



Concentrated iron pyrite mine waste as an amendment for alkaline soils
by Troy C Smith

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Soils
Montana State University
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Abstract:

Many agricultural-soils in the western U.S. are alkaline. Soil pH's above 7.0 cause several essential plant nutrients, including iron and sulfur, to become unavailable to plants. These soils often require additional fertilizer, and can be very difficult to correct for agricultural purposes. Sulfur has been identified as one of the best amendments for highly alkaline soils. Many forms of sulfur have been used to amend these soils. Most forms are either only moderately effective, or are expensive to apply.

The mining industry commonly extracts sulfur rich minerals as a waste product. Although other countries have tried these waste products, very little research has been done in the United States to test these materials as an alternative soil amendment to alleviate iron and sulfur deficiencies on alkaline soils.

The Golden Sunlight gold mine in Montana produces a high sulfur by-product. The material contains approximately 55 % finely ground pyrite. Pyrite is composed of iron and sulfur and when allowed to oxidize will acidify, releasing these elements. It was felt this pyrite material would be a good amendment for alkaline soils.

A study was designed to test the benefit of applying finely ground pyrite to several soils varying in alkalinity. The research included a laboratory and field study. In the laboratory, samples of the pyrite, and five soils amended with the pyrite, were kept moist and monitored for chemical parameters that would measure the rate of pyrite oxidation. The samples were monitored for one year. Field test plots were also constructed on one of the alkaline soils tested in the laboratory to evaluate the effect of pyrite applications on a sulfur demanding crop.

The results indicated that applications of finely ground pyrite were very effective at lowering soil pH and increasing plant available iron and sulfur. The results also showed that due to the relatively slow oxidation of the pyrite, successful application rates for very alkaline soils may often exceed 10,000 kg/hectare.

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A thesis submitted in partial fulfillment
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Master of Science

in

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Bozeman, Montana**

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APPROVAL

of a thesis submitted by

Troy C. Smith

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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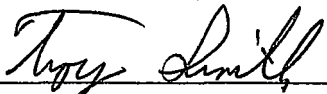
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ABSTRACT

Many agricultural soils in the western U.S. are alkaline. Soil pH's above 7.0 cause several essential plant nutrients, including iron and sulfur, to become unavailable to plants. These soils often require additional fertilizer, and can be very difficult to correct for agricultural purposes. Sulfur has been identified as one of the best amendments for highly alkaline soils. Many forms of sulfur have been used to amend these soils. Most forms are either only moderately effective, or are expensive to apply.

The mining industry commonly extracts sulfur rich minerals as a waste product. Although other countries have tried these waste products, very little research has been done in the United States to test these materials as an alternative soil amendment to alleviate iron and sulfur deficiencies on alkaline soils.

The Golden Sunlight gold mine in Montana produces a high sulfur by-product. The material contains approximately 55% finely ground pyrite. Pyrite is composed of iron and sulfur and when allowed to oxidize will acidify, releasing these elements. It was felt this pyrite material would be a good amendment for alkaline soils.

A study was designed to test the benefit of applying finely ground pyrite to several soils varying in alkalinity. The research included a laboratory and field study. In the laboratory, samples of the pyrite, and five soils amended with the pyrite, were kept moist and monitored for chemical parameters that would measure the rate of pyrite oxidation. The samples were monitored for one year. Field test plots were also constructed on one of the alkaline soils tested in the laboratory to evaluate the effect of pyrite applications on a sulfur demanding crop.

The results indicated that applications of finely ground pyrite were very effective at lowering soil pH and increasing plant available iron and sulfur. The results also showed that due to the relatively slow oxidation of the pyrite, successful application rates for very alkaline soils may often exceed 10,000 kg/hectare.

INTRODUCTION

Calcareous and high pH agricultural soils often produce lower crop yields than neutral soils. The lower yields are usually a result of alkaline induced nutrient deficiencies, increased salt content, or poor soil structure. Consequently, alkaline agricultural soils typically require greater amounts of fertilizer, and often micronutrient applications such as iron. These soil problems can be expensive to correct. Many high sulfur materials have been used to amend alkaline soils. Elemental sulfur has been shown to be an effective amendment because of its ability to produce acid and neutralize soil alkalinity (Follett et al., 1981). Sulfide minerals such as iron pyrite have been tried worldwide as amendments for alkaline soils. Very little research has been conducted in the U.S., partially because sulfide minerals are often associated with unwanted heavy metals.

Iron pyrite has the chemical formula FeS_2 , and when exposed to oxygen and water produces plant available ferrous iron (Fe^{2+}) and sulfate (SO_4^{2-}). Sulfuric acid is also produced as one of the by-products from the decomposition of iron pyrites. The reaction rate for the decomposition of iron pyrites is dependent on particle size, surface area, the composition of the matrix encompassing the pyrite, and surrounding environmental factors.

Golden Sunlight Mines, Inc. is a large gold mine located near Whitehall, Montana which produces a concentrated iron pyrite by-product. This by-product is relatively low in heavy metals other than iron. Since it was known that crop yields from alkaline soils could theoretically increase with iron pyrite additions, it was of interest to learn how the iron pyrite by-product could affect these soils. This study was conducted to identify beneficial agricultural uses for the iron pyrite by-product that could lead to an alternative means of eliminating iron and sulfur deficiencies in calcareous and high pH soils.

Thesis Objectives

- To determine the rate of soil acidification and related iron and sulfur release during a one-year period from the oxidation of pyrite added to five different soils.
- To determine the effects of pyrite applications on alkaline Montana soils in relation to pH and plant available iron and sulfur levels.

BACKGROUND

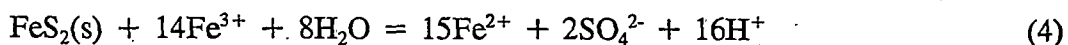
Soil Chemistry

Alkaline soils (soil pH above 7.0) are common in semi-arid agricultural environments. It is known that soil alkalinity affects plant nutrient availability. Many essential plant nutrients in the soil such as phosphorus, sulfur, and iron become less available to the plant as the soil pH is elevated above 7.0 (Follet et al., 1981). Nutrient requirements vary between agricultural crops, consequently, specific nutrient deficiencies due to soil alkalinity also vary. Plant available iron deficiencies are one of the more common problems associated with alkaline soils (Follet et. al., 1981).

Alkaline soil problems are often corrected with commercially available products which contain either sulfur or acid. Commercially available products include the chemicals ammonium sulfate, gypsum, elemental sulfur, and sulfuric acid. These products are either low acid producers, or are hazardous to handle.

Iron Pyrite

Iron pyrite (referred to as pyrite) is a naturally occurring mineral often found as a by-product of metal and coal mining. Pyrite exposed to water and oxygen will weather according to the following reactions (Hossner, 1988):



The oxidation of pyrite does not always include equation number 4, due to the large amounts of ferric iron required. The rate of reaction is dependent on particle size, surface area, oxygen, moisture and temperature. These reactions can also be catalyzed by thiobacillus bacteria. Thiobacillus ferrooxidans can play an important role in the oxidation rate of pyrite (NTIS, 1991). The conversion of ferrous iron to ferric iron is the rate-limiting step in the oxidation of pyrite (equation 2). Iron-oxidizing bacteria can catalyze this step, thus accelerating this conversion and the oxidation of pyrite (Stumm and Morgan, 1981).

Pyrite oxidation is directly related to surface area (Vlek and Lindsay, 1978). Finely disseminated "framboidal" pyrite will oxidize much more rapidly than larger crystalline pyrites (Caruccio and Ferm, 1974). Crystalline pyrite, if finely ground, may also oxidize rapidly.

Oxygen and water are shown to be essential to pyrite oxidation in the above reactions. In air-dried soils, pyrite oxidation practically ceases (Barrau and Berg, 1977). Oxygen diffusion through certain materials can also limit pyrite oxidation.

Temperature has been shown to have a significant effect on the rate of pyrite oxidation. A 10° C increase in temperature can produce a two-fold increase in the rate of pyrite oxidation (Smith and Shumate, 1970). This is partially a result of biological activity.

Smith and Shumate (1970) have shown that pH affects the rate at which ferrous iron is converted to ferric iron, thus affecting the rate of pyrite oxidation. In the absence of iron-oxidizing bacteria, the ferrous to ferric iron conversion occurs rapidly at a pH above 6.0. In the presence of iron-oxidizing bacteria, the ferrous to ferric iron conversion occurs most rapidly between pH 2.4 and 3.6 (NTIS, 1991). Acidic micro-environments are sufficient for bacterial iron oxidation (Barrau and Berg, 1975). The presence of calcium carbonate can slow the oxidation of pyrite by inhibiting bacterial interaction and creating less soluble iron hydroxides (Caruccio et al., 1981).

Golden Sunlight Pyrite Material

Golden Sunlight Mine produces a concentrated tailing material that is primarily pyrite and has no appreciable heavy metal content other than iron. Golden Sunlight's gold ore contains approximately 4 to 7% pyrite. In the milling process about 40% of this pyrite is removed in a gravity circuit to increase gold recovery. The pyrite material removed in the gravity circuit is composed of approximately 55% pyrite by weight. The remaining 45% is composed primarily of feldspars and silica. After the gold is removed this material becomes a by-product. Approximately 400 tons of pyrite enriched tailing is produced per day.

A concentrated pyrite tailing composite sample was created by blending equal weights of monthly samples from July, 1989 to January, 1990. The sample was submitted to Chen Northern Laboratories, Inc. in Billings for heavy metal analysis.

Tests were conducted in accordance with the U.S. Environmental Protection Agency Manual SW-846 Test Methods for Evaluating Solid Waste, 3rd Edition, November, 1986 and Method 1311 published June 29, 1990 in 40 CFR Part 302. The results of the analysis for the Toxicity Characteristics Leaching Procedure (TCLP) have been adjusted for spike recovery and are summarized in Table 1.

Table 1. Pyrite material TCLP Metal Concentration Data (ppm).

Metal	Test Extract	EPA Extract Limit
Ag	<0.040	5.0
As	0.020	5.0
Ba	<0.200	100
Cd	0.145	1.0
Cr	0.150	5.0
Hg	0.0006	0.2
Pb	<0.040	5.0
Se	0.006	1.0

Since all the test extracts were less than the EPA extract limits, the pyrite material is deemed non-hazardous by the EPA method based on heavy metal content.

Table 2 summarizes total metal analyses for monthly composite samples from July, 1989 through January, 1990 (Rhoades, 1982).

Table 2. ICP multielement concentrations of pyrite material composite samples.

Month	Year	Ag (oz/ton)	Al (%)	As (ppm)	Au (oz/ton)	Ba (ppm)	Bi (ppm)	Ca (%)	Cd (ppm)	Ce (ppm)	Co (ppm)	Cu (ppm)	Li (ppm)	Cr (ppm)	Hg (ppm)
July	1989	0.0496	2.21	128	0.0223	>2000	32	0.87	1	40	53	410	11	79	0.604
August	1989	0.0204	2.85	96	0.0186	1558	24	0.19	1	33	46	217	10	64	0.617
September	1989	0.0496	2.62	96	0.0212	1891	29	0.19	<1	42	58	225	15	97	0.478
October	1989	0.0408	2.62	99	0.0215	1971	40	0.15	<1	44	57	209	10	69	0.448
November	1989	0.0467	2.49	106	0.0207	1745	38	0.14	<1	46	54	208	10	55	0.449
December	1989	0.0525	2.78	115	0.0207	>2000	39	0.22	<1	37	50	354	15	88	0.798
January	1990	0.0321	2.97	89	0.0206	>2000	32	0.23	<1	37	53	271	11	76	0.667
Maximum		0.0525	2.97	128	0.0223	>2000	40	0.87	1	46	58	410	15	97	0.798
Average		0.0418	2.64	104	0.0208		33	0.28		40	53	268	12	75	0.580
Std. Dev.		26	9	12	5		16	85		10	7	28	18	13	0.121

Table 2 continued.

Month	Year	Mg (%)	Mo (ppm)	Na (%)	Nb (ppm)	Ni (ppm)	Pb (ppm)	Sc (ppm)	Sr (ppm)	Te (ppm)	Ti (%)	V (ppm)	Zr (ppm)	Se (ppm)
July	1989	0.25	48	0.37	18	73	56	4	215	3.7	0.08	41	47	2.2
August	1989	0.19	46	0.66	21	59	65	4	182	2.8	0.08	40	46	2.7
September	1989	0.32	52	0.32	15	83	109	5	178	4.0	0.09	51	50	3.0
October	1989	0.22	57	0.55	21	69	115	4	188	4.6	0.07	40	40	3.8
November	1989	0.20	56	0.41	17	73	112	4	158	4.1	0.07	37	41	3.3
December	1989	0.24	62	0.48	18	71	213	4	183	5.0	0.08	47	48	3.2
January	1990	0.25	55	0.74	20	60	78	4	191	3.6	0.08	41	44	3.5
Maximum		0.32	62	0.74	21	83	213	5	215	5.0	0.09	51	50	3.8
Average		0.24	54	0.50	19	70	106	4	185	4.0	0.08	43	45	3.1
Std. Dev.		17	10	29	11	11	46	8	9	17	8	10	8	.49

A composite sample of pyrite material was collected in November, 1990 and submitted to the U.S.B.M. Research Center in Reno, Nevada for semi-quantitative mineralogical analysis.

The sample consisted of:

64% Pyrite (28% Fe and 36% S)

13% Quartz

23% Feldspar

100%

LITERATURE REVIEW

Research results have shown that pyritic mine waste can be utilized as a source of iron, sulfur and acid in alkaline soils. Soils amended with pyrite show increased Fe availability as a direct result of the oxidation of the pyrite (Vlek and Lindsay, 1978). Pyrite forms have not been extensively used or commercialized as a soil amendment in the United States. No known attempt has been made to use pyrite from Montana gold mines to amend alkaline soils in Montana.

Many sulfur rich minerals have been used to improve agricultural soil conditions. All of the many acid-forming sulfur minerals tested appear to be suitable for reclamation of alkaline soils. Unfortunately, only limited data are available comparing the effectiveness of alternative sulfur materials under a wide range of soil conditions (Sulphur Institute, 1979).

Pyrite has been studied as an amendment for alkaline soils in Europe for many years. Odelien (1967) in Norway found that pyrite was initially slow to react with soil but showed a marked increase in response after the second year. This was probably due to the cool soil temperatures of Norway which inhibited microbiological activity. In Holland it was discovered that a cultivated soil which had been amended with pyrite in 1844 still contained 0.2% pyrite after 100 years (Harmsen et al., 1954).

Sulfur deficiencies in cropped soils have long been recognized in India. Results of a study with different sulfur forms in India indicated that pyrite produced an equivalent amount of available sulfur as gypsum (Tiwari, 1990). Tiwari also showed pyrite can prevent Fe chlorosis in plants and can improve the availability of phosphorus, manganese, and zinc. Pyrite not only contains these micronutrients as impurities, but enhances the availability of native micronutrients by reducing alkalinity. Tiwari found that "a pyrite application rate of 250 kg ha⁻¹ helped correct lime-induced chlorosis and improved the millable cane percentage and yield of sugarcane. Pyrite doses up to 400 kg ha⁻¹ increased the number and dry weight of N fixation nodules, and showed significant increase in chickpea grain and straw yield." The purity and particle size of the pyrite used in Tiwari's study is not known.

Two studies from Australia and New Zealand found that pyrite amendments were effective in correcting iron and sulfur deficiencies in corn (Banath and Holland, 1976). The effective applied rates ranged from 190 to 760 kg ha⁻¹ of 50 percent < 9 micrometer pyrite. It was found that approximately 10% of the pyrite was oxidized the first growing season (Banath and Holland, 1976). In a different study it was found that "priming" with small amounts of sulfuric acid increased the oxidation of pyrite (Metson et al., 1971). Metson also found that organic matter and calcium carbonate significantly increased the oxidation rate of pyrite. This appears to contradict what was previously stated by Caruccio.

Barrau and Berg (1977) at Colorado State University found that the extremely high rates of 90,000 and 270,000 kg ha⁻¹ were effective at reclaiming very alkaline soils.

A now defunct company in the Southwestern United States produced a product called "Iron Sul". The product was produced from a copper processing waste containing the iron salt jarosite. The jarosite was mixed with sulfuric acid, dried and sold as an effective iron fertilizer (Ryan and Stroehlein, 1976).

Following procedures similar to those developed by Iron Sul, a company in Arizona is currently reprocessing pyritic tailing from a closed copper concentrator. They are concentrating the ferric iron produced from the tailing and creating an iron fertilizer called "Ironite". Ironite contains approximately 4.5% soluble iron and 15% sulfur.

A review of available literature indicated that pyrite can be an effective agricultural soil amendment for alkaline soils, but scientific data are limited and the results vary. It also appeared that the United States is behind the rest of the world in evaluating pyrite as an alkaline soil amendment.

MATERIALS AND METHODS

Study Plan

A study was designed to characterize how soil pH, plant available iron, and sulfur change due to the addition of pyrite. The study was also intended to identify crop responses from the addition of pyrite to soil. Five soils varying in alkalinity and texture were identified for this study. The alkalinity varied from non-alkaline to calcic and sodic soils. Approximately 50 kgs of each soil were collected in plastic buckets and brought to the MSU greenhouse for drying and homogenizing. A sample of each soil was analyzed by the MSU Soil Testing Laboratory for pH, EC, percent CaCO_3 equivalent, plant nutrients, DTPA extractable iron, SO_4^{2-} , total sulfur, SAR, ESP, texture and 1/3 bar water content. These data are summarized in Table 3. The analytical methods for these and all other parameters discussed in this document are listed in Table 4.

Table 3. Initial data for all five soils.

Soil	Append. A desig.	pH (paste)	EC (mmhos/cm)	SAR	CaCO ₃ (%)	SO ₄ ²⁻ (mg/kg)	Fe (mg/kg)	Ca (mg/l)	O.M. (%)
1	RB	4.4	0.56	0.2	0.2	3.0	30.0	54	0.7
2	MC	8.2	0.70	0.1	3.9	7.2	3.9	109	1.4
3	KP	8.0	1.38	1.4	18.0	32.4	7.0	153	1.5
4	KC	8.5	0.90	6.5	3.0	16.3	9.4	43	1.3
5	SM	7.9	18.83	89.6	1.9	773.2	5.8	456	0.5
Soil	Na (mg/l)	NO ₃ ⁻ (mg/kg)	P (mg/kg)	K (mg/kg)	Mg (mg/l)	Sand (%)	Silt (%)	Clay (%)	Text.
1	6	15.8	12.8	100	11	83	8	9	ls
2	6	3.7	6.1	422	11	48	35	17	l
3	75	21.0	34.1	170	75	47	23	30	scl
4	162	8.0	14.6	670	3	23	27	50	c
5	7400	32.4	30.9	2106	36	50	27	23	scl
Soil	Classification							Soil Series	
1	Ustic Torripsamment, frigid, mixed							Yetall	
2	Borollic Calciorthid, coarse-loamy, mixed							Amesha	
3	Borollic Calciorthid, coarse-loamy, mixed							Amesha	
4	Borollic Calciorthid, fine-loamy, mixed							Delphill	
5	Typic Haploboroll, coarse-loamy, mixed							Chinook	

These data show that soil 1 is non-buffered, soils 2 and 4 are well buffered, soil 3 is highly buffered, and soil 5 is saline-sodic.

Table 4. Soil analytical methods.

Parameter	Analytical Method
pH Electrical Conductivity (EC)	Rhoades, 1982, p. 167-179 Saturated water paste extract
Sodium Adsorption Ratio (SAR) Ca, Mg, Na, K	Rhoades, 1982, p. 167-219 Soluble Cations
CaCO ₃	Allison and Moodie, 1965, p. 1388 Gravimetric Method for loss of carbon dioxide
Sulfate (SO ₄ ²⁻)	Bardsley and Lancaster, 1965, p. 1111 Acetate Soluble Sulfate
Iron	Olson and Roscoe, 1982, p. 309 DTPA extractable iron
Nitrate (NO ₃ ⁻)	Keeney and Nelson, 1982, p. 676 Nitrate by colorimetric methods
Organic Matter	Sims and Haby, 1970 Colorimetric determination of soil organic matter
Phosphorus	Olsen and Sommers, 1982, p. 416-418
Particle Size Distribution	Day, 1965 Hydrometer method
Hot Water Extractable SO ₄ HCL Extractable SO ₄ HNO ₃ Extractable S Total S	Sobek et al., 1978 Acid-base accounting

Approximately 10 kgs of Golden Sunlight Mine's pyrite material were collected, dried and purged with nitrogen gas to prevent oxidation until ready for use. The pyrite material was analyzed for pH, EC, available iron, sulfate and texture. It should be noted that these parameters characterize the pyrite prior to oxidation.

These data are summarized in Table 5.

Table 5 Initial pyrite analysis.

pH (paste)	EC (mmhos/cm)	DTPA Fe (mg/kg)	SO ₄ ²⁻ (mg/kg)	Texture
2.9	3.74	656	2907	93% < 27 micrón (silt)

A laboratory petri dish study was designed to evaluate pyrite application rates to the chosen soils. Six rates were selected which were thought to cover all reasonable agricultural applications. To simulate field moisture conditions, the dishes were wetted to approximate field capacity moisture content, then checked weekly and re-wetted when the dish moisture content was approximately at wilting point. The study was designed to periodically evaluate changes in soil chemistry over a one-year period. The length of time between evaluations would depend on changes in chemistry. This study is outlined in the section "Bench Top Study."

The laboratory study was designed to allow identification of chemical changes in the soils from the addition of the pyrite material over time. It was realized that field conditions could not be fully modeled in the laboratory, so it should be noted that certain natural variables such as leaching, ultra violet light and temperature were not part of the petri dish study.

A replicated field study using soil number 2 from Steve McDonnell's farm near Three Forks, Montana was also implemented. This study is outlined in the section "Field Test Plots."

Bench Top Study

A petri dish study was designed to evaluate the five soils amended with the six pyrite rates shown in Table 4 below. The study was replicated four times in a randomized complete block design for statistical comparison.

For all of the five soils, 50 grams were placed in each of six plastic petri dishes. Each dish was amended with one of the pyrite material rates shown in Table 4. This created six treatments per soil. The treatments were replicated four times for a total of 24 dishes per soil. An additional petri dish replicated four times containing only 50 grams of Golden Sunlight pyrite material were added to the treatment list for a total of 124 petri dish treatments. The entire study was then duplicated 10 times to allow for 10 sequential destructive analyses for identification of treatment responses. This created a total of 1240 petri dish treatments.

Table 6. Petri dish pyrite material amendment rates.

Rate	Grams pyrite material/dish	% pyrite material by weight	Kg pyrite material/ hectare
1	0.00	0.0	0
2	0.25	0.5	10,000
3	0.50	1.0	20,000
4	2.50	5.0	100,000
5	5.00	10.0	200,000
6	10.00	20.0	400,000

After amending all petri dishes, they were stirred with a spatula, wetted to field capacity with distilled water and stirred again. The amount of water used for each soil is shown in Table 5. After wetting, all the dishes were loosely covered with a petri dish lid and an initial weight was recorded. All the dishes were set up by August 1, 1991. Each week the dishes were reweighed and if a dish had lost at least one half the initial water content (approximately wilting point for these soils), it was wetted with distilled water until the initial weight was re-established.

Table 7. Petri dish initial water content.

Soil	Rate	Water (mls)
1	1	5
1	2	5
1	3	5
1	4	5
1	5	6
1	6	6
2	1	9
2	2	9
2	3	9
2	4	9
2	5	10
2	6	11
3	1	9
3	2	9
3	3	9
3	4	9
3	5	10
3	6	11
4	1	13
4	2	13
4	3	13
4	4	13
4	5	14
4	6	15
5	1	9
5	2	9
5	3	9
5	4	9
5	5	10
5	6	11

Initially, every two weeks, and then again at progressively longer time intervals for one year, a complete set of petri dishes from all five soils and pyrite material were taken from the set for analysis. Table 6 shows the frequency of analysis and the parameters analyzed. The parameters pH and EC were measured by weighing out ten grams of material from each dish into a beaker, adding 20 milliliters of distilled water, stirring for one minute and measuring pH and EC with bench top electrodes. If the samples were to be analyzed for iron and sulfur, then the remaining 40 grams of soil and pyrite material were pulverized and submitted to the MSU Soil Testing Laboratory for DTPA extractable iron and sulfate sulfur analyses.

Table 8. Petri dish schedule of analysis.

Run	Day	pH	EC	Fe	SO ₄ ²⁻
1	13	X		X	X
2	28	X		X	X
3	64	X			
4	91	X	X		
5	118	X			
6	152	X			
7	184	X			
8	225	X	X		
9	293	X			
10	378	X	X	X	X

Data are summarized in the results section.

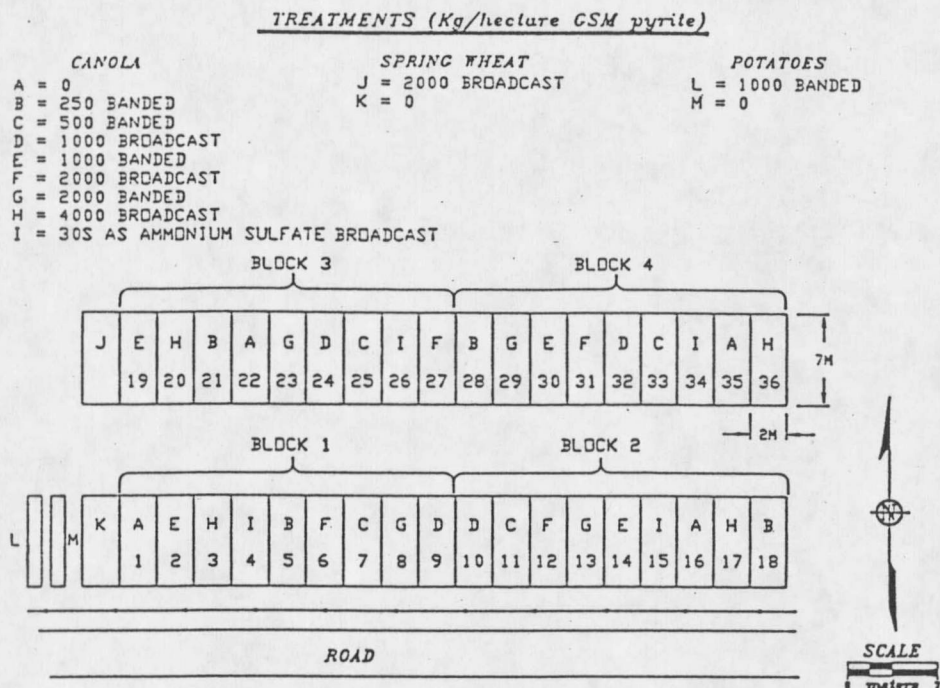
Field Test Plots

To determine crop responses to pyrite additions, a crop with high sulfur and other nutrient requirements was desired. Canola fits this description and was the crop chosen for this study. The study was implemented on soil number 2 because of its alkalinity and agricultural history.

A fallow field was chosen for the study site. A composite soil sample was collected from the site and analyzed for nutrient availability. Data are summarized above in Table 2. Based on these data, the entire study site was fertilized with 120 kg N/hectare, 50 kg P/hectare, and 20 kg K/hectare.

Test plots were established on the site to evaluate various rates of pyrite added to the soil. Using a hand broadcaster and a double disk drill, both broadcast and banded pyrite applications were evaluated in the study. To account for field variability the plots were randomized and replicated in four separate complete blocks. The study layout is shown in Figure 1.

Figure 1. Test plot study design.



The test plots were established and seeded May 1, 1991. All broadcast treatments were rototilled for mixing to a 10 cm depth. A sprinkler irrigation system supplied by a 3000 gallon water truck was constructed to irrigate the plots. Leaf tissue samples were collected from each plot prior to flowering to identify any increases in tissue iron or sulfur from the pyrite. The plots were harvested at the appropriate time and the canola seed was compared by plot for yield and quality responses to the various pyrite rates. During harvest, soil samples were collected from each plot to determine soil responses to the pyrite. Test plots amended with pyrite banded below the crop, were sampled by collecting composite samples from within the band area, and 5 cm from the band. The results are summarized in the section "Field Test Plots."

Demonstration Plots

As a supplement to the study to further identify visible vegetation responses to pyrite over a variety of soils, non-replicated test plots were established in several locations. To enhance the pyrite reactivity, the pyrite material was prilled using lignin sulfonate and "primed" with an addition of 2% sulfuric acid by weight.

One quarter acre test plots were established on soil numbers 3 and 4. Broadcast application rates were 2000 kg/hectare of pyrite material. After application, soil number 3 was seeded to potatoes and soil number 4 to grass as part of the government conservation reserve program. Several test plots with various application rates and sizes were also constructed at the Three Forks golf course. The soils were determined to be alkaline and slightly saline. The largest plot involved broadcasting 2000 kg/hectare of pyrite material over a one half hectare fairway. This plot was compared to a smaller adjacent plot where a recommended rate of the commercially produced "Ironite" product was applied. Additional visual trials include pyrite material applications on several lawns and agricultural fields in the Three Forks and Whitehall, Montana areas.

RESULTS

Bench Top Study

The specific objectives of the bench top study were to determine soil responses to the various pyrite material rates and identify differences in responses between the five soil types. To achieve the stated objectives, the study was constructed with a randomized complete block design, with four blocks for statistical comparison. To determine if these data met the objectives, analysis of variance was used to identify significant differences between treatments and soils. These data were also interpreted graphically to predict successful treatment rates. To smooth these data for purposes of graphing, the replications were averaged prior to plotting.

These data were collected as outlined in Table 6. The entire data set can be found in Appendix B. The soils were analyzed for pH, EC, available iron, and sulfate. These soil parameters were chosen because they are directly linked to the oxidation of pyrite. These parameters are dependent on each other and time. For the purposes of this discussion each parameter will be evaluated separately in the following sections.

Most of the parameters were analyzed for variance using all replications from each treatment for each soil across time. This created a two-way analysis of variance. The replications are random, and replication, soil, and time are completely

independent from each other. These data are assumed to have a normal distribution, since only four data points exist for any given soil treatment.

pH was chosen as the main parameter to track soil responses to the various treatments. All pH values were used for the analysis of variance and regression tests to determine soil responses to the six pyrite rates over time.

Comparisons were made between the five soils for each pyrite rate. The analysis of variance is summarized in Table 9 below. The capital letters following each mean in each column signify significant similarities or differences between means based on the least significant difference (LSD) value.

Table 9. pH mean separation test between soils for each pyrite rate over time.

Soil No.	Rate No. 1	Rate No. 2	Rate No. 3	Rate No. 4	Rate No. 5	Rate No. 6	Overall mean
1	5.59 A*	4.59 A	4.33 A	3.32 A	3.18 A	3.14 A	4.02 A
2	7.88 B	7.84 C	7.71 B	7.58 B	7.45 CB	7.26 D	7.62 C
3	7.84 B	7.87 C	7.85 C	7.69 C	7.66 D	7.57 E	7.75 D
4	7.88 B	7.44 B	7.76 B	7.60 B	7.34 B	6.91 C	7.54 B
5	9.05 C	8.83 D	8.69 D	8.05 D	7.50 C	5.88 B	8.00 E
LSD(.05)	0.0474	0.0749	0.0609	0.0407	0.1126	0.1190	0.0366

* Means followed by the same letter in columns are not significantly different (P=0.05)

Table 9 shows significant differences between soil pH means for each rate. Rate number 1 (control) shows similarities between soils 2, 3, and 4 over time in the absence of treatment. These three soils have similar pH means because soils 2 and 4 are well buffered and soil 3 is highly buffered. The overall means show that all soils are also significantly different over time with all rates for each soil averaged.

Table 10 summarizes how time affected pH for each rate over all soils. The overall means identify significant differences between all rates and the lower case LSD values show the significant responses directly correlating with the treatment rate increments.

Table 10. pH mean separation test between times for each rate over all soils.

Time	Rate No. 1	Rate No. 2	Rate No. 3	Rate No. 4	Rate No. 5	Rate No. 6
1	7.63 C*	7.57 F	7.59 G	7.23 E	7.04 F	6.90 G
2	7.70 DE	7.43 ED	7.38 F	7.10 D	6.89 F	6.73 F
3	7.51 AB	7.27 ABC	7.16 B	6.78 B	6.71 E	6.41 E
4	7.45 A	7.18 A	7.02 A	6.68 A	6.66 DE	6.24 D
5	7.66 CD	7.33 BCD	7.25 CD	6.85 C	6.71 E	6.56 EF
6	7.53 B	7.25 AB	7.20 CB	6.86 C	6.64 DEC	6.17 D
7	7.80 F	7.43 ED	7.26 CD	6.63 A	6.34 AB	5.91 C
8	7.66 CD	7.42 ED	7.37 FE	6.78 B	6.52 DC	5.94 C
9	7.76 FE	7.52 EF	7.19 CB	6.90 C	6.49 BC	5.67 B
10	7.76 FE	7.36 CD	7.23 ED	6.66 A	6.26 A	4.99 A
LSD(.05)	0.0671	0.1060	0.0861	0.0576	0.1592	0.1683
Overall mean	7.65 f**	7.38 e	7.27 d	6.85 c	6.63 b	6.15 a

* Means followed by the same letter in columns are not significantly different (P=0.05)

** Means are compared within the row.

pH

Due to the significant interaction between rate and time, a model was developed to correlate the variables. The multiple regression equation modeling each treatment response for each soil was determined by using analysis of variance to

check the various linear and quadratic factors. All factors were determined significant. as shown in Table 11. The model describing all soils is shown below:

$$\text{pH} = \beta_0 - \beta_1 \text{rate} - \beta_2 \text{day} + \beta_3 \text{rate}^2 + \beta_4 \text{day}^2 - \beta_5 \text{rate} \times \text{day}.$$

The multiple regression coefficients for each soil are listed in Table 9.

Table 11. Multiple regression coefficients calculated from pH data for each soil.

Soil No.	β_0 (Intercept)	β_1 (Rate)	β_2 (Day)	β_3 (Rate ²)	β_4 (Day ²)	β_5 (Rate x Day)	R ²
1	5.590	-0.6390	-0.6197E-02	0.4872E-01	0.9604E-05	-0.1742E-03	0.712
2	7.818	-0.9131E-01	-0.5172E-03	0.5188E-02	0.2800E-05	-0.1150E-03	0.612
3	7.881	-0.5516E-01	-0.7202E-03	0.3118E-02	0.2536E-05	-0.3511E-04	0.409
4	7.475	0.2630E-01	0.4743E-03	0.9263E-03	-0.1062E-04	-0.8203E-03	0.656
5	8.765	-0.1164	-0.1487E-02	0.3965E-03	0.1064E-04	-0.1227E-02	0.946

The model was used to create three-dimensional graphs showing the pH data from all six pyrite material rates for each soil for a 378-day period. Figures 2 through 6 show the graphs for all five soils. It should be noted that these figures are not proportionally scaled on the z axis. Figure 7 shows the actual pH values for the pyrite material.

Figure 2. Effect of rate of pyrite application on pH during a 378-day period (soil 1).

SOIL NO. 1

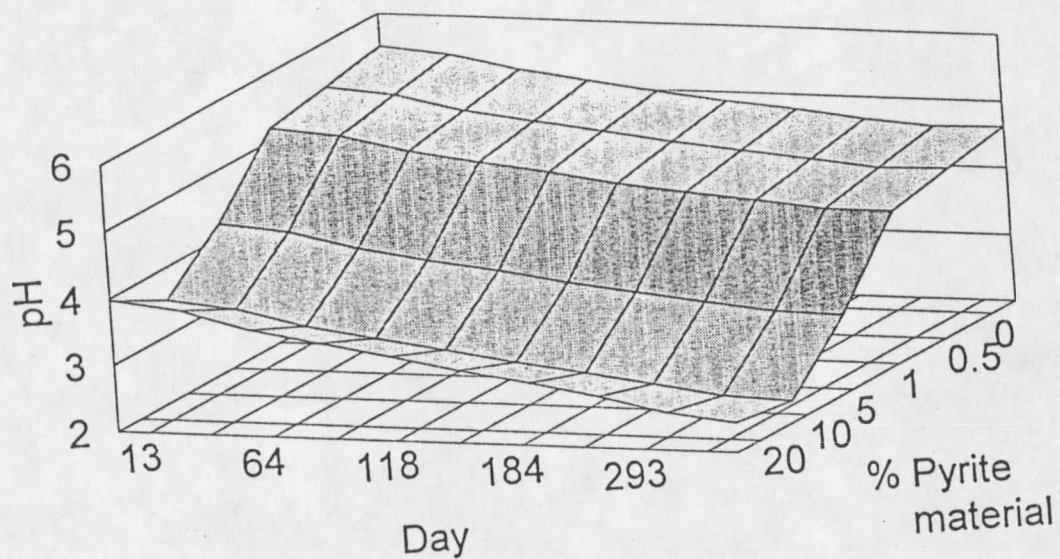


Figure 3. Effect of rate of pyrite application on pH during a 378-day period (soil 2).

SOIL NO. 2

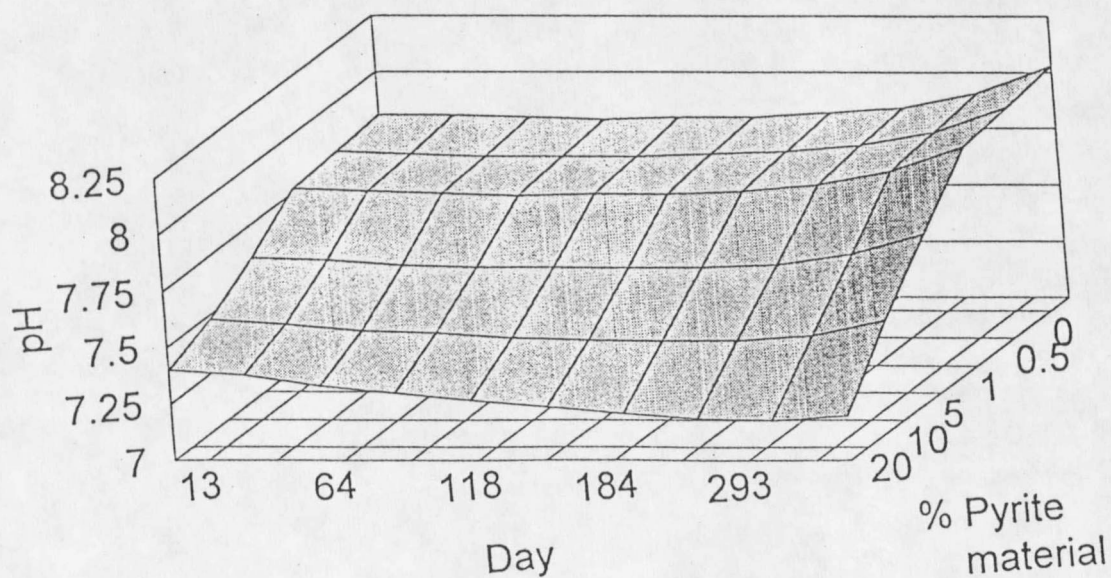


Figure 4. Effect of rate of pyrite application on pH during a 378-day period (soil 3).

SOIL NO. 3

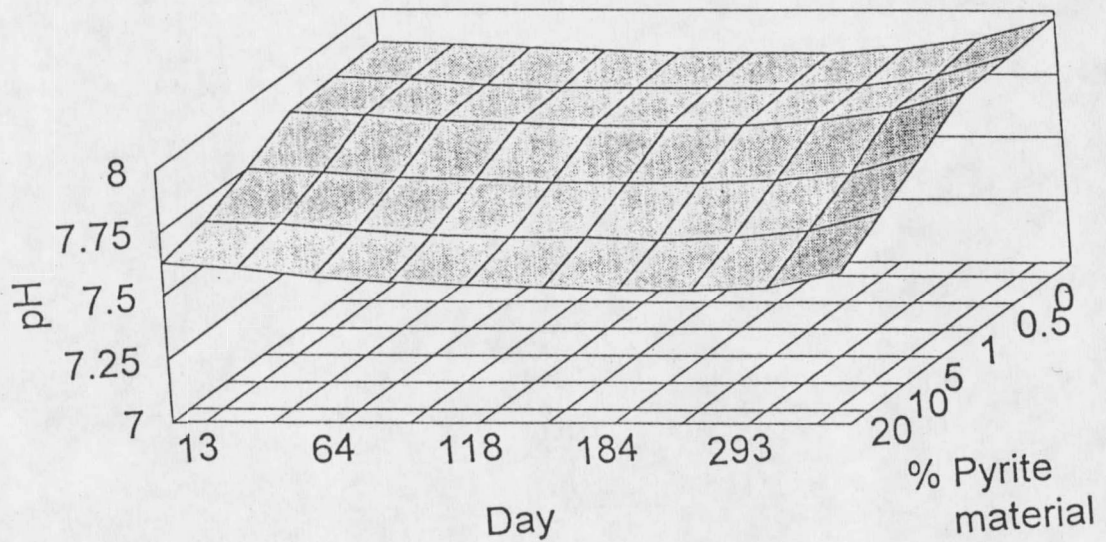


Figure 5. Effect of rate of pyrite application on pH during a 378-day period (soil 4).

SOIL NO. 4

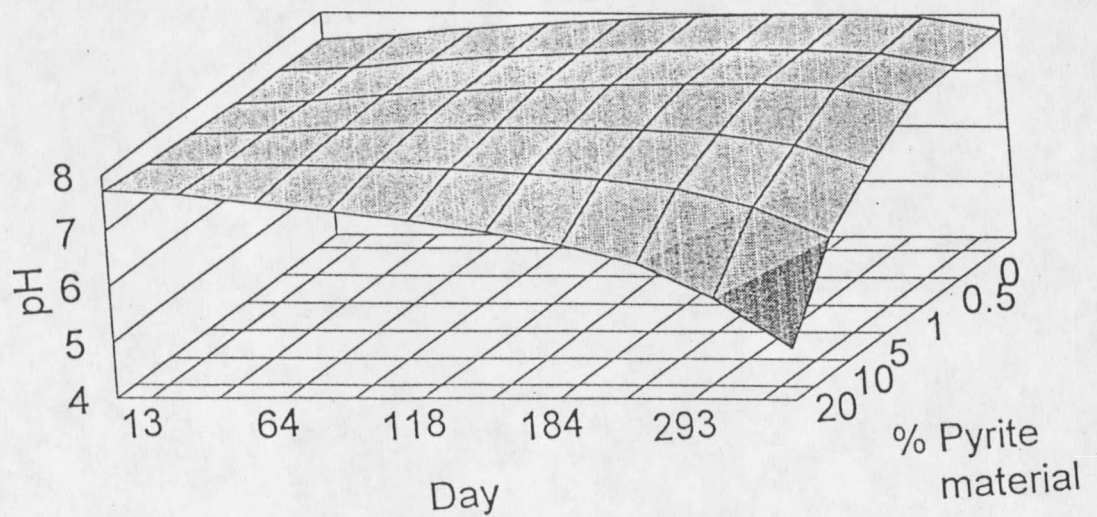


Figure 6. Effect of rate of pyrite application on pH during a 378-day period (soil 5).

SOIL NO. 5

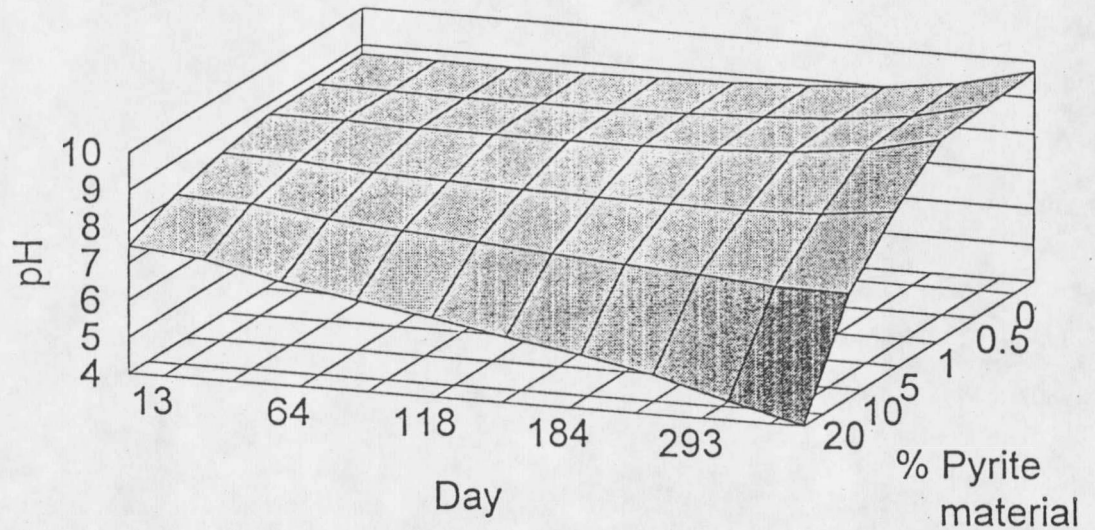
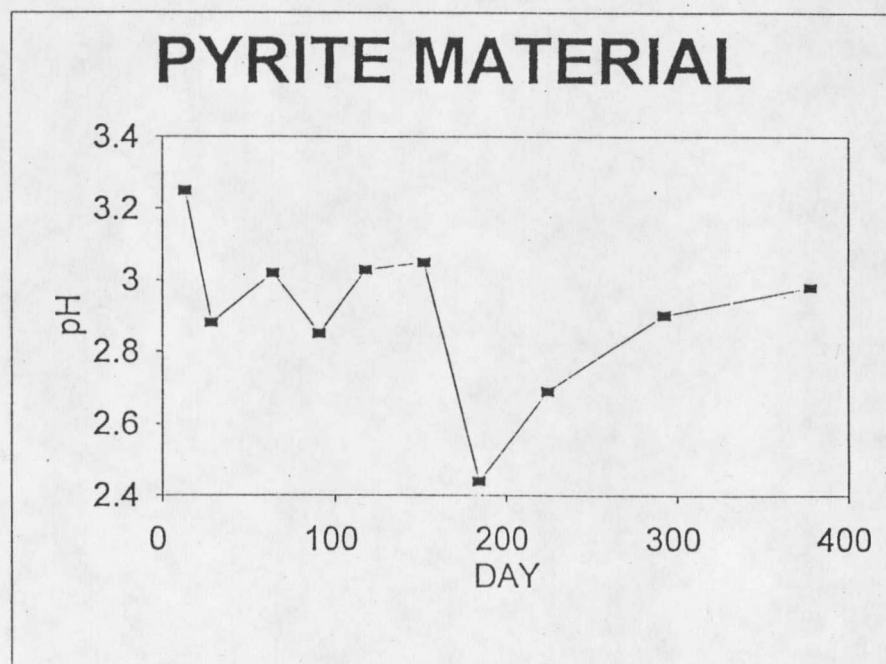


Figure 7. Changes in pyrite material pH during a 378-day period.



The pyrite material had an acidic pH prior to initiating the research. Linear regression indicated very little additional reduction in pH with time. The computed analysis indicated an R^2 value of 0.09 with 8 degrees of freedom, an x coefficient of -0.00056, and a standard error coefficient of 0.000634. The regression seemed to indicate that the data scatter was greater than any significant changes in pH.

These data were tested for significant pH responses from each pyrite rate over time. The analyses are summarized in Tables 12 and 13. Table 12 is very similar to Table 9 except Table 12 shows significant difference comparisons between rates.

Table 12. pH mean separation test between rates for each soil over time.

Rate	Soil No. 1	Soil No. 2	Soil No. 3	Soil No. 4	Soil No. 5	Overall mean
1	5.59 E*	7.88 E	7.84 C	7.88 E	9.05 F	7.65 F
2	4.59 D	7.84 E	7.87 C	7.74 D	8.83 E	7.38 E
3	4.33 C	7.71 D	7.85 C	7.76 D	8.69 D	7.27 D
4	3.32 B	7.58 C	7.69 B	7.60 C	8.05 C	6.85 C
5	3.18 A	7.45 B	7.66 B	7.34 B	7.50 B	6.63 B
6	3.14 A	7.26 A	7.57 A	6.91 A	5.88 A	6.15 A
LSD(.05)	0.0902	0.0434	0.0405	0.1135	0.0965	0.0366
Overall mean**	4.02 a***	7.62 c	7.75 d	7.54 b	8.00 e	6.99

* Means followed by the same letter in columns are not significantly different (P=0.05)

** LSD (0.05) = 0.0335.

*** Means are compared within the row.

Table 13. pH mean separation test between times for each soil over all rates.

Time	Soil No. 1	Soil No. 2	Soil No. 3	Soil No. 4	Soil No. 5	Overall mean
1	4.94 F*	7.73 E	7.86 D	7.81 FG	8.29 E	7.33 H
2	4.56 E	7.74 E	7.78 CB	7.65 DE	8.30 E	7.20 G
3	4.05 C	7.39 A	7.64 A	7.56 CBD	8.23 E	6.97 E
4	3.76 B	7.52 B	7.68 A	7.47 CB	7.94 CBD	6.87 B
5	4.38 D	7.56 CB	7.65 A	7.71 FE	7.99 D	7.06 F
6	3.78 B	7.65 D	7.77 CB	7.57 CDE	7.93 CBD	6.94 CDE
7	3.74 B	7.62 CD	7.75 B	7.53 CBD	7.83 B	6.89 CB
8	3.76 B	7.71 E	7.76 CB	7.87 G	7.65 A	6.95 DE
9	3.94 C	7.61 CD	7.78 CB	7.42 B	7.85 CB	6.92 CBD
10	3.33 A	7.71 E	7.80 C	6.79 A	7.97 CD	6.72 A
LSD(.05)	0.1165	0.0560	0.0523	0.1465	0.1246	0.0473
Overall mean**	4.02 a***	7.62 c	7.75 d	7.54 b	8.00 e	6.99

* Means followed by the same letter in columns are not significantly different (P=0.05).

** LSD (0.05) = 0.0335.

*** Means are compared within the row.

These data show a significant response to time for each soil over all rates.

These data also show each rate to have a significant effect across all five soils.

Tables 10 and 11 prove the responses to be a direct result of rate and time.

Effective Rates For Soil pH Amendment

Assuming an optimum agricultural final soil pH between 7.0 and 7.5, the best pyrite material rate for each soil was identified from the regression model for a one-year period. The selected rates have model derived final pH's within the optimum

range, with significantly different treatment means from all other rates. Table 14 shows the optimum experimental treatment for each soil. It should be noted that for all soils the treatment effect model has a negative slope, indicating a continued change in pH with time. For this reason, Table 14 also shows adjusted optimum pyrite material application rates to ensure that the buffering capacity of the soil is not exceeded. The rates were adjusted using an equation developed in 1978 to predict the percent of CaCO_3 required to buffer the amount of acid potentially produced from pyrite (Sobek et al., 1978). Sobek found:

$$\% \text{CaCO}_3 = \% \text{sulfur} \times 3.125$$

Table 14. Optimum and adjusted rates to correct soil pH to a 15 cm depth after one year.

Soil No.	Untreated Soil pH	CaCO_3 %	Optimum Rate No.	Optimum Rate* (kg/hectare)	Adjusted Rate** (kg/hectare)
1	5.59	0.2	1	0	0
2	7.88	3.9	5	200,000	69,340
3	7.84	18.0	6	400,000	320,000
4	7.88	3.0	4	100,000	53,340
5	9.05	1.9	4	100,000	33,780

* May acidify soil after one year.

** Adjusted not to exceed soil's buffering capacity.

EC

Electrical conductivity was measured in a 2:1 water to soil solution for all treatments at three different time intervals as shown in Table 6. These data are presented in Figures 8 through 13.

Figure 8. Effect of rate of pyrite material application on electrical conductivity during a 378-day period (soil 1).

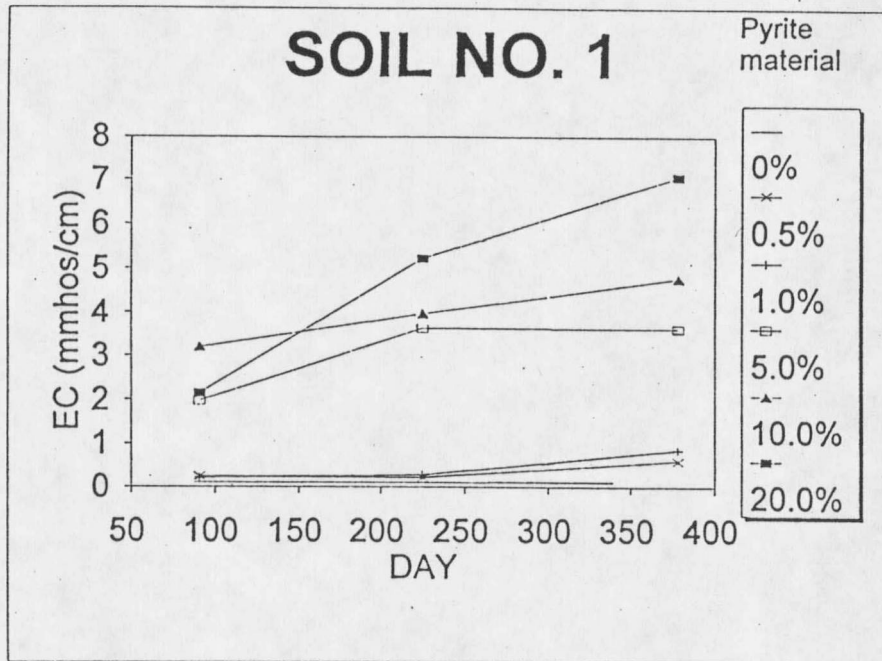


Figure 9. Effect of rate of pyrite material application on electrical conductivity during a 378-day period (soil 2).

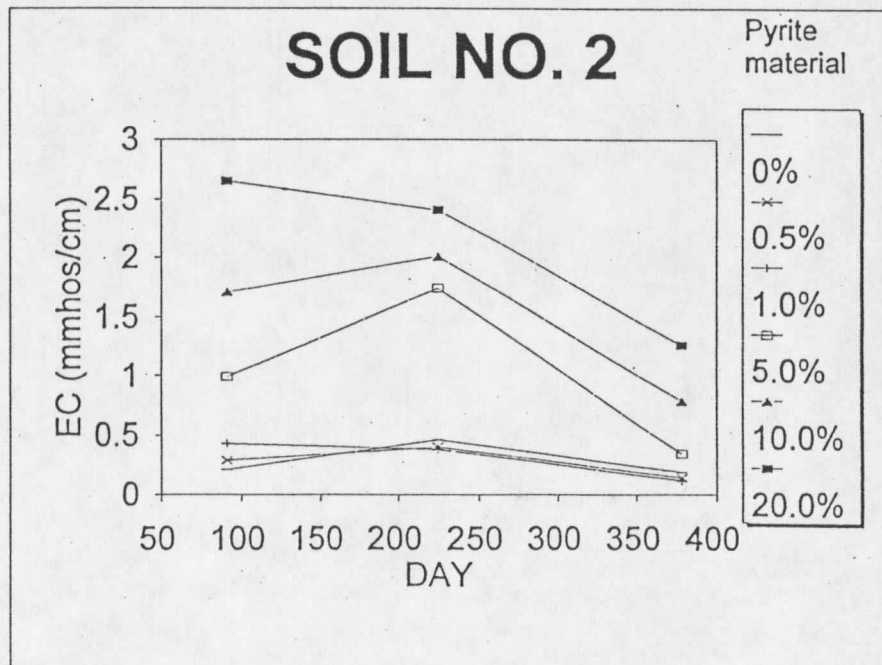


Figure 10. Effect of rate of pyrite material application on electrical conductivity during a 378-day period (soil 3).

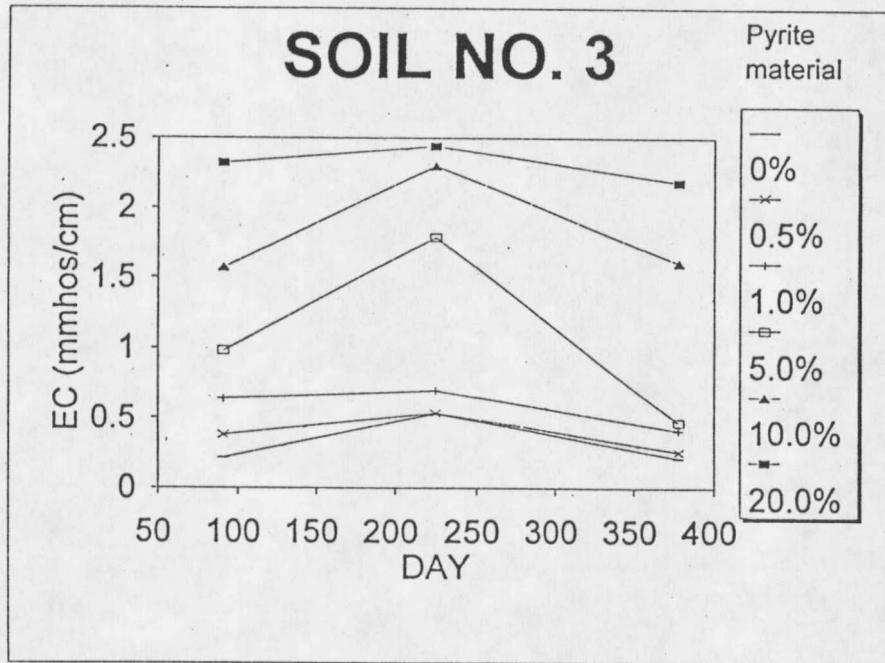


Figure 11. Effect of rate of pyrite material application on electrical conductivity during a 378-day period (soil 4).

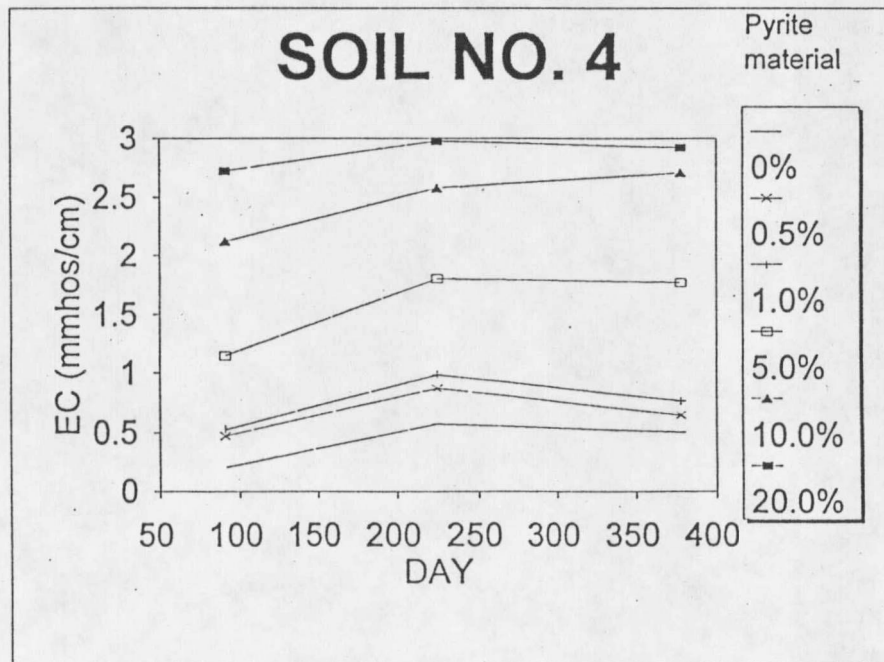


Figure 12. Effect of rate of pyrite material application on electrical conductivity during a 378-day period (soil 5).

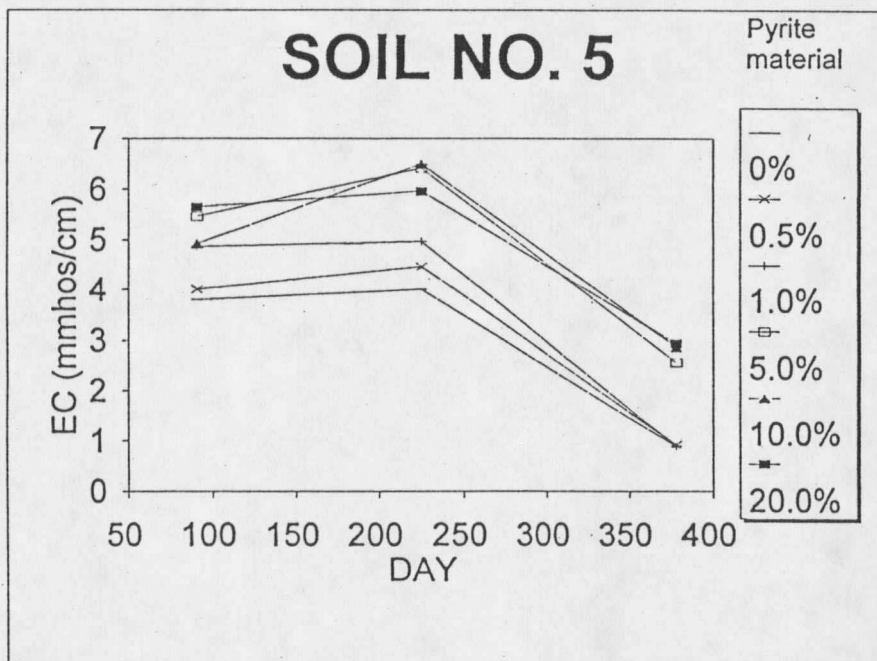
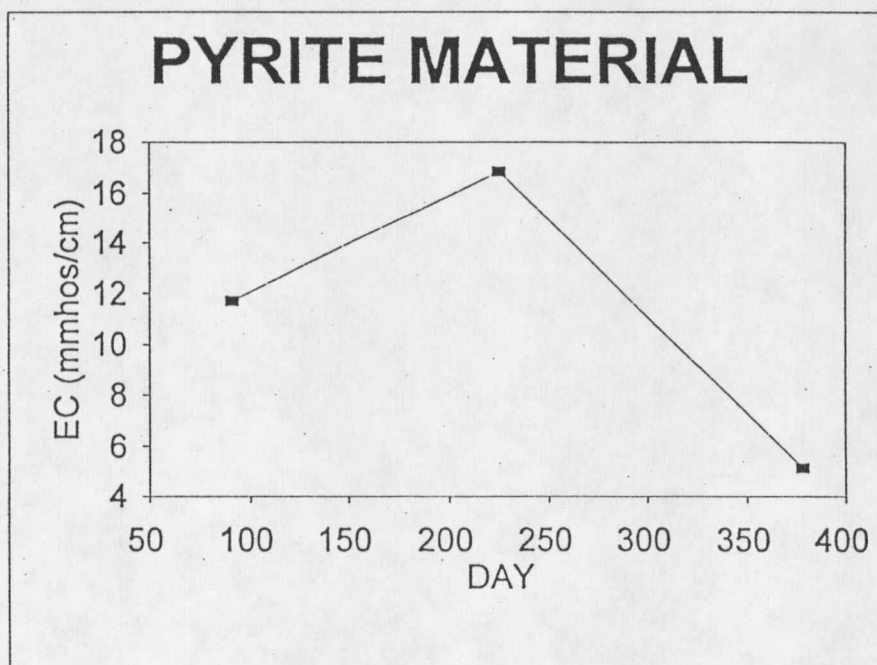


Figure 13. Changes in pyrite material electrical conductivity during a 378-day period.



These data show a significant decrease in electrical conductivity between the second and last data points in almost all cases. It is possible that the soils are attenuating the salts created from the oxidation of the pyrite material. More probably, because the tests were evaluated in an enclosed system with continuous salt production, the last measurement is an analytical error. For this reason, and the fact that only three measurements per treatment were taken, no statistical comparisons were made. These data show significant increases in soil electrical conductivity for rates five and six when compared to background levels.

Fe

Available iron responses to the six pyrite material rates were measured at three times as shown in Table 6. The iron is reported as milligrams of iron per kilogram of soil. Figures 14 through 18 show the treatment responses for each soil. Figure 19 shows the increase in available iron with time for the pyrite material.

Figure 14. Effect of rate of pyrite material application on plant available iron during a 378-day period (soil 1).

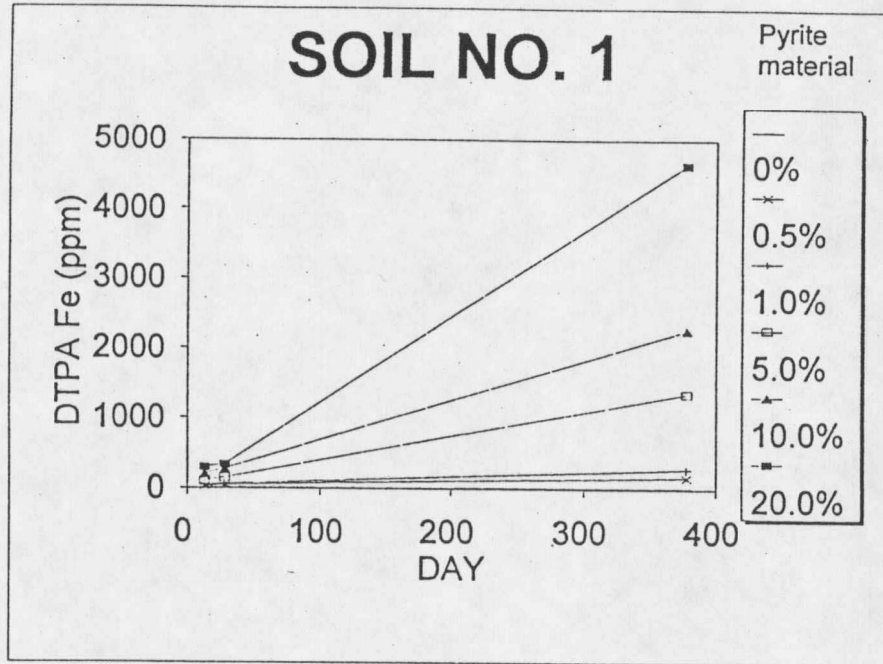


Figure 15. Effect of rate of pyrite material application on plant available iron during a 378-day period (soil 2).

