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The effects of abandoned coal mines on stream water chemistry in the Big South Fork National River and Recreation Area, Tennessee and Kentucky

Maria Christine Leary

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To the Graduate Council:

I am submitting herewith a thesis written by Maria Christine Leary entitled "The effects of abandoned coal mines on stream water chemistry in the Big South Fork National River and Recreation Area, Tennessee and Kentucky." I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Geography.

Carol Harden, Major Professor

We have read this thesis and recommend its acceptance:

Stephen Nodvin, Sally Horn

Accepted for the Council:
Carolyn R. Hodges

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)

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Dr. Carol Harden,
Major Professor

We have read this thesis
and recommend its acceptance:

Sally P. Horn

Stephen C.

Accepted for the Council:

CW Minkel

Associate Vice Chancellor
and Dean of the Graduate School

THE EFFECTS OF ABANDONED COAL MINES ON STREAM WATER CHEMISTRY IN THE BIG SOUTH FORK NATIONAL RIVER AND RECREATION AREA, TENNESSEE AND KENTUCKY

A Thesis for the
Master of Science Degree

University of Tennessee, Knoxville

Maria Christine Leary
December, 1991

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Jeffry Rodin was the person who sparked my interest in graduate school and who I turned to when I needed an escape. Thanks Kid.

ABSTRACT

Both surface and deep coal mining have occurred in the vicinity of Big South Fork National River and Recreation Area (BISO) in eastern Tennessee and Kentucky. Mine drainage constituents have entered many tributary streams of the Big South Fork River through surface and subsurface flow. Because some streams have contamination levels potentially harmful to humans, a current priority of the National Park Service is reclamation of contaminated surface water in BISO.

A database of available water quality data from BISO and adjacent watersheds was compiled. Data from BISO (1981-1990), O'Bara *et al.* (1981), and the current study (1990) comprise a nine-year overview of sulfate, hardness and iron concentration levels. These three parameters were used to evaluate general stream characteristics and seasonal water chemistry changes, and their usefulness as indicators of acid mine drainage impacts was assessed. Sulfate was determined to correspond best, followed by hardness and then iron, to the potential amount of acid mine drainage entering a stream. Sulfate, however, is not recommended as a single indicator because it does not represent the stream's ability to buffer or neutralize the acid drainage.

Water samples were collected from thirteen different sites in five streams, in October of 1990. Each site was analyzed for the following: Ca^{2+}, Mg^{2+}, Na^+, K^+, NH_4^+, PO_4^{3-}, Al, Cl^-, Fe, SO_4^{2-}, NO_3^-, As, Ba, B, Br, Cd, Cr, Cu, F, Mn, Mo, Ni, Pb, Se, Si, Sr, Ti and Zn, as well as, alkalinity, pH, specific conductance and discharge. Baseline levels for natural stream chemical concentrations were determined from the concentrations of the two unmined surveyed streams. The baseline values were compared to EPA drinking water standards to develop reclamation target levels. All but Fe, Al, Se, and Pb were within the regulation concentration levels.

Through downstream comparison of the chemical concentrations, one tributary, Roaring Paunch Creek, was determined to be presently affected by deep mining acid mine drainage contaminants, as well as surface mining.

Stream chemistry concentrations at base flow condition were modeled by combining the recency of mining abandonment with the extent of surface disturbance. The model describes three stages of stream impacts from mining: 1) extensive - recently mined, large disturbance; 2) moderate - abandoned 15 to 25 years ago, medium disturbance; and 3) low - abandoned greater than 25 years, little disturbance. It also indicates how factors such as geology, seasonal changes and other land usage may affect the concentration levels in a stream.

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Chapter 1

INTRODUCTION

The Problem of Coal Mine Drainage

Coal has been an important economic resource of eastern Tennessee and Kentucky. Extensive coal mining near the Big South Fork of the Cumberland River watershed has resulted in the contamination of many streams by mine drainage. The management of Big South Fork National River and Recreation Area (BISO) is especially concerned about stream contamination from mining disturbance because of increased use of the park and its waterways (Dickenson, personal communication, 1991). The water in some BISO streams does not meet standards set by state health regulations for levels of pH or for major, minor, and trace chemical constituents (Barrass, personal communication, 1990).

Coal was excavated in the Big South Fork River watershed by both surface and deep mining (Barclay and Parsons, 1983). Surface mining operations were preferred over deep mining operations because of higher coal recovery, greater production, lower costs, better health and safety conditions, and greater flexibility in operation. Surface mining was done mainly by contour strip mining along hillsides, where the coal was mined as far back into the mountains as was economically feasible (Gaydos *et al.*, 1982). Contour surface mines are an environmental hazard, as they are difficult to reclaim because of the high-walls, benches, and spoil piles left behind after mining (Vaughan, 1967).

During the mining process, the bedrock layers surrounding the mined coal beds are excavated and then relocated to the edge of the mining site. This results in the exposure of minerals within the bedrock and has the potential of weakening the bonds between elements in the minerals in the rock. The weathering process becomes accelerated and minerals within the rock become subject to oxidation, dissolution and transport from the rock.

Coal can be classified either according to its degree of metamorphism or by sulfur content. Generally in the BISO region, the coal has medium to high levels of sulfur (Heine *et al.*, 1979). It is the sulfur in the coal and the surrounding bedrock that reacts with water to create acid mine drainage (Stumm and Morgan, 1981).

Mine drainage becomes acidified when pyrite (FeS_2) in the spoil piles (or from other mining disturbances) is oxidized and sulfuric acid is produced. Acid mine drainage entering surface or ground waters usually lowers the pH of the water, unless large quantities of carbonate minerals are available to neutralize the acid (Infanger and Hood, 1980; Knapp, 1987). Even if the pH is not affected, the natural stream chemistry may be changed because of the elevated concentrations of dissolved solids and suspended particles downstream from mining sites. These changes in stream chemistry can be detected both during and subsequent to coal excavation (Minear and Tschantz, 1976).

Mine drainage, whether it is acidic or not, concerns resource managers because of its potential to damage the environment by increasing the transport of heavy metals through a watershed (Krothe *et al.*, 1980). Not only is surface water affected, but subsurface water located near the surface also becomes contaminated as chemical elements infiltrate through surface materials into the water table (Lund and Dillon, 1987).

Streams adjacent to mining areas can be contaminated by mine drainage as the result of two mechanisms. First, during storm runoff periods, surface runoff can carry large quantities of both suspended and dissolved solids from mining sites into streams. Second, streams can be impacted when contaminated ground water discharges into them (Brown *et al.*, 1980). The extent of damage from acid mine drainage is influenced by the proximity of watershed streams and the height of the water table with respect to the mined area. The closer the hydrologic network is to the spoil piles, the more extensive the damage (Infanger and Hood, 1980).

The Purpose of this Study

The purpose of this study was to investigate the chemical dynamics of mine drainage in BISO. Two approaches were taken. The first approach involved compiling available stream databases from previous studies within BISO and neighboring watersheds. The compilation provided a nine-year chemical background on sulfate, hardness, and iron, which was used to evaluate relatively long-term effects and general seasonal water chemistry changes within BISO. The second approach involved a field-based water sampling project designed to obtain an extensive chemical analysis of current stream water conditions.

Within this framework were two objectives:

1) To investigate the relationship of sulfate, hardness and iron concentrations to acid mine drainage, reviewing the effects of the extent of mine disturbance and the length of the abandonment period on these parameters; and
2) To determine baseline concentration levels for natural stream chemistry in unmined streams of BISO.

A number of organizations, including the National Park Service, the Soil Conservation Service, the Land Reclamation Division of the Tennessee Department of Environment and Conservation, and the Kentucky and Tennessee offices of the U.S. Geological Survey (USGS) are working within the Big South Fork River basin to improve the quality of streams that have been degraded by coal mining. One of the largest projects being conducted concurrently with this work is a restoration program for Bear Creek, a severely contaminated tributary of the Big South Fork of the Cumberland River, which the city of Oneida, Tennessee would like to utilize as a future drinking water source. The work described in this project was done in cooperation with the above agencies and was designed to provide information on stream chemistry that could be utilized by the interagency working group to develop guidelines for the clean-up of streams in the area.

Chapter 2

REVIEW OF ACID MINE DRAINAGE AND PREVIOUS RESEARCH

The Chemical Basis of Acid Mine Drainage

The extent of acid drainage from coal mines is controlled by hydrology, geology, topography, climatology, coal chemistry, mining method and mine location (Baker, 1975). Acid mine drainage originates with a complex set of interactions between chemical elements in soils, bedrock, water and microbiological organisms. Four stages occur in the generation of acid mine drainage: 1) chemical oxidation of pyrite or other sulfide minerals, which produces an acid; 2) neutralization of the acid in the water by carbonate minerals until all carbonate elements have been used; 3) chemoautotrophic bacterial acceleration of acidification as the pH decreases; and 4) oxidation of ferrous iron to ferric iron which, in turn, catalyzes the oxidation of more sulfide minerals (Ferguson and Erickson, 1987).

The basic chemical reactions which describe acid mine drainage generation are as follows:

$$FeS_2 + 7/2\ O_2 + H_2O = Fe^{2+} + 2H^+ + 2SO_4^{2-} \tag{2.1}$$

$$Fe^{2+} + 1/4\ O_2 + H^+ = Fe^{3+} + 1/2\ H_2O \tag{2.2}$$

$$Fe^{3+} + 3H_2O = Fe(OH)_3\ (s) + 3H^+ \tag{2.3}$$

and/or

$$14Fe^{3+} + FeS_2 + 8H_2O = 15Fe^{2+} + 16H+ + 2SO_4^{2-} \tag{2.4}$$

The oxidation of sulfide to sulfate (equation 2.1) occurs rapidly when the pyrite is in contact with oxygen in water, and releases iron and sulfuric acid (H_2SO_4). Upon entering the stream, ferrous iron (Fe^{2+}) is oxidized by oxygen or microorganisms to form ferric iron (Fe^{3+}) (equation 2.2). The ferric iron may stay in solution if pH is less than 3.0, or precipitate out to form insoluble ferric hydroxide, commonly named "yellow boy" (equation 2.3). Alternatively, ferric iron may react with additional pyrite to release sulfuric acid and ferrous iron, acidifying the water again (equation 2.4). At this point ferrous iron is capable of re-entering the system as per equation 2.2 (Baker, 1975; Infanger and Hood, 1980; O'Bara *et al.*, 1982). Every mole of pyrite yields four moles of acidity by the end reaction (Infanger and Hood, 1980).

As pH descends into the acidic range, biological oxidation becomes more significant than the chemical process in breaking down the ferrous iron into ferric iron. Compared to chemical oxidation, microbial oxidation of ferrous iron to ferric iron greatly accelerates the acid production by several orders of magnitude (Knapp, 1987; Lund and Dillon, 1987). One of the prime bacteria species necessary for the effective oxidation of pyrite in low pH conditions is *Thiobacillus ferrooxidans* (Stumm and Morgan, 1981). Chemoautotrophic bacteria are dependent on the oxidation of reduced iron and sulfur to produce energy for growth. The bacteria function between pH 5.0 and pH 1.5, optimally between pH 3.2 and 2.8, as shown in Figure 2.1. At pH levels less than 2.0, the primary oxidation mechanism becomes chemical again, although microbial oxidation still continues (Knapp, 1987).

Lowering the pH of a stream through input of acid mine drainage causes increased dissolution and mobilization of trace elements in the water. The final change in stream chemistry will depend upon the surrounding geochemistry of soils and sediments, which determines the natural water chemistry. The effects of coal mine drainage on stream chemistry can therefore differ from region to region due to differences in local geology. For example, shale, containing aluminum silicate minerals, produces a more alkaline discharge because of the liberation of its hydroxide ion when water passes through it, buffering the acid mine drainage as follows:

$$Al_2Si_2O_5(OH)_4 + 5H_2O = 2Al^{3+} + 2H_4SiO_4\ (aq) + 6OH^- \qquad (2.5)$$

(Geidel and Caruccio, 1977). Another example of buffering occurs when limestone components in the soil or bedrock raise the pH of the acid mine drainage:

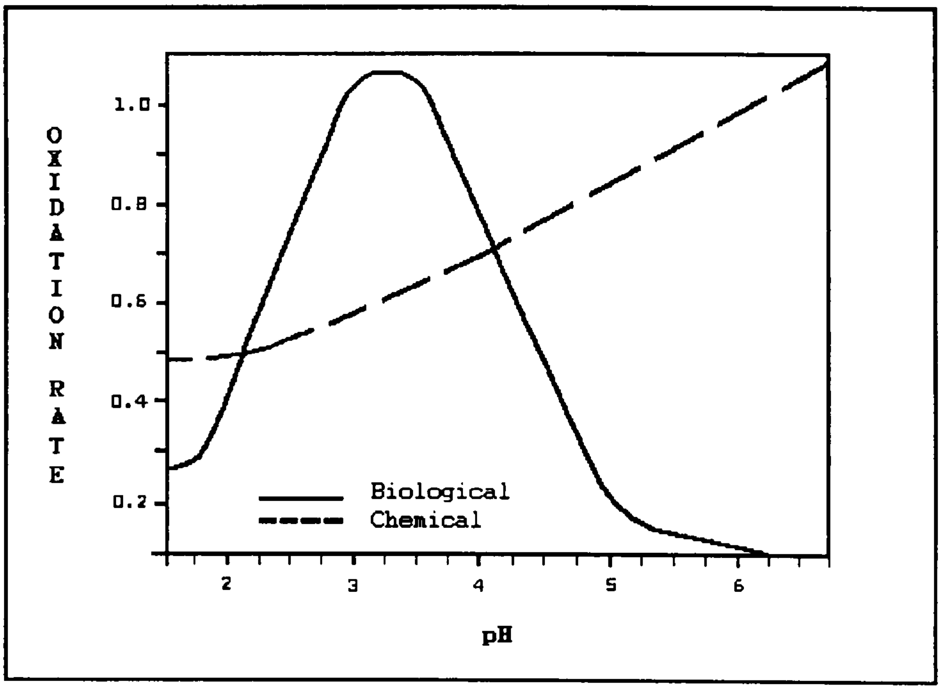

Figure 2.1 Effects of pH on Biological and Chemical Pyrite Oxidation Rates
Source: Knapp, 1987

$$2H^+ + SO_4^{2-} + CaCO_3 = Ca^{2+} + SO_4^{2-} + H_2O + CO_2. \qquad (2.6)$$

Where pyrite reacts directly with limestone (in the presence of oxygen and water), acidity also decreases:

$$FeS_2 + 2CaCO_3 + 15/4O_2 + 3/2H_2O = Fe(OH)_3 + 2SO_4^{-2} + 2Ca^{2+} + 2CO_2 \qquad (2.7)$$

Other chemical reactions, such as ion exchange on clay surfaces, gypsum precipitation, and acid-induced dissolution of other minerals, also decrease the development of stream acidity from acid mine drainage (Ferguson and Erickson, 1987).

Stream chemistry reflects the input from surface runoff, ground water discharge and interflow[1]. Each of these contributes a unique chemistry to the stream that is related to the

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[1] Infiltrated water which moves downslope as lateral, unsaturated flow in the soil zone.

composition of the material through which it flows (Fetter, 1988). Surface runoff generally contains lower levels of total dissolved solids than ground water. It thus dilutes the stream chemistry during high runoff periods (Hem, 1989). Interflow is representative of the soil mineralogy; the ability of interflow to dissolve elements from the soil and bedrock is inversely dependent on slope steepness (Phillips and Stewart, 1990). The slow movement of ground water allows the maximum quantity of elements to be dissolved and transported through the watershed.

The type of soil surrounding a mined surface is a major control of the quantity and chemistry of water draining from the disturbed area (Curtis, 1972). Certain soil factors affect drainage characteristics more so than others (Hesse, 1971). These are:

1. Permeability - increased soil permeability decreases stream contamination, yet may escalate water table contamination.
2. Depth - deep soils decrease surface runoff and absorb some of the acid mine drainage constituents before they reach the stream or water table.
3. Clay content - clay may decrease acid mine drainage over a relatively short time period through pH neutralization by absorbing hydrogen ions and releasing calcium, magnesium, aluminum, potassium and iron into the water.
4. Natural soil acidity - low soil pH amplifies the acid mine drainage processes.

Stream chemistry also can vary as a function of the sediment supply from upstream activities. Mines contribute sediment both while they are in production and after abandonment (Baker, 1975; Minear and Tschantz, 1976; Tolbert, 1978). Sediment loading from a mined region will vary according to soil type, length and degree of slope, climate, amount of rainfall, and disturbance size. Mine-related sediment originates in processing plant waste disposal areas, spoil piles, roads and tailings ponds (Baker, 1975). Studying east Tennessee watersheds, Tschantz (1977) found that steeply sloped watersheds that had been disturbed by contour strip mining had total sediment yields approximately one thousand times greater than similar, nonmined watersheds.

Suspended sediments in streams perform an important role in transporting adsorbed cations, especially when the sediments contain clay minerals. Clay has a high adsorption capacity due to its high surface area and ion activity level (Fetter, 1988). Such constituents as aluminum, iron and other trace elements can be effectively transported by clay adsorption in the BISO region because of the existence of shale formations (which through dissolution release clay sediments (Hem, 1989)) and the presence of a natural clay layer (Pomerene, 1964). Deposits of sediment located downstream from mined areas are often loaded with inorganics and heavy metals (Mills, 1988). Elevated stream concentrations of trace elements introduced by mining disturbances can be toxic to aquatic life (Tolbert, 1978, O'Bara *et al.*, 1982).

For resource managers, one problem in managing acid mine drainage is a "contaminant lag." After the initial excavation, the impacts of acid mine drainage may be delayed from a few weeks to years (Lund and Dillon, 1987). The lag time may be related to the distance of the stream from the mining source and the amount of precipitation; it is also influenced chemically by the availability of carbonate minerals to buffer the mine drainage. The lag time for ground water contamination from acid mine drainage is greater than that for surface water. Ground water moves slowly and, consequently, usually remains contaminated many years after surface waters have been flushed of acid mine drainage (Fetter, 1988; Lund and Dillon, 1987).

Another management problem is determining the duration of the production of acid mine drainage in streams. It depends upon the amount of sulfur and iron in the bedrock, the presence of sediment sinks along the stream bed, the amount of precipitation, and the degree of ground water contamination (Curtis, 1972). Generally, in the Eastern United States, mines that were closed approximately fifteen to twenty years ago are still producing high levels of contamination. Acid mine drainage has been found to persist at some sites for more than fifty years following closure (Erickson, 1987; Curtis, 1972).

Acid Mine Drainage History in the Big South Fork Region

The importance of coal mine drainage as a water pollution source in the eastern coal region was cited as early as 1933 by Carpenter and Herndon. They studied the quantity of acid mine drainage produced with respect to the coal vein characteristics and the area's ability to buffer the acidic drainage. Shoup (1940) first sampled the tributary streams of the Big South Fork River. He determined conductivity, turbidity, pH, dissolved oxygen, and alkalinity and observed the aquatic activity in the streams. O'Bara *et al.* (1982) classified benthic macroinvertebrates and fish in all BISO watershed streams according to acid mine drainage contamination and other parameters. O'Bara is currently updating his study and linking it with a geographic information system (O'Bara, personal communication, 1991). Rikard and Kunkle (1986, 1990) did an extensive chemical survey of all streams within BISO. Bakaletz is currently studying the effects of acid mine drainage on freshwater mussels (Bakaletz, personal communication, 1991).

Curtis (1971, 1972) investigated the effects of sedimentation on streams and the duration of contamination in eastern Kentucky. Minear and Tschantz (1976) and Tschantz (1977) did extensive studies in the New River Basin on sedimentation and downstream effects from mining areas. Rose (1975), Tolbert (1978), and Dickens (1982) worked with Minear and Tschantz in the New River Basin, adjacent to the southern portion of BISO. Rose studied water chemistry, Tolbert studied the ability of benthic insect communities to withstand acid mine drainage contamination, and Dickens studied the effects of various saturation levels on spoil pile sedimentation and chemistry. Parker and Carey (1980) also worked in the New River Basin, comparing the uncontaminated Clear Fork River with the New River.

Herricks and Cairns (1974) in West Virginia, Parker and Carey (1980) in the New River Basin, and Rikard and Kunkle (1986) in BISO considered sulfate to be the best single chemical indicator of coal mining activity in their study areas. Sulfate was chosen over pH and turbidity because the latter two are more affected by geology. Thus, pH and turbidity measurements can be the same in streams with very different chemical compositions. Measured by themselves, pH and turbidity may not indicate or may under represent the occurrence of acid mine drainage in an affected stream. This is shown by some BISO streams that have elevated levels of acid mine drainage, yet pH readings above neutral (Rikard and Kunkle, 1990).

Caruccio and Geidel (1980), showed that the total sulfate content of water by itself is not a good predictor of acid mine drainage production because of the influence of calcium in the surrounding bedrock. They found that acid generated by sulfur oxidation in water is buffered and at times suppressed by the calcareous material present in rocks. If sulfur oxidation occurs in water that passes through carbonate rock, the dissolution of calcium and magnesium can raise the pH of water and impart a high level of acid neutralizing capacity. When water is super-saturated with respect to calcium and magnesium before entering the bedrock containing sulfides, the release of sulfate can be reduced. Infanger and Hood (1980) related the differences between various stacking positions of bedding to the potential for acidification. When limestone or an alkaline shale was bedded above the coal bed, the super-saturated carbonate solution would decrease the ability of pyrite to react and thereby reduce the acidifying process. This did not occur when coal was bedded above limestone.

Sulfate concentration levels in unmined streams at BISO were found to be less than 208 μeq/l[2], according to the Rikard and Kunkle (1986) study. In the New River Basin, higher sulfate values resulted where shale formations were more prominent than sandstone, yet this area still had values of sulfate less than 416 μeq/l for undisturbed streams (Parker and Carey, 1980). The lower detection limit for both studies was 208 μeq/l, even though typical sulfate concentrations in unmined watershed streams in BISO ranged from 21 to 42 μeq/l (O'Bara *et al.*, 1982). Sulfate concentrations from streams in coal mined watersheds in both studies ranged from the 100s to the 1000s of μeq/l.

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[2] microequivalents per liter

Chapter 3

BIG SOUTH FORK NATIONAL RIVER AND RECREATION AREA

The Big South Fork National River and Recreation Area (BISO) is a unit of the National Park Service and is located along the border of eastern Kentucky and Tennessee (Figures 3.1 and 3.2). The largest towns near the park are Oneida to the east and Jamestown to the west in Tennessee, and Whitley City to the east in Kentucky. The National Recreation Area and its watersheds lie within Scott, Pickett, Fentress, and Campbell counties in Tennessee, and McCreary, Whitley and Wayne counties in Kentucky. Contiguous to BISO are two other public properties: Pickett State Park in Tennessee, and Daniel Boone National Forest in Kentucky.

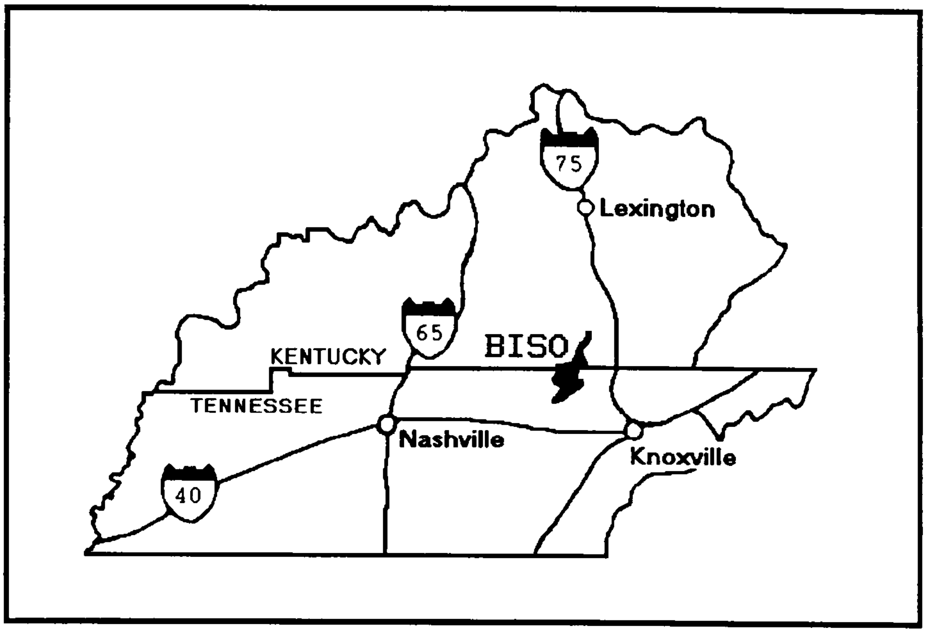

Figure 3.1 Big South Fork National River and Recreation Area Location Map

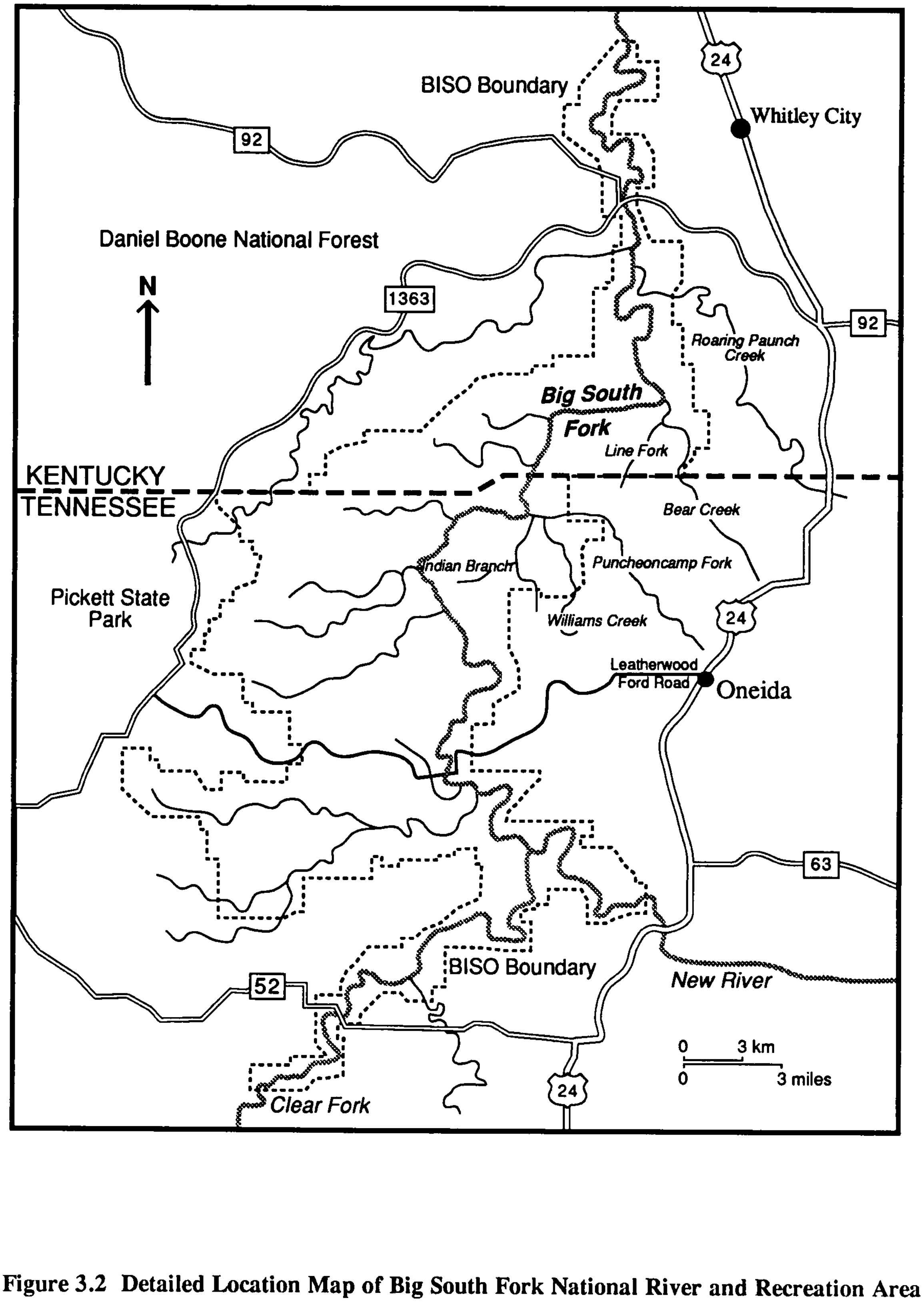

Figure 3.2 Detailed Location Map of Big South Fork National River and Recreation Area

BISO was established by Congress in 1974 under Public Law 93-251, which authorized the purchase of 123,000 acres of land in the states of Tennessee and Kentucky. The U.S. Army Corps of Engineers was responsible for developing the area for recreational use and the National Park Service manages the area (Barclay and Parsons, 1983).

Topography

BISO is located on the Cumberland Plateau within the Appalachian Physiographic Province and is dissected by multiple streams. Elevations range from 400 to 650 meters with slope gradients generally 20 to 60 percent. The Big South Fork of the Cumberland River originates at the confluence of Clear Fork River and New River at the southern park border. The Big South Fork is the dominant surface drainage for the area and has cut a gorge 100 to 150 meters deep (Gaydos *et al.*, 1982). There are seventeen other streams within BISO, but the majority of their watersheds lie outside the park boundaries (Rikard and Kunkle, 1986).

Climate

The annual air temperature in this region, as measured in Allardt, Tennessee, averages about 13° C, with yearly extremes ranging from -21° C to above 37° C. The daytime temperature remains above 32° C for about six weeks per year. The frost-free period between April and October provides an average growing season of 160 days (Gaydos *et al.*, 1982).

Mean annual precipitation is 127 cm, ranging between 89 cm and 178 cm, of which 38 cm usually fall as snow. Most precipitation occurs in late October through early December, February and May according to data from the Oneida Weather Station and BISO (Figure 3.3). The area develops thunderstorms during roughly 45 days per year. These often produce heavy rainfall in combination with damaging winds and extreme temperature changes (Gaydos *et al.*, 1982).

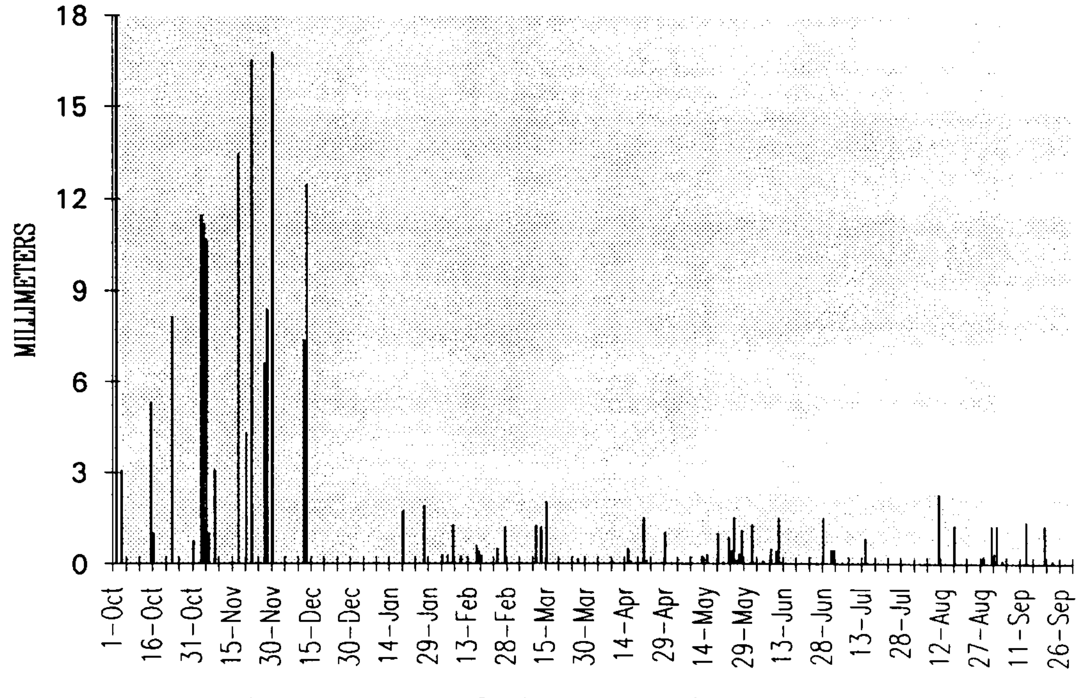

Figure 3.3 Daily Precipitation Data At Oneida Weather Station From October1985 through September 1986

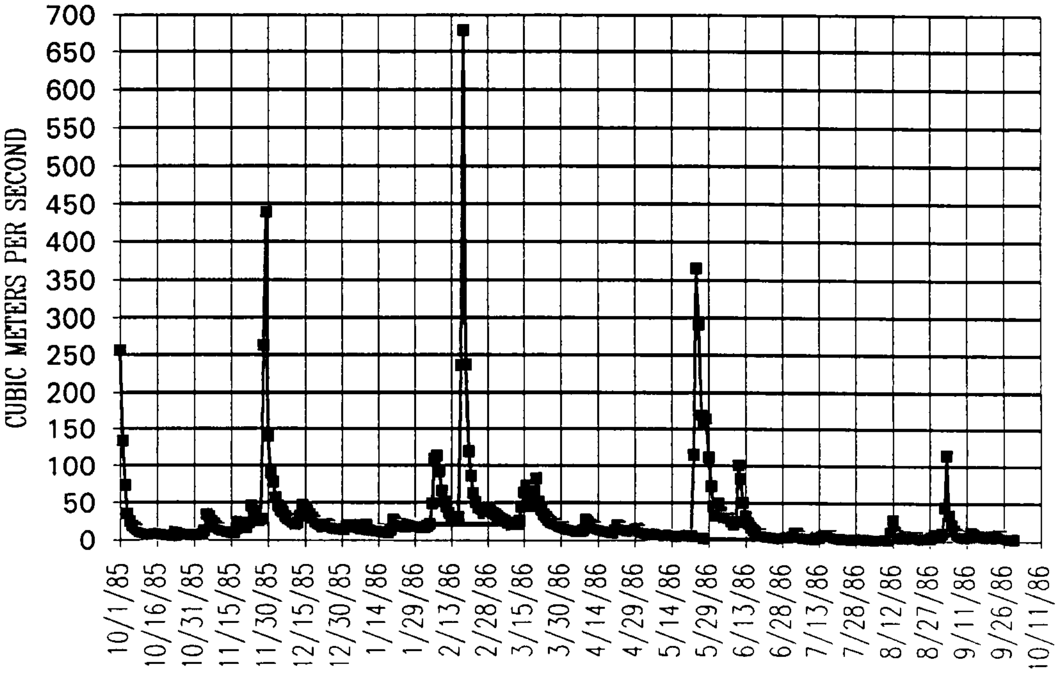

Figure 3.4 Daily Discharge Of The Big South Fork River At Leatherwood Ford Source: TN-USGS, Lowery (1987)

Stream Hydrology

Gaging Stations

Two United States Geological Survey (USGS) gaging stations are located on the Big South Fork of the Cumberland River, at Leatherwood Ford and Stearns. Figure 3.4 shows average daily discharge for the Big South Fork River at Leatherwood Ford, Tennessee, for the water year 1985-86 as determined by the USGS-TN (Lowery *et al.*, 1987). The average annual runoff for the Big South Fork of the Cumberland River at Leatherwood Ford is 51 cubic meters per second (m^3/sec) based on data from 1979 to 1986 from TN-USGS. The maximum discharge during this period was 300 (m^3/sec) and the minimum discharge was 5.9 (m^3/sec) (Lowery *et al.*, 1987).

Stream Classifications

Rikard and Kunkle (1986) classified the streams of BISO into four categories: clean, slightly polluted, moderately polluted, and severely polluted (Table 3.1). The authors used the parameters of temperature, pH, conductance, dissolved oxygen, alkalinity, acidity, hardness, chloride, iron, manganese, sulfate, turbidity, and bacteria to classify BISO streams into the categories (Table 3.2). The majority of the seventeen tributary streams were classified as moderately polluted or cleaner, with Roaring Paunch Creek, Bear Creek and the lower portion of Rock Creek (downstream from White Oak Junction) the only streams rated as severely polluted. Figure 3.5 shows where the streams are located.

Soils

Soils in BISO are related to elevation because of their relationship to the various relatively horizontal geologic formations. The soils in this region vary from sandy to a clay loam, depending on the underlying geology. Soil depth ranges from 0 to 250 cm (Gaydos *et al.*, 1982). The following detailed soils descriptions were derived from Bryne *et al.* (1970).

Table 3.1 Classification of Big South Fork National River and Recreation Area Streams. Source: Rikard and Kunkle (1986)

CLEAN	SLIGHTLY POLLUTED	MODERATELY POLLUTED	SEVERELY POLLUTED
Bandy Creek	Clear Fork	New River	Roaring Paunch Ck
Grassy Fork	N. White Oak Creek	Pine Creek	Bear Creek
Station Camp Ck	Williams Creek	Puncheoncamp Fork	Lower Rock Creek
Upper Rock Creek	Laurel Fk, N.Wh Oak	White Oak Creek	
No Business Ck			
Laurel Fk, Stn. Camp			

Most stream level soils are either Tate stony sandy loam or Tate-Trappist stony complex with a 30 to 50 percent slope. As hillsides rise from the stream, the soils grade to Dekalb and Tate sandy loams, with the highest elevation soils Muse-Trappist silt loam with clay.

The Tate series includes deep soils that are well drained. It is the most extensive soil in the area and is formed on colluvium which moved down slope from sandstone and shale bedrock. Tate soils have a high moisture capacity, low pH and moderate fertility.

The Dekalb series soils occupy the steeply sloping areas. Formed in the residuum that weathered from acidic sandstone, these soils tend to be moderately deep and excessively drained.

The Muse series are well drained, deep soils similar to the Tate series. Muse soils are loams derived from the residuum of shale and sandstone. They are strongly acidic, moderately fertile, and they occupy shallower slopes, thus allowing for more cultivation than the Tate series (Bryne *et al.*, 1970).

Table 3.2 Concentration Levels of Parameters used for Determining Water Quality Categories
Source: Rikard and Kunkle (1986)

Criterion	Clean/ Sandstone-influenced	Clean/ Limestone-influenced	Slightly Polluted	Moderately Polluted	Severely Polluted
Conductivity (μS/cm)	<30	<60	>30	>100	>150
pH	5.5 - 7.0	6.0 - 7.5	6.0 - 7.5	6.0 - 7.5	extreme <5.0
Chlorides (mg/l)	<5.0	<5.0	<5.0	>5.0	>5.0
Iron (mg/l)	<0.2	<0.2	<0.2	most<0.2	most>0.2
Manganese (mg/l)	<0.5	<0.5	<0.5	most<0.5	most>0.5
Sulfates (mg/l)	<10	<10	<10	>20	most>50
Alkalinity (mg/l)	<5.0	most>10	>10	most>20	most<20; extreme <2.5
Hardness (mg/l)	<20	>20	>20	most>60	few>100
Turbidity (NTU units)	<10	<10	<10	few>10	few>10

"Most" means >75% of the samples have the indicated reading;
"Few" means <25% of the samples have the indicated reading.

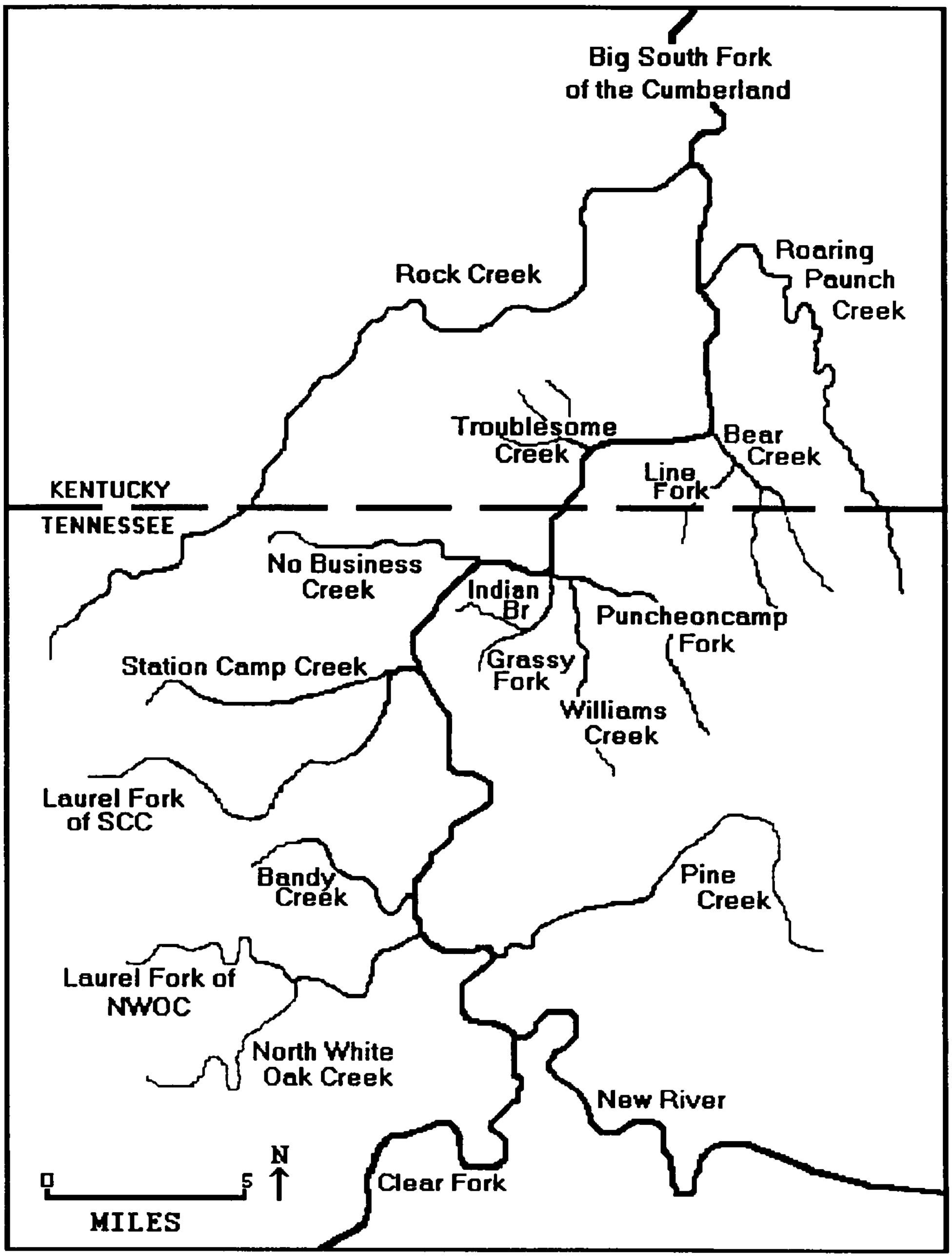

Figure 3.5 BISO Streams Analyzed by Rikard and Kunkle
Source: O'Bara *et al.*, 1982

Geology

The Big South Fork of the Cumberland River cuts through rocks of Pennsylvanian age in eastern Tennessee and Kentucky. These rocks are composed of conglomerate, sandstone, siltstone, and shale, with small amounts of interbedded coal. The thickness of this sequence is approximately 875 meters and the rocks dip shallowly to the southeast (Gaydos *et al.*, 1982).

The upper layers of this sequence (Breathitt Formation) are predominantly thicker shales and siltstones with some thinly interbedded sandstone layers (Figure 3.6). In the lower Pennsylvanian Lee Formation, the dominant layers are composed of sandstone with some interbedded shale, siltstone, conglomerate and coal (Figure 3.6). The Corbin member of this formation contains an argillaceous (clayey) component in both the shale and the sandstone layers. Throughout this sequence, the sandstone weathers to a coarse- to medium-grained material. Most of the stream beds in the Big South Fork watershed are on bedrock that is either shale or conglomerate (Pomerene, 1964).

Underneath the Pennsylvanian series lie the Mississippian-aged Pennington and Bangor Formations, which are composed of slate, limestone, dolomite, and conglomerate to fine-grained sandstones. The combined thickness ranges from 32 to 165 meters (Figure 3.6). These rocks are exposed in some portions of Kentucky, north of BISO, in deeply cut gorges (Pomerene, 1964; Gaydos *et al.*, 1982) and thus have had some influence on ground water chemistry in the BISO area.

The important coal beds in the New River watershed on the southern boarder of BISO, are the Big Mary, Jellico, Pewee, and Coal Creek (Dickens, 1982). In McCreary County, Kentucky, the major coal beds are the River Gem, Barren Fork, and Stearns (Pomerene, 1964).

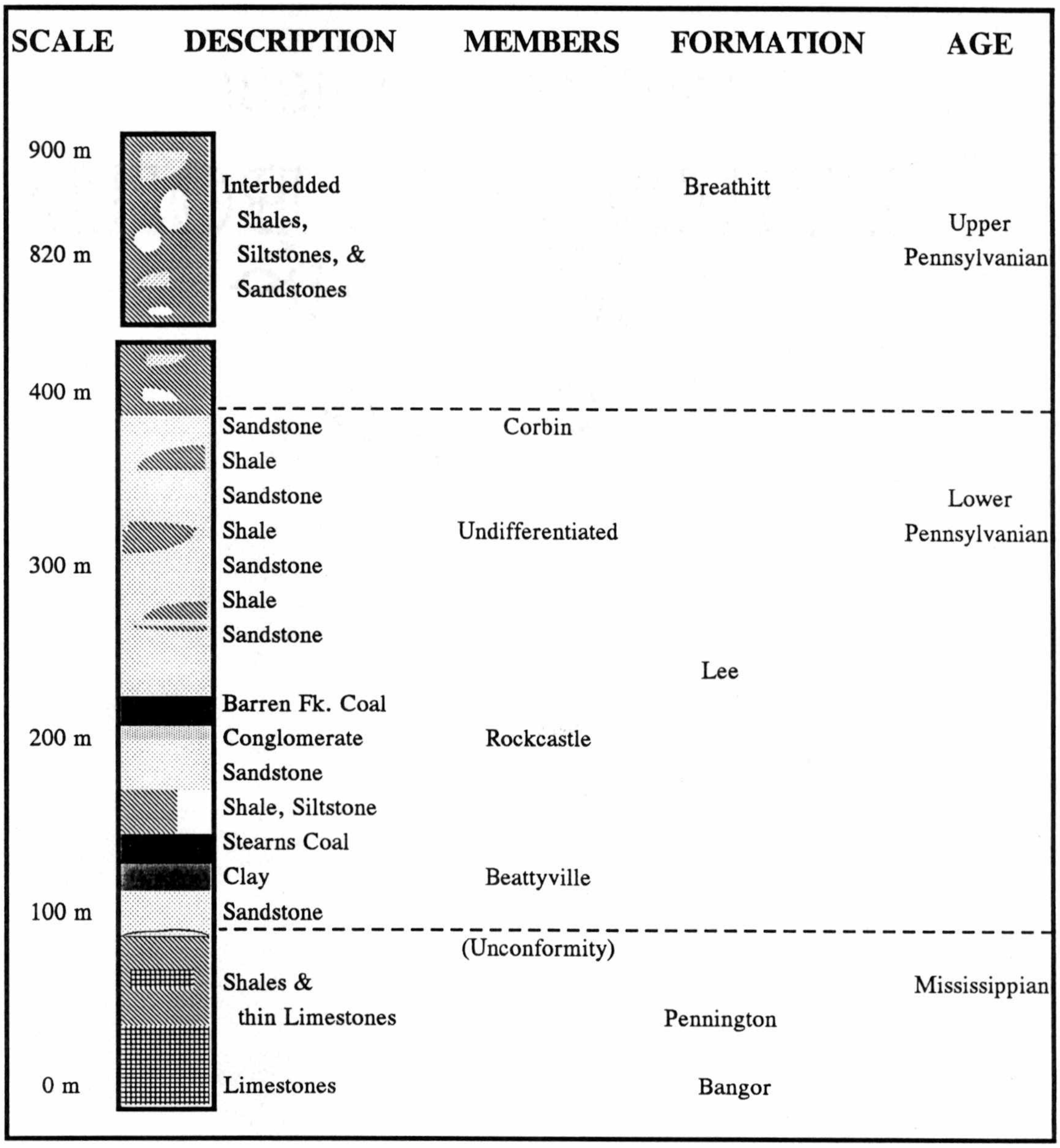

Figure 3.6 Geologic Column of Tennessee and Kentucky Along the Big South Fork River
Source: Pomerene, 1964

Land Use History

The earliest mining activity recorded in the BISO area was in the middle of the 1820s. Coal was extracted at the surface in the vicinity of Roaring Paunch Creek and was floated downstream on river barges (Barclay and Parsons, 1983). The first underground mining began about 1898 along Roaring Paunch Creek. Underground mines were operated in this area by the Stearns Coal Company until 1974. Maximum yearly output was reached in the early 1960s, and decreased rapidly afterwards as surface mining became more economically feasible (Barclay and Parsons, 1983).

Surface mining began in the BISO region during the mid 1940s (Dickens, 1982). Currently, surface mining is only active in small areas south of the park boundary (Baker, personal communications, 1990). Disturbance from surface mining has taken place in the headwaters of many BISO streams, although no surface mining has occurred within the park boundaries. Most of the surface mining took place in the late 1960s to the mid 1970s on the eastern side of BISO, before the Federal Surface Mining Control and Reclamation Act of 1977 was enacted. During the early 1980s the price of coal rose to compensate for the new regulatory standards, making it economically feasible to remove greater amounts of overburden, so surface mining operations increased (Dickens, 1982). Since then, the extent of mining has decreased in this area as coal veins have been stripped beyond the point of diminishing returns (Baker, personal communications, 1990).

Rugged terrain and generally poor soils limited the amount of agriculture in the study area. The few family farms were located along the stream valleys and floodplains. In 1976, four percent of the southeast portion of the Cumberland Mountains region was agricultural (Gaydos *et al.*, 1982). Outside the park boundary, current agricultural products are mainly poultry, livestock and grain.

Widespread timber extraction during the first three decades of the twentieth century occurred throughout the entire region. A railroad was built to support logging and concurrent mining activities (Dickens, 1982). Spotty timbering took place from the 1940s until the area was designated as a National Recreational Area in 1974. Most of the area was cleared at least once, with some locations having multiple cuttings of timber pines from 1940 through 1974, on a twenty-year harvesting rotation (Shrunk, personal communications, 1990).

Within the park boundaries there are over one hundred and fifty oil and natural gas well sites (O'Bara *et al.*, 1982). Not all of the oil and natural gas mineral rights belong to BISO, and actively producing sites exist (Cornelius, personal communications, 1991). There are also many abandoned sites, some of which have been improperly sealed. The main exploitation of these resources occurred in the late 1970s and early 1980s (Dickens, 1982). Brine solutions, which are by-products of oil and gas drilling, have elevated chloride concentrations in certain BISO streams (Richard and Kunkle, 1986).

Fisheries

Over forty fish species and a variety of benthic macroinvertebrates and unique mussels live in the waters of BISO. In areas severely damaged by pollution, aquatic life is restricted to the few benthic macroinvertebrate species that tolerate the low pH and the high aluminum and iron concentrations (O'Bara *et al.*, 1982).

Recreational Uses

BISO recreational activities include camping, boating, rafting, canoeing, swimming, hiking, bicycling, horseback riding, picnicking, sightseeing, four-wheel driving, hunting and fishing.

Chapter 4

METHODS AND STUDY SITES

Database Compilation

All available water sample data from studies within the Big South Fork National River and Recreation Area (BISO) region were compiled into one database.[3] The data are from eleven studies shown in Table 4.1. The parameters analyzed in each study are listed in Appendix 1 and the methods and detection limits are in Appendix 2.

Site Selection of Present Study

The five streams chosen for the present research were selected on the basis of six criteria: 1) their location in relation to Bear Creek, a tributary of the Big South Fork River, where related studies were concurrently being conducted; 2) the amount, type and time since abandonment of mining within their watersheds; 3) the presence of perennial base flow discharge; 4) the locations of previous BISO sampling sites; 5) the potential for multiple sampling locations along streams; and 6) the ease of access to the streams. From April through September 1990, reconnaissance studies were conducted to select sampling site locations. The parameters to be analyzed and compared were: pH, specific conductivity, alkalinity, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, F^-, Cl^-, Br^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, Fe, Al, B, Ba, Co, Cr, Cu, Mn, Mo, Ni, P, Pb, Se, Si, Sr, Ti and Zn (Appendix 3).

Multiple sites were sampled on three of the five streams to evaluate chemical trends downstream from coal mined areas with varying abandonment time periods. Roaring Paunch Creek (the most extensively and recently mined) had four sampling sites. Puncheoncamp Fork

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[3] The database and original data sets are held by Cooperative Park Studies Unit at the University of Tennessee, Forestry Office, 274 Ellington Plant and Science Bldg., Knoxville, 37901-1071. The data are in ASCII format for IBM compatible computers.

Table 4.1 Compiled Data for Big South Fork National Recreation Area Database

SOURCE	SAMPLING DATES	PURPOSE
Leary	October 5-7, 1990	Water Chemistry for Thesis
Bakeletz	August 6 & 20, 1990	Water Quality for Bear Creek Project
Eagle	May 1990	Water Quality for Bear Creek Project
BISO	Janunary 1982 - December 1990	General Monthly Water Quality Sampling
Mills	April & June 1988, January & May 1989	Intensive Water Quality Survey
KY USGS	September 1981 - October 1989	General Water Quality Study
Barrass	October 1988	Water Quality for Bear Creek Project
Richardson	September 1987 & August 1988	Water Quality Study for Thesis
TN USGS	February - September 1984	General Water Quality Study
O'Bara	June & October 1981	Water Quality for U.S. Army Corps
Dyer	February - November 1978	Intensive Water Quality Study for U.S. EPA

SOURCE	STREAMS SAMPLED
Leary	Indian Branch of Grassy Fork, Line Fork of Bear Creek,
	Puncheoncamp Fork of Williams Creek, Roaring Paunch Creek and Williams Creek
Bakeletz	Bear Creek
Eagle	Bear Creek
BISO	All major Big South Fork tributary streams in Park
Mills	Rock Creek and tributaries: White Oak Creek and Jones Branch
KY USGS	Big South Fork River at Stearns
Barrass	Bear Creek
Richardson	Clear Fork, New River and Big South Fork River
TN USGS	Big South Fork at Leatherwood Ford
O'Bara	All major Big South Fork tributary streams in Park
Dyer	Pemberton Branch of Brimstone Creek, Scott County

and Williams Creeks (similar in extent of mining but different in the time of abandonment) had three sites. Indian Branch of Grassy Fork and Line Fork of Bear Creek (unmined watersheds) each had one site (Figure 4.1).

Listed below are descriptions of the sampling sites, with multiple sampling sites on one stream numbered by starting at the mouth and increasing upstream.

Sampling Sites and Their Characteristics

SITE: (IB) INDIAN BRANCH OF GRASSY FORK OF WILLIAMS CREEK
Location: Latitude 36° 33' 16" Longitude 84° 28' 58"
7.5 minute Topographic map: Barthell SW, TN/KY
Watershed size: 77 hectares
Elevation at sampling site: 413 meters
Mined areas: none
Other land uses: forest, abandoned dry oil wells

SITE: (LF) LINE FORK OF BEAR CREEK
Location: Latitude 36° 35' 50" Longitude 84° 32' 30"
7.5 minute Topographic map: Oneida N, TN/KY
Watershed size: 1096 hectares
Elevation at stream site: 416.6 meters
Mined areas: none
Other land uses: cattle farming, forest

SITE: (PU1) PUNCHEONCAMP FORK OF WILLIAMS CREEK
Location: Latitude 36° 34' 36" Longitude 84° 35' 53"
7.5 minute Topographic map: Oneida N, TN/KY
Watershed size: 2903 hectares
Elevation at stream site: 269 meters
Mined areas: none
Other land uses: agricultural, residential, abandoned oil and gas wells, and forest

SITE: (PU3) PUNCHEONCAMP FORK OF WILLIAMS CREEK
Location: Latitude 36° 33' 46" Longitude 84° 33' 16"
7.5 minute Topographic map: Oneida N, TN/KY
Watershed size: 1658 hectares
Elevation at stream site: 406.8 meters
Mined areas: abandoned strip mines before 1978
Other land uses: agricultural, residential, forest

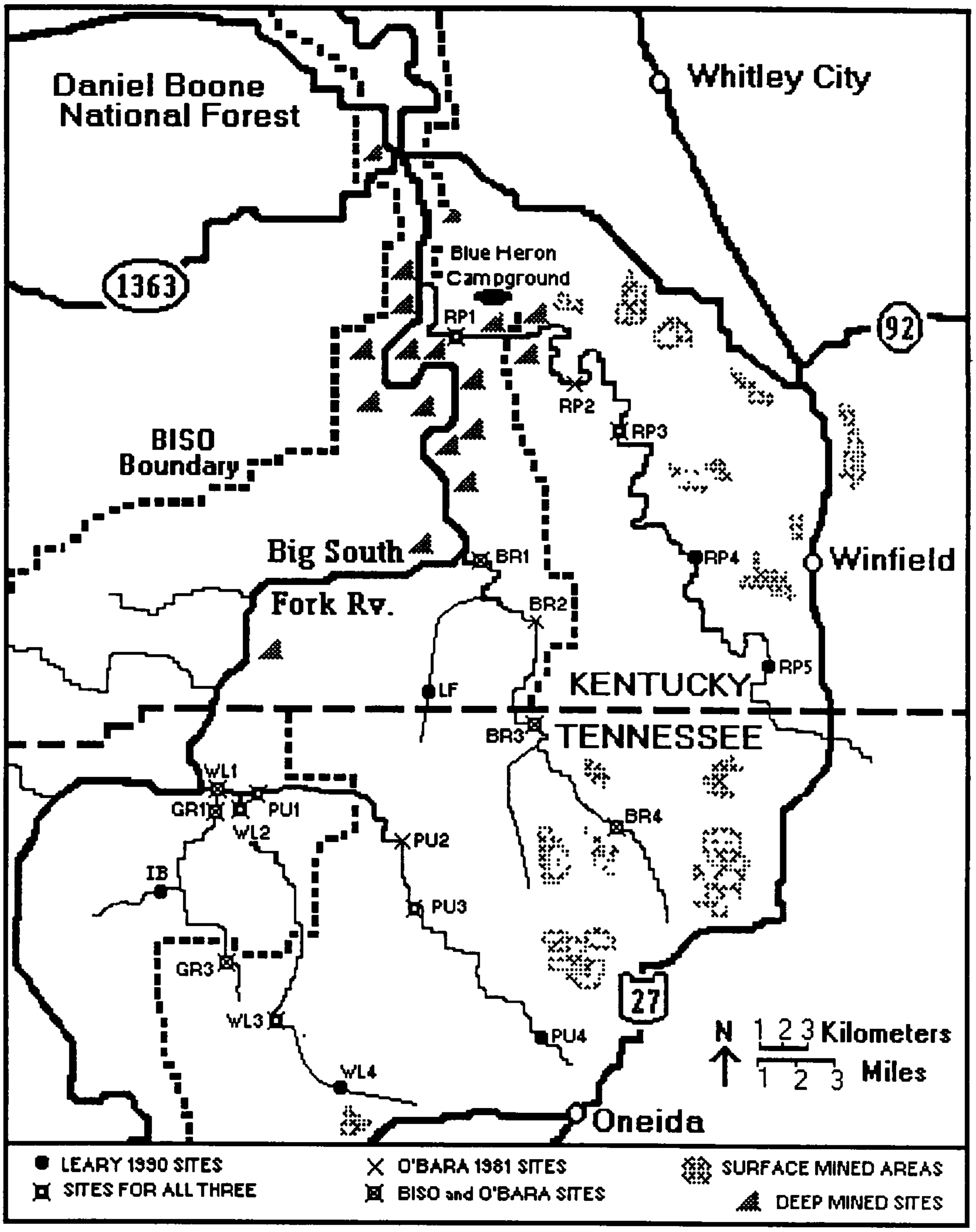


Figure 4.1 Sampling Site Locations for the Present Study and Related Sites from the Compiled Database

SITE: (PU4) PUNCHEONCAMP FORK OF WILLIAMS CREEK
Location: Latitude 36° 32' 30" Longitude 84° 33' 14"
7.5 minute Topographic map: Oneida N, TN/KY
Watershed size: 529 hectares
Elevation at stream site: 419.9 meters
Mined areas: overlapping mine site from PU3
Other land uses: gas and oil wells - active and abandoned, agricultural, forest

SITE: (RP1) ROARING PAUNCH CREEK
Location: Latitude 36° 40' 47" Longitude 84° 32' 24"
7.5 minute Topographic map: Barthell, KY
Watershed size: 12,567 hectares
Elevation at stream site: 270.6 meters
Mined areas: deep mines abandoned in 1975
Other land uses: forest

SITE: (RP3) ROARING PAUNCH CREEK
Location: Latitude 36° 40' 05" Longitude 84° 29' 47"
7.5 minute Topographic map: Whitley City, KY
Watershed size: 10,992 hectares
Elevation at stream site: 334.6 meters
Mined areas: strip mining site abandoned before 1982
Other land uses: forest, residential

SITE: (RP4) ROARING PAUNCH CREEK
Location: Latitude 36° 37' 36" Longitude 84° 28' 58"
7.5 minute Topographic map: Whitley City, KY
Watershed size: 8257 hectares
Elevation at stream site: 364.2 meters
Mined areas: multiple strip mines abandoned in 1982
Other land uses: forest, residential

SITE: (RP5) ROARING PAUNCH CREEK
Location: Latitude 36° 36'51" Longitude 84° 29' 26"
7.5 minute Topographic map: Winfield, TN/KY
Watershed size: 6477 hectares
Elevation at stream site: 367.4 meters
Mined areas: strip mining site abandoned before 1982
Other land uses: abandoned dry oil wells, forest

SITE: (WL2) WILLIAMS CREEK
Location: Latitude 36° 34' 30" Longitude 84° 35' 58"
7.5 minute Topographic map: Oneida N, TN/KY
Watershed size: 2735 hectares
Elevation at stream site: 269 meters
Mined areas: none
Other land uses: abandoned gas and oil wells, forest

SITE: (WL3) WILLIAMS CREEK
Location: Latitude 36° 31' 54" Longitude 84° 36' 10"
7.5 minute Topographic map: Oneida N, TN/KY
Watershed size: 1432 hectares
Elevation at stream site: 419.9 meters
Mined areas: strip mining abandoned before 1959
Other land uses: abandoned gas and oil wells, agricultural, forest

SITE: (WL4) WILLIAMS CREEK
Location: Latitude 36° 31' 14" Longitude 84° 35' 18"
7.5 minute Topographic map: Oneida N, TN/KY
Watershed size: 897 hectares
Elevation at stream site: 426.5 meters
Mined areas: overlapping mine site WL3
Other land uses: abandoned gas and oil wells, agricultural, forest.

Water Sampling

Stream water sampling took place between October 5-7, 1990. The daytime temperatures in Oneida averaged 26°C. During this period it did not rain, although BISO reported that three centimeters of rain had fallen during the previous two days, with precipitation ending approximately by noon on October 4, 1990 (Cornelius, personal communication, 1990). The storm contained scattered cells throughout the region that produced periods of initially intense downpour, diminishing to a steady sprinkle. The entire study area most likely received precipitation, yet Puncheoncamp Fork site PU3, was the only site with evidence of elevated stream flow and increased suspended sediment at the time of sampling. Although no specific soil moisture tests were done, the moisture content seemed to be below saturation because the trails and areas along streams were not muddy and clay particles did not stick to our waders.

Because discharge at Puncheoncamp Fork site PU3 had higher than base flow conditions on October 5, this site was resampled eleven days later. No measurable rain had occurred during the interim. The flow on October 16 appeared normal, based on previous flow observations at this site and low levels of suspended sediment. The two sets of data are listed in Appendix 3 as PU3 (October 5, 1990) and PU3.2 (October 16, 1990).

For stream water collection, a hand-held sample bottle was filled in the middle of the stream where the current actively moved and a depth integrated sample was collected as recommended by Hem (1970). The bottles were capped under water in all locations except in Line Fork where this was impossible. At site LF, the bottles were filled at a trickle waterfall that collected all flow, and then sealed with a full cap of water.

At each site four polyethylene bottles were filled with a total of 1250 ml of stream water. Samples to be analyzed for trace elements and metals had 0.33 ml of ultrapure nitric acid added to acidify each sample to pH less than 2.0. Samples to be analyzed for major inorganic elements were filtered in the field at each location using 0.4 micron nucleopore filter paper and a Millipore filter system with a Nalgene hand operated vacuum. The papers were changed approximately every 200 ml to improve clarity and efficiency. Replicate samples were taken at sites PU1 and RP3.

Chemical Analyses

Of the 1250 ml of water collected at each site, a 500 ml sub-sample bottle was sent to the U.S. Geological Survey (USGS) Analytical Laboratory in Doraville, Georgia for cation/anion tests and a 250 ml sub-sample was sent to the USDA Forest Service Experiment Station's Analytical Laboratory (Fort Collins, Colorado) for metals and trace element tests. A 500 ml sample bottle for each site was kept at University of Tennessee as a back-up.

Analyses done by USGS included: pH, specific conductivity, and Gran alkalinity. Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, F^-, Cl^-, Br^-, NO_3^-, PO_4^{3-} and SO_4^{2-} were measured on a dual channel Dionex ion chromatography system. The results of the tests were referenced with US EPA standards and rerun through the instrument if the standard results were not within ten percent of true value.

The elements -- Al, Fe, As, B, Ba, Cd, Cr, Co, Cu, Mn, Mo, Ni, Pb, Se, Si, Sr, Ti

Spectrophotometer. The results were also referenced with US EPA standards and rerun through the instrument if results were not within ten percent of true value. Fe and Mn can be present in water at multiple oxidation states. In this work, concentrations for these elements are expressed as: Fe^{2+} and Mn^{2+}.

The pH in the field was measured each evening for that day's samples using 250 ml of stream water. CO_2 was added by bubbling, to equilibrate each sample to 300 ppm concentration of CO_2. The purpose of adding CO_2 to the sample is to eliminate possible variations in atmospheric levels of CO_2 from the fluctuations in seasonal levels (Hillman *et al.*, 1986). The following equation, which combines Henry's Law and the first dissociation constant for carbonic acid, was used to estimate bicarbonate concentrations from the pH of 300 ppm CO_2-equilibrated stream samples:

$$HCO_3^-(\mu eq/l) = ((.00030*10^{-1.41}*10^{-6.381})/10^{-pH})*10^6. \qquad (4.1)$$

Following the procedures of Hillman *et al.* (1986), pH readings were taken before any CO_2 was added and thereafter at one minute intervals until the pH leveled off.

Discharge Methods

Discharge measurements were taken at the same time that the water samples were collected using a sodium bromide tracer. Bromide was chosen as the tracer because of its conservatism with other stream elements and its low background concentrations within most natural streams (Levy and Chambers, 1987). Bromide discharge measurements were taken at all sampling sites except RP1, LF and PU4. Sites LF and PU4 had insufficient base flow to add the tracer. At site RP1, discharge was too great to be accurately determined with the tracer method.

The theory behind using a tracer is that over a determined time period a constantly injected solution will reach an equilibrium value with the stream at a downstream location. The stream discharge, determined by a tracer, is obtained by measuring the tracer

The stream discharge, determined by a tracer, is obtained by measuring the tracer concentration of the solution being injected into the stream and the dilution of the tracer at a designated distance downstream. At this distance downstream, the tracer has reached its equilibrium concentration value. Discharge then can be determined by comparing the equilibrium dilution concentration with the original concentration. The total discharge at each site was calculated as follows:

$$Q_t = [(q_i * C_i)/C_o] - q_i. \tag{4.2}$$

Where Q_t is the total discharge (l/min), q_i is the injection rate of the tracer (l/min). C_i is the concentration of the tracer injected (mg/l), and C_o is the observed concentration of the tracer (mg/l) (Zellweger *et al.*, 1986).

The bromide salt was dissolved into a 40 liter container of stream water to create the injection solution. The solution was injected into the streams using a Geotech Series II peristaltic pump at varing rates (0.8 - 1.5 l/min) as suggested by Hoelscher (personal communication, 1990). The effectiveness of this procedure was confirmed at a USGS gaging station in Knoxville, Tennessee where both the gaging station and the bromide injection technique produced similar discharge estimates.

To measure the discharge at each site, a total of six 100 ml water samples were taken, one of the injection solution and five downstream at five minute intervals for twenty-five to thirty-five minutes depending on stream size (the larger the stream the longer the time). The length from the injection site to the bromide sampling site ranged from approximately 10 to 70 meters, depending on the discharge, the stream width to depth ratio, and the ability to avoid pooled areas (length increases as any one of these variables increases).

An ionic strength adjustor (ISA) of 2M sodium nitrate was added to each sample in the ratio of 1:10 (1 unit ISA: 10 units sample). The adjustor was used to eliminate any background interference within the samples from other ions present. Samples were analyzed on an Orion Research digital pH/mV/temp meter at the University of Tennessee. Plotted against time, the five bromide readings from each site rose, plateaued and then fell, to signify the end of the injection. The plateau values (which signify the maximum mixing concentration) were used to determine the discharge.

Discharges at sites RP1 and PU4 were estimated by timing a floating object over a specific distance and averaging the measured cross-sectional area along the stream distance. Both locations for the discharge measurements were chosen because of their fairly consistent rectangular shape and lack of pools. At site PU4, where the water averaged 5 cm deep and 38 cm wide over a distance of 3.5 m, two methods were used -- a red food coloring dye and a small stick. At site RP1, length was 32 m, width averaged 7.5 m, 10 cm, and depth averaged 35 cm. Two rate measurements with twigs as floats were taken in the main current and one along the edge and the average calculated. Discharge for LF was measured by timing the collection of 500 ml at a tiny waterfall where all flow was collected.

Chapter 5

RESULTS

Sulfate, Hardness and Iron Concentrations in BISO Water

Analysis of long-term water quality data on Big South Fork National River and Recreation Area (BISO) streams resulted in a general chemical description, relative to previous acid mine drainage impacts, of the following streams: Williams Creek, Grassy Fork of Williams Creek, Puncheoncamp Fork of Williams Creek, Roaring Paunch Creek, and Bear Creek. The data sets reviewed include monthly monitoring data collected and measured by the Big South Fork National River and Recreation Area resource managers over nine years (1981-1990), survey data from a scientific study in June and October 1981 by O'Bara *et al.*, and data collected for the present study during October of 1990. The three combined data sets -- BISO, O'Bara *et al.*, and the current field study -- all had multiple sampling sites (Figure 4.1). In this discussion, data from the overlapping locations were reviewed. Through this long-term review, an overview of sulfate, hardness and iron concentrations was developed to provide background information on seasonal maximum and minimum values and to determined the generalized stream concentration characteristics.

Sulfate

Sulfate measurements from all BISO data sets showed a broad range of concentrations from as low as 42 μeq/l (Grassy Fork) in apparently unimpacted streams to values as high as 2700 μeq/l (Roaring Paunch Creek) in streams clearly impacted from coal mine drainage (Table 5.1). As the amount of mining disturbance increased, there was an increase in sulfate concentration levels. The low and high detection limits imposed on sulfate analyses in the BISO monitoring set constrain this review. The lower detection limit to these data was imposed through the use of a commercial analytical technique (Hach barium sulfate turbidity), in which the lower detection limit for sulfate is high. The upper detection limit in the BISO

Table 5.1 Sulfate Maximum and Minimum Concentrations In Stream Water

Stream Site	Minimum	Date	Maximum	Date	Researcher
Grassy Fork	208*	-	291	3/23/83	BISO
	62	Oct-81	166	Jun-81	O'BARA
Williams Creek-1	208*	-	175	9/14/83	BISO
	62	Oct-81	187	Jun-81	O'BARA
Williams Creek-2	208*	-	229	2/22/83	BISO
	62	Oct-81	187	Jun-81	O'BARA
			71	10/7/90	LEARY
Williams Creek-3	208*	-	580	7/11/83	BISO
	83	Oct-81	187	Jun-81	O'BARA
			119	10/5/90	LEARY
Puncheoncamp Fork-1	208*	-	805	3/23/83	BISO
	21	Jun-81	104	Oct-81	O'BARA
			85	10/7/90	LEARY
Puncheoncamp Fork-3	208*	-	1665*	-	BISO
	125	Oct-81	458	Jun-81	O'BARA
	94	10/5/90	670	10/16/90	LEARY
Roaring Paunch-1	208*	-	1665*	-	BISO
	728	Jun-81	2184	Oct-81	O'BARA
			1004	10/6/90	LEARY
Roaring Paunch-3	208*	-	1665*	-	BISO
	666	Jun-81	3227	Oct-81	O'BARA
			931	10/6/90	LEARY
Bear Creek-1	208*	-	1665*	-	BISO
	1206	Jun-81	2707	Oct-81	O'BARA
Bear Creek-3	208*	-	1665*	-	BISO
	1248	Jun-81	4160	Oct-81	O'BARA

Units in microequivalents per liter
- denotes multiple samples with this value
* denotes detection limits of procedure used

sulfate data was the result of a failure to incorporate dilution procedures in the analysis of samples with concentrations above the standard analytical range. As a result of these limitations, the long-term minimum and maximum sulfate concentrations for BISO data are not known.

Hardness

BISO and O'Bara *et al.* reported the hardness of the water, rather than the individual elements which usually comprise the hardness measurement. Elements of hardness vary with the individual stream characteristics. Potential elements include calcium (Ca^{2+}), magnesium (Mg^{2+}), iron (Fe), aluminum (Al), manganese (Mn), strontium (Sr), and zinc (Zn) (Anon., 1985). In most surface waters Ca^{2+} and Mg^{2+} are the primary contributors to the hardness value. Hardness, therefore, is defined as a characteristic of water that represents the total concentration of the Ca^{2+} and Mg^{2+} ions, expressed as equivalents of $CaCO_3$. In order to compare the BISO and O'Bara hardness data with the current study values, the October 1990 $[Ca^{2+}]$ and $[Mg^{2+}]$ concentrations were summed to estimate hardness.

The greater the amount of mining in each study watershed, the greater the upper range in hardness values measured: Grassy Fork < Williams Creek < Puncheoncamp Fork < Roaring Paunch Creek < Bear Creek. The lowest measured hardness value was 38 μeq/l in Grassy Fork, and the highest was 4746 μeq/l in Roaring Paunch Creek (Table 5.2). Since this was the only reviewed parameter not constrained by detection limits, it was useful to show the full range of potential fluctuation in the other concentration values (Figures 5.1-5.5). Except on the unmined streams, there was a general increase in the hardness values and the range of fluctuation from the end of 1987 to 1989.

Iron

The general range of iron measurements from all three data sets was from 1 μeq/l

Table 5.2 Hardness Maximum and Minimum Concentrations in Stream Water

Stream Site	Minimum	Date	Maximum	Date	Researcher
Grassy Fork	38	2/16/84	119	3/25/86	BISO
	40	Jun-81	60	Oct-81	O'BARA
Williams Creek-1	89	6/13/83	175	9/14/83	BISO
	160	Jun-81	200	Oct-81	O'BARA
Williams Creek-2	80	5/16/84	185	11/11/83	BISO
	140	Jun-81	190	Oct-81	O'BARA
			259	10/7/90	LEARY
Williams Creek-3	49	3/7/83	580	7/11/83	BISO
	180	Jun-81	210	Oct-81	O'BARA
			393	10/5/90	LEARY
Puncheoncamp Fork-1	178	6/13/83	829	11/1/82	BISO
	200	Jun-81	250	Oct-81	O'BARA
			135	10/7/90	LEARY
Puncheoncamp Fork-3	179	11/1/82	1803	11/11/83	BISO
	489	Oct-81	500	Jun-81	O'BARA
			409	10/5/90	LEARY
Roaring Paunch-1	84	10/27/82	4746	9/19/86	BISO
	519	Jun-81	959	Oct-81	O'BARA
			758	10/6/90	LEARY
Roaring Paunch-3	239	3/6/84	1873	3/12/82	BISO
	54	Jun-81	759	Oct-81	O'BARA
			947	10/6/90	LEARY
Bear Creek-1	317	5/13/85	2048	11/1/83	BISO
	999	Jun-81	1499	Oct-81	O'BARA
Bear Creek-3	558	1/26/86	2155	11/3/88	BISO
	1419	Jun-81	2298	Oct-81	O'BARA

Units in microequivalents per liter
Leary concentrations are calcium and magnesium values added together
BISO and O'Bara concentrations are hardness as calcium carbonate

(Puncheoncamp Fork) to 114 μeq/l (Roaring Paunch). The BISO data set was constrained with a minimum detection limit of 7 μeq/l. This minimum detection level was considered a high lower detection limit for both natural and coal mined watershed streams, since 25 of the 96 samples from the O'Bara *et at.* stream study had concentrations less than the minimum detection level for iron. The BISO value of 2 μeq/l in Williams Creek site three, analyzed at Tennessee Technological University, also represents a much lower iron concentration than the normal lower detection limit used by BISO (Table 5.3). The concentrations of iron in these data were less variable than sulfate or hardness throughout the five streams. In all five streams, most of the iron concentrations were at or near the minimum detection limit; some streams had values above this limit (Table 5.3). As with sulfate and hardness, iron concentration tended to decrease and level off downstream in all but Roaring Paunch Creek (Figures 5.1-5.5).

Sulfate, Hardness and Iron Characteristics of Individual Streams

In the following section the streams are arranged by increasing coal mining disturbance to better reflect the relationship between sulfate, hardness and iron concentrations in stream water and the extent of mining disturbance. The long-term trends for the weighted annual concentrations of the individual streams were not possible to obtain because discharge was not recorded in the BISO and O'Bara *et al.* data sets.

Grassy Fork of Williams Creek

Grassy Fork of Williams Creek sulfate and iron concentrations remained consistently low throughout the years of sampling. Hardness values also remained relatively low, but varied more between the maximum and minimum values than did sulfate and iron (Figure 5.1). Grassy Fork showed the most consistency in hardness values between the upstream and downstream sites of all the reviewed streams.

Table 5.3 Iron Maximum and Minimum Concentrations In Stream Water

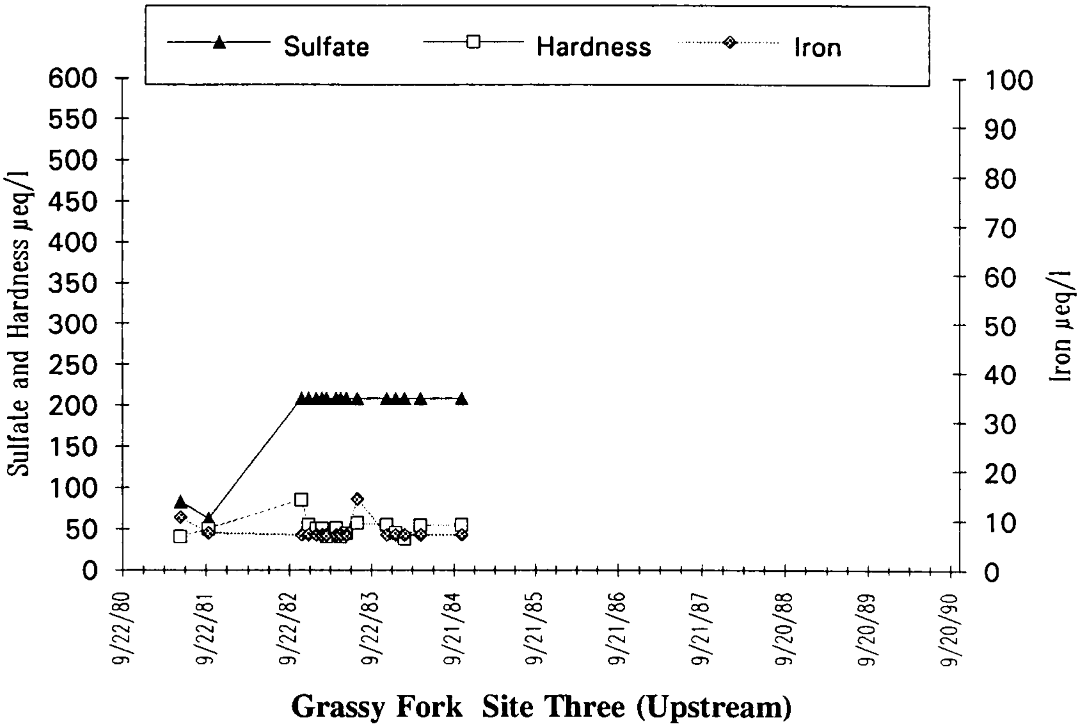
Stream Site	Minimum	Date	Maximum	Date	Researcher	Over**
Grassy Fork	7*	-	7*	-	BISO	
	5	Oct-81	8	Jun-81	O'BARA	
Williams Creek-1	7*	-	7*	-	BISO	
	8	Jun-81	9	Oct-81	O'BARA	
Williams Creek-2	7*	-	9	11/13/84	BISO	1 day
	11	Oct-81	14	Jun-81	O'BARA	
			10	10/7/90	LEARY	
Williams Creek-3	2	2/28/90	42	8/4/88	BISO	13 days
	26	Jun-81	31	Oct-81	O'BARA	
			16	10/5/90	LEARY	
Puncheoncamp Fork-1	7*	-	18	11/11/83	BISO	3 days
	1	Oct-81	4	Jun-81	O'BARA	
			4	10/7/90	LEARY	
Puncheoncamp Fork-3	7*	-	66	9/17/86	BISO	9 days
	7	Jun-81	15	Oct-81	O'BARA	
			20	10/5/90	LEARY	
Roaring Paunch-1	7*	-	22	11/5/87	BISO	19 days
	47	Jun-81	104	Oct-81	O'BARA	
			114	10/6/90	LEARY	
Roaring Paunch-3	7*	-	18	12/9/86	BISO	11 days
	7	Oct-81	15	Jun-81	O'BARA	
			5	10/6/90	LEARY	
Bear Creek-1	7*	-	32	7/29/87	BISO	9 days
	6	Oct-81	10	Jun-81	O'BARA	
Bear Creek-3	7*	-	57***	7/29/87	BISO	24 days
	19	Jun-81	36	Oct-81	O'BARA	

Units in microequivalents per liter

* denotes detection limits of procedure used

** Over = number of days over the 7.16 ueq/l lower concentration limit during the nine years of data collection

*** The highest concentration was 2864 ueq/l, which is a possible error



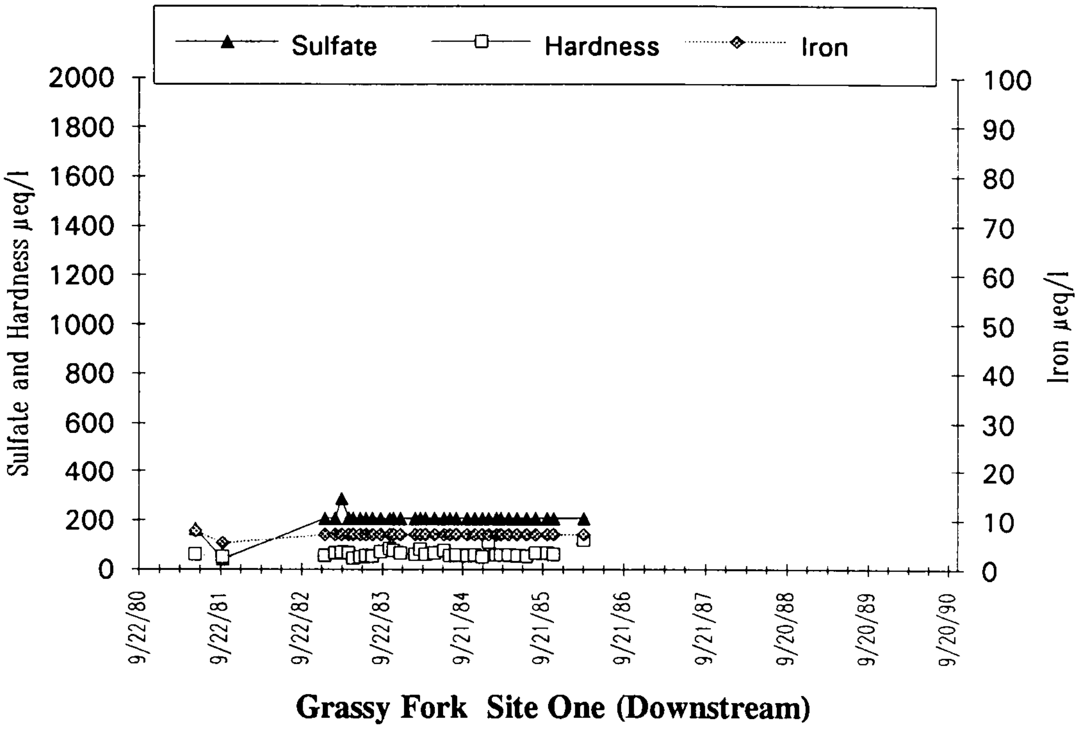
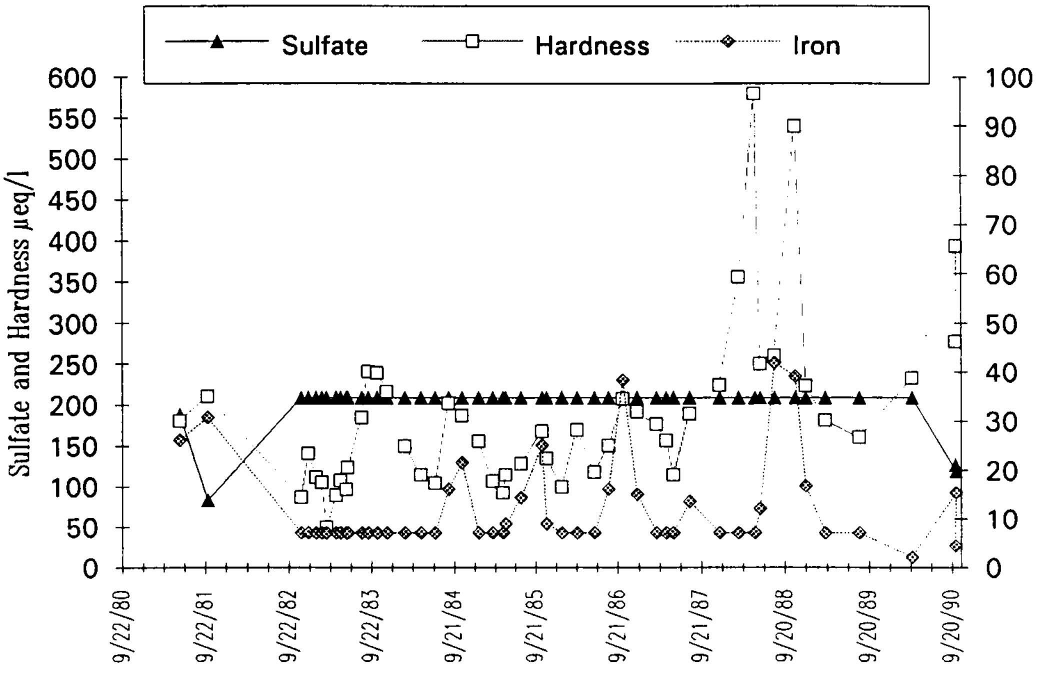
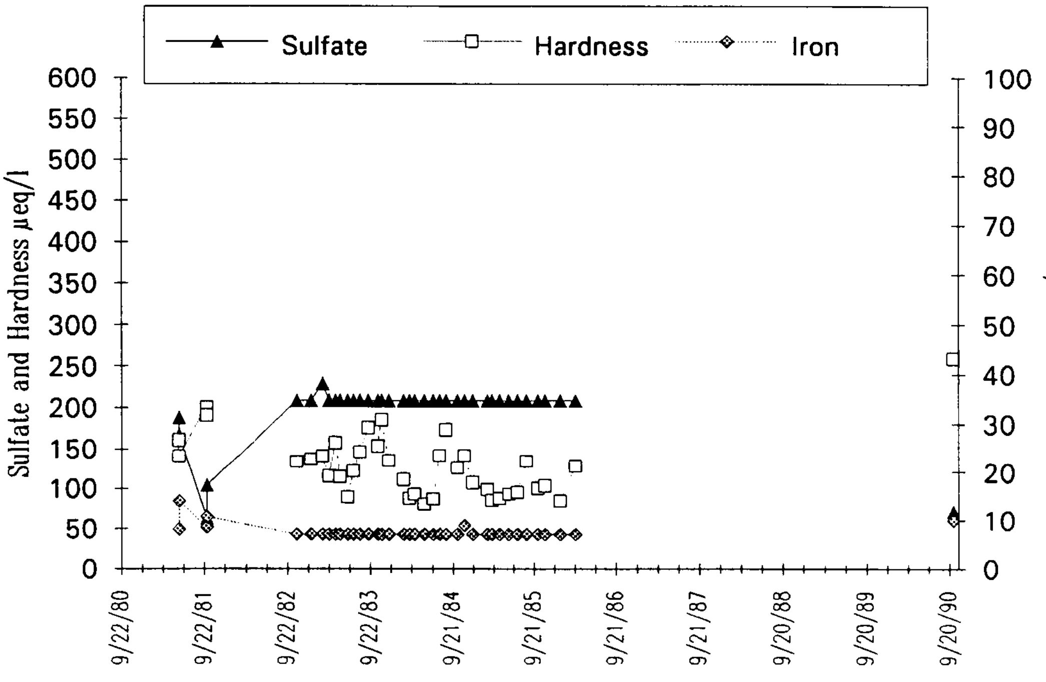


Figure 5.1 Grassy Fork Sulfate, Hardness and Iron Concentrations Over Time

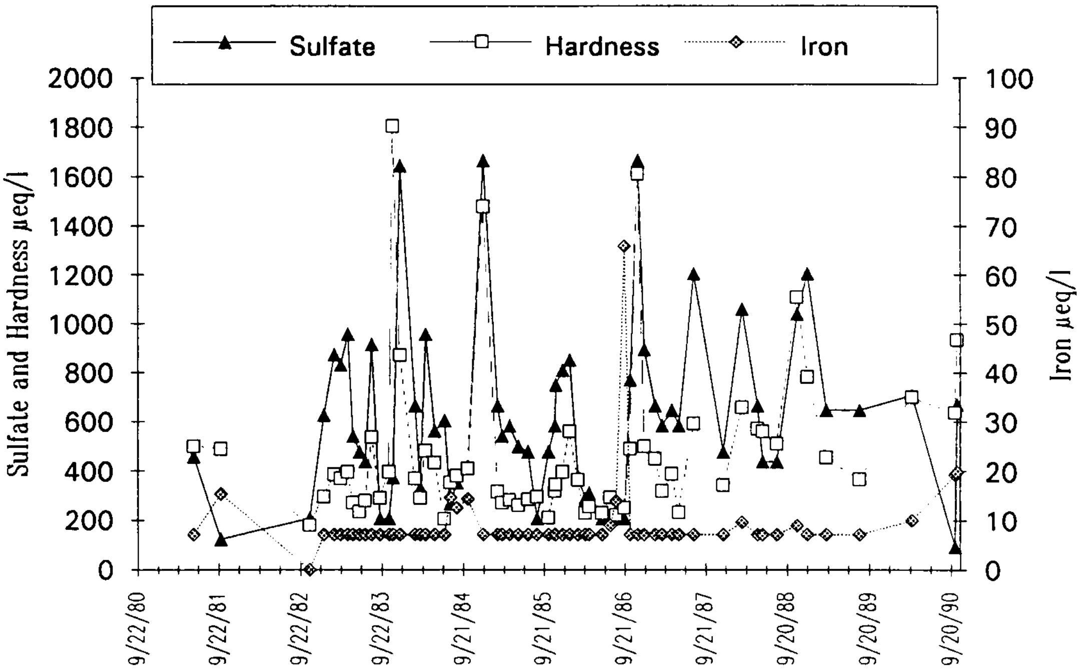


Williams Creek Site Three (Upstream)

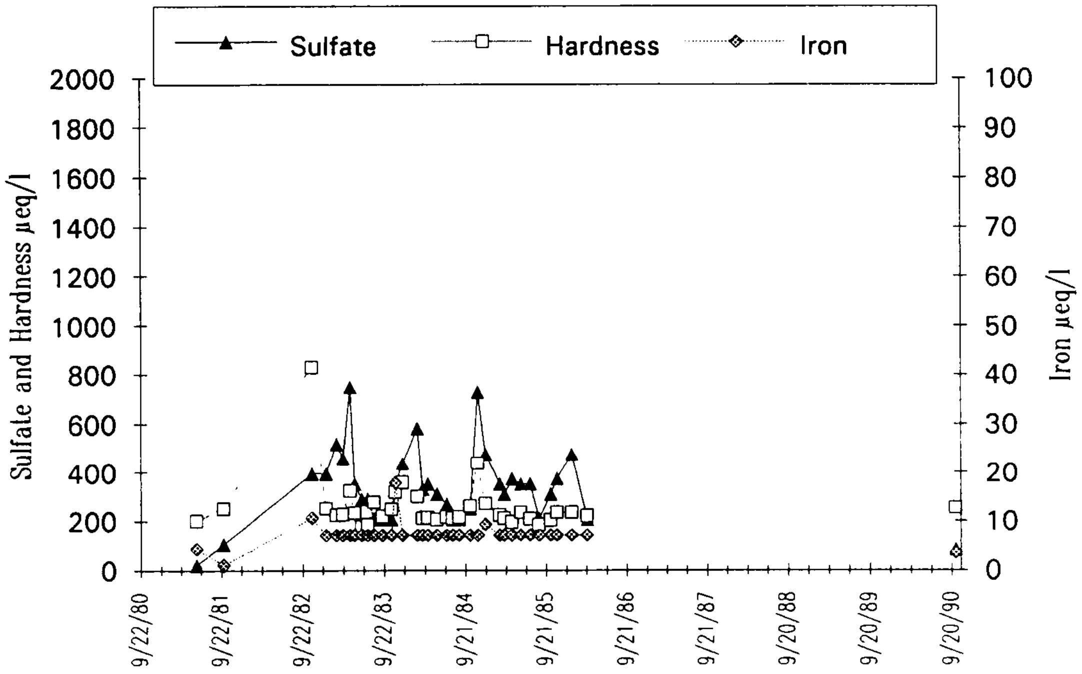


Williams Creek Site Two (Downstream)

Figure 5.2 Williams Creek Sulfate, Hardness and Iron Concentrations Over Time

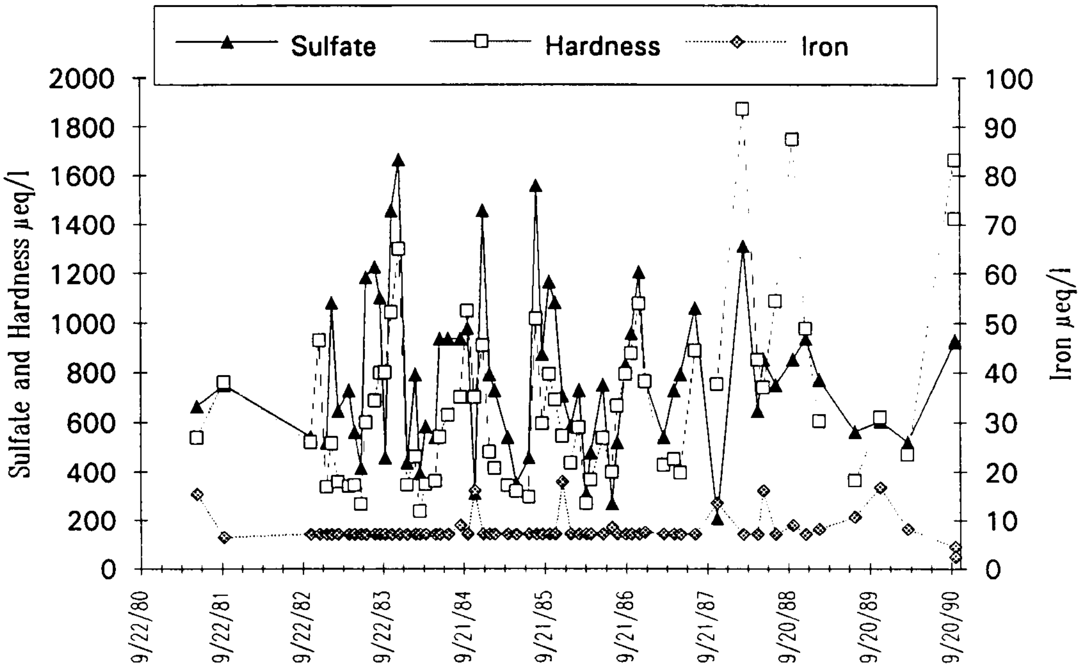


Puncheoncamp Fork Site Three (Upstream)

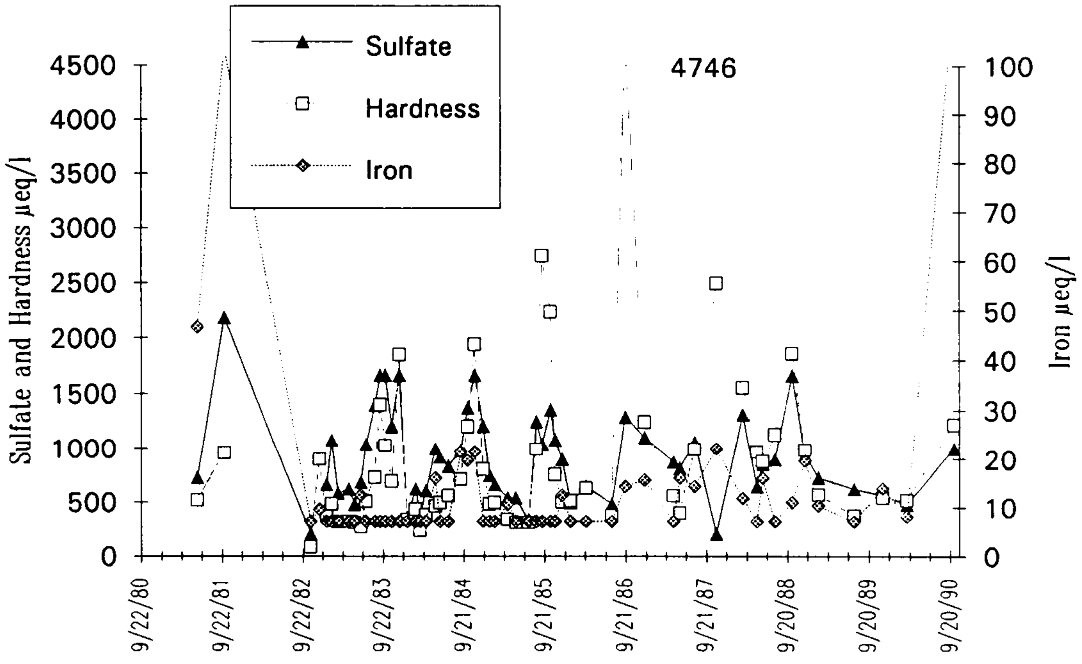


Puncheoncamp Fork Site One (Downstream)

Figure 5.3 Puncheoncamp Fork Sulfate, Hardness and Iron Concentrations Over Time

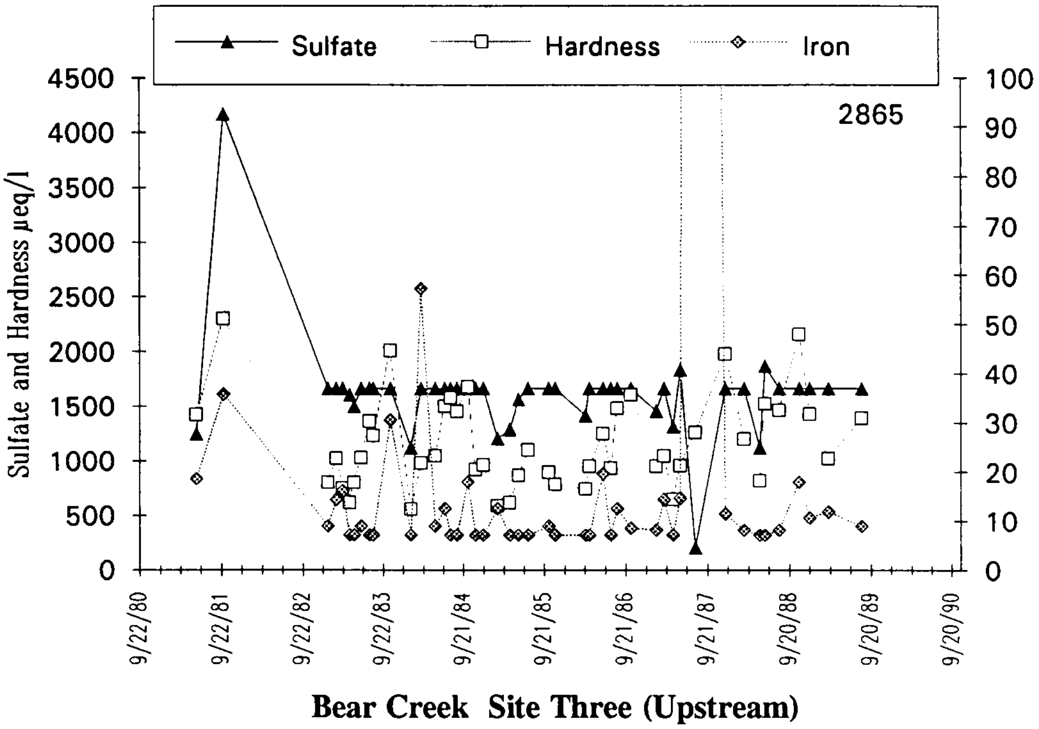


Roaring Paunch Creek Site Three (Upstream)



Roaring Paunch Creek Site One (Downstream)

Figure 5.4 Roaring Paunch Creek Sulfate, Hardness and Iron Concentrations Over Time



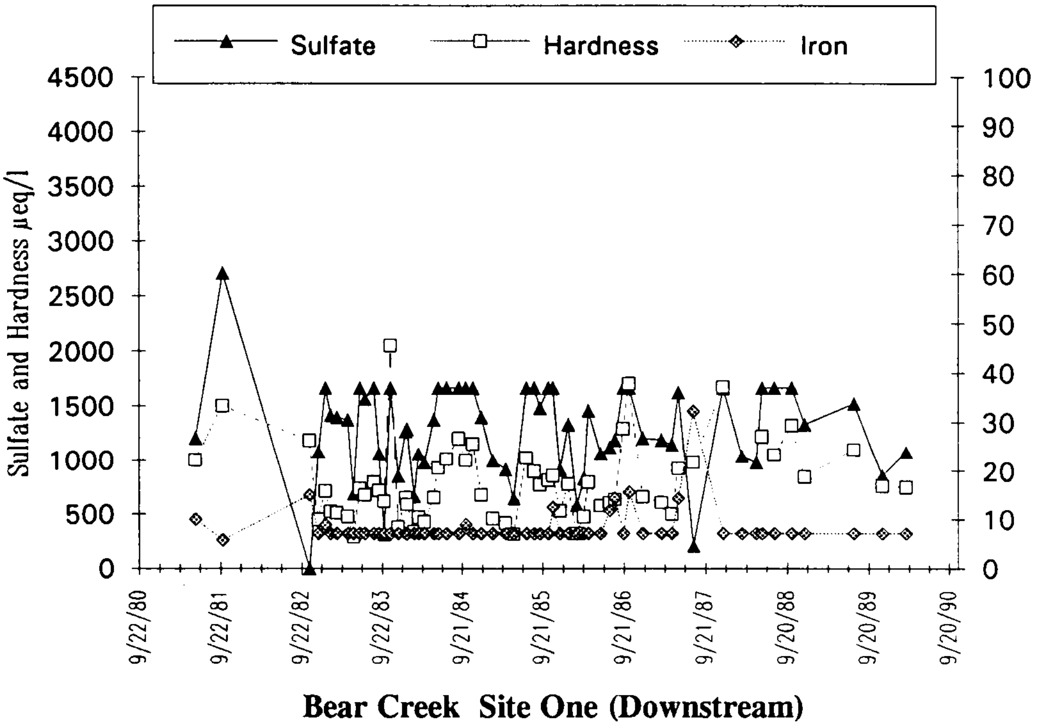


Figure 5.5 Bear Creek Sulfate, Hardness and Iron Concentrations Over Time

Williams Creek

Williams Creek, with minor surface mining disturbance, exhibited sulfate concentrations similar to those of Grassy Fork -- primarily remaining at the lower detection limit. Hardness and sulfate concentrations in Williams Creek were usually lower than those of other surface mined streams. However, iron concentrations were more consistently elevated in the upstream site of Williams Creek than in locations impacted by surface mining on the other streams, except Bear Creek. During the last three years of monitoring, both iron and hardness values varied more and had higher maximum values (Figure 5.2).

Puncheoncamp Fork of Williams Creek

Puncheoncamp Fork had generally higher maximum sulfate and hardness concentrations than Williams Creek or Grassy Fork, coinciding with the increased amount of surface mining disturbance. Hardness, at the upstream site, became generally more concentrated from May of 1987 to October 1990, as it had in Williams Creek. Upstream sulfate and hardness concentrations values were more concentrated than the downstream values (Figure 5.3), whereas iron concentrations showed marked differences between Puncheoncamp Fork site three, which was impacted by acid mine drainage, and site one downstream. In fact, the lowest iron concentration (1.1 μeq/l) for the entire O'Bara *et al.* study was that at the downstream stream site in Puncheoncamp Fork.

Roaring Paunch Creek

Roaring Paunch Creek showed trends in sulfate concentrations similar to those in Puncheoncamp Fork, but concentrations were at higher levels. Hardness and iron concentrations showed an even greater range between sites than in Puncheoncamp Fork. Unlike the first three streams, downstream hardness and iron values were higher than upstream values. Unexpectedly, the upstream site on Roaring Paunch Creek had iron concentrations below the majority of those measured in other streams sampled by O'Bara *et al.* (1982) and current study data sets (Figure 5.4).

Bear Creek

The highest sulfate values in the BISO area showed in Bear Creek. Sulfate concentrations at the upstream site were notably at the upper detection limit over the nine-year time period. This did not occur for any other stream. At the upstream site on Bear Creek, iron concentrations were highly variable throughout the nine year period, yet they almost entirely leveled off to the lower detection limit at the downstream site. Of the three chemical parameters reviewed, Bear Creek hardness values were the most similar between the upstream and downstream sites, decreasing a little at the downstream site (Figure 5.5).

Seasonal Trends in the BISO Database

Seasonal trends in each stream for sulfate, hardness and iron were examined by categorizing the ten highest and lowest concentration values for each stream element in the nine-year BISO record. The seasonal categories are designated as: Spring (March through May), Summer (June through August), Fall (September through November) and Winter (December through February) (Table 5.4).

Highest concentrations for all three parameters were most often encountered during the Fall. Although sulfate concentrations and hardness values were usually highest in the Fall, sulfate also showed high concentrations in the Spring and Summer. Hardness also showed high values during the Spring. Iron, one the other hand, only had its highest concentrations during the Fall (Table 5.4).

The lowest concentrations of sulfate were measured most often during the Fall, with some low concentrations measured during Summer as well. Hardness values were usually low in the Spring and Summer, but it was not uncommon to also find extremely low values during

Table 5.4 Seasonal Ranking of Highest and Lowest Sulfate, Hardness, and Iron Concentrations in Stream Water

Parameter	Conc.	Spring	Summer	Fall	Winter
Sulfate	High	H2		X, H1	
	Low		L2	X, L1	
Hardness	High	H2		X, H1	
	Low	X, L1	L2		
Iron	High		H2	X, H1	
	Low	below detection limit			

X = season concentrations most often measured
H1 = highest concentration, H2 = second highest concentration
L1 = lowest concentration, L2 = second lowest concentration

the Fall and Winter. Because of the relatively high lower detection limit placed on iron concentrations, it is not possible with these data to determine when the lowest concentrations normally occurred (Table 5.4). The October 1990 water samples generally were in the middle concentration ranges between the highest and lowest values measured in the other studies. Therefore, these measurements may not be the highest levels usually reached during the Fall months.

1990 Water Chemistry of Individual BISO Streams

While the previous section focused on sulfate, hardness and iron over a long-term basis, this section evaluates a wider spectrum of chemical species measured during low flow conditions for this project in October 1990. In the discussion that follows, the streams sampled in October are separated according to whether their watersheds were unmined or mined in order to establish what may be the typical "natural" stream chemistry baseline concentrations for a Big South Fork National River and Recreation Area (BISO) stream. The data from the October 1990 water sampling are given in Appendix 3.

Streams Unaffected by Acid Mine Drainage

Indian Branch of Grassy Fork

The watershed of Indian Branch of Grassy Fork has never been mined. It appears to be the least disturbed of the study, with horse and foot trails and a dirt road on the watershed divide as the primary disturbances. The pH value was 5.8 for Indian Branch, the lowest pH measurement for streams in the study area. Indian Branch also had the lowest chemical concentrations (Appendix 3), conductance (10 μs/cm) and alkalinity (205 μeq/l). In Indian Branch, sulfate (SO_4^{2-}), chloride (Cl^-) and calcium (Ca^{2+}) were the predominant ions in solution. Zinc (Zn), boron (B), and lead (Pb) were the trace elements with the highest concentrations.

Indian Branch is a first order stream that has a relatively consistent elevation of 413 m. The discharge of Indian Branch had an approximate perennial flow of 3.4 liters per second (l/s), as measured on October 6, 1990.

Line Fork of Bear Creek

The pH of Line Fork was 6.4, which was lower than that of the streams disturbed by mining. Line Fork's conductivity of 70 μs/cm and alkalinity of 8999 μeq/l were both above the values for these parameters in the studied streams that had little to moderate mining disturbance. The overall levels of chemical species concentrations were also elevated compared to those found in other streams with little mining disturbance. For Line Fork, the predominant ions in solution were Ca^{2+}, Cl^- and magnesium (Mg^{2+}) and the most prominent trace elements were B, Zn, and fluoride (F). Both Line Fork and Indian Branch had similar concentrations (within ten percent of each other) of arsenic (As), cadmium (Cd), copper (Cu), lead (Pb), molybdenum (Mo), nickel (Ni), silicon (Si) and Zn.

Line Fork had an almost stagnant discharge on October 6, 1990 with a flow of 0.08 l/s, although the flow increased with precipitation events throughout the summer and fall. The elevation was 419 m for most of the stream length. Like Indian Branch, Line Fork is a first order stream.

Streams Affected by Acid Mine Drainage

Three of the five streams studied have been directly impacted by surface and/or deep mining at some time in the past. These streams were: Williams Creek, Puncheoncamp Fork of Williams Creek and Roaring Paunch Creek (Figure 4.1, p.26).

The average specific conductivity value from each stream (obtained by averaging values from multiple sites on the same stream) was used to generalize the extent of chemical species in each stream that was affected by acid mine drainage. In order of increasing conductance they are Williams Creek (50 μs/cm), Puncheoncamp Fork of Williams Creek (88 μs/cm), and Roaring Paunch Creek (219 μs/cm). The alkalinity values of these streams have the same increasing order: Williams Creek (4586 μeq/l), Puncheoncamp Fork of Williams Creek (8676 μeq/l), and Roaring Paunch Creek (12,309 μeq/l). The values for conductivity and alkalinity in Williams Creek were less than those for Line Fork.

Williams Creek

Williams Creek had a pH ranging from 7.0 at WL4, to a downstream value of 7.6 at WL2. The predominant ions in solution were Ca^{2+}, Mg^{2+} and either Cl^- or SO_4^{2-} depending on the sampling site. Ca^{2+}, Cl^-, Mg^{2+} and potassium (K^+) concentrations were four times greater than those of Indian Branch, although still less than the concentrations in Line Fork. Nitrate (NO_3^-) measurements in Williams Creek ranged from 0.7 to 71 μeq/l; the latter value is unusually high, and is most likely due to the bovine activity surrounding the creek.

The predominant trace elements in solution were B, Zn, and F. The Zn concentrations for the upstream sites on Williams Creek were the lowest in the study area, with values of 6.2 and 6.5 μeq/l. Many of the trace element concentrations in Williams Creek were similar to (or slightly lower than) those in Indian Branch.

The discharge of Williams Creek increased downstream from 2.4 l/s at WL4 to 26.8 l/s at site WL2. The initial stream gradient was low with an approximate elevation of 425 m, the stream dropped quickly in elevation, and at its mouth had an elevation of 269 m. The stream was third order at each site.

Puncheoncamp Fork of Williams Creek

The pH of Puncheoncamp Fork of Williams Creek ranged from 6.5 to 7.3. This is the greatest range in pH values for streams sampled during this project. The pH value of 6.5 was measured at site PU4, which had an alkalinity of more than double the other downstream sites in Puncheoncamp Fork.

Except for the unusually large SO_4^{2-} concentration at PU3.2, the predominant ions in solution were Ca^{2+}, Mg^{2+} and Cl^-. Thus, Puncheoncamp Fork has water chemistry characteristics similar to Line Fork. The middle site on Puncheoncamp Fork (PU3) showed the greatest concentration of aluminum (20 μeq/l) measured in this study.

The predominant trace elements in solution in Puncheoncamp Fork were Mn, Zn, B and F. The last three were the same elements that were predominant in Williams Creek and Line Fork. The manganese concentration in Puncheoncamp Fork (26 μeq/l) was the highest for all five sampled streams.

The first sampling sites on Puncheoncamp Fork and Williams Creek were both just above the confluence of these two streams (Figure 4.1). They had similar chemical concentrations (within ten percent of each other) of As, B, Br, Ca, Cd, Cr, Mg, Mn, Mo, Si, Sr, and Zn. Their discharges were also similar, with 25.6 l/s for Puncheoncamp Fork and 26.8 l/s for Williams Creek. Thus the overall hydrology and chemistry of these two streams are similar. Although Williams Creek is consistently a third order stream, Puncheoncamp Fork is second order at the two upstream sampling sites and third order at the downstream site.

Roaring Paunch Creek

The pH of Roaring Paunch over four sampling sites ranged from 7.2 (RP1) to 7.6 (RP3), and showed no systematic upstream or downstream variation. Conductivity was greater upstream at RP4 (311 μs/cm) than at the mouth (RP1) (188 μs/cm), as was the alkalinity (14,411 μeq/l at RP4, and 8346 μeq/l at RP1).

The water in Roaring Paunch Creek had the highest concentration of chemical species of the three mined streams. The predominant ions in the stream water were SO_4^{2-}, Ca^{2+} and Mg^{2+}. Sulfate concentrations were approximately ten to twenty times larger than at the most concentrated site on each of the other streams sampled in the Leary (1990) study .

RP1 on Roaring Paunch contained the highest iron concentration, 114 μeq/l, while the other three sites on Roaring Paunch Creek had iron concentrations of 2 to 5 μeq/l. The dominant trace elements in the Roaring Paunch stream water were B, F, and Zn, which were also dominant in the other studied streams except for Indian Branch. Zinc concentrations were similar at all sites in Roaring Paunch Creek, ranging from 12.5 to 12.9 μeq/l.

Roaring Paunch had the largest discharge of all the studied streams, increasing from 48 l/s at RP5 to a downstream value of 1020 l/s at RP1. Elevations at the sampling sites were from 367 m (RP5) to 271 m at the mouth. The stream gradient is gentle until RP3, where it drops 70 m over a distance of nearly 23 km. Roaring Paunch Creek is a fourth order stream.

Chapter 6

DISCUSSION

Determination of Natural Stream Chemistry of Unmined BISO Watersheds

Coweeta Hydrologic Laboratory, NC, Walker Branch Watershed, TN, and Fernow Experimental Forest, WV were reviewed for similarities to BISO's unmined watersheds. Of these three, Walker Branch Watershed, because of its dolomite bedrock, was the only one not used in a comparison of water chemistry between unmined BISO streams and regional natural streams. The purpose of this comparison was to determine whether the chemical concentrations found in October 1990 in the unmined streams at BISO were within the long-term annual average chemical concentrations of similar watersheds which have been well characterized. Within this study's 1990 October water sampling, Indian Branch of Grassy Fork and Line Fork of Bear Creek were the only streams that were located within unmined watersheds. Streams were chosen for comparison from Coweeta Hydrologic Watershed and Fernow Experiment Forest based on similarities in: 1) rock type, 2) soils, 3) stream order, and 4) land use (Table 6.1). For this analysis, October 1990 stream water chemistries of Indian Branch and Line Fork were compared with the ten-year weighted chemistries of the Coweeta streams WS2 and WS18 (Swank, 1988) and the Fernow WS4 stream 16-year annual average chemistries (Edwards and Helvey, 1991), using the concentrations of Ca^{2+}, Mg^{2+}, Na^+, K^+, NH_4^+, SO_4^{2-}, NO_3^- , and Cl^- (Table 6.2).

The major chemical species concentrations in Line Fork were quite different from those in Indian Branch. This variance between the two unmined watersheds was probably related to the differences between their discharges. Rikard and Kunkle (1986), Gaydos *et al.* (1982) and Hem (1989) state that as the discharge decreases, the chemical species concentrations in a stream increase. Thus, the trickle flow of Line Fork was probably more concentrated than Indian Branch and is likely to represent maximum concentration levels in

Table 6.1 Site Characteristics of BISO, Coweeta and Fernow Watersheds

		BISO				COWEETA				FERNOW	
Geology		Sandstone Shale Limestone				Metasandstone Granite				Shale Sandstone	
Soils		Ultisols deeply weathered ~2m depth				Ultisols deeply weathered ~7m depth				Inceptisol ~120 cm depth	
		CEC	B.S.%	pH		CEC	B.S. %	pH		B.S.%	pH
	0-2 cm	15.3	8	5.0	0-10 cm	11.6	17.2	4.74	A horizon	~12	4.3
	2-40 cm	15.7	8	4.5	10-20 cm	9.4	18.8	4.89	B horizon	~17	4.6
	40-85 cm	15.6	10	4.5	20-30 cm	6.8	19.1	5.02	C horizon	~20	4.7
	85-150 cm	12.2	14	4.5	30-40 cm	7.2	27.7	5.11			
					40-50 cm	6.2	16.1	5.14			
					50-60 cm	6.0	11.7	5.13			
Elevation		~400 m				~700 m				~950 m	
Stream Order		first				first				second	
Precipitation		89-178 cm year round discharge -highest Feb. -lowest Sept.-Oct.				180-250 cm year round discharge -highest Feb. -lowest Sept.-Oct.				~150 cm year round	
Vegetation		hardwoods				hardwoods				hardwoods	

Table 6.2 Stream Water Chemistry of Unmined Regional Streams

Location	Ca^{2+}	Mg^{2+}	Na^+	K^+	NH_4^+	SO_4^{2-}	NO_3^-	Cl^-
Indian Branch	24	22	21	0	0	42	0	30
Line Fork	241	161	108	0	43	117	0	208
Coweeta WS2	29	27	53	13	0.2	94	0.2	19
Coweeta WS18	18	17	21	6	0.3	24	1.3	14
Fernow	68	51	22	16	-	90	16	2

Note: all values are in μeq/l

unmined watersheds of BISO. For this reason Line Fork water chemistry is not compared with the other regional watersheds.

The concentrations of Ca^{2+}, Mg^{2+}, Na^+ and SO_4^{2-} in Indian Branch were within the range of natural stream chemistries observed at the Coweeta. Fernow had higher values of Ca^{2+}, Mg^{2+}, Na^+ and SO_4^{2-} likely related to the higher amounts of atmospheric sulfur deposition at Fernow, relative to Coweeta and BISO (Turner *et al.*, 1990), resulting in elevated transport of sulfate cations through the Fernow watershed. The Indian Branch Cl^- concentration was higher than the Cl^- concentrations in Coweeta and Fernow (Table 6.2). BISO Cl^- concentrations are generally elevated because of brine pumped out with the oil and natural gas resources in the area (Gaydos *et al.*, 1982). The K^+, NH_4^+ and NO_3^- values were all less than those in Coweeta and Fernow (Table 6.2). The lower concentrations of K^+, NH_4^+ and NO_3^- in Indian Branch compared to the regional streams are likely an artifact of the differing periods of measurement. The longer period of observation at Coweeta and Fernow provided a larger data set, in which seasonal concentration changes, related to vegetation growth and animal activity, are better represented (Hem, 1989). The unusually low K^+ concentrations may be a result also of differences in soils and/or geology. The concentration measurements of Indian Branch are thus seen to be similar to natural stream water chemistry, as depicted by regional water chemistry, and should be representative of unmined BISO streams. Other natural BISO stream concentrations may vary somewhat in relation to watershed differences and seasonal effects.

Chemical Concentrations to be Used During Reclamation

Stream chemistry concentration targets for reclamation projects in BISO streams may be determined by using Indian Branch as an example of a free-flowing, unmined stream with low concentrations of chemical species, and Line Fork as an example of an unmined stream at low- to stagnant flow, with concentrated chemical species levels. The Federal Government usually mandates that contaminated water be cleaned to the Environmental Protection Agency's (EPA) drinking water standards in stream and ground water reclamation projects (Fetter, 1988). BISO natural stream element concentration levels are compared to the EPA drinking water maximum concentration limits in Table 6.3. Indian Branch and Line Fork are used for the determination of maximum and minimum concentration levels in BISO.

All elements , except Fe, Pb, Se, and Al, were within the EPA standards for both maximum and minimum concentrations. The iron and lead concentrations in unmined BISO streams periodically become more concentrated than EPA standards allow; the aluminum and selenium concentrations were above EPA limits at minimum and maximum levels (Table 6.3). Aluminum, when taken in large dosages by humans, can cause nausea and skin problems, and may contribute to Alzheimer's disease (King, 1985). Selenium, in large doses, can cause indigestion and abdominal pain (King, 1985). Lead causes multiple health problems leading to cancer and birth defects, even at low levels (King, 1985). Iron is generally not harmful to humans, but EPA has determined iron guidelines based on taste, color and odor.

Recommended concentration levels for reclamation projects must be based on the EPA maximum standards for elements. In setting this target for BISO, it should be realized that the natural levels of Al and Se that occur may not allow the EPA standards to be met in all cases.

Table 6.3 Composition of BISO Natural Streams Compared to EPA Standard Concentration Levels

Element	EPA MAX MG/L	BISO MAX* MG/L	BISO MIN* MG/L
Aluminum	**0.05**	**0.50**	**0.24**
Arsenic	0.05	0.01	0.00(L)
Barium	1.0	0.03	0.01
Cadmium	0.01	0.00	0.00
Chloride	250.00	3.36	0.52
Chromium	0.05	0.02	0.01
Copper	1.0	0.03	0.01
Fluoride	2.0	0.14	0.02
Iron	**0.3**	**0.57**	0.20
Lead	**0.05**	**0.07**	0.05
Manganese	0.05	0.04	0.01
Molybdenum	--	0.00	0.00
Nickel	--	0.01(I)	0.00
Nitrate	10.00	0.25	0.00
Selenium	**0.01**	**0.07**	**0.03**
Silver	0.05	--	--
Sodium	200.00**	2.48	0.49
Sulfate	400.00**	5.59	2.01
Zinc	5.00	0.25 (I)	0.20

* BISO MAX and BISO MIN were based upon a composite of Indian Branch (I), and Line Fork (L) streams. Unless otherwise noted, BISO Max is based on Line Fork and BISO Min on Indian Branch.

** World Health Organization (WHO) water quality guidelines

Sources: EPA Federal Register, 1986; WHO, 1984.

Sulfate, Hardness and Iron Concentrations in Stream Water Impacted by Acid Mine Drainage

The Extent of Mining Disturbance and the Time of Abandonment

The effects of surface mining on stream water chemistry are related to both the size of the area disturbed and the time since disturbance occurred. Within this study it was not possible to separate these two functions, since the amount of mining disturbance increases with the recency of mining activity within each watershed. Thus to relate sulfate, hardness and iron concentrations in BISO to the period of abandonment and the extent of mining disturbance within the studied watersheds, the heightened stream concentrations of these three parameters from the long-term data set were averaged and plotted relative to the combined effects of both age and extent of mining disturbance (Figure 6.1). The streams were broken down into three categories of mining disturbance: Extensive--- recently abandoned, large surface disturbance; Moderate -- medium-sized disturbance areas with abandonment periods of 15 to 25 years; and None -- no impact from mining.

Maximum sulfate concentrations were highly elevated in recently mined watersheds with large amounts of disturbed area. Hardness increased to a lesser extent than sulfate in the more highly impacted mined watersheds, then leveled off similarly in mined areas abandoned for longer periods of time. Iron responded the least to increase in disturbance size and recency of abandonment (Figure 6.1). As a result, sulfate and hardness could be viewed as primary indicators of acid mine drainage and iron as a secondary indicator.

Sulfate as a Single Indicator of Mining Effects on Stream Water

Although sulfate has been used as an indicator of acid mine drainage by Rikard and Kunkle (1990), Ferguson and Erickson (1987), Parker and Carey (1980), Geidel and Caruccio (1977), and Minear and Tschantz (1976), among others, there continues to be controversy about its suitability as a single indicator of acid mine drainage. Dyer and Curtis (1983), for

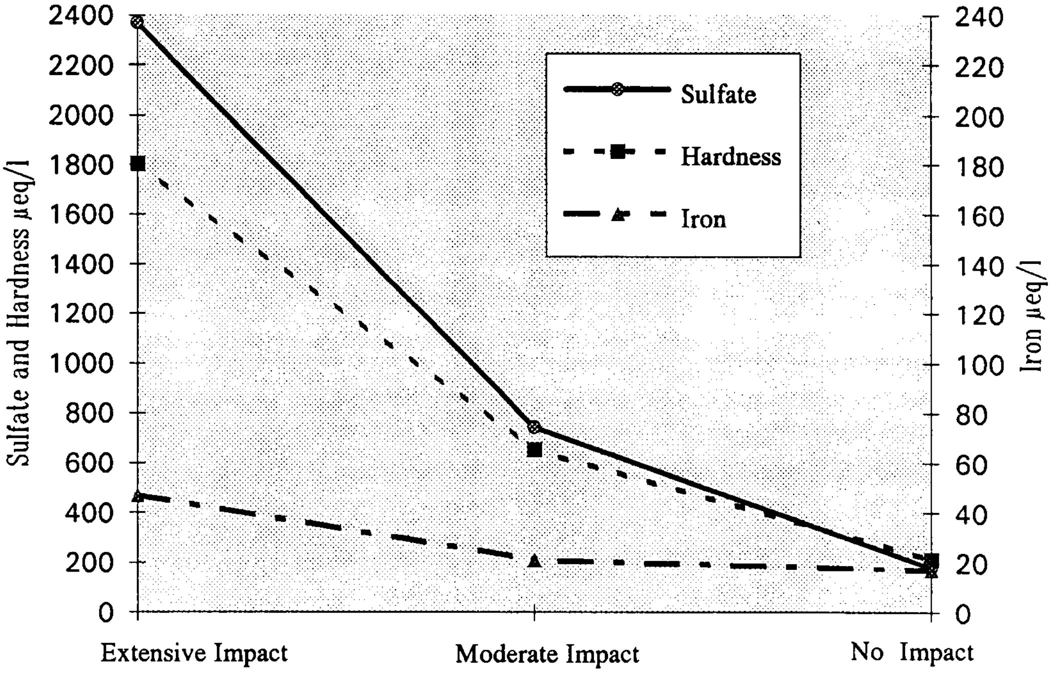


Figure 6.1 Maximum Sulfate, Hardness and Iron Concentrations Compared to the Age and the Extent of Mining Disturbance

example, argued that pH is the best indicator of water quality related to acid mine drainage in eastern Tennessee and Kentucky streams.

Before determining if sulfate is the best single indicator of acid mine drainage, an examination of acid mine drainage effects on a watershed stream is called for. Generally, the effects from acid mine drainage are considered by humans to be negative. This is because streams often become more acidified, increase in trace element levels and turn visually degraded. Acid mine drainage, though, does not always have negative impacts on a watershed stream; rather it can be neutral or beneficial depending on the watershed soils, geology and the flow path through the watershed of the acid mine drainage. As found in studies reviewed by the National Acid Precipitation Program, watersheds having a greater proportion of their water flowing through shallow, more acid soils will have surface waters more acidic or with lower acid neutralizing capacity, than watersheds in which a large proportion of the water flows through deeper, more weatherable materials (Turner *et al.*, 1990). The longer the hydrologic flow path, the longer the time available for the water to acquire solutes through biogeochemical reactions. This same situation can occur with acid mine drainage. Since sulfate is a mobile anion (Ruess and Johnson, 1986), it is capable of transporting base cations out of the soils and out of weathered rocks. This in turn can cause a rise in the base cation concentration of the watershed stream and actually improve the stream water. As determined by Caruccio and Geidel (1980), increased Ca^{2+} and Mg^{2+} concentrations in the watershed from mining disturbance produces a rise in stream pH levels. This increase in stream pH reduces the impact of acid mine drainage on the stream. When the pH is above 7.0, mine drainage is no longer considered acidic (Paine, 1987). Thus,in certain soils and geology formations, the sulfate from acid mine drainage can result in an elevation of stream pH, thereby resulting in an alkalization rather than acidification of a stream. The rise of the pH is generally considered a beneficial efect, yet streams may still contain elevated levels of trace metals that diminish the improved quality of acid mine drainage.

The "positive" change in pH from acid mine drainage in a watershed can be seen in the October 1990 stream water chemistry data from this study. Indian Branch, an unmined stream, had the lowest pH value (5.83) of all the studied streams. On the other hand, the pH values in streams impacted by mining were higher and relatively constant, i.e., Williams Creek - 7.03, Puncheoncamp Fork - 7.01, and Roaring Paunch Creek - 7.30 (Figure 6.2).

Maximum sulfate, $[Ca^{2+}+Mg^{2+}]$, chloride, alkalinity and conductivity values showed similar patterns to each other as the amount of surface mining disturbance increased (Figure 6.2). Of these parameters, sulfate has low biological interactions and is highly mobile; it is considered the best indicator of the amount of acid mine drainage entering a watershed. To use sulfate or any of the other five parameters to represent singly the impact of acid mine drainage on the stream water chemistry could be only partially accurate, because

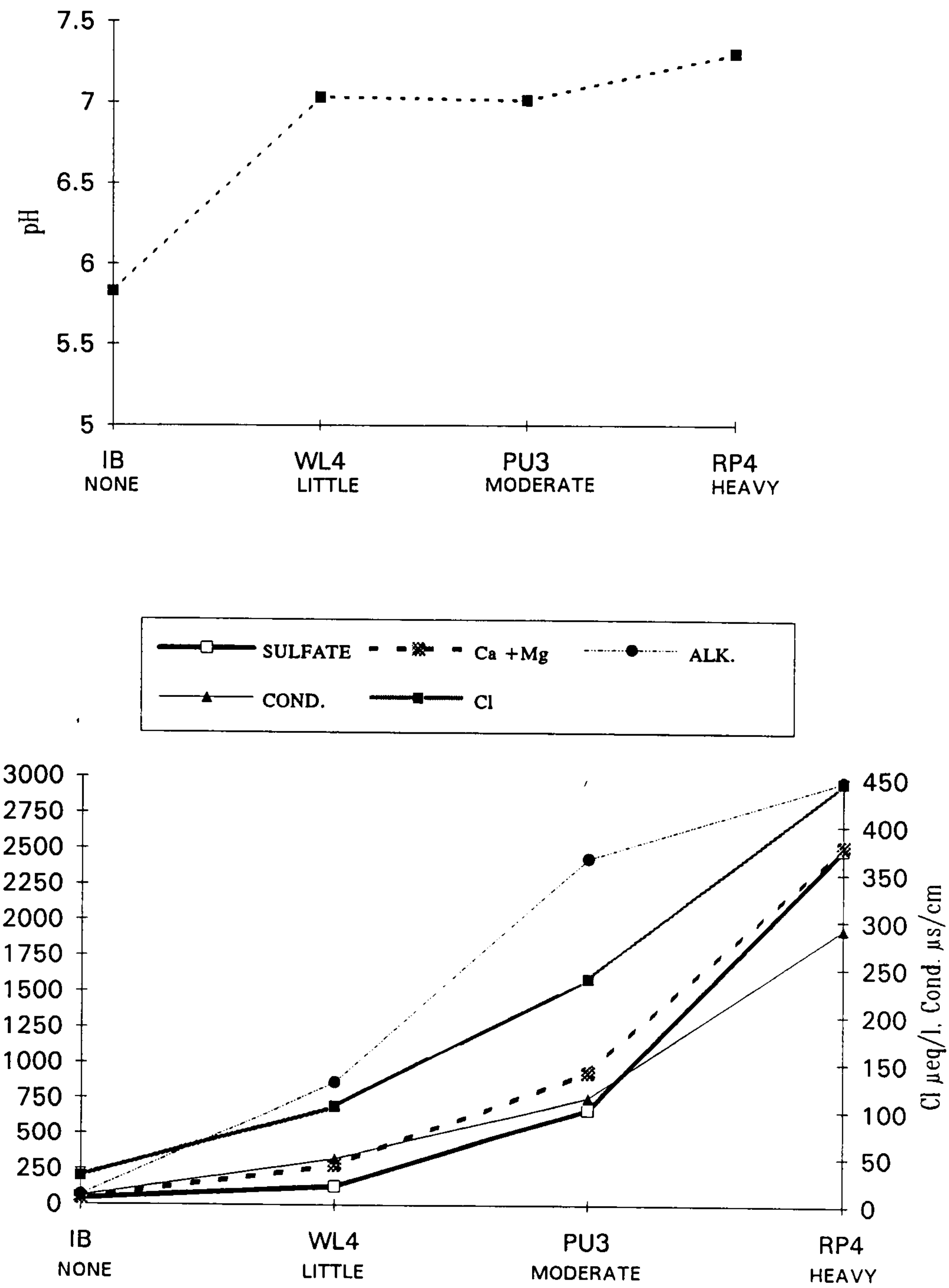


Figure 6.2 Stream Water Concentrations Compared to Increasing Surface Mine Drainage Input

each one alone does not show the synergistic interactions of the watershed and stream.

This is shown by the downstream movement of parameters in the Puncheoncamp Fork and Roaring Paunch Creek (Figure 6.3). In Puncheoncamp Fork, from PU4 (not affected by mine drainage) to PU3 (where mine drainage affected the stream), the pH increased from 6.52 (PU4) to 7.01 (PU3). In the same stream segment the SO_4^{2-} concentration increased 534 μeq/, the Ca^{2+} increased 93 μeq/l and Mg^{2+} increased 136 μeq/l. At the same time, the alkalinity proportionately decreased 1674 μeq/l from PU4 to PU3. In order for this to happen, a buffering and/or neutralization of the acid in the stream from mine drainage is likely to have occurred (Figure 6.3).

Similarly in the Roaring Paunch Creek between sites RP5 and RP4 the alkalinity proportionately decreased 1191 μeq/l, while increases occurred in the SO_4^{2-} (1350 μeq/l), Ca^{2+} (350 μeq/l) and Mg^{2+} (593 μeq/l). Although the pH rose in Puncheoncamp Fork, in the Roaring Paunch the pH decreased slightly from 7.48 (RP5) to 7.30 (RP4). This decrease in pH indicates that the amount of acid entering the stream was slightly more than what could be neutralized and/or exchanged by the surrounding calcareous material (Figure 6.3).

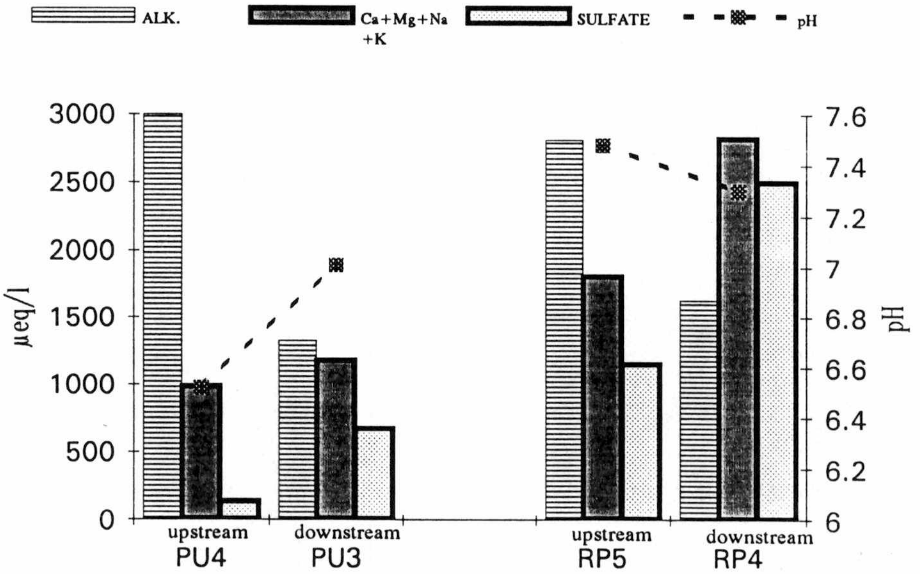


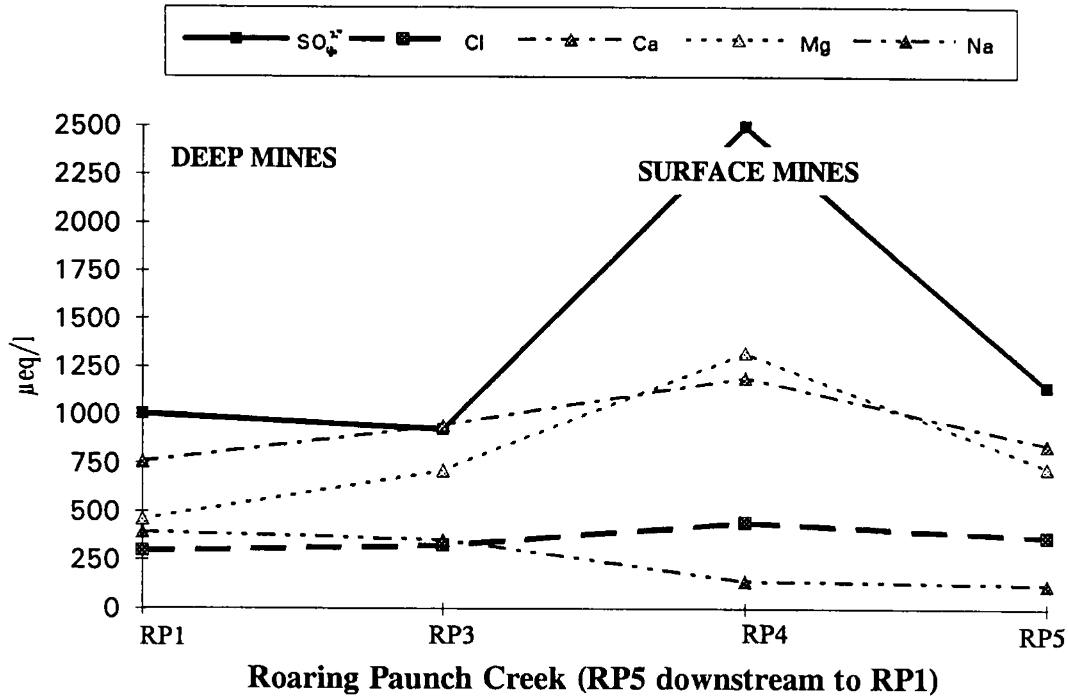
Figure 6.3 Interactions between Sulfate input from Acid Mine Drainage and the Calcareous Elements in Puncheoncamp Fork and Roaring Paunch Creek

Sulfate concentrations may be highly related to the amount of acid mine drainage created at a mined site. However, due to chemical reactions occurring within the watershed, stream sulfate concentrations do not necessarily indicate the type of effects acid mine drainage will have on stream water chemistry in BISO watersheds, and is therefore not a good *single* indicator.

Deep Mining Influence on Stream Water Chemistry:
The Case of Roaring Paunch Creek

Deep mining had occurred until 1974 along the Roaring Paunch Creek from approximately RP2 downstream to the convergence with the Big South Fork of the Cumberland River (Barclay and Parsons, 1983). Surface mining had occurred outside the park boundary from RP3 upstream, until the mid 1980's (Baker, personal communication, 1990). Water chemistry in Roaring Paunch Creek may thus have been impacted by both surface and deep mining.

Concentration changes in the October 1990 Roaring Paunch Creek data did not decrease with downstream transport, as was found in the other streams. Instead a rise, fall and then a second rise occurred from sites RP5 to RP1 (Figure 6.4). From sites RP5 to RP4, increases in concentrations were measured for most of the chemical species, especially SO_4^{2-}, Ca^{2+}, Mg^{2+} and Cl^- (Table 6.4). This initial increase in chemical concentrations paralleled the increase in surface mining disturbance. In the next reach, from RP4 to RP3, the concentrations declined with increasing discharge as the stream flowed through unmined areas (Figure 6.4). It was anticipated that the species concentrations would continue to decrease downstream, yet from Roaring Paunch sites RP3 to RP1 (where deep mining occurred), species concentrations increased for SO_4^{2-}, Na^+, Al, Fe, Mn, Si, and Pb (Figure 6.4).



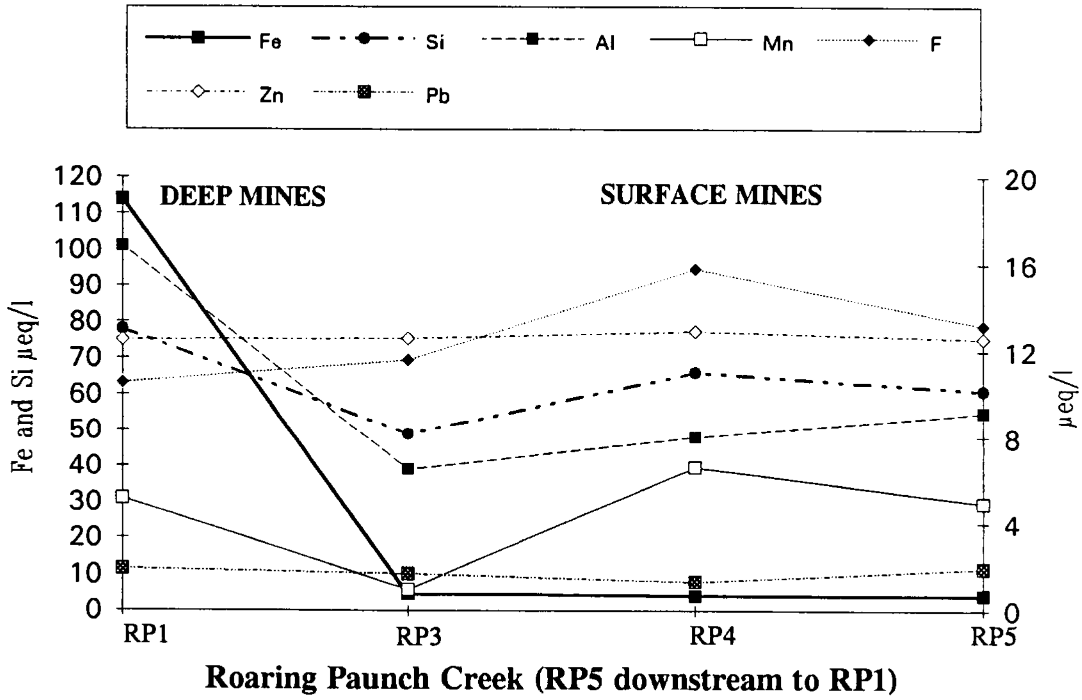


Figure 6.4 Downstream Trends of Chemical Species in Roaring Paunch Creek

Table 6.4 **Downstream Chemical Concentration Changes in Roaring Paunch**

Site	pH	Sulfate	Calcium	Iron	Silicon	Aluminum	Manganese
RP 5	7.48	1148	848	4	61	9	5
RP 4	7.30	2498	1197	4	66	8	7
RP 3	7.56	931	947	2	49	7	1
RP 1	7.20	1004	758	114	78	17	5

Note: all concentrations are in μeq/l, except silicon - μmol/l

In determining whether the acid mine drainage entering the stream between RP3 and RP1 was from surface mining or deep mining, three approaches were used: 1) review of potential transport methods for sulfate, iron and silicon; 2) review of formations disturbed by deep mining in Roaring Paunch Creek; and 3) review of characteristics of deep mining constituents in other areas.

The input of sulfate and iron into the stream water at RP4 and RP1 could be from either upstream surface mining sources alone, or from a combination of surface mining upstream and deep mining downstream. Since there was a decrease in sulfate export from RP4 to RP3, then an increase at RP1, for there to be only the upstream source, the source of SO_4^{2-} entering RP1 would have been transported primarily through subsurface flow from upstream surface mining sites. If the same upstream source impacts Roaring Paunch at both RP4 and RP1, SO_4^{2-} export would be expected to remain similar, since sulfate tends to be a conservative ion in solution (Stumm and Morgan, 1981). Yet, comparing RP4 to RP1 the sulfate export increased by 764 meq/s (Table 6.5). Thus sulfate, in this scenario, behaved in an unconservative manner. The increase in SO_4^{2-} at RP1 was therefore not likely to be from an upstream surface mined site because of the difference in SO_4^{2-} concentrations and export.

Elevated iron concentrations shown in the present study were not necessarily unusual, since the O'Bara *et al.* (1982) October iron concentrations measured 104 μeq/l at site RP1.

Table 6.5 Downstream Export of Sulfate and Silicon in Roaring Paunch Creek

Sites	RP5 upstream	RP4	RP3	RP1 downstream
Sulfate export	55	260	142	1024
Silicon export	3	7	8	80

Note: all export values in meq/s

They also measured an iron concentration of 34 μeq/l at site RP2 (O'Bara *et al.* in October 1981). In both data sets the largest rise in the iron concentration appears to be from RP2 to RP1, along the reach where the abandoned deep mines are located.

Elevated iron concentrations at site RP1 indicate that the contaminated water entering Roaring Paunch Creek was from either deep mining or from upstream subsurface transport, which passed through rocks containing high iron content. According to a study by Gaydos *et al.* (1982), in eastern Tennessee and Kentucky coal fields, high iron concentrations are most likely to occur where ground water has moved through beds of black shale or coal. The Beattyville Shale member (composed of black shales) and the Stearns Coal formations were the most disturbed during the deep mining operations in the area, and may be contributing to the elevated iron concentrations in Roaring Paunch Creek.

To determine if the rise in iron was from deep mining or subsurface flow, the silicon component was examined. A rise in silicon is often used as standard chemical test to depict a ground water source entering surface water (Hem, 1989). Since silicon is generally unrelated to acid mine drainage, the increased silicon export can be used as an independent indicator of ground water input (Table 6.5). The silicon concentration and export in the stream water at site RP1 was the highest for all the low flow samples taken during the present study. Hence, the high silicon export potentially indicates that the water came from a deeper ground water source than subsurface flow. This finding suggests that the increase in iron of 112 μeq/l was related to ground water movement through the disturbed shale and coal formations.

Herricks and Cairns (1974) characterized deep mining acid drainage in the Appalachians by elevated concentrations of H^+, Fe and SO_4^{2-}. From RP3 to RP1 the H^+ concentration increased slightly, as shown by the drop in pH from 7.56 to 7.2, yet the iron concentration increased dramatically from 2 µeq/l (RP3) to 114 µeq/l (RP1) and the sulfate concentration rose from 924 µeq/l to 1004 µeq/l (Table 6.4). This increase in concentrations of H^+, Fe and SO_4^{2-} from RP3 to RP1 corresponded with the findings of Herricks and Cairns study, strongly suggesting an impact from deep mining production of acid mine drainage in the stream water chemistry downstream from RP3.

Although deep mining ended approximately sixteen years ago, it has been shown in other Appalachian locations that drainage from deep mines tends to be higher in volume, to be more moderate in contaminant concentration and to continue for longer periods of time than drainage from surface mined sites (Appalachian Regional Commission, 1969; Erickson, 1987). The deep mining along the Roaring Paunch Creek follows this pattern with its moderate SO_4^{2-} and trace element concentrations. Therefore the increase of mine drainage contaminants in the Roaring Paunch Creek at RP1 is likely to be primarily from abandoned deep mines, rather than the abandoned surface mines upstream.

BISO Base Flow Stream Water Chemistry Model

A summary of the stream water chemistry found in this study during October 1990 can be used to design a model for BISO base flow surface water conditions. This project has shown that changes in stream water chemistry from input of acid mine drainage reflect the combination of both the timing of mine abandonment and the extent of mining disturbance. The model has four main categories (Figure 6.6) based on a combination of the extent of mining disturbance, the time of mining abandonment, and other factors that influence natural stream chemistry, i.e., geology, seasonal fluctuations, and watershed land use.

There are three stages in the long-term effects on stream chemistry from surface mining production of acid mine drainage, as long as the acid mine drainage does not directly enter the stream. Initially, a watershed neutralizes the increased acidity that would enter streams through the dissolution of calcareous elements in the surrounding rocks and soils. During this time period there may be an increase in alkalinity, with conductivity and base cations concentrations increasing in the stream water. The suspended sediment load is generally highest during this time period because of the disturbances caused by the mining activity (Tschantz, 1977).

In the second stage, the base cations concentrations decrease due to the leaching of calcareous elements from the rocks and soils. This results in a drop in pH, and an increase in elements such as Al, Fe, Mn, Cr, and Zn. As the pH is lowered, the water is capable of carrying increased amounts of most dissolved elements (Stumm and Morgan, 1981).

The third stage, characterized by a decrease in acid production, results from the diminishing availability of pyrite. This is represented by stream pH beginning to rise. If the ground water has been contaminated by acid mine drainage infiltrating into it, the ground water will now become the primary contributor of acid mine drainage contaminants in area streams (Lund and Dillon, 1987). This change in source of acid mine drainage from surface runoff and interflow to contaminated ground water is shown by a decrease in mining contaminants concentrations. Low level contamination continues until ground water contamination tapers off to an insignificant level. Each of these three stages could vary in length from months to centuries.

Generally in BISO a widespread increase in concentration of SO_4^{2-}, Ca^{2+}, Mg^{2+}, Na^+, and Cl^- is related to the recency and presence of mining. Fe, Zn, Mn, B, F and Sr are the trace elements most closely related mining disturbance. Their concentrations increase with the magnitude of mining disturbance and decrease as the period of mining abandonment increases. Concentrations of Al, Si, Br, Pb, As, Se and Cr are elevated in currently mined locations and locations abandoned less than ten years. These elements tend to fluctuate more as the time since abandonment increases and local geology becomes a more dominant influence.

The model, schematically presented in Figure 6.5, summarizes the perspective developed in this thesis: that certain ranges of stream water constituents may be expected for streams with different periods of mining abandonment and amounts of disturbance, but that actual ranges also reflect geologic, soil, seasonal and land use factors. Based on mining history, the concentrations shown in Figure 6.6 are predicted for BISO streams. The key ions to examine in BISO streams are Ca^{2+}, Mg^{2+}, SO_4^{2-}, Cl^- and NO_3^-; trace elements should be used if the classification is a borderline case. The nature of changes to these ranges associated with geology, seasonal variation and various land uses are summarized in Figure 6.7.

The age of mining is generally difficult to determine by examining Office of Surface Mining records. With information on the extent of mining, this model can be used for water studies on streams impacted by mining to estimate the age of mining, or to determine approximately how much longer a stream would be impacted from acid mine drainage.

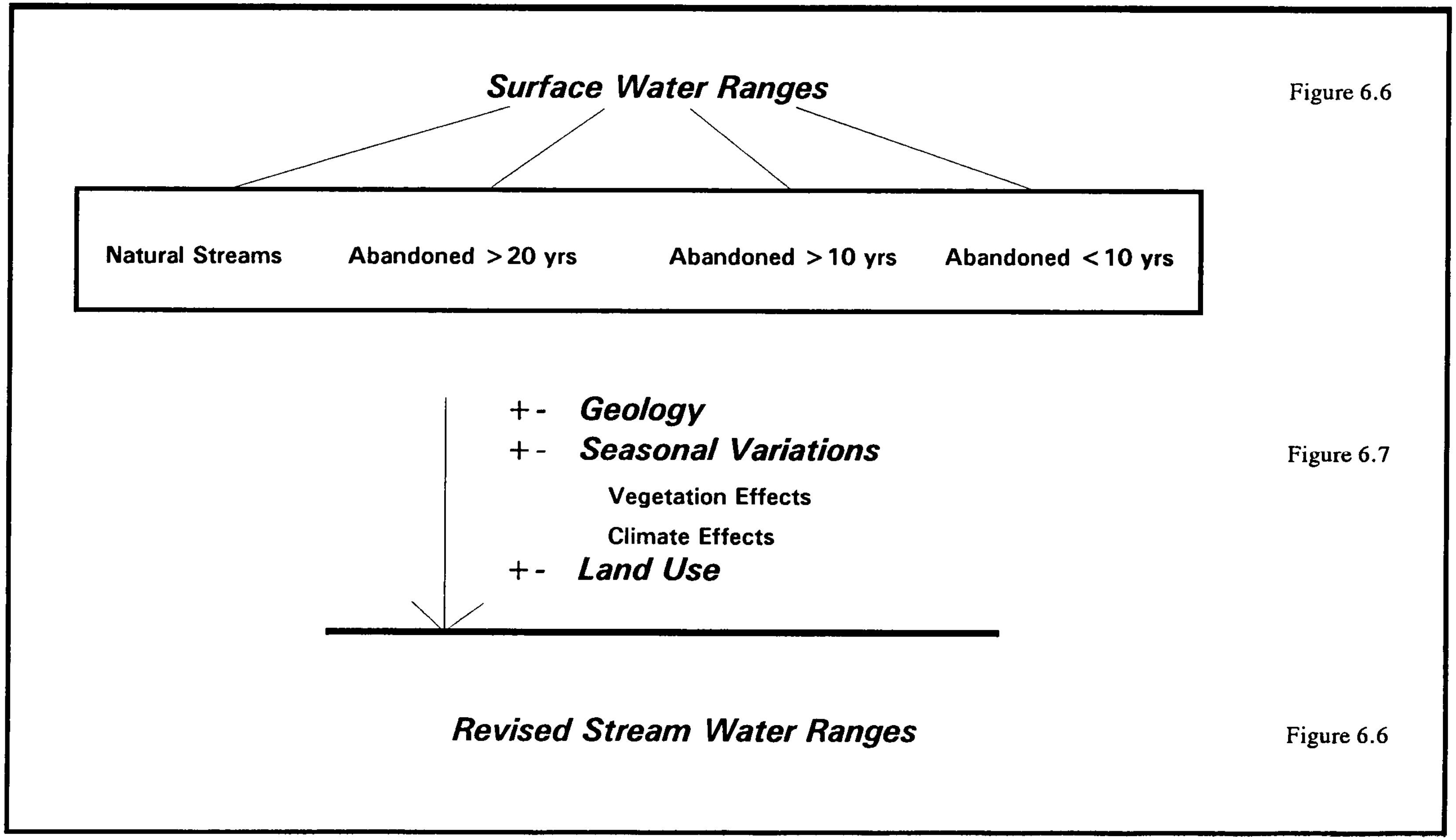


Figure 6.5 Base Flow Model for Big South Fork Area Stream Water Chemistry

Natural Streams		Low Impact		Moderate Impact		Extensive Impact	
Ca	<241 *	Ca	135 - 300	Ca	340 - 600	Ca	650 - 1359
SO_4^{2-}	<116	SO_4^{2-}	60 - 150	SO_4^{2-}	85 - 750	SO_4^{2-}	800 - 2750
Mg	<162	Mg	90 - 200	Mg	200 - 300	Mg	550 - 1500
Cl	<208	Cl	80 - 200	Cl	200 - 280	Cl	280 - 500
Na	<108	Na	30 - 110	Na	110 - 200	Na	110 - 400
F	<8	F	3.0 - 6.0	F	7.0 - 11	F	10 - 20
Zn	<8	Zn	5.0 - 8.5	Zn	7.0 - 11	Zn	11 - 16
Sr	<.34	Sr	0.3 - 0.8	Sr	0.70 - 1.5	Sr	1.5 - 3.5
Fe	<21	Fe	3.0 - 20	Fe	3.0- 110	Fe	2.0 - 150
B	<10	B	5.0 - 10	B	10 - 30	B	10 - 20
Mn	<1.5	Mn	0.5 - 3.5	Mn	15 - 45	Mn	1.0 - 60

Relationship of Other Elements to Acid Mine Drainage

Highly Related	Related	Unrelated
Al	Cr	Ti
Si	Ba	Mo
Br	Se	Cu
Pb	Ni	Cd
	As	

* All concentrations in μeq/l

Figure 6.6 Surface Water Chemistry Ranges for Mining Impacted Streams

GEOLOGY

Sandstone	Shale	Conglomerate	Clay Layer
If highly weathered - increase in infiltration rate + potential water table contamination	If highly weathered + increased lateral movement + increase in Al and Si	Quartz pebbles + increase in Si	+ absorbs hydrogen ion + increase in suspended sediment + increase in Al and Si
Argillaceous Composition - increase in neutralization + increase in suspended sediment + increase in Al and Si	Calcareous elements + increase Ca and Mg - neutralizes acid drainage		

SEASONAL VARIATIONS

Vegetation Effects

Spring - Summer	Fall - Winter
Plant growth - decrease in N, Ca, K, P, Mg	Vegetation die off + increase in K, P, Ca, Mg, N

Climatic Effects

Winter - Spring	Summer - Fall
High water table - dilution of Ca, Mg, trace elements + increase in Si	Low flow + increase in Ca, Mg, SO_4^{2-} - decrease in N, P,
Surface runoff dominant -- controlled by land use and composition of precipitation	Ground water dominant + rain events cause surges of chemical species

LAND USE

Oil and Natural gas wells
- + increase in Cl & Na Concentrations

Agriculture
- + increase in N,

Deep Mining
- + increase in H , Fe, $SO_4$2-, CO_2

Industrial Pollution
- + increase in trace metals -- Cd, Cr, Pb, Ni, Sr, Zn

Figure 6.7 Factors Affecting Natural Stream Chemistry

Chapter 7

CONCLUSIONS AND RECOMMENDATIONS

The management staff of Big South Fork National River and Recreation Area (BISO) is currently working with other Tennessee and Kentucky state agencies in order to improve the water quality of the park streams. One of the principal contaminators of area streams is acid mine drainage from abandoned coal mines.

Using water chemistry data collected from streams affected by varying degrees of coal mining disturbance, this project investigated the relationship of sulfate, hardness and iron concentrations to acid mine drainage, proposed baseline concentration levels for unmined streams of BISO and developed a stream water chemistry model for BISO streams.

Conclusions

Acid Mine Drainage in BISO Streams

Of the five intensively studied streams, Roaring Paunch Creek was the most heavily contaminated by acid mine drainage, as it was located in the most recently mined watershed with the greatest extent of disturbance. The Roaring Paunch watershed was able to neutralize the acid mine drainage entering the stream through cation exchange and/or carbonate weathering processes. These processes caused the pH in Roaring Paunch to be higher than pH levels of unmined streams.

Generally, concentrations of constituents associated with acid mine drainage tend to decrease downstream from their point of introduction, unless additional contaminated subsurface water enters the stream at downstream locations. Ground water contaminated by deep mine drainage contains elevated levels of hydrogen, sulfate and iron (Herricks and Cairns, 1980). Because of the rise in concentrations of these elements and others, the mining contamination entering Roaring Paunch Creek near the mouth was concluded to be from abandoned deep mines and not solely from the abandoned surface mines upstream.

Puncheoncamp Fork of Williams Creek was moderately contaminated. The mines in this watershed had been abandoned for a longer period than those in the Roaring Paunch Creek watershed, and the level of contamination entering the stream had decreased as pyrite levels presumably diminished. The concentration levels of major chemical species were therefore less in Puncheoncamp Fork than in Roaring Paunch Creek. Although the amount of acid mine drainage entering the stream was lower in Puncheoncamp Fork than in Roaring Paunch Creek, Puncheoncamp Fork still had a slightly lower pH value than Roaring Paunch, and higher concentrations of aluminum, iron and manganese. Trace element concentrations in Puncheoncamp Fork were generally equal to those of Roaring Paunch Creek.

Williams Creek drains the area with the longest period (approximately thirty-six years) of mining abandonment. In this stream, the sulfate concentration at the upstream site (WL4) indicated that acid mine drainage could possibly still be entering the stream at low levels. Overall, the water chemistry of Williams Creek was less chemically concentrated than that of Line Fork, an unmined stream.

Indian Branch of Grassy Fork was determined to be more representative of natural stream chemistry in unmined BISO watersheds than Line Fork of Bear Creek. This is because, in comparison with regional watershed stream chemistry studies at Coweeta Hydrologic Laboratory and Fernow Experimental Forest, Line Fork had concentrations greatly above their annual average levels. The differences in concentrations between Indian Branch and Line Fork were presumed to be related to the differences in discharge of the two streams.

Sulfate, Hardness and Iron as Indicators of Acid Mine Drainage

Sulfate was a better indicator of the extent of mining disturbance and the age of mining abandonment than hardness or iron. Although sulfate was a good indicator of the potential for acid mine drainage contamination in a stream, it did not always reflect the actual extent of stream acidification resulting from acid mine drainage entering a stream, as shown by Roaring Paunch Creek. Hardness generally increased with the increase in mining disturbance, because of the input of sulfate increasing cation transport through a watershed. Yet, an increase in hardness alone does not necessarily indicate an impact from acid mine drainage. If elevated levels of hardness were associated with elevated levels of sulfate, then this indicated that the acid mine drainage being produced was possibly being neutralized by cation exchange and weathering processes improving the stream. Iron was not considered a good indicator of acid mine drainage because iron concentrations fluctuated inconsistently with the amount of mining disturbance, probably because concentrations were more strongly related to stream pH and local geology.

Rikard and Kunkle (1986) determined the acid mine drainage indicators in BISO to be sulfate, iron, aluminum, manganese, zinc, specific conductance and low pH. With the addition of trace element from this study, the indicators I found most directly related to acid mine drainage from surface mining were sulfate, calcium, magnesium, chloride, boron, fluorine, manganese, strontium, zinc, and conductance. Iron and aluminum were found to be good indicators of deep mining, but not surface mining because their occurrence seemed to be primarily controlled by stream pH and the local geology.

Future studies of acid mine drainage in BISO streams should continue to use sulfate, in combination with pH and hardness (or calcium and magnesium), to determine the stream's ability to neutralize the acid mine drainage. For more extensive studies of acid mine drainage, Al, F, B, Zn, Sr, Fe and Mn should also be determined, with the understanding that these are influenced by acid mine drainage, but inconsistently reflect the extent of mining disturbance because they are also affected by pH and the chemical composition of the rocks. Silicon may be used as an indicator of where the contamination is entering from, i.e., surface runoff or deep ground water.

BISO Base Flow Stream Water Chemistry Model

Concentrations of acid mine drainage parameters in BISO stream waters can be estimated based on a combination of the period of abandonment and the extent of mining as indicated in the base flow model for streams of BISO (Figure 6.5). Three different stages occur related to the acid mine drainage impacts on stream water chemistry. Initially a BISO watershed will neutralize the acidity entering streams through cation exchange and weathering processes. Once the capacity for these two processes is exhausted, the continued pyrite oxidation and production of acid mine drainage would result in lowered stream pH, causing an increase in iron, aluminum and other trace elements. The last stage is recognized by the decreasing production of acidity and by the change in the source of acid mine drainage, from primarily surface runoff to contaminated ground water. Acid mine drainage contamination continues until the ground water contamination becomes insignificant. Depending on the size of the watershed, the size of the mining disturbance, and the geologic and soils properties, these stages could occur from years to centuries.

Using the factors which influence the stream water chemistry, i.e. type of mining, age of mining, geology, seasonal fluctuations in climate and vegetation and other land use in the watershed, estimates of stream element concentrations affected by mining can be determined (Figures 6.5-6.7). In general, Ca^{2+}, Mg^{2+}, Na^{+}, SO_4^{2}, Cl^{-}, Fe, Zn, Mn, B, F and Sr concentrations are related to the recentness and the extent of mining. Elevated concentrations of Al, Si, Br, Pb, As, Se and Cr are most likely observed in currently mined locations or locations abandoned less than ten years. These elements tend to fluctuate in concentration levels as the period of mining abandonment increases.

Recommendations

Baseline Chemistry for Reclamation Projects

In determining the baseline stream chemical levels for improving water quality for recreational and aquatic activity in the BISO area, the EPA drinking water maximum allowable concentrations are suggested for all chemical species. It should be understood that iron and selenium levels may not be attainable targets for all reclamation projects because these elements were shown to have natural concentration levels above EPA acceptable limits, as in the unmined streams of Indian Branch and Line Fork. Where concentrations levels exceed the EPA maximum standard, a posted warning should alert stream users, but not prevent recreational water activities, because of the relatively minimal health risk to humans. It is also recommended that further studies be done on the natural stream chemistry in BISO and the amount of human contact expected within the contaminated streams.

Management Recommendations for Mined Watersheds

From the results found in this study, especially related to the stream water chemistry of Roaring Paunch Creek and Pauncheoncamp Fork, it appears that with good management, stream water quality can be improved in BISO. The ability to minimize the stream degradation, due to acid mine drainage input, is related to preventing direct contact of acid mine drainage with the watershed streams. There are multiple methods for achieving this goal.

1. Focus on preventing direct movement of acid mine waters into streams through use of well designed reclamation activities such as:
    a. covering open surface mine sites and coal veins with non-acid soils, these would include soil material with high base saturation and weatherable carbonates,
    b. using holding ponds to insure maximum infiltration into the soil and bedrock,
    c. redirecting overland flow paths to create the greatest distance possible between source site and stream entry site.

2. Limit activities which would accelerate water movement through deep mines.

3. Review alternatives to the proposed lake in the Bear Creek watershed, since flooding the area could potentially increase acid mine drainage into the water by limiting the natural buffering ability of the watershed.

4. In determining the stream priority list for reclamation projects, put streams affected by recent surface mining and deep mines first. Source areas closest to streams and/or in the primary water-movement paths should have the highest priority.

Stream Monitoring Recommendations for BISO Management

The following recommendations are suggested for future monitoring of BISO streams.

1. Eliminate the maximum sulfate detection limit by utilizing dilution techniques as needed.

2. Improve the minimum sulfate detection limit by utilizing an enhanced analytical procedure.

3. Keep the monthly sampling program as consistent as possible. Along with this program, which was previously designed by Rikard and Kunkle (1986), design short term projects that incorporate weather extremes such as storm events, spring thaws, or extended summer droughts. Within these short term projects, in addition to the standard monthly analysis, also analyze for the recommended trace elements, i.e. boron, fluorine, manganese, strontium and zinc. If deep mines were operated in the area or if the pH is below neutral, then include iron and aluminum in the analysis.

4. Utilize the analysis of specific constituents described in this report as related to deep mining to assess possible contamination and/or leakage from deep mines at BISO.

Chapter 8

FUTURE RESEARCH

The National Park Service will continue to coordinate further studies in Big South Fork National River and Recreation Area (BISO) to monitor the influence of mining on the stream water quality and aquatic life. I recommend the following objectives for future watershed research:

1. Sample during high discharge conditions, i.e., saturated soil periods in spring and storm events;
2. Determine whether, during storm flows, sulfate concentration peaks occur at the same time in streams affected by acid mine drainage that they do in undisturbed watershed streams.
3. Examine flow paths and the capacity of groundwater to carry acid mine drainage elements;
4. Define partial runoff source areas within the watersheds;
5. Map in detail the geology of Scott County, including the geochemical composition.

High Discharge Sampling in Spring

There are two important reasons for examining high discharge conditions in Spring. First, the chemical contribution from the entire watershed land surface to the stream water chemistry can be determined most accurately during saturated conditions, when runoff is maximized. Second, the slower movement of ground water throughout the late Fall and Winter months will increase the amount of soluble substances dissolved from the soil and rocks (Phillips and Stewart, 1990). Combining these two factors, samples collected during the spring should represent the maximum influence of the watershed on the stream chemical composition.

Storm Event Sampling

Under normal conditions a stream's base flow is composed primarily of subsurface water. During a storm flow an initial surge of surface runoff, usually containing increased amounts of suspended solids, comprises the hydrograph rising limb. Sampling during this period is important because generally at this time many of the chemical species in the stream have reached their maximum concentrations (Elwood and Turner, 1989; Trudgill, 1986). Tracers can be used to mark ground water flow into the stream versus the surface water component. In doing this, the ground and surface water component percentage can be determined for the stream. The role each component plays in transporting acid mine drainage, i.e., over the land surface versus through ground water flow, can be studied (Castro and Hornberger, in press). Learning more about the sources of stream water will provide information on whether ground or surface water most influences the watershed, and on which component contributes more to acid mine drainage in the stream. This information will aid in determining the methods to be used for improving the stream water quality.

Improved knowledge of the sulfate concentration peak, as related to a storm event on a stream disturbed by mining, would help researchers determine when to sample in order to acquire maximum sulfate levels. This is important since sulfate is one of the prime indicators of acid mine drainage.

Ground Water Movement

Numerous deep mines throughout the Big South Fork River gorge makes understanding the direction of ground water flow important for the determination of acid mine drainage transport patterns. The soils in this region have the ability to also transport acid mine drainage elements into ground water through infiltration. Contaminated ground water can influence streams either by initially introducing acid mine drainage constituents into clean surface water or by being a secondary source for streams already affected (McWhorter, 1979).

For a full watershed dynamics study, it is important to know ground water flow direction, transmissivity[4] and chemical composition, in addition to surface water characteristics. Improved knowledge of ground water characteristics will aid in understanding ground water as a transport medium for acid mine drainage and its effect on stream water at ground water discharge locations.

Partial Source Area Impacts

Knowing the locations of micro drainage sources aids in the reclamation process of a watershed. This is determined by studying the effective drainage area of a watershed. This is the portion of the watershed that contributes water and sediment to the main stream channel. The extent of the watershed contributing water sediment changes with fluctuations in ground saturation (Campbell, 1985). It is rare for all surface and subsurface locations within a watershed to contribute to the stream's chemical composition (Trudgill, 1986). Discharge into a stream is usually from microflow patterns, referred to as partial source areas of a watershed. Areas within a watershed that contribute to stream discharge consistently, because of their topographic location, soil type and land use, determine the "normal" stream chemistry (Hewlett and Hibbert, 1967).

Because of these partial source areas, most surface mined areas contribute runoff into streams only during certain saturation conditions. Those contributing the most are likely to be the source areas closest to streams, in the floodplain, or near a riparian zone. The amount of acid mine drainage entering a stream is then related to spoils pile locations and to the extent of mining disturbances with respect to the microflow drainage patterns and storm runoff through these areas. Therefore, depending on the ground saturation level at the time of water sampling, stream water chemistry may only partially represent the watershed's entire area.

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[4] The movement ability of groundwater, computed as permeability multiplied by aquifer depth.

This becomes an important factor during reclamation of the abandoned mines and for water sampling of maximum concentrations.

Geology

The geology of Scott County, Tennessee has only been mapped at a scale of 1:250,000 (USGS, 1966). The New River Basin south of BISO and McCreary County, Kentucky directly north of Scott County, have both been mapped in greater detail (1:24,000). Future detailed mapping of Scott County would improve the understanding of the specific geologic formations through which water flows en route to the streams in the southern BISO watersheds.

The geology and soils of an area play an important part in either buffering or amplifying acid mine drainage effects on the stream water chemistry. A study of the geochemical composition of the rock minerals in this area would improve understanding of which rock types are contributing the majority of the elements in the stream water chemistry.

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APPENDICES

Appendix 1

Parameters Analyzed in Previous Projects

Data File	Dates	Interval	AREA SQ. KM	Q CFS	Q CMS	VEL MS	T Deg C	ALK UEQ/L	Acid MG/L
Bakaletz, Steve	Aug. 6,20 , 1990	daily						x	
Barrass, Andy	October 24, 1988	daily							
BISO	1982-1990	monthly					x	x	
Dyer, Ken U.S. EPA	Feb.- Nov 78	monthly	x	x	x		x	x	
Eagle, Tim	May 1, 1990	daily							
Leary, Maria	October 5-7, 16,1990	daily	x	x	x		x	x	
Mills, Mike U.S.G.S.	Jan, May-89; Apr, Jul-88	monthly						x	x
O'Bara, Christopher	June, Oct. 1981	monthly		x	x		x	x	
Richardson, John	Sept. 87 - Aug. 88	monthly				x	x		
U.S.G.S., KY - Stearns	Oct. 1980 - Sept. 1988	daily	x	x	x		x	x	
U.S.G.S., TN	Oct. 1985 - Sept. 1986	daily	x	x	x		x		
Leatherwood Ford	Feb 84 - Sept 84	3-monthly	x	x	x		x		

Data File	Location of Analysis	pH LAB	NH4 UEQ/L	Ca UEQ/L	Mg UEQ/L
Bakaletz, Steve	Tenn. Tech. University, Cookeville, TN	x	x	x	x
Barrass, Andy	Tennessee State Environmental Lab, Knoxville				
BISO	Tenn. Tech. University, Cookeville, TN	x			
Dyer, Ken U.S. F.S.	Surface Mined Area Reclam. Research Unit, NFS, Berea, KY	x		x	x
Eagle, Tim	Standard Laboratories, Jacksboro, TN	x			
Leary, Maria	USGS - Doraville, GA and USDAFS - Fort Collins, CO	x	x	x	x
Mills, Mike U.S.G.S.	Kentucky Department for Natural Resources Analytical Laboratory	x	x	x	x
O'Bara, Christopher	Tenn. Tech. University, Cookeville, TN	x			
Richardson, John	Tenn. Tech. University, Cookeville, TN	x			
U.S.G.S., KY - Stearns	USGS - Arvada, CO	x			
U.S.G.S., TN	USGS - Arvada, CO	x			
Leatherwood Ford		x			

Appendix 1

Data File	Na UEQ/L	K UEQ/L	Al UMOL/L	Cl UEQ/L	SO4 UEQ/L	NO3 UEQ/L	N UMol/l	P UEQ/L	HCO3 UEQ/L	D.O. MG/L	COND UM/CM	HARD MG/L
Bakaletz, Steve	x	x	x	x	x		x				x	x
Barrass, Andy			x									
BISO				x	x							x
Dyer, Ken U.S. EPA	x	x	x	x	x	x			x		x	
Eagle, Tim			x		x						x	x
Leary, Maria	x	x	x	x	x	x		x			x	
Mills, Mike U.S.G.S.	x	x	x	x	x	x	x	x		x	x	x
O'Bara, Christopher			x		x					x	x	x
Richardson, John		x	x							x	x	x
U.S.G.S., KY - Stearns										x	x	x
U.S.G.S., TN										x	x	
Leatherwood Ford										x	x	

Data File	TURB NTU	SS MG/L	DS MG/L	Ag UEQ/L	As UEQ/L	B UEQ/L	Ba UEQ/L	Be UEQ/L	Br UEQ/L	Cd UEQ/L	Co UEQ/L	Cr UEQ/L
Bakaletz, Steve	x	x			x					x		x
Barrass, Andy					x					x		x
BISO	x											
Dyer, Ken U.S. F.S.	x		x			x	x	x			x	
Eagle, Tim			x		x							x
Leary, Maria					x	x	x		x	x		x
Mills, Mike U.S.G.S.	x	x	x	x	x		x	x		x		x
O'Bara, Christopher	x	x										
Richardson, John	x											x
U.S.G.S., KY - Stearns	x	x	x									
U.S.G.S., TN	x	x										
Leatherwood Ford		x										

Appendix 1

Data File	Cu UEQ/L	F UEQ/L	Fe UEQ/L	Hg UEQ/L	Li UEQ/L	Mn UEQ/L	Mo UEQ/L	Ni UEQ/L	Org C.	Pb UEQ/L	Se UEQ/L
Bakaletz, Steve	x	x	x	x		x		x		x	
Barrass, Andy	x		x	x		x		x		x	
BISO											
Dyer, Ken U.S. EPA	x		x		x	x		x		x	
Eagle, Tim			x			x					
Leary, Maria	x	x	x			x	x	x		x	x
Mills, Mike U.S.G.S.	x	x	x	x		x		x	x	x	x
O'Bara, Christopher			x								
Richardson, John	x		x			x				x	
U.S.G.S., KY - Stearns											
U.S.G.S., TN											
Leatherwood Ford											

Data File	Si MG/L	Sr UEQ/L	Ti UEQ/L	Zn UEQ/L
Bakaletz, Steve				x
Barrass, Andy				x
BISO				
Dyer, Ken U.S. F.S.	x	x		x
Eagle, Tim				x
Leary, Maria	x	x	x	x
Mills, Mike U.S.G.S.				x
O'Bara, Christopher				
Richardson, John				
U.S.G.S., KY - Stearns				
U.S.G.S., TN				
Leatherwood Ford				

Appendix 2 Methods and Detection Limits in Data Sets

INSTRUMENTS USED

Atomic Absorption, Chel-ext (AAC)
Atomic Absorption, Cold Vapor (AACV)
Atomic Absorption, Direct (AAD)
Atomic Absorption, Hydride (AAH)
Atomic Absorption, Flameless (AAF)
Atomic Absorption, Graphite Furnace (AAG)
Atomic Emmission, DC plasma (AE)
Bausch and Lomb Spectronic 20 Spectrophotometer (BLS)
Colorimetry, Discrete Analyzer (CDA)
Dionex Ion Chromatography, Auto (DIC)
Electrometry, Glass Electrode, Auto (EGE)
Electrometry, Automated (EA)
Inductively Coupled Plasma (ICP)
Ion Chromatography with Conductivity Detection (ICC)
Mettler Autotitrator, 0.02 Sulfuric Acid for 25ml (MAT)
Nephelometric Turbidity Units (NTU)
Spectraspan III Emmission Spectrometer (SES)
Technicon Auto Analyzer II (TAA)
Titrimetry, Electrometric as Calcium Carbonate (TIE)
Turbidimetric Technique, Hach Chemical Co. MODEL 16800 (TTH)
Wheatstone Bridge Conductivity Meter (WBC)
Wet Oxidation (WO)
Yellow Springs Instruments (YSI)

OTHER ABBREVIATIONS

DCT - Detection Limits, MG/L
DVT - Deviation Levels, MG/L
DPL - Detection Percision Level, MG/L

REFERENCES FOR ANALYSES

National Water Quality Lab Service Catalog
U.S.G.S. Open File Report 86-232
Reston , VA 22092

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16th Ed. APHA - AWWA - WPCF
Washington, D.C. 1985

Methods for Chemical Analysis of Water and Wastes
EPA -600/4-79-020
Cincinnati, OH. 1983

Field and Laboratory Methods Applicable to Overburdens and Mine Soils
EPA-600/2-78-054
Cincinnati, OH. 1978

Elements	Conversion From MG/L to UEQ/L	Leary, Maria		
		METHO	DTC	DVT
Alkalinity	MG/L*2/100.19*1000			
Dis. Oxygen				
pH		EGE	4	0.01
Conductivity				
Hardness				
Turbidity				
Sus. Solids				
Dis. Solids				
Acidity				
Aluminum	MG/L/26.98*1000	ICP	0.104	0.4%
Ammonia	MG/L*1/14.007*1000	DIC	3 uS -N	10.0%
Arsenic	MG/L*3/74.92*1000	ICP	0.014	10.0%
Barium	MG/L*2/137.34*1000	ICP	0.02	2.0%
Beryllium	MG/L*2/9.012*1000	ICP	0.003	10.0%
Bicarbonate	MG/L*1/61.019*1000			
Boron	MG/L*3/10.81*1000	ICP	0.005	6.0%
Bromide	MG/L*1/79.904*1000	DIC	10 uS	10.0%
Cadmium	MG/L*2/112.4*1000	ICP	0.004	10.0%
Calcium	MG/L*2/40.08*1000	ICP	0.01	0.7%
Chloride	MG/L*1/35.45*1000	DIC	10 uS	10.0%
Chromium	MG/L*3/51.996*1000	ICP	0.007	10.0%
Colbalt	MG/L*2/58.9332*1000	ICP	0.007	10.0%
Copper	MG/L*3/63.546*1000	ICP	0.006	10.0%
Floride	MG/L*1/18.9984*1000	DIC	10 uS	10.0%
Iron	MG/L*2/55.847*1000	ICP	0.007	10.0%
Lead	MG/L*4/207.2*1000	ICP	0.04	10.0%
Lithium	MG/L*1/6.941*1000			
Magnesium	MG/L*2/24.305*1000	ICP	0.1	8.0%
Manganese	MG/L*2/54.938*1000	ICP	0.002	1.0%
Mercury	MG/L*2/200.59*1000			
Molybdenum	MG/L*3/95.94*1000	ICP	0.003	10.0%
Nickel	MG/L*2/58.71*1000	ICP	0.01	10.0%
Nitrate	MG/L*1/62.0067*1000	DIC	10 uS -N	0.3%
Nitrogen	MG/L *3/14.007*1000			
Organic Carbon				
Phosphate	MG/L*3/30.974*1000	DIC	3 uS -P	3.0%
Potassium	MG/L*1/39.102*1000	ICP	0.5	5.0%
Selenium	MG/L*2/78.96*1000	ICP	0.075	10.0%
Silicon		ICP	0.27	0.1%
Silver	MG/L*3/107.868*1000			
Sodium	MG/L*1/22.989*1000	ICP	0.1	8.4%
Strontium	MG/L*2/87.62*1000	ICP	0.001	1.1%
Sulfate	MG/L*2/96.06*1000	DIC	10 uS	0.1%
Titanium	MG/L*4/47.90*1000	ICP	0.001	10.0%
Zinc	MG/L*2/65.37*1000	ICP	0.8	1.3%

Elements	Barrass, Andy			Bakaletz, Steve		
	METHOD	DTC	DVT	METHOD	DTC	DVT
Alkalinity				Gram titration		
Dis. Oxygen						
pH				Electro. meter		
Conductivity				WBC		
Hardness				ICP		
Turbidity				Hach Dig. Titra.		
Sus. Solids				Dried at 85 degrees C		
Dis. Solids						
Acidity						
Aluminum	AAD		22.50%	ICP	0.04	
Ammonia				Colorimetric		
Arsenic	AAD	<.194	13.80%	ICP	<.005	
Barium						
Beryllium						
Bicarbonate						
Boron						
Bromide						
Cadmium	AAD	<.01		ICP	<.005	
Calcium				ICP	0.01	
Chloride				ICC		
Chromium	AAC			ICP	<.005	
Colbalt						
Copper	AAD			ICP	<.01	
Floride				Colorimetric, SPADNS		
Iron	AAD			ICP	0.007	
Lead	AAC			ICP	<.001	
Lithium						
Magnesium				ICP	0.03	
Manganese	AAD			ICP	0.002	
Mercury	AACV			AAH		
Molybdenum						
Nickel	AAD			ICP	0.015	
Nitrate						
Nitrogen				Persulfate Method		
Organic Carbon						
Phosphate						
Potassium				ICP	0.01	
Selenium						
Silicon				ICP	0.27	
Silver						
Sodium				ICP	0.03	
Strontium						
Sulfate	Gravimetric		4.70%	ICC		
Titanium						
Zinc	AAD			ICP	0.002	

Elements	BISO		
	METHOD	DTC	DVT
Alkalinity	Hach dig. titra. using sulfate and		
Dis. Oxygen	bromcresol green and red		
pH	YSI Model 58 meter		
Conductivity	Orion Model 399A/F meter		
Hardness	Beckman Model RB-5-6 meter		
Turbidity	Hach Dig. Titra.		
Sus. Solids	Hach Model 2100 Turbidimeter		
Dis. Solids			
Acidity			
Aluminum			
Ammonia			
Arsenic			
Barium			
Beryllium			
Bicarbonate			
Boron			
Bromide			
Cadmium			
Calcium			
Chloride			
Chromium			
Colbalt			
Copper			
Floride			
Iron	BLS		
Lead			
Lithium			
Magnesium			
Manganese	BLS		
Mercury			
Molybdenum			
Nickel			
Nitrate			
Nitrogen			
Organic Carbon			
Phosphate			
Potassium			
Selenium			
Silicon			
Silver			
Sodium			
Strontium			
Sulfate	BLS		
Titanium			
Zinc			

Elements	**O'Bara, Christopher**			**Dyer, Ken U.S. EPA**		
	METHOD	DTC	DVT	METHOD	DTC	DVT
Alkalinity	Gram titration			MAT	pH 5.64	
Dis. Oxygen	Winkler					
pH	Electro. meter			Markson digi-sense Meter		
Conductivity	WBC			YSI		+-30%
Hardness	ICP					
Turbidity	Nephlometric			BLS	450 nm	
Sus. Solids	Dried at 85 degrees C					
Dis. Solids				alk./acidity - all ions		
Acidity						
Aluminum	ICP	0.004		SES	0.2	+-10%
Ammonia						
Arsenic						
Barium				SES	0.5	
Beryllium				SES	0.01	+-0.01
Bicarbonate				Alk., pH, & Ionic strength		
Boron				SES	0.05	+-10%
Bromide						
Cadmium						
Calcium				SES	0.05	+-10%
Chloride				TAA	0.2	+-.42%
Chromium						
Colbalt				SES	0.1	+-20%
Copper				SES	0.02	+-20%
Floride						
Iron	ICP	0.007		SES	0.05	+-10%
Lead				SES	0.1	
Lithium				SES	0.05	+-25%
Magnesium				SES	0.05	+-10%
Manganese				SES	0.05	+-20%
Mercury						
Molybdenum				SES	0.25	
Nickel				SES	0.03	+-10%
Nitrate	CDA			TAA	.04 N	0.31%
Nitrogen						
Organic Carbon						
Phosphate						
Potassium				SES	0.1	+-10%
Selenium						
Silicon	ICP	0.27		SES	0.1	+-20%
Silver						
Sodium				SES	0.05	+-10%
Strontium				SES	0.03	+-20%
Sulfate	ICC			TTH		+-30%
Titanium						
Zinc				SES	0.3	+-10%

Elements	Richardson, John METHO	 DTC	 DVT	Eagle, Tim METHOD	 DTC	 DVT
Alkalinity						
Dis. Oxygen	YSI					
pH	Orion SA 250			Meter		
Conductivity	Beckman Meter		+-2%	Meter		
Hardness	Hach Digital Tritrator			ICP		
Turbidity	TTH					
Sus. Solids						
Dis. Solids				Gravimetric		
Acidity						
Aluminum	ICP	Mar-<.1 May-<.02		AAD		22.50%
Ammonia						
Arsenic				AAD	<2.0	13.80%
Barium						
Beryllium						
Bicarbonate						
Boron						
Bromide						
Cadmium	ICP	<.01				
Calcium						
Chloride						
Chromium	ICP	<.01		AAC	<10.0	
Colbalt						
Copper	ICP	<.01				
Floride						
Iron	ICP	0.007		AAD		
Lead	ICP	<.05				
Lithium						
Magnesium						
Manganese	ICP	0.002		AAD		
Mercury						
Molybdenum						
Nickel	ICP	<0.01				
Nitrate						
Nitrogen						
Organic Carbon						
Phosphate						
Potassium	ICP	Mar <1.0				
Selenium						
Silicon						
Silver						
Sodium						
Strontium						
Sulfate				Gravimetric		4.70%
Titanium						
Zinc	ICP	<.01		AAD		

Elements	**Mills, Mike U.S.G.S.**			**U.S.G.S.**		
	METHOD	DTC	DPL	METHOD	DTC	DPL
Alkalinity	TIE			TIE		
Dis. Oxygen				Winkler		
pH	EGE	4	0.01	EGE	4	0.01
Conductivity	EA	1	<1	EA	1	<1
Hardness						
Turbidity				Nephlometric		
Sus. Solids						
Dis. Solids						
Acidity	TIE	0.1	0.09			
Aluminum	AE	0.1				
Ammonia	CDA	0.01	0.02			
Arsenic	AAH	<0.001	0.05			
Barium	AE	<0.001	0.16			
Beryllium	AE	<0.001	0.15			
Bicarbonate						
Boron						
Bromide						
Cadmium	AAG	0.001	0.02			
Calcium	AAD	0.01	0.07			
Chloride	IC	0.01	0.04			
Chromium	ADG	0.005	0.01			
Colbalt						
Copper	AAG	0.0005	0.02			
Floride	IC	<0.1				
Iron	AE	<.001	0.06			
Lead	AAG	<.002	0.03			
Lithium						
Magnesium	AAD	0.01	0.04			
Manganese	AAG	0.002	0.06			
Mercury	AAF	0.0001	0.04			
Molybdenum						
Nickel	AAG	0.001	0.01			
Nitrate	CDA	0.01	0.08			
Nitrogen	ICA	0.01	0.04			
Organic Carbon	WO	0.1	0.04			
Phosphate						
Potassium	AAD	0.1	0.14			
Selenium	AAH	0.001	0.04			
Silicon						
Silver	AAC	0.001	>.14			
Sodium	AAD	0.01	0.01			
Strontium						
Sulfate	ICA	0.01	0.03			
Titanium						
Zinc	AAG	0.0005	0.08			

Appendix 3

October 1990 Sampling Data Analysis

SITE	LATITUDE			LONGITUDE			Elev	AREA	DATE	Q	Q	Water Temp
	DEG	MIN	SEC	DEG	MIN	SEC	Meters	Hectares		CFS	L/S	Deg C
LEARY, IB	36	33	16	84	28	58	413	77	10/7/90	0.1	3.44	13.5
LEARY, LF	36	35	50	84	32	30	417	1096	10/5/90	0.0	0.08	15.0
LEARY, PU1	36	34	36	84	35	53	269	2903	10/7/90	0.9	25.60	14.0
LEARY, PU1.2	36	34	36	84	35	53	269	2903	10/7/90	0.9	25.60	14.0
LEARY, PU3	36	33	46	84	33	16	407	1658	10/5/90	0.4	10.83	14.0
LEARY, PU3.2	36	33	46	84	33	16	407	1658	10/16/90	0.1	2.83	13.5
LEARY, PU4	36	32	30	84	33	14	420	529	10/5/90	0.1	1.97	14.5
LEARY, RP1	36	40	52	84	32	34	269	12567	10/6/90	36.0	1020.45	14.5
LEARY, RP3	36	40	5	84	29	47	335	10992	10/6/90	5.5	154.22	14.0
LEARY, RP3.1	36	40	5	84	29	47	335	10992	10/6/90	5.5	154.22	14.5
LEARY, RP4	36	37	36	84	28	58	364	8257	10/6/90	3.7	103.75	14.0
LEARY, RP5	36	36	51	84	29	26	367	6477	10/6/90	1.7	48.00	14.0
LEARY, WL2	36	34	30	84	35	58	269	2735	10/7/90	1.0	26.82	14.0
LEARY, WL3	36	31	54	84	36	10	420	1432	10/7/90	0.2	4.45	14.0
LEARY, WL4	36	31	14	84	35	18	427	897	10/5/90	0.1	2.39	14.5

Note: * indicates sample concentration was below the minimum measuring limit

Appendix 3

SITE	pH Field	pH LAB	COND μM/CM	Alkalinity MG/L	ALK μEQ/L	Ammonia MG/L	NH4-N μEQ/L	Calcium MG/L	Ca μEQ/L	Magnesium MG/L	Mg μEQ/L
LEARY, IB	5.9	5.83	10	10.3	205.6	0.00	0.00	0.48	23.94	0.27	22.22
LEARY, LF	7.3	6.41	70	450.8	8998.9	0.06	42.84	4.84	241.42	1.96	161.31
LEARY, PU1	7.3	7.12	41	221.0	4411.6	0.00	0.00	2.79	139.17	1.39	114.40
LEARY, PU1.2		7.16	40	218.7	4365.7	0.00	0.00	2.72	135.67	1.40	115.22
LEARY, PU3	7.1	7.25	130	531.3	10605.9	0.00	0.00	8.20	409.02	2.75	226.32
LEARY, PU3.2	6.9	7.01	121	365.6	7298.1	0.00	0.00	10.80	538.70	4.80	395.04
LEARY, PU4	7.1	6.52	108	836.6	16700.3	0.64	45.70	8.95	446.43	3.15	259.25
LEARY, RP1	7.7	7.20	188	418.1	8346.1	0.00	0.00	15.19	758.18	5.60	460.88
LEARY, RP3	7.5	7.43	198	720.9	14390.7	0.00	0.00	18.99	947.72	8.70	716.01
LEARY, RP3.1		7.56	196	721.9	14410.6	0.00	0.00	15.99	798.08	7.60	625.48
LEARY, RP4	7.5	7.30	311	447.2	8927.0	0.00	0.00	23.99	1197.12	16.10	1325.03
LEARY, RP5	7.7	7.48	201	775.2	15474.6	0.10	7.14	16.99	847.96	8.90	732.47
LEARY, WL2	7.4	7.59	38	237.1	4733.0	0.00	0.00	3.10	154.63	1.27	104.52
LEARY, WL3	7.1	7.35	61	322.5	6437.8	0.00	0.00	4.95	246.91	1.78	146.49
LEARY, WL4	6.6	7.03	52	129.6	2587.1	0.04	2.86	3.17	158.12	1.45	119.33

Appendix 3

SITE	Sodium	Na	Potassium	K	Phosphate	PO4-P	Aluminum	Al	Chloride	Cl
	MG/L	μEQ/L	MG/L	μEQ/L	MG/L	μEQ/L	MG/L	μMOL/L	MG/L	μEQ/L
LEARY, IB	0.49	21.31	0.58	14.85	0.000	0.0	0.24	8.75	0.52	29.68
LEARY, LF	2.48	107.83	5.34	136.70	0.000	0.0	0.50	18.46	3.36	207.78
LEARY, PU1	2.04	88.70	1.50	38.40	0.000	0.0	0*	0*	2.28	118.73
LEARY, PU1.2	2.01	87.39	1.51	38.66	0.000	0.0	0.14	5.37	2.70	118.73
LEARY, PU3	13.89	604.37	2.94	75.26	0.003	0.3	0.54	20.05	4.16	252.31
LEARY, PU3.2	3.30	143.48	3.89	99.58	0.000	0.0	0.00	0.07	3.75	237.47
LEARY, PU4	4.20	182.62	3.75	96.00	0.000	0.0	0.14	5.30	4.38	267.15
LEARY, RP1	9.10	395.67	2.90	74.24	0.003	0.3	0.45	16.83	11.70	296.83
LEARY, RP3	8.20	356.54	4.00	102.40	0.003	0.3	0.18	6.52	10.40	326.52
LEARY, RP3.1	7.90	343.50	3.50	89.60	0.003	0.3	0.18	6.82	10.40	311.70
LEARY, RP4	3.30	143.48	6.11	156.16	0.003	0.3	0.22	8.01	2.21	445.25
LEARY, RP5	2.90	126.09	3.70	94.72	0.003	0.3	0.25	9.19	2.90	371.04
LEARY, WL2	0.87	37.83	2.09	53.50	0.000	0.0	0.13	4.71	1.46	89.05
LEARY, WL3	1.56	67.83	3.75	96.00	0.000	0.0	0.25	9.41	3.31	148.42
LEARY, WL4	1.27	55.22	3.02	77.31	0.000	0.0	0.26	9.53	3.35	103.89

Appendix 3

SITE	Iron MG/L	Fe µEQ/L	Nitrate MG/L	NO3-N µEQ/L	Sulfate MG/L	SO4 µEQ/L	Arsenic MG/L	As µEQ/L	Barium MG/L	Ba µEQ/L	Boron MG/L	B µEQ/L
LEARY, IB	0.20	7.00	0.00	0.00	2.01	41.87	0*	0*	0.01	0.19	0.02	6.38
LEARY, LF	0.57	20.24	0.00	0.00	5.59	116.46	0.00	0.12	0.03	0.42	0.03	9.44
LEARY, PU1	0.10	3.62	0.00	0.00	4.08	85.00	0*	0*	0.01	0.15	0.01	3.89
LEARY, PU1.2	0.05	1.88	0.00	0.00	4.10	85.42	0.04	1.64	0.01	0.19	0.02	6.38
LEARY, PU3	0.54	19.32	0.12	8.57	4.53	94.37	0.01	0.40	0.02	0.28	0.03	6.94
LEARY, PU3.2	0.55	19.85	0.00	0.00	32.14	669.57	0*	0*	0.02	0.35	0.05	14.71
LEARY, PU4	2.79	99.84	0.11	7.85	6.53	136.04	0.00	0.00	0.04	0.57	0.08	23.03
LEARY, RP1	3.18	113.91	0.02	1.43	48.20	1004.15	0.05	1.96	0.03	0.44	0.05	13.04
LEARY, RP3	0.13	4.51	0.01	0.71	44.40	924.99	0.06	2.28	0.03	0.42	0.04	11.38
LEARY, RP3.1	0.07	2.40	0.01	0.71	44.70	931.24	0.05	1.80	0.03	0.41	0.04	11.66
LEARY, RP4	0.11	3.95	0.00	0.00	119.90	2497.88	0.06	2.20	0.03	0.50	0.04	12.21
LEARY, RP5	0.12	4.15	0.00	0.00	55.10	1147.90	0.05	2.00	0.02	0.29	0.04	12.21
LEARY, WL2	0.28	10.09	0.01	0.71	3.42	71.25	0*	0*	0.03	0.39	0.02	5.83
LEARY, WL3	0.43	15.51	0.25	17.85	5.70	118.75	0.00	0.04	0.03	0.36	0.03	7.49
LEARY, WL4	0.12	4.44	1.00	71.40	6.10	127.08	0.01	0.28	0.03	0.50	0.03	8.88

Appendix 3

SITE	Bromide	Br	Cadmium	Cd	Chromium	Cr	Copper	Cu	Fluoride	F	Lead	Pb
	MG/L	µEQ/L	MG/L	µEQ/L	MG/L	µEQ/L	MG/L	µEQ/L	MG/L	µEQ/L	MG/L	µEQ/L
LEARY, IB	0.13	1.63	0.00	0.07	0.02	1.15	0.02	1.13	0.02	1.05	0.07	1.39
LEARY, LF	0.49	6.13	0.00	0.05	0.02	1.33	0.03	1.27	0.14	7.37	0.07	1.43
LEARY, PU1	0.16	2.00	0*	0*	0*	0*	0.02	0.99	0.08	4.21	0*	0*
LEARY, PU1.2	0.05	0.63	0.00	0.07	0.01	0.81	0.02	0.99	0.08	4.21	0.06	1.14
LEARY, PU3	38.00	475.61	0.00	0.05	0.01	0.81	0.01	0.66	0.17	8.95	0.04	0.83
LEARY, PU3.2	0.08	1.00	0*	0*	0*	0*	0*	0.00	0.16	8.42	0*	0*
LEARY, PU4	0.33	4.13	0.00	0.02	0.01	0.52	0.01	0.38	0.18	9.47	0.03	0.52
LEARY, RP1	0.24	3.00	0.01	0.11	0.02	0.92	0.02	0.80	0.20	10.53	0.10	1.89
LEARY, RP3	0.20	2.50	0.01	0.09	0.02	0.92	0.02	0.80	0.22	11.58	0.09	1.68
LEARY, RP3.1	0.35	4.38	0.00	0.07	0.02	1.04	0.01	0.61	0.21	11.05	0.07	1.37
LEARY, RP4	0.22	2.75	0.00	0.07	0.02	0.92	0.01	0.66	0.30	15.79	0.07	1.33
LEARY, RP5	0.13	1.63	0.01	0.11	0.02	1.27	0.02	0.99	0.25	13.16	0.10	1.93
LEARY, WL2	0.04	0.50	0.00	0.05	0.01	0.75	0.01	0.61	0.06	3.16	0.04	0.79
LEARY, WL3	0.34	4.26	0.00	0.05	0.03	1.62	0.03	1.42	0.10	5.26	0.07	1.39
LEARY, WL4	0.37	4.63	0.00	0.07	0.02	0.92	0.02	1.13	0.07	3.68	0.05	1.04

Appendix 3

SITE	Manganese	Mn	Molybdenum	Mo	Nickel	Ni	Selenium	Se	Silicon	Strontium	Sr
	MG/L	μEQ/L	MG/L	μEQ/L	MG/L	μEQ/L	MG/L	μEQ/L	μmol/L	MG/L	μEQ/L
LEARY, IB	0.03	1.02	0.00	0.03	0.01	0.27	0.04	0.91	67.65	0.01	0.11
LEARY, LF	0.04	1.49	0.00	0.06	0.01	0.24	0.07	1.82	74.41	0.02	0.34
LEARY, PU1	0.05	1.82	0*	0*	0*	0*	0*	0*	75.13	0.02	0.41
LEARY, PU1.2	0.01	0.47	0.00	0.03	0.01	0.20	0.06	1.47	60.88	0.01	0.30
LEARY, PU3	0.14	5.13	0.00	0.06	0.01	0.24	0.05	1.19	82.25	0.03	0.57
LEARY, PU3.2	0.71	25.81	0.00	0.00	0.00	0.03	0.01	0.20	75.13	0.04	0.96
LEARY, PU4	1.14	41.50	0*	0*	0.01	0.17	0.02	0.48	70.50	0.03	0.78
LEARY, RP1	0.14	5.13	0.01	0.25	0.01	0.48	0.04	1.11	77.62	0.10	2.33
LEARY, RP3	0.04	1.57	0.01	0.22	0.02	0.51	0.07	1.72	50.56	0.09	2.01
LEARY, RP3.1	0.03	0.98	0.01	0.16	0.01	0.41	0.03	0.73	49.13	0.09	2.03
LEARY, RP4	0.18	6.59	0.01	0.19	0.02	0.72	0.05	1.17	66.23	0.10	2.28
LEARY, RP5	0.14	4.91	0.01	0.25	0.01	0.48	0.07	1.77	61.24	0.08	1.71
LEARY, WL2	0.01	0.36	0.00	0.03	0.00	0.07	0.03	0.71	60.88	0.02	0.34
LEARY, WL3	0.03	1.16	0.00	0.13	0.01	0.37	0.03	0.76	64.09	0.02	0.34
LEARY, WL4	0.02	0.62	0.00	0.03	0.01	0.37	0.04	1.04	52.34	0.02	0.39

Appendix 3

SITE	Titanium MG/L	Ti μEQ/L	Zinc MG/L	Zn μEQ/L
LEARY, IB	0.01	0.92	0.25	7.65
LEARY, LF	0.02	1.84	0.24	7.37
LEARY, PU1	0.04	3.09	0.31	9.61
LEARY, PU1.2	0.01	0.84	0.23	7.04
LEARY, PU3	0.02	1.42	0.27	8.32
LEARY, PU3.2	0.00	0.00	0.30	9.12
LEARY, PU4	0.01	0.50	0.27	8.17
LEARY, RP1	0.01	0.75	0.41	12.51
LEARY, RP3	0.01	0.67	0.41	12.57
LEARY, RP3.1	0.01	0.58	0.41	12.67
LEARY, RP4	0.01	0.67	0.42	12.88
LEARY, RP5	0.01	0.92	0.41	12.57
LEARY, WL2	0.01	0.58	0.25	7.74
LEARY, WL3	0.01	1.09	0.20	6.24
LEARY, WL4	0.01	0.92	0.21	6.55

VITA

Maria Christine Leary was born in Detroit, Michigan on December 3, 1963 to Jim and Joan Leary. She is the third of five children. She attended Farmington schools until her senior year of high school, when she moved to Adrian, Michigan, her current permanent residence.

Desiring first hand life experience, she attended four universities to better understand the geography of the United States. Those universities are: Oakland University in Rochester, Michigan, Indiana University of Pennsylvania, California State University, Chico, and Michigan State University, in East Lansing.

After finishing her Geography degree she worked and traveled in the Southwest for a year, then managed the family-owned TCBY frozen yogurt store, where she earned enough money to learn to fly private planes and travel to the Soviet Union.

She accepted the offer from the University of Tennessee, Knoxville Geography Department to study there beginning in August 1989. She completed her research and graduated in December 1991.

Upon finishing this degree, she plans to continue to travel internationally, primarily in Australia before becoming employed full time, and continuing to live an exuberant life.