

Sulfuric Acid as an Amendment for Reclaiming Soils High in Boron¹

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ABSTRACT

Laboratory results indicated that sulfuric acid can effectively aid in reclaiming soils high in boron. Results of a study, using 80-cm columns of a soil high in B, indicated that a surface application of 3.22 metric tons/ha of concentrated (96%) H₂SO₄ followed by leaching with 3 pore volumes, p.v. of water was nearly as effective in reducing the level of water-soluble soil B as was leaching with 16 p.v. of water. A direct pH effect on B adsorption affinity can explain the enhanced reclamation effect at the soil surface but cannot account for the beneficial effect found at lower soil column depths. Data suggested that competition by silicate ion for adsorption sites may be contributing to the enhanced desorption of B at lower soil depths.

Additional Index Words: boron toxicity, pH, adsorption, Fe-Al hydrous oxides, silica.

TOXIC CONCENTRATIONS of boron may occur naturally in arid region soils or they may develop because of irrigation with waters containing high amounts of B. Since many crops are quite sensitive to B, this excessive B must be eliminated from agricultural soils. The current recommended practice for reclaiming soils with excessive B is by extensive leaching with water, because B is relatively immobile in alkaline soils (Reeve et al., 1955; Rhoades et al., 1970; Bingham et al., 1972). A method to facilitate the leaching of B below the root zone, while conserving water, would be valuable.

The adsorption of B by soils has been shown to be pH dependent (Eaton and Wilcox, 1939; Midgley and Dunklee, 1939; Berger and Truog, 1945; Olson and Berger, 1946; Hingston, 1964; Okazaki and Chao, 1968; Bingham et al., 1971). Olson and Berger (1946) reported that alkalization (pH >7) of soil increased its capacity to fix B and that this additional adsorbed B could be released by acidification to the original soil pH. Lime-induced B deficiency has frequently been observed in acid soils, and is believed to be the result of increased B adsorption resulting from the increased pH and not a direct effect of calcium per se (Eaton and Wilcox, 1939; Olson and Berger, 1946; Hatcher et al., 1967). However, under certain conditions Ca has been credited with increasing B precipitation in salt solution studies with aluminum and silica (Parks and Shaw, 1941).

Most of the B in arid soils is adsorbed by the mineral portion of the soil, although organic matter also has a capacity to adsorb B (Berger and Truog, 1945; Olson and Berger, 1946; Parks and White, 1952). Reports are available in the literature indicating that clay minerals will adsorb B (Parks and White, 1952; Hingston, 1964; Fleet, 1965; Sims and Bingham, 1967; Couch and Grim, 1968) with the primary adsorption sites for B being Al and iron oxides and/or hydrous oxides (Schauer et al., 1956; Hatcher et al., 1967; Sims and Bingham, 1968a, 1968b).

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Adsorption of B by these adsorbents is pH-dependent, and adsorption is maximum at pH 8 to 9 for hydroxy-Fe compounds and at pH 7 for hydroxy-Al compounds (Schauer et al., 1956; Sims and Bingham, 1968a, 1968b). Boric acid molecules (H₃BO₃) predominate for pH values below 7, and borate ions (H₂BO₃⁻) make up an increasing proportion of the boron in solution with increasing pH.

This paper reports the results of research investigating the potential use of sulfuric acid as a soil amendment to facilitate leaching of B. Sulfuric acid was chosen because of the above observations of pH dependence, the apparent reversibility of B adsorption, and because of an expected H₂SO₄ surplus (McKee, 1969; Miyamoto et al., 1975) in the southwestern U.S. Arid soils high in B are also frequently high in sodium (Na) (Bingham et al., 1971). The beneficial use of H₂SO₄ in sodic soil reclamation is well established. Thus, H₂SO₄ may be beneficial for reclaiming soils high in both Na and B levels.

MATERIALS AND METHODS

Three calcareous soils, high in water-soluble B, were investigated. These soils were the same as those used in a B-leaching study by Rhoades et al. (1970). The soils were air-dried and the 1-mm fraction retained. Some properties of these soils are shown in Table 1.

Boron concentrations were determined using carmine (Hatcher and Wilcox, 1950). Aluminum and Si were determined either colorimetrically using methods of Hsu (1963) and Kilmer (1965), respectively, or by atomic absorption spectrophotometry. The acid titratable basicity (ATB₀), a measure of all the base constituents in the soil with which acid may readily react, was determined using the method of Miyamoto et al. (1973). The other physical and chemical characterizations were determined in accordance with the procedures described in USDA Handbook no. 60 (U.S. Salinity Laboratory Staff, 1954). Alkali-resistant, low-B glassware or plastic containers were used during the experiment.

The initial portion of this investigation consisted of a batch equilibrium study to determine the effects of varying amounts of H₂SO₄ on the soluble B levels in the soil solution. Acid application rates were calculated to achieve neutralization of the soil ATB₀ to 0, 10, 25, 50, 75, 100, and 200%. The acid was added to a 0.01M CaCl₂ solution (to prevent soil dispersion) and the solution was mixed with the soil to give a 1:1 soil-solution

Table 1—Soil chemical and physical characteristics.

Soil no.†	CEC‡	Surface area	SP§	pH¶	ECₑ††	ATB‡‡	Organic carbon	Boron conc.§§
	meq/100 g	m ² /g	%		mmho/cm	eq/kg	%	µg/ml
3660	28.2	193	54	8.2	2.7	1.21	0.43	6.1
3568	10.2	60	26	9.5	55.8	0.66	0.55	12.3
3582	14.0	62	29	9.4	5.0	1.47	0.48	1.2

† Soils also used by Rhoades et al. (1970b); soil 3660, Lethent, a fine, montmorillonitic, thermic xerollic natrargids, from Westside Project Area of San Joaquin Valley in California, soil 3568, Warm Springs, a fine-loamy, mesic aeric calciaqualls, from Utah; and soil 3582, Bramwell, a fine-silty, mixed, mesic aeric calciorthids from Idaho.

‡ Cation exchange capacity.

§ Saturation paste water content.

¶ pH of 1:1 extract.

†† Electrical conductivity of saturation extract.

‡‡ Acid titratable basicity.

§§ Boron concentration in the 1:1 extract.

ratio. Slurries were allowed to stand for various periods (5 min, and 1 and 3 days) with occasional mixing. The 1:1 soil-CaCl₂ solution slurries were centrifuged and the extracts analyzed to determine B, pH, Si, and Al.

Another study was made to investigate the effect of readjusting the pH of the 1:1 soil-CaCl₂ solution extract to its original value after addition of acid. To the 1:1 slurries for soil 3568, H₂SO₄ was added at rates to neutralize the ATB₀ to 0, 25, 50, 75, and 100%, allowed to remain for 1 day with occasional mixing and then alkalized by using 10N NaOH. The three treatments were as follows: (i) acidification and extraction, (ii) acidification, extraction, and alkalization of the extract, and (iii) acidification, alkalization, and extraction. Solution extracts were centrifuged and analyzed for pH, B, Si, and Al.

A column leaching study was made using 3.1-cm ID plexiglas columns constructed by joining 5-cm segments to form 80-cm long columns. Air-dry soil 3568 was packed to an average bulk density of 1.52 g/cm³. A volume of 0.5M CaCl₂ solution slightly greater than the estimated saturation pore volume, p.v., was applied to all columns and allowed to drain overnight. The saturation p.v. was the volume retained by each column. The volume of leachate was subtracted from the amount added for leaching. A 10N H₂SO₄ solution was applied to the surface at amounts equal to 0, 0.64, 1.61, and 3.22 metric tons/ha of surface area. After effervescence (~ 10 min), a volume of 0.01M CaCl₂ solution equal to 3 p.v. less the volume of the applied acid, was applied to each column using a mariotte constant-head delivery system. Three p.v. were chosen because the benefit of the acid is mostly dissipated after that much leaching (data not presented). Nearly uniform water flow rates were always observed. For comparison, check columns were leached with 16 p.v. of 0.01M CaCl₂ (no acid applied) to remove the leachable B from this soil (Rhoades et al., 1970). The effect of delay in applying leaching water after application of H₂SO₄ was also investigated for delay periods of 10 min and 2 and 6 hours.

After leaching, the columns were segmented and the soil segments retained for analysis. Based upon weights, the soil samples were brought to a 1:1 soil-water ration with deionized water, were allowed to stand for 1 day with occasional mixing, and were analyzed for B, pH, Al, and Si. Also, air-dried soil samples of each segment were extracted with 0.5N NaOH according to the method of Jackson (1965), and extractable Al and Si were determined.

RESULTS

Boron concentrations and the resultant pH values in the 1:1 soil-water extracts as affected by H₂SO₄ application rates (in terms of relative percent neutralization on ATB₀) and length of acid-soil contact time are presented in Table 2. Treating soil with H₂SO₄ was effective (though in some cases only temporarily) in bringing B into solution. Acid application rate, length of acid-soil contact time, and soil type all affected the B concentration. The B concentration in solution for all soils decreased with time though the amount varied with soil type and percent ATB₀ neutralized. Certain percent equivalent ATB₀ neutralizations also caused the B concentration to decrease.

The B concentration for the 1- and 3-day intervals of soil 3660 varied unlike those of the other two soils, resulting in relatively low B values for ATB neutralizations of 25, 50, 100, and 200%. Based on pH solubility relations of Al and previous reports (Parks and Shaw, 1941; Schauer et al., 1956; Sims and Bingham, 1968b), Al was suspected of causing the observed effect on soluble B levels in solution. The concentrations of Al in the 1:1 extract for the 1-day interval were 0.2, 2.6, 0.1, 0, 7.5, and 14.2 μg/ml for % ATB₀ neutralizations of 0, 10, 25, 50, 75, and 100,

respectively. The relative amounts of water-soluble B and Al tended to parallel each other, suggesting a cause and effect relationship.

Alkalinization of acidified soil 3568 slurries produced different B levels depending upon whether the soil solution was extracted before or after the base was added. Table 3 shows the results for the analysis of pH, B, Si, and Al. The B levels for the acidified-alkalized-extracted treatment were lower than those for the acidified-extracted and the acidified-extracted-alkalized treatments, especially at higher acid rates. The Si and Al values were considerably decreased by adding the base either before or after extraction. A whitish precipitate, primarily colloidal silica, was present in the acidified-extracted-alkalized treatment.

Results of the 80-cm long column study showed that surface application of H₂SO₄ and subsequent leaching effectively removed B from the soil profile (Fig. 1). At the highest rate of H₂SO₄ applied (3.22 metric tons/ha) enough acid was added to neutralize the total basicity to a depth of approximately 3.5 cm. Yet the depth of effective B removal upon leaching (3 p.v.) extended throughout the entire 80-cm depth profile. Extract pH and water-soluble 0.5N NaOH extractable (amorphous) Al and Si were analyzed on the segments of the treated columns. Only the pH and water-soluble Si data showed any measurable differences in concentration; and those differences were relatively small as compared to the values obtained in the batch equilibrium study.

The effects of 10 min, and 2- and 6-hour time intervals between applying the acid application and leaching were also studied (data not presented). There was no difference in average water-soluble B levels between the 10-min and the 2-hour time intervals. However, for the 6 hour interval, average water-soluble B levels increased 50% over that of the lesser time intervals.

DISCUSSION

Decreasing the soil pH by H₂SO₄ treatment effectively increased the concentration of water-soluble B in the soils studied. However, readsorption of B occurred with time (Table 2). Hingston et al. (1972) suggested that the specific adsorption of an anion involves the formation of a coordination complex at an oxide surface. The decrease in B adsorption with decreasing pH may be the result of loss in, or competition for, such coordination sites. The study of the alkalinization of acidified soil 3568 (Table 3) indicated that readsorption of B is only minimal if the solid phase is removed before readjusting the pH to its original value. The B readsorption in the acidified-extracted-alkalinized study and the acidified-alkalinized-extracted study (Table 3) were likely a result of B fixation on coprecipitated hydrous oxides. These data agree with that of others that the major sites for B adsorption for mineral soils are Al and/or Fe-hydroxy compounds present as coatings on or associated with clay minerals (Hatcher et al., 1967; Sims and Bingham, 1968b), or clay mineral and particularly micaceous-type clay minerals (Hingston, 1964; Couch and Grim, 1968; Fleet, 1965; Sims and Bingham, 1967).

The effect on pH of surface application of H₂SO₄ to the columns was not expected to extend below a few centimeters depth. However, the beneficial effect of the H₂SO₄

Table 2—Concentration of B and pH in the 1:1 soil-water extract for three time intervals between acid application and extraction.

Soil no.	% ATB ₀ neutralized	5 min		1 day		3 days	
		μg/ml	pH	μg/ml	pH	μg/ml	pH
		3660	0	3.4	7.5	6.1	8.2
	10	9.7	6.7	9.5	8.0	7.4	8.1
	25	13.2	6.0	6.8	7.5	3.1	8.0
	50	19.0	2.4	4.8	6.7	2.3	7.4
	75	20.6	1.4	17.6	3.7	17.2	4.1
	100	24.0	1.1	7.1	2.5	5.6	2.5
	200	24.0	0.6	8.6	1.3	4.4	1.5
3568	0	7.4	8.3	12.3	9.5	13.1	9.3
	10	20.0	6.1	20.1	8.0	19.2	8.2
	25	26.4	5.5	22.8	6.9	21.6	7.8
	50	32.0	2.4	28.8	6.3	24.7	6.1
	75	36.0	1.6	30.4	3.9	28.8	5.0
	100	35.0	1.2	32.4	2.2	28.3	3.0
	200	36.0	0.8	32.4	1.0	30.4	1.4
3582	0	1.2	7.8	1.2	9.4	1.8	9.2
	10	2.5	6.2	2.0	8.2	1.7	8.1
	25	3.2	6.1	3.1	7.3	3.0	7.8
	50	5.6	3.0	2.7	7.4	1.4	8.1
	75	6.6	1.7	4.0	6.7	4.0	7.1
	100	7.0	1.2	6.5	3.4	7.0	3.4
	200	7.8	0.7	9.0	1.0	10.3	1.2

Table 3—Effect of readjusting soil 3568 to its pre-acid treatment pH on the concentrations of water soluble B, Si, and Al.

% ATB ₀ neutralized	Acidified-extracted				Acidified-extracted-alkalized				Acidified-alkalized-extracted			
	pH	B	Si	Al	pH	B	Si	Al	pH	B	Si	Al
	μg/ml											
0	9.5	12.3	45	0.1	9.5	12.3	45	0.1	9.5	12.3	45	0.1
25	6.9	22.8	70	0.2	8.9	22.3	53	0.1	9.0	13.0	49	0.2
50	6.3	28.8	85	0.8	9.2	21.5	60	0.2	9.2	10.0	50	0.2
75	3.9	30.4	175	2.9	9.1	26.0	62	0.2	9.3	12.5	59	0.2
100	2.2	32.4	325	11.2	8.9	23.5	44	0.2	8.9	8.5	53	0.2

treatment in enhancing the ease of B removal by leaching extended over the entire 80-cm depth. Also, B released in the upper soil depths was not reabsorbed in the deeper depths where the pH was unaffected by the acid treatment. The boron species in solution is also affected by pH, however, this effect on adsorption is uncertain (Hingston, 1964; Sims and Bingham, 1968a). The possibility of competitive anion adsorption between sulfate (SO_4^{2-}) and borate $[\text{B}(\text{OH})_4^-]$ ions exists, but only with soils that were directly affected by H_2SO_4 (i.e., acidic pH). Therefore, only that soil which was affected by the H_2SO_4 (reduced pH and increased hydrous oxides) will demonstrate any appreciable competitive anion adsorption by SO_4^{2-} . Though definitive information is lacking concerning the mechanism(s) by which B reclamation enhancement occurs with surface application of H_2SO_4 , enough information exists to suggest a causal effect. Treatment of soil with H_2SO_4 , causes the Si concentration to increase considerably (Table 3). Results of analysis of the columns for water-soluble Si (data not presented) showed Si concentration increased as acid application increased. These values were conservative since they represent the Si concentration about 1 week after acid application. McPhail et al. (1972) demonstrated that the adsorption of B on hydrous oxides of Al or Fe is decreased as the amount of Si adsorbed on the surface is increased. However, the reverse case, where B was initially adsorbed and the effect B had on the subsequent adsorption of Si was not performed. They stated that the reduced B

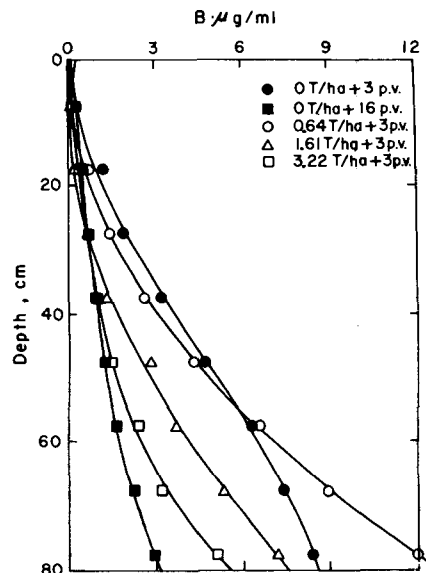


Fig. 1—Column study illustrating concentration of water soluble B with depth (Soil 3568) for four acid application rates and 3 p.v. of leaching water and a treatment of 16 p.v. of leaching water and no acid.

adsorption could be caused by either the increased solution concentration of monosilicic acid, thus resulting in direct competition between monosilicic acid and boric acid for adsorption sites, or by changes in the oxide surface after Si adsorption. The amounts of Si brought into solution with acidification are much greater than that for B. This Si could compete for adsorption sites at deeper soil depths during leaching, which may result in the lack of reabsorption of desorbed boron and even the desorption of adsorbed B from lower depths.

Data presented here indicated that surface application of H_2SO_4 with subsequent leaching can effectively aid in removal of B. The best results can be expected if soil is leached immediately after acid is applied and if the soil hydraulic conductivities are relatively high.

The consequences of B reclamation of ground water quality is of legitimate concern. Regardless of whether H_2SO_4 is used in conjunction with water or not, leaching the B below the rootzone is the desired result. An examination of Fig. 1 suggests that the ground water contamination may actually be less if H_2SO_4 is used as a reclamation aid, for more of the desorbed B is reabsorbed at shallower depths and in higher concentrations.

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