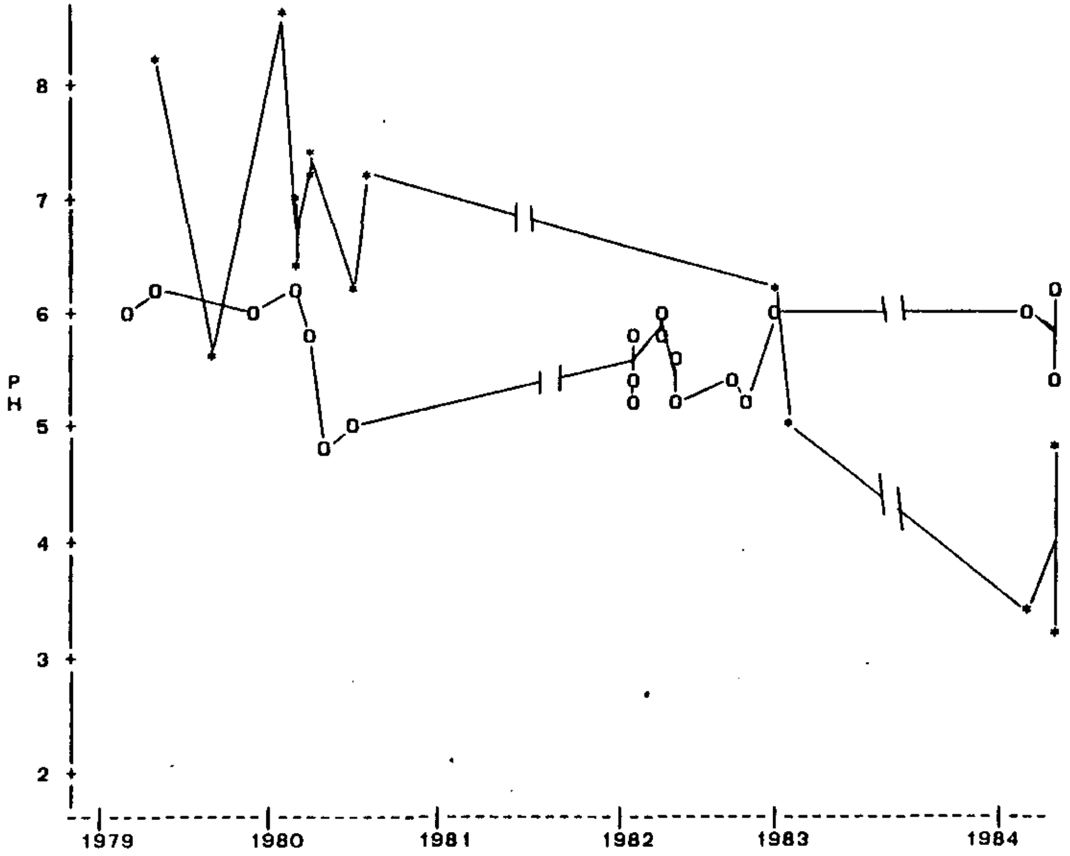

Figure 13. Plot of pH values over time. Tar Creek site 26 (*) and mine discharge site 28 (O) is shown.

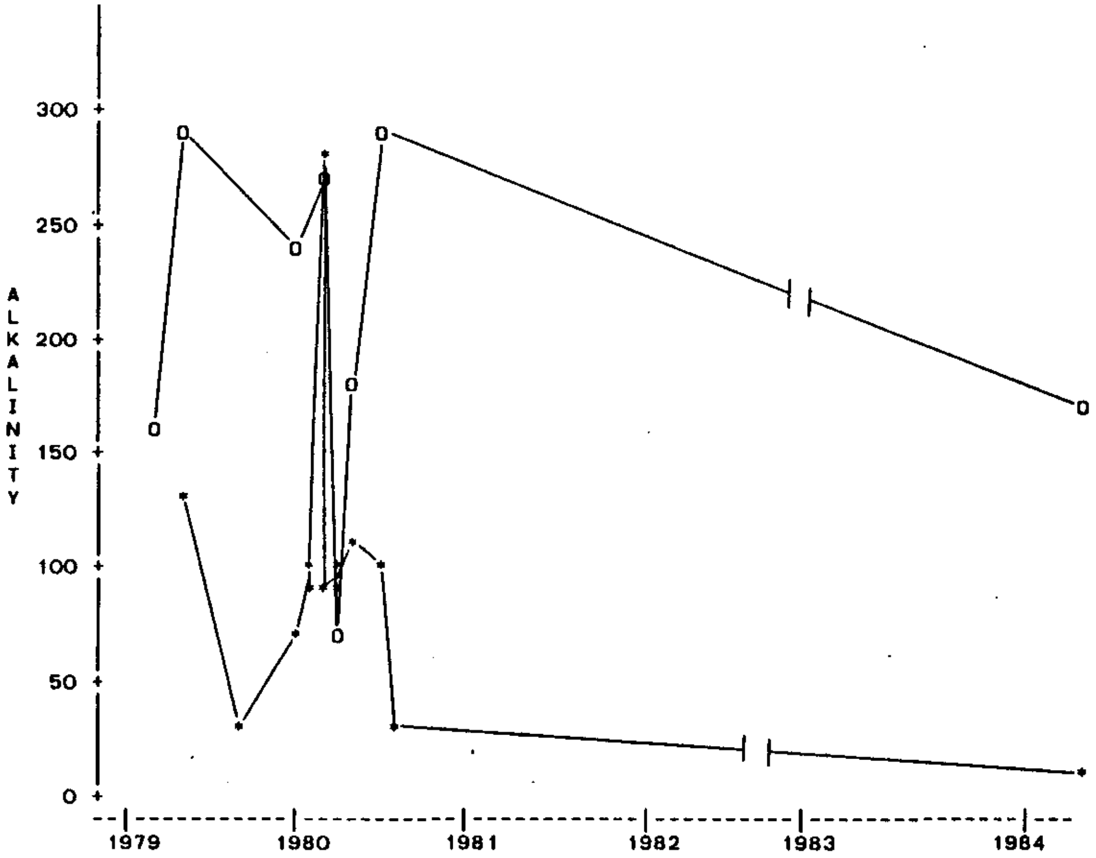

Figure 14. Plot of alkalinity (mg/L) over time. Tar Creek site 26 (*) and mine discharge site 28 (O) are shown.

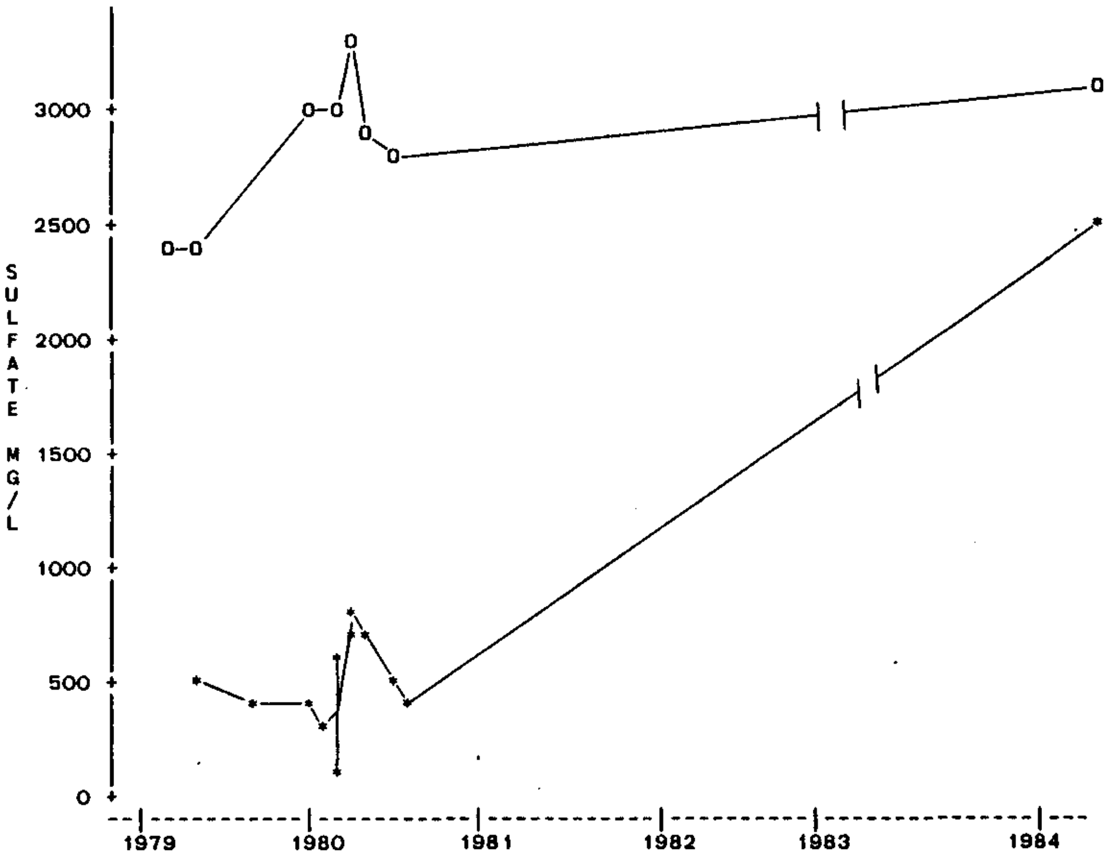

Figure 15. Plot of sulfate concentration (mg/L) over time. Tar Creek site 26 (*) and mine discharge site 28 (O) are shown.

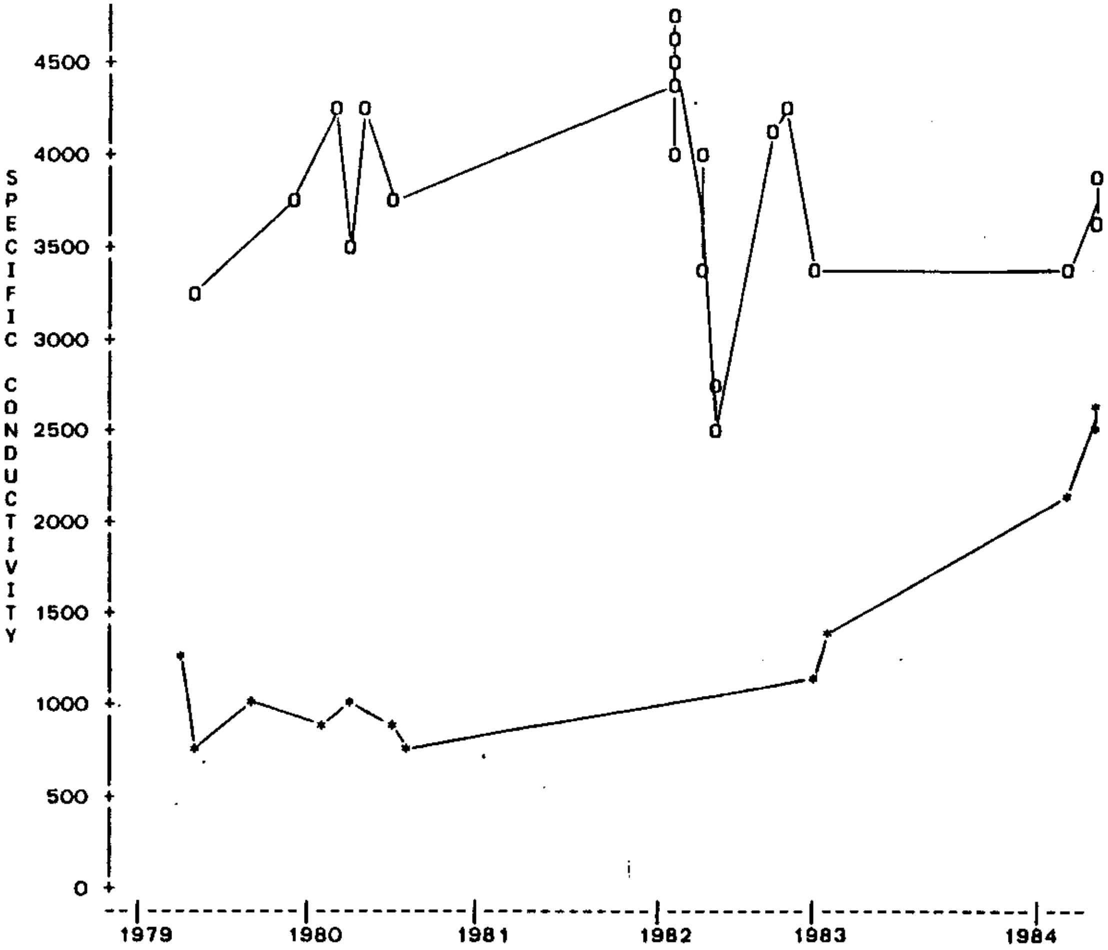

Figure 16. Plot of specific conductivity (umhos/cm) over time. Tar Creek 26 (*) and mine discharge site 28 (O) are shown.

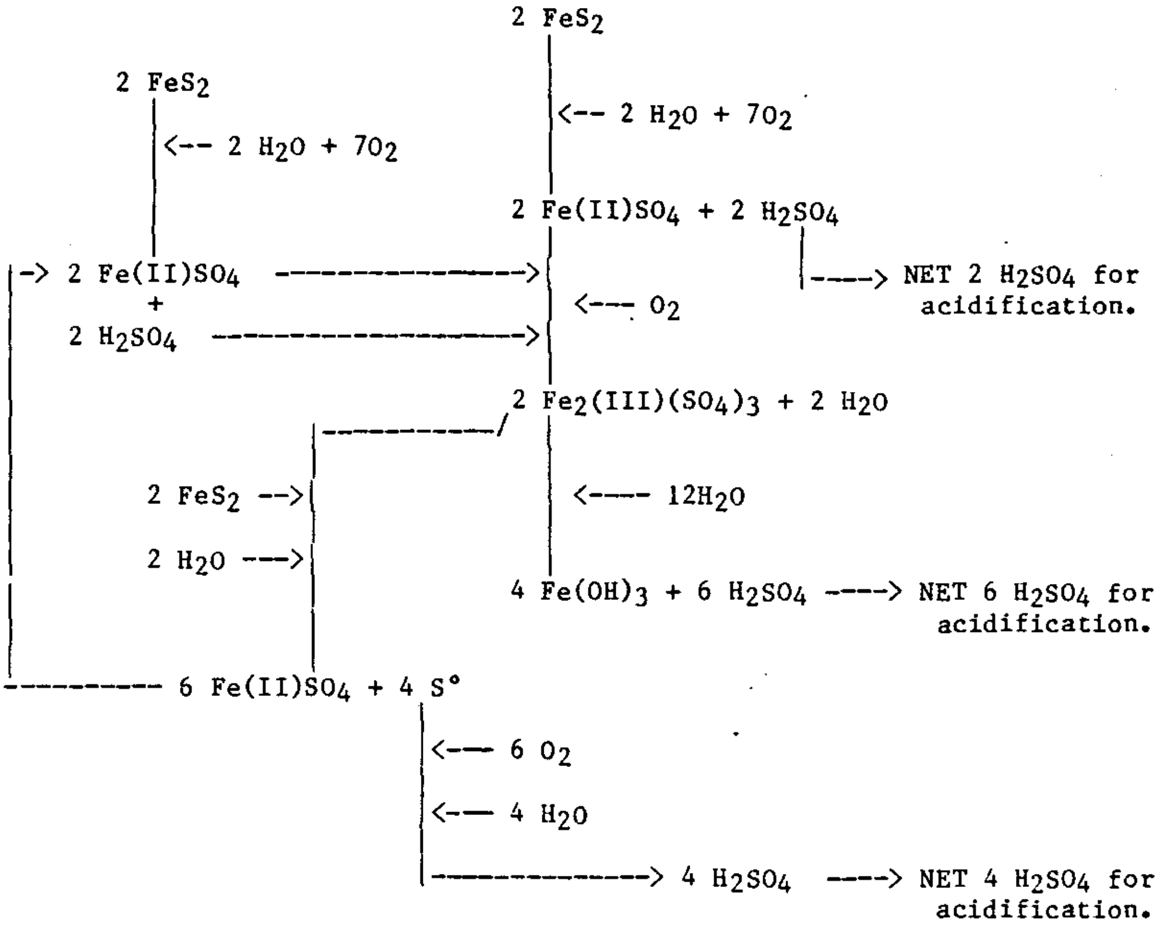

Figure 12. Summary of chemical reactions of iron sulfide with oxygen and water.