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INFLUENCES OF ACID MINE DRAINAGE ON WATER CHEMISTRY OF BLACKWATER RIVER WATERSHED

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The Department of Chemistry
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Master of Science

By

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TO MY DEAR FAMILY

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ABSTRACT

Acidic mine drainage flow from active and abandoned coal mines has been a major source of water pollution in the Appalachian Mountain region of the eastern USA. Water samples were collected and analyzed from Blackwater River watershed during 2 years (September 1996 – May 1998). The water quality measurements determined that the Beaver Creek and North Fork tributaries were affected by acid mine drainage but not Yellow Creek. Beaver Creek and North Fork stations had high sulfate and manganese markers of acid mine drainage, whereas Yellow Creek was slightly acidic with low sulfate and manganese. North Fork was the primary source of acid mine drainage in the watershed in spite of attempts at remediation. Slightly elevated aluminum concentration downstream showed signs of influence of acid mine drainage by dispersion of metals. Lastly, the relation of iron concentration with humic acid of Black Bear stations differed with season. This change may be due to increased iron influx in the Spring.

I. Introduction

A. Main Characteristics of Coal

Coal is an organic substance, primarily carbon with varying proportions of hydrogen, oxygen, nitrogen, and sulfur. Oxygen is present mainly in carboxyl, ketone, hydroxyl (phenolic and alcoholic) and methoxy groups, but the distribution of these functional groups varies with rank, as described below. Nitrogen is found in amines and in aromatic rings (e.g. pyridyl units). Sulfur is found in thiols, sulfides and aromatic rings (e.g. thiophenic units). Sulfur is a common constituent of coal in inorganic form, usually as pyrite. Also, coals are usually classified as either humic or sapropelic. Humic coals are formed mainly from vascular plant remains. They tend to be bright, exhibit stratification and go through a peat stage involving humification (i.e. formation of humic material). The major organic components derive from the humification of woody tissue and have a lustrous, black/dark-brown appearance. In contrast, the less common sapropelic coals are not stratified macroscopically and are dull. They are formed from fairly fine grained organic muds in quiet, oxygen-deficient shallow waters. Normally they do not go through a peat stage but follow the diagenetic path of hydrogen-rich kerogens (polymeric organic material from which hydrocarbons are produced with increasing burial and heating) (1,2).

B. Acid Mine Drainage Chemistry in Aquatic Environment

When mineral deposits that contain sulfides are mined, they have the potential to produce acid mine drainage (AMD). This includes the mining of coal, copper, gold, silver, lead and uranium. Coals and shales of marine origin tend to contain higher concentrations of sulfide than strata from freshwater palaeoenvironments. Chemically, pyrite, the most important mineral, is iron disulfide (FeS_2). Marcasite, an orthorhombic polymorph of FeS_2, is more reactive than pyrites. Variations in pyrite morphology such a crystallinity, particle size and reactivity all affect its breakdown; in particular, crystalline forms are less subject to weathering and oxidation than amorphous forms (1,3).

Upon exposure to oxidizing conditions, the sulfide minerals oxidize in the presence of water and oxygen to form highly acidic, sulfate-rich drainage. Metal composition and concentrations depend on the type of sulfide mineral and the amount present. In the Appalachian coal fields, the oxidation of iron disulfides and subsequent conversion to hydrogen ions occur through several reactions. The following four chemical equations are accepted to explain the processes.

$$FeS_2 + 7/2\ O_2 + H_2O = Fe^{+2} + 2\ SO_4^{-2} + 2\ H^+ \qquad [1]$$

$$Fe^{+2} + 1/4\ O_2 + H^+ = Fe^{+3} + 1/2\ H_2O \qquad [2]$$

$$Fe^{+3} + 3\ H_2O = Fe(OH)_3 + 3\ H^+ \qquad [3]$$

$$FeS_2 + 14\ Fe^{+3} + 8H_2O = 15\ Fe^{+2} + 2\ SO_4^{-2} + 16\ H^+ \qquad [4]$$

In reaction 1, iron sulfide is oxidized thereby releasing ferrous iron (the reduced form of iron), sulfate, and acidity. Ferrous iron in reaction 2 can be oxidized to form ferric iron. Ferric iron can then either be hydrolyzed and form hydroxide and acidity (reaction 3), or it can directly attack pyrite and act as a catalyst in generating much greater amounts of ferrous iron, sulfate, and acidity (reaction 4) (1,3,4).

It is clear from these reactions that the pyrites can remain in their reduced state in undisturbed strata as long as they are anaerobic. While there are a few cases of naturally occurring acid streams, most occur as a result of mining activities (1,3).

Ascertaining which is the rate limiting step has been the subject of some controversy. It was considered that the reaction of FeS_2 and O_2 (reaction 1) was the rate limiting step (1). In

1970, Singer and Stumn were able to show that it was the oxidation of the ferrous iron (iron (II) - reaction 2) and that it was therefore irrelevant whether the FeS_2 was pyrite or marcasite. Reaction 2 is the rate limiting step because ferrous iron conversion to ferric ion is rather slow under abiotic (or strictly chemical) conditions. But iron-oxidizing bacteria, namely *Thiobacillus ferrooxidans*, greatly enhance and accelerate iron oxidation which in turn greatly speeds acid generation (3). Under these biotic conditions, acid generation is increased up to a million times (4).

Acidity is caused by the liberation of hydrogen ions (H^+) in all of the reaction steps except reaction 2. Production of acid mine drainage can occur long after mines have been abandoned if piles of waste rock are in contact with air and water (1). Acidity is commonly measured by pH values, which are easy to collect and compare. pH is an intensity factor, measuring the concentration (or, more strictly, activity) of hydrogen ions whereas what is most important in situations with acid mine drainage is not the concentration alone but the availability of hydrogen protons; in other words, their excess over other ions. This quantity is referred to as 'total acidity' and is reported in the same units as alkalinity (usually mg/L $CaCO_3$) (3). Moreover, the bright orange color water and the stains on the rocks in streams are called "Yellow-Boy," or ferric hydroxide formed during reaction 3 above (4).

C. Effects of Acid Mine Drainage on the Biota

Through the decades, thousands of acres of land were disturbed in surface mining operations and miles of underground workings (tunnels) in deep mines were abandoned as the coal was mined out. Hundreds of miles of streams were contaminated with mine drainage and sediment, and the acres of abandoned surface-mined land presented a scar on the landscape.

Some of the worst degradation has occurred in the Appalachian Coal Region. This very important environmental issue is facing the mining industry and West Virginia today (4,5).

Acid mine drainage impacts stream and river ecosystems through acidity, ferric ion (Fe^{3+}) precipitation, oxygen depletion and release of metals associated with coal and metal mining such as aluminum (Al^{3+}), zinc (Zn^{2+}) and manganese (Mn^{2+}) (7-10).

There is a general agreement that under conditions of high acidity there is a drastic reduction in the number of species of blue-green algae, bryophytes and higher plants, invertebrates and fish; however, in many of the studies those species which are able to tolerate the acidity thrive in the absence of competition and predators (1,7-10).

A few highly specialized organisms are able to survive in the most highly acidic environments. Prime among these is a flagellated single celled organism (*Euglena mutabilis)*, by far and away the species most often recorded as abundant in acid mine drainage. However, it is not exclusively confined to this habitat as it has been reported from non acid mine drainage affected localities (1). Nonetheless, it is particularly well suited to the extreme acidic conditions encountered in some acid mine drainages, with some growth detectable in the laboratory at pH as low as 1.3 (1,8). There are a variety of difficulties facing any autotrophic organism which grows in highly acidic environments: concentrations of bicarbonate are either very low or non-existent, there are difficulties in maintaining a constant internal pH and there are often high concentrations of heavy metals. On the other hand, organisms which can overcome these problems may face relatively little competition for resources. Not surprisingly acidophilic organisms have been extensively studied both in the field and in the laboratory (1,7,8).

Extensive experiments on the effects of nutrients on the growth of algae in acid lakes have been performed in Cheat Lake in West Virginia. This artificial lake has a number of strip mines and deep coal mines in its catchment and has a typical pH of about 4.8. Laboratory assays of Cheat Lake water showed that below pH 5.5 algal growth was limited both by the inorganic carbon supply and by phosphorus; however, above pH 5.5 phosphorus alone could stimulate growth. (1).

Interpretation of the effects of acid mine drainage on invertebrates is complicated by the variety of factors involved; in addition to the acidity itself there may be problems from high concentrations of suspended solids, from precipitation of iron (III) hydroxide and from elevated concentrations of heavy metals. There are a number of species of invertebrates which are able to tolerate the acidity. In particular, midge fly organisms of the Chironomidae family are frequently found at high densities. Examples include a strip mine lake in Kansas (pH 3.2-3.6) dominated by the subfamily of *Tendipes* sp., acid reaches of the Taff Bargoed. South Wales (pH > 3.5) dominated by the *Conchapelopia pallidula* subfamily and a stream in West Pennsylvania affected by acid mine drainage (pH 2.6-3.0; total acidity, 456-1130 mg/L $CaCO_3$) dominated by the subfamily of *Tendipes riparius* (1,7).

The pH of lake water is often inversely correlated with concentrations of trace metals in the water column, especially Al, Cd, Fe Mn, Pb and Zn. Experimental reductions of pH in lakes and streams confirmed that increased H^+ concentrations can cause increases in metal concentrations. The amount of change and the affected metal ions depend on the geological nature of the watershed, the chemical and physical characteristics of the water body and its sediments, characteristics of each metal, and the amount of atmospheric deposition of such metals as Pb, Cd and Zn (1,7-10).

Concentrations of trace metals can be more than 100,000 times greater in aquatic plants and more than 10,000 times greater in invertebrates than in the water. The effects of pH on metal assimilation by or adsorption to plants and invertebrates vary among metals, organisms, and aquatic sites to such a degree that generalizations about the role of pH in the movement of metals into living organisms and through trophic levels are not possible. Reviews of Al, Cd, Pb and Hg revealed that Pb concentrations in aquatic invertebrates and Al, and possibly Pb, concentrations in aquatic plants seem to increase in low pH environments (7-10).

The chemistry and toxicity of aluminum in dilute (low ionic strength) acidic aquatic environments are of some interest because: (1) aluminum is an important pH buffer, (2) aluminum may influence the cycling of important elements like phosphorus and dissolved organic carbon (DOC), and (3) aluminum is potentially toxic to aquatic and terrestrial organisms (9,10). Aluminum toxicity to aquatic organisms is related to its solubility and chemical speciation, two properties largely dependent on pH. A large amount of aluminum toxicity data has been generated from studies conducted in the neutral to acidic pH range, partially due to the concern over mobilization of aluminum from the terrestrial to the aquatic environment by acid rain. Aluminum hydroxide complexes are presumed to be the primary toxic forms of aluminum to fish at low pH due to interactions of these complexes with gill tissue resulting in impaired ionoregulatory and respiratory function (8-10).

Studies at neutral and acidic pH have shown that aluminum toxicity to freshwater fish can be attenuated by increasing DOC concentrations in exposure water. Humic substances are a major component of DOC in natural waters and complex metal ions including aluminum which may result in decreased availability of toxic aluminum species to the gills of aquatic organisms.

In 6 days of exposure at pH 4.5, the mortality rate in rainbow trout (*Oncorhynchus mykiss*) exposed to 0.33 mg/L aluminum and approximately 10 mg DOC/L compared to those exposed to 0.07 mg/L aluminum without DOC was similar (8).

Hardness (Mg^{2+} and Ca^{2+}) has also been implicated in reducing aluminum toxicity at neutral and acidic pH, although these effects are not due to complexation of aluminum species. Binding of calcium to the gill surface of fish appears to be essential for proper maintenance of ionoregulatory systems (8). Displacement of calcium from these sites by aluminum and H^+ has been proposed, partially due to the higher affinity of cationic aluminum species for these sites. The observed loss of electrolytes in fish exposed to low pH and aluminum may be due to the displacement of calcium from the gill surface, which presumably could be reduced by increasing the calcium concentration in the exposure medium (8-10).

Laboratory studies of prolonged exposure to sublethal Al have shown that acclimation (i.e. increased resistance to lethal Al) occurs with time, which may explain the continued presence of fish populations in acidified softwater lakes and rivers containing levels of Al in excess of 100 μg/L. The acclimation process results from a "damage/repair" phenomenon involving physiological, biochemical, and structural changes at the gills. In juvenile brook trout (*Salvelinus* fontinalis), the initial damage phase (lasting 4-5 days) was characterized by the accumulation of gill Al, reduction in whole-body electrolyte, severe gill histopathologies, and impaired oxygen delivery to tissues (whole-body lactate levels were elevated). Acclimation was observed from day 10 onwards and was accompanied by at least partial recovery of whole-body ion and lactate levels and a progressive reduction in total gill Al (8,10).

The specificity of acclimation to Al is unknown because the mechanism of acclimation is probably designed to combat the mechanism of toxicity of metal, it is possible that metals with similar modes of toxic action will elicit similar acclimatory responses and thus may exhibit crossover resistance. Cu has similar effects to Al in freshwater fish; both can impair respiratory gas exchange during acute exposure and both interfere with the active influx and passive efflux components of branchial ion transport. Therefore, Cu is a likely candidate for testing crossover resistance during acclimation to Al (8,10).

D. Description of the Blackwater River Watershed

Approximately 20,000 Km of streams and rivers in the United States are impacted by acid mine drainage, and about 85 to 90% of these streams receive acid mine drainage from old, abandoned surface and deep mines (3). This research is focused in one region of West Virginia, the Blackwater River watershed in Tucker County. The Blackwater River watershed cover 5781 Km within Tucker and Grant counties in the north-east-central part of West Virginia (Figure 1). Acid mine drainage from some of 65 abandoned mines has essentially sterilized the aquatic biota for 18 Km and excluded the stream as a sport fishery. As seen in Figure 2, the Blackwater River rises between Canaan and Cabin mountains (elevation 991 m), flows southwest and joins the Dry Fork to form the Black Fork of the Cheat River at Hendricks (elevation 520 m), a total of 49 Km with a total fall of 471 m. Its principal tributaries, in descending order, are Yellow Creek, Beaver Creek, North Fork, Finley Run and Tub Run (11).

The color of the Blackwater is a dark, reddish-brown apparently due to lightly dissolved organic carbon and iron oxides from red mauch chunk shales that compose the principal portion of the sedimentary deposits (11).

E. Coal Mining and Reclamation of the Blackwater Watershed

The West Virginia Stream Restoration was initiated in 1992 to work on the Blackwater River watershed which is still severely impacted by acid mine drainage. The first coal mining in the Blackwater River watershed occurred on Beaver Creek, and it is presently receiving acid mine drainage pollution from abandoned surface and deep mines (3,11).

The Davis Rotary Drum Limestone Treatment Station was constructed by the West Virginia Division of Environmental Protection (WVDEP) on the Blackwater River approximately 1 Km above the mouth of Beaver Creek. The drum rotates and brings out fresh limestone to be used. The station was placed into operation in late September 1994. This station was designed to neutralize the acid loads from Beaver Creek, rehabilitating the Blackwater River downstream to its confluence with the North Fork. A dry-powder limestone slurry doser was also installed in conjunction with the rotary drum facility to provide supplemental treatment during high flow intervals when the capacity of the rotary drum station was exceeded. With the improvement in water quality, trout were reintroduced 7.2 Km down to the North Fork (3,11,12).

The North Fork of the Blackwater River has abandoned deep mine sites at Thomas, Coketon and Douglas that are major sources of acid mine drainage. “Coketon” is the term for the central mining facility of the Davis Coal & Coke Company between Thomas and Douglas. The most significant and striking cultural resources of the site are the rows of coke ovens which line both sides of the valley. An entire bank of ovens stands free in the middle of the site while both walls of the hollow are lined with the brick and stone ovens. A combination of abandoned surface and deep mines show a dramatic increase of acid mine drainage pollution loads that occurs between the upper North and Douglas. WVDEP was involved in the development of methods to reduce the acid loads of the North Fork of the Blackwater River. Much of the disturbed surface mined land has been reclaimed and a large anoxic limestone drain (ALD) has been constructed at the Douglas Highwall location (3,11,12).

The ALD was designed to:

1. Remove Fe^{+3} in the water by: 1) adsorption or precipitation of Fe^{+3} in the organic material overlaying the limestone, and 2) microbial Fe^{+3} reduction producing soluble Fe^{+2} in the anaerobic sediment,
2. Remove the dissolved oxygen in the water by consumption of the oxygen through organic matter decomposition,
3. Add alkalinity to the water by: 1) microbial sulfate reduction in the anaerobic zone of the organic material, and 2) limestone dissolution from the ALD, and
4. Precipitate metals in the catchment basin before the water is discharged into the North Fork of the Blackwater River (12).

F. Objective of This Research

The goal of this research is to determine which tributaries or sites of the Blackwater River Watershed are contaminated with acid mine pollution. To determine these affected sites, an understanding of the relationship of pH, acidity, sulfate (SO^{2-}_4) to the major, minor and trace metal concentrations is developed.

II. Experimental

A. Sample Collection

The water samples were collected from Blackwater River watershed located in the north-east-central part of West Virginia seen in Figure 1. The station collection dates and the map showing the station locations are in Table I and in Figure 2, respectively. Also, a map of a section of North Fork showing ALD station locations is in Figure 3.

High-density polyethylene bottles were used to store the sampling. Prior to field use, they were cleaned with detergent and tap water then rinsed with 5 x 1 L of distilled water. Ten mL of 1M nitric acid were dispensed into each and the bottles were sealed and shaken. The acid was rinsed with one volume of distilled water and the clean bottles were capped and stored for transport (13). Collection was made by rinsing the bottle with one volume of the sample, pouring this out, and then collecting a bottle full of sample by placing the opening of the bottle completely underneath the surface of the water and pointed downstream. The bottle was then capped and labeled with a letter.

B. Water Quality Measurements

Water quality samples were analyzed in the field and lab for the following parameters:

pH	Aluminum	Potassium	Sulfate
Total Alkalinity	Zinc	Sodium	Silica
Total Hot Acidity	Iron	Strontium	Tannin and Lignin
Manganese	Calcium	Barium	

All analyses were done in accordance with the published standard methods (13) and all the reagents were bought from Hach Company (Colorado, USA).

1. Field Measurements

a. pH Measurements

A Sentron hand-held pH meter was used to make measurements at each site. The instrument was calibrated before measurements using pH 4.00 and pH 7.00 certified buffer solutions.

b. Total Alkalinity Measurements

The unfiltered 100 mL water sample was titrated using bromcresol green-methyl red as an indicator and 1.600 N sulfuric acid as a titrant.

When alkalinity is due entirely to carbonate or bicarbonate content, the pH at the equivalence point of the titration is determined by the concentration of carbon dioxide at that stage. Carbon dioxide concentration depends, in turn, on the total carbonate species originally present and any losses that may have occurred during titration. Total alkalinity is the term traditional used for the quantity measured by titration to 4.5 because of the bromcresol green-methyl red indicator. Dissolved gases contributing to acidity or alkalinity, such as carbon dioxide, hydrogen sulfide or ammonia, may be lost or gained during sampling, storage or titration. The effects were minimized by titrating to the end point promptly after opening sample container, avoiding vigorous shaking or mixing.

1. Lab Measurements

a. Total "Hot" Acidity Measurements

The pH of the unfiltered 100 mL water sample was adjusted to pH 4.0 or less by using 1.600 N sulfuric acid to keep the ions in solution. Five drops of 30% hydrogen peroxide solution were added. Then, the solution was boiled for 2-5 min. The treated 100 mL water sample was titrated using phenolphthalein as an indicator and 1.600 N sodium hydroxide as a titrant. This method applied for acid mine drainage samples because they contain hydrolyzable metal ions such as iron, aluminum, or manganese. These metals were treated with hydrogen peroxide to ensure oxidation of any reduced forms of polyvalent cations, and boiled to hasten hydrolysis.

In a sample containing only carbon dioxide-bicarbonate-carbonates, titration to pH 8.3 at 25 °C corresponds to stoichiometric neutralization of carbonic acid to bicarbonate. Because the color change of phenolphthalein indicator is close to pH 8.3, this value generally is accepted as a standard end point for titration of total acidity. In the interferences, samples containing oxidizable or hydrolyzable ions, the reaction rates at room temperature may be slow enough to cause drifting end points.

b. High Range Silica Measurements

Ammonium molybdate was acidified with an acid reagent to about pH 1.2. The acidic solution reacted with silica and any phosphate present to produce heteropoly acids. Citric acid was added to destroy the molybdophosphoric acid but not the molybdosilicic acid. The intensity of the yellow color was proportional to the concentration of molybdate silica. The interferences were tannin, large amounts of iron, color, turbidity, sulfide and phosphate. Distillated water was used as the blank to correct color and turbidity interferences. Treatment with citric acid eliminated interference from phosphate and decreased interference from tannin.

c. Sulfate Measurements

Sulfate ion was precipitated in an acetic medium with barium chloride so as to form barium sulfate crystals of uniform size. The amount of turbidity formed was proportional to the sulfate concentration. The color and turbidity interferences were corrected by filtering each sample and using distilled water as the standard to which barium chloride was added. Silica and calcium may interfere at levels above 500 and 20,000 mg/L as $CaCO_3$, respectively.

d. Tannin and Lignin Measurements

Tannin and lignin aromatic hydroxyl groups reduced tungstophosphoric and molybdophosphoric acids after adding sodium carbonate solution. As a result, blue color was produced. Sulfite interference was removed by adding 1 mL of formaldehyde to the sample before running the test. Ferrous iron caused a positive interference. Two mg/L of ferrous iron produced a color equivalent to about 1 mg/L of tannic acid. About 0.2 g of sodium pyrophosphate was added to the sample before running the test to eliminate interference due to levels up to 20 mg/L of ferrous iron.

C. Instrumentation

The inductively coupled plasma-atomic emission spectrometer (ICP-AES) consisted of a Varian model Liberty 110. The ICP-AES was interfaced with a computer and its operation conditions are listed in Table II.

The portable colorimeter consisted of a Hach model DR/700. Tannin and Lignin, Silica and sulfate had their own specific operation conditions that were explained in the published methods (13).

1. ICP-AES Analysis

The water samples were filtered through a 0.45 µm (type HA) filter membrane. The filtered water samples were analyzed for Al, Mn, Fe, Zn Ca, Sr, Ba, Mg, Na and K with ICP-AES using standards and blanks. The standard concentrations of the metals are listed in Table III. Distilled water was used as the blank.

2. Colorimeter Analysis

The filtered water samples were analyzed for silica, sulfate and tannin and lignin with the colorimeter using 420 nm, 450 nm and 690 nm wavelengths, respectively. A detailed procedure was explained in the published methods (13).

III. Results and Discussion

The concentration range (ppm), the reproducibility (SD), the limit of detection (LOD) and the limit of quantification (LOQ) of major, minor and trace metals analyzed by ICP-AES and inorganic species analyzed by the Hach Kits are given in Table IV.

The results of the analyses will be presented by sampling location going downstream along the Blackwater River (Figure 2). Samples were collected throughout the year at many of the stations; however, no significant seasonal variation was detected for any parameter in the Blackwater and North Forks stations.

Acid mine drainage consists of a low pH, sulfate rich water with high amounts of acidity. The acidity is comprised of mineral acidity (Al, Fe, Mn and other metals depending on the geologic deposit) and also hydrogen ion acidity measured in mg/L $CaCO_3$ (3).

The Blackwater River stations located above Yellow Creek, included BW001 (Canaan Valley), BW002 (Blackwater at Camp 70) and BW003 (Blackwater at Gauging Station) and the one directly below Yellow Creek was BW006 (Tables V and VI). These stations were within normal levels of major, minor and trace analytes for North American rivers (Table VII). Low levels, particularly of sulfate and trace metals associated with mine drainage (Al, Mn and Fe), support this conclusion. One of the differences between the stations above and below Yellow Creek was the decrease of pH from 6.5 at the above stations to 5.0 at the below station (Table VIII). This difference was due to the low buffered BW004 station. BW004 is a wetland area covered by moss generally of 1 or 2 genera, Polytrichum and Sphagnum, and thus can be best described as a peat bog (14). BW004 had low pH (3.8) but was only slightly acidic (9 mg/L) and the other parameters in Table VIII had low concentrations. Then, BW004 was naturally low in pH due to the decomposition of the plant cover in the bog that leads to the production of organic acids often called "humic" acids. The bog first drained into Yellow Creek and afterwards into station BW005. The BW004 and 5 stations shared uniform levels of most analytes (Table IX). Al was slightly elevated (up to 0.35 ppm) in some samples because the particles of the complex clay minerals went through the filter paper. Mainly, the sulfate and Mn were low in BW004 and 5 stations.

The station on the Blackwater River below BW006 but above the Liming Plant was BW007 (Figure 2). Both BW006 and 7 showed little or no influence by the high acidity water from Yellow Creek on any of the parameters measured (Table VIII). This is due in part to the much higher flow volume of Blackwater River compared to that of Yellow Creek.

The WV Department of Natural Resources (WVDNR), the WV Division of Environmental Protection (WVDEP) and our group collected and analyzed samples from BW007 over a period of 8 years (Table VI). These groups showed constant levels of most analytes. In our year of analysis, BW007 had higher acidity and lower alkalinity values compared to those reported by WVDNR and WVDEP. These values represent a single sampling and not an average. Also, some samples from this station had high concentration of Al (up to 1.40 ppm) and Fe (up to 2.10 ppm) reported by WVDNR and WVDEP. The reason for the Al elevated values was because at non-acid-producing mine sites, the downstream transport of metals is primarily in the sediment load due to the low solubility of metals in water at neutral or higher pH (15). The high Fe value may be due to analytical error. If the exclusions are disregarded, WVDNR, WVDEP and our parameter results suggested that during the 8 years of analysis, BW007 was not affected by acid mine drainage because of its high pH, low acidity, sulfate and Mn.

The regions adjacent to stations BW001 to BW008 have little or no history of mining activities. However, the water was not likely to be affected by acid mine drainage. The production of pyrite occurs in nature but not only as it is exposed by erosion and natural weathering thereby generating negligible acidity or alkalinity levels. This small amount of acid is naturally diluted or neutralized by surrounding rocks so that it is not seen or noticed.

Alkalinity of a solution is defined as the capacity of a solution to react with strong acid. It is determined by titration to specific end-points, namely, pH=4.5-methyl orange, and pH=8.3-phenolphthalin. A measured volume of the water is titrated with a strong acid such as HCl. Several different solute species contribute to the alkalinity of an unpolluted water sample; however, the titration with acid does not specifically identify them. Alkalinity may be reported in several ways, the most common is in terms of an equivalent amount of $CaCO_3$, usually meq/L $CaCO_3$ (1,15).

$$\text{meq/L } CaCO_3 = \frac{\text{mg/L } CaCO_3}{50}, \text{ where 50 is the equivalent weight of } CaCO_3$$

The natural base content of overburden materials (alkali and alkaline earth reactions, commonly present as carbonates or exchangeable cation in clays) is important in evaluating the future chemical producing potential of the materials. The amount of alkaline material in unweathered overburden could be enough to equal or overwhelm the acid producing potential of the material. Of the many types of alkaline compounds present in rocks, carbonates are the only alkaline compounds which occur in sufficient quantities to be considered as effective deterrents to acid mine drainage. Noncarbonate contributors to alkalinity include hydroxide, silicate, borate and the organic ligands, especially acetate and propanoate. The inclusion of these ions in the alkalinity value will be important if they are present in significant amounts (1,3,15).

In overburden containing alkaline and pyritic material, the alkaline material may be sufficient to neutralize the acid formed from pyrite. Higher alkalinities also help control bacteria and restrict ferric iron activity which are both known to accelerate acid generation. A balance of the acid producing potential and neutralizing capacity of an overburden sample will indicate the ultimate acidity or alkalinity that might be expected in the material upon complete weathering (3).

The stations located downstream from BW008 were confronted with a greater quantity of abandoned surface and/or deep mines. Thus, relatively large volumes of pyritic material were exposed to the air resulting an increased levels of Mn, Al, Fe, SO^{2-}_4 and acidity into underground and surface waters. Sulfur in coal and coal-bearing rocks can occur as organic sulfur, sulfate sulfur, and pyritic sulfur. Pyritic or sulfide sulfur is the predominant sulfur species in the majority of coal and associated rocks and is the sulfur form of greatest concern. Of all the sulfide minerals that may be present, pyrite predominates and is the major acid producer (1,3,15).

The traditional approach for treating acid mine drainage is collecting the contaminated drainage in ponds and treating it with alkaline reagents to neutralize acidity and precipitate metals, and raise pH. The six primary chemicals used in treatment are listed in Table X. Each chemical has characteristics that make it more or less appropriate for a specific condition. The best choice among alternatives depends on both technical and economic factors. The technical factors include acidity levels, flow, the types and concentrations of metals in the water, the rate and degree of chemical treatment needed, and the desired final water quality. The economic factors include prices of reagents, labor, machinery and equipment, the number of years that treatment will be needed, the interest rate, and risk factors (3,11).

The Blackwater River stations located below the dam and across the river from the Davis Liming Plant were BW008, 8a and 8b, where the rotary drum limestone station was constructed (Figure 2). The WVDNR maintains this "Liming Plant" and it has been treating a portion of the river flowing over the dam with limestone to increase the buffering capacity of the river. This increased buffering capacity was intended to neutralize acid mine drainage added to the river further downstream. The stations BW008, 8a and 8b showed that most of the analytes had consistent levels (Table XI), except for slightly higher Ca values. Also, there was a sharp alkalinity increase from 13 mg/L at BW008 to 76 mg/L at BW008b. This was probably due to the incomplete mixing of the liming plant outflow with the bulk of the river water at BW008b.

In Table XII, our Below Dam values (the average concentration of the BW008, 8a and 8b parameters) are compared to those reported by WVDEP and WVDNR. The samples collected over a 4 year period showed consistent values for most parameters. We observed a significantly lower Al concentration (0.08 ppm versus 0.43 ppm - 0.55 ppm) than previously reported. Also observed was a slightly higher Ca concentration (16.0 ppm versus 14.0 - 14.2 ppm). The lower Al may be related to an increased effectiveness of the limestone treatment. One of the main differences between the Above Dam station (BW007) and the Below Dam station (BW008, 8a, 8b) was that the alkalinity of the water increased from 1.4 mg/L at above Dam station to 44.5 mg/L at below Dam station as shown in Table VIII. Nonetheless, there was a little increase of average pH and major metal concentrations. These metal concentrations should have been higher because calcite contains mainly Ca (1002 ppm) and dolomite is compose of Ca (501 ppm), Mg (304 ppm) and salts (15). Even though the pH values reported by WVDEP and WVDNR (Table XII) ranged from 6.1 to 8.6, the alkalinity and Al concentrations ranged up to

160 mg/L and 1.00 ppm, respectively because dissolved Al concentration increases with pH above 7.0. The solubility of Al^{+3} will be explained next.

Although pH values are easy to collect and compare, pH is neither a true indication of acidity, nor is it a good determining factor for the extent of acid mine drainage. The streams with the lowest pH values are not necessarily those with most damaged biota. pH is an intensity factor, measuring the concentration (or more strictly activity) of hydrogen ions whereas what is most important in acid mine drainage is not the concentration alone but the availability of hydrogen ion to neutralized bases; that is, to react with hydroxyl ions and in so doing to convert all carbonate species to carbon dioxide. This quantity is usually referred as total acidity and is reported in the same unit as alkalinity (mg $CaCO_3$/L) (1,11,15). Usually, high acidity is accompanied by a low pH in acid mine drainage but there are some cases where the pH is higher than 4.5, for instance Beaver Creek station (BW009) observed in Table XIII.

The BW009 station was another tributary into Blackwater River. Its average pH (5.1) was lower than those of the stations above Beaver Creek on Blackwater River. Nonetheless, the average pH (5.1) of this station compared to the pH (4.2) of BW005 could have mistakenly taken as moderate. Most of the analytes in BW009 had consistent levels and they were much higher than those of BW005, excluding Fe. The strip mines upstream in Beaver Creek contributed high acidity, Al, Mn, Ca, Mg, Na and elevated sulfate. The release of these high concentrations was because acidity increases the decomposition rate of clay minerals, feldspars and carbonates. High concentrations of Mn and sulfate will always appear as markers in waters contaminated with acid mine drainage pollution, such as in BW009 but not in BW005.

On the contrary, BW005 and BW009 had identically low average concentrations of Fe because the pH (4.2 - 5.1) was too high for Fe^{+3} to be soluble in water. According to Kelly (1), the drop in pH is accompanied by a rise in the solubility of metals, making possible very high aqueous concentrations. Iron, aluminum and manganese are acid soluble, so merely neutralizing the water (increasing the pH) will precipitate these ions.

Iron can exist in 2 forms in acid mine drainage, ferrous (unoxidized) and ferric (oxidized). The ferric (Fe^{+3}) form will begin to precipitate around pH 3.5 forming ferric hydroxide ($Fe(OH)_3$). Including a more complicated oxyhydroxide hydrates such as $Fe(OH)_3(H_2O)_2$ and iron (III) hydroxysulfate complexes as $Fe(OH)(SO)_4$ which form the yellowish-orange precipitate commonly called yellow boy (Figure 4). The ferrous (Fe^{+2}) ion converts to a solid bluish-green ferrous hydroxide ($Fe(OH)_2$) at a pH of 8.5 or greater. It is usually advantageous to oxidize the ferrous iron to the ferric state rather than to rely upon ferrous precipitation at high pH's. This oxidation is accomplished by increasing the pH above 7.0 and introducing air into the water to provide oxygen. The oxidation rate of ferrous iron is strongly pH dependent and proceeds extremely slow below pH 6.0 (1,3).

Aluminum (Al^{+3}) generally precipitates as aluminum hydroxide ($Al(OH)_3$) at a pH above 5.0 but also enters in solution again as $Al(OH)^-_4$ complex at pH of 8.0. The color of the aluminum hydroxides flocks are almost white (1,3).

Manganese precipitation is variable due to its oxidation states, but will generally precipitate at a pH of 9.0 to 9.5. Sometimes, however, a pH of 10.5 is necessary for complete removal of manganese. For example, manganese (II) precipitated as MnO_2 (brownish-black flocks) and manganese (IV) as $Mn(OH)_4$ (white flocks). The role of hydrolysis products in influencing the solubility of Al(III), Fe(III) and Zn (II) (hydro)oxides is illustrated in Figures 5a, 5b and 5c, respectively (1,3,16).

WVDEP and WVDNR also collected samples from BW009 (Table XIII) reporting a pH range of 4.6-5.8 and the consistent elevated acidity, sulfate, Al and Mn concentrations. For unpolluted water, Ca should be greater than sulfate but the sulfate values reported by these groups were about 2-3 orders of magnitude greater than Ca values. As a result, Beaver Creek was the first source of acid mine drainage to enter the Blackwater River.

The Beaver Creek effluent was diluted with a larger water mass of Blackwater River. The resulting water dilution was collected at BW010 station (Blackwater Falls) shown in Figure 2 (Table XIII). The sample collection and analysis of BW010 was on 10/12/96, its pH and alkalinity were high and its minor and trace metals were low because of the efforts of the Davis Liming Plant trying to turn the Blackwater River into an alkaline stream. Altogether, the stations from BW001 to BW010 showed no significant change in the concentrations of Zn, Sr, Ba, silica and Tannin and Lignin (T&L).

The results of the analyses will be represented by station location along North Fork going downstream into Blackwater River (Figure 2). The North Fork stations were divided into 2 groups: above mining (NF019, 20, 21 and 1) and below mining (NF002, 3, 12, 12a, 13, 14, 15, 15a, 16, 17 and 18). First the above mining stations will be discussed, followed by the discussion of below mining stations.

The average pH at NF019 (Thomas Dam), and NF001 (Coketon Bridge) was greater than 6.0 with similar levels of most analytes (Table XIV). Both stations had high pH and low concentrations of Al, Mn and Fe, consistent with the absence of acid mine drainage. NF001 contained high sulfate, Ca, Mg and Na concentrations suggesting upstream limestone treatment and sulfate leaching from the Wolf Welding (NF020) and Snyder Run (NF021) stations.

NF021 drains old strip mined areas according to USGS quadrangle maps. The low sulfate and Mn indicated that little acid mine drainage was introduced into the watershed via Snyder Run. The station NF020 had a moderate average pH of 5.5 and a high alkalinity of 37 mg/L while the constant levels of remaining analytes were several times higher than the values in NF001, NF019 and NF021 (Table XIV). The elevated sulfate and Mn in NF020 were indicative of acid mine drainage pollution which has been neutralized (pH 5.4). The outflow from the mine was milky white in color probably due to $Al(OH)_3$ precipitate. The fact that orange-yellow flocs from $Fe(OH)_3$ were not seen perhaps because they had precipitated inside the mine or further downstream. This acid stream may have joined the less acidic river, which diluted the acidity and triggered the decomposition of the floc (1). Elevated Ca, Mg, Na, K and alkalinity indicate limestone remedation was used within the mine. Based on pH alone, one would expect Al concentration around 0.1 ppm; however, 0.39 ppm was observed. Aluminum hydroxide is a whitish gel. When filtered, the particles went through the filter membrane under vacuum causing a higher Al concentration.

The concentration of Al reported by WVDNR at NF020 was much higher than expected for the reported pH (>6) (Table XV). As discussed previously, we believe that $Al(OH)_3$ must have passed through the filter membrane for the WVDNR samples as well. The difference in sulfate, Al, Mn and Fe between our data and WVDNR may be was the result of variations in water flow at the mine. Higher water drainage into the mine in 1998 could have resulted in a more diluted output.

For the below mining group, the receiving drainage stations from Douglas mines consisted of NF002a (Mine portal before Douglas Dozer), NF002b (Douglas Dozer outlet), NF002c (Hold pond drain) and NF002d (Drain downstream from dozer). Their locations are shown in Figure 2.

The outflow of 3 portals of the Douglas mine feed into a common duct (17). Stations NF002a and 2b exit the duct near the uppermost portal and NF004 (Grate of top of ALD) was located below the most downstream portal. NF002a feed into a holding pond that drains at station NF002c. Initially during our sample collection (September 97 - March 98), the holding pond received the majority of the water from the upper portal. The holding pond was about 1-2 feet in depth (0.3 - 0.6 m). Later, the dike at NF002c was breached and the pond drained. Both, NF002a and 2c stations had a very low pH and similar concentrations of most parameters. An increased proportion of the upper drainage exited at a drum dozer at NF002b. NF002d was located in the slew at the outlet of the dozer to compare the water after immediate impact of the dozer on the outflow at NF002b. The discharge at NF002b and 2d had a very low pH with constant levels of most analytes. During 1998, the accumulation of some limestone fines and pebbles in the slew was observed. These showed an orange stain indicating $Fe(OH)_3$ had formed on the surface of the limestone.

Finally, NF002a, 2b, 2c and 2d stations were characterized to have been severely impacted by acid mine drainage. These stations not only had a very low pH and very high concentrations of sulfate and Mn markers but also contained other high major, minor and trace metal concentrations. The acidity gradually dissolves the sediments adjacent to the coal formation to varying degrees depending on the water's acidity level and the rock's hardness and composition. Upon contact with surrounding acid producing rocks, more acid, metals and sulfate may be released (3,15).

In Table XVII, our Douglas Mine station values (the average of NF002a, 2b, 2c and 2d concentration parameters) are compared to those in the WVDEP and WVDNR reports. WVDEP, WVDNR and our group shared a very low pH (3.0) with highly uniform concentrations of most parameters. Based on this, these groups agreed that Douglas mine discharge was critically affected by acid mine drainage. This acidic drainage was never successfully neutralized because the operation of the dozer was highly variable throughout the sampling period. For example, prior to the last collection (May 1998) the drum had been removed. In addition, the average concentrations of sulfate and Ca reported by WVDEP and WVDNR were 10 and 2.5 times more than our values, respectively. Because our values for Beaver Creek agreed with WVDEP and WVDNR, we rule out errors in methodology. We have no explanation of those differences.

Water drained from the stations NF019, 20, 21, 1, 2 were mixed and diluted while flowing down along the North Fork until it was collected at NF003 station (North Fork @ concrete abutment). The precise location of this station was shown in Figure 3. NF003 station had low average pH, with high acidity, major and trace metal concentrations, (Table XVII). The exclusion was the sulfate value because it was within the normal limits for the average river (Table VII).

Because the Douglas Drum Dozer failed as a treatment for acid mine drainage pollution in this region, the Douglas Highwall project was made to treat this water with a passive system called Anoxic Limestone Drains (ALD). This system is located below the Douglas Dozer (Figure 2) and it consists of 11 stations which are NF004, 5, 6, 7, 8, 9, 10, 10a, 10b, 10c, and 11. See description of the stations in more detail in Table I and location in Figure 3.

According to Skousen (17), in the late summer of 1997, WVDEP renewed the organic matter and limestone of the ALD/Wetland Treatment System. Water passing through the system causes limestone dissolution, raising pH and adding alkalinity. They were trying to improve the water rate percolating through the limestone bed. Acid mine drainage depletes the buffering ability of water by neutralizing carbonate and bicarbonate ions to form carbonic acid (H_2CO_3). The reactions to produce carbonic acid are the following:

$$H^+ + CO^{-2}_3 \Leftrightarrow HCO^-_3 \qquad [4]$$

$$H^+ + HCO^-_3 \Leftrightarrow H_2CO_3 \qquad [5]$$

Once exposed to acid mine drainage, the affected carbonate buffering system is not able to control changes in pH as well. The buffering system is completely destroyed below a pH of 4.2 where all carbonate and bicarbonate ions have been converted to carbonic acid. The carbonic acid readily breaks into water and carbon dioxide (18).

$$H_2CO_3 \Leftrightarrow H_2O + CO_2 \qquad [6]$$

In October 6, 1997 (Table XVIII), the NF010, 10a and 11 stations had pH values in the 6s with much lower metal concentrations than in the other stations. Likewise, NF010a, b and c samples were collected at different locations within the same wetland in the same date but the pH for each station was 6.6, 4.2, and 4.3, respectively. Naturally, NF010b and c with pH of ~4.3 had higher Al and Mn concentrations than in NF010a because at low pH values the metal ions remain soluble. Meanwhile, the variance of the major and minor concentrations was minor among the 3 stations. These concentrations were constantly high because of the limestone layer and the high sulfate values were from the Douglas mines effluent. The water of NF010b and c stations were slightly acidic (pH ~4.3) due to the presence of humic acids produced by decaying vegetation.

The following collecting date was in January 5, 1998 (Table XVIII). The pH values in the 3s were observed in NF007, NF009 and NF011 stations. The water samples of the rest of the stations were not collected and analyzed on January 5, 1998. The reasons for the decrease of the pH from 6 in October 97 to 3 in January 98 were not answer by WVDEP because they did not know the exact length of time and the cause for the ALD/Wetland Treatment System to deteriorate. Since its construction in August 1993, the system developed a diversity of problems (3). For example, it was calculated that based on 240 gpm and 500 mg/L acidity, treatment longevity of this drain with its 19,000 tons of limestone was estimated to be 60 years (3,11). Organic material has a finite capacity to adsorb metals; so the longevity based on the capacity of the organic material may be less than 60 years. Nonetheless, practically the ALD/Wetland Treatment System has not been effective at water flow water greater than 100 gpm (17).

The motive of the high pH values in the NF010, 10a and 11 stations in October 1997 may be due to the contribution of water that had percolated through fresh limestone bed. Otherwise, the low pH values in the NF007, NF009 and NF011 stations on January 1998 were instead the contribution of water that had eroded a new way out of the treatment system or had gone through a bright orange stained limestone. Normally, much of the Fe^{+3} in the water should have been precipitated or absorbed onto the organic material in the surface of the wetland. After October 1997, when the Fe^{+3} came into contact with limestone, the limestone was covered by $Fe(OH)_3$. This hindered carbonate dissolution and made it less reactive for neutralization. Another probability was the coating of limestone or plugging of limestone pores by aluminum hydroxides or other precipitation of insoluble metal compounds.

Water contaminated from the station NF011 (ALD outlet) was mixed and diluted with water of the stations NF012 (Middle Run) and NF013 (Lined Run @ Middle Run). Water while going through NF012a station (Outlet of the culvert @ Middle Run) was collected and analyzed (Table XIX).

When comparing NF012 and NF013 stations (Table XIX), the concentrations of most parameters in NF012 were consistently low and opposite to those in NF013. The only exception was the high sulfate values at both stations. Consequently, NF012 was not affected by acid mine drainage even though the sulfate value was high (18.0 ppm). The absence of acid mine drainage at this station was reinforced by the moderate pH, low acidity, Al, Fe and Mn concentrations. Since the water of this station drained from a sector of the Douglas Highwall project, sulfate leached from mines surrounding the project. The NF013 station had very low pH with extremely high acidity, and high fluxes of sulfate, Al, Mn and Fe straight from a mine. It displayed severe impact of acid mine drainage.

NF012a station (Table XIX) represented diluted water which had a low sulfate but the low pH was accompanied with high acidity, major and trace metal concentrations, i.e., NF012a station was contaminated with acid mine drainage. NF014 station (North Fork above Long Run) was located further down from NF012a (Figure 2). Because of this station location, there was evidence to suggest that the mine drainage waters of station NF012a became worse as the water flowed down along North Fork. The evidence was the increase of sulfate, Mn and other major metal concentrations from NF012a to NF014 stations (Table XIX).

NF012, 12a and 13 stations (Table XIX) showed a trend relating Al and Fe concentrations with pH. As the average pH decreased from 5.4 in NF012 to 3.8 in NF012a and to 2.6 in NF013, the average concentrations of Al and Fe increased. The average Al increased from

0.13 ppm in NF012 to 3.18 ppm in NF012a and to 9.18 ppm in NF013. The average Fe increased from 0.18 ppm in NF012 to 0.35 ppm in NF012a and to 12.32 ppm in NF013. Consequently, pH has been shown to be directly proportional to the log concentrations of Al and Fe but the relation was only slight for Mn concentration (Figure 5). Manganese was one of the indicators of acid mine drainage that works as a dilution factor. Manganese concentration correlates with the Mn input by acid mine drainage versus the flow rate of the water in the stream. It was significant that the average Mn concentrations increased from 0.04 ppm in NF012 to 0.62 ppm in NF012a and to 1.13 in NF013 were smaller than the increments of Al and Fe average values in Table XIX.

Moreover, Zn also works as a dilution factor but was not an acid mine drainage marker like Mn. Table VIII showed that in almost every station influenced by acid mine drainage, both Mn and Zn emerged together and behaved in the same manner. For example, as the pH decreased, the Zn concentration increments from NF012 to NF012a and to NF013 were much smaller than the increments of Mn concentrations. The exception was the Wolf Welding mine portal (NF020) which emitted acid mine drainage containing high Mn and low Zn concentrations. Most of the time, high Sr concentrations were observed in stations affected by severe acid mine drainage pollution, such as station NF002. The low pH with high acidity influence the elements released by increasing the rate of decomposition of clay minerals, feldspars and carbonates which include toxic metals, especially Al, but also silica (1). This is the reason for the increase of silica in stations where the Al was high. Otherwise, there was not any significant difference in Ba and Tannin and Lignin concentrations among Blackwater, and North Fork stations (Table VIII).

The stations NF015 (Long Run @ North Fork) and NF015a (Long Run @ Forest Rd.) contributed acid mine drainage to North Fork. Station NF015 was also analyzed by WVDNR from 1/25/95 to 3/11/97 and we continued the analysis from 5/16/97 to 5/16/98. During our year of analysis (Table XX), the acid mine drainage improved just a little as evidenced by the lower concentrations of acidity, major, and minor and trace metals compared to those reported by WVDNR. NF015 and NF015a had a pH range from 3.2 to 3.4 with constant levels of some analytes. These analytes contained high concentrations of sulfate, Al, Mn and Fe, indicating contamination by acid mine drainage.

Because NF016 (North Fork above Falls @ gate) was the last station on North Fork, water masses of every upstream station flowed through this station before entering into Blackwater River (Figure 2). This station had a low pH with consistent levels of most analytes (Table XX). Likewise, this station reflected mainly acidic metal rich drainage because of the sulfate dilution and this value was within the range of normal levels for the average river (Table VII). Accordingly, North Fork was definitely the major source of acid mine drainage to the Blackwater River. Concluding, as the North Fork stream flowed into the Blackwater River, dilution occurred to improve the acid mine pollution.

The NF017 (Finley Run @ Forest Rd.) and NF018 (Tub Run @ Forest Rd.) distributed acid mine drainage straight into the Blackwater River (Figure 2). Both stations had low pH but NF017 had most of the concentrations greater than in NF018 (Table XXI). Their acidity, major, minor and trace metal concentrations were high, resulting from acid mine drainage contributions to both stations. The strip mines upstream of NF017 and NF018 contributed approximately equal Mn concentrations but different sulfate values. These variations presumably depended on the type of coal (3,19).

The final station BW011 (Hendricks) was located almost at the mouth of the Blackwater River (Figure 2) and the carbonate bearing sandstone was between NF018 and BW011 stations (17). The WVDEP, WVDNR and our group collected and analyzed samples from BW011 station during three years (Table XXI). These groups had high pH with constant levels of most analytes. WVDEP, WDNR and our group agreed that BW011 station was slightly influenced by acid mine drainage even though there was a decrease of major, minor and trace metal concentrations, specially Mn and Fe reported by our group. In addition, their average alkalinity and acidity were low. All of these resulted because of the many types of neutralization treatment systems along the Blackwater watersheds. As neutralization occurred, one of the ways to lose metals from solution was by adsorption, a process dependent upon pH. As the pH rose, metals were absorbed onto suspended particles and sediments. The metals were transported over great distances because the velocity of the water flow was high enough to keep particles in suspension, leading to widespread contamination (1,20). Changes in flow of the Blackwater River may have lead to the settling or resuspension of particulate material. Thus, the sediments could have contained higher concentrations of metals at points where the river flow was particularly low (20,21). If the metals were deposited in sediments near the source of acid, they were easily re-released into the ecosystem should a rush of acid water flow from the upstream source (1). Furthermore, sulfate values in BW011 were high primarily because of the sulfate leaching from the strip mines upstream in NF017 and 18 stations.

The stations of the Black Bear bog were composed of BB001a, 1b, 1c, 2a, 2b, 3 and 4. Their location and description are in Figure 2 and Table I, respectively. The pH of these stations ranged from 4.9 to 6.3 with constant levels of most analytes (Tables XXII and XXIII). The exceptions were the BB004 station, plus the readings of 1.71 ppm and 1.00 ppm Fe for BB002a and BB003 on 5/16/98, respectively. Water quality parameters of the remaining stations were within normal limits for river water (Table VII), particularly, low sulfate and trace metal concentrations (Tables XXII and XXIII). Conversely, the acidity, sulfate and trace metal concentrations in BB004 station were much higher for pH 5.3. The reason for these conditions was because humic acids have a complicated chemical structure. The carboxyl and hydroxyl functional groups of these polyaromatic ligands offer many binding sites for metal ions. According to Barsdate (21), humic acids form a stable chelation with Co, Mn, Al, Fe and others as long as the pH is keep high. The more highly brown colored waters contain the greater amounts of associations of humic acids with metals.

BB002a, 3 and 4 had pH of 5.3, 6.2 and 4.9 with Fe concentrations of 28.2 ppm, 1.00 ppm, and 1.71 ppm, respectively (Table XXIII). At these pH values, the Fe should have already precipitated out. Thus, these high Fe concentrations were amazingly unexpected. The explanation would be that Fe was in chelation with humic acids, keeping Fe in solution at these pH values. In general, retention of metallic cations by humic acids and brown coals was favored by increasing pH (2). According to Killops (2), chelation of Al and Mn with humic acids would not be expected because it has been found that Fe is absorbed most efficiently and Al and Mn least.

When Yellow Creek (BW004 and 5) and Black Bear stations (BB) were compared, a unique relation between Fe and Tannin and Lignin (T&L) was detected (Tables IX, XXII and XXIII). In Figure 6, the data points of BW004 and 5 stations were distributed along T&L axis.

Otherwise, the relationship of Fe with T&L concentrations of BB stations revealed divergence with season. Figure 7 showed the May 98 (Spring) and the October 97 (Fall) trend lines. In the Spring trend line, Fe concentrations were high but T&L concentrations were low. Instead, in the Fall trend line, Fe concentrations were low but T&L concentrations were high.

The behavior of the May 98 trend line could have been due to Spring rain and snow melt may have brought additional trace metals from surrounding highlands to the wetland. Another possibility was that the Fe in May 98 collecting period may contain greater amount of aliphatic organic matter than the aromatic organic matter in the October samples. Aliphatic compounds should give a lower response to the T&L test (22). It is likely that both processes are taking place.

Biological productivity especially actively algal growing tissue and blooms should be higher in Spring than Fall. According to Sieburth and coworker (23), the rainfall speeds up the generation of dissolved organic matter (DOM) and this DOM can chelate Fe and other metals. Appreciable excretion rates of the unicellular algae have focused attention on the phytoplankton as the primary source of dissolved matter in fresh waters (23). Probably the increase of Fe input and the higher DOM are responsible for the higher Fe/humic acid ratio seen in the May samples. Future work in this area should monitor chlorophyll *a* as a measure of productivity and the dissolved organic carbon, which may help to resolve the relative contributions of both mechanisms.

The October 97 trend line behavior could have been due to the lower rainfall conditions in Summer, this would increase the decomposition of the peat. This condition produced higher level of humic acids and the detection for tannin and lignin were referred simply as the concentrations of humic acids. A successive dilution of extracted moss provided by Dr. Persinger was measured for T&L concentrations using our portable colorimeter. Figure 8 showed that the data points were linear and the R-square was 0.9985. Moreover, humic substances are found in brown coals, soils, and seawater and both marine and lacustrine sediments. They can be leached, particularly from acidic soils, and account for almost all the organic carbon in fresh waters, imparting the characteristic brown coloration to waters. Further studies are necessary to clarify and understand the different effects. It would be essential to extract humic acids from plant communities in the four seasons and determine some chemical differences using IR, NMR, LC-MS and other appropriate techniques. If run off effect was the factor, additional sampling would be necessary, especially from the vernal pools such as station BB004.

IV. Conclusions

In this research, we demonstrated the importance of water chemistry to determine which streams contributed acid mine drainage to the Blackwater River. Mine acid came from both active and abandoned mines. In these mines, the refuse coal that remained in contact with the air and percolating water for a long period of time, oxidation of pyrite in the coal has resulted in the production of mainly high acidity, sulfate and Mn. These are the properties can be used to monitor the impact of acid mine drainage in any aquatic system.

The water quality of the Blackwater River watershed ranged from excellent to poor. The impact of acid mines on the stations from Canaan Valley to Blackwater Falls was negligible. Yellow Creek and Beaver Creek contributed "natural" acidic water and acid mine pollution into Blackwater River, respectively. The greatest and most degrading acid mine problems existed in the North Fork stream because no company or individual claimed responsibility for reclaiming abandoned mine lands (AML), no treatment of the acid mine drainage occurred and continual contamination of surface and groundwater resources resulted. Even more, the ALD and Douglas Drum Dozer constructed on North Fork to remediate acid mine pollution failed. Evidence of acid mine drainage is present well downstream. Further, long term water treatment of Blackwater River tributaries especially the North Fork is necessary to remediate the problem. Until then, continued monitoring is recommended.

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Appendix

Table I. Sample Collection Dates and Description of Stations in the Blackwater River Watershed

Station	**Description**	**Collection Dates**								
		9/7/96	10/12/96	2/15/97	3/15/97	5/16/97	6/10/97	10/6/97	1/5/98	5/16/98
BB#	**Black Bear :**									
BB001a	@ the large pond in the near side							x		x
BB001b	@ the large pond in the middle							x		
BB001c	@ the large pond in the far side							x		x
BB002a	@ the top of Y drainage channel									x
BB002b	@ the bottom of Y drainage channel							x		x
BB003	@ Beaver Pond at the edge in cattails							x		x
BB004	@ shallow depression near knoll									x
BW#	**Yellow Creek and Blackwater :**									
BW001	Canaan Valley	x	x	x	x		x	x	x	x
BW002	Blackwater at Camp 70								x	x
BW003	Blackwater at Gauging Station							x	x	x
BW004	Yellow Creek at bog						x	x		
BW004	Yellow Creek at bog drain							x		x
BW005	Yellow Creek at Camp 70 Road				x	x		x	x	x
BW006	Blackwater below Yellow Creek					x				x
BW007	Blackwater above Dam							x	x	x
BW008	Blackwater below Dam across from Davis Liming Station	x	x							
BW008a	Blackwater below Dam at opposite bank from Liming Station	x					x	x		
BW008b	Blackwater below Dam at the Liming Station bank									x
BW009	Beaver Creek	x	x	x	x		x	x	x	x
BW0010	Blackwater Falls		x							
BW0011	Hendricks	x		x	x					
NF#	**North Fork :**									
NF001	@Coketon Bridge	x		x	x		x			x
NF002a	Drain at portal mine pool (before Dozer)	x		x	x		x	x	x	x
NF002b	Drum dozer outlet					x	x	x		x
NF002c	Holding pond drain		x		x	x				
NF002d	drain downstream from dozer		x			x	x			
NF003	North Fork at concrete abuttment	x			x		x			x
NF004	Grate of top of ALD							x	x	x
NF005	ALD at position C						x			x
NF006	ALD at position H					x	x			
NF007	ALD at Beaver Pond (J)								x	x
NF008	ALD at position K									x
NF009	Letter "L" Weir								x	
NF010	Pool above pipe "M"						x	x		

NF010a	North Fork "wetlands" below weir at pipe "M"							x		
NF010b	North Fork "wetlands" next to limestone pile							x		
NF010c	North Fork "wetlands" in algae mat and reeds							x		
NF011	Outlet of ALD					x	x	x		x
NF012	Middle Run						x	x	x	x
NF012a	Outlet of the culvert at Middle Run									x
NF013	Lined Run at Middle Run						x	x	x	x
NF014	North Fork above Long Run							x		x
NF015	Long Run at North Fork					x		x	x	x
NF015a	Long Run at Forest Rd.					x	x			
NF016	North Fork above falls @ gate					x		x		x
NF017	Finley Run at Forest road						x			x
NF018	Tub Run at Forest Rd.					x	x			x
NF019	Thomas Dam	x								
NF020	Wolf Welding mine portal								x	x
NF021	Snyder Run									x

Table II. Operation Conditions of ICP-AES

Plasma Gas Settings:	
Plasma	15.0 L/min
Auxiliary	1.50 L/min
Nebulizer	150 kPa

Common Conditions:	
Power	1.00 KW
Pump Speed	25.0 rpm
Rinse Time	10 s
Sample Delay	30 s

Table III. Concentration (ppm) Range of Metal Standards

Elements	**Conc. (ppm)**
Al	0.796-49.8
Mn	0.160-10.00
Zn	0.241-15.1
Fe	0.165-10.3
Ca	0.800-50.0
Sr	0.081-5.09
Ba	0.080-5.00
Mg	0.831-51.9
Na	0.839-52.4
K	0.280-17.5

Table IV. Figure of Merits for the Elements and Tests

Element or Test	Range (ppm)	Sample SD[1]	Blank SD	LOD[2]	LOQ[3]
Al	ND[4] - 35.25	0.09	0.002	0.006	0.021
Mn	ND - 7.87	0.04	0.0001	0.0002	0.001
Fe	ND - 11.88	0.07	0.0001	0.0002	0.001
Ca	0.87 - 56.52	0.05	0.01	0.03	0.1
Mg	0.13 - 54.48	0.07	0.0007	0.002	0.007
Zn	ND - 1.30	0.004	0.0001	0.0002	0.001
Sr	ND - 0.28	0.0003	0.00001	0.00002	0.00006
Na	0.20 - 5.05	0.02	0.0001	0.0002	0.001
K	0.14 - 2.40	0.005	0.004	0.01	0.04
Ba	ND - 0.28	0.0001	0.00001	0.00002	0.00007
Sulfate	ND - 55.9	0.3	0.09	0.28	0.93
Tannin & Lignin	0.4 - 9.1	0.1	0.05	0.14	0.47
Silica	1.2 - 21.7	0.1	0.03	0.08	0.27

[1] SD = Standard Deviation; [2] Limit of Detection; [3] Limit of Quantification and [4] Not Detected.

Table V. Parameter Results of BW001, BW002 and BW003 Stations

Station	**BW001**	**BW002**	**BW003**
Date Range	9/7/96 - 5/15/98	1/6/98 - 5/15/98	10/5/97 - 1/6/98
pH Range	6.1 - 7.5	6.2 - 6.9	5.9 - 6.8
Avg.	6.6	6.6	6.3
Alkalinity Range[1]	11 - 18	19	18
Avg.	14	19	18
SO^{2-}_4 Range (ppm)	2.0 -14.4	0.9 - 4.8	0.9 - 6.4
Avg.	4.9	2.8	2.9
Al Range (ppm)	0.03 - 0.28	0.04 - 0.10	0.03 - 0.10
Avg.	0.10	0.07	0.07
Mn Range (ppm)	ND - 0.03	ND - 0.02	ND
Avg.	ND	0.01	ND
Zn Range (ppm)	ND - 0.03	ND	ND
Avg.	0.01	ND	ND
Sr Range (ppm)	0.01 - 0.02	0.02 - 0.03	0.02 - 0.03
Avg.	0.02	0.03	0.03
Ba Range (ppm)	0.02 - 0.03	0.03 - 0.23	0.02 - 0.03
Avg.	0.02	0.13	0.02
Fe Range (ppm)	0.03 - 0.27	0.07 - 0.29	0.06 - 0.26
Avg.	0.15	0.18	0.19
Ca Range (ppm)	11.1 - 14.9	9.17 - 14.4	9.12 - 17.0
Avg.	12.5	11.8	13.4
Mg Range (ppm)	0.75 - 0.97	0.56 - 0.93	0.57 - 1.06
Avg.	0.84	0.75	0.84
Na Range (ppm)	1.73 - 2.48	1.40 - 1.80	1.42 - 1.79
Avg.	2.42	1.60	1.59
K Range (ppm)	0.39 - 0.57	0.27 - 0.37	0.24 - 0.52
Avg.	0.45	0.32	0.37
Silica Range (ppm)	1.3 - 2.0	1.3 - 1.6	1.5 - 1.6
Avg.	1.7	1.5	1.6
T&L Range (ppm)	0.9 - 5.7	0.8 - 6.2	0.9 - 6.7
Avg.	4.3	3.5	4.5

[1] **(mg/L CaCO$_3$)**

Table VI. WVDNR, WVDEP and Our Parameter Results of BW006 and BW007 Stations

Group	**Our**	**Our**	**WVDNR**	**WVDEP**
Station	**BW006**	**BW007**	**BW007**	**BW007**
Date Range	5/17/97 - 5/15/98	6/10/97 - 5/15/98	11/11/88 - 9/13/94	9/27/94 - 4/24/95
pH Range (ppm)	4.5 - 5.4	5.8 - 6.7	5.7 - 7.9	6.1 - 7.8
Avg.	5.0	6.2	7.0	6.2
Acidity Range[1]	23	22	0 - 15	1 - 9
Avg.	23	22	2	2
Alkalinity Range[1]	1.4	1.4	3 - 50	2 - 44
Avg.	1.4	1.4	18	20
SO_4^{2-} Range (ppm)	0.5 - 9.0	0.9 - 6.6	1.0 - 15.0	1.0 - 11.4
Avg.	4.7	2.6	7.2	6.9
Al Range (ppm)	ND- 0.36	0.04 - 0.46	0.13 - 1.40	0.30 - 1.10
Avg.	0.20	0.17	0.42	0.55
Mn Range (ppm)	ND - 0.09	ND	ND - 0.41	0.04 - 0.14
Avg.	0.04	ND	0.06	0.09
Zn Range (ppm)	ND - 0.01	ND	-	-
Avg.	0.01	ND	-	-
Sr Range (ppm)	0.02	0.02 - 0.02	-	-
Avg.	0.02	0.02	-	-
Ba Range (ppm)	0.01	0.02 - 0.02	-	-
Avg.	0.01	0.02	-	-
Fe Range (ppm)	ND - 0.25	0.07 - 0.28	0.28 - 2.10	0.30 - 0.60
Avg.	0.13	0.20	0.83	0.45
Ca Range (ppm)	11.6	7.65 - 15.2	7.47 - 13.8	3.44 - 20.0
Avg.	11.6	12.1	10.2	10.1
Mg Range (ppm)	0.76	0.48 - 0.97	-	-
Avg.	0.76	0.77	-	-
Na Range (ppm)	1.21	1.47 - 1.54	-	-
Avg.	1.21	1.47	-	-
K Range (ppm)	0.42	0.21 - 0.55	-	-
Avg.	0.42	0.39	-	-
Silica Range (ppm)	3.9	1.1 - 1.7	-	-
Avg.	3.9	1.4	-	-
T&L Range (ppm)	0.5 - 0.8	0.8 - 6.5	-	-
Avg.	0.6	4.5	-	-

[1] **(mg/L $CaCO_3$)**

Table VII. Averaged Major, Minor and Trace Constituents of the North American Rivers

Station	**Average River**
$S0^{2-}_4$ (ppm)	11.5
Al (ppm)	<0.1
Mn (ppm)	<0.1
Fe (ppm)	<0.3
Ca (ppm)	14.8
Mg (ppm)	4.37
Na (ppm)	6.00
K (ppm)	2.74

Table VIII. Our Average Parameter Results

Station	pH	Acidity^1	Alkalinity^1	SO_4^{-2} ^{2}	Al^2	Mn^2	Zn^2	Sr^2	Ba^2	Fe^2	Ca^2	Mg^2	Na^2	K^2	Silica^2	T&L^2
BW001 - BW003	6.5	-	17	3.5	0.08	ND	ND	0.02	0.06	0.17	12.5	0.81	1.87	0.38	1.6	4.1
BW004	3.8	9	-	6.7	0.14	0.07	0.01	0.01	0.01	0.16	1.72	0.53	0.37	0.24	1.6	1.6
BW005	4.2	-	-	6.0	0.23	0.06	ND	ND	0.01	0.12	-	-	-	-	0.09	3.6
BW006	5.0	23	1.4	4.7	0.20	0.04	0.01	0.02	0.01	0.13	11.6	0.76	1.21	0.42	3.9	0.6
BW007	6.2	22	1.4	2.6	0.17	0.00	ND	0.02	0.02	0.20	12.1	0.77	1.47	0.39	1.4	4.5
BW008 - 8b	6.4	-	45	2.9	0.08	0.00	ND	0.03	0.02	0.17	16.0	0.9	1.83	0.46	2.6	3.0
BW009	5.1	15	7.5	45.4	0.40	0.54	0.04	0.03	0.02	0.08	19.8	3.7	3.25	0.69	1.6	2.3
BW010	7.6	-	46	-	0.11	ND	ND	-	-	0.03	-	-	-	-	-	-
BW011	6.1	-	8	28.2	0.97	0.11	0.01	-	-	0.10	-	-	-	-	-	0.6
NF001	6.5	-	17	39.0	0.17	0.03	ND	0.09	0.02	0.09	26.1	4.1	3.55	0.88	-	0.2
NF002	3.0			45.3	24.0	6.42	1.05	0.24	0.01	5.34	25.7	53.5	4.58	2.01	10.2	2.0
NF003	4.2	36	-	12.5	3.35	1.33	0.18	0.12	0.02	0.02	43.6	14.4	3.62	1.18	7.7	1.1
NF012	5.4	3	-	18.0	0.13	0.04	0.01	0.02	0.01	0.18	11.0	1.6	0.44	0.61	1.5	2.5
NF012a	3.8	29	-	7.70	3.18	0.62	0.12	0.05	0.01	0.35	30.0	6.7	1.16	1.10	5.8	1.7
NF013	2.6	129	-	28.7	9.18	1.13	0.25	0.08	0.01	12.3	40.7	11.5	0.78	1.59	3.5	0.3
NF014	4.1	29	-	14.8	3.28	1.73	0.23	0.14	0.03	0.03	52.7	15.7	3.54	1.40	3.5	2.1
NF015	3.2	83	-	22.8	5.37	0.33	0.12	0.05	0.02	3.26	22.8	4.2	2.12	0.65	4.2	1.4
NF015a	3.4	-	-	13.1	3.61	0.23	0.08	-	-	2.99	-	-	-	-	-	0.7
NF016	3.9	36	-	12.7	0.18	0.12	4.9	1.27	0.02	0.04	48.8	14	3.13	1.28	3.5	1.5
NF017	3.0	72	-	29.9	6.39	0.48	0.19	0.02	0.01	3.1	9.48	3.8	0.33	0.8	4.1	1.2
NF018	3.5	22	-	18.6	2.32	0.27	0.07	0.01	0.01	0.63	3.14	1.2	0.23	0.48	2.0	0.9
NF019	6.4	-	17	-	0.01	ND	ND	-	-	0.06	-	-	-	-	-	-
NF020	5.5	-	37	54.1	0.39	0.95	0.04	0.22	0.04	ND	37.5	14.2	4.61	1.82	2.9	1.7
NF021	5.4	-	18	15.7	0.12	0.03	ND	0.06	0.02	0.13	17.1	2.35	3.13	0.91	1.53	0.15
BB001 - BB003	5.9	-	16	5.50	0.08	0.02	0.01	0.05	0.06	0.65	10.0	0.75	0.65	0.50	1.8	3.1
BB004	5.3	138	31	27.0	1.03	0.28	0.12	0.03	0.06	28.2	12.3	1.77	2.84	1.71	10.5	9.0

^{1}(mg$CaCO_3$/L) and ^{2}(ppm).

Table IX. Parameter Results of BW004 and BW005 Stations

Station	**BW004**	**BW005**
Date Range	6/10/97 - 5/15/98	3/15/97 - 6/10/97
pH Range	3.2 - 4.1	4.0 -4.4
Avg.	3.8	4.2
Acidity Range[1]	6 - 14	-
Avg.	9	-
SO^{2-}_4 Range (ppm)	1.4 - 9.5	1.6 - 8.9
Avg.	6.7	6.0
Al Range (ppm)	0.09 - 0.35	0.16 - 0.28
Avg.	0.14	0.23
Mn Range (ppm)	0.03 - 0.14	0.05 - 0.07
Avg.	0.07	0.06
Zn Range (ppm)	ND -0.15	ND
Avg.	0.02	ND
Sr Range (ppm)	ND - 0.01	ND
Avg.	0.01	ND
Ba Range (ppm)	0.01 - 0.02	0.01 – 0.02
Avg.	0.01	0.01
Fe Range (ppm)	ND - 1.01	0.09 - 0.16
Avg.	0.16	0.12
Ca Range (ppm)	1.23 - 3.12	-
Avg.	1.72	-
Mg Range (ppm)	0.29 - 0.69	-
Avg.	0.53	-
Na Range (ppm)	0.26 - 0.44	-
Avg.	0.37	-
K Range (ppm)	0.12 - 0.32	-
Avg.	0.24	-
Silica (ppm)	1.2 - 1.9	1.6 - 1.6
Avg.	1.6	1.6
T&L (ppm)	ND - 4.0	0.7 - 8.4
Avg.	0.9	3.6

[1] **(mg/L $CaCO_3$)**

Table X. Chemical Compounds Used in Acid Mine Drainage Treatment[1]

Common Name	**Formula**	**Conversion Factor**[2]	**Neutralization Efficiency**[3]	**1996 Cost**[4] $ per ton or gal.	
				Bulk	**<Bulk**
Limestone	$CaCO_3$	1.00	30%	$ 10	$ 15
Hydrated Lime	$Ca(OH)_2$	0.74	90%	$ 60	$100
Pebble Quicklime	CaO	0.56	90%	$ 80	$240
Soda Ash	Na_2CO_3	1.06	60%	$200	$320
Caustic Soda (solid)	$NaOH$	0.80	100%	$680	$880
20% Liquid Caustic	$NaOH$	784	100%	$0.46	$0.60
50% Liquid Caustic	$NaOH$	256	100%	$1.10	$1.25
Ammonia	NH_3	0.34	100%	$300	$680

[1] Taken from Ref. 3 (Table 1).

[2] The conversion factor may be multiplied by the estimated tons acid/yr to get tons of chemical needed for neutralization per year.

[3] Neutralization Efficiency estimates the relative effectiveness of the chemical in neutralizing acid mine drainage acidity. For example, if 100 tons of acid/yr was the amount of acid to be neutralized, then it can estimated that 82 tons of hydrated lime would be need to neutralize the acidity in the water (100(0.74)/0.90).

[4] Price of chemical depends on the quantity being delivered. Bulk means delivery of chemical in a large truck, whereas <Bulk means purchased in small quantities.

Table XI. Parameter Results of BW008, BW008a and BW008b Stations

Station	**BW008**	**BW008a**	**BW008b**
Date	9/7/96 - 10/12/96	2/15/97 - 10/5/97	5/15/98
pH Range	5.9 - 7.1	6.4 - 7.2	6.0 - 6.2
Avg.	6.3	6.7	6.1
Alkalinity Range[1]	13	-	18 - 134
Avg.	13	-	76
SO^{2-}_4 Range (ppm)	-	3.7 - 5.9	0.8 - 1.3
Avg.	-	4.8	1.1
Al Range (ppm)	0.03 - 0.08	0.03 - 0.07	0.12
Avg.	0.06	0.05	0.12
Mn Range (ppm)	ND	ND	ND
Avg.	ND	ND	ND
Zn Range (ppm)	ND	0.02	ND
Avg.	ND	0.02	ND
Sr Range (ppm)	-	-	0.03 - 0.03
Avg.	-	-	0.03
Ba Range (ppm)	-	0.03	0.01 - 0.01
Avg.	-	0.03	0.01
Fe Range (ppm)	0.10 - 0.12	0.13 - 0.24	0.18 - 0.24
Avg.	0.12	0.19	0.21
Ca Range (ppm)	-	15.6	15.0 - 17.8
Avg.	-	15.6	16.4
Mg Range (ppm)	-	0.97	0.68 - 0.81
Avg.	-	0.97	0.74
Na Range (ppm)	-	1.45	1.39 - 1.45
Avg.	-	1.45	2.22
K Range (ppm)	-	0.53	0.36 - 0.41
Avg.	-	0.53	0.39
Silica Range (ppm)	-	-	1.7 - 3.5
Avg.	-	-	2.6
T&L Range (ppm)	-	3.8 - 7.0	0.6 - 0.7
Avg.	-	5.4	0.7

[1] **($CaCO_3$ mg/L)**

Table XII. WVDNR, WVDEP and Our Parameter Results of Below Dam Station

Group Station	**WVDEP Below Dam**	**WVDNR Below Dam**	**Our Below Dam**
Date Range	10/18/94 - 4/24/95	9/27/94 - 3/11/97	9/7/96 - 5/15/98
pH Range	7.0 - 8.2	6.1 - 8.6	5.9 - 7.2
Avg.	7.7	7.6	6.4
Acidity Range[1]	0 - 1	0 - 15	-
Avg.	1	1	-
Alkalinity Range[1]	47 - 116	36 - 160	13 - 134
Avg.	71	76	45
SO^{2-}_4 Range (ppm)	1.4 - 11.6	1.0 - 13.0	0.8 - 5.9
Avg.	6.9	6.8	2.9
Al Range (ppm)	0.20 - 1.00	0.14 - 1.00	0.03 - 0.12
Avg.	0.55	0.43	0.08
Mn Range (ppm)	0.04 - 0.18	0.08 - 0.62	0.00 - 0.00
Avg.	0.10	0.08	0.00
Zn Range (ppm)	-	-	ND
Avg.	-	-	ND
Sr Range (ppm)	-	-	ND - 0.03
Avg.	-	-	0.03
Ba Range (ppm)	-	-	0.01 - 0.03
Avg.	-	-	0.02
Fe Range (ppm)	0.30 - 0.90	0.25 - 1.80	1.7 - 3.5
Avg.	0.63	0.74	0.17
Ca Range (ppm)	7.84 - 23.0	14.2 - 23.0	15.0 - 17.8
Avg.	13.9	14.2	16.0
Silica Range (ppm)	-	-	1.7 - 3.5
Avg.	-	-	2.6
T&L Range (ppm)	-	-	0.6 - 7.0
Avg.	-	-	3.0

[1] ($CaCO_3$ mg/L)

Table XIII. WVDEP, WVDNR and Our Parameter Results of BW009 and BW010 Stations

Group	**WVDEP**	**WVDNR**	**Our**	**Our**
Station	**BW009**	**BW009**	**BW009**	**BW010**
Date Range	9/27/94 - 4/24/95	9/27/94 - 3/11/97	9/7/96 - 5/15/98	10/12/96
pH Range	4.6 - 5.8	4.5 - 5.8	4.6 - 5.7	7.6
Avg.	4.6	4.9	5.1	7.6
Acidity Range[1]	1 - 31	0 - 42	15	-
Avg.	10	14	15	-
Alkalinity Range[1]	1 - 4	1 - 4	0 - 15	46
Avg.	2	2	7.5	46
SO^{2-}_4 Range (ppm)	39.6 - 97.6	22.0 - 97.6	42.1 - 51.3	-
Avg.	56.4	47.8	45.4	-
Al Range (ppm)	0.60 - 3.10	0.60 - 3.10	0.13 - 0.66	0.11
Avg.	1.47	1.24	0.40	0.11
Mn Range (ppm)	0.55 - 1.00	0.30 - 1.36	0.24 - 1.23	ND
Avg.	0.67	0.65	0.54	ND
Zn Range (ppm)	-	-	ND - 0.07	-
Avg.	-	-	0.04	-
Sr Range (ppm)	-	-	0.03 - 0.04	-
Avg.	-	-	0.03	-
Ba Range (ppm)	-	-	0.01 - 0.03	-
Avg.	-	-	0.02	-
Fe Range (ppm)	0.6 - 7.40	0.49 - 7.40	0.00 - 0.22	0.03
Avg.	1.83	1.20	0.08	0.03
Ca Range (ppm)	8.00 - 27.2	8.0 - 27.2	14.4 - 26.2	-
Avg.	15.2	15.3	19.8	-
Mg Range (ppm)	-	-	2.61 - 4.89	-
Avg.	-	-	3.66	-
Na Range (ppm)	-	-	4.47 - 2.74	-
Avg.	-	-	3.25	-
K Range (ppm)	-	-	0.45 - 0.97	-
Avg.	-	-	0.69	-
Silica Range (ppm)	-	-	1.5 - 1.7	-
Avg.	-	-	1.6	-
T&L Range (ppm)	-	-	0.4 - 4.3	-
Avg.	-	-	2.3	-

[1] **($CaCO_3$ mg/L)**

Table XIV. Parameter Results of NF001, NF019, NF020 and NF021 Stations

Station	NF001	NF019	NF020	NF021
Date Range	9/8/96 - 5/16/98	9/7/96	1/5/98 - 5/16/98	5/16/98
pH Range	6.0 - 7.2	6.4	5.4 - 5.5	5.4
Avg.	6.5	6.4	5.5	5.4
Alkalinity Range[1]	16 - 21	17	37	18
Avg.	17	17	37	18
SO^{2-}_4 Range (ppm)	34.1 - 48.1	-	52.3 - 56.0	15.7
Avg.	39.0	-	54.1	15.7
Al Range (ppm)	0.11 - 0.22	0.01	0.18 - 0.59	0.12
Avg.	0.17	0.01	0.39	0.12
Mn Range (ppm)	ND - 0.06	ND	0.86 - 1.04	0.03
Avg.	0.03	ND	0.95	0.03
Zn Range (ppm)	ND	ND	0.02 - 0.06	ND
Avg.	ND	ND	0.04	ND
Sr Range (ppm)	0.09	-	0.19 - 0.25	0.06
Avg.	0.09	-	0.22	0.06
Ba Range (ppm)	0.02	-	0.03 - 0.05	0.02
Avg.	0.02	-	0.04	0.02
Fe Range (ppm)	ND - 0.21	0.06	ND - 0.01	0.13
Avg.	0.09	0.06	ND	0.13
Ca Range (ppm)	26.1	-	16.3 - 58.7	17.1
Avg.	26.1	-	37.5	17.1
Mg Range (ppm)	4.09	-	12.3 - 16.1	2.35
Avg.	4.09	-	14.2	2.35
Na Range (ppm)	3.55	-	3.95 - 5.27	3.13
Avg.	3.55	-	4.61	3.13
K Range (ppm)	0.88	-	1.71 - 1.94	0.91
Avg.	0.88	-	1.82	0.91
Silica Range (ppm)	-	-	2.9	1.53
Avg.	-	-	2.9	1.53
T&L Range (ppm)	ND - 0.4	-	0.2 - 3.1	0.15
Avg.	0.2	-	1.7	0.15

[1] **($CaCO_3$ mg/L)**

Table XV. WVDNR and Our Parameter Results of NF020 Station

Group	**WVDNR**	**Our**
Station	**NF020**	**NF020**
Date Range	9/17/96 - 12/3/96	1/5/98 - 5/16/98
pH Range	6.0 - 6.7	5.4 - 5.5
Avg.	6.3	5.5
Acidity Range[1]	1 -1	-
Avg.	1	-
Alkalinity Range[1]	17 - 33	37
Avg.	26	37
SO^{2-}_4 Range (ppm)	54 - 177	52.3 - 56.0
Avg.	123.2	54.1
Al Range (ppm)	0.86 - 3.65	0.18 - 0.59
Avg.	1.61	0.39
Mn Range (ppm)	0.58 - 1.62	0.86 - 1.04
Avg.	1.09	0.95
Zn Range (ppm)	-	0.02 - 0.06
Avg.	-	0.04
Sr Range (ppm)	-	0.19 - 0.25
Avg.	-	0.22
Ba Range (ppm)	-	0.03 - 0.05
Avg.	-	0.04
Fe Range (ppm)	0.05 - 1.37	ND - 0.01
Avg.	0.32	ND
Ca Range (ppm)	-	16.3 - 58.7
Avg.	-	37.5
Mg Range (ppm)	-	12.3 - 16.1
Avg.	-	14.2
Na Range (ppm)	-	3.95 - 5.27
Avg.	-	4.61
K Range (ppm)	-	1.71 - 1.94
Avg.	-	1.82
Silica Range (ppm)	-	2.9
Avg.	-	2.9
T&L Range (ppm)	-	0.2 - 3.1
Avg.	-	1.7

[1] **($CaCO_3$ mg/L)**

Table XVI. Parameter Results of NF002a, NF002b, NF002c and NF002d Stations

Station	**NF002a**	**NF002b**	**NF002c**	**NF002d**
Date Range	9/7/96 - 5/16/98	5/16/97 - 5/16/98	10/12/96 - 5/16/97	10/12/96 - 5/16/97
pH Range	2.7 - 3.4	2.6 - 3.8	2.9 - 3.1	2.7 - 3.1
Avg.	2.9	3.2	3.0	2.9
SO_4^{2-} Range (ppm)	41.0 - 50.5	32.7 - 51.6	45.1 - 52.0	37.6 - 45.3
Avg.	45.6	45.5	48.6	41.4
Al Range (ppm)	23.8 - 35.3	14.3 - 31.9	24.0 - 27.3	18.4 - 20.9
Avg.	26.9	24.1	25.1	19.7
Mn Range (ppm)	6.49 - 7.87	6.89 - 7.94	6.33 - 7.66	3.97 - 4.75
Avg.	7.16	7.41	6.83	4.29
Zn Range (ppm)	1.03 - 1.30	1.02 - 1.29	1.16 - 1.17	0.68 - 0.86
Avg.	1.14	1.15	1.14	0.78
Sr Range (ppm)	0.21 - 0.23	0.22 - 0.26	-	-
Avg.	0.23	0.24	-	-
Ba Range (ppm)	ND - 0.02	ND	-	-
Avg.	0.01	ND	-	-
Fe Range (ppm)	2.42 - 11.9	3.52 - 8.30	2.02 - 5.10	2.46 - 7.49
Avg	6.08	6.49	3.09	5.68
Ca Range (ppm)	20.7 - 24.2	23.01 - 32.68	-	-
Avg.	22.5	27.8	-	-
Mg Range (ppm)	51.7 - 56.6	52.0 - 54.5	-	-
Avg.	54.0	53.0	-	-
Na Range (ppm)	4.21 - 5.05	4.35 - 4.95	-	-
Avg.	4.52	4.65	-	-
K Range (ppm)	1.83 - 2.02	2.02 - 2.07	-	-
Avg.	1.98	2.05	-	-
Silica Range (ppm)	9.7 - 11.5	9.9	-	-
Avg.	10.5	9.9	-	-
T&L (ppm)	0.6 - 9.0	0.6 - 5.7	0.5 - 1.3	0.7 - 4.1
Avg.	2.2	2.4	0.9	2.4

Table XVII. WVDEP, WVDNR and Our Parameter Results of Douglas Mine and NF003 Stations

Group Station	**WVDEP Douglas Mine**	**WVDNR Douglas Mine**	**Our Douglas Mine**	**Our NF003**
Date Range	4/21/94 - 4/24/95	4/21/96 - 3/11/97	9/7/96 - 5/16/98	9/8/96 - 5.16/98
pH Range	2.8 - 3.1	2.6 - 3.4	2.6 - 3.8	3.7 - 4.8
Avg.	3.0	3.0	3.0	4.2
Acidity Range[1]	67 - 375	67 - 394	-	36
Avg.	283	267	-	36
Alkalinity Range[1]	0 - 1	0 - 1	-	-
Avg.	1	1	-	-
SO^{2-}_4 Range (ppm)	380 - 730	254 - 730	32.7 - 52.0	12.5
Avg.	606.0	502.0	45.3	12.5
Al Range (ppm)	25.4 - 41.1	18.0 - 51.5	14.3 - 35.3	0.31 - 6.05
Avg.	33.6	29.1	23.9	3.35
Mn Range (ppm)	4.63 - 8.40	2.13 - 9.22	3.97 - 7.94	0.77 - 1.94
Avg.	6.58	5.74	6.42	1.33
Zn Range (ppm)	-	-	0.68 - 1.30	0.09 - 0.26
Avg.	-	-	1.05	0.18
Sr Range (ppm)	-	-	0.21 - 0.26	0.12
Avg.	-	-	0.24	0.12
Ba Range (ppm)	-	-	ND - 0.02	0.02
Avg.	-	-	0.01	0.02
Fe Range (ppm)	4.30 - 28.0	4.30 - 50.6	2.02 - 11.9	0.01 - 0.03
Avg.	20.6	17.8	4.46	0.02
Ca Range (ppm)	38.0 - 120	38.0 - 120	20.7 - 32.7	43.6
Avg.	62.4	63.4	25.2	43.6
Mg Range (ppm)	-	-	51.7 - 56.6	14.4
Avg.	-	-	53.5	14.4
Na Range (ppm)	-	-	4.21 - 5.05	3.62
Avg.	-	-	4.58	3.62
K Range (ppm)	-	-	1.83 - 2.07	1.18
Avg.	-	-	2.01	1.18
Silica Range (ppm)	-	-	9.7 - 11.5	7.7
Avg.	-	-	10.2	7.7
T&L (ppm)	-	-	0.6 - 5.7	0.2 - 2.6
Avg.	-	-	2.0	1.1

[1] **(mg/L $CaCO_3$)**

Table XVIII. Parameters Results of Stations in ALD/Wetland Treatment System

Station	Date	pH	Acidity[1]	SO_4^{-2}[2]	Al[2]	Mn[2]	Zn[2]	Sr[2]	Ba[2]	Fe[2]	Ca[2]	Mg[2]	Na[2]	K[2]	Silica[2]	T&L[2]
NF004	10/6/97	2.7	-	38.3	24.6	4.99	0.87	0.20	0.01	8.45	15.0	37.6	3.01	2.05	-	2.9
	1/5/98	2.8	-	51.1	20.8	3.48	0.82	0.19	0.02	8.42	15.6	29.4	3.19	1.95	10.7	7.6
	5/16/98	2.6	189	31.8	17.5	3.30	0.66	0.17	0.00	7.16	13.8	26.7	3.45	1.88	21.5	0.4
NF005	6/10/97	2.7	-	28.1	15.3	2.48	0.53	-	-	7.51	-	-	-	-	-	2.1
	5/16/98	2.5	202	39.6	17.5	3.24	0.64	0.17	0.00	7.37	13.4	26.0	3.42	1.87	20.5	0.3
NF006	6/10/97	2.7	-	29.8	15.4	2.56	0.53	-	-	7.60	-	-	-	-	-	5.5
	5/16/98	2.7	184	34.5	17.6	3.24	0.66	0.17	0.00	7.13	14.4	26.3	3.43	1.89	9.0	0.5
NF007	1/5/98	2.9	-	51.9	21.0	2.90	0.59	0.21	0.03	3.06	17.8	23.3	4.17	2.18	12.0	4.3
	5/16/98	2.7	184	37.0	18.0	3.69	0.66	0.19	0.00	5.99	16.1	26.5	3.66	1.98	9.7	0.3
NF008	5/16/98	2.8	179	41.3	17.7	3.22	0.63	0.19	0.01	2.81	17.1	26.6	3.80	2.06	9.3	0.3
NF009	1/5/98	3.1	-	47.8	17.7	2.61	0.56	0.19	0.03	0.78	17.5	23.0	4.31	2.01	10.0	4.2
NF010	6/10/97	2.8	-	30.6	14.6	2.36	0.48	-	-	5.10	-	-	-	-	-	2.4
	10/6/97	6.2	-	37	0.99	1.13	0.33	0.27	0.03	0.00	38	34.7	3.56	2.32	-	6.8
NF010a	10/6/97	6.6	-	37.4	1.99	1.46	0.11	0.28	0.03	0.00	32.3	33.5	3.43	2.40	-	8.2
NF010b	10/6/97	4.2	-	38.7	6.40	3.45	0.48	0.27	0.03	0.03	33.4	35.6	3.34	2.21	-	9.1
NF010c	10/6/97	4.3	-	40.3	6.58	3.51	0.50	0.27	0.03	0.02	34.2	35.9	3.44	2.27	-	8.4
NF011	6/10/97	2.8	-	29.6	14.9	2.38	0.48	-	-	4.58	-	-	-	-	-	2.7
	10/6/97	6.6	-	36.6	2.00	1.74	0.04	0.28	0.03	0.00	42.2	33.1	3.55	2.39	-	8.5
	1/5/98	3.2	-	50.2	16.7	2.49	0.55	0.20	0.03	0.19	21.1	23.7	4.25	2.00	9.6	9.4
	5/16/98	3.0	131	24.6	16.0	2.89	0.57	0.20	0.01	2.01	21.1	25.9	4.19	2.08	8.9	0.5

[1] **(mg/L $CaCO_3$)** and [2] **(ppm).**

Table XIX. Parameter Results of NF012, NF012a, NF013 and NF014 Stations

Station	NF012	NF013	NF012a	NF014
Date Range	6/10/97 - 5/16/98	6/10/97 - 5/16/98	5/16/98	10/6/97 - 5/16/98
pH Range	4.7 - 6.2	2.3 - 2.8	3.8	4.0 - 4.1
Avg.	5.4	2.6	3.8	4.1
Acidity Range[1]	3	129	29	29
Avg.	3	129	29	29
SO^{2-}_4 Range (ppm)	1.2 - 28.8	20.8 - 45.9	7.7	12.1 - 17.4
Avg.	18.0	28.7	7.7	14.8
Al Range (ppm)	0.06 - 0.22	6.29 - 15.6	3.18	2.99 - 3.57
Avg.	0.13	9.18	3.18	3.28
Mn Range (ppm)	0.00 - 0.07	0.78 - 1.69	0.62	1.44 - 2.02
Avg.	0.04	1.13	0.62	1.73
Zn Range (ppm)	ND - 0.04	0.21 - 0.38	0.12	0.20 - 0.26
Avg.	0.01	0.28	0.12	0.23
Sr Range (ppm)	0.01 - 0.02	0.06 - 0.10	0.05	0.11 - 0.16
Avg.	0.02	0.08	0.05	0.14
Ba Range (ppm)	0.01 - 0.01	ND - 0.03	0.01	0.02 - 0.03
Avg.	0.01	5.4 - 6.2	0.01	0.03
Fe Range (ppm)	0.10 - 0.27	7.69 - 15.7	0.35	0.03 - 0.04
Avg.	0.18	12.32	0.35	0.03
Ca Range (ppm)	6.40 - 16.3	32.1 - 50.5	30.0	41.6 - 63.9
Avg.	11.01	40.67	30.0	52.7
Mg Range (ppm)	0.96 - 2.35	9.62 - 15.0	6.66	12.8 - 18.6
Avg.	1.64	11.5	6.66	15.7
Na Range (ppm)	0.31 - 0.57	0.50 - 1.28	1.16	3.33 - 3.74
Avg.	0.44	0.78	1.16	3.54
K Range (ppm)	0.32 - 0.87	1.34 - 1.91	1.10	1.17 - 1.64
Avg.	0.61	1.59	1.10	1.40
Silica Range (ppm)	1.3 - 1.6	5.4 - 3.9	3.5	3.5
Avg.	1.5	5.8	3.5	3.5
T&L	0.2 - 3.9	0.1 - 3.9	0.3	0.3 - 3.9
Avg.	2.5	1.7	0.3	2.1

[1] (CaCO3 mg/L)

Table XX. WVDNR and Our Parameters Results of NF015, NF015a and NF016 Stations

Group	**WVDNR**	**Our**	**Our**	**Our**
Station	**NF015**	**NF015**	**NF015a**	**NF016**
Date Range	1/25/95 - 3/11/97	5/16/97 - 5/16/98	6/10/97 - 5/17/98	5/16/97 - 5/16/98
pH Range	2.8 -7.3	2.8 - 4.1	2.9 - 3.9	3.7 - 4.1
Avg.	3.4	3.2	3.4	3.9
Acidity Range[1]	1 - 254	83	-	36
Avg.	98	83	-	36
SO^{2-}_{4} Range (ppm)	8.0 - 546	10.0 - 52.2	8.8 - 17.3	6.90 - 18.5
Avg.	119	22.8	13.1	12.7
Al Range (ppm)	0.32 - 26.70	0.71 - 11.1	0.57 - 6.64	3.55 - 6.39
Avg.	8.06	5.37	3.61	4.90
Mn Range (ppm)	0.06 - 6.81	0.12 - 0.54	0.05 - 0.42	0.88 - 1.71
Avg.	0.71	0.33	0.23	1.27
Zn Range (ppm)	-	0.04 - 0.19	ND - 0.15	0.13 -0.23
Avg	-	0.12	0.08	0.18
Sr Range (ppm)	-	0.04 - 0.06	-	0.10 - 0.14
Avg.	-	0.05	-	0.12
Ba Range (ppm)	-	0.01 -0.02	-	0.02 - 0.02
Avg.	-	0.02	-	0.02
Zn Range (ppm)	-	0.04 - 0.19	ND - 0.15	0.13 - 0.23
Avg.	-	0.12	0.08	0.18
Sr Range (ppm)	-	0.04 - 0.06	-	0.10 - 0.14
Avg.	-	0.05	-	0.12
Fe Range (ppm)	0.20 - 23.1	0.03 - 5.18	0.07 - 5.82	0.01 - 0.10
Avg.	6.59	3.26	2.99	0.04
Ca Range (ppm)	14.2 - 56.0	17.3 - 29.8	-	41.0 - 56.5
Avg.	30.4	22.8	-	48.8
Mg Range (ppm)	-	3.04 - 5.30	-	11.2 - 15.8
Avg.	-	4.16	-	13.5
Na Range (ppm)	-	1.21 - 3.65	-	2.99 - 3.27
Avg	-	2.12	-	3.13
K Range (ppm)	-	0.40 - 0.81	-	1.08 - 1.48
Avg.	-	0.65	-	1.28
Silica Range (ppm)	-	3.7 - 4.7	-	3.5
Avg.	-	4.2	-	3.5
T&L Range (ppm)	-	0.2 - 3.2	0.7	0.1 - 4.2
Avg.	-	1.4	0.7	1.5

[1] **($CaCO_3$ mg/L)**

Table XXI. WVDEP, WVDNR and Our Parameter Results of NF017, NF018 and BW011 Stations

Group Station	**Our NF017**	**Our NF018**	**WVDEP BW011**	**WVDNR BW011**	**Our BW011**
Date Range	6/1097 - 5/16/98	5/16/97 - 5/16/98	10/25/94 - 4/24/95	10/25/94 - 3/11/97	9/8/96 - 3/15/97
pH Range	2.9 - 3.0	3.2 - 3.8	6.1 - 7.0	4.7 - 7.4	5.9 - 6.2
Avg.	3.0	3.5	6.5	6.4	6.1
Alkalinity Range[1]	-	-	8 - 18	7 - 18	8
Avg.	-	-	8	7	8
Acidity Range[1]	72	22	3 - 9	0 - 20	-
Avg.	72	22	3	5	-
SO^{2-}_4 Range (ppm)	12.5 - 47.3	10.3 - 25.1	28.1 - 45.3	14.0 - 145.0	28.2
Avg.	29.9	18.6	35.5	39.0	28.2
Al Range (ppm)	5.69 - 7.09	1.25 - 4.45	1.10 - 2.30	0.69 - 7.30	0.13 - 2.64
Avg.	6.39	2.32	1.55	1.61	0.97
Mn Range (ppm)	0.43 - 0.53	0.19 - 0.37	0.21 - 0.44	0.12 - 0.98	0.04 - 0.17
Avg.	0.48	0.27	0.30	0.33	0.11
Zn Range (ppm)	0.19 - 0.19	0.04 - 0.12	-	-	ND - 0.02
Avg.	0.19	0.07	-	-	0.01
Sr Range (ppm)	0.02	0.01	-	-	-
Avg.	0.02	0.01	-	-	-
Ba Range (ppm)	0.01	0.01	-	-	-
Avg.	0.01	0.01	-	-	-
Fe Range (ppm)	2.64 - 3.56	0.18 - 1.27	0.80 - 1.30	0.51 - 4.50	0.00 - 0.26
Avg.	3.10	0.63	1.00	1.17	0.10
Ca Range (ppm)	9.48	3.14	9.70 - 28.8	9.70 - 33.6	-
Avg.	9.48	3.14	15.2	16.5	-
Mg Range (ppm)	3.82	1.18	-	-	-
Avg.	3.82	1.18	-	-	-
Na Range (ppm)	0.33	0.23	-	-	-
Avg.	0.33	0.23	-	-	-
K Range (ppm)	0.80	0.48	-	-	-
Avg.	0.80	0.48	-	-	-
Silica (ppm)	4.1	2	-	-	-
Avg.	4.1	2	-	-	-
T&L (ppm)	0.6 - 1.7	0.2 - 2.2	-	-	0.6
Avg.	1.2	0.9	-	-	0.6

[1] ($CaCO_3$ mg/L)

Table XXII. Parameter Results of BB001a, BB001b and BB001c

Station	**BB001a**	**BB001b**	**BB001c**
Date Range	10/4/97 & 5/16/98	10/4/97	10/4/97 & 5/16/98
pH Range	5.7 - 6.1	6.1	5.6 - 6.1
Avg.	5.9	6.1	5.9
Alkalinity Range[1]	9	-	7
Avg.	9	-	7
Acidity Range[1]	1	-	-
Avg.	1	-	-
SO^{2-}_4 Range (ppm)	3.1	-	4.4 - 8.7
Avg.	3.1	-	6.6
Al Range (ppm)	0.01 - 0.05	0.02	ND - 0.02
Avg.	0.03	0.02	0.01
Mn Range (ppm)	ND	ND	ND - 0.01
Avg.	ND	ND	0.01
Zn Range (ppm)	ND	ND	ND - 0.04
Avg.	ND	ND	0.02
Sr Range (ppm)	0.02 - 0.03	0.01	0.01 - 0.03
Avg.	0.03	0.01	0.02
Ba Range (ppm)	0.03 - 0.03	0.03	0.02 - 0.03
Avg.	0.03	0.03	0.03
Fe Range (ppm)	0.09 - 0.26	0.07	0.11 - 0.42
Avg.	0.18	0.07	0.27
Ca Range (ppm)	5.21 - 8.01	5.36	5.83 - 8.62
Avg.	6.61	5.36	7.23
Mg Range (ppm)	0.68 - 0.83	0.59	0.62 - 0.95
Avg.	0.76	0.59	0.79
Na Range (ppm)	0.52 - 0.64	0.58	0.48 - 1.03
Avg.	0.58	0.58	0.78
K Range (ppm)	0.42 - 0.56	0.60	0.43 - 0.49
Avg.	0.49	0.60	0.46
Silica Range (ppm)	1.2	-	-
Avg.	1.2	-	-
T&L	0.6 - 4.7	4.9	0.9 - 5.1
Avg.	2.7	4.9	3.0

[1](CaCO3 mg/L)

Table XXIII. Parameter Results of BB002a, BB002b, BB003 and BB004 Stations

Station	**BB002a**	**BB002b**	**BB003**	**BB004**
Date Range	5/16/98	10/4/97 & 5/16/98	10/4/97 & 5/16/98	5/16/98
pH Range	4.9	5.6 - 6.1	6.2 - 6.3	5.3
Avg.	4.9	5.9	6.2	5.3
Alkalinity Range[1]	0	18	45	31
Avg.	0	18	45	31
Acidity Range[1]	-	-	-	138
Avg.	-	-	-	138
SO^{2-}_4 Range (ppm)	5.0	2.6 - 14.5	2.5 - 2.9	27.0
Avg.	5.0	8.9	2.7	27.0
Al Range (ppm)	0.32	0.05 - 0.14	0.05 -0.17	1.03
Avg.	0.32	0.10	0.11	1.03
Mn Range (ppm)	0.17	ND - 0.03	ND - 0.03	0.28
Avg.	0.17	0.02	0.02	0.28
Zn Range (ppm)	0.03	ND	ND	0.12
Avg.	0.03	ND	ND	0.12
Sr Range (ppm)	0.21	ND - 0.03	0.03 - 0.09	0.03
Avg.	0.21	0.02	0.06	0.03
Ba Range (ppm)	0.20	ND - 0.05	0.02 - 0.03	0.06
Avg.	0.20	0.03	0.03	0.06
Fe Range (ppm)	1.71	0.07 - 0.77	0.20 - 1.00	28.2
Avg.	1.71	0.42	0.6	28.2
Ca Range (ppm)	7.74	0.96 - 12.1	14.5 - 31.7	12.3
Avg.	7.74	6.53	23.1	12.3
Mg Range (ppm)	0.94	ND - 0.83	0.65 - 1.41	1.77
Avg.	0.94	0.42	1.03	1.77
Na Range (ppm)	1.28	ND - 0.48	0.51 - 0.93	2.84
Avg.	1.28	0.24	0.72	2.84
K Range (ppm)	0.55	0.30 - 0.85	0.21 - 0.57	1.71
Avg.	0.55	0.58	0.39	1.71
Silica Range (ppm)	2.9	1.7	1.8	10.5
Avg.	2.9	1.7	1.8	10.5
T&L	2.8	1.6 - 3.9	1.0 - 5.9	9.0
Avg.	2.8	2.8	3.5	9.0

[1] **($CaCO_3$ mg/L)**

Figure 1. Location of the Blackwater Falls.

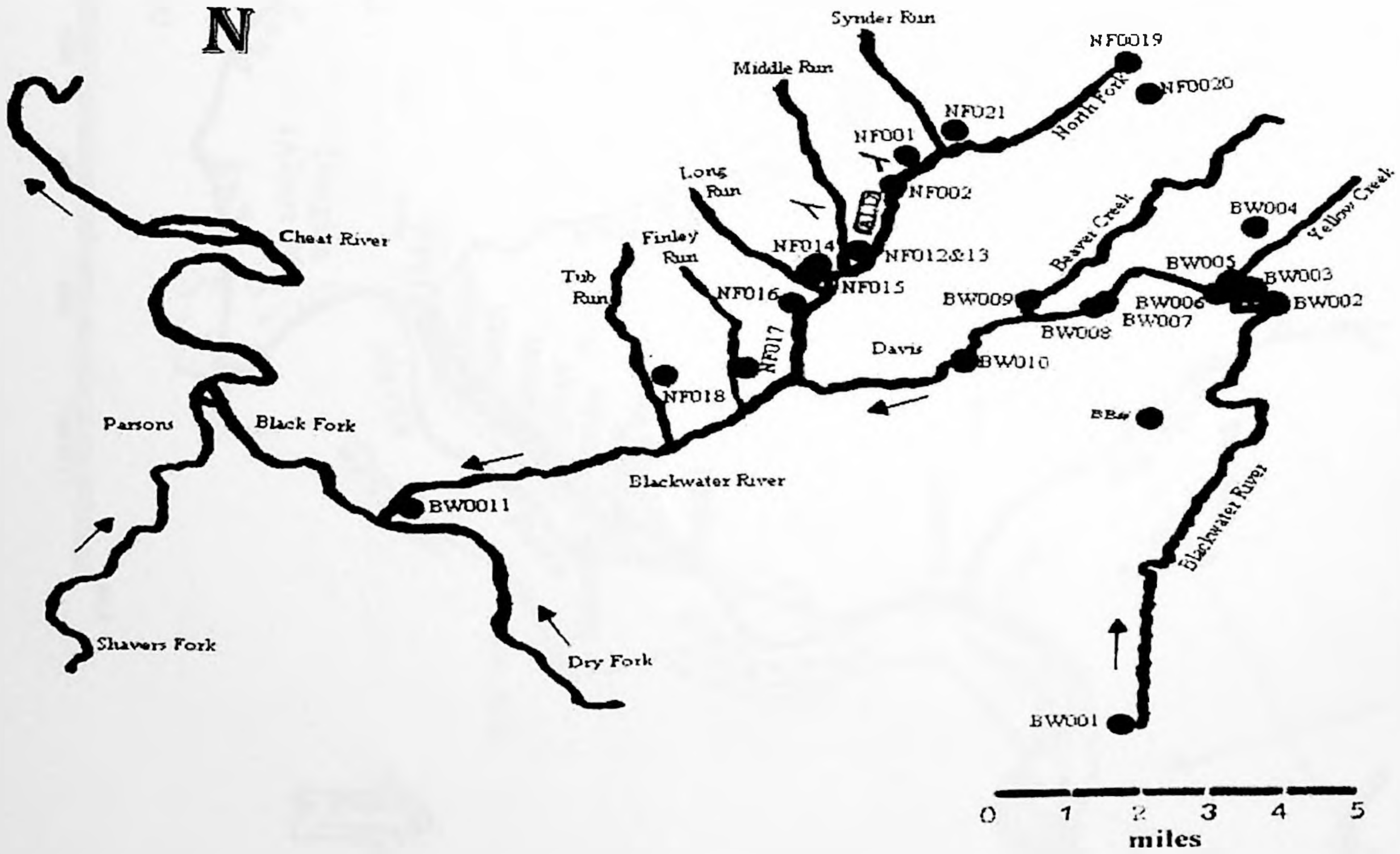

Figure 2. Map of Blackwater River Station Locations.

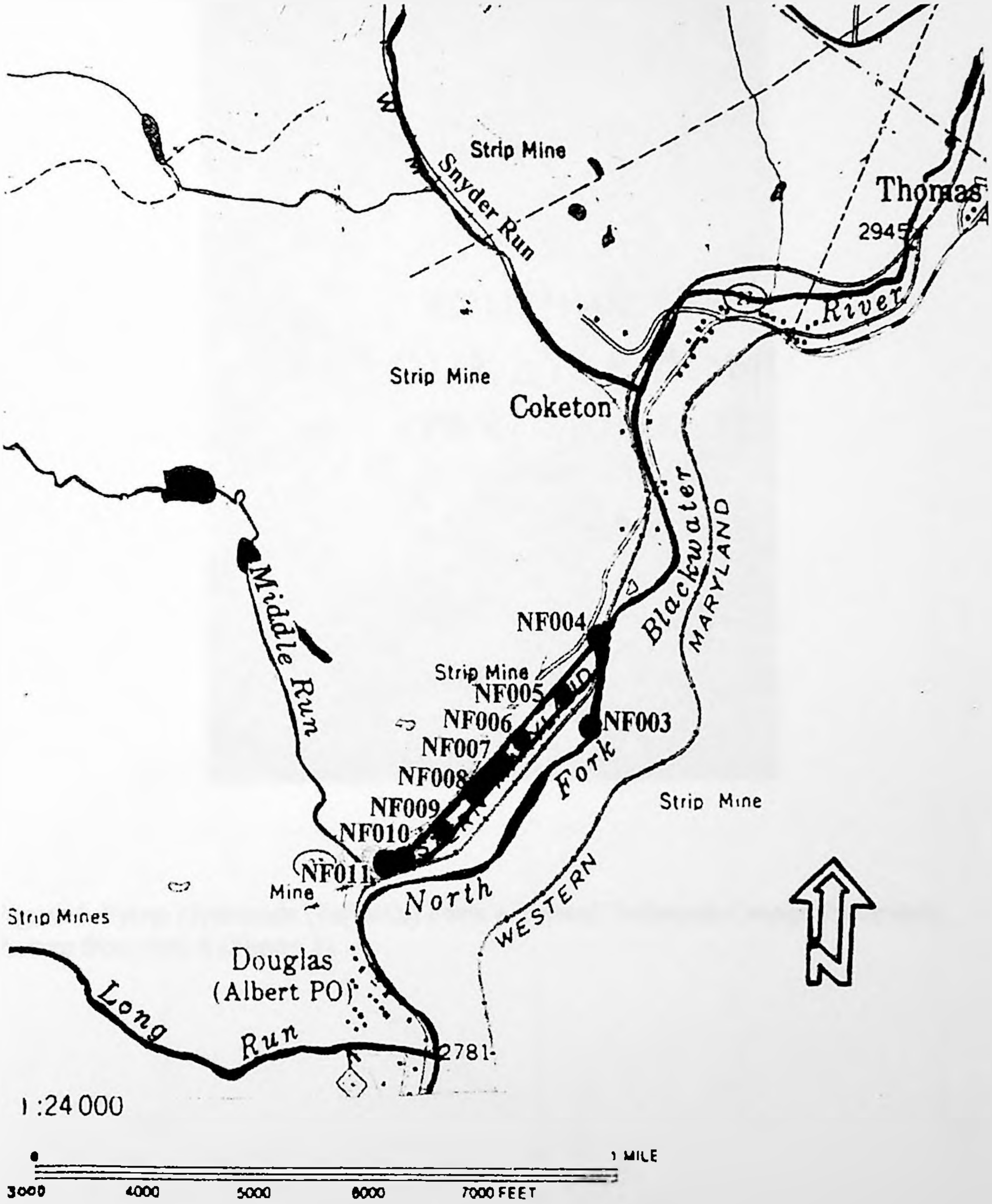

Figure 3. ALD Station Locations in a Section of North Fork.

Figure 4. Ferric Hydroxide ($Fe(OH)_3$) Form a Typical Yellowish-Orange Precipitate. Picture from Ref. 4 (Figure 3).

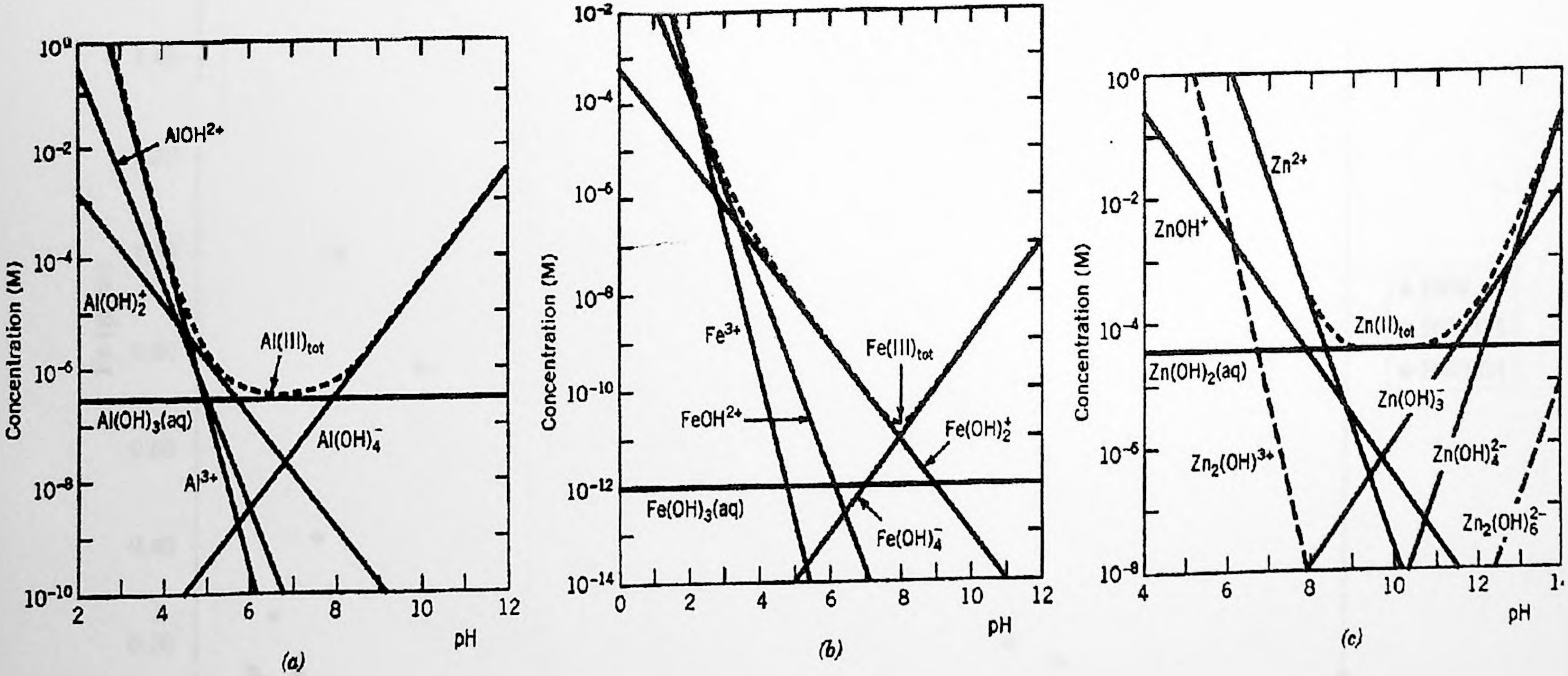

Figure 5. Effects of Hydrolysis on Solubility of (Hydr)oxides: (a) Solubility of α-$Al(OH)_3(s)$ (Gibbsite), (b) Solubility of Amorphous $FeOOH(s)$, and (c) Solubility of Amorphous $Zn(OH)(s)$. Data from Ref. 16 (Table 6.8).

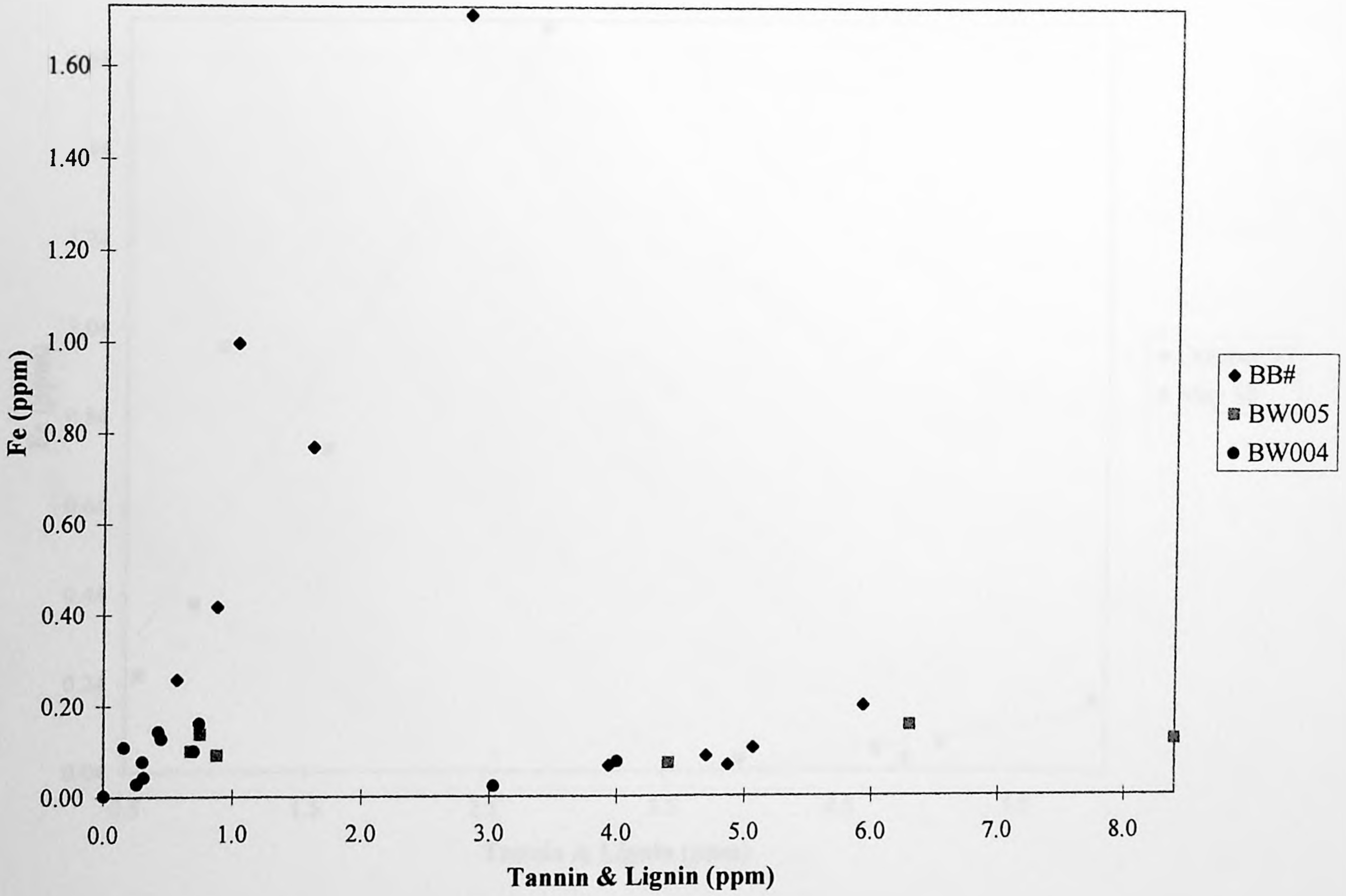

Figure 6. Relation Between Fe and Tannin and Lignin Concentrations in Yellow Creek Bog (BW004), Yellow Creek at Camp 70 Rd. (BW005) and Black Bear Stations (BB#).

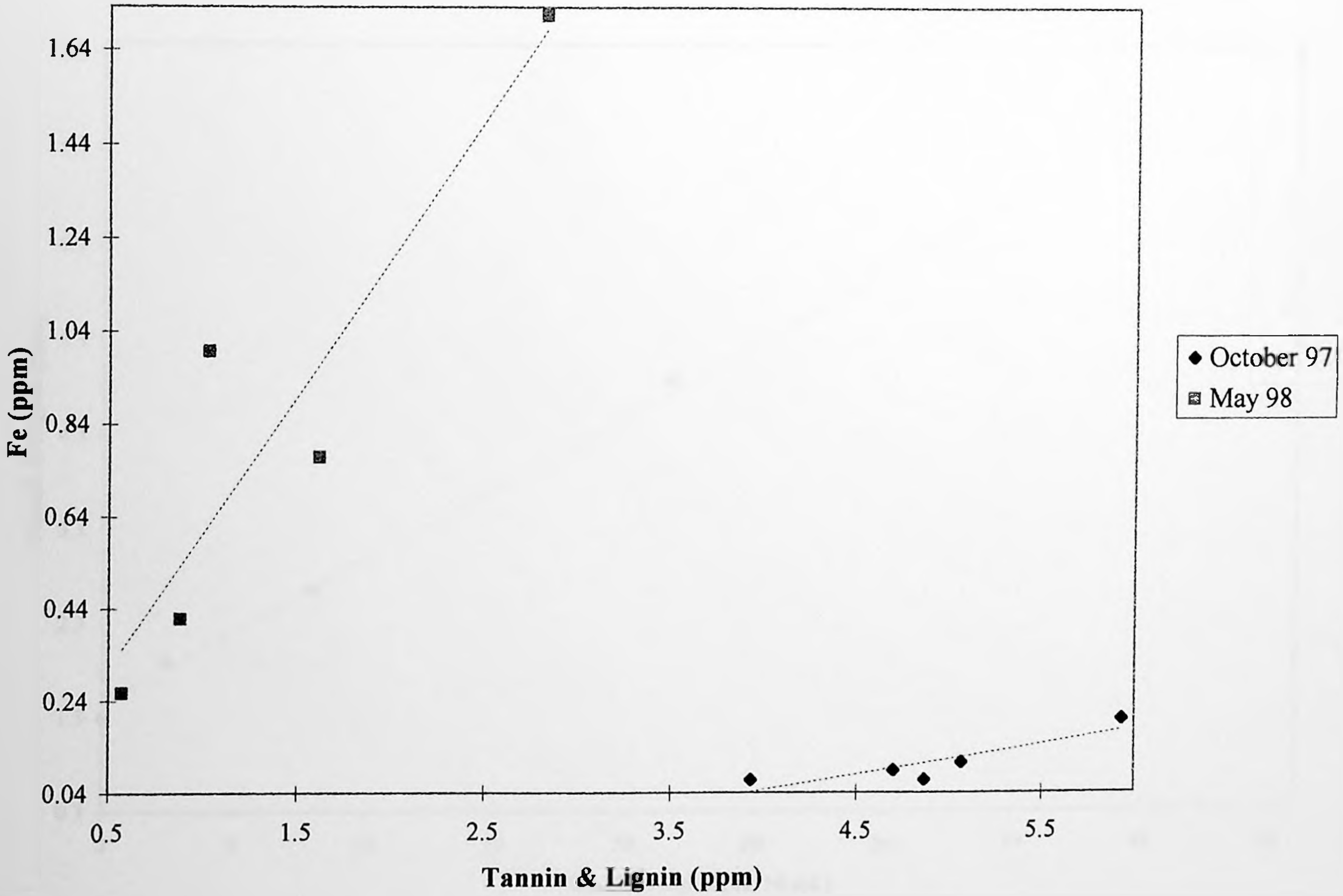

Figure 7. Variation of Trend Lines with Season of Black Bear Stations.

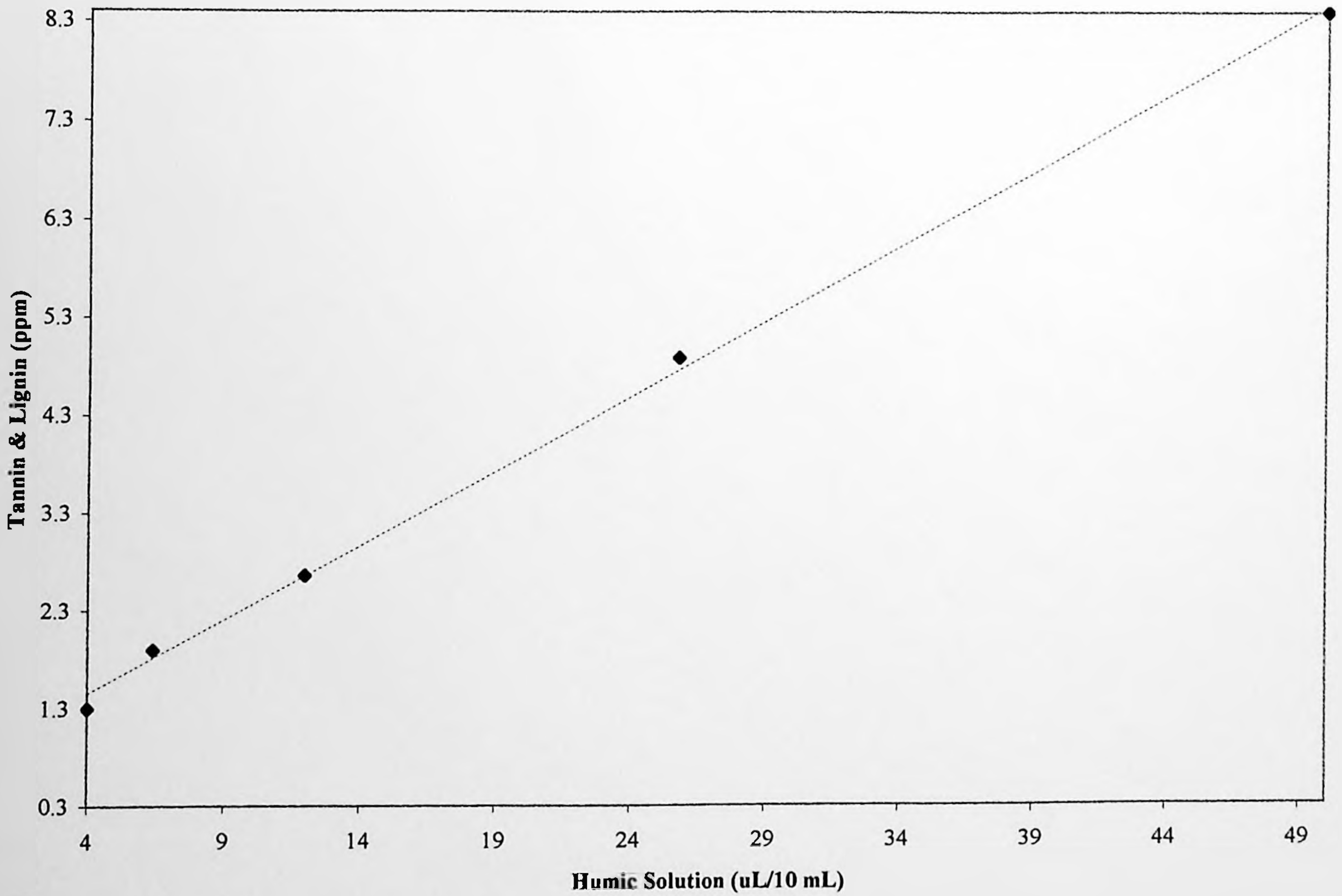

Figure 8. Tannin and Lignin Concentrations of a Diluted Humic Solution.