Acidic Drainage Abatement Through Surficial Application of Limestone Quarry Waste and Limeplant Flue Dust, Jonathan Run, Centre County, PA

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Abstract

Acid pollution of springs, a lake, and stream resulted from I-80 highway construction near Snow Shoe, Centre County, Pennsylvania, where extensive cuts and fills were required in pyritic rocks. Oxidation of pyrite contained in extensive fill embankments and in spoil deposits caused fish kills and overall water quality degradation down valley. Surficial application of a mixture of limestone fragments and lime flue dust (600 metric tons/ha) with aged sawdust (225 m^3 /ha) and vegetation reduced acid production within a treatment area. Water quality and flow data were monitored from June 1973 to December 1977 for both a control and treatment area. Iron, calcium, magnesium, aluminum, sulfate, acidity, pH, and temperature were measured.

Prior to treatment, pH was directly related to discharge. Annual peak sulfate *concentrations at* the treated versus an untreated site down gradient were 374 versus 500 mg/1 (1973-74,

pretreatment), 100 versus 250 mg/1 (1974-75), and 20 versus 260 mg/1 (1975-76). The pH values at the treatment site increased from 4.0 to 5.8 and from 3.9 to 4.4 for the control plot. Fluxes of sulfate concentration indicate that the treatment not only neutralizes acid but also slows its production, indicating that when the pH is higher than 4.5 to 5.0, bacterial catalysis is unimportant in pyrite oxidization, and the water's buffer capacity can neutralize the acid.

The method should have application on most disturbed lands, but when lime flue dust is used in *combination with* quarry wastes, it should be aged or well blended with soil to prevent pavement development.

INTRODUCTION

The Problem

Traditionally, acid mine drainage problems have been attacked using two approaches: treatment and abatement. Here, abatement is taken to mean the reduction or prevention of production of acid. While treatment techniques are concerned with the removal of the dissolved species after acid reaction, primarily through neutralization and precipitation, abatement techniques are concerned with preventing these substances from entering water initially. Intuitively, abatement procedures appear more attractive because they have the potential of working indefinitely whereas treatment technologies require the collection and open-ended processing of mine water that may require decades before acid die off concentrations reach acceptable levels.

In the simplest of terms, production of acid by the oxidation of pyrite requires the presence of reactive pyrite, oxygen and water. Acid reactions are very slow under abiotic, low pH conditions and it has been shown that catalyzing effect of the iron-oxidizing bacteria are required to account for the amount of acid produced. Acid mine drainage abatement techniques are designed to remove one of these required ingredients. It should be clear that this is not easily accomplished despite extensive state of the art mine reclamation efforts resulting from the Surface Mine Reclamation Act of 1977 and previous reclamation practices. However, the inhibition of acid reactions at their source offers the most attractive cost-effective and long-term means for reducing water quality impacts resulting from surface coal mining activities.

Objective of This Report

The nature and benefits of a field demonstration resulting from the surficial application of limestone quarry waste and limeplant flue dust on pyrite bearing strata disturbed by highway construction will be reviewed. Alkaline bearing waste products were applied to the top of disturbed strata in hopes of inhibiting acid reactions during a four year study that involved detailed water quality and flow monitoring at a treatment and control plot.

Intervention Options

Acid abatement techniques are designed to remove or reduce one or more of the required ingredients responsible for acid reactions. Oxygen, water, pyrite or catalytic bacteria. These are briefly discussed below.

Control of oxygen:

One of the earliest abatement techniques suggested for subsurface mines was the procedure of mine sealing (Leitch and others, 1930). The goals are two-fold. The first is to reduce the flow of acidic water from a mine. These ..water seals" are generally ineffective in greatly reducing flow from mines; the water flows around the seal. The second goal is to prevent oxygen from entering the mine. However, acid can probably form under partial pressures of oxygen less than 10-60 atmospheres (Barnes and Romberger, 1968, p. 378). As a result, air seals are generally ineffective in the abatement of acid. Other suggestions for the removal of oxygen include extensive grouting and the introduction of inert gases into the mine (West Virginia University, 1970).

It is difficult, costly or impracticable to prevent oxygen contact with pyrite in strip spoil deposits on a field scale. oxygen may be dissolved in infiltrating surface and groundwater, it may diffuse into spoil backfill deposits, move in response to barometric pressure changes and by convection. The latter process appears to be more important than previously realized because the amount of acid generated by some surface mines can not be accounted for by diffusion processes and the amount of oxygen dissolved in percolating mine waters.

In copper dump leaching experiments and computer models, Cathles and Apps (1975) have shown that convection of air through pore spaces in mine tailings is a major control on the rate of acid production and the rate of copper leaching. In the interior of rapidly oxidizing waste and overburden piles, the availability of O_2 in low permeability spoils may similarly restrict the rate of acid production, but in the initial stages of slow oxidization, O_2 is not likely to be a limiting factor.

Available oxygen has been measured in unsaturated mine spoil to greater depths than can be accounted for by diffusion in the ongoing acid abatement demonstration near Clarion, Pa. This suggests that convective air circulation must take place. Most likely, convection is induced by buoyancy resulting from warn air heated within spoil caused by exothermic pyrite oxidation reactions. More effective reduction of air circulation may be possible through the selective placement of poorly permeable topsoil and spoil deposits provided that areas of concentrated air entry can be identified (Parizek, 1985).

Vegetation, plant root respiration and decaying organic matter within incipient soils do not appear to be adequate oxygen sinks in many eastern mines lacking extensive topsoil to eliminate oxygen. Biological processes have been shown to reduce available oxygen, however. Kosowski (1973) for example, reported that the establishment of a plant cover on a one-foot thick layer of imported soil reduced the production of acid from the underlying mine spoil by 91%. To optimize vegetation growth, however, reclaimed mines may have to be placed into agricultural production to insure continued productivity of organic matter or be treated repeatedly with sewage sludge.

Some years ago, it was common practice to place toxic spoil near the pit floor where it might be saturated by groundwater following mine reclamation. This practice was developed because water quality improvements were noted when some subsurface mine workings were flooded after being abandoned. Presently, toxic spoils are being isolated higher within backfill spoil where they are less likely to become saturated. These pods of toxic spoil may be capped with low permeability materials but data are lacking that demonstrate that this practice is adequate.

Removal of water:

In the humid east, it is not feasible to completely prevent water from entering coal mines. Because acidic drainage is commonly mixed with better quality water after it leaves a mine site, the acid load is often a better indicator of an acid problem than is acidity. Reducing the discharge from a mine may result in higher acidities but lower acid loads. Schemes for reducing the discharge from a mine include surface diversions, paving, bypass wells (Parizek, 1971; Parizek and Tarr, 1972), the planning of mines to reduce discharge (mining downdip, coal barriers, and restoral of strip mines to original contour) extensive revegetation to maximize interception and transpiration, compaction of topsoil and the elimination of detention storage depressions to reduced infiltration. Reshaping of backfills to a concave profile to reduce infiltration, erosion and siltation also has been suggested by Gardner (1985).

Permeability of the spoil backfill controls in part, the rate of infiltration and percolation of water in mine spoil. These factors influence the availability of water at depth. Spoils with integrated surface slopes, low infiltration capacities and low permeability at depth will promote more surface runoff. A lush vegetation cover will maximize interception and transpiration further reducing water availability within spoil. However, capillary water and even humidity within spoil banks are suitable for pyrite oxidation. Acid salts stored within spoil deposits can be flushed and carried to the water table whenever gravitational water becomes available.

Laboratory experiments conducted by Geidel (1979) show that acid concentrations increase as the duration between flushing increase up to the point where soil moisture is depleted and vertical percolation ceases. Therefore, total acid loads may be similar for spoils with frequent and less frequent flushings all other variables remaining the same.

Aside from more drastic steps to isolate toxic spoils from ground and infiltrating surface waters through the use of liners or engineered caps, it will be difficult in many field settings to completely eliminate the entry of water. Where spoil backfills are located above the water table following closure, some success may be achieved by constructing capillary barriers that prevent deep percolation of soil water. Here, finer-grained topsoil is placed above a coarse-grained subsoil layer that prevents water entry.

Pyrite removal:

It is common practice to return coal preparation wastes to the mine from which the coal was produced. These waste products are typically enriched with potentially reactive pyrite. For sites lacking a natural neutralization or buffer capacity and that are likely to produce acid, it may be prudent to exclude tipple wastes from these mines or to require special handling procedures.

Control of bacteria:

Decreasing the activity of Thiobacillus sp. and Ferrobacillus sp. will slow the ferrous iron oxidation rate and thereby slow the production of acid. The schemes for doing this include the use of bacteriocides (Shearer and others, 1970; Barnes and Romberger, 1968), the use of bromo-substituted phenols to inhibit metabolism (Aleem, 1972), the introduction of heterotrophic bacteria to eat the iron bacteria (Walsh and Mitchell, 1972), the removal of attachments for the stalked bacteria Metallogenium (Walsh and Mitchell, 1972), and the increase of the pH in the neighborhood of the bacteria (Clark, 1966; Caruccio and Parizek, 1967; Walsh and Mitchell, 1972. Laboratory scale studies have been made of some of these suggestions; others have only been suggested. The last technique suggested is being reported upon in the present study. Successful field studies using bactericides have been reported upon by Kleinman (1979) and will not be discussed here. This approach to acid inhibition has the disadvantage of having to be repeated from time to time to maintain a sterile environment.

Bacterial catalysis of the oxidation of ferrous iron is important only at low pH's. At pH's above about 5.0 or 5.5, abiotic oxidation is rapid, (Fig. 1). Above a pH of about 4, the abiotic oxidation rate is second order with respect to pH (Singer and Stumm, 1969a). A decrease in pH from 6 to 5 results in a decrease in the ferrous iron oxidation rate of two orders of magnitude. As the pH continues to decrease until at a pH of about 3.5 the reaction rate becomes zero-order with respect to pH. At these low pH's the abiotic rate is very slow. Without bacterial catalysis oxidation of pyrite would not result in acidic discharges.

The bacteria that catalyze the oxidation of ferrous iron at low pH's are the chemoautotrophic Thiobacillus ferrooxidans and Ferrobacillus ferrooxidans. These bacteria use the oxidation of ferrous iron as a source of energy. According to Lau, Shumate, and Smith (1970) they increase the oxidation of pyrite by maintaining a high ferric to ferrous iron ratio in contact with the pyrite, allowing the ferric iron to oxidize the pyrite. The total production of acid is dependent in part on the number of cells near the pyrite surface. The bacteria intercept ferrous iron produced at or near the pyrite surface and oxidize it, resulting in more ferrous iron, which in turn oxidize more pyrite.

The iron-oxidizing bacteria may increase the reaction rate by more than six orders of magnitude at low pH (Singer and Stumm, 1970). However, their activity decreases as the pH is either raised or lowered from the optimal pH of about 3.5. F. ferrooxidans appears to be more important than T. ferrooxidans in the bacterial catalysis of the reaction (Silverman and others, 1967; Bounds and Colmer, 1972), although both are important.

Walsh and Mitchell (1972a, 1972b) investigated the characteristics of a bacterium identified as an iron bacterium of the species Metallogenium.

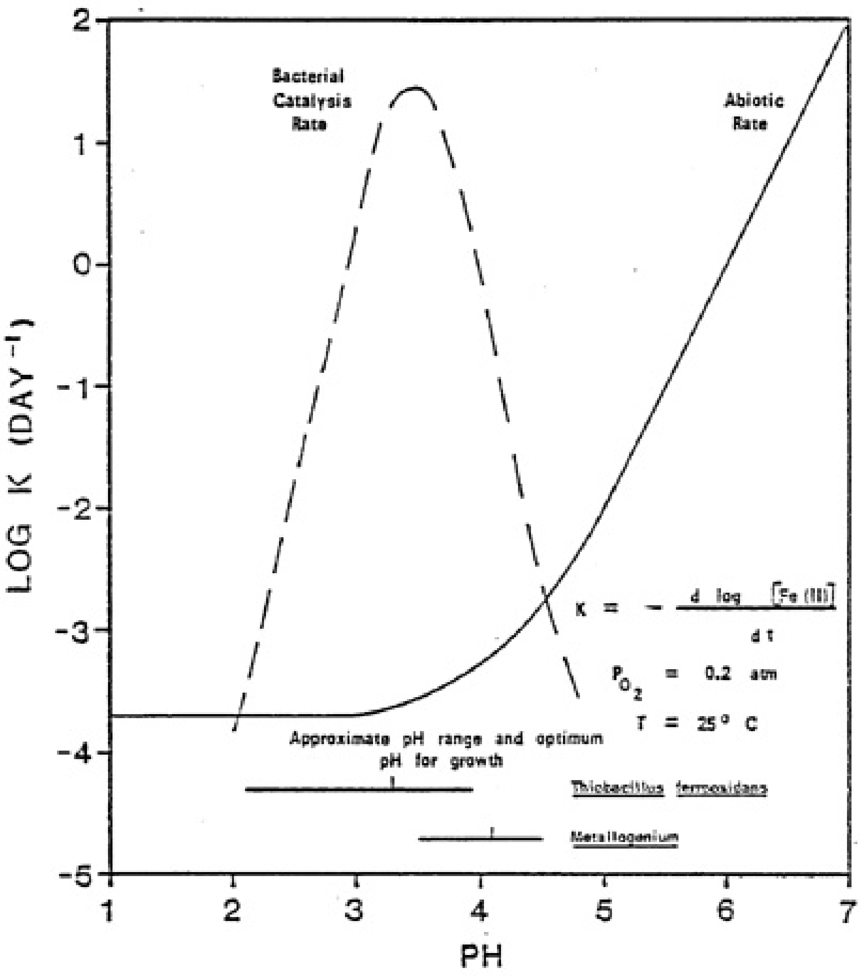

Figure 1. Reaction rate as a function of pH for the oxidation of ferrous iron. (Abiotic curve is from Stumm and Morgan, 1970; bacterial catalysis curve is suggested by pH limits on activity of the iron-oxidizing bacteria and the suggestion by Singer and Stumm, 1969, that bacterial catalysis may result in the increase of the reaction rate over the abiotic rate by six orders of magnitude).

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This bacterium is important in the catalysis of the iron-oxidation reaction by <u>T. ferrooxidans.</u> T. <u>ferrooxidans </u>is most active as pH's near 3.5, where it increases the reaction rate greater than 300 times under laboratory conditions. Waters enter acid-producing strata with pH commonly above 5.5, where abiotic oxidation can produce enough acid to lower the pH to approximately 4.5 before the reaction rate decreases to a point where the pH cannot decrease much further in the amount of time the water remains in the acid-producing strata. The iron oxidation-pyrite oxidation cycle (reactions b" and "c" of Stumm and Morgan, 1970) must take 93 cycles to produce acidic effluent with a total iron concentration of 300 mg/l from influent water containing 0.5 mg/l of iron (Walsh and Mitchell, 1972a, p. 809). At pH 4.5 the abiotic iron oxidation rate is 0.7 mg/1-day if the initial ferrous iron concentration is 250 mg/l, and lower for lower initial ferrous concentrations. At this pH, T. ferrooxidans is not very active. The reaction would almost be stopped if it were not for the presence of Metallogenium. Metallogenium is most active at pH 4.1, where the iron oxidation due to Metallogenium is 59 mg/1-day for an initial ferrous iron concentration of 250 mg/l. Metallogenium therefore, bridges the gap between the rapid abiotic oxidation rates at pH's greater than about 5.0 and the rapid oxidation rate due to T. ferrooxidans at pH's near 3.5. The activity of Metallogenium is low at pH 5.0 and above (Waddell, et al, 1978).

As the pH is raised above 4.5 or 5.0, the activity of the iron-oxidizing bacteria decreases and the rate of acid production due to bacterial catalysis decreases. Figure I illustrates this decrease in acid production. The bacterial catalysis curve is hypothetical. Its shape and magnitude is suggested by the estimate of Singer and Stumm for the increase in oxidation rate caused by bacterial catalysis and by the decrease in bacterial activity with increasing pH. At pH's greater than 5.0 or 5.5, the abiotic reaction rate is great enough for the reaction to proceed without bacterial catalysis (Waddell, et al, 1978).

The production of acid is not instantaneous. Consider water travelling through pyrite-bearing material. If the water has a low buffer capacity, production of acid will occur rapidly at first, but the rate will decrease as the pH decreases. As acid production continues, the pH will drop to a point where the reaction is slow. With continued production of acid, the pH will continue to slowly drop until Metallogenium begins to catalyze the reaction. This pH is about 4.5. Walsh and Mitchell suggest that a pH of 4.7 is too high for Metallogenium to significantly catalyze the reaction. As the catalysis by Metallogenium becomes important, the reaction rate increases. The pH drops rapidly and T. ferrooxidans and F. ferrooxidans begin to catalyze the reaction. the result is water with a low pH and high sulfate and metal concentrations. Production of acid will stop when the pH becomes too low for the bacteria to function or when the water flows out of the acid-bearing material. The flow path and flow rate of the water determine in part the amount of acid produced (Waddell et al, 1978).

Consider now a second case. Suppose the water travelling through the pyrite-bearing material first travels through calcite-bearing material and dissolved enough calcite to give the influent water a high total bicarbonate content and thus a high buffer capacity at near neutral pH's. When this water comes in contact with pyrite, abiotic production of acid will lower the pH of the water. Much of the acid produced will be neutralized by the reaction of the dissolved carbonate species with the hydrogen ion produced by the dissolution of pyrite. As the pH decreases, the rate of acid production also decreases. Also, as the pH decreases below about 6.3, the buffer capacity of the water decreases. At the point where the buffer capacity is a minimum, the reaction rate is also near its minimum. If the transit time of the water through the pyrite-bearing material is short enough, the reaction will not be able to proceed long enough to overcome the remaining buffer capacity, and the pH will be lowered to the point where bacterial catalysis becomes important. The pH will not fall below about 4.5 or 5.0 and the total production of acid will be low. If, however, the transit time is too long, or the amount of dissolved carbonate is too low, the slow production of acid will be able to exhaust the remaining buffer capacity and bacterial catalysis will cause the pH to drop rapidly and the production of acid to increase greatly (Waddell, et al, 1978).

The buffer capacity of the water has two effects. First, it neutralizes the acid produced.

Second, if sufficient buffer capacity remains in the pH range of 4.5 to 5.0 ' the gap between rapid abiotic reactions and bacterial catalysis, the slow production of acid combined with the neutralizing effect of the dissolved carbonate will result in very slow decrease in pH so that bacterial catalysis may not become significant (Waddell, et al, 1978).

If an abatement scheme based on the inhibition of the iron-oxidizing bacteria is effective, the discharge should have lower concentrations of sulfate and a higher pH than if the treatment were not applied.

PREVIOUS WORK

Studies done by Caruccio (1968), Caruccio and Parizek (1968), Parizek and Tarr (1972) and Gang and Langmuir (1974) Parizek (1982) as well as others, have emphasized the importance of calcareous material on the production and abatement of acidic coal mine drainage. Dutcher et al (1967), Parizek and Tarr (1972) note that in Pennsylvania, Illinois, Indiana, and Ohio, calcareous glacial drifts are present which serve as sources for alkalinity in groundwater. Mine discharges in these areas tend to be slightly alkaline or neutral if extensive chemical leaching of the drift has not occurred (Bobo and Eikenberry, 1982; Parizek, 1979). In some parts of western Pennsylvania, calcareous shales and limestones provide a source of alkalinity within mine spoil deposits (Parizek and Tarr, 1972). Caruccio and Parizek (1968) noted the difference between water chemistry of units adjacent to calcareous rocks and areas lacking calcareous rocks.

The observations of Biesecker and George (1966), Caruccio and Parizek (1967), and others led to a demonstration study by Waddell, Parizek, and Buss (1980). They investigated an early attempt at a field scale application of acid suppression concept through the surficial application of limestone quarry waste and limeplant flue dust on an area of central Pennsylvania impacted by acidic drainage from a highway roadcut. Excess rock fill and highway embankments contained reactive pyrite and was the source of acid. Discharges at the site had pHs as low as about 4 prior to treatment with limestone quarry waste and flue dust at a rate of about 99 metric tons/ha Sawdust, grass seed, and fertilizer were added to promote vegetation and thereby increase the carbon dioxide partial pressure in the root zone. Significant improvements in water quality parameters such as pH, specific conductance, and sulfate were seen after 1 to 1 1/2 years of monitoring.

Geidel and Caruccio (1984) investigated a small basin in east central Ohio. Their study involved the application of a dolomitic limestone on a reclaimed strip mine surface. Seeps were monitored for changes in chemical parameters characteristic of acid mine drainage. Some decreases in the acidity and sulfate concentrations of the waters were observed, but these were not attributed to the calcareous material applied to the site.

The importance of calcareous materials in neutralizing or inhibiting acidic reactions was further investigated by Hornberger, Parizek and Williams (1981). Their study included leaching experiments on bedrock overburden samples collected from marine, brackish and freshwater depositional environments, comparison of leaching data with mine drainage chemistry obtained from mines located in each setting, sulfur analyses, and microscopic examination of coal samples.

Work by Williams, et al (1982) expanded these efforts to identify major factors controlling acid mine drainage to a degree allowing pre-mining prediction of surface mining effects and application of improved inhibition and amelioration methods. Both field and laboratory experiments were so designed to evaluate quality effects of many major rock types, paleoenvironments of sedimentation and stratigraphic sequence. Samples were included from strata containing high, medium and low total sulfur values, low and high calcium carbonate contents and various pyrite types.

Possible inhibiting and neutralizing effects of calcium carbonate were tested through a series of controlled leaching experiments, in which known amounts of calcite were added to high sulfur, non-calcareous acid-producing coal and brackish shale samples. These laboratory column leaching tests demonstrated that carbonate placed above the acid-producing unit both neutralizes and inhibits acid production; whereas carbonate placed below the sample only neutralizes acid (Williams, et al, 1982). Similar field scale results were observed by these investigators. Most Kittanning and Clarion mines with limestone produced no acid. Mines without limestone were major sources of acid-mine drainage. All backfilled Freeport Mines lacking sandstone produced neutral to alkaline drainages. Some Freeport Mines with major sandstone units produced acidic drainages, others did not.

The results from these experiments have demonstrated that pyrite amount and the presence or absence of calcareous units are the major factors controlling acid generation. Marine and brackish shales and channel sandstones are major acid-producers, whereas calcareous units function as acid inhibitors or neutralizers (Williams, et al, 1982).

More recently an acid abatement demonstration was initiated by Parizek al (198 4) on a surf ace mine containing up to 27.4 ft of spoil and excessive tipple waste. Two 1.01 ha treatment plots receiving 161.7 and 191 t/ha of a mixture of limestone quarry waste and limeplant flue dust and 1.01 ha control plot were included in the demonstration which is still in progress. Both water in the unsaturated zone and groundwater are being monitored in this three year demonstration. Two 3.6 x 3.6 m wide and 1. 2m deep trench lysimeter plots also are included in the study that received 91.8 and 183.8 metric tons/ ha of limestone quarry waste (Henke, 1985). These plots were fertilized, mulched, seeded and monitored to determine their infiltration and evapotranspiration rates, and alkalinity loading rates resulting from the treatments under central Pennsylvania's climate conditions.

JONATHAN RUN FIELD DEMONSTRATION

Introduction

The demonstration area is not directly related to coal mining, but has acidic discharge. Interstate-80 construction across part of the Allegheny Front in Centre County, PA, required extensive cut-and-fill operations through pyrite bearing strata of Mississippian age and coal and pyrite bearing strata of Pennsylvania age. The area is located in Boggs Township, at the intersection of I-80 and Route 144 (Figure 2). Prior to I-80 construction, local property owners reported water quality to be good in Jonathan Run. The stream and a recreational lake supported trout.

Construction of extensive rock cuts and fills was accompanied by a deterioration of water quality in Jonathan Run and of water discharging from several springs downslope of the highway. Trout in a pond located below the highway died shortly after construction..

Rerouting of acidic discharge past the pond improved its quality but not enough to support trout because other springs nourishing the pond also were impacted by acid.

Background water quality monitoring began in July 1973 and continued until December 1977. Stream and spring gaging stations were constructed by June 1974. The relationship between the treatment area, piezometers, gaging stations and I-80 are shown in Figure 2.

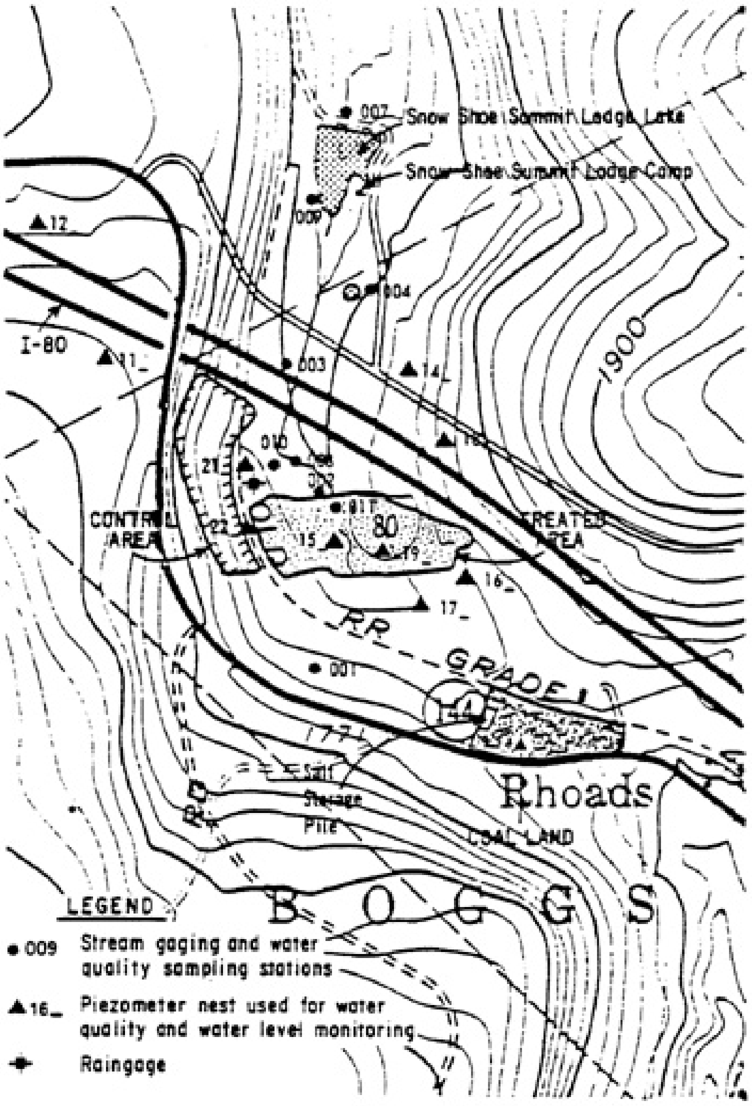

Figure 2. Location of treated and control areas, coal yard and sampling sites.

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Field Setting

I-80 is from 20 to 60 meters above the bottom of the valley. The embankment is approximately 150 meters wide. A staging area used during construction is located south of the highway. It consists of a relatively flat area, a small loading ramp and an asphalt pad.

This low relief area was formed by placing a zero to three meter thickness of rock fill from the nearby roadcuts over an area of about 3.9 hectares. This area runs perpendicularly to Jonathan Run and is about 300 meters long and 120 meters wide. This area of fill material is in effect a permeable dam that sometimes causes a small pond to form at the upstream edge of the fill. This area received the pollution abatement treatment in 1974 and is referred to as the "treated area".

The area south of the highway was also used for permanent storage of excess fill material from the roadcuts. One large pile was built on the west side of Jonathan Run. The top of this pile is nearly flat and is almost at the same level as the highway at the east end of the roadcut west of the site. It is 12 to 15 meters above the low relief area below. This pile is from 60 to 90 meters wide. Its eastern edge is steep. This pile was not treated and is referred to as the "control area", even though its hydrologic setting is different from that of the treated area.

Another, smaller storage pile is present at the site, and is included within the treated area. Its thickness ranges from 0 to 10 meters, decreasing to the east. It is about 55 meters long and about 45 meters wide at its eastern end and about 20 meters wide at its western end.

Water infiltrating into the highway embankment flows to lower areas both south and north of the embankment. As a result, there is a marshy area to the south. Water in this area has emerged as springs at the base of the fill material in the treated area. Part of it comes from overland flow, especially during the spring and fall. However, much of it is water discharges from diffuse seeps, originating from both the embankment and the higher areas surrounding the site. Numerous dead trees are present in this marshy area and water is acidic, having a pH of about 4. The tree kills were probably caused by the acidic water and the high water table.

Dead trees are also present immediately downstream from a small coal yard at Rhoads. This coal yard is a coal crushing and storage facility that is located at the surface water divide of Jonathan Run. Runoff from this yard has carried suspended coal and shale particles into the woods north of the coal yard indicating that this runoff does enter the Jonathan Run drainage system. A small "alluvial fan" has formed where these fine-grained materials have been deposited immediately north of the abandoned railroad right of way about 30 meters northwest of the northwest corner of the coal yard. There are numerous dead trees here. Dead trees may also be observed at several places immediately north of the coal yard. These tree kills and coal particle accumulations all postdate the 1971 investigations indicating that runoff from the coal yard to Jonathan Run has occurred more frequently since 1971.

Construction

Treatment began on May 28, 1974. Delivery of the limestone fragment -lime plant flue dust mixture began a day or two earlier. The mixture was purchased from the Marblehead Lime Company and was picked up at their plant at Pleasant Gap, Pennsylvania. The mixture consists of approximately 50 percent minus 1/4 inch limestone and 50 percent flue dust. The chemical analyses of these materials are in Tables I and 2. This limestone mixture is often referred to as quarry waste produced from sceening operations and contains an abundance of fine-grained rock particles. It has limited demand, hence, is termed quarry waste. It should not be confused with overburden waste material stripped from quarries that may contain fresh and weathered rock mixed with soil deposits.

Spreading of the limestone fragment-flue dust mixture began on May 28. This was done by two lime-spreader trucks. The mixture was thrown from each truck by two rotating discs. The mixture was loaded into the trucks by a backhoe with a front bucket. The loader was not in constant use. Spreading of the mixture required from eight to ten hours over a two-day period.

Spreading of the sawdust as mulch was begun and completed on June 1. The trucks used to spread the lime also spread the sawdust. No chemical analyses are available for the sawdust, but at least two-year old or older sawdust was specified.

This application rate of the limestone-flue dust mixture was 597 metric tons per hectare (267 tons per acre). This rate is great enough to give a thickness of 3.4 centimeters over the area if applied uniformly. Application was fairly uniform although some areas had a thickness of about six centimeters.

The sawdust was applied at a rate of 224 cubic meters per hectare cubic yards per acre), resulting in a layer 2.24 centimeters thick, if applied uniformly.

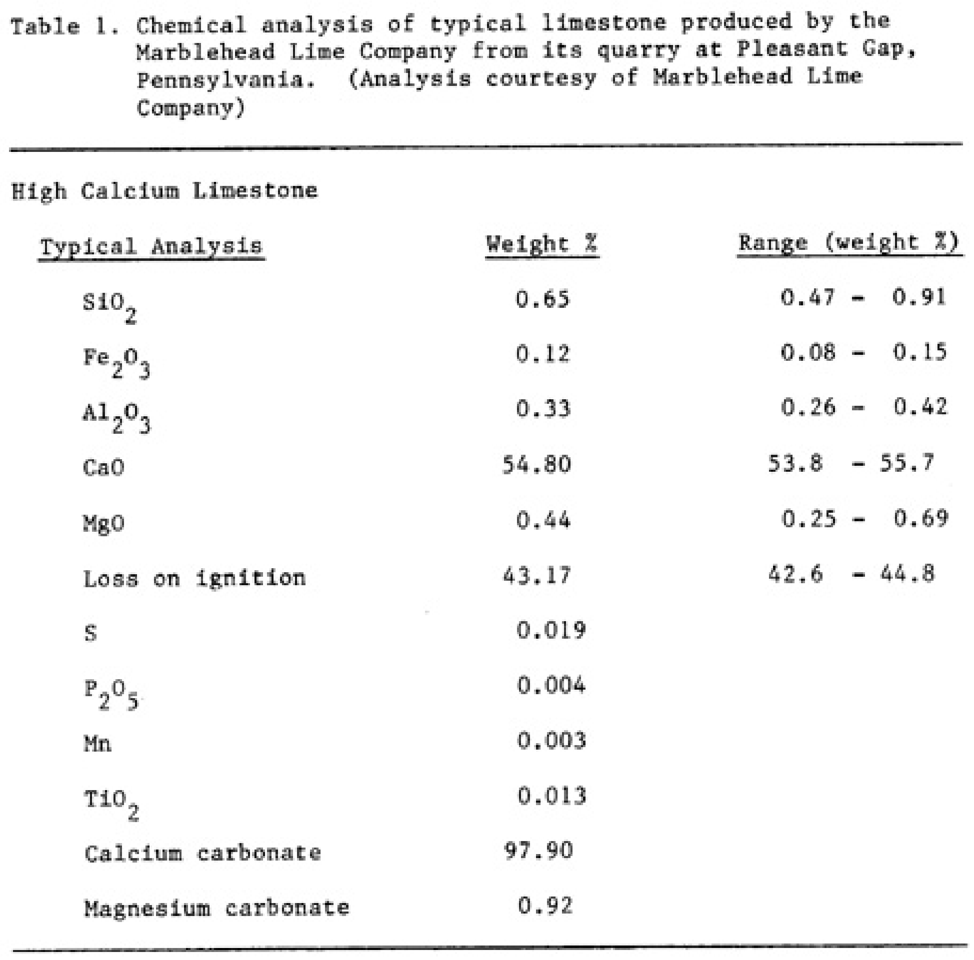
On June 4, 1974, an attempt was made to mix the two layers together. A light tractor pulling a disc or typical farm harrow was used. The quality of mixing was poor largely because of the rocky nature of the spoil being mixed and light weight of the equipment employed.

On the afternoon of the fourth, fertilizer (10-6-4, with 50 percent of the total nitrogen derived from ureaform) was applied at a rate of 350 kilograms per hectare (312 pounds per acre).

Application of various seed mixtures was done on June 5, 1974. The area was split into two parts of approximately equal area. The boundary between the two areas paralleled Interstate 80. Mixture I was applied in the northern area, mixture 2 in the southern area (Table 3).

On the same day the area was mulched with wheat straw at a rate of 125 bales per hectare (50 bales per acre). Nothing was applied to hold the mulch in place in hope that it would be held by seedlings and plant rootlets. High winds during the next few days blew much of the straw mulch away. This exposed much of the seed to the sun and allowed the seed bed to dry out.

Table 1. Chemical analysis of typical limestone produced by the Marblehead Lime Company from its quarry at Pleasant Gap, Pennsylvania. (Analysis courtesy of Marblehead Lime Company)



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High Calcium Limestone

Typical Analysis	Weight %	Range (weight %)
SiO_2	0.65	0.47 - 0.91
Fe_2O_3	0.12	0.08 - 0.15
Al_2O_3	0.33	0.26 - 0.42
CaO	54.80	53.8 - 55.7
MgO	0.44	0.25 - 0.69
Loss on ignition	43.17	42.6 - 44.8
S	0.019	
P_2O_5	0.004	
Mn	0.003	
TiO_2	0.013	
Calcium carbonate	97.90	
Magnesium carbonate	0.92	

Table 2. Means and standard deviations of chemical analyses of weekly composites of flue dust. Flue dust is a waste product of a cleaning process, hence its high available calcium oxide content.

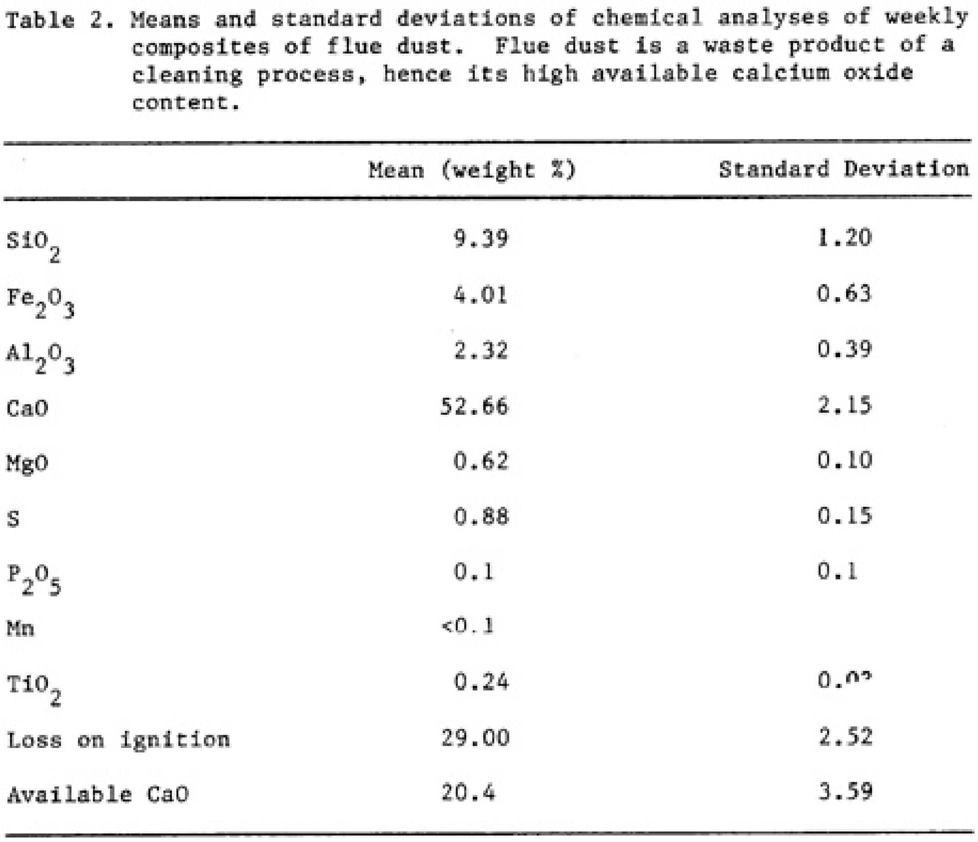

Table 2. Means and standard deviations of chemical analyses of weekly composites of flue dust. Flue dust is a waste product of a cleaning process, hence its high available calcium oxide content.

	Mean (weight %)	Standard Deviation
SiO_2	9.39	1.20
Fe_2O_3	4.01	0.63
Al_2O_3	2.32	0.39
CaO	52.66	2.15
MgO	0.62	0.10
S	0.88	0.15
P_2O_5	0.1	0.1
Mn	<0.1	
TiO_2	0.24	0.03
Loss on ignition	29.00	2.52
Available CaO	20.4	3.59

Table 3. Seed mixtures applied to the treated area.

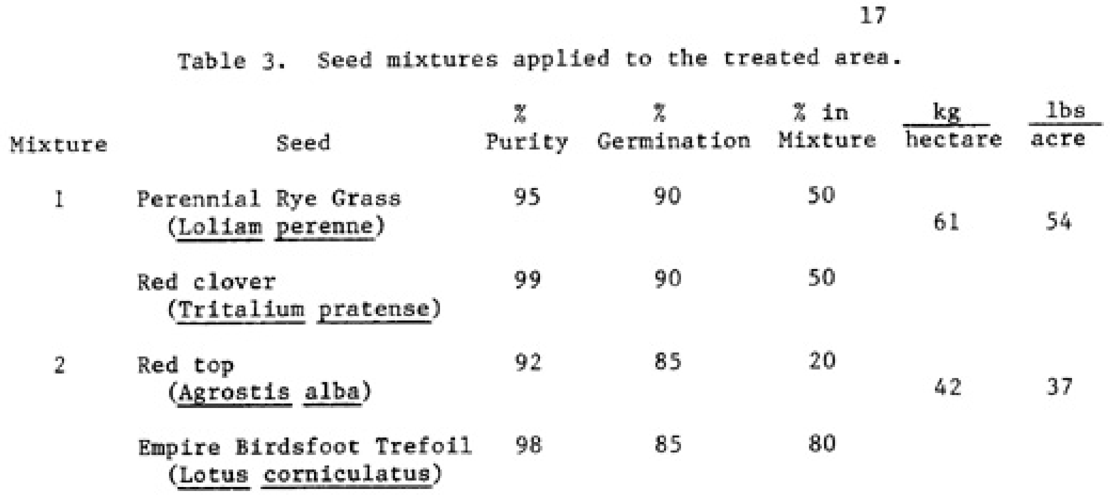

Table 3. Seed mixtures applied to the treated area.

Mixture	Seed	% Purity	% Germination	% in Mixture	kg/hectare	lbs/acre
1	Perennial Rye Grass (*Loliam perenne*)	95	90	50	61	54
	Red clover (*Tritalium pratense*)	99	90	50		
2	Red top (*Agrostis alba*)	92	85	20	42	37
	Empire Birdsfoot Trefoil (*Lotus corniculatus*)	98	85	80		

Within a few days a high intensity rain storm washed additional mulch, sawdust, and seed from the site. This was followed by a hot dry spell which further complicated the revegetation program.

During the time that the treatment was being applied, the four wiers were being installed. A backhoe was used to install three of the wiers. The fourth (at site 003) was installed by hand. A plastic sheet was laid down at each site beneath the pool created on the upstream side of the weir to limit leakage around and below the weir.

Problems encountered during treatment

Because of the simplicity of the treatment, few logistical problems were encountered during the application of the treatment. The major expense was the procurement, transport, and spreading of the material. The site had been previously graded to a smooth surface so that little grading was necessary. The cost of the treatment was about $4500 per acre. Approximately 60 percent of this cost was for the purchase, transport, and spreading of the material; 30 percent was for seed, fertilizing, seeding, and mulching the area; and the remaining 10 percent was for digging trenches and grading.

Casting the material with lime spreader proved to be a very satisfactory way of applying the material, but with one major drawback. The limestone-flue dust mixture was spread in a very dry condition; and, because the material is fine-grained, casting the material more than a few meters caused a large dust cloud. This would be unacceptable at many construction sites. Unless the dust problem can be solved, another method of spreading must be found. Advantages of this method include its speed and the uniform thickness which results.

Flue dust is collected to prevent air pollution during the production of lime. When it is removed from the "bag house", it is in a very dry state. Part of the flue dust delivered to the site was this dry, fresh material. When the fresh material is allowed to get wet, it hardens as it dries. If aged rather than fresh flue dust had been used, after crushing it first for easier handling, the dust problem would not have developed. This would involved greater expense but may be necessary at future job sites.

The absence of something to hold the mulch in place allowed the mulch to be blown away and extensive erosion to occur when heavy rains fell about a week after the treatment was applied. The underlying fill was exposed in several places.

A major problem was first noticed about a month after the treatment. The seeds germinated within two weeks after they were spread. By the end of the fourth week, most of the young seedlings had died. Investigation showed that a hard crust had formed over most of the treated area, killing the seedlings. A lack of rain during the period did not help. This pavement was formed by a chemical reaction between the incompletely mixed flue dust sawdust, rocky soil and water. The flue dust, being calcined limestone, contained calcium hydroxide which reacted with silica (contained in the dust) and water. The pavement could not be penetrated with a shovel, or with a tractor-mounted rototiller. Careful inspection of the treated area revealed numerous small (less than two square meters) areas where the pavement had not formed. In these areas the sawdust and limestone-flue dust mixture had been well blended as intended. In the areas where the pavement did form, the two materials were poorly mixed. Part of this problem may have been eliminated had aged flue dust been used as intended, rather than "hot", dry baghouse dust as provided by Marblehead Lime Company.

The pavement was almost completely broken up by March 1975, probably because of numerous freeze-thaw cycles that occurred during the 1974-75 winter when the snow pack was thin. The pavement was still present in areas where the treatment layer was more than about six centimeters thick and where there were not the temperature extremes to cause the pavement to break up.

To improve on the vegetation cover that was still scant in the spring of 1975, the site was reseeded in August 1976, asphalt emulsion was applied to additional straw mulch to improve the seedbed along with additional fertilizer. This resulted in a good stand of vegetation by the summer of 1977 which is even better established at present, spring 1986. This grass cover crop was considered desirable to the treatment process because it should add CO_2 to soil water by the decay of organic matter, plant root respiration, action of soil microorganisms, etc.

Choice of parameters for evaluating treatment

In the study the parameters temperature, specific conductance, pH, acidity, alkalinity, and the concentrations of iron, calcium, magnesium, aluminum, sulfate, and chloride were measured. Discharges were measured where possible. Of these variables, the acidity, alkalinity, pH and sulfate concentration are the best measures of the progress of the reactions. The acidity is a measure of the amount of dissolved material which resists increases in pH. It is a function of pH, dissolved gases and metals, and the oxidation and hydrolysis states of the metals. The alkalinity is a measure of the amount of dissolved material that resists decreases in pH, and is primarily an indicator of the bicarbonate content of the water. If the measured alkalinity is zero, the water has little reserve to oppose reductions in pH. The pH is important not only for ecological reasons but as an indicator of the ferrous iron oxidation rate. The system of reactions produces, among other things, dissolved iron and sulfate. The iron concentration is a function of the pH, the oxidation potential, and whether iron has been removed by the precipitation of ferric oxyhydroxide. The iron concentration is therefore difficult to interpret, hence has not been used. The sulfate concentration is an indicator of how much pyrite has been oxidized. For each mole of pyrite oxidized one mole of sulfate is produced. Removal of sulfate can happen by the precipitation of sulfate minerals, such as gypsum, jarosite, alunite, and basalunite. Mineral equilibria calculations indicate that the waters from the demonstration area may be saturated with respect to jarosite, alunite, and basalunite, but not with gypsum. The sulfate concentrations, when considered in connection with discharge, provide estimates of the amount of pyrite oxidized. Whether the amounts of jarosite, alunite, and basalunite within the areas upstream of the sampling point are increasing, remaining constant, or decreasing with time determines whether the sulfate concentrations given estimates below, the same as, or above the actual rate of pyrite oxidation.

MONITORING RESULTS

Introduction

Water quality monitoring began on springs (001, 002, 003, 004) in July 1973, on Beech Creek (005, 006) about 1.5 km to the west. Site 005 is the exit point of a drain in the embankment of the highway and site 006 is upstream from where acidic water from another I-80 embankment enters Beech Creek. These latter two stations were for background and comparison purpose only because neither are located within a watershed likely to be impacted by the treatment.

Just before treatment construction, sites 007, 008 and 009 were added. One was an outfall from the recreation pond (Snow Shoe Summit Lodge Lake) and two were weir sites on

Jonathan Run. Later, 010 was added which is at the downstream end of a trench from the control area. Site 011 is at the downstream end of the trench running down the middle of the treated area. Sampling was every two weeks until June 1976, after which samples were taken every three weeks. Wells were sampled less frequently.

Summary, Chemistry of Surface and Spring Waters

Table 4 gives the mean and standard deviation of the different variables for each of the regularly sampled sites and includes data to June, 1976. All variables except temperature and pH are approximately log-normally distributed, but the summary statistics for the transformed data are not presented here. For sites 001, 002, 003, and 004 both pretreatment and posttreatment data are included. The discharge data for site 002 are correlated data from the stream gage at Beech Creek (Waddell et al., 1978).

In terms of different measures (pH, sulfate, and acidity) of the production of acid, the sites can be ranked, from least to most, in the order

001, (007, 002), 004, (008, 003), 009

Table 4. Summary statistics for the regularly sampled sites (from Waddell, et al., 1978).

Site:	001		002		003		004		007		008		009	
	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s
Temp (°C)	8.34	0.545	9.95	5.57	9.19	1.05	9.20	0.77	13.02	7.58	14.02	8.32	11.43	5.02
SpC (μmhos)·25°C	47.69	11.89	624.	560.	430.	142.	224.	48.6	128.	23.4	634.	332.	749.	256.
pH	5.58	0.16	5.14	0.59	4.16	0.23	4.88	0.22	4.06	0.24	4.34	0.39	3.92	0.22
Fe_{tot} (mg/l)	0.26	0.51	1.88	3.93	0.75	0.54	0.20	0.32	0.12	0.11	2.5	3.0	2.6	1.8
Ca (mg/l)	2.49	0.64	17.0	16.3	21.1	7.74	12.4	2.75	6.74	0.85	30.1	19.2	34.9	14.4
Mg (mg/l)	1.0	0.3	3.0	2.6	8.4	2.9	5.6	1.4	2.9	0.4	6.6	3.6	10.5	3.9
Al (mg/l)	0.4	0.4	1.3	2.3	20.2	8.8	3.7	2.7	1.2	0.39	14.9	11.5	39.7	19.7
SO_4 (mg/l)	3.6	1.41	50.1	63.8	197.	86.1	56.7	18.9	26.7	5.9	171.	102.	332.	134.
Cl (mg/l)	34.2	55.7	301.	237.	34.7	58.2	41.9	20.2	19.2	5.8	234.	180.	69.1	27.5
Acidity (mg $CaCO_3$/l)	6.2	4.0	23.7	37.8	164.	64.0	29.1	11.6	15.9	6.0	234.	180.	281.	137.
Alkalinity (mg $CaCO_3$/l)	1.99	1.09	1.12	1.44	0		0.06	0.25	0		0		0	
Dis (l/sec)			676.	525.	6.66	4.12	7.10	3.73			6.55	5.89	16.0	12.3
No. of samples	46		51		61		62		41		41		39	

where the parentheses indicate approximately equal ratings. The position of site 002 is largely determined by the effect of the treatment on this site. If only the pretreatment data are considered, the ranking is

001, 007, 004, 002, (008, 003), 009.

The rankings of sites 007, 008, and 009 have been estimated from posttreatment data. if only posttreatment data are considered the ranking is

(001, 002), 007, 004, (008, 003), 009.

The treatment has primarily affected the location of site 002 in this ranking. This indicates that the area treated was located outside of the watersheds of other sampling stations or the treatment area was still too small to overcome acid production within the larger subwatersheds.

The chemistry of water in the demonstration area appear to be affected by three different processes. The first process is the production of acid by the dissolution of pyrite and the reactions that occur between the reaction products. The second is the mixing of waters of different chemistries, such as the dilution of acid water by unpolluted water. The third is the pollution of the water by road salt. Chloride levels have been used in deciphering the flow system in the study area and are not related to pyrite oxidation reaction (Waddell et al., 1978).

Two aids were employed to increase the understanding of the first two processes. The first is the program WATEQ, which computes mineral equilibrium relations given a water analysis (Truesdale and Jones, 1974; Waddell, 1978). The second is statistical analyses including factor analysis, which attempts to find the relationship among variables.

Site 001

Spring 001 was included for baseline comparison. This spring is the most pristine of any of the sampling sites. It is up- or cross-hydraulic-gradient from both the coal yard and Interstate-80, and no acid problem is associated with it. It reflects ground water least affected by man's activities. Its sulfate concentrations are the lowest of all the sampling sites. It is located down-gradient from Route 144, and its discharge contains variable but moderate concentrations of chloride ion (Waddell et al., 1978).

The flow from the spring is steady (not flashy), but with seasonal variation. Its flow ceases during the late summary and early fall. No precise measurements of its flow were made, but visual estimates of its flow range between 0 and 40 liters per second, averaging about 6 liters per second (Waddell et al., 1978).

The temperature of site 001 varies between 7.0 and 9.5^{0}C, indicating that the flow path of the water is deep enough so that seasonal variations are suppressed. The specific conductance varies little from about 50 micromhos. The pH varies from about 5.4 to 5.8. The sulfate concentration ranges from 0.5 to 6.0 mg/l. The acidity has never been above 16 mg $CaCO_3$ /l (Waddell et al., 1978).

Despite the low concentrations of dissolved species in the water seasonal variations are present in the calcium and magnesium concentrations. The concentrations are highest during the late summer when evapotranspiration is high.

The other variables that were measured do not exhibit easily discernible seasonal variations. The aluminum concentration may vary through the year on a cyclical basis, but the evidence for an annual cycle is not strong. Iron concentrations, generally around 0.2 mg/l, have increased to greater than 1.0 mg/l, during two of the three summers considered. All other variables appear to vary nonsystematically.

Samples from site 001 are undersaturated with respect to calcite, dolomite, and gypsum. They are supersaturated with respect to iron oxide phases (hematite, magnetite, and maghemite) and goethite. The mean of pIAP (negative log of the IAP) with respect to ferric hydroxide is 37.1. This number is the same as pK (negative log of the equilibrium constant for freshly precipitated amorphous ferric hydroxide (pK = 37.1, Langmuir, 1975, personal communication). Freshly precipitated amorphous ferric hydroxide may control the concentration of iron in the waters at site 001 (Waddell et al., 1978).

The sum of the carbonate species averages about .007 molar for site 001. The maximum buffer capacity (at pH 6.35) due to dissolved carbonate is approximately 0.58 C_T (total carbonate) (Langmuir, 1978, personal communication). For site 001, this is about 0.41 meg/pH. At pH's near 5.5, the buffer capacity is about 0.3 C_T, or 0.21 meg/pH.

Site 002

Site 002 is a spring that emerges from the downstream edge of the fill material placed for use as a staging area. The flow of this spring, as well as the flow from the numerous other springs near site 002, emerges at the contact between the fill material and the underlying colluvium. The discharge ranges from zero to an estimated three liters per second. Estimates are based on comparisons with the flow measured at site 008. Flow ceases during the late summer and early fall, and sometimes during the winter as flow does at site 001.

Site 002 shows evidence of acid production. Suspended ferric hydroxide is sometimes present in the water at site 002. Its sulfate content has been as high as 350 mg/l. The acid is produced as water flows through the fill material up-gradient from the spring (Waddell et al., 1978).

Site 002 discharges water whose temperature varies greatly, but smoothly, through the year. The temperature of the water at site 001 is nearly constant. The mean and standard deviation, respectively, of the water temperature at site 001, and 002, respectively, are 8.34 and 0.55^0C, and 9.95 and 5.57^0C. This suggests that the flow from site 001, is relatively deep, but that the flow from site 002 is either shallow or has been recently recharged, so that seasonal atmospheric changes affect it. This implies flow through the layer of fill material up-gradient of the site (Waddell et al., 1978).

Water discharging from site 002 has two different origins. Part of the precipitation falling on the treatment fill material infiltrates the fill.. It flows to the northern (downstream) edge of the fill appearing as seeps or springs such as 002, or flows to the center of the valley. The second source is a deeper flow system discharging into the valley. A multi-piezometer installation in the middle of the valley demonstrates an upward hydraulic gradient. The deeper piezometer, open at forty feet below the surface, flows sometimes during the spring and fall. The water discharging at site 002 is probably a mixture of water from deep and shallow flow systems (Waddell et al., 1978).

Site 002 is the site that should show the greatest change as a result of the treatment, because of its location immediately down-gradient from the treatment area.

The water quality of this site is greatly affected by the reactions that occur in the treated area. The water quality varies greatly through time. The concentrations of iron, calcium, magnesium, aluminum, sulfate, and acidity increase during the drier months. The chloride concentration increases during the spring with mobilization of chloride from road salt by the spring thaw.

Plots of the pH, and the concentrations of sulfate, acidity and alkalinity through time are presented in Figures 3 through 6. In addition, the fluxes (concentration times discharge) of calcium, sulfate, and acidity are plotted through time Figures 7 through 10, using correlated discharge data from Beech Creek (Waddell et al., 1978).

The pH was about 4.0 when sampling began. Beginning in 1974, the pH began to increase until at about the time of treatment the pH was about 5.0. A few days after the treatment was applied at the end of May, 1974 a pH of 4.71 was measured. Whether a decrease in the pH had begun because of decreasing discharges at this time of year, or whether the measurement was an error or a random variation is not known. The rising pH before treatment is correlated with increasing flow at Beech Creek so that the change in pH is probably related to dilution. After treatment, the pH increased approximately 5.5. One measurement at the end of 1975 was 4.02 and one late in 1977 was 4.77. The cause of these low values is unknown, and could be due to measurement error since only two low values have been observed since treatment. Alternatively, these low measurements could be associated with periods of abnormally low discharges. The variation in the pH related to changes in discharge (if changes in discharge were responsible for changes in pH before treatment) has disappeared or decreased. The alkalinity of the samples increased from zero before treatment (only three samples had measurable alkalinities) to from one to six mg $CaCO_3$/l after treatment (Figure 6). This largely reflects the increase in pa because of the treatment. The buffer capacity also has increased as a result of treatment as expected and can be counted upon to help neutralize acidic drainage. After treatment, the total carbonate averages about 0.0009 molar. The maximum buffer capacity due to dissolved carbonate is about 0.5 meq/pH, and at pH 5.5, about 0.24 meq/pH. This is greater than that at site 001. The increase in buffer capacity is probably responsible for decreased sensitivity of the pH to variations in discharge. The buffer capacity resists decrease in the pH during the drier periods. This is an important attribute of the treatment system that can be maximized by applying limestone to ground-water recharge areas (Waddell et al., 1978).

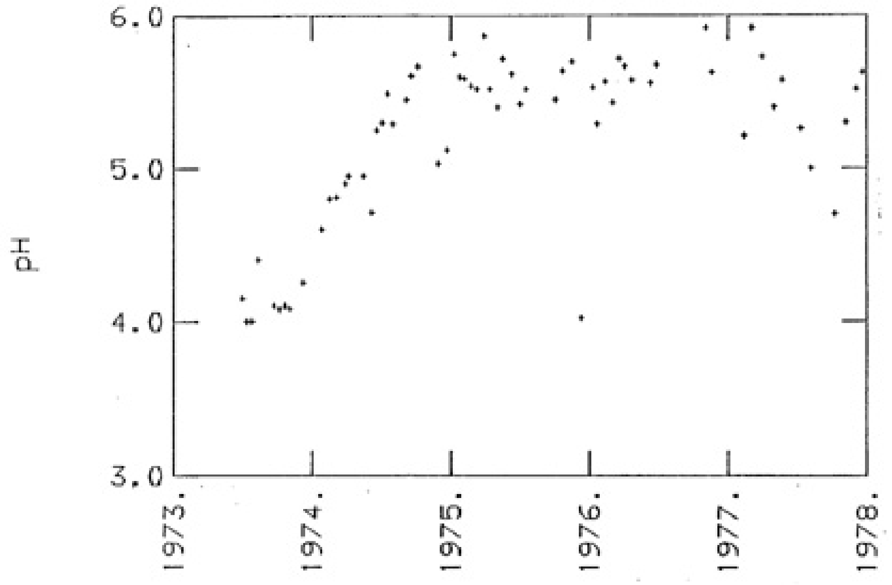

Figure 3. Plot of pH through time for site 002 (from Waddell et al., 1978).

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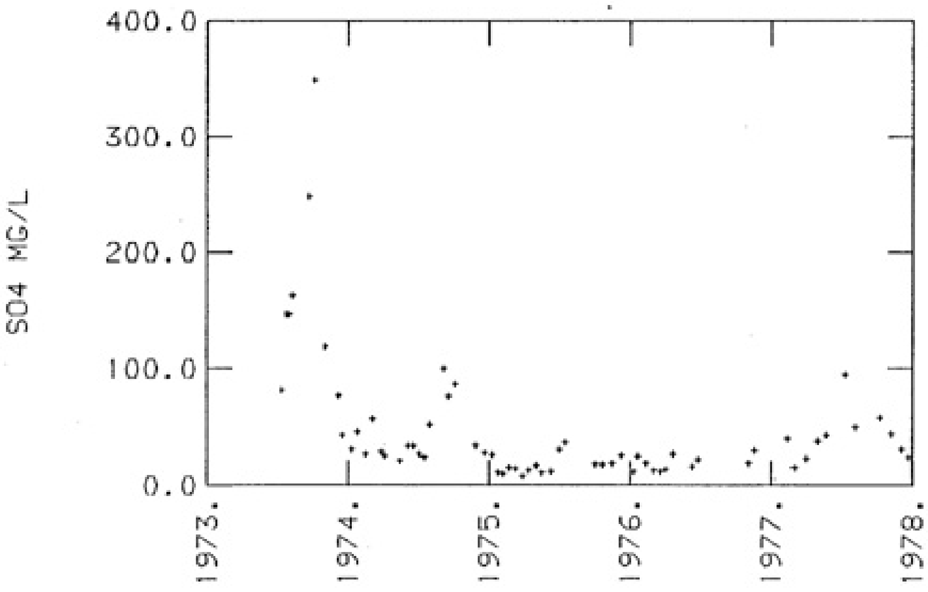

Figure 4. Plot of concentration of sulfate through time for site 002 (from Waddell et al., 1978).

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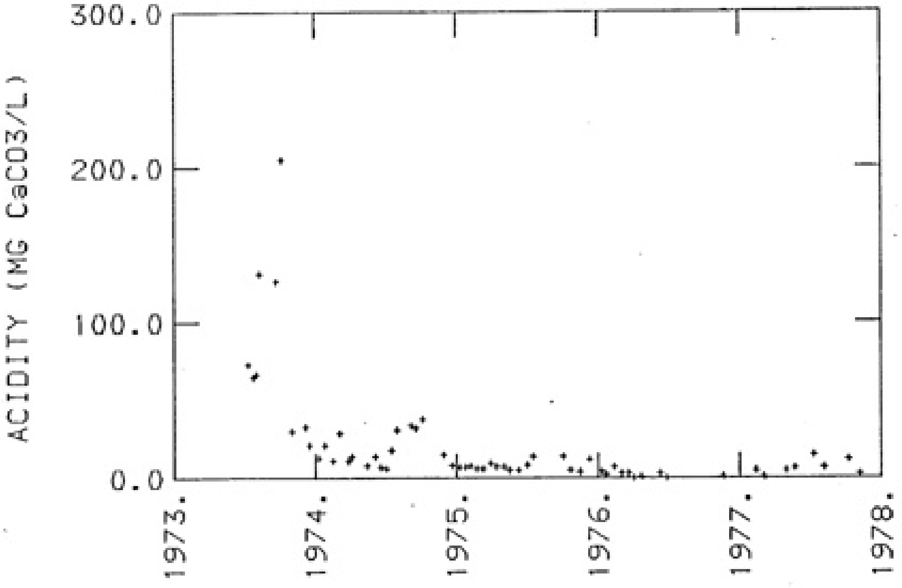

Figure 5. Plot of acidity through time for site 002 (from Waddell, et al., 1978).

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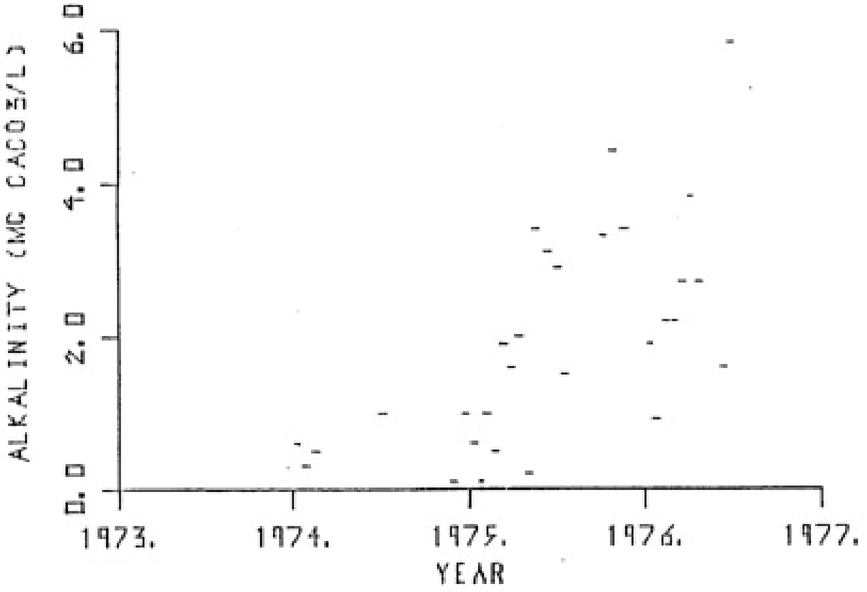

Figure 6. Plot of alkalinity through time for site 002 (from Waddell, et al., 1978).

Figure 6. Plot of alkalinity through time for site 002 (from Waddell, et al., 1978).

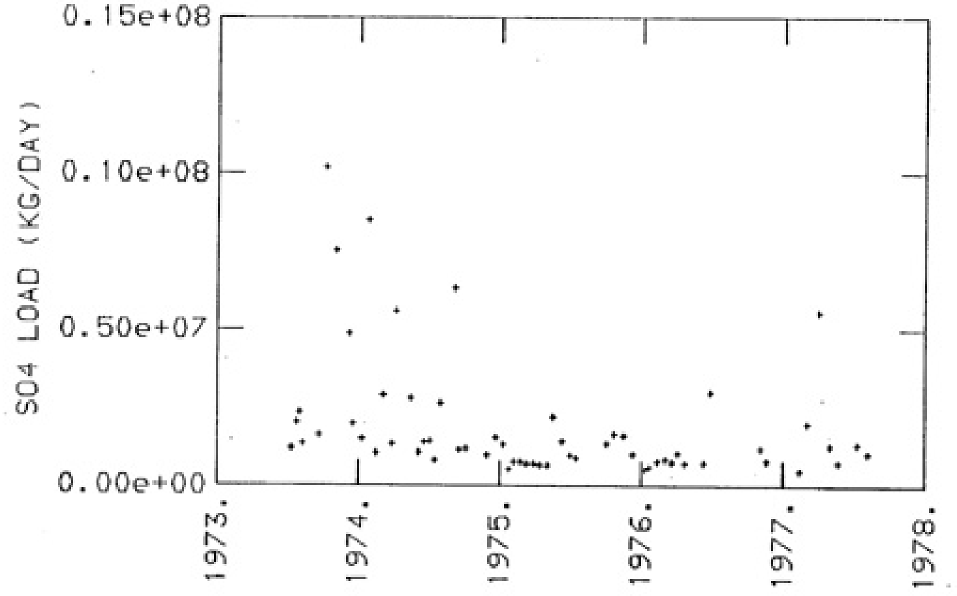

Figure 7. Plot of sulfate load through time for site 002 (from Waddell, et al., 1978).

Figure 7. Plot of sulfate load through time for site 002 (from Waddell, et al., 1978).

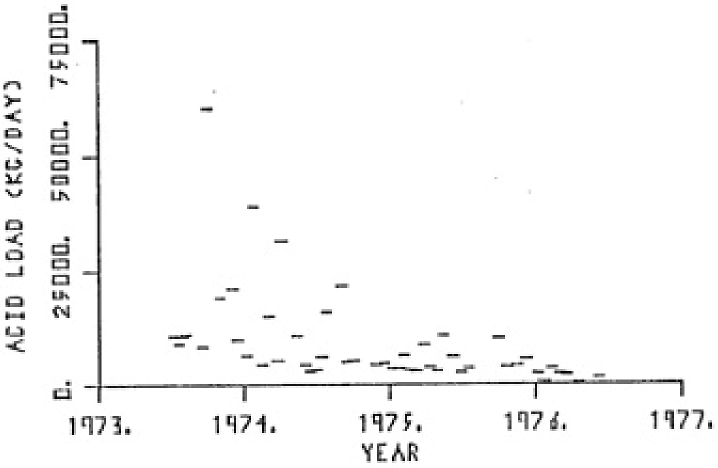

Figure 8. Plot of acid load through time for site 002 (from Waddell, et al., 1978).

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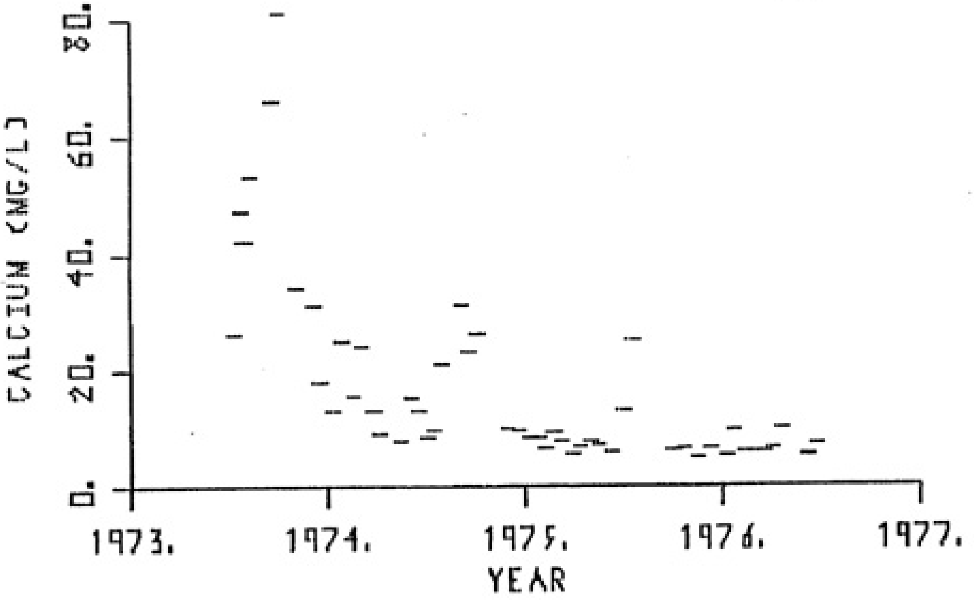

Figure 9. Plot of concentration of calcium through time for site 002 (from Waddell, et al., 1978).

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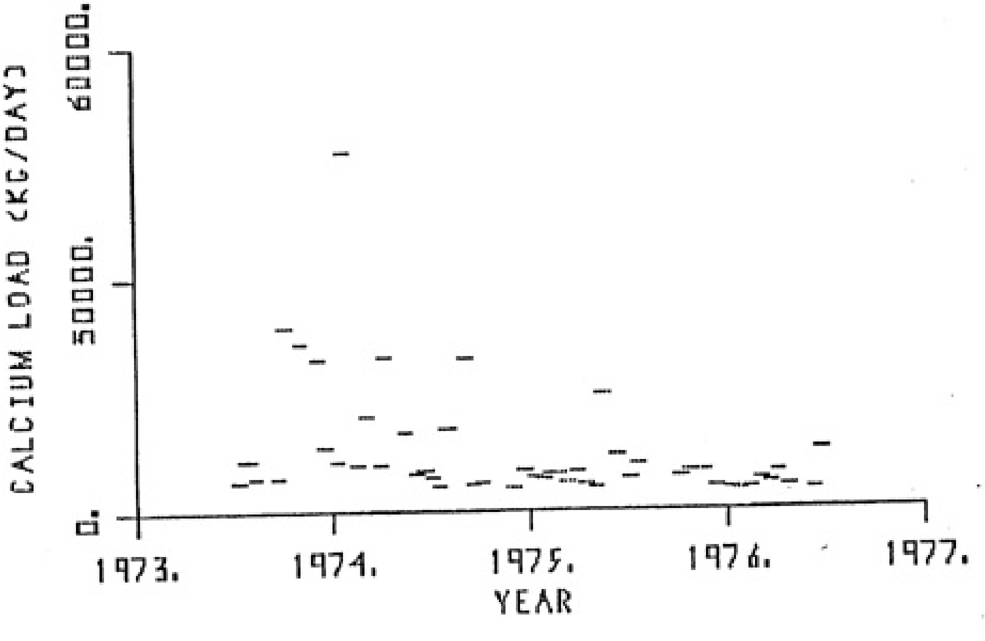

Figure 10. Plot of calcium load through time for site 002 (from Waddell, et al., 1978).

Figure 10. Plot of calcium load through time for site 002 (from Waddell, et al., 1978).

The peaks of the sulfate concentration and the acidity are smaller after treatment than before. Also, the seasonal peaks of the fluxes of sulfate and acidity from site 002 are smaller after treatment than before (Figures 7 and 8). Because the fluxes also decreased, the reduction in concentrations are not due to increases in discharge, and the accompanying amount of dilution, but must, in part, be due to treatment (Waddell et al., 1978).

When the treatment concept was proposed it was thought that the technique would result in higher concentrations of calcium because of the dissolution of the calcite and calcium oxide. The reverse was found to be true. Both the concentration and the flux of calcium decreased after treatment (Figures 9 and 10). The calcium concentration of the water increases as the sulfate concentration does, suggesting that the production of acid mobilized calcium. Glaeser (1972) reports small amounts of calcite in the Pocono in the roadcut east of the study area. Perhaps this calcite is the source of the calcium. A second possible source may be calcium sorbed into clay minerals. Decreases in the pH will replace sorbed calcium by hydrogen ions. The aluminum concentration is also positively correlated with the sulfate concentration, and has decreased after treatment. The aluminum in the water probably is mobilized by the destruction of clay minerals by low pH water. According to Langmuir (1975, personal communication), pH's of 3 or 4 will begin to destroy clay minerals. Thin sections of sandstones from the roadcut west of the study area contained a micaceous matrix and chlorite, although the dominant mineral was quartz. This matrix material in the sandstones, and the clay minerals in the shales could provide the aluminum found in the samples. The magnesium concentrations are also positively correlated with the calcium and sulfate concentrations. The magnesium may be contributed by the destruction of chlorite (Waddell et al., 1978).

The decrease in the concentration of aluminum after treatment may be caused by either the reduction in the destruction of clay minerals with increasing pH, or by controls imposed on the maximum aluminum concentrations by the precipitation of amorphous aluminum hydroxide, or both. Assuming a pK for the dissolution of aluminum hydroxide of 32.9 at 8^0C, the waters from site 002 are undersaturated with respect to amorphous aluminum hydroxide. The pIAP's range from 33.5 to 35.4, and average about 34.4. The waters are slightly oversaturated with respect to crystalline gibbsite. Saturation indices (log (LAP/K_{eq})) range from -0.05 to 1.13, where a positive, zero, or negative saturation index indicates supersaturation, saturation, or undersaturation, respectively (Waddell et al., 1978).

The waters are undersaturated with calcite, and supersaturated with iron oxides. The pIAP values for amorphous ferric hydroxide range from 35.2 to 38.8, compared with pK values of 37.1 for freshly precipitated ferric hydroxide and 38.5 for aged ferric hydroxide. The pIAP values average 36.6. The samples were not filtered prior to acidifying so that suspended ferric hydroxides were included in some of the samples. The samples were probably not greatly supersaturated with respect to ferric hydroxides, and freshly precipitated ferric hydroxide probably controls the iron concentrations in the water (Waddell et al., 1978).

Because the water chemistry of site 002 shows seasonal changes, being of poorer quality when flow is low and dilution is less, it is necessary to consider discharge when interpreting the chemical data. Unfortunately, no flow data are available for 002, hence, the flow of the South Fork of Beech Creek at Route 144 was used to simulate the discharge of 002 in the factor analyses.

Regression lines as well as the pretreatment $SO_4{}^{2-}$ data for treatment site 002 using both the dilution and dominant source models are plotted in figure 42 of Waddell (1978) and includes data until June 1976. The regression lines for the periods P_1, P_2 P_3 and P_4 are plotted in Waddell (1978) and equations for these lines are given in Appendix A of Waddell et al., (1978).

It is apparent from data presented in Waddell (1978) that the dilution model for SO_4^{2-} fits the data better than the dominant source model. This agrees with the idea that the discharge at site 002 is a mixture of water that has traveled down through the fill material, picking up a high sulfate load, and relatively pure, upward flowing water. If this model is valid, the flux of sulfate from the fill material must increase with increasing discharge because the slope of the regression line is greater than -1 (Waddell et al., 1978). The fact that SO_4^{2-} was reduced demonstrates that the acid forming reactions were being suppressed by the treatment and that the acidity simply was not lower because of increased buffering by the alkalinity added to the system by the treatment.

<u>Site 003</u>

Site 003 was the outfall of a spring that is buried beneath the highway embankment. After the weirs were installed, it became difficult to reach the original sampling site because of the weir pool created, and the site was changed to the down-stream end of the weir pool.

According to local residents, this spring discharged good quality water before I-80 construction. During construction, a galvanized steel culvert was emplaced running from the spring to the north edge of the highway embankment. At the present time the quality of the discharge is poor. Because of the conduit, the hydraulic head at the spring is close to zero, and the spring, or at least the buried end of the conduit, is a sink for both the original discharge of the spring (probably laterally moving or upwelling groundwater) and flow: moving down through the highway embankment material. This water flowing through the embankment is the cause of the poor water quality of this site (Waddell et al., 1978).

Figures 11 through 14 are plots of the pH, and concentrations of sulfate, acidity, and calcium through time. The pH does not vary appreciably through time. There is a sharp jump in the plot that occurred during March, 1974. The cause is unknown. It is not related to the change in the sampling site; that did not occur until June 1, 1974. It was feared that this increase might be due to a change in the pH buffer used for calibration of the pH meter. Such a change would have caused all sites to display such a jump because the same buffer was used for all sites. Site 003 is the only site displaying such an abrupt change. Whatever the cause, the shift has continued through to the present. The greater spread in the measurements, after June, 1974, is probably due to the movement of the sampling site to an area downstream from the weir pool (Waddell et al., 1978).

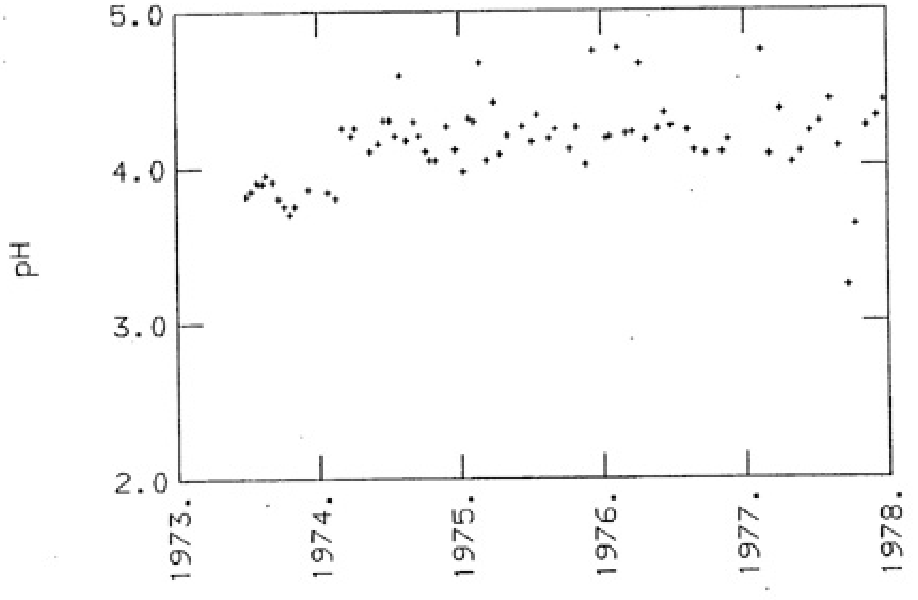

Figure 11. Plot of pH through time for site 003 (from Waddell, et al., 1978).

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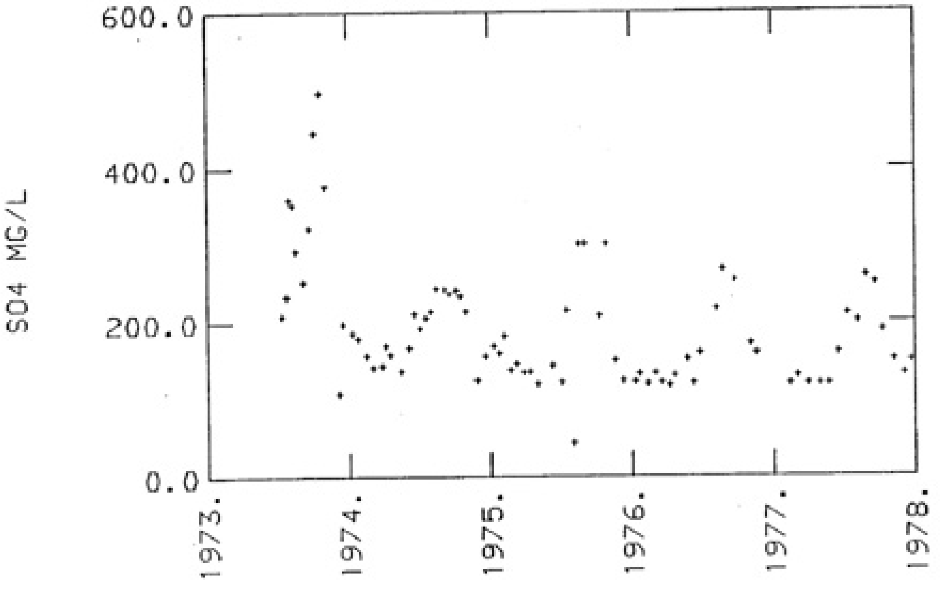

Figure 12. Plot of concentration of sulfate through time for site 003 (from Waddell, et al., 1978).

Figure 12. Plot of concentration of sulfate through time for site 003 (from Waddell, et al., 1978).

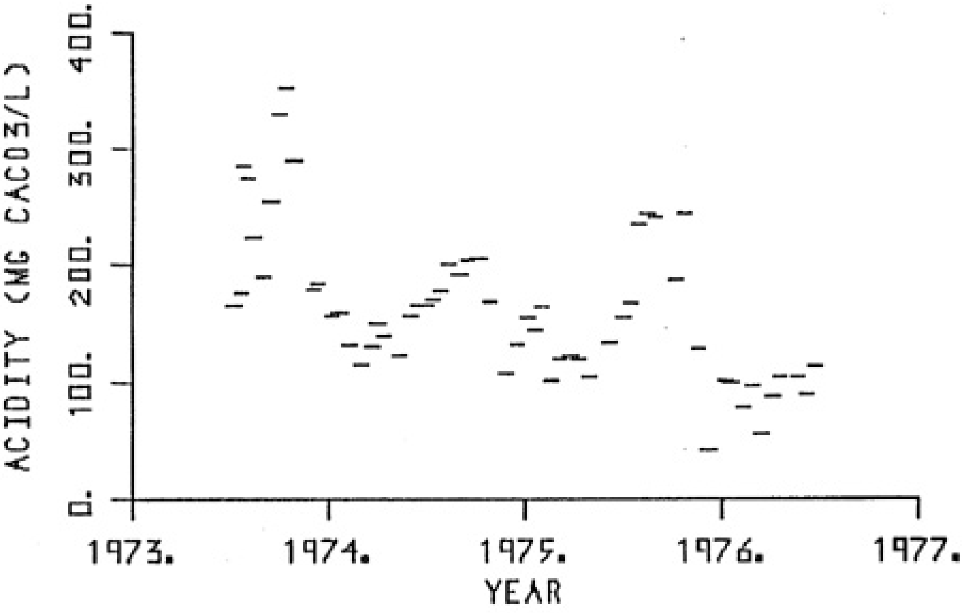

Figure 13. Plot of acidity through time for site 003 (from Waddell, et al., 1978).

Figure 13. Plot of acidity through time for site 003 (from Waddell, et al., 1978).

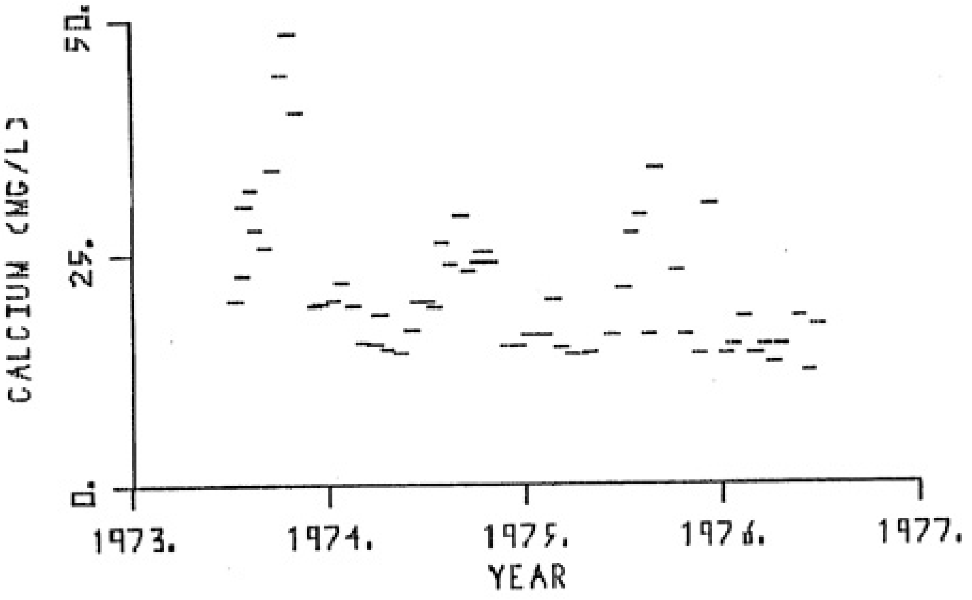

Figure 14. Plot of concentration of calcium through time for site 003 (from Waddell, et al., 1978).

Figure 14. Plot of concentration of calcium through time for site 003 (from Waddell, et al., 1978).

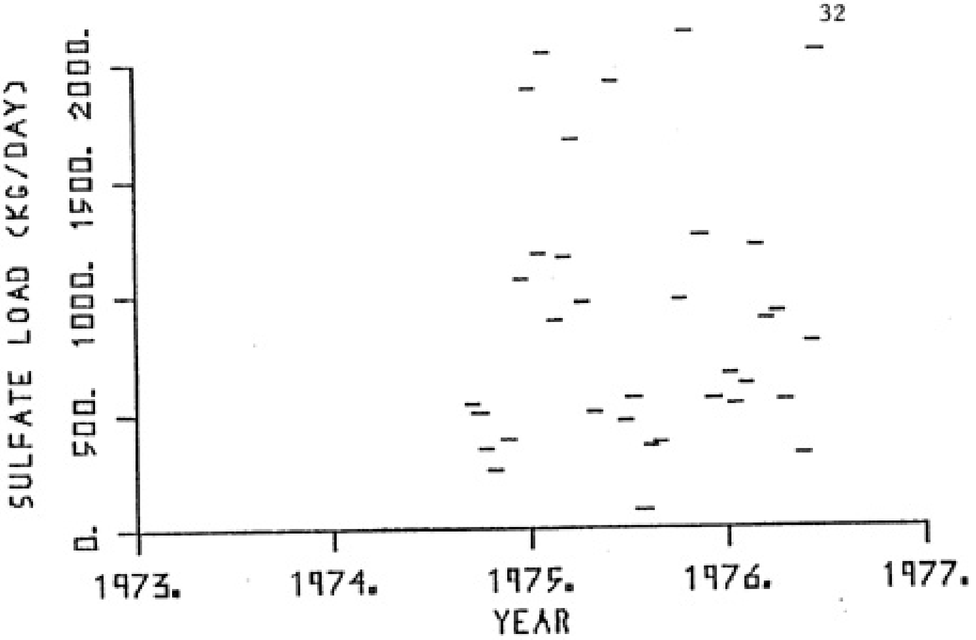

Figure 15. Plot of sulfate load through time for site 003 (from Waddell, et al., 1978).

Figure 15. Plot of sulfate load through time for site 003 (from Waddell, et al., 1978).

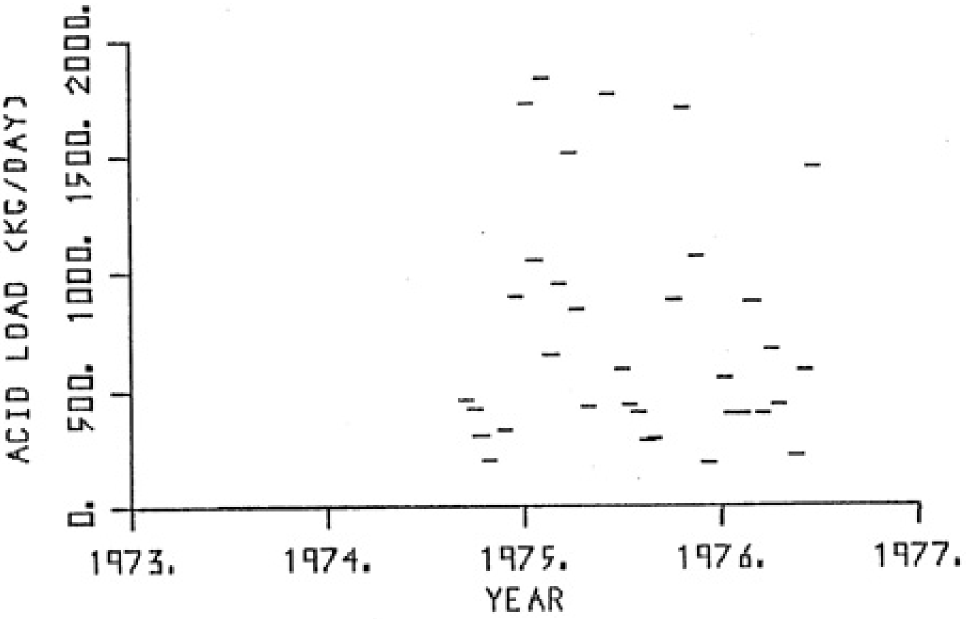

Figure 16. Plot of acid load through time for site 003 (from Waddell, et al., 1978).

Figure 16. Plot of acid load through time for site 003 (from Waddell, et al., 1978).

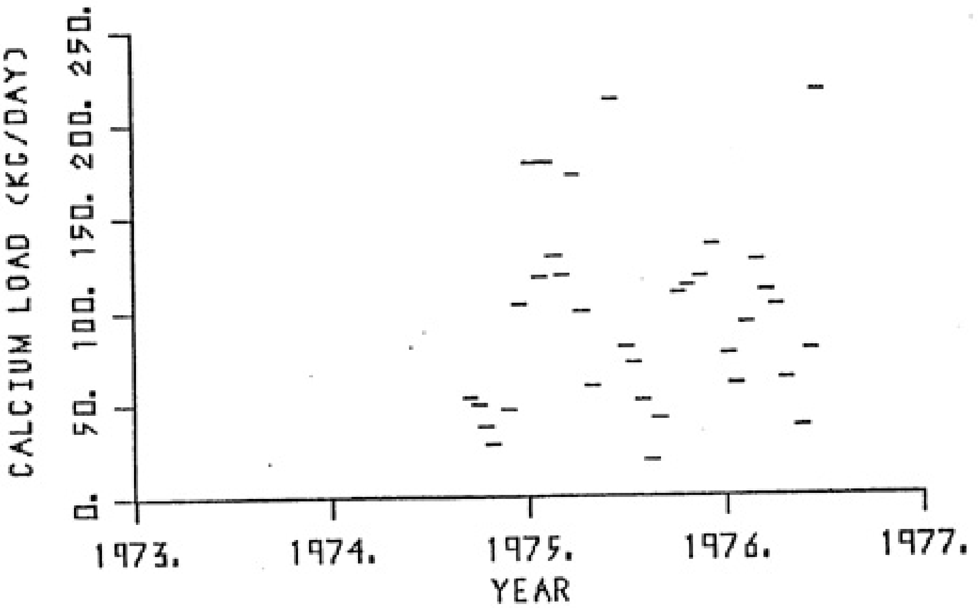

Figure 17. Plot of calcium load through time for site 003 (from Waddell, et al., 1978).

Figure 17. Plot of calcium load through time for site 003 (from Waddell, et al., 1978).

The plots of sulfate, acidity, and calcium through time are similar to those at site 002. However, the seasonal peaks related to times of low discharge at site 003 are higher than those at site 002.

The peak during the late summer of 1976 is barely discernible at site 002. Two low pH values observed at 003 late in 1977 (Figs. 11) correlate with extremely low flows noted that year and do not appear to be due to measurement error. Plots of the fluxes of sulfate, acidity, and calcium (Figs. 15 to 17) do not show easily discernible seasonal cycles, although they hint at lows during the late summer. Changes in discharge counteract changes in concentrations (Waddell et al., 1978).

Changes in water quality

In order to test the effectiveness of the treatment, the Kruskall-Wallis One-Way Analysis of Variance (KRWAL ANOVA) nonparametric test was used. Even though nonparametric techniques do not use all the available information, a non-parametric technique, or distribution-free technique, was chose because the parametric techniques assume a normal distribution. The distribution of the population is probably lognormal, but log transformations of the data did not always result in a normal population. Siegel (1965) suggests using nonparametric techniques when the number of observations is low. A more conservative approach in this situation is to use a nonparametric technique in-testing the data. Parametric techniques such as regression and factor analyses were used but only to determine relations among variables, not to test for significance.

To properly analyze time-dependent data, time-series techniques are well suited.

Unfortunately, these require more data than were available or affordable. In order to minimize the effects of non-independence, the data were divided into three groups. Each group contains data for one year, so that seasonal effects are minimized. These three groups are P_1 (June 1, 1973 to May 30, 1974); P_2 (June 1, 1974 to May 30, 1975); P_3 (June 1, 1975 to May 30, 1976); and P_4 (June 1, 1976 to May 30, 1977). The period P_5 (June 1, 1977 to December 31, 1977) was not included in the analysis because it was for a partial water year and would introduce a bias if treated equally to P_1 P_2 P_3 and P_4 data. The first group contains the pretreatment data and the last three groups contain the posttreatment data (Waddell et al., 1978).

The Kruskall-Wallis One-Way Analysis of Variance was used (Siegel, 1965). The test is based on rankings of the data rather than the data themselves, and requires at least ordinal-rank data.

The analyses were performed in two different manners. First, analyses were done on the pH, sulfate, and acidity data for sites 001, 002, 003, and 004 for the periods 1973-74, 1974-75, 1975-76, and 1976-77 and for the pH, sulfate, acidity, pH-load, sulfate-load and acidity-load for sites 002, 003, 004, 008, and 009 for the periods 1974-74, 1975-76, and 1976-77. Also, the analysis was performed on the pH, sulfate, acidity, and their respective loads for site 002, for the periods 1973-74, 1974-75, 1975-75, and 1976-77. The significance levels of the results are presented in Table 4a for P_1 vs

Table 4. Results of the Kruskall-Wallis One-Way Analysis of Variance, with the sites considered individually (from Waddell et al., 1978).

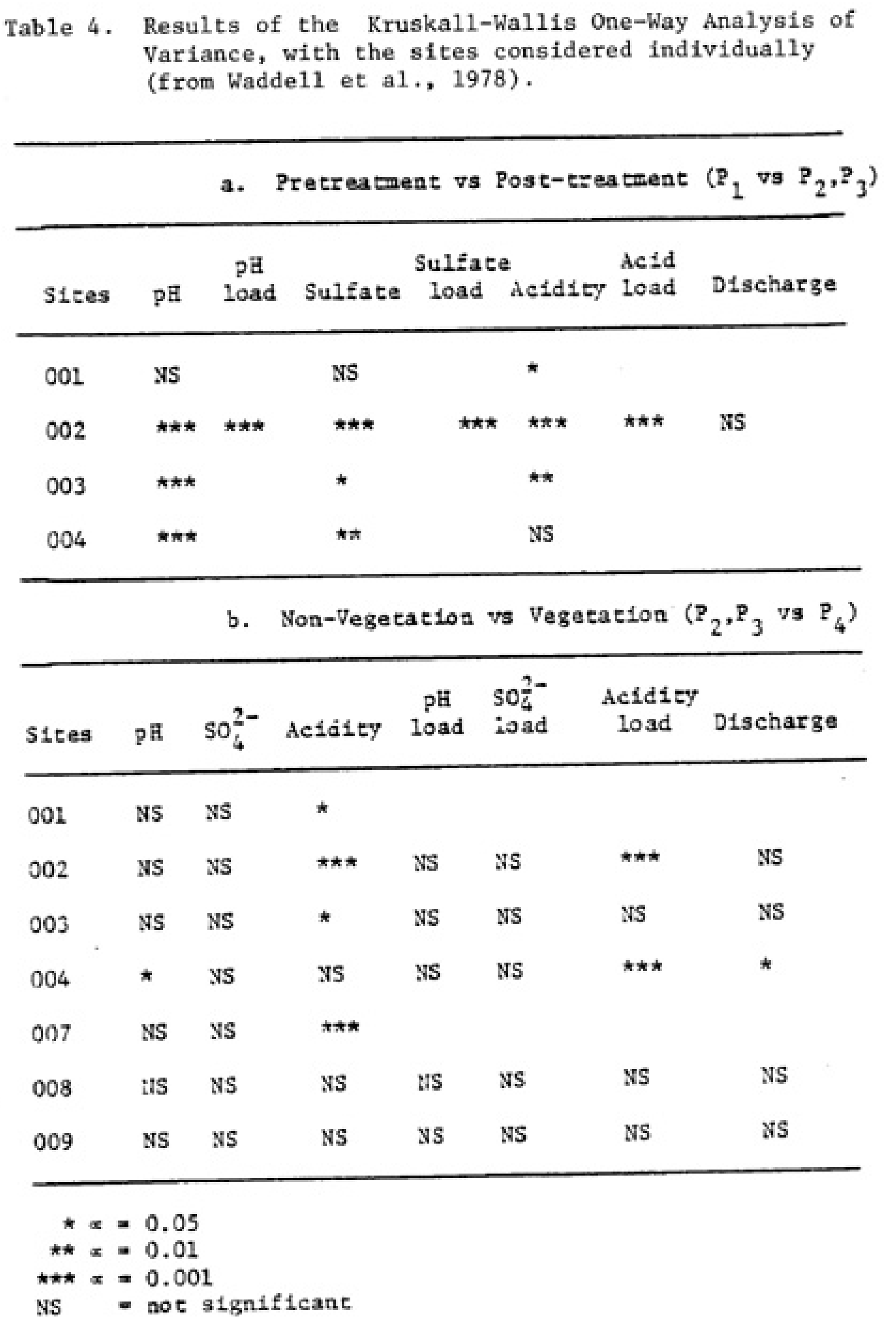

Table 4. Results of the Kruskall-Wallis One-Way Analysis of Variance, with the sites considered individually (from Waddell et al., 1978).

a. Pretreatment vs Post-treatment (P_1 vs P_2,P_3)

Sites	pH	pH load	Sulfate	Sulfate load	Acidity	Acid load	Discharge
001	NS		NS		*		
002	***	***	***	***	***	***	NS
003	***		*		**		
004	***		**		NS		

b. Non-Vegetation vs Vegetation (P_2,P_3 vs P_4)

Sites	pH	SO_4^{2-}	Acidity	pH load	SO_4^{2-} load	Acidity load	Discharge
001	NS	NS	*				
002	NS	NS	***	NS	NS	***	NS
003	NS	NS	*	NS	NS	NS	NS
004	*	NS	NS	NS	NS	***	*
007	NS	NS	***				
008	NS	NS	NS	NS	NS	NS	NS
009	NS	NS	NS	NS	NS	NS	NS

* α = 0.05
** α = 0.01
*** α = 0.001
NS = not significant

P_2, P_3 (Pretreatment vs Post-treatment) and P_2, P_3 vs P_4 (Non-vegetation vs Vegetation).

In these tests, the population sampled is the value of a variable for the particular periods. For example, in Table 4b, the test for the pH values for site 002 is a test to see if there is a significant difference between three different populations, each being composed of the measurements of the pH of the water at site 002 for the period June 1974-May 1977. Each entry in the table represents a separate test.

The significance level (a) is the probability of rejecting the null hypothesis when it should have been accepted. The smaller the significance level, the more stringent is the test.

The test for site 001; which is up-hydraulic-gradient from the treatment and should not be affected by it, but may be affected by changes along highway 144, shows that there is no significant change in either pH or sulfate concentration, but there is (a = 0.05) a change in the acidity (Table 4b). Examination of the data suggests that during 1975-76, the acidity values are lower than in 1973-74 or 1974-74. The reason is not known.

Site 002 has experienced significant changes (a = 0.001) in acidity concentration and acidity load (Table 4b). The discharge data used (Beech Creek) did not change significantly so the changes in load primarily reflect changes in concentration. There was an increase in pH and decreases in both sulfate and acidity concentrations, indicating that the water quality did improve because of the treatment. When only the post-treatment periods (1974-75 and 1975-76, P_2 and P_3) were considered (Table 30b of Waddell, 1978), there were significant changes only in acidity (a = 0.01) and acid load (a = 0.05) indicating that most of the change in water chemistry at site 002 occurred between 1973-74 and 1974-75 (P_1 and P_2) the time of the treatment. The change in acidity between 1974-75 P_2) and 1975-76 (P_3) was a slight decrease.

Site 003 also experienced significant changes in acidity concentration (Table 4b) (a = 0.05). Plots of these variables through time indicate that an improvement in water quality has occurred. The exact cause of this improvement is not known but we believe that the treatment site partially overlapped the watershed area of control site 003. However, the most abrupt change in pH occurred at the end of February 1974, before the treatment was applied. This may be due to an increase in the discharge of the spring because of the snow melt that year, and reflected normal pretreatment seasonal water quality variability. Comparison with site 004 shows a similar, but smaller increase at the same time which supports this explanation. Site 002 shows an increase at the same time, but a more gradual one (Waddell et al., 1978).

These results indicate that there is a difference between the pretreatment and post-treatment data. This may be due to the treatment, or to some other factor such as a change in the amount of precipitation, although the test for changes in the discharge at Beech Creek indicated that no significant change in flow had occurred over the period considered. To be certain, however, that the change in chemistry was related to the treatment rather than another change, a second set of analyses was performed. The treatment should affect site 002 the most and site 001 the least. The effect on the other sites should be intermediate if there is an effect at all. The following analyses, test not the data at each site, but the difference between the measurements at two different sites. For example, the differences in the pH measurements at site 001 and 002 were tested to see if the magnitude of the differences changed through the three periods of time. The results of these analyses are in Table 5 (Waddell et al., 1978).

The first six pairs of sites were used to help evaluate the changes at site 002 in reference to other sites. The significance levels of the changes in the differences between site 001 and site 002 are not surprising because the chemistry of site 001 changed little and the chemistry of site 002 changed greatly. The chemistry of site 001 changed about the same as at site 004. There were also significant changes in the differences between sites 002 and 004. From these results it can be seen that sites 001 and 004 changed little, and site 002 changed significantly with respect to these two sites. Similar arguments allow other combinations of sites to be evaluated for their relative degree of change. Doing this for all combinations of sites 001, 002, 003, and 004 results in the following rankings with regard to change in the three parameters:

pH: (001, 003, 004), 002

so 4 : 001, 004, 003, 002

Acidity: 004, 001, 003, 002

where the rankings are (left to right) from sites of least change to sites of greatest change, and where the parentheses indicate that the rankings inside the parentheses indicate that the rankings inside the parentheses are ties in rank (Waddell et al., 1978).

From these rankings, it may be said that the greatest overall change in chemistry has occurred at site 002, followed by site 003, and that the sites with the least amount of change were sites 001 and 004. From this, and from knowledge of the flow system and site locations, it can be concluded that the changes observed are a result of a change near site 002, and one almost definitely caused by the treatment.

Table 5. Results of Kruskall-Wallis One-Way Analysis of Variance of the difference in the measured parameters between two sites (from Waddell, et al., 1978).

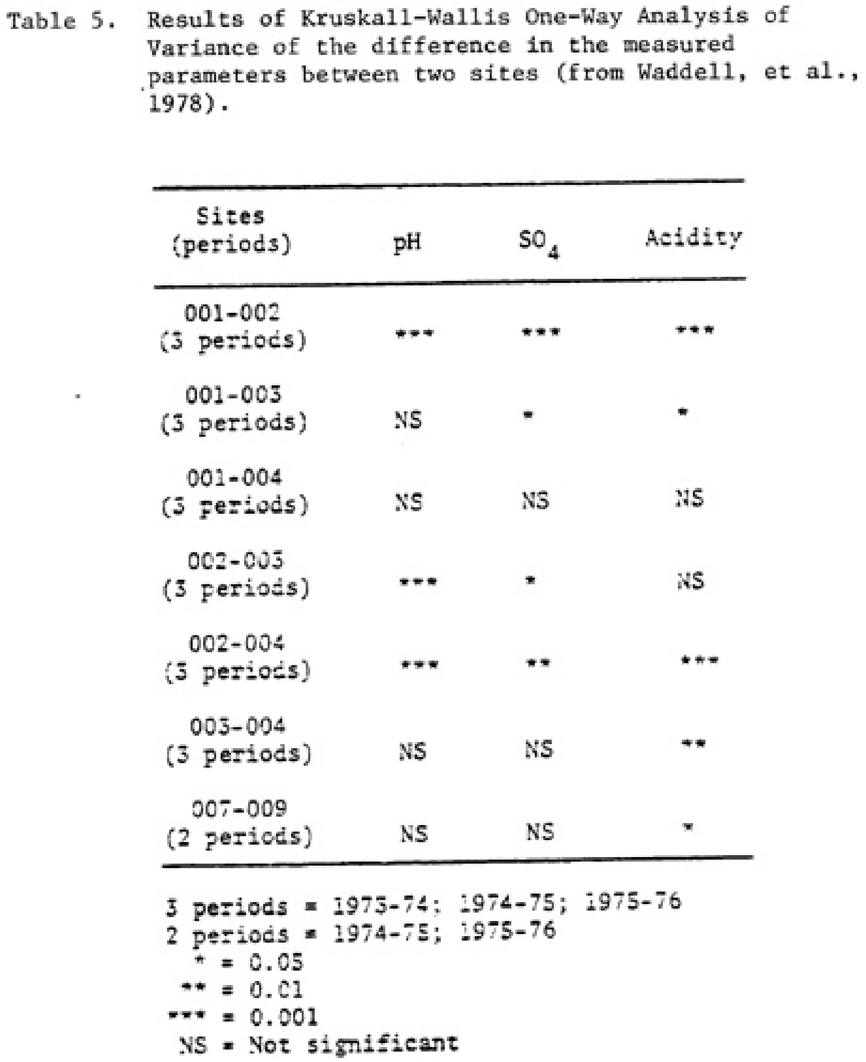

Table 5. Results of Kruskall-Wallis One-Way Analysis of Variance of the difference in the measured parameters between two sites (from Waddell, et al., 1978).

Sites (periods)	pH	SO_4	Acidity
001-002 (3 periods)	***	***	***
001-003 (3 periods)	NS	*	*
001-004 (3 periods)	NS	NS	NS
002-003 (3 periods)	***	*	NS
002-004 (3 periods)	***	**	***
003-004 (3 periods)	NS	NS	**
007-009 (2 periods)	NS	NS	*

3 periods = 1973-74; 1974-75; 1975-76
2 periods = 1974-75; 1975-76
* = 0.05
** = 0.01
*** = 0.001
NS = Not significant

CONCLUSIONS

The effectiveness of the abatement technique has been demonstrated for a relatively thin layer of pyrite bearing rockfill deposits. To reach this goal, many factors were considered: the presence of long term trends in the quality of water, the effects of discharge on concentration, the ground-water flow system, and mineral equilibria and kinetic controls on the water chemistry. Secondary goals of the investigation were concerned with understanding these factors.

1) No chemical evidence of long-term trends not attributable to treatment was found. In only two sites (002, 003) were possible trends found, both showing an improvement in quality. Samples were collected for only one year before treatment, so no long-term trends could be detected at these two sites before the treatment. Any trends noted since treatment should have been caused by it (Waddell, et al, 1978).

2) Increases in discharge result in improvement of water quality through dilution. Almost all of the factor analyses that include discharge indicate that the discharge-related factor contains higher percentages of the variation in the data set than do other factors. Two different regression models used in the analysis point out different properties of the relation between concentration and discharge, and the use of both is worthwhile when the data are available (Waddell, et al, 1978).

3) The effect of discharge may be decreased by looking at the flux of the constituent past a point, rather than its concentration. Plots of the fluxes of sulfate and acidity for all sites except site 002 show no noticeable trend in flux with time. However, the fluxes of these variables at site 002 have decreased greatly with time due to the treatment.

The dilution model estimates that for site 002 the change in log flux of sulfate with change in log discharge are 0.40 and 0.25 for the pretreatment and post-treatment data. The rate of change has decreased since treatment was applied. The dominant source model predicts that the sulfate concentration in the dominant source is 48 and 4.6 mg/l, for pretreatment and post-treatment data, respectively (Waddell, et al, 1978).

4) Two different flow systems are active in the treated area. Water recharged on the tops of hills is discharged in the valley. It is generally of good quality except for pollution by road salt. Because this water is discharging upwards into the treated area, it is not possible to treat it before it reaches the sites of acid production. This decreases the effect of the treatment. Treatment in recharge areas, on the other hand, puts favorable quality water into storage that will help to buffer the system (Waddell, et al, 1978).

5) The chemistry of the water at the study area is partially controlled by the solubility of ferric hydroxide and aluminum hydroxide. Precipitation of these phases produces protons, counteracting the increase in pH caused by the treatment. Ferric hydroxide cannot precipitate near pyrite surfaces but can precipitate within the fill material. Aluminum hydroxide can also precipitate within the fill (Waddell, et al, 1978).

6) The rate of the production of acid appears to be controlled by pH. The amount of acid produced determined by, among other things, the residence time of the water in the fill material and the oxidation rate of ferrous iron. At pH's of 3.0 to 4.0, bacterial catalysis is

very important. Above a pH of about 5.5 or 6.0, the oxidation reaction occurs rapidly without the influence of bacteria. If the pH ranges of significant bacterial catalysis and rapid abiotic oxidation overlap considerably, the rate of the production of acid at its minimum will be great enough that the buffer capacity of the water will quickly be exhausted and the pH will decrease into the range where bacterial catalysis is important. If this is the case, the main effect of the treatment will be the neutralization of acid until the buffer capacity is exhausted. The effect of the treatment would probably not be noticeable. However, if the range of overlap is small, the production of acid will be so slow that the pH will not decrease into the range of bacterial catalysis unless the residence time is very long. The decrease in the production of acid will be significant (Waddell, et al, 1978).

7) The fluxes of acidity and sulfate, and thus the production of acid, at site 002 decreased by a factor of four after the treatment was applied. The flux of sulfate at site 002 has not been above 25,000 kg/day (using discharge data for Beech Creek) since November, 1974 (Fig. 7) when the pH reached about 5.5. The pH has not increased above this level, except for random variation around the mean, since that time (Fig. 3). The maintenance of the pH at 5.5 at site 002 since January, 1975, suggests that the pH where bacterial catalysis becomes important is somewhere below 5.5. Except for one measurement, the lowest pH measured at site 002 since January 1974, has been about 5.2. Thus, it appears that the pH where bacterial catalysis becomes important is below 5.2. At pH 5.2, the oxidation rate is too slow to produce enough acid to deplete the buffer capacity of the water during the time the water remains in the fill material (Waddell, et al, 1978).

8) We conclude that the treatment has been effective in reducing the production of acid in the treatment area. Statistical testing using conservative tests indicate that there have been significant decreases in the production of acid. Concentrations and fluxes have decreased. The discharge at Beech Creek has not varied significantly when considered on a year to year basis. The differences in the pH and sulfate values between sites 002 and 003 have significantly increased, as expected if the treatment caused the changes (Waddell, et al, 1978).

9) The treatment did not seem to be effective in improving the quality of the water in Jonathan Run to a point where the normal aquatic community can be restored. The contributions of acid by the untreated highway embankment, the control area, and ground-water discharge to the stream are too great. If the quality of Jonathan Run is to improve, these contributions of acid must be decreased by expanding the treatment (Waddell, et al, 1978).

10) The success of the treatment in the Jonathan Run study area does not insure its success in all settings. The amount of acid produced depends on the residence of time of the water and the rate of oxidation of ferrous iron. If the residence time is too long, and flux of alkaline water too small, even the slow production of acid will eventually deplete the buffer capacity of the water and lower the pH into the range of bacterial catalysis. The larger the disturbed area and the longer the residence time of water within rock spoil, the higher the buffer capacity must be after it leaves the treatment layer (Waddell, et al, 1978).

11) Because of the similarity between the hydrologic and chemical settings in the Jonathan Run study area and in many strip mines, we conclude that this abatement technique has very good chances of reducing the production of acid from both active and abandoned strip mines,

from other highway sites, or from anywhere that pyrite bearing strata are disturbed. Its use is especially promising where earth-moving equipment is already available at the site and where sources of waste limeplant flue dust and limestone fragments can be found nearby. However, many more field demonstrations will be required under a variety of mining, overburden, climatic and geochemical settings before the limitations and benefits of the alkaline topdressing acid abatement scheme is adequately understood. We still have not established the alkaline material loading requirements given acid-base accounting data nor the benefits to be achieved by applying alkaline material at various positions within mine spoil during backfilling operations. These are the incentives for undertaking the current demonstration project at an abandoned mine site in Clarion County, PA and following the progress of other investigators.

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