

**ADSORPTION OF COPPER, CADMIUM, AND ZINC ON  
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ACID MINE DRAINAGE: THE EFFECT OF SEASONAL  
CHANGES IN DISSOLVED ORGANIC CARBON**

by

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## INTRODUCTION

The release of metal-rich, acidic waters from abandoned mining operations is a major problem in Colorado and throughout the Western United States. In Colorado, over 600 km of stream reach are estimated to be affected by such releases (Wentz, 1974). The metals released adversely affect stream biota, including fish. It is therefore important to understand the chemical processes which influence metal transport in these waters. This report details studies of the role of suspended sediments with respect to the transport of several important trace metals in a stream impacted by acid mine drainage. The role of streambed sediments was studied in the same system as part of an earlier project, also funded by a grant from the Colorado Water Resources Research Institute (Macalady, et al., 1990)

Specifically, this report details research which examined the role of dissolved organic carbon (DOC) as it affects the adsorption and transport of copper, cadmium and zinc by suspended iron oxyhydroxide particles. Seasonal changes in particulate chemistry caused by changes in DOC were also examined. This study, like the previous study of streambed sediments (Macalady, et al., 1990), focuses on St. Kevin Gulch, a small sub-alpine stream located seven kilometers northwest of Leadville, Colorado (Figure 1). The stream receives acidic, metal-rich tailings effluent, which produces elevated concentrations of sulfate and several metals, including iron, manganese, aluminum, zinc, copper and cadmium (McKnight, et al., 1988).

Hydrous iron oxides (HIO) are the dominant minerals in this system, as in most streams contaminated by acid-mine drainage. These minerals can control aqueous concentrations of various metals through adsorption/precipitation reactions, which in turn depend on the chemical and electrical properties of the HIO surfaces. The net charge on HIO surfaces is pH dependent due to the amphoteric nature of surface hydroxyl groups. A net positive surface charge is expected at pH's below the point of zero charge (pH 7-9 for HIO, Parks, 1967). Modification of surface can occur as a result of adsorption of cations or anions, anion sorption being especially important at low pH. In most natural waters, suspended particles have a ubiquitous net negative charge. This observation has been related to the presence of organic coatings (Hunter and Liss, 1982) resulting in part from the sorption of DOC by the particles. Sorption of DOC in acidic streams by HIO has been shown to be an important geochemical process which selectively removes fractions of DOC (McKnight, et al., personal communication). In acid mine drainage systems, extensive fresh HIO surfaces and low DOC allow the existence of positively-charged surfaces (Newton and Liss, 1987; Ranville, et al., 1989). Sulfate ion is weakly sorbed at low pH and can

partially neutralize HIO surfaces, but has been shown not to produce a net negative surface charge (Rajan, 1978).

HIO are formed in acidic streams by oxidation of ferrous iron sulfides, subsequent hydrolysis of ferric iron, and resulting precipitation of HIO phases (Nordstrom, et al., 1979). HIO generally form as small particles with high specific surface areas. As a consequence of these high surface areas and the presence of strong metal-binding surface sites, these minerals are strong sorbants for metals (Dzombak and Morel, 1990). Modification of HIO surfaces by sorbed or coprecipitated anions may enhance their sorptive capacities. Incorporation of silica has been shown to enhance cadmium sorption (Anderson and Benjamin, 1985). Sorption of DOC increases sorption of copper on HIO (Tipping, et al., 1983) and aluminum oxides (Davis, 1984).

Because HIO formation occurs in the presence of organic matter, incorporation of organic matter into the structure of newly-formed HIO may be important. This process would result in less surface-active HIO-associated organic matter than would be the case for sorbed DOC and could possibly limit the influence of organic matter on surface charge and adsorption characteristics of HIO.

Extensive investigations of St. Kevin Gulch are part of a larger study of acid-mine drainage contaminated streams being conducted by the Water Resources and Geologic Divisions of the U.S. Geological Survey in Denver, Colorado. The Colorado School of Mines has participated in these studies through participation by several faculty and graduate students, supported in part by the Colorado Water Resources Research Institute. The work reported herein represents the second phase of this support to the principal investigator and the doctoral degree research of James F. Ranville and Kathleen S. Smith.

### OBJECTIVES

The objectives of this study are part of the overall goal of developing a comprehensive understanding of the factors which influence the transport of trace metals in streams contaminated by acid-mine drainage. This will, in turn, enable the design of effective remediation programs to counteract the deleterious effects of acid-mine drainage on Colorado's waters. Specifically, this research was designed to test the hypothesis that seasonal changes in stream water chemistry, particularly of DOC, determine the sorption and transport of trace metals by suspended sediments in St. Kevin Gulch. The detailed objectives of the research included:

1. to isolate and characterize the suspended sediments and DOC from St. Kevin Gulch waters at various times during the field

season (collection times based on stream discharge);

2. to determine the extent of DOC incorporation into and onto the isolated suspended sediments and synthetic iron oxyhydroxides;

3. to determine the extent of copper, cadmium and zinc adsorption onto suspended sediments and synthetic iron oxyhydroxides as a function of the presence of various levels of DOC and sulfate; and

4. to determine if seasonal changes in DOC, water chemistry or suspended sediment composition affect metal sorption.

#### EXPERIMENTAL METHODS

Prior to the initiation of this research, a series of sample sites was selected along St. Kevin Gulch (Figure 1). SK-11 is far above the main influence of acid-mine drainage, but still shows indications of some contamination. SK-15 lies just above, and SK-20 just below the confluence of a significant, year-round stream of tailings effluent (acid-mine drainage) with St. Kevin Gulch. Site SMG lies along Single Mill Gulch, a small tributary less contaminated than St. Kevin Gulch. SK-25 lies just below the confluence of Single Mill Gulch and St. Kevin Gulch, and SK-49 lies about one kilometer further downstream.

Procedures for sampling and chemical characterizations of stream water and particulates were summarized in our previous report (Macalady, et al., 1990). This report also summarized methods for electrophoretic mobility determinations of particle surface charges. Field determinations of stream pH, temperature and conductivity were made using standard methods.

#### Field Studies

Samples of water and suspended sediments were collected from up to six sites (SK-11, 15, 20, 25, and 49 and SMG) over a three-year period beginning in 1988. Most of the results reported herein are based on the 1989 and 1990 samples. Field measurements of pH, conductivity and temperature were recorded. Water samples included raw water and 0.1  $\mu\text{m}$  (micrometer) filtered water (using tract-etched polycarbonate membranes). Anion analyses were performed by ion chromatography (IC) on unacidified, filtered water samples. DOC analyses were performed on glass-fiber filtered samples using a high temperature persulfate oxidation method with coulometric detection of evolved carbon dioxide. Surface charge on the suspended particles was determined by measuring electrophoretic mobility (EM) of particles present in the raw samples at ambient concentrations using a light-scattering technique.

Two size fractions of suspended sediments were collected from large-volume water samples (60 liters or more) that had been

screened through a 63 um nylon mesh. A direct filtration using 147 millimeter, 5 um porosity, track-etched polycarbonate filters was used to collect silt-sized fractions. Filters were changed after 4 liters were processed to minimize clogging of the filters. Colloidal size fractions were collected using tangential-flow ultrafiltration of the 5 um filtrate using 100,000 molecular weight membranes. Suspended sediment samples were removed from both filter types by placing the filters individually into Teflon bags along with some sample water and gently rubbing the particles off the filters from outside the bags. The resulting suspensions were each split into two portions and half were freeze-dried for organic carbon analyses. The other half of each sample was stored at 4° C. for future experiments.

#### Laboratory Experiments

In order to investigate the effects on EM of co-precipitation of DOC by HIO, and the effects of organic carbon on the removal of metals, laboratory experiments were performed under more controlled conditions which simulated the stream. In one set of experiments, 100 ml samples of water collected from site SK-20 were diluted with distilled water to 220 ml and the pH raised to 4.0 using NaOH to simulate dilution and pH increase at SK-25 occurring as a result of the addition of water from Single Mill Gulch, a near-neutral tributary (see Figure 1). No additional iron was added to the experiments so the amount of HIO formed more accurately simulates what forms in the stream. The precipitation was performed in the presence of calcium sulfate at a final sulfate concentration of approximately 150 mg/L. Calcium sulfate was used to more closely match the major element chemistry of stream water at SK-25.

Three types of organic matter were used to provide total organic carbon of similar concentrations ranging from 0.7 to 2.6 mg Carbon/L. These included Suwannee River Fulvic Acid (SR-FA), selected because it is well-characterized and serves as a "standard" fulvic acid (Averett, et al., 1989). Also included were a fulvic acid isolated from Single Mill Gulch (SMG-FA) using procedures outlined in Thurman and Malcolm (1981), and a rotary-evaporated concentrate of Single Mill Gulch water which is referred to as whole organic matter (SMG-DOM). The organic matter was added prior to the precipitation of HIO, so the experiments represent both coprecipitation and sorption. Phase separations were accomplished by vacuum filtration using washed 0.1 um polycarbonate filters. (After filter washing, filtered distilled water had DOC concentrations similar to unfiltered distilled water). The filtrates were analyzed for DOC, metals and anions. Aliquots of the unfiltered suspensions were acidified to dissolve the HIO and were also analyzed for DOC, metals and anions. Electrophoretic mobilities were also determined on the suspensions.

In a similar set of experiments, the effect of pH on EM was studied in samples with initial DOC's from 0 to about 2.6 mg/l and pH adjustments with NaOH. This same set of experiments was used to evaluate metals removal by the precipitated HIO, so additional ferric iron was added via a 50 mg Fe/L ferric nitrate solution to achieve a final total iron concentration of approximately 14 mg Fe/L.

## RESULTS AND DISCUSSION

Characterization of the suspended sediments in St. Kevin Gulch included measurements of electrophoretic mobilities of the particles as a function of season, DOC and particulate organic carbon, as well as infrared studies. Figure 2 shows the seasonal variations in electrophoretic mobilities of suspended sediments for three sampling seasons (1988, 89 and 90). Electrophoretic mobility is a measure of the surface charge in the shear plane of the particles (a region of the diffuse layer), which is approximately equivalent to the outer Helmholtz plane.

The data in Figure 2 show distinct seasonal variations in particle surface charge. During the spring, when runoff is greatest, charges are generally negative. During this time of year, input of particles and DOC from surface runoff is important, as is scouring of the streambed of HIO particles from previous year's deposits. The presence of silicates from the surrounding land and high DOC levels provide the necessary conditions for the observed negative surface charges. The iron content of the suspended sediments is lowest during this time of year, perhaps also as a result of detrital silicates from surrounding land areas. The high DOC's provide sufficient DOC to cause the HIO particles to have a net negative charge. During this early part of the seasons, little streambed evidence for HIO precipitation is present.

As the season progresses, water levels fall, as do DOC concentrations. Iron concentrations of suspended sediments increase, and evidence for HIO precipitation as determined by observations of streambed deposits, increases. Thus there is apparently not enough DOC to cause the net surface charge of the suspended HIO particles to become negative. These seasonal variations illustrate the dual importance of hydrology and stream chemistry in determining the surface character of suspended sediments.

Figure 3 further illustrates the dependence of surface charge on DOC. At higher DOC concentrations, the suspended particles have a net negative surface charge, at lower DOC's, there is not enough organic carbon to cause the particles to have a net negative charge. This is further illustrated by the relationships between surface charge and organic carbon content of the suspended sediment particles themselves (Figure 4). A surprisingly linear

relationship between weight percent carbon and electrophoretic mobility is observed.

Figures 5 and 6 show the infrared (IR) spectra of freeze-dried silt and colloidal fractions, respectively for samples collected during the 1990 field season. IR spectra were determined using KBr pellets on a Perkin-Elmer 580 spectrometer. The spectra are in many ways typical of HIO particles, showing water bands at 3500 and 1640  $\text{cm}^{-1}$ . Organic matter is evident from the carbon-hydrogen bands at 2850, 2920 and 2950  $\text{cm}^{-1}$ . Carbonyl bands at 1710-1720  $\text{cm}^{-1}$  are partially obscured by overlap with water and Fe-OH bands, but can be seen as a shoulder on the 5/19 silt and 6/4 colloidal spectra. Organic matter is most obvious in the 6/4 silt sample, which corresponds to the highest percent organic carbon of any of the samples tested. The 950-1200  $\text{cm}^{-1}$  region shows a broad silicate region and sulfate peaks at 1170, 1125, 1050 and 970  $\text{cm}^{-1}$ . The lack of important silicate bands at 3600 and 3700  $\text{cm}^{-1}$  except in the early-season silt spectra indicates the minor importance of silicates during much of the season.

Figure 7 shows the solid state  $^{13}\text{C}$  NMR of Single Mill Gulch fulvic acid, which was taken using cross-polarization-magic angle spinning NMR. This fulvic acid sample was isolated from Single Mill Gulch at a site above most influences from mining activities. The spectrum is very similar to that of Suwaunee River fulvic acid, and shows the sample to be low in aromaticity, high in carbonyl and acid carbons, and high in saturated carbon. The importance of this spectrum is that it shows that SMG-FA can be expected to have the high metal-binding capacity that is typical of fulvic acids.

In summary, these experiments characterize the suspended particles in St. Kevin Gulch and the organic matter which may be incorporated into the particles by sorption and/or coprecipitation with HIO. They show that seasonal variations in suspended sediment surface charge, due in part to the incorporation of DOC into the particles, might be expected to have a strong influence on trace metal partitioning to the suspended sediments.

Laboratory experiments were conducted to serve two main purposes. First to characterize the dependence of surface charge, as measured by EM, on the DOC concentration during the precipitation of the HIO particles. Figure 8 illustrates the results of these experiments. As can be seen, the surface charge of HIO particles depends upon the solution DOC concentration. The ideal result of these trials would have been a relationship which mimics the results shown for actual stream particles, as shown in Figure 3. However, a quantitative correspondence is not evident. The changes in stream particle charge apparently occur at much lower DOC levels than used in the laboratory trials. Also, the stream results match more closely to those observed for the SW-FA than



for those for the Shingle Mill Gulch organic carbon trials.

The reasons for these differences are not known. However, there are some reasonable conjectures which might explain some of the observed differences. The SW-FA sample comes from an environment low in metals, where precipitation of HIO is absent, whereas, the SMG-FA and SMG-DOM samples come from an environment rich in metals and may have already been fractionated by processes similar to the precipitation of HIO. Also, the stream environment provides a continuous, if low concentration, source of DOC. Therefore, as HIO forms in the stream, unlike in the laboratory, the DOC available has a more or less constant source of those fractions of the DOC which are most susceptible to incorporation into the precipitating HIO, or to sorption on the freshly formed HIO surfaces. Thus a lower total DOC might be expected to have a greater net effect on surface charge than is observed in the laboratory trials.

In any event, it is clear from these trials and the field studies, that DOC has a marked effect on the surface charge of the suspended HIO particles. The question remains as to whether or not such seasonal differences in surface charge have a concomitant effect on the coprecipitation, sorption and transport of trace metals such as zinc, copper and cadmium. To determine whether or not this is the case was the purpose of the second set of laboratory experiments.

This second set of trials was also used to check the dependence of HIO surface charge on both pH and the levels of DOC in the solution from which the HIO was forming. In these trials, experimental procedures were similar to those used for the DOC/EM trials described above (see experimental section). However, unlike those trials, as illustrated in Figure 8, ferric iron was added (as ferric nitrate in a 50 mg Fe/L solution) to achieve a ferric iron concentration of approximately 14 mg/L before precipitation was initiated by pH elevation. This was done to assure adequate quantities of precipitated HIO for metals analyses, since the same experiments were used to test for trace metal removal during precipitation. In these trials, pH was adjusted with 0.1 N NaOH and samples were equilibrated for 48 hours before separation of particulate phases with 0.1  $\mu$ m washed Nucleopore membrane filters. Metals and DOC concentrations were then measured in both the supernatant and particulate phases.

Figure 9 shows the dependence of EM on pH and organic matter concentrations in these trials (solid curves in these and all subsequent graphs are second order polynomial fits of the data). Note that within experimental uncertainties ( $\pm 0.1$   $\mu$ m/sec/volt.cm), the presence of organic matter lowers the EM at all pH's. The EM is higher in all cases than those shown in Figure 8, due to the additional ferric iron present in these trials. The shape of these curves is interesting, as a maximum in

EM occurs at about pH = 5.5 for all four additions of DOC. This may be because the DOC itself becomes more negative as pH increases, and metals which neutralize the OM are transformed from cations to hydroxy complexes. This may cause the surface charge of the HIO precipitate to decrease above pH = 5.5.

Figures 10 and 11 show the effect of these experiments on the DOC levels in solution. The total carbon curve (10a) shows the rather high distilled water blanks which are an unexplained part of all of these trials and the consistent recovery of the total DOC added throughout the experiments. The final DOC and percent carbon removed curves (Figures 10b, 11a and 11b) show that 50-70 percent of the added DOC is removed during the coprecipitation/sorption experiment. The curves for zero added DOC are suspect, due to the high carbon blanks and the fact that these analyses were near the detection limit for the DOC determinations.

The removal of iron from these solutions is illustrated in Figures 12, 13 and 14. Figure 12 shows the total and dissolved iron for the trials with SMG-DOM. An apparent analytical error is obvious for the pH = 5.0 points. The apparent decrease in total iron for the trials with added DOC is unexplained, and may also be an analytical artifact. Figure 13 shows the same for the SR-FA trials. Again, an analytical artifact at pH = 4.5 for the dissolved iron concentration may obscure the trend for the intermediate DOC trial, though the total iron results show consistent recoveries of the added iron. Figure 14 illustrates the consistently increasing iron removal, as expected, as the pH increases. In general, the presence of DOC decreases the amount of iron precipitated at all pH's. The analytical precision of the iron analyses is generally smaller than the sizes of the points in Figures 12-14.

The removal of metals during these trials is the central issue of this research. The dependence of metal removal during the precipitation of HIO and subsequent metal sorption was determined in the same series of experiments represented in Figures 9-14. In each case, metals were determined in the particulate and supernatant phases by ICP-AES. Figures 15 and 16 show the total and dissolved copper for these trials with SMG-DOM and SW-FA respectively. Figure 17 shows the percent of the initial copper which was removed by coprecipitation/sorption processes. This latter figure shows the expected increase in removal as the pH is increased, but shows no evidence that the presence of organic matter increases metal removal. If anything, there is slight evidence from these trials that the presence of organic matter decreases the removal of copper to particulate phases. No differences between SMG-DOM and SW-FA are apparent. The removal of zinc during coprecipitation/sorption is illustrated in Figures 18-20. Figures 18 and 19 summarize analytical results for SMG-DOM and SW-FA respectively. There is

considerably more scatter in these data, for unknown reasons. Figure 20 shows the expected slight increase of metal removal as the pH increases. Again, however, there is no evidence that the presence of dissolved organic matter during coprecipitation/sorption has any substantial effect on metal removal, this time for zinc.

Similar analyses for several other metals (results not shown) show that for cadmium, manganese and lead, no effect of organic matter on metal removal can be substantiated. The results for lead are less certain, as stream lead levels are close to the analytical detection limit.

## CONCLUSIONS

The central issue of this research and the research which preceded it, is the possible influence of organic matter on the removal of harmful trace metals (to suspended or bed sediments) by hydrous iron oxides in streams contaminated by acid mine drainage. The hypotheses which guided the research involved the idea that the presence of organic matter, through its effect on the surface and precipitation characteristics of the hydrous iron oxides, would increase the extent to which such harmful trace metals are removed to the sediment phases.

The results of the experiments detailed in this report illustrate that the surface charge of suspended particulates in St. Kevin Gulch does indeed depend seasonally upon the levels of dissolved organic carbon (DOC) in the stream and the presence or absence of detrital silicates during high water flow periods. Organic matter lowers the surface charge, making it negative during much of the field seasons. However, this surface charge variation, and the coprecipitation/sorption of solution DOC, has little effect on the removal of copper, zinc or cadmium from the stream water. In fact, removal of these metals in the presence of organic matter is not substantially different than removal in the absence of significant DOC.

Thus, the conclusion of this research add considerably to preceding study of bed sediments (Macalady, et al., 1990), and confirm that the removal of trace metals to particulate phases can be viewed solely in terms of the behavior expected for hydrous iron oxides (HIO). Metals are removed, but in a manner dependant upon the pH of the stream environment in which the HIO precipitate, independent of the presence of dissolved organic matter.

This study has added significance in that it is the first recorded study which shows the variations in surface charge of suspended particulates with stream hydrology and chemistry. It is the only study which shows that surface charge can actually change from positive to negative during the year, despite the fact that the particulates are dominated by hydrous iron oxides during the entire year. Further fundamental research into the factors controlling surface charge is needed in order to enable accurate modelling of these variations.

FIGURE CAPTIONS

- Figure 1 Map of study site, St. Kevin Gulch, Colorado. Sampling sites are shown. The influence of a year-round stream of mine tailings is located between sites SK-15 and SK-20.
- Figure 2 Seasonal variations in electrophoretic mobilities of suspended sediments for sites along St. Kevin Gulch: A. 1988 field season, B. 1989 field season, C. 1990 field season.
- Figure 3 Electrophoretic mobility of suspended sediment as a function of dissolved organic carbon (DOC) for the 1988 and 1989 field seasons.
- Figure 4 Electrophoretic mobility as a function of weight percent carbon in the suspended sediments, 1990 field season.
- Figure 5 Infrared spectra of the suspended silt fraction in St. Kevin Gulch as a function of sampling date for the 1990 field season.
- Figure 6 Infrared spectra of the suspended colloidal fraction in St. Kevin Gulch as a function of sampling date for the 1990 field season.
- Figure 7 Solid state  $^{13}\text{C}$ -Nuclear Magnetic Resonance spectrum for a fulvic acid sample isolated from water from Single Mill Gulch.
- Figure 8 Electrophoretic mobility as a function of dissolved organic carbon for hydrous iron oxides coprecipitated in water from site SK-20 (collected 9/18/90). Three sources of organic carbon are represented: SMG-FA, fulvic acid isolated from Single Mill Gulch water; SR-FA, Suwannee River fulvic acid, a "standard" fulvic acid; and SMG-DOM, unfractionated organic matter isolated from Single Mill Gulch water. Background sulfate concentration is approximately 150 mg/L.
- Figure 9 Electrophoretic mobility versus pH for hydrous iron oxides coprecipitated from diluted SK-20 water in the absence of added DOC and with two different concentrations of Single Mill Gulch organic matter and Suwannee River fulvic acid. Ferric iron has been adjusted to approximately 14 mg Fe/L. See text for experimental details.

- Figure 10 Total carbon (A) and residual dissolved organic carbon (B) in the coprecipitation experiments described in Figure 9.
- Figure 11 Percent of the dissolved organic carbon removed in the coprecipitation experiments described in Figures 9 and 10. (A). SMG-DOM, (B). SR-FA.
- Figure 12 Total iron (A) and residual dissolved iron (B) as a function of pH in the SMG-DOM coprecipitation experiments described in Figures 9, 10 and 11.
- Figure 13 Total iron (A) and residual dissolved iron (B) as a function of pH in the SR-FA coprecipitation experiments described in Figures 9, 10 and 11.
- Figure 14 Percent iron removed by coprecipitation of hydrous iron oxides with dissolved organic matter as a function of pH and added organic matter. See Figure 9 and text for experimental details. (A). SMG-DOM, (B). SR-FA.
- Figure 15 Total copper (A) and residual dissolved copper (B) as a function of pH after coprecipitation of hydrous iron oxides with various levels of SMG-DOM. See Figure 9 and text for experimental details.
- Figure 16 Total copper (A) and residual dissolved copper (B) as a function of pH after coprecipitation of hydrous iron oxides with various levels of SR-FA. See Figure 9 and text for experimental details.
- Figure 17 Percent copper removed as a function of pH as a result of coprecipitation of hydrous iron oxides with various levels of SMG-DOM (A) and SR-FA (B). See Figure 9 and text for experimental details.
- Figure 18 Total zinc (A) and residual dissolved zinc (B) as a function of pH after coprecipitation of hydrous iron oxides with various levels of SMG-DOM. See Figure 9 and text for experimental details.
- Figure 19 Total zinc (A) and residual dissolved zinc (B) as a function of pH after coprecipitation of hydrous iron oxides with various levels of SR-FA. See Figure 9 and text for experimental details
- Figure 20 Percent zinc removed as a function of pH as a result of coprecipitation of hydrous iron oxides with various levels of SMG-DOM (A) and SR-FA (B). See Figure 9 and text for experimental details.

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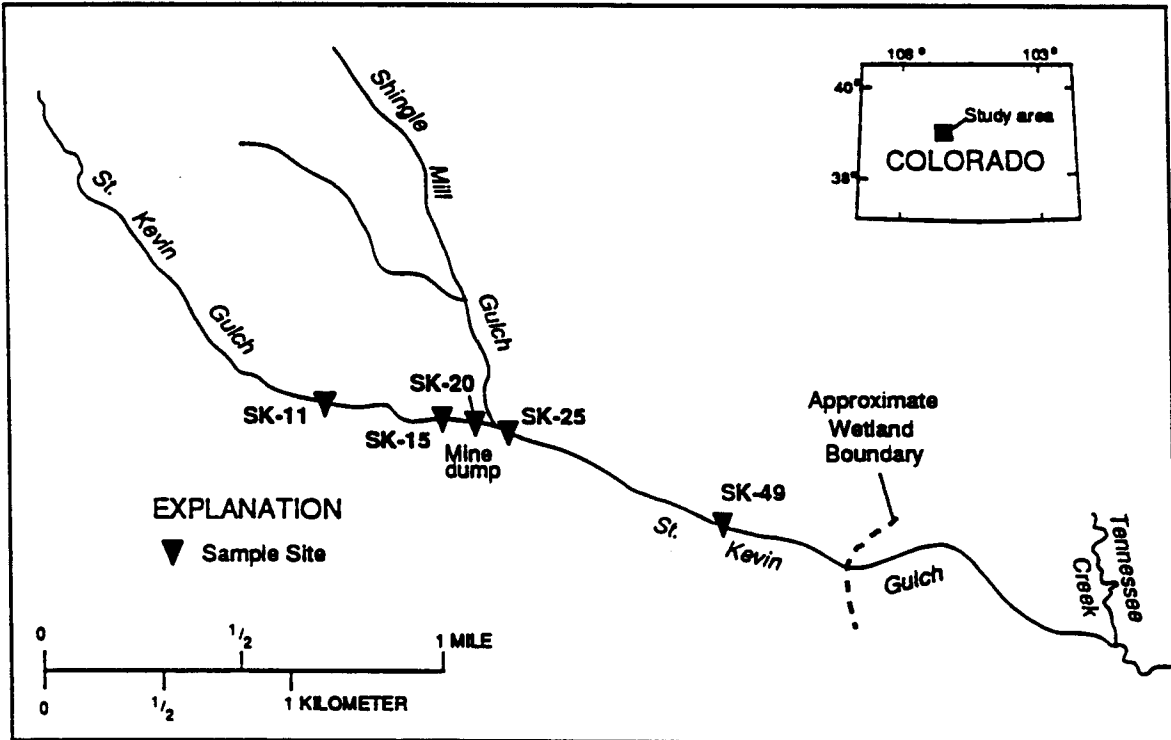


FIGURE 1

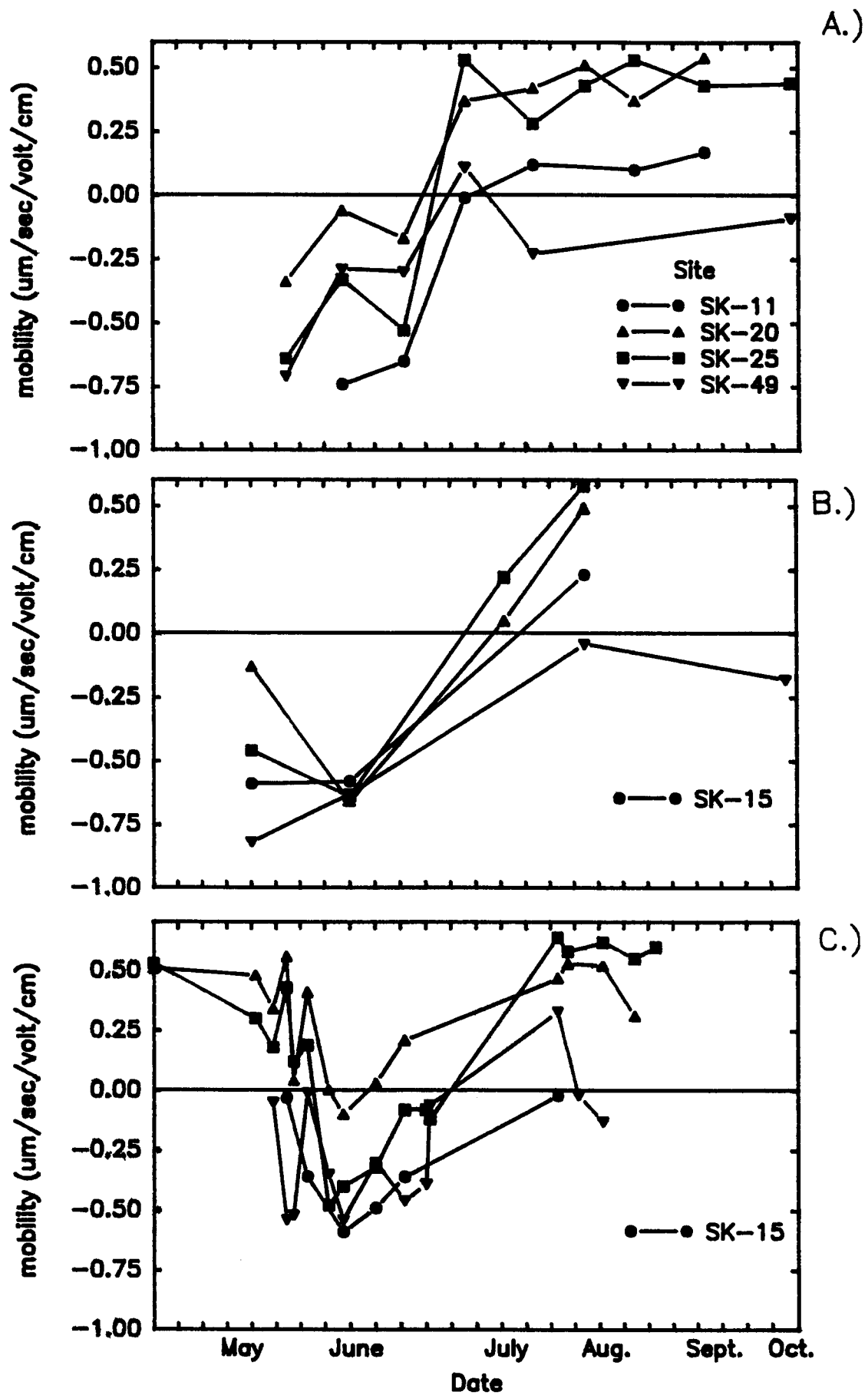


FIGURE 2

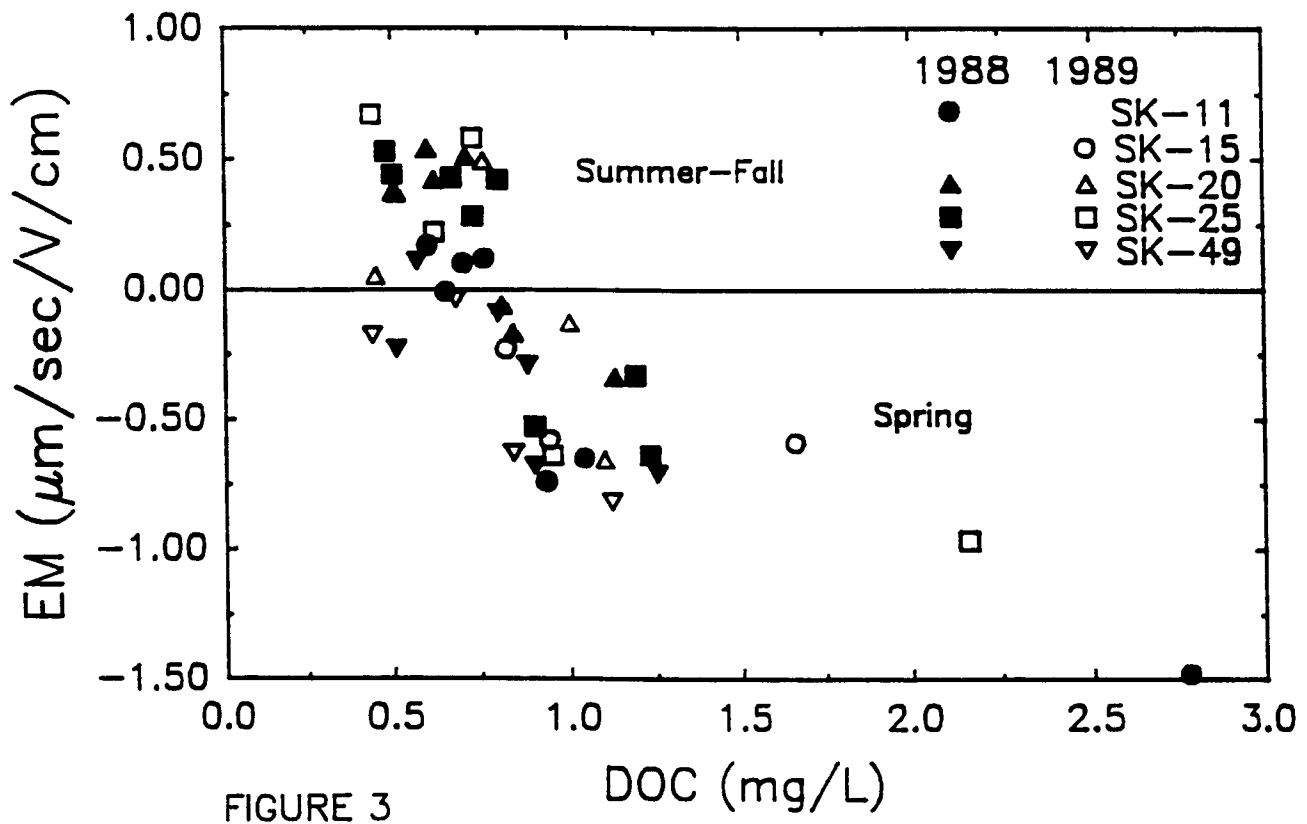


FIGURE 3

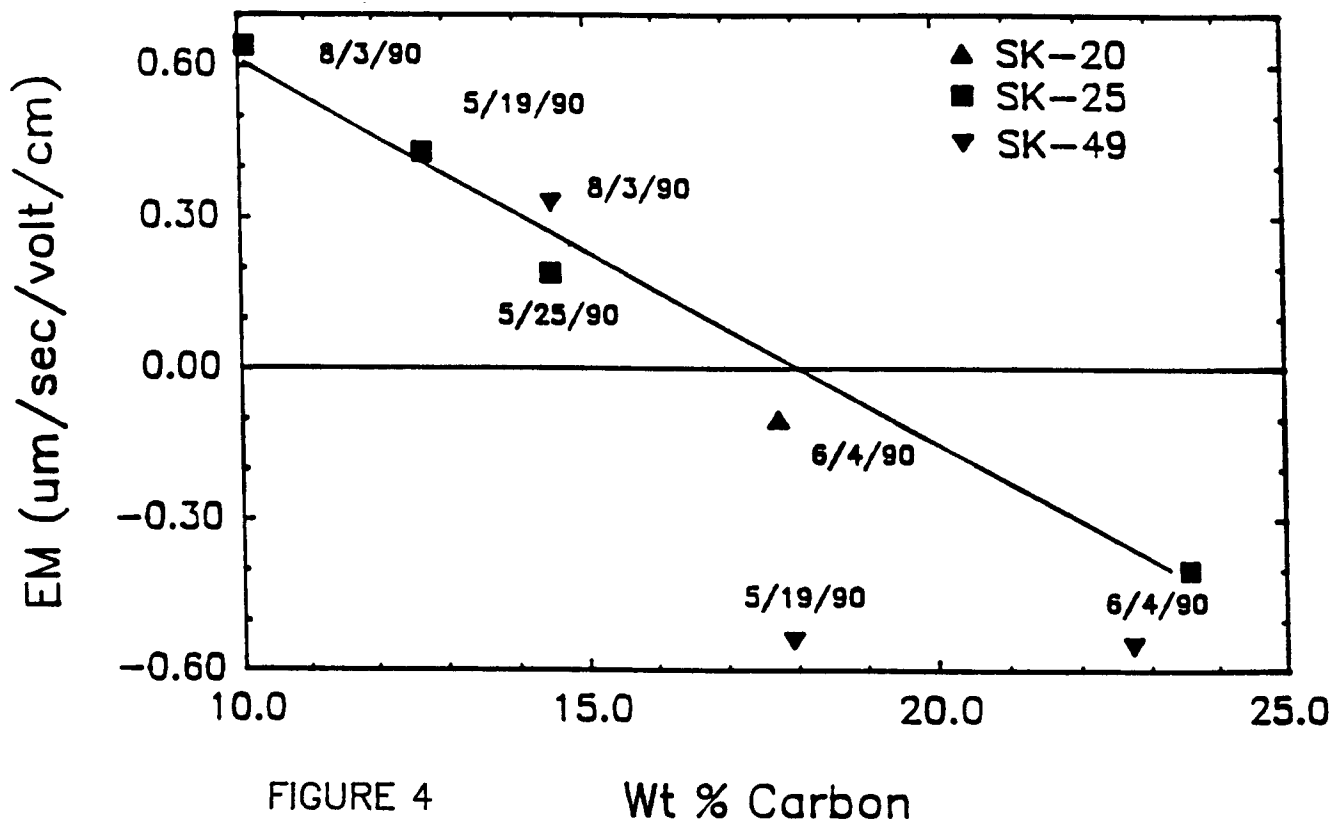


FIGURE 4

Wt % Carbon

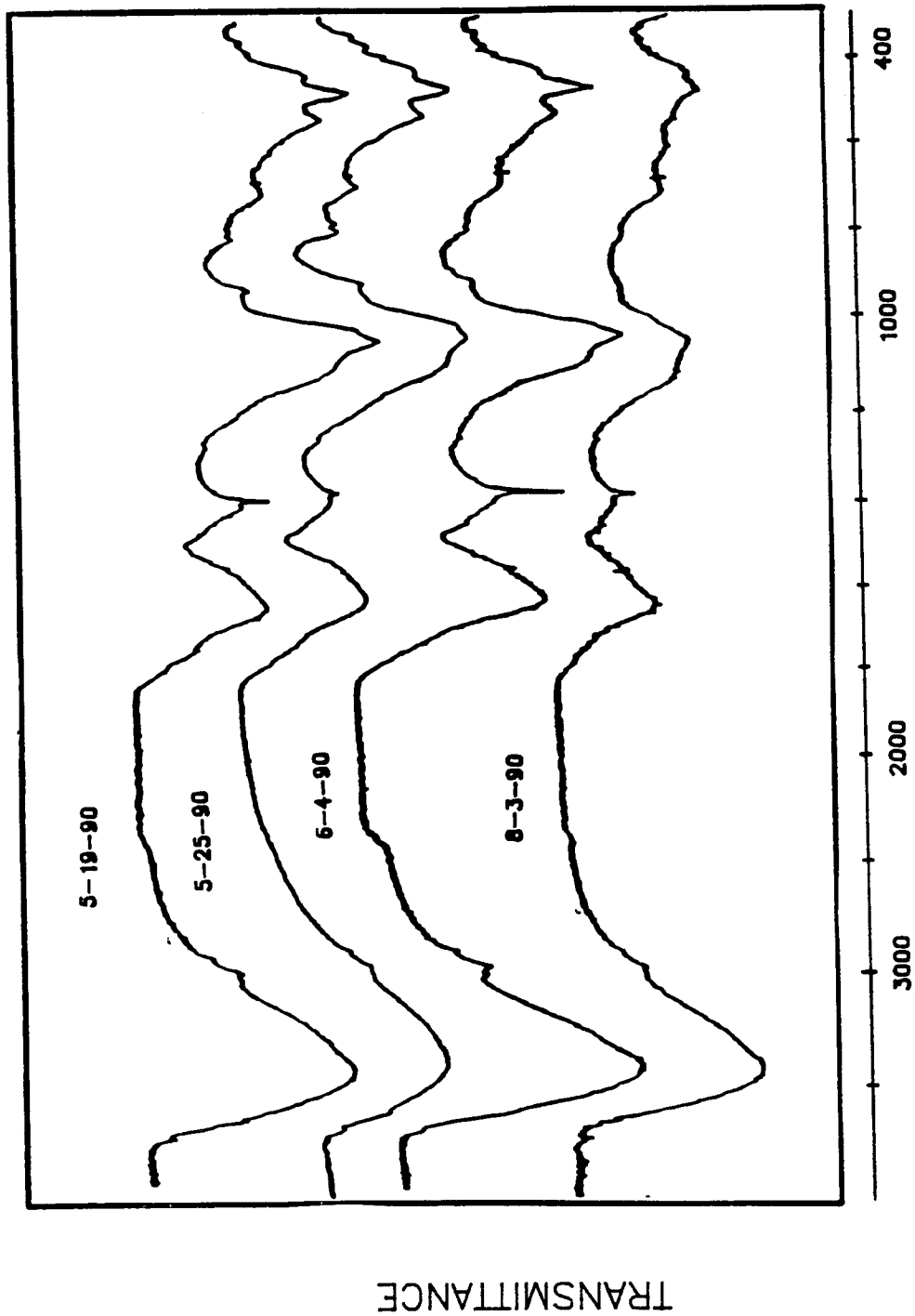


FIGURE 5

FREQUENCY (  $\text{cm}^{-1}$  )

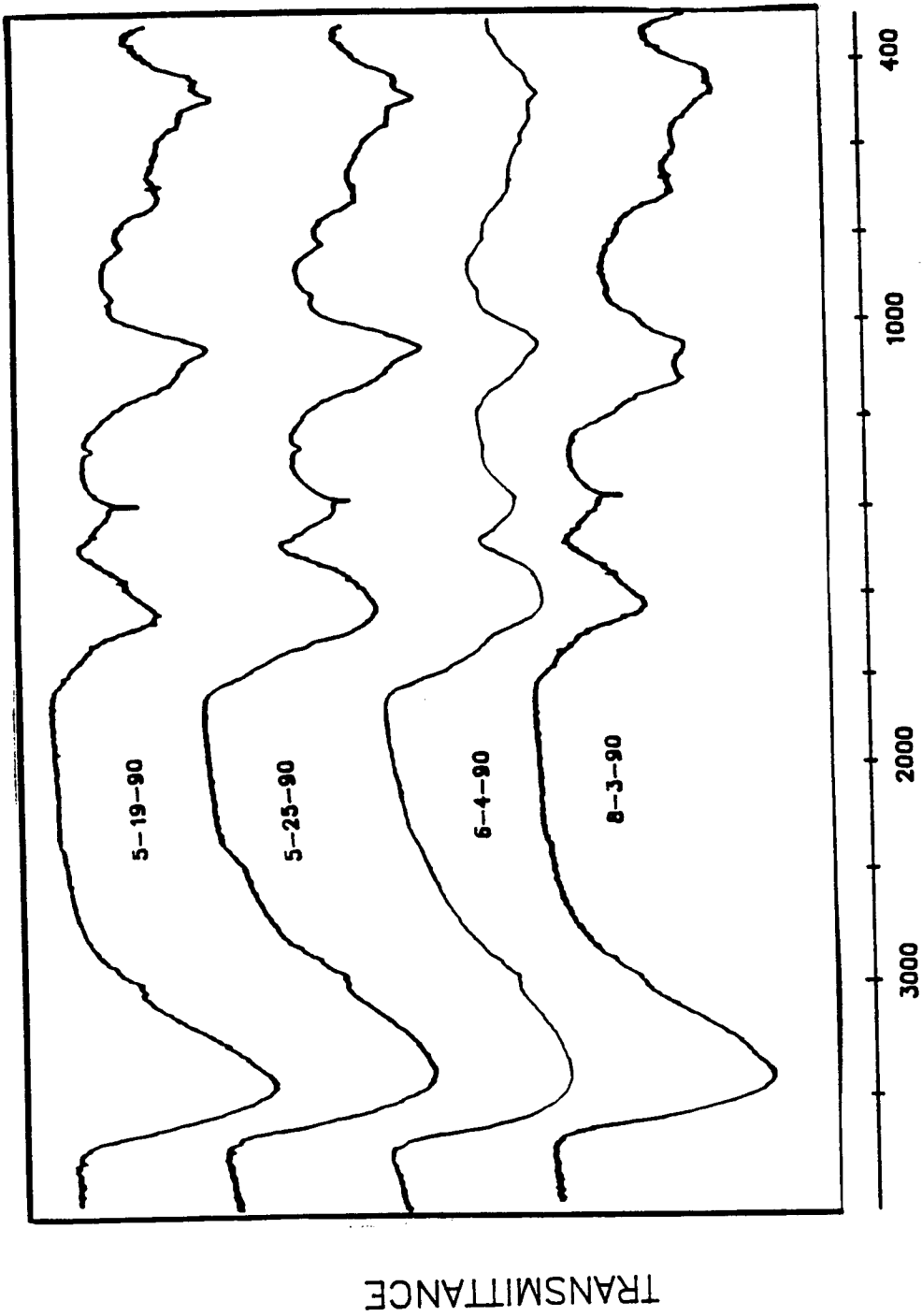


FIGURE 6

FREQUENCY (  $\text{Cm}^{-1}$  )

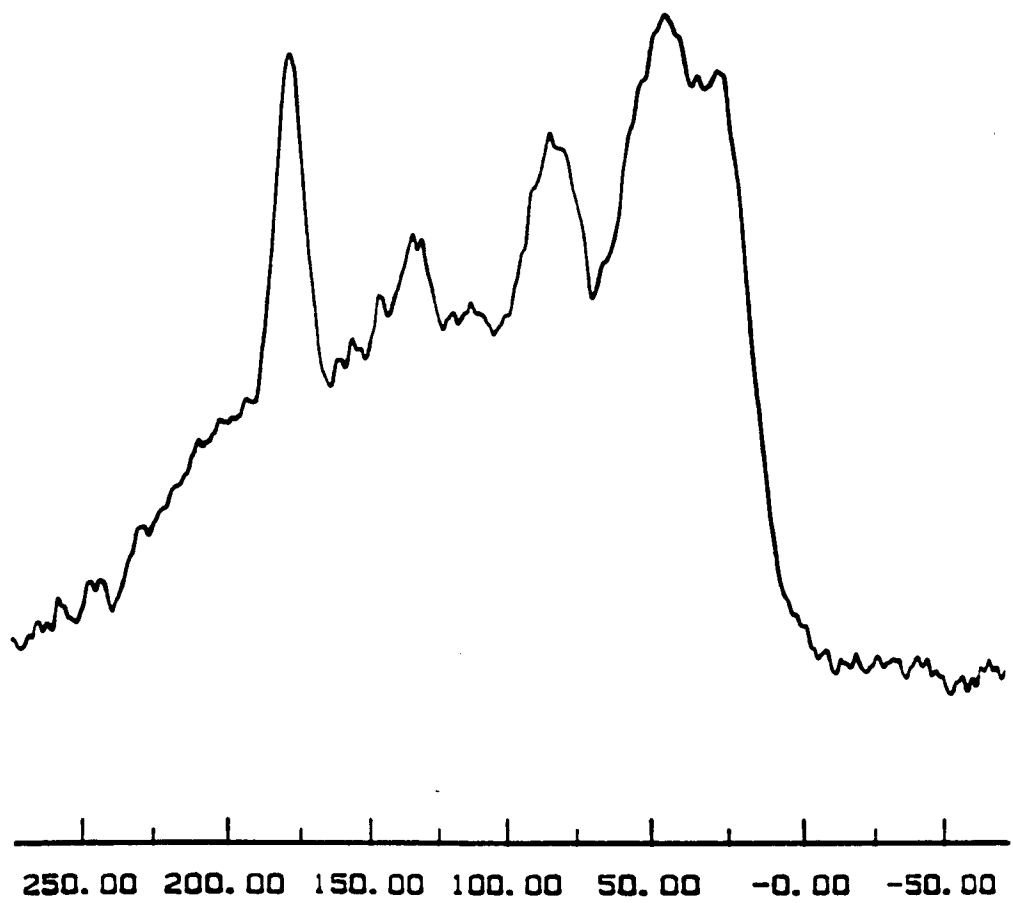


FIGURE 7

CHEMICAL SHIFT ( PARTS PER MILLION )

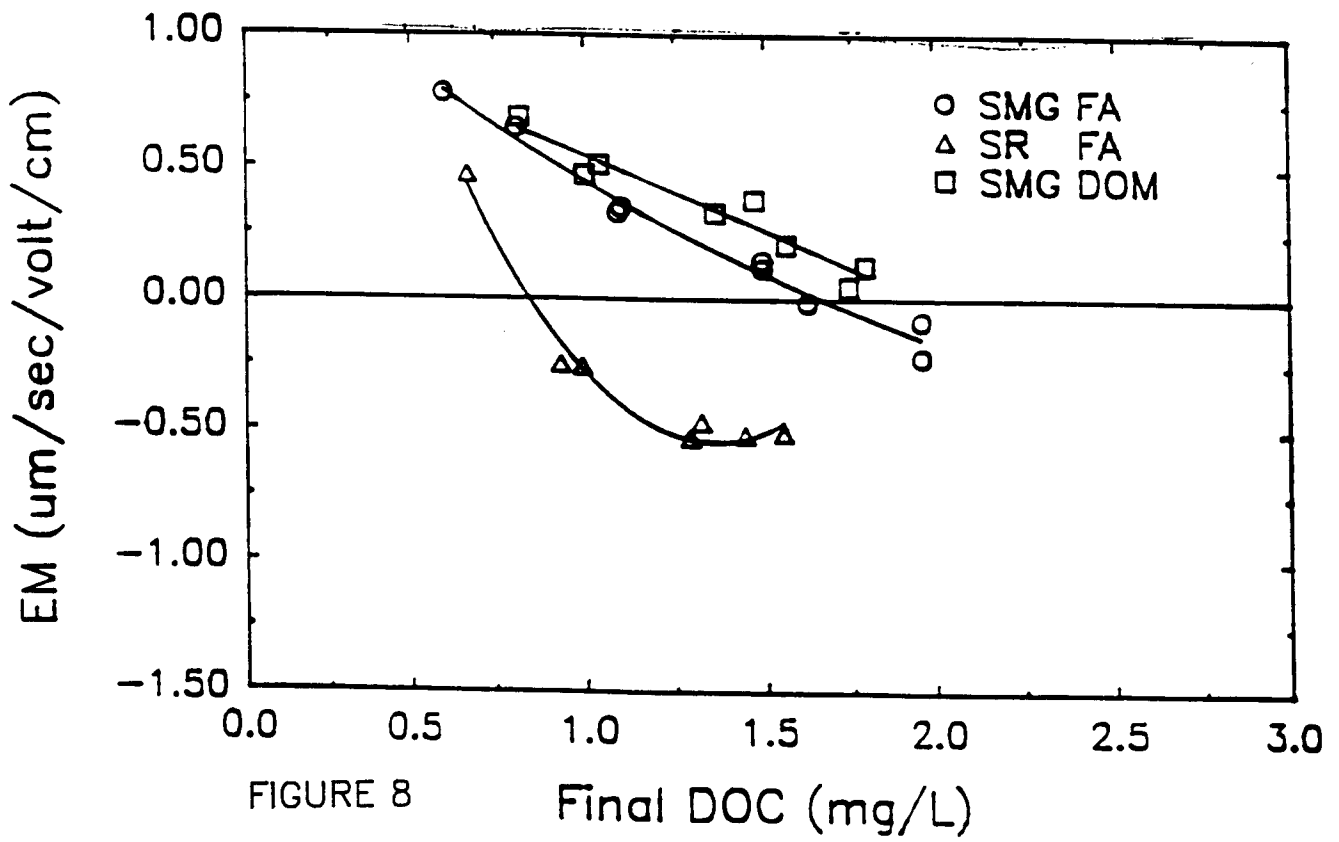
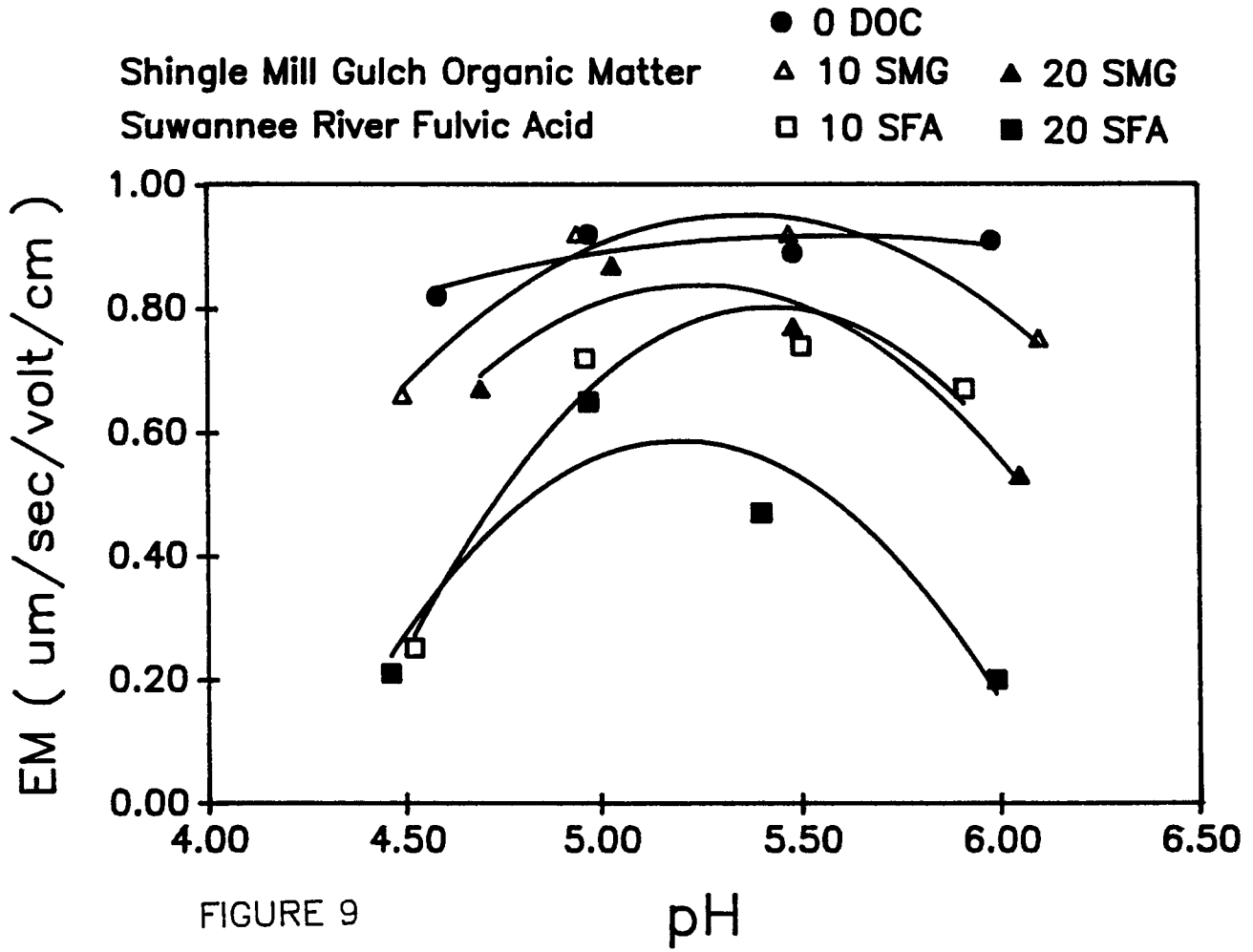


FIGURE 8

Final DOC (mg/L)

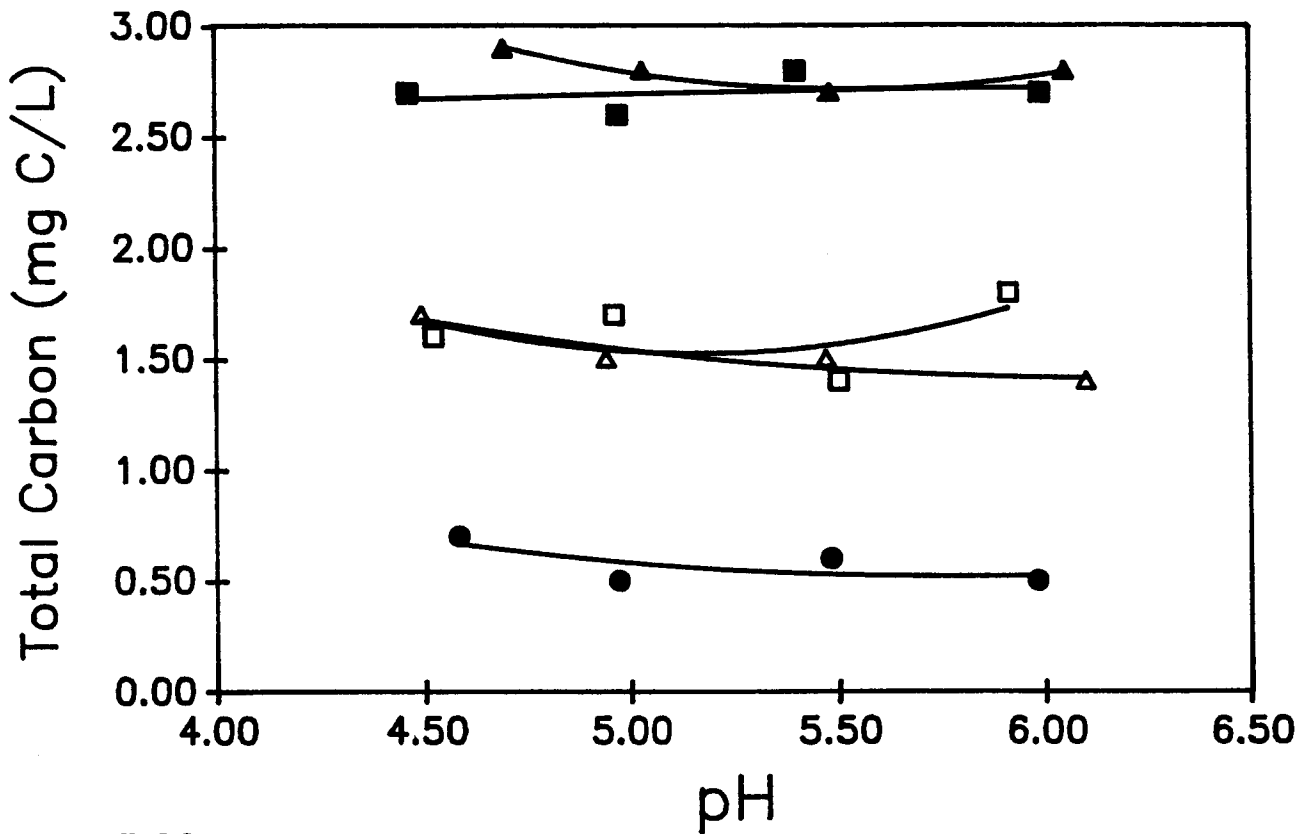




Shingle Mill Gulch Organic Matter  
 Suwannee River Fulvic Acid

● 0 DOC    ▲ 10 SMG    ▲ 20 SMG  
 □ 10 FA    ■ 20 FA

A.)



B.)

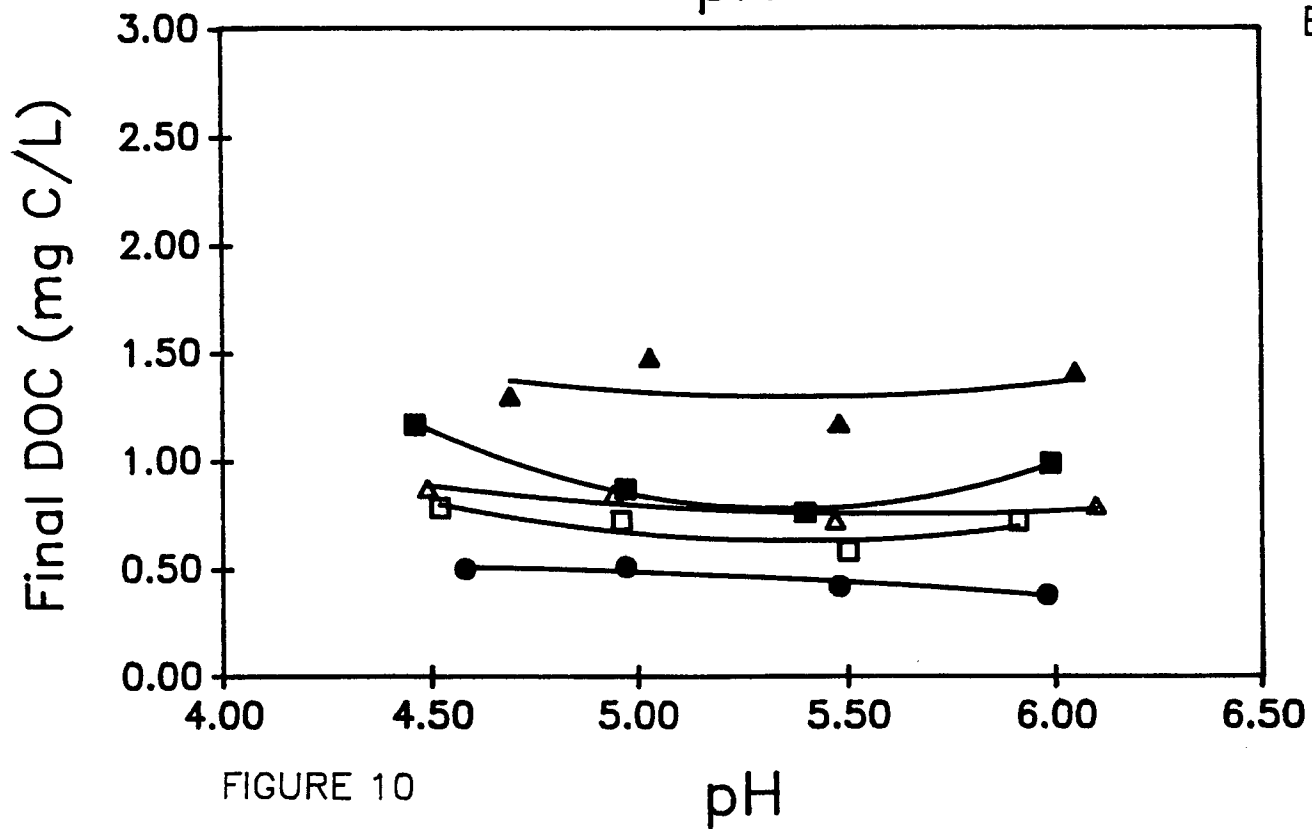


FIGURE 10

pH

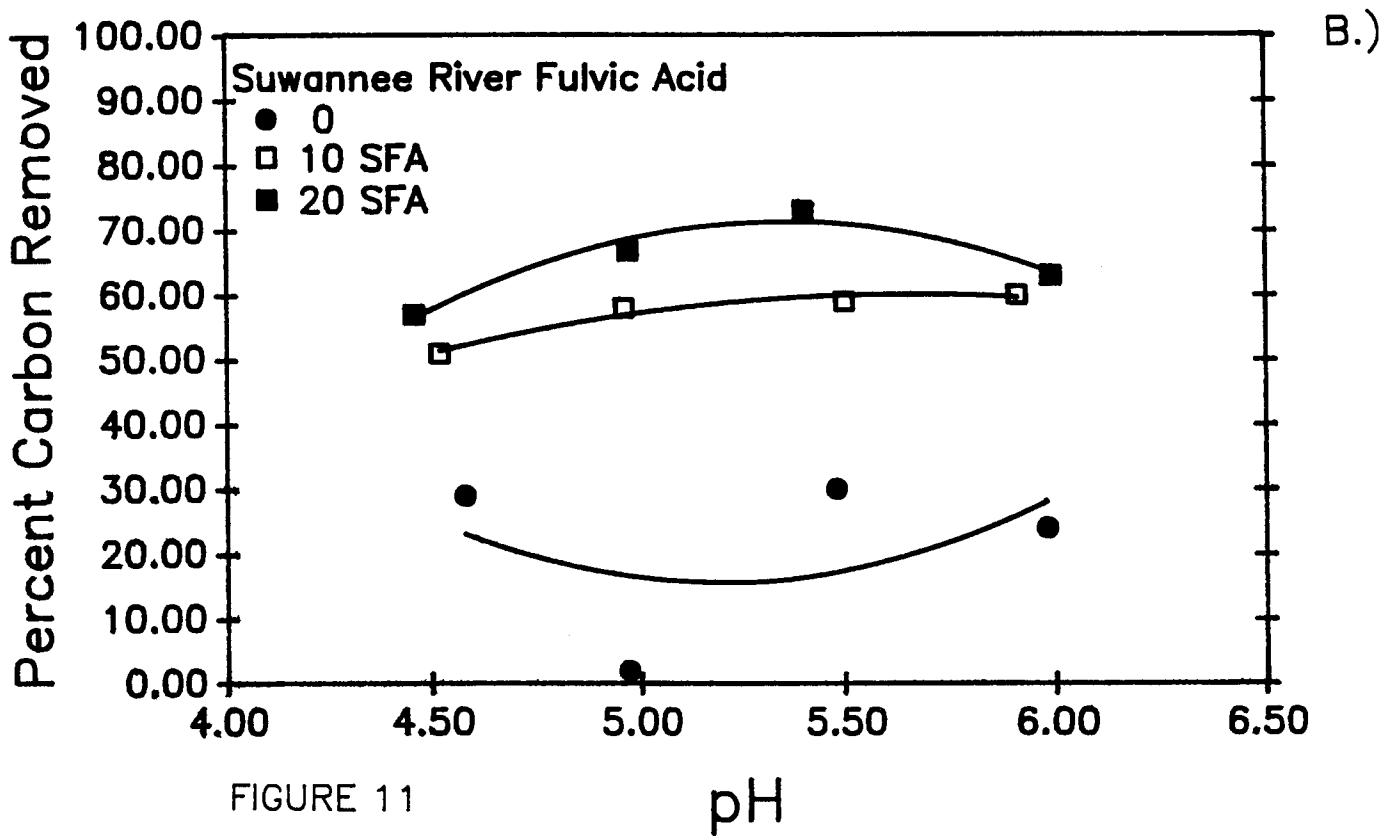
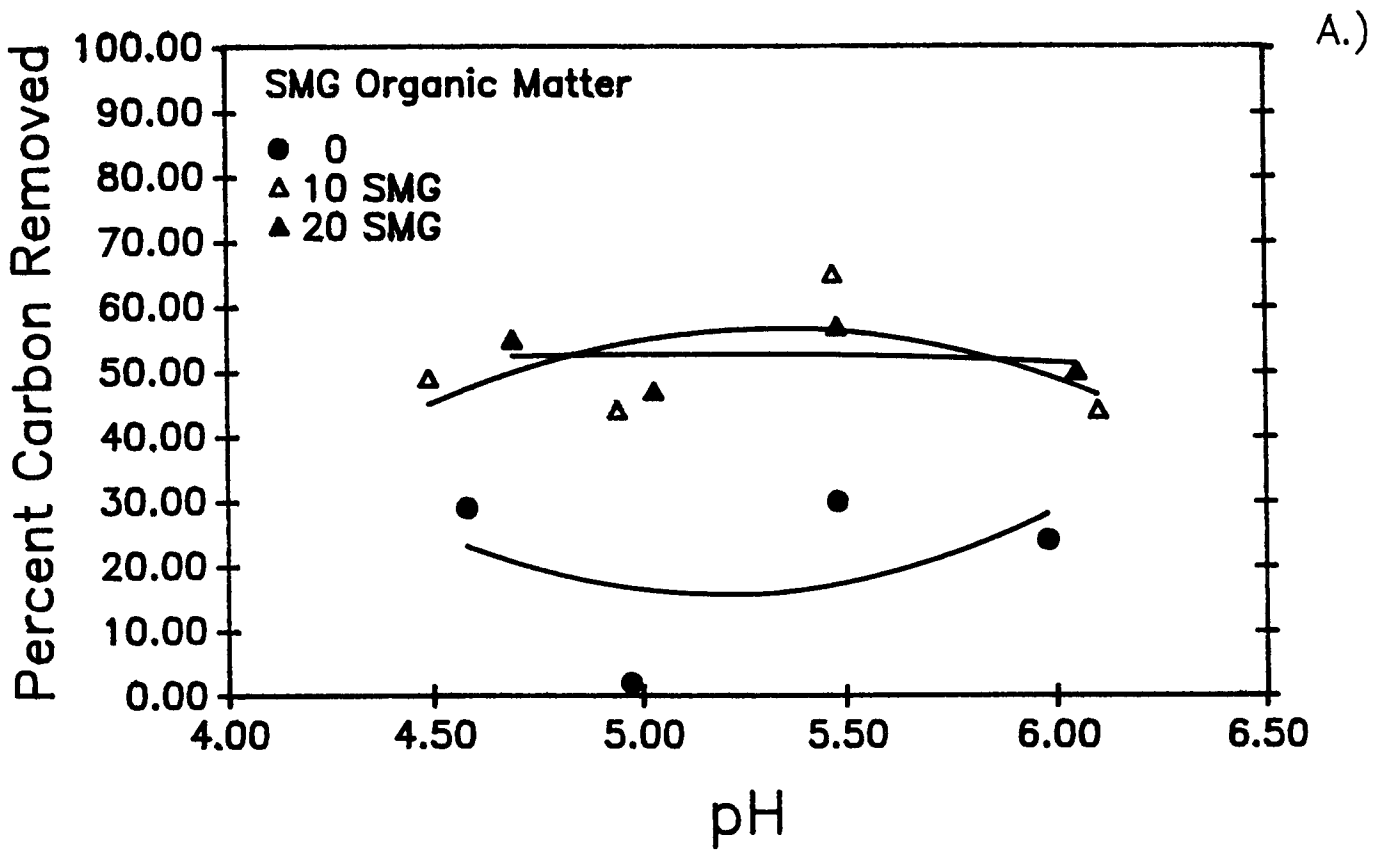
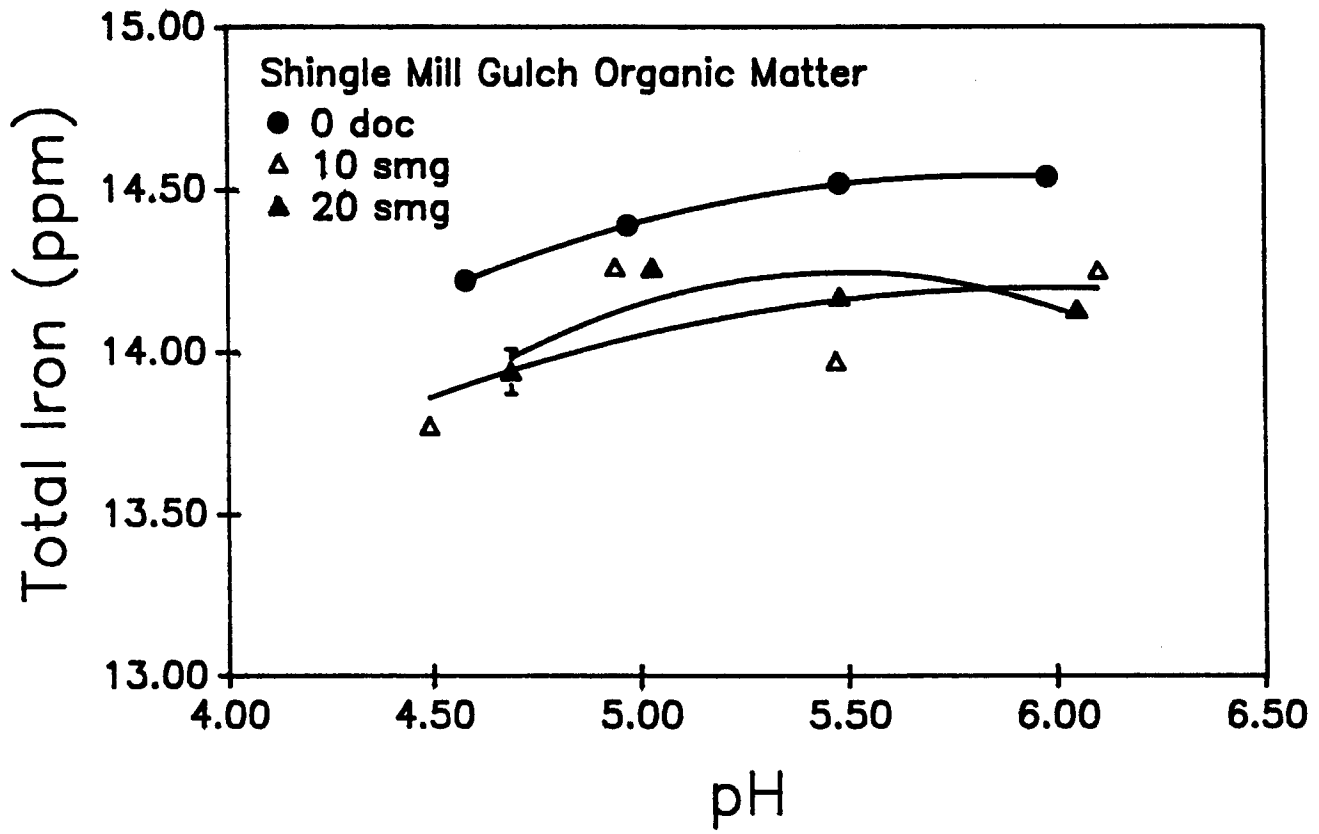
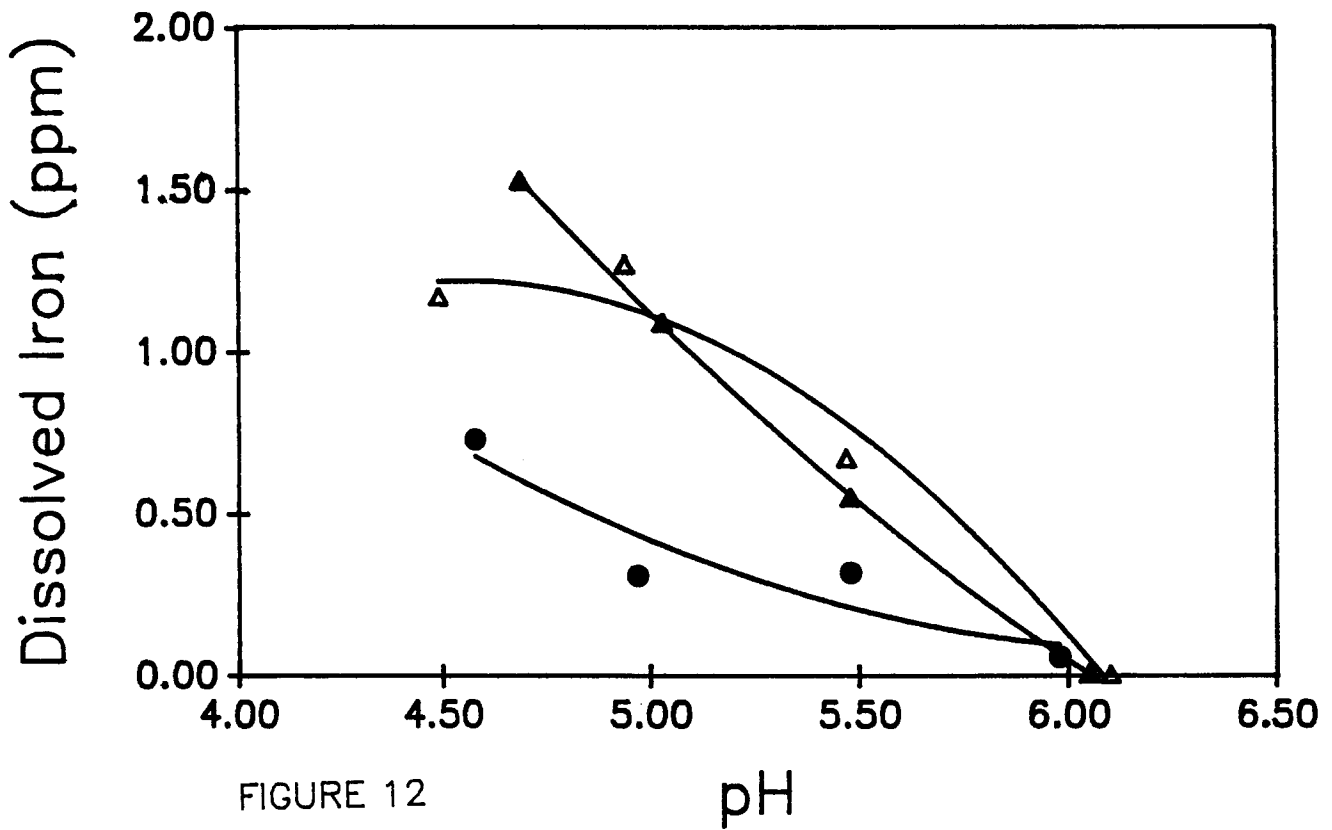


FIGURE 11



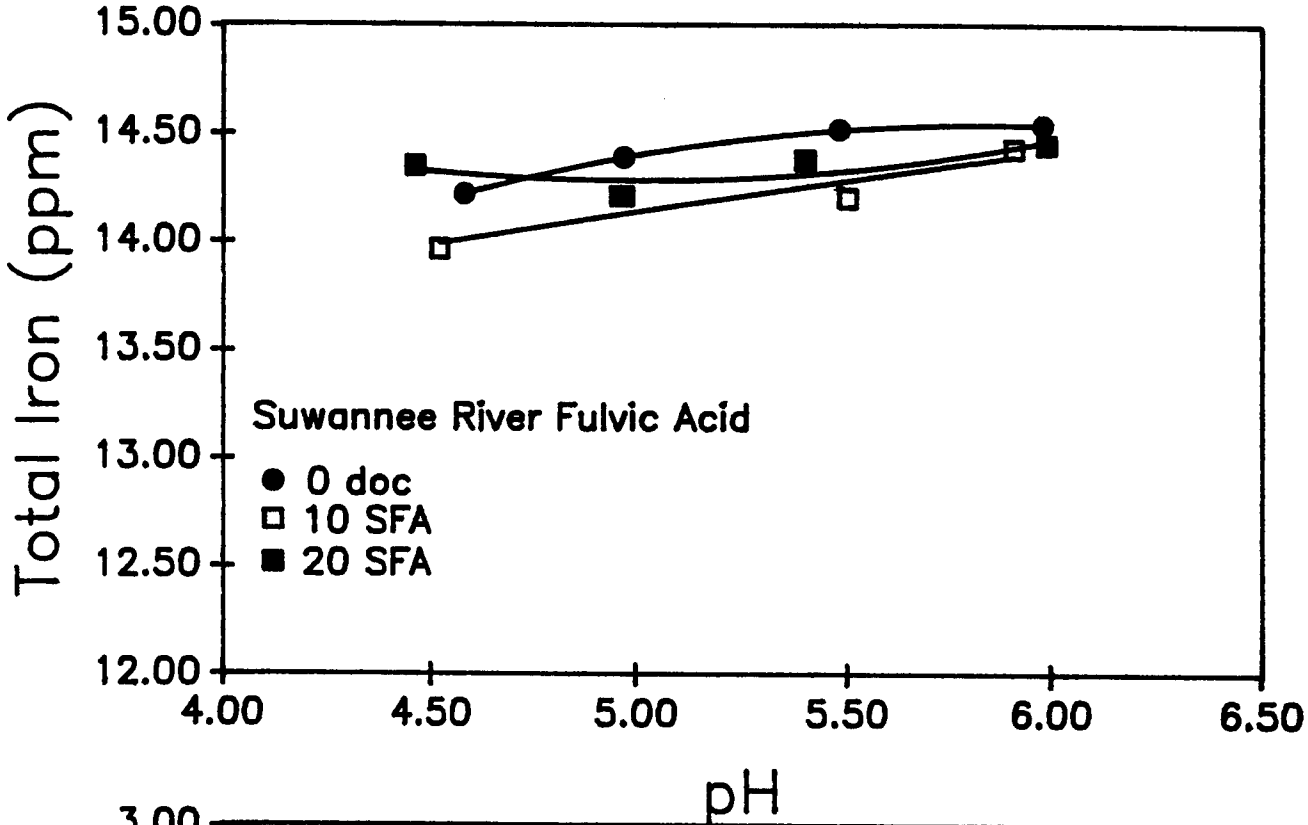
A.)



B.)

FIGURE 12

A.)



B.)

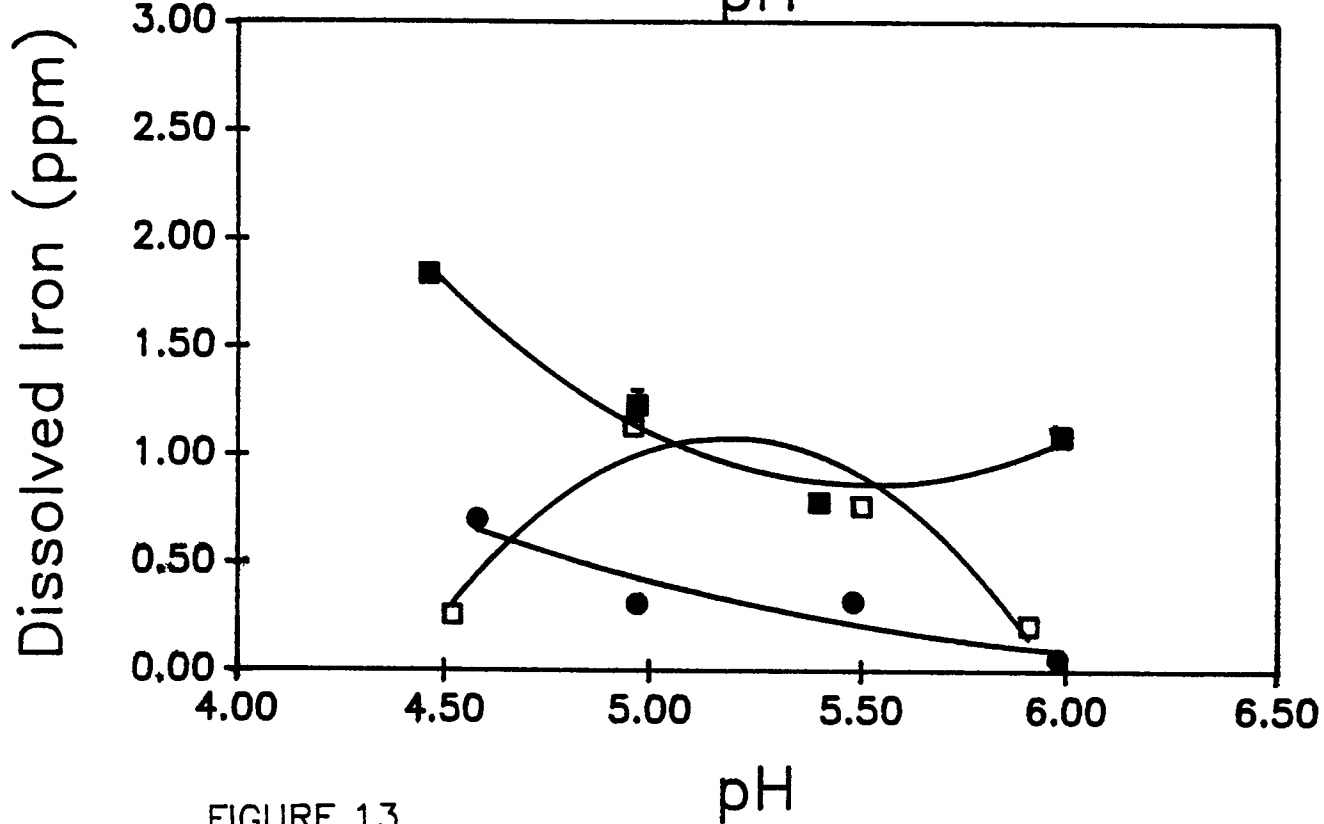
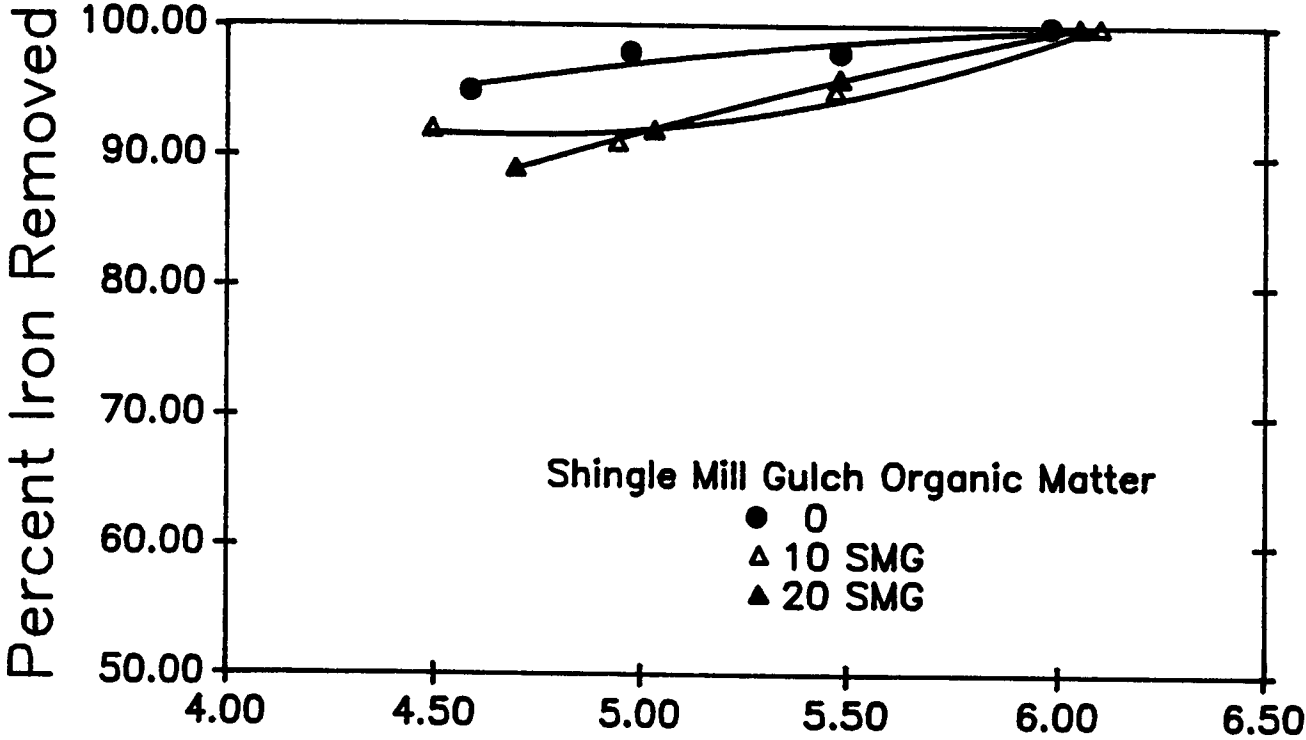


FIGURE 13

A.)



B.)

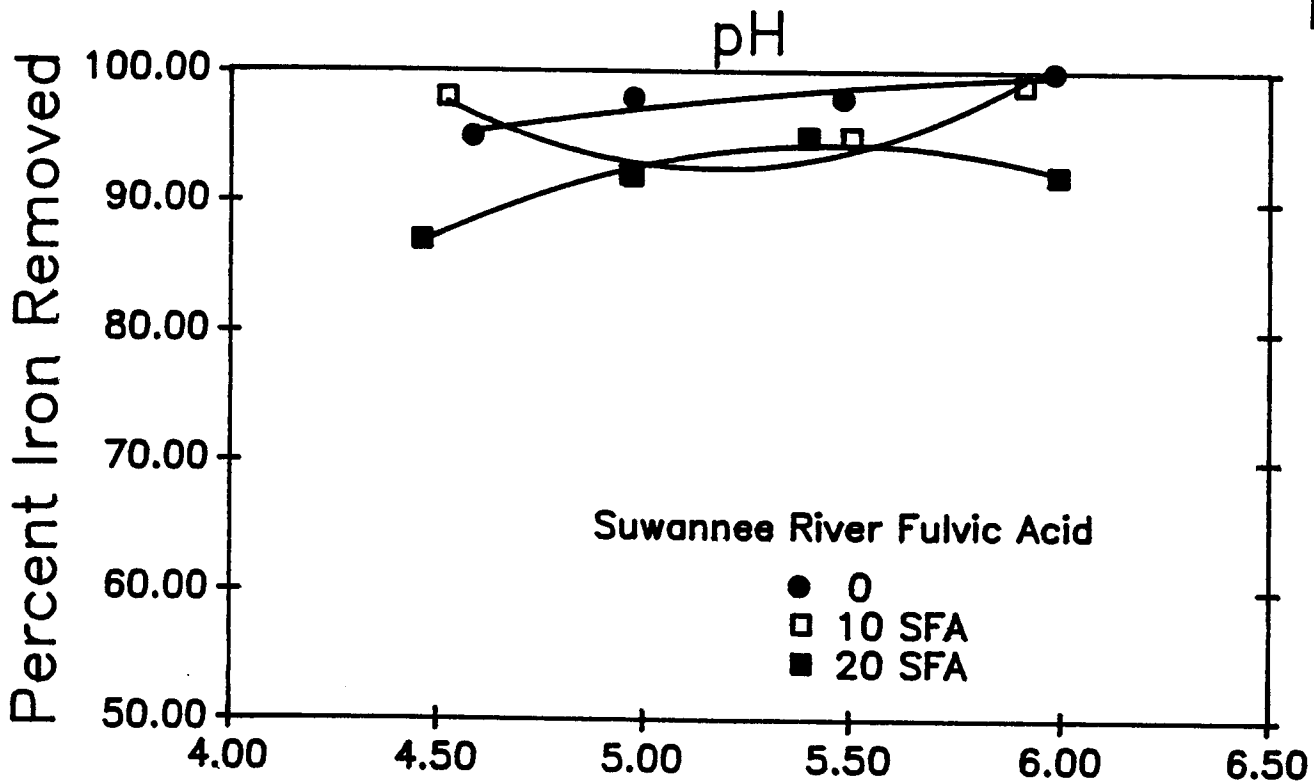
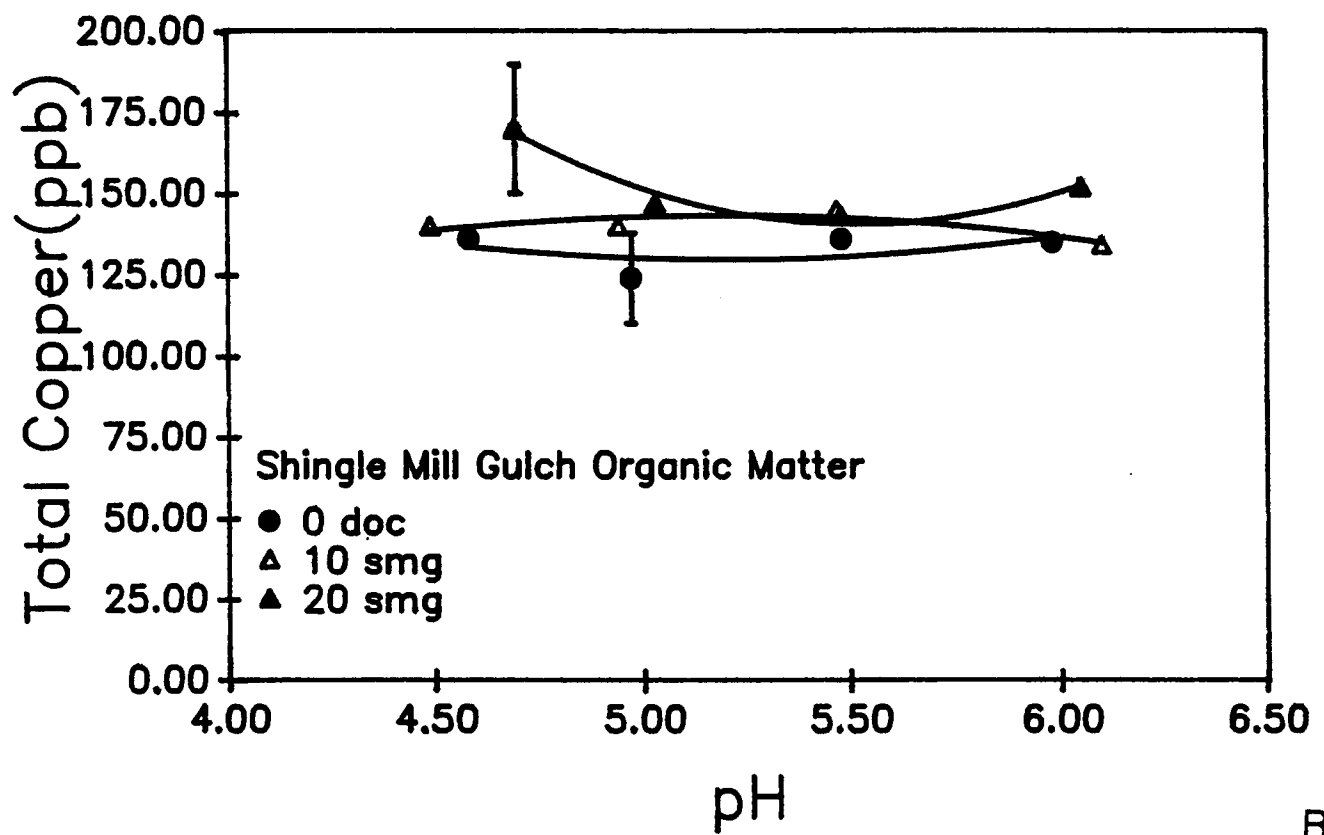


FIGURE 14

pH

A.)



B.)

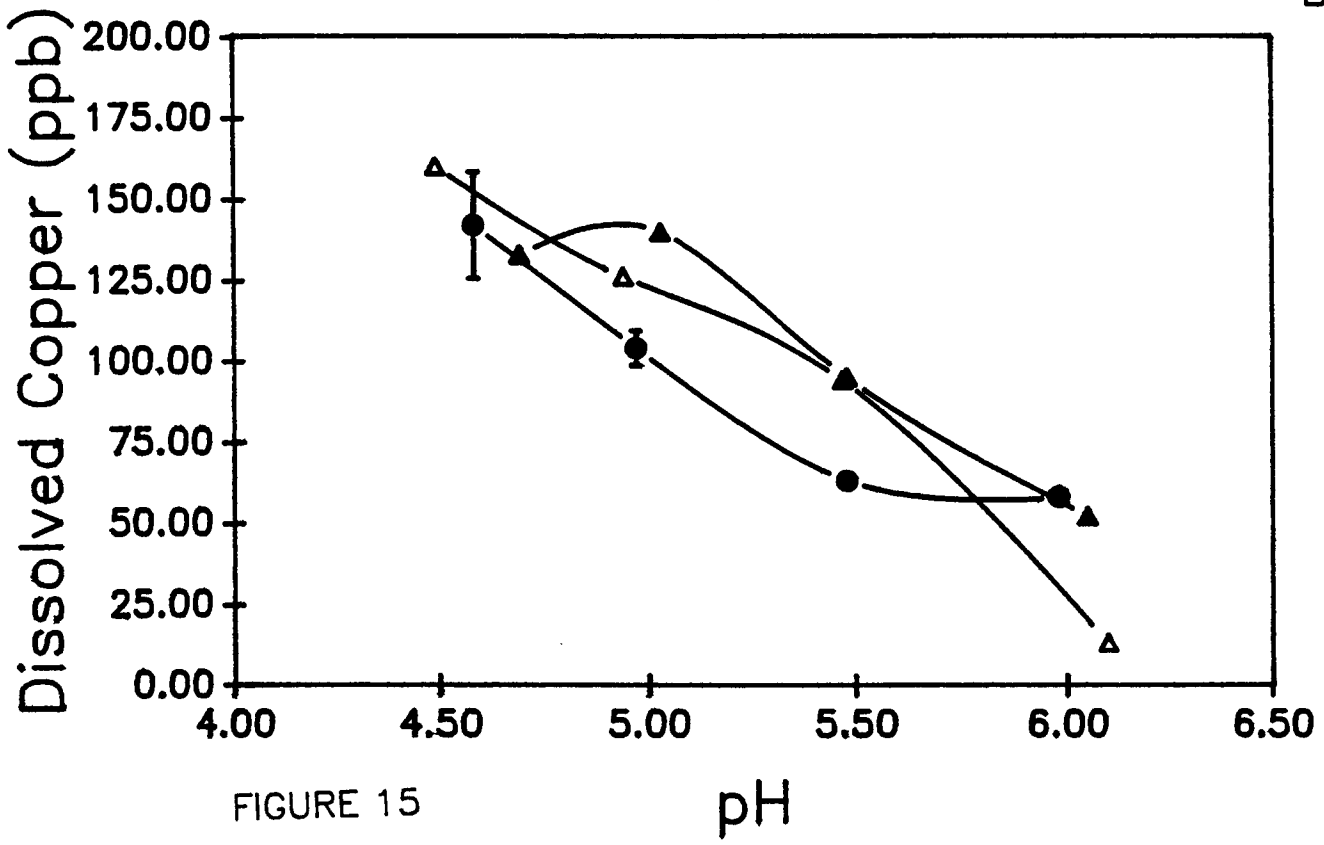
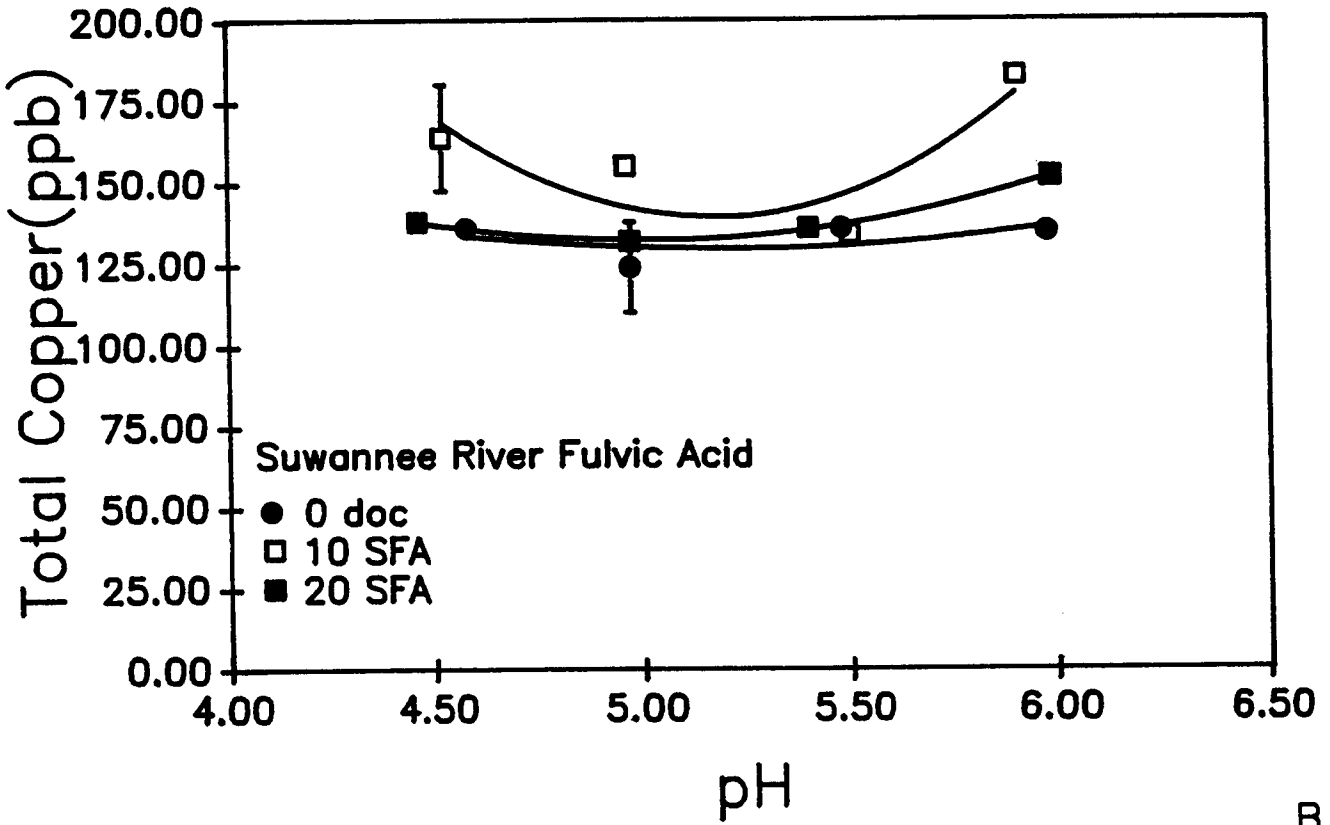


FIGURE 15

A.)



B.)

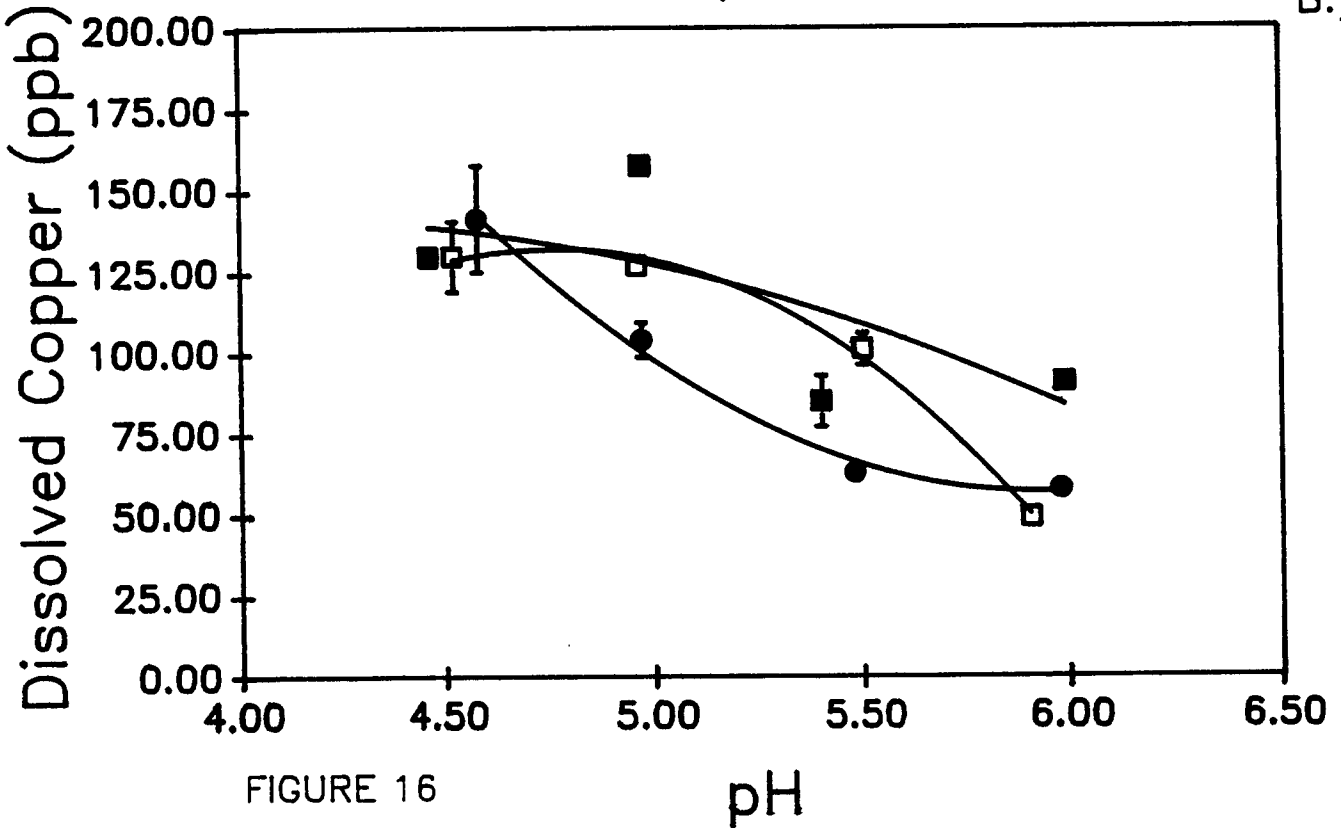


FIGURE 16



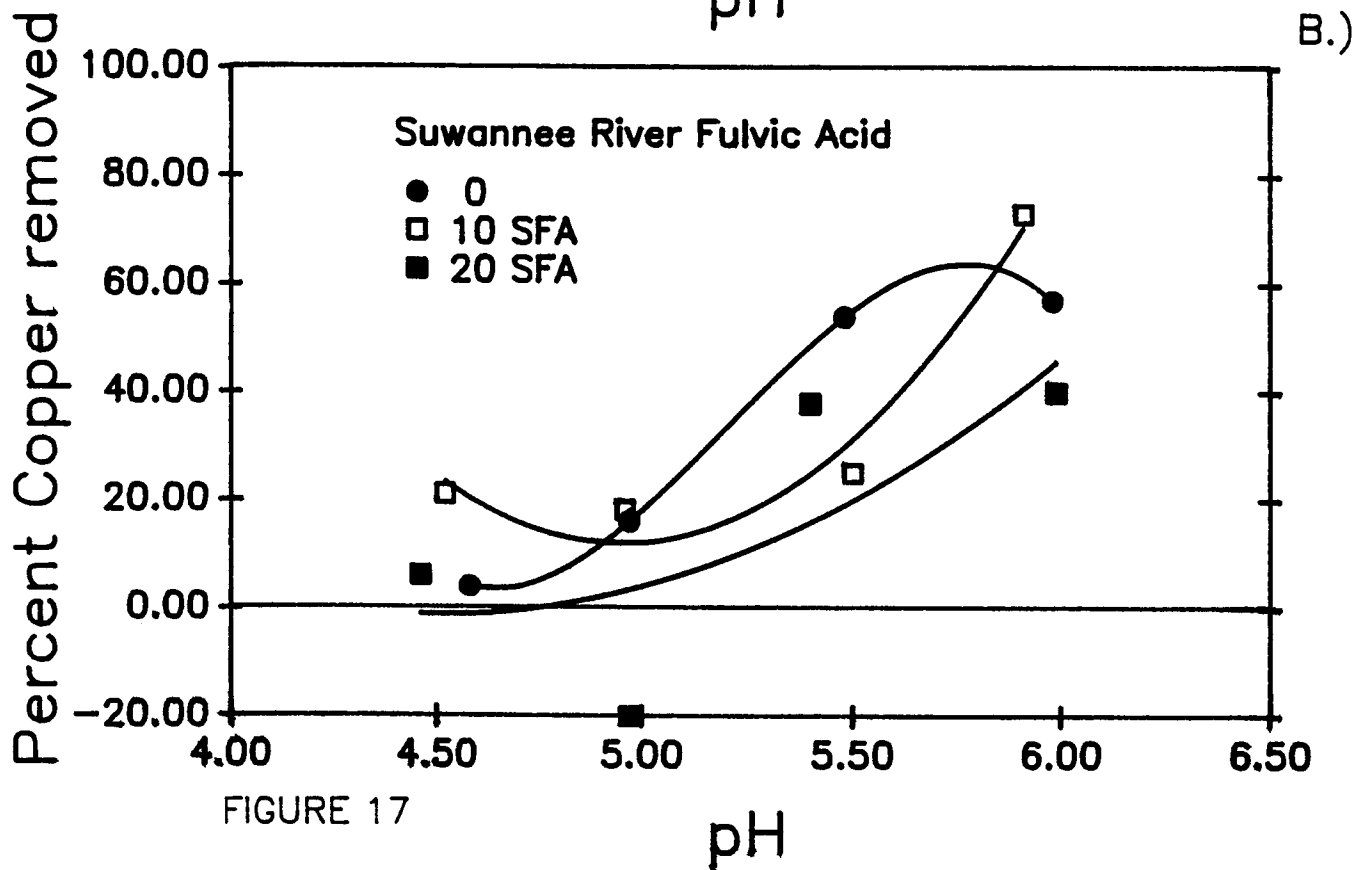
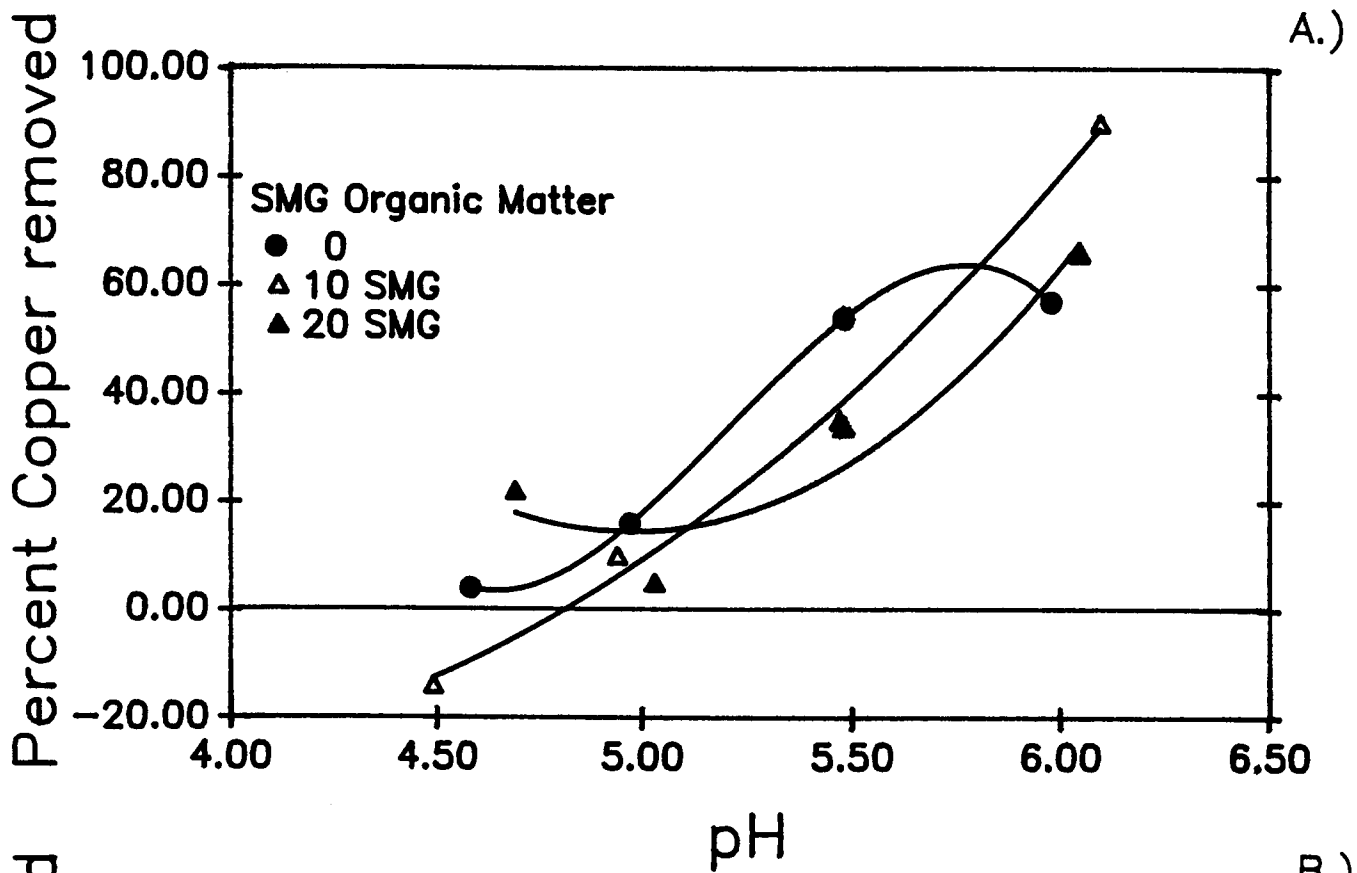


FIGURE 17

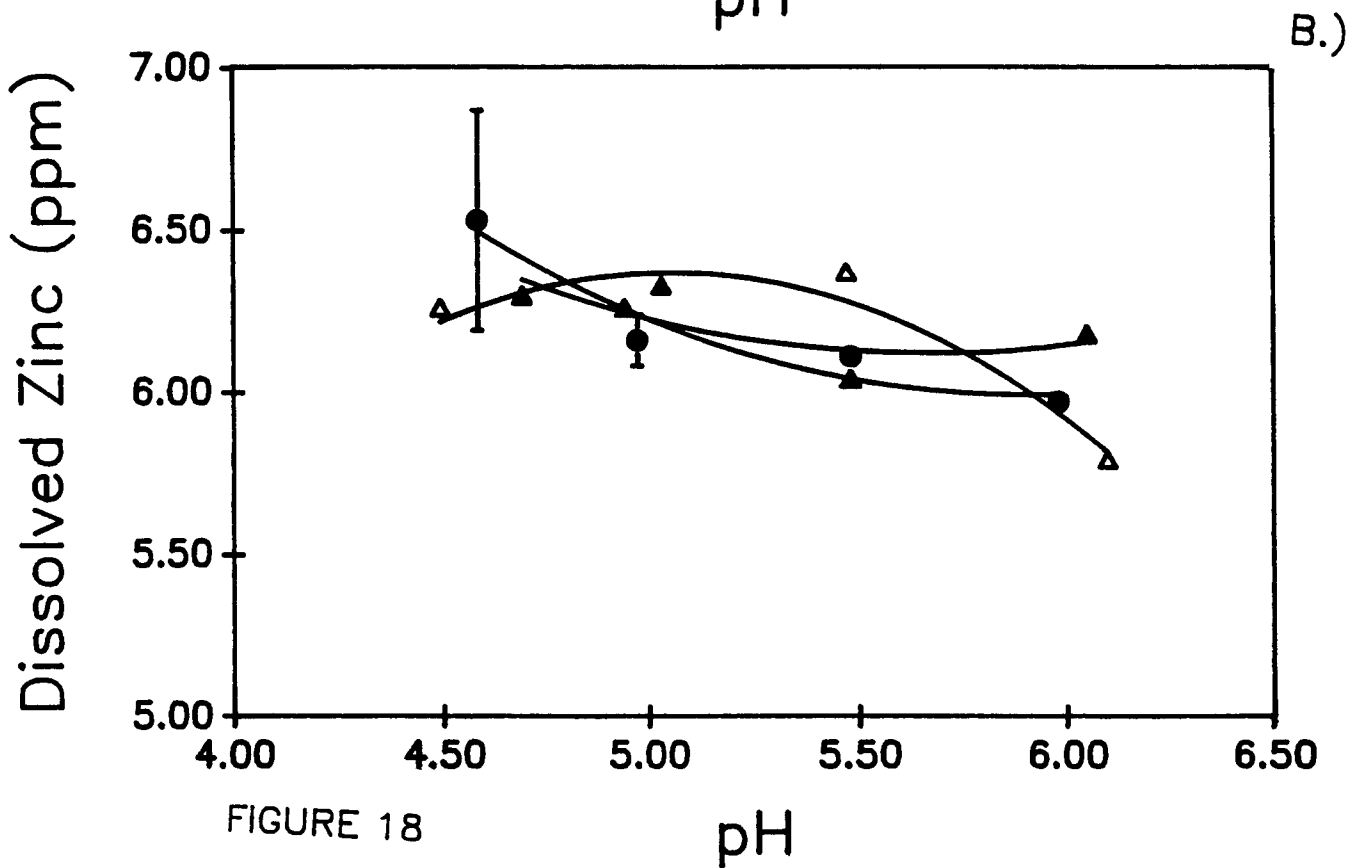
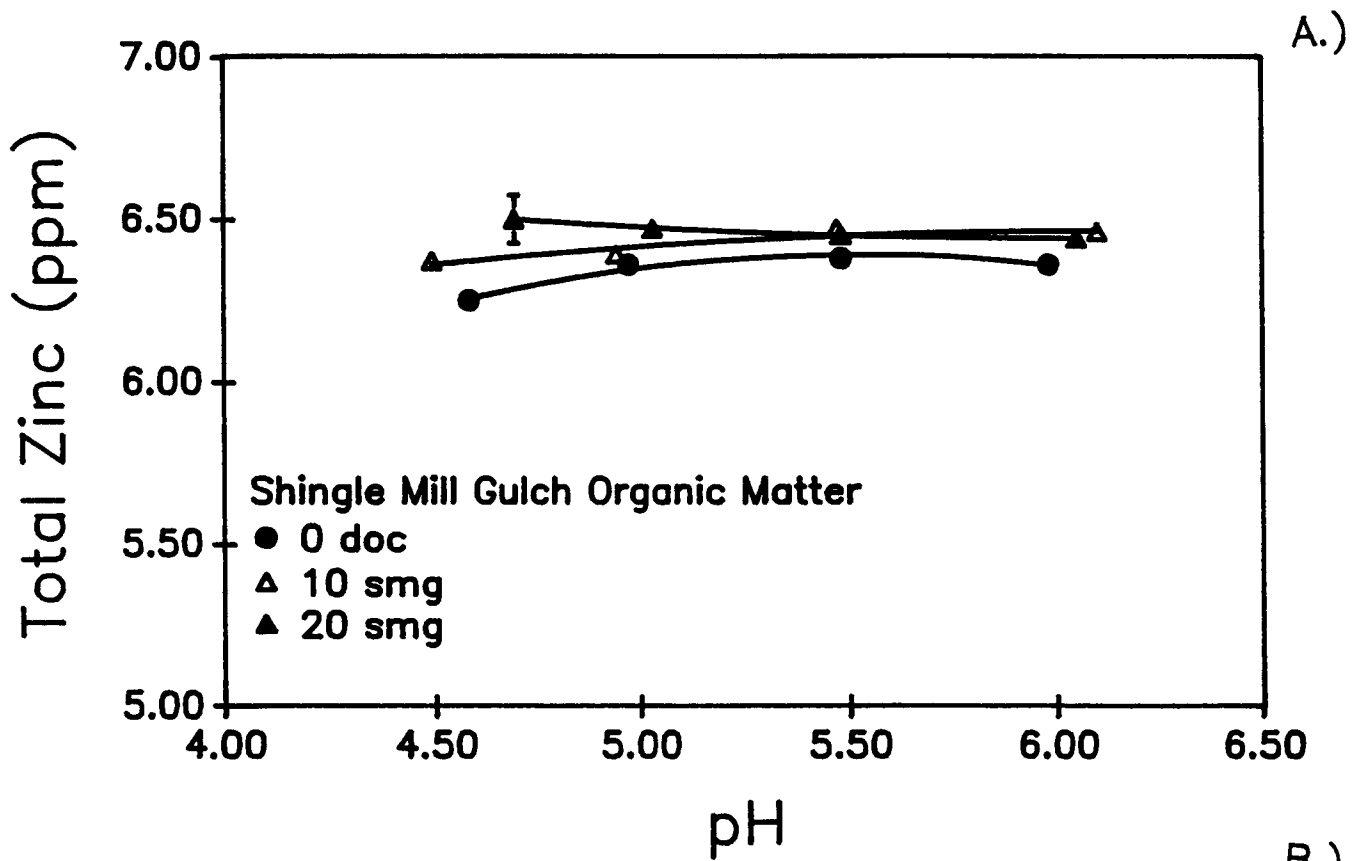
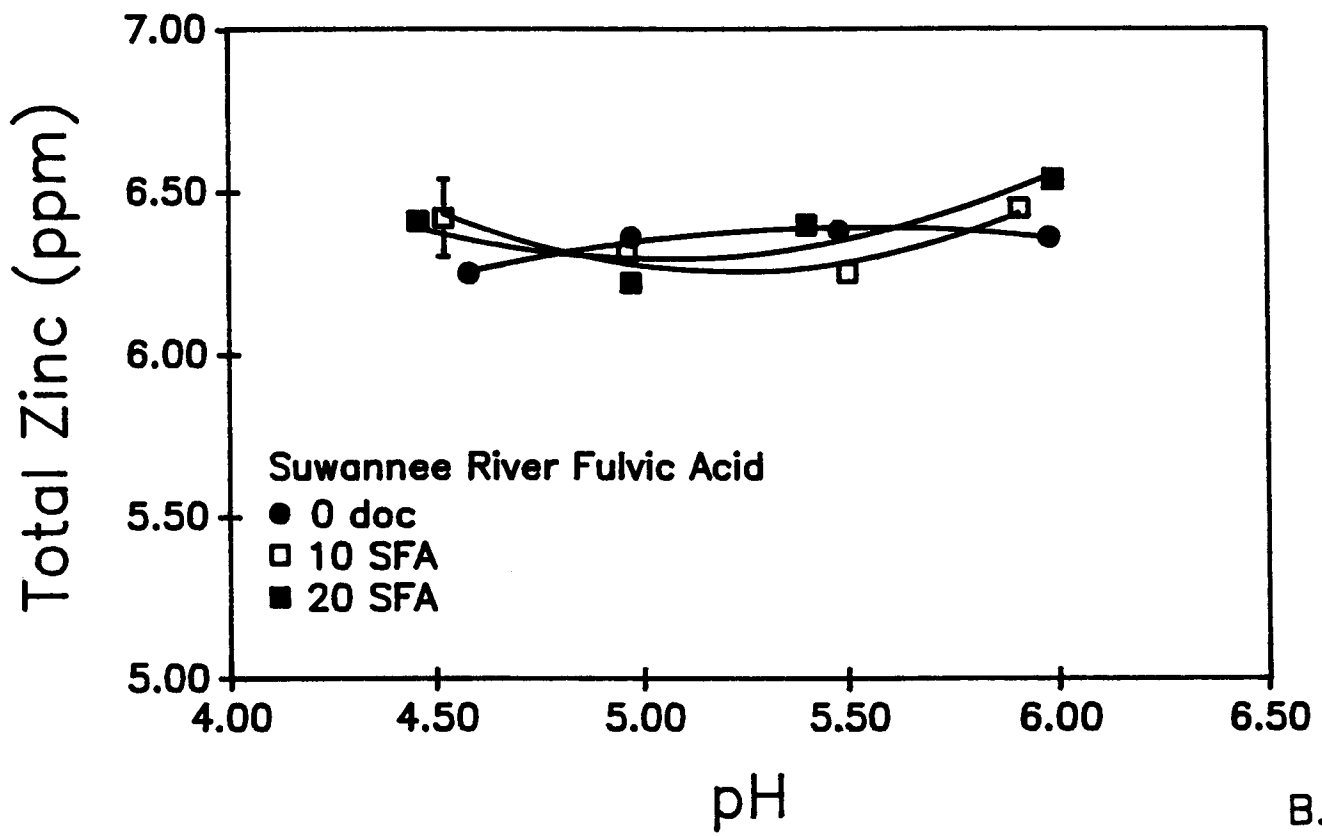


FIGURE 18

pH

A.)



B.)

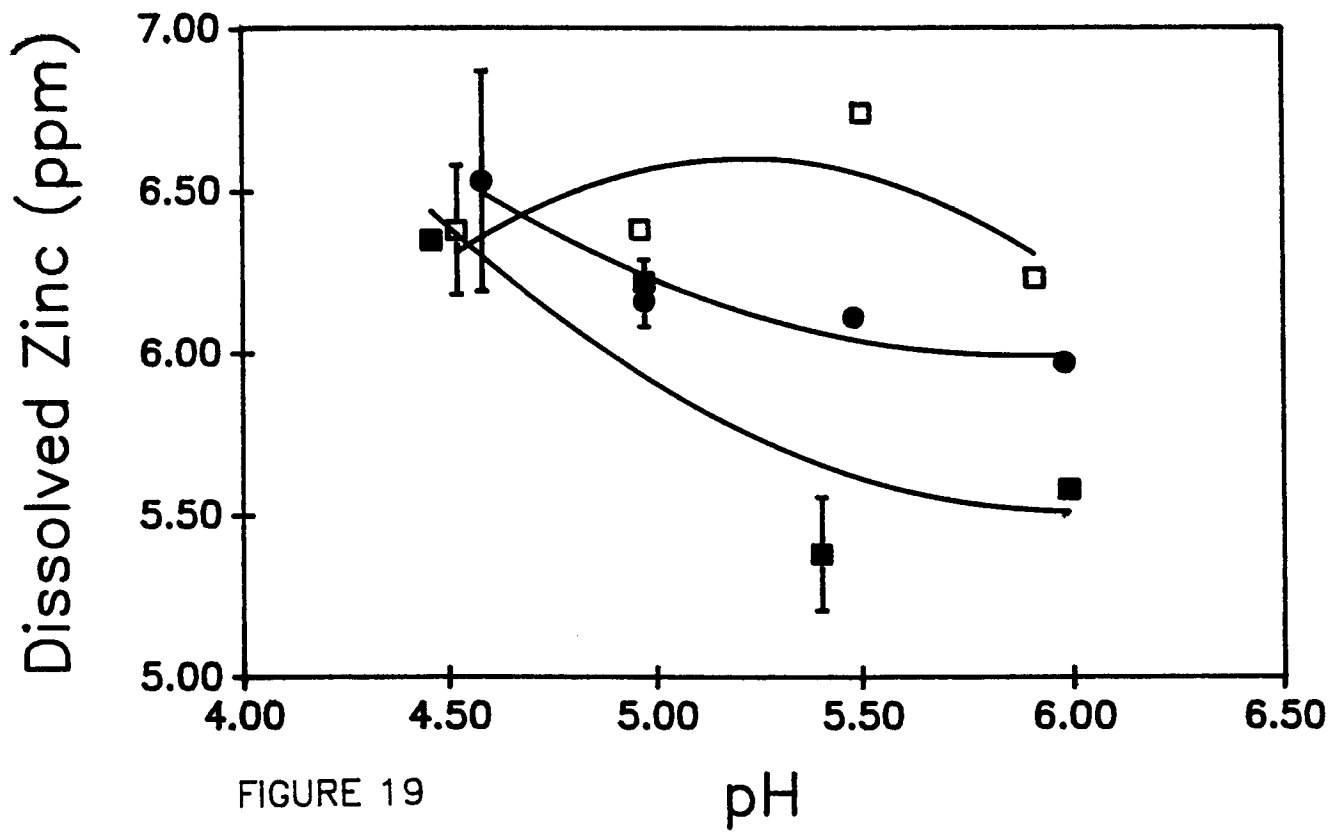


FIGURE 19

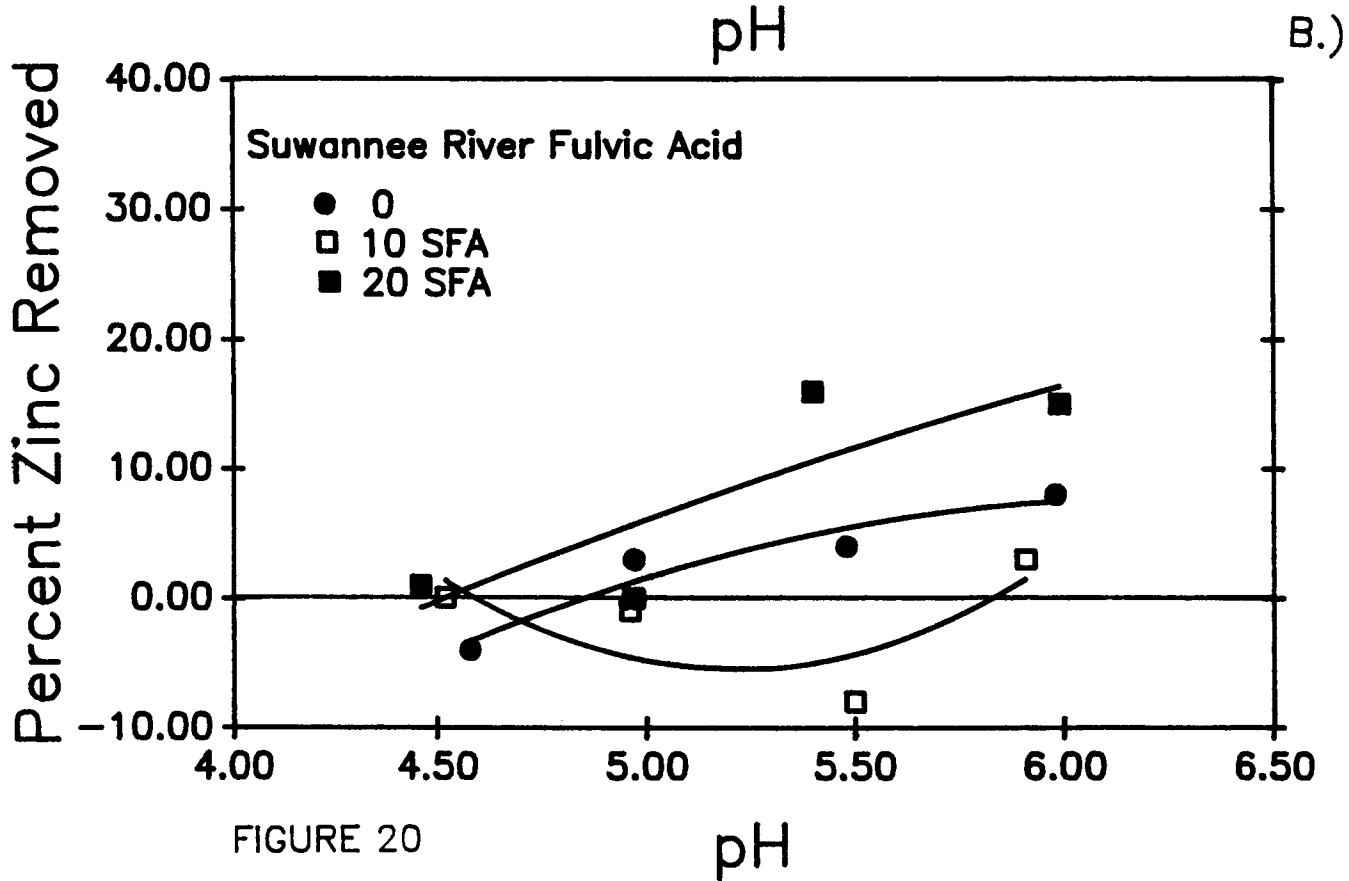
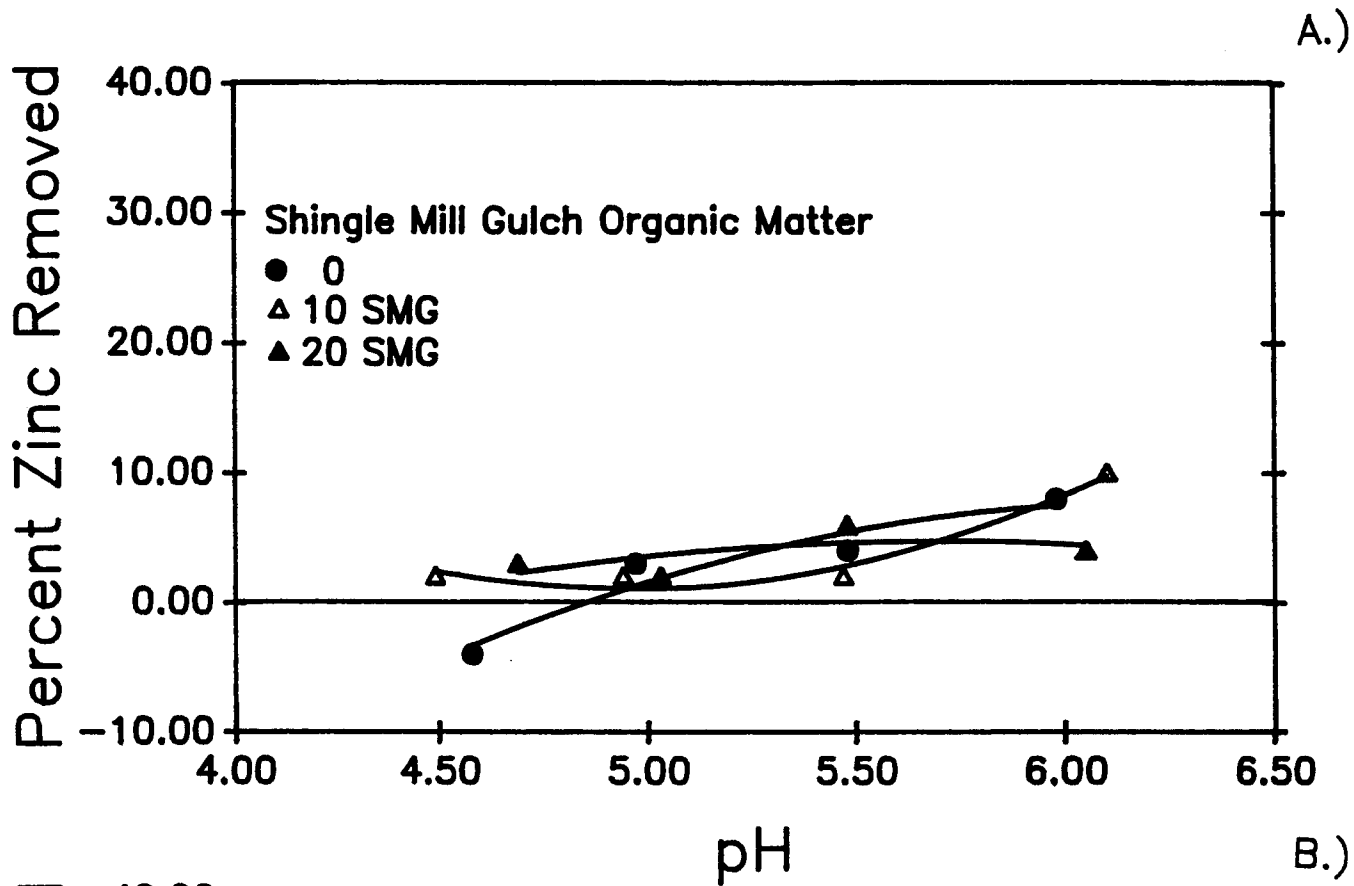


FIGURE 20