Effect of Surface-applied Sulfuric Acid on Growth and Nutrient Availability of Five Range Grasses in Calcareous Soils

J. RYAN, J. L. STROEHLEIN, AND S. MIYAMOTO

Highlight: *In a greenhouse pot study, the application of concentrated sulfuric acid to two calcareous soil surfaces significantly increased growth of five range grasses: Lehmann lovegrass (*Eragrostis lehmanniana *Nees.), Wilman lovegrass (*E. superba *Peyr.), atherstone lovegrass (*E. atherstonei *Stapf.), weeping lovegrass (*E. curvula *(Schrad.) Nees.), and blue panicgrass (*Panicum antidolale *Retz.). These species varied in their response to soil applied phosphorus (P), iron (Fe), and sulfuric acid. The effectiveness of* H_2SO_4 *was attributed principally to increased solubility of these elements. Sulfuric acid, being produced in large quantities in the Southwest, may prove to be a suitable alternative to existing Fe and P fertilizers.*

Maintenance and improvement of Southwestern rangelands depends mainly on grazing management without significant use of fertilizers. However, several studies have shown that fertilization, particularly with nitrogen (N), can increase pasture output and quality (Holt and Wilson, 1961). Responses to applied phosphorus (P) are less well documented and generally occur in the presence of adequate N (Burkholder, 1967), and where P is deficient in the soil (Martin et al., 1957). Research on micronutrient fertilization of rangelands is limited, with no evidence of any response to applied iron (Fe) despite the fact that Kuykendall (1956) estimated that soils in the Western states were generally low in available Fe. Bales (1965) observed growth responses of mixed chaparral vegetation to a micronutrient mixture, but did not specifically attribute responses to Fe.

Recent work has shown that sulfuric acid (H_2SO_4) can increase Fe availability (Ryan et al., 1973) and P availability (Ryan and Stroehlein, 1973) in deficient soils. Other benefits include improved water penetration into sodic soils (Yahia et al., 1975) resulting in better stand establishment. In view of the projected surplus of H_2SO_4 from copper smelting in the Southwest and the high cost of rangeland fertilization, the possible use of acid as an amendment for range soils or its disposal under controlled conditions on these extensive areas is worthy of consideration. This paper examines the effect of H_2SO_4 on growth and P and Fe nutrition of five grass species grown in the Southwest.

Experimental Procedure

Two calcareous soils were used in the study. The Cave soil is representative of extensive areas of noncultivated soils in Southern Arizona and is used for desert range, wildlife, and urban development. It is highly calcareous, overlying an indurated lime hardpan (caliche), and was shown to be low in available Fe (Ryan et al., 1973). The Comoro soil, formed on recent alluvium and widely used for irrigated agriculture and rangeland, is low in available P (Ryan and Stroehlein, 1973). The respective pH values (water:soil, 5:1) were 8.3 and 8.1, while $CaCO_3$ contents were approximately 20 and 8%, respectively.

The soils, taken from surface horizons, were sieved through a 2-mm screen and 1.5-kg lots potted. The soil treatments were 50 ppm Fe on a weight basis as $FeSO_4 . 7H_2O$; 300 ppm P as $Ca(H_2PO_4)_2$ mixed uniformly with the soil; and 1, 5, and 10 ml concentrated H_2SO_4 applied to the soil surface, equivalent to 1.1, 5.5, and 11.0 tons per hectare on an area basis. A series of untreated pots served as controls. The H_2SO_4 treated pots were leached with two pore volumes of water to remove excess soluble salts produced by acidification. After drying, the pots were seeded with five species of range grass: Lehmann lovegrass (*Eragrostis lehmanniana* Nees.), Wilman lovegrass (*E. superba* Peyr.), atherstone lovegrass (*E. atherstonei* Stapf.), weeping lovegrass (*E. curvula* (Schrad.) Nees.), and blue panicgrass (*Panicum antidolale* Retz.). All treatments were replicated three times in a randomized block design. Plants were grown from December 12, 1973, to July 23, 1974, with three harvests taken on April 29, June 9, and July 23, respectively. At the beginning of each growth period 200 ppm N as NH_4NO_3 were added solution. The pots were watered to field capacity as necessary with no precise measurements made of the amount of water used.

After drying at 65°C for 24 hours the plant weights were recorded. The material was digested with nitric-perchloric acid and analyzed for P and Fe by standard methods. Fresh samples of the material were also extracted with methanol to determine chlorophyll content according to Johnson (1974). After the final harvest the potted soil was analyzed for DTPA-extractable Fe and available P by CO_2-saturated extraction.

Results

Growth responses occurred with both Fe and P application on each soil. Increases were greatest for Fe on the Cave soil and for P on the Comoro soil; consequently only these data are presented. Dry matter yields from the Fe treated (50 ppm) and untreated Cave soil for three harvests are presented in Table 1. In the first harvest, all species responded to Fe, the order being weeping lovegrass, Wilman lovegrass, Lehmann lovegrass, blue panicgrass, and atherstone. In general, the relative responses increased with time, reflecting decreased growth on the untreated soil and sustained growth on the Fe treated pots. All species responded to the P treatment (300 ppm) in the first harvest, but the magnitude of the response

Authors are research associate, associate professor, and research associate, Department of Soils, Water and Engineering, University of Arizona, Tucson, 85721.

The study is a contribution of the Arizona Agricultural Experiment Station as Journal number 2379, supported in part by the Arizona Mining Association.

Manuscript received September 18, 1974.

Table 1. Yield (g/pot) response of range grasses to applied Fe (50 ppm) for three harvests from the Cave soil (average of three replications).

Grass species	Harvest 1 Control	Harvest 1 Fe	Harvest 1 Percent increase	Harvest 2 Control	Harvest 2 Fe	Harvest 2 Percent increase	Harvest 3 Control	Harvest 3 Fe	Harvest 3 Percent increase
Lehmann lovegrass	1.4	2.5**	78	1.8	6.6**	300	1.8	4.2**	133
Wilman lovegrass	2.5	5.1**	104	1.8	4.7**	161	1.3	6.5**	400
Blue panicgrass	3.2	4.2*	31	0.7	2.7**	286	0.5	4.8**	860
Atherstone	2.1	2.3	9	1.7	3.7**	118	0.6	3.9**	550
Weeping lovegrass	0.2	2.3**	1050	0.1	3.8**	3700	0.0	4.4**	–

* $P \leqslant 0.05$.
**$P \leqslant 0.01$.

decreased in subsequent harvests (Table 2).

The effect of surface applied H_2SO_4 on dry matter yield is presented in Table 3 for the Cave soil. Without exception, yields were increased with increasing levels of acid. This response persisted throughout the three harvests with the magnitude varying with the species. The most noteworthy exception to the general pattern occurred with weeping lovegrass, which produced significant growth only at the highest acid level. Data from the Comoro soil exhibited a pattern (Table 4) similar to that obtained from the Cave soil.

In the absence of a reliable measure of physiologically active Fe in plant tissue by total Fe analysis, the chlorophyll concentration was chosen to quantify greenness in the plant, thereby reflecting active Fe (Johnson, 1974). Visual differences in color appeared in the second growth period and were accentuated in the third. Color variation was apparent in all species except Lehmann lovegrass on the Cave soil, and only in blue panicgrass on the Comoro soil. Consequently, only these data are presented in Table 5. Highest values were obtained from the Fe soil treatment, while the untreated and the P treated pots were generally pale green to chlorotic. The application of H_2SO_4 consistently increased chlorophyll concentrations of all species listed, but generally not to the extent of the Fe treatment.

Analyses of the soil after the final harvest for CO_2-extractable P and DTPA-extractable Fe revealed the P and Fe treatments significantly increased these values in the soil (Table 6). The lowest level of H_2SO_4 had no effect on soil values, while extractable P in the surface 3 cm of the Cave soil was increased by the 5 ml H_2SO_4 treatment. Both P and Fe were increased to a depth of 6 cm for both soils by the highest acid rate. In the case of P, all layers were influenced for the Comoro soil. The highest level of H_2SO_4 resulted in only a slight decrease in pH to 7.0 in the top 3 cm of the Comoro soil, and to 7.8 for the Cave soil.

Table 2. Yield (g/pot) response of range grasses to applied P (300 ppm) for three harvests from the Comoro soil (average of three replications).

Grass species	Harvest 1 Control	Harvest 1 P	Harvest 1 Percent increase	Harvest 2 Control	Harvest 2 P	Harvest 2 Percent increase	Harvest 3 Control	Harvest 3 P	Harvest 3 Percent increase
Lehmann lovegrass	2.8	5.5**	96	0.8	0.8	0	–	–	–
Wilman lovegrass	1.9	3.1**	63	2.4	3.3*	38	3.4	3.5	3
Blue panicgrass	3.1	3.9**	26	1.9	1.9	0	5.5	5.5	0
Atherstone	1.8	2.6*	44	2.2	2.3	5	2.4	2.4	0
Weeping lovegrass	0.4	0.5	25	0.2	0.2	0	0.3	0.3	0

* $P \leqslant 0.05$.
**$P \leqslant 0.01$.

Table 3. Effect of soil applied H_2SO_4 (0, 1, 5, 10 ml/pot) on dry matter yields (g/pot) of range grasses grown on the Cave soil (average of three replications).

Species	Harvest 1 0	Harvest 1 1	Harvest 1 5	Harvest 1 10	Harvest 2 0	Harvest 2 1	Harvest 2 5	Harvest 2 10	Harvest 3 0	Harvest 3 1	Harvest 3 5	Harvest 3 10
Lehman lovegrass	1.4	2.5**	3.6**	4.6**	1.8	4.2**	5.5**	8.7**	1.8	2.7*	3.7**	5.3**
Wilman lovegrass	2.5	3.9**	4.2**	5.8**	1.8	3.3**	3.6**	4.8**	1.3	1.7	2.3*	4.4**
Blue panicgrass	3.2	4.5**	4.5**	5.1**	0.7	1.6**	1.9**	2.9**	0.5	0.6	1.8**	2.8**
Atherstone	2.3	2.8*	3.7**	4.7**	1.7	1.8	3.6**	4.0**	0.6	0.6	1.6**	2.3**
Weeping lovegrass	0.2	0.5	0.7*	2.1**	0.1	0.1	0.5*	2.7**	0.0	0.1	0.2	1.2**

Response to H_2SO_4: * $P \leqslant 0.05$, ** $P \leqslant 0.01$.

Table 4. Effect of soil applied H_2SO_4 (0, 1, 5, 10 ml/pot) on dry matter yields (g/pot) of range grasses grown on the Comoro soil (average of three replications).

Species	Harvest 1 0	Harvest 1 1	Harvest 1 5	Harvest 1 10	Harvest 2 0	Harvest 2 1	Harvest 2 5	Harvest 2 10	Harvest 3 0	Harvest 3 1	Harvest 3 5	Harvest 3 10
Lehman lovegrass	2.8	3.7**	6.1**	13.1**	0.8	1.1	2.0**	4.3**	–	–	–	–
Wilman lovegrass	1.9	2.5*	5.9**	9.9**	2.4	3.7**	4.1**	6.2**	3.4	4.3**	5.7**	7.2**
Blue panicgrass	3.1	3.5	5.8**	4.3**	1.9	2.3*	2.8**	3.6**	3.3	4.6**	5.0**	5.6**
Atherstone	1.8	4.1**	10.1**	9.5**	2.3	2.6	3.9**	4.7**	2.4	3.5**	5.9**	7.1**
Weeping lovegrass	0.4	0.4	3.0**	7.0**	0.2	0.7*	2.9**	6.6**	0.3	0.4	1.3**	6.7**

Response to H_2SO_4: * $P \leqslant 0.05$, ** $P \leqslant 0.01$.

Table 5. Chlorophyll concentration (mg/g of plant material) in range grasses at third harvest treated with phosphorus, iron, and sulfuric acid (average of three replications).

Soil	Grass species	Control	$Ca(H_2PO_4)_2H_2O$ (300 ppm P)	$FeSO_4.7H_2O$ (50 ppm Fe)	H_2SO_4 (ml/pot) 1	5	10
Cave	Wilman lovegrass	2.4	2.7	6.0	4.1	4.8	5.0
	Blue panicgrass	4.3	3.4	5.7	3.5	4.3	5.1
	Atherstone	1.9	2.6	9.6	3.3	3.7	5.0
	Weeping lovegrass	–	–	6.6	–	–	1.5
Comoro	Blue panicgrass	2.5	3.0	5.0	2.5	3.7	5.1

Discussion

In view of the absence of any convincing benefits from fertilization of rangelands with micronutrients (Bales, 1965; Eckert et al., 1961; and Retzer, 1954) the responses to Fe are of particular interest and point to a severe information deficiency on this aspect of rangeland. As Fe availability is low in calcareous soils, primarily due to high soil pH (Hodgson, 1963), and since these soils are widespread in the West, we can reasonably infer that Fe deficiency poses a limitation on growth of nonnative plants. While plants vary in their sensitivity to low Fe availability, these data clearly show that weeping lovegrass is poorly adapted to Fe deficient soils. Lehmann and Wilman lovegrasses would probably be most competitive with other adapted species.

The continued response to Fe in contrast to that for P indicates that Fe has a proportionately greater influence on established grasses. The absence of a response to P after the initial harvest may have been due to gradual immobilization of the applied P and/or development of a mature rooting system resulting in greater exploitation of native soil P than fertilizer sources. These data suggest that fertilizer P could be effectively used to stimulate early growth and establishment after reseeding. With the supply of water and N being at optimum levels in this study, responses to both Fe and P are higher than expected in the field.

Application of H_2SO_4 stimulated growth of all species. Previous studies with acidification of calcareous soils on nutrient solubility (Pratt, 1961; Ryan et al., 1974) as well as soil data (Table 6) and chlorophyll concentration (Table 5) infer that the increased growth was largely due to increased Fe and P solubility in the soil. A consideration of the responses to Fe and P (Tables 1, 2) suggests that Fe had a proportionately greater influence on growth, particularly in the second and third harvests.

Table 6. CO_2-extractable P (ppm) and DTPA-extractable Fe (ppm) from soils treated with phosphorus, iron, and sulfuric acid.

Treatment	Sampling depth	Soils: Comoro P	Comoro Fe	Cave P	Cave Fe
Control	–	2.0	3.0	2.2	2.8
50 ppm Fe	–	1.5	5.6	4.0	9.2
300 ppm P	–	9.0	2.8	13.0	2.6
H_2SO_4 (ml/pot)	0–3 cm	2.3	4.0	2.0	3.4
1	3–6 cm	1.5	4.4	2.0	2.4
	6–9 cm	1.3	2.8	2.0	2.8
	9–12 cm	2.0	3.8	1.5	3.2
5	0–3 cm	2.5	4.2	5.0	3.8
	3–6 cm	1.5	4.2	2.5	3.0
	6–9 cm	2.0	3.0	2.0	3.4
	9–12 cm	2.5	4.0	1.5	3.2
10	0–3 cm	7.0	17.0	4.5	5.2
	3–6 cm	7.0	10.1	3.0	4.6
	6–9 cm	5.0	4.4	2.5	3.6
	9–12 cm	5.0	2.6	2.5	3.6

The low rate of H_2SO_4 is within the range of practical field application. However, data in Table 6, taken after three harvests, indicate that such a rate would not have a persistent effect. In general, DTPA-extractable Fe values less than 2.1 ppm are considered deficient, while CO_2-extractable P values less than 3.0 ppm are usually deficient, depending on the type of crop grown. The highest rate of 11 tons H_2SO_4/hectare further increased growth, having only the slightest effect on soil pH. In view of the high buffering capacities of Southwestern calcareous soils, they may be used to safely dispose of large quantities of acid if surpluses develop as predicted by McKee (1969). While surface application of H_2SO_4 may be technically most feasible, other methods such as placement or soil injection may be more efficient in terms of plant growth (Ryan and Stroehlein, 1973).

The potential benefits of H_2SO_4 use on rangelands include increased livestock carrying capacity and reduced erosion as a result of better vegetative cover. The latter aspects are important for exposed soil surfaces resulting from open pit and strip mining. Sulfuric acid has also been shown to increase water penetration into sodium-affected calcareous soils (Yahia et al., 1975). Using H_2SO_4, therefore, may not only improve productivity of existing range soils but would render previously barren areas productive. As some range soils are deficient in S as shown by Martin (1958) in California, responses from the sulfate of H_2SO_4 may also occur. While these studies point to such possibilities, the practical problems of field application, such as water management to adequately leach salts produced by acidification, will be the concern of future work. Since the use of P and Fe fertilizers on rangeland is generally uneconomical due to high costs and low returns, H_2SO_4 may prove to be a suitable alternative, if and when sulfuric acid disposal becomes a reality.

Literature Cited

Bales, R. L. 1965. Ecology of cleared chaparral site under different nutrient treatments. MS thesis, Univ. of Ariz.

Burkholder, D. A. 1967. Interspecific differences among five Southwestern desert grasses as affected by varying moisture and fertilizer levels. MS thesis, Univ. of Ariz.

Eckert, R. E., A. T. Bleak, and J. H. Robertson, 1961. Effects of macro- and micronutrients on the yield of crested wheatgrass. J. Range Manage. 14:149-155.

Hodgson, T. F. 1963. Chemistry of micronutrient elements in soils. Advance. Agron. 15:110-154.

Holt, G. A., and D. G. Wilson. 1961. The effect of commercial fertilizers on forage production of a Southern Arizona desert grassland range. J. Range Manage. 14:252-256.

Johnson, G. V. 1974. A simple procedure for quantitative analysis of turfgrass color. Agron. J. 66:457-459.

Kuykendall, J. R. 1956. The occurrence of iron chlorosis in the United States with particular respect to the occurrence of lime induced chlorosis. *In:* A. Wallace (ed.), Symposium on the use of metal chelates in plant nutrition. p. 24-28. The National Press, Palo Alto, California.

Martin, W. E. 1958. Sulfur deficiency widespread. Calif. Agr. 12(11):10-12.

Martin, W. E., L. J. Berry, and W. A. William. 1957. Range fertilization in a dry year. Fourth Progress Report. Agr. Ext. Serv., Univ. of Calif.

McKee, A. G., and Co. 1969. System study for control of emissions by the primary nonferrous industry. U.S. Federal Clearing House P B 1, 4.

Pratt, P. F. 1961. Phosphorus and aluminum interactions in the acidification of soils. Soil Sci. Soc. Amer. Proc. 25:467-469.

Retzer, J. L. 1956. Fertilization of some range soils in the Rocky Mountains. J. Range Manage. 7:69-73.

Ryan, J., and J. L. Stroehlein. 1973. Use of sulfuric acid on phosphorus deficient Arizona soils. Prog. Agr. in Arizona 25(6):11-13.

Ryan, J., S. Miyamoto, and H. L. Bohn. 1973. Prevent chlorosis with use of sulfuric acid. Prog. Agr. in Arizona 25(2):3-5.

Ryan, J., S. Miyamoto, and J. L. Stroehlein. 1974. Solubility of manganese, iron, and zinc as affected by application of sulfuric acid to calcareous soils. Plant and Soil 40:421-427.

Yahia, T. A., S. Miyamoto, and J. L. Stroehlein. 1975. Effect of surface applied sulfuric acid on water penetration into dry calcareous and sodic soils. Soil Sci. Soc. Amer. Proc. (in press).