estimate can be made of the maximum ammoniation rate for each size without leaving ammonia in the air.

Fraction	Unscreened	-4
		+16
Lb. NH_3 per unit P_2O_5	5.7	4.0

The air analysis is evidently a more sensitive indicator than the product analysis. Ten per cent of ammonia in the drum atmosphere represents about 0.51 gram of ammonia, equivalent to 0.42 gram of nitrogen, or only 0.021% of the 2000 grams of product.

If other ammoniation equipment or techniques were used, limiting ammoniation rates would probably differ from those found in this study. These particular limits are thus less important than the general conclusion that fine superphosphate absorbs ammonia better than coarse.

					- 60	-100
>	+30	+40	+50	+60	+100	
	5.2	5.7	6.0	6.3	6.6	7.0

All the superphosphate used in this study, even that designated as original product, had been passed through a 4mesh sieve. Lumps retained on a 4mesh sieve would presumably be even poorer absorbers than the 4- to 16-mesh fraction, the coarsest one included in this study.

Acknowledgment

The authors wish to thank H. B. Baird, Jr., for aid in the analytical work.

Literature Cited

- Assoc. Offic. Agr. Chemists, Washington, D. C., "Methods of Analysis," 7th ed., 1950.
- (2) Datin, R. C., Worthington, E. A., and Poudrier, G. L., Ind. Eng. Chem., 44, 903-5 (1952).
- (3) Frear, G. L., Comm. Fertilizer, 81, No. 3A, 29 (1950).
- (4) Kumagai, R., Rapp, H. F., and Hardesty, J. O., J. Agr. Food Снем., 2, 25–30 (1954).

Received for review September 17, 1954. Accepted December 20, 1954. Presented before the Division of Fertilizer and Soil Chemistry, Symposium on Fertilizer Technology, at the 126th Meeting of the AMERICAN CHEMICAL SOCIETY, New York, N. Y., 1954.

MINOR PLANT NUTRIENTS

Less-Soluble Boron Compounds for Correcting Boron Nutritional Deficiencies

N. R. PAGE and H. P. COOPER Agronomy Department, South Carolina Agricultural Experiment Station, Clemson, S. C.

Crop response to annual applications of boron on the coastal plain soils of the southeastern United States is often inconsistent. Fluctuations in the supply of available boron from highly soluble boron compounds is thought to be a predominant reason. Lysimeter studies show that the leaching of moderately soluble boron compounds is less affected by rainfall than leaching of soluble compounds. Availability and crop response to slowly soluble boron compounds are reported. Slowly soluble boron compounds have advantages in preventing toxicity and in the possible elimination of special fertilizer formulations containing boron.

LARGE AREAS in the southeastern section of the United States lack sufficient boron for the maximum production of many crops (7). In the past, these deficiencies have generally been corrected by the application of highly soluble boron compounds.

Most of the soils in this area have a relatively low exchange capacity, are low in organic matter, and are subjected to heavy leaching rains. Under these conditions of soil and rainfall, highly soluble boron compounds may either supply toxic amounts of boron to plants under favorable moisture conditions or be leached by heavy rains to such an extent that an adequate supply of boron is not maintained in the root zone throughout the growing season. These fluctuations in the supply of available boron to the plants are probably a major reason for the often observed inconsistent response to annual applications of boron.

Recently (2, 7, 8) there has been interest in the use of less-soluble boron compounds as a means of minimizing some of the problems encountered in the use of highly soluble sources. By decreasing the seasonal fluctuations in the supply of available boron, these compounds would

Table I. Effect of Three Annual Applications of Equivalent Rates of Colemanite and Fertilizer Borate on Accumulation of Water-Soluble Boron in Soils

			И	/ater-Soluble Bor	on, P.P.M.			
	Cecil sl		Dunbar sl		Nosbig fsl		Lakeland s	
	1 st	3rd	1 st	3rd	1 st	3rd	1 st	3rd
Treatments	year	year	year	year	year	year	year	year
None	0.066	0.057	0,102	0.106	0.083	0.056	0.067	0.053
Colemanite ^a	0.118	0.142	0.162	0.157	0.162	0.130	0.111	0.114
Fertilizer borate ^a	0.147	0.128	0.152	0.143	0.122	0.089	0.085	0.058

^a Equivalent to 20 pounds per acre of borax.

Soils. Cecil sandy loam, Dunbar sandy loam, Nosbig fine sandy loam, and Lakeland sand.

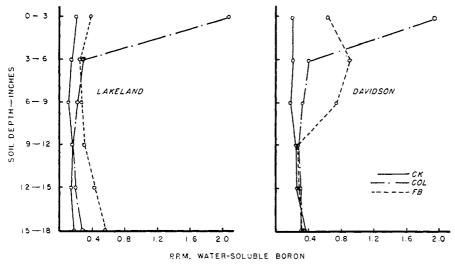


Figure 1. Effect of type of rainfall on comparative movement of colemanite and fertilizer borate in soils

Ck. Check, no boron compounds applied to soil

Col. Colemanite

FB. Fertilizer borote

Surface application of 40 pounds per acre of borax equivalent following 4 inches of water applied to simulate heavy leaching rain

probably tend to reduce the danger of toxicity and provide a more uniform and continuous supply of boron throughout the growing season. This would probably result in a more efficient use of the applied boron, which would be reflected in higher yields and more consistent response.

Reaction of Soluble and Moderately Soluble Boron Compounds under Field Conditions

In a study comparing the response from fertilizer borate to that of several less-soluble boron minerals that could be supplied commercially, colemanite, a calcium borate mineral approximately one half as soluble a fertilizer borate, gave the highest and most consistent yield response. It has been observed in both greenhouse and field experiments that the moderately soluble colemanite is less toxic to seedlings than equivalent rates of the highly soluble forms such as borax or fertilizer borate. This difference is most pronounced on light sandy soils. If the plants are sampled from 30 to 45 days after the boron compounds are applied, the analysis usually shows the plants treated with colemanite contain at least as much boron as the plants treated with the highly soluble sodium borates. These facts have also been observed by other workers (2, 8). In a study of boron accumulation in several soils under field conditions, colemanite and fertilizer borate were applied annually for 3 years at a rate equivalent to 20 pounds of borax per acre. As shown in Table I, annual applications of colemanite, at this rate, do not increase the water-soluble boron content of the soils to any greater extent than fertilizer borate.

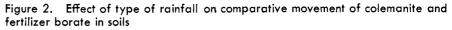
Lysimeter Studies of Boron Movement in Soils

In order to explain these observations and to clarify the movement of boron in the soil profile, a leaching experiment was set up with colemanite and fertilizer borate on Lakeland sand, representative of the light sandy soils of the coastal plains and a Davidson clay, one of the heavier soils of the Piedmont.

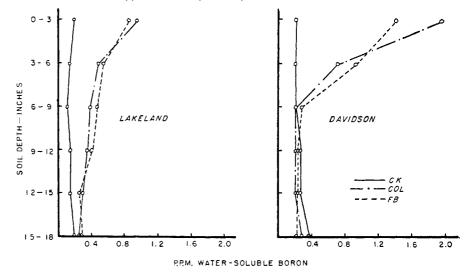
Experimental Procedures Twelve inches of subsoil and 6 inches of topsoil were placed in lysimeters and either 40 pounds per acre of fertilizer borate or an equivalent amount of colemanite was broadcast over the surface. Each compound on both soil types received the following types and quantities of simulated rainfall: 4 inches of water as a single application in a manner to simulate a heavy leaching rain, and 5, 10, 15, and 20 inches of total water added at the rates of 0.5 and 1 inch applied alternately at 3-day intervals. On the third day after the end of each treatment, the soil was removed in 3-inch layers and analyzed for water-soluble boron. The results are summarized in Figures 1, 2, and 3.

In South Carolina, it is Discussion common to have cloudof Results bursts or periods of heavy rainfall in the spring during the planting season. As shown in Figure 1, most of the colemanite remains in the top 3 inches of the soil, when subjected to this type of rainfall, in both the Lakeland sand and the Davidson clay. On the other hand, most of the fertilizer borate has moved past the 18-inch depth in the Lakeland sand and, even in the heavy Davidson clay, a considerable portion has moved into the 9-inch layer. This variation, owing to different solubility rates, partially explains the different response of seedlings to applications of colemanite and the sodium borates. Following periods of heavy rainfall, the highly soluble sodium borates may be leached from the root zone and therefore fail to supply the crop with the necessary boron. Yet, under conditions of favorable soil moisture with little leaching, the sodium borates will supply excessive amounts of available boron to the seedlings at the time of least requirement. This high initial availability often results in toxicity to the young plants and offsets beneficial effects that otherwise might be obtained.

Because colemanite requires a longer period of time to dissolve in the soil solution, it is not so subject as the sodium borates to leaching during the first weeks following application. The solubility



Surface application of 40 pounds per acre of borax equivalent following 5 inches of water added at rates of 0.5 and 1 inch applied alternately at 3-day intervals



VOL. 3. NO. 3. MARCH 1955 223

product is sufficiently high, however, that under conditions where leaching rains have not occurred, its movement in the soil soon approaches that of fertilizer borate (Figure 2). The slight lag in the movement of colemanite through the soil probably explains why plant material taken from colemanite-treated plots 30 to 45 days after application usually contains more boron than plants treated with equivalent rates of fertilizer borate.

As shown in Figure 3, most of the colemanite and fertilizer borate has moved past the 18-inch depth in Lakeland sand after 20 inches of rain. In the heavier Davidson clay, the boron compounds have not moved much past the 9-inch depth, although some leaching into the 15-inch level is indicated. Kubota and coworkers (3) also found that the rate of boron movement through various soils is related primarily to the texture, with the most rapid movement occurring in soils of light texture. As South Carolina has a normal rainfall of from 45 to 50 inches a year, these data indicate that up to 40 pounds per acre of both colemanite and fertilizer borate would be leached from the root zone following a year of normal rainfall. These data substantiate the field experiments on boron accumulation (Table I), which show that three annual applications of these two boron compounds did not increase the concentration of water-soluble boron in the soil over that of the first application.

While this experiment compared the movement of fertilizer borate and colemanite through the soil profile, it is logical to assume that the same general relations would hold for other boron compounds having approximately the same solubility products.

Slowly Soluble Boron Compounds

Because crops vary widely in their tolerance to boron, it is necessary now to make special fertilizer formulations for specific crops. The moderately soluble colemanite, while affording initial protection to seedlings, cannot be added safely at rates much higher than the sodium borates. So, although it eliminates some of the fluctuations in the supply of boron to the plant, special fertilizer formulations are still required. If special

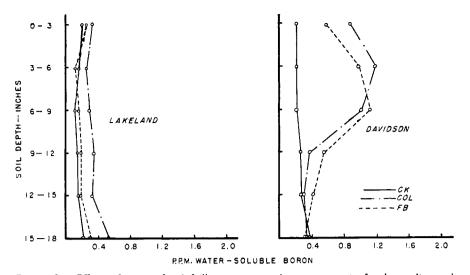


Figure 3. Effect of type of rainfall on comparative movement of colemanite and fertilizer borate in soils

Surface application of 40 pounds per acre of borax equivalent following 20 inches of water added at rates of 0.5 and 1 inch applied alternately at 3-day intervals

formulations for specific crops are to be eliminated, boron compounds must be available that will not produce toxicity in boron-sensitive crops but will supply sufficient boron to meet the requirements of most plants. Slowly soluble borosilicate or soft-glass frits have shown promise in limited tests.

McHargue and Calfee (4) in 1933 reported that a borosilicate was superior to soluble borates for lettuce. Muckenhirn (5) in sand cultures and Winsor (8) in field experiments have also used borosilicates successfully to control boron deficiency.

The borosilicate and other minor element frits are produced by the same general process used to prepare sheet steel cover-coat or ground-coat porcelain enamels. The boron and/or other minor elements are added to the regular raw materials, which are then heated until the mass is completely molten. The molten mass is quickly cooled by pouring it directly into a large volume of cold water. The fritted glass is then ground to the desired particle size.

The availability of the minor elements in the frits may be varied by altering the percentage composition of the minor element or elements concerned, the matrix, the melting and cooling process, and the particle size. In general, they are slowly soluble compounds which will supply the minor elements to plants without any danger of toxicity. As shown in Table II, a complete minor element frit may be added to soybeans, a boron-sensitive crop, at rates up to 200 pounds per acre under field conditions without producing visual toxicity symptoms or decreasing the vield.

Wynd (9) indicates that the minor elements in the frits may become available to plants through direct contact with the roots. Wheat was grown in the greenhouse in adjoining pots containing either an iron frit of large particle size or quartz sand. Both pots were supplied from the same bottle of a nutrient solution lacking iron by an automatic pumping and leveling device which caused the nutrient solution to rise to the surface of the pots. The excess solution from both pots was returned to the bottle and used again. The plants growing in the iron frit appeared normal, while those growing in sand culture developed iron chlorosis, indicating that very little of the iron in the frit was going into solution.

Presentation and Discussion of Results

In some work (7) finely ground boro-

silicate frits have been applied as a topdressing to well established stands of crimson clover. They increased the yield of forage and seed as well as the boron content of the plant, indicating that the boron in the frits does dissolve in the soil water. It is probable that when borosilicate frits are mixed with the soil the boron becomes available both by solution and through direct contact with the roots.

An experiment was initiated this year in stainless steel cylinders on a Durham sandy loam soil to compare the accumulative and residual effect of colemanite and several boron frits on the yield and

 Table II. Comparative Effect of Colemanite and a Minor Element Frit on Boron Content and Yield of Soybeans

Treatments	<i>L</i> Ь.	Boron Content of Soybean Leaves, P.P.M.	Yield of Soybeans, Bu./Acre
None		27.04	23.6
Colemanite	5	43.64	22.5
RL-95	50	33.64	25.7
RL-95	100	37.12	27.6
RL-95	200	46.80	25.7

All values are averages of three replicates. RL-95 = 5% Fe₂O₃; 2% each of B_2O_3 , MnO₂, CuO, ZnO; and 0.1% MoO₃.

quality of alfalfa and a mixture of ladino clover and alta fescue. The effect of the boron compounds on the yield of alfalfa and the clover-fescue mixture and the total quantity of boron removed in five cuttings of alfalfa-and four cuttings of the clover-fescue mixture are shown in Tables III and IV.

Although the data are too limited to allow conclusions as to the accumulative and residual effects of the frits in the soil, they show that the boron contained in the frits is available to plants and that plants respond to applications of the frits.

Obviously, the rate of 100 pounds per acre required for frits RL-95 and RL-13 is both expensive and so large that they cannot be used in mixed fertilizers. However, if the rates could be reduced so that 10 to 15 pounds per acre would supply the boron requirements of most crops, the borosilicate frits could be used in general fertilizer mixtures.

The availability of the minor elements in the frits may be increased by raising the percentage composition. Although the response was not so great as for RL-95 and RL-13, Tables III and IV show that 20 pounds per acre of a 15% B₂O₃ borosilicate frit, FN-176-C, increased both the yields and the boron uptake of alfalfa and 10 pounds per acre increased the yield of the clover-fescue mixture. This particular lot of FN-176-C was coarsely ground (70% minus 20 plus 100, 15% minus 100 plus 200 and 15% minus 200 mesh),

while the corresponding frits RL-95 and RL-13 were finely ground (25% minus 20 plus 100, 30% minus 100 plus 200, and 45% minus 200 mesh). The availability of FN-176-C could be increased both by decreasing the particle size and by altering the matrix. The significance of the matrix on the availability of the boron in the frits is demonstrated by frits RL-13 and RL-95. As seen in Tables III and IV, 100 pounds of RL-95 containing 2% B₂O₃ supplied more boron to the plants than an equal amount of RL-13 containing 5% B₂O₃.

These data indicate that it is possible to produce borosilicate frits of sufficient availability so that 10 to 15 pounds per acre will supply the boron requirements of most crops. These compounds should give more control of the boron supply, so that annual variations in yield response due to fluctuations in the supply to the plants would be minimized. With the elimination of the danger from boron toxicity, special fertilizer formulations for specific crops would not be necessary, and boron could be included in general crop fertilizers.

Before the slowly soluble boron compounds can be used generally, however, extensive work will be required to determine rates of application, availability to plants, and residual effects in the soil. While accurate methods for determining the total boron content of the borosilicates have been proposed (6), it will also be necessary to develop methods of chemical analysis that will accurately reflect their boron-supplying power.

Acknowledgment

This research was supported in part by a grant from Ferro Corp., Cleveland, Ohio. The colemanite was supplied by the Pacific Coast Borax Co.

Literature Cited

- (1) Beeson, K. D., Soil Sci., 60, 9-13 (1945).
- (2) Jacob, A., and coworkers, Landwirtsch. Forsch., 6, No. 1 (1954).
- (3) Kubota, J., and coworkers, Soil Sci. Soc. Am. Proc., 13, 130-4 (1948).
- (4) McHargue, J. S., and Calfee, R. K., Plant Physiol., 8, 305-13 (1933).
- (5) Muckenhirn, R. J., J. Am. Soc. Agron., 28, 824-42 (1936).
- (6) Naftel, J. A., and Fajans, E. W., J. Assoc. Offic. Agr. Chemists, 37, 537-44 (1954).
- (7) Page, N. R., and Paden, W. R., Agron. J., 46, 337-8 (1954).
- (8) Winsor, H. W., Soil Sci., 69, 321-33 (1950).
- (9) Wynd, F. L., Lloydia, 14, 1-33 (1951).

Received for review September 17, 1954. Accepted January 14, 1955.

Table III. Effect of Boron Compounds on Yield and Quantity of Boron Removed by Five Cuttings of Alfalfa

Treatments		B_2O_3 in	Oven-Dry Hay, Lb./Acre		Boron Removed, G./Acre	
		Compounds,	Yield	Gain over no	Total for	Gain over no
	LD.	Lb. % Yie	riela	treatment	cuttings	treatment
None			13,299		118.49	
Colemanite	10	33.5	16,117	2818ª	206.83	88.34ª
RL-95	100	2	14,371	1072	181.10	62.61ª
RL-13	100	5	15,353	2054 ^b	178.14	59.65 ^a
FN-176-C	20	15	14,221	922	154.93	36.44 ^b
All values are ave	rages of four rei	plicates.				
		of B_2O_3 , MnO_2 , ZnO_2	, CuO; and 0.1%	MoO ₃ .		
Hay. L.S.D. 0.02	5 = 1484.	Boron removed.	L.S.D. 0.05 = 3	6.00.		

L.S.D. 0.05 = 1484. Hay. Boron removed.

^a Significant at 1% level.
^b Significant at 5% level.

Table IV. Effect of Boron Compounds on Yield and Quantity of Boron Removed by Four Cuttings of Mixture of Ladino Clover and Alta Fescue

L.S.D. 0.01 = 53.46.

Treatments Lb.		B_2O_3 in	Oven-Dry	Oven-Dry Hay, Lb./Acre		Boron Removed, G./Acre	
		Campounds, %	Yield	Gain over no treatment	Tatal for 4 cuttings	Gain over no treatment	
None Colemanite RL-95 RL-13 FN-176-C	5 100 100 10	33.5 2 5 15	12,617 12,287 13,567 13,910 12,960	-330 +947 +1293a +343	85.88 97.95 113.21 104.97 85.06	+12.07 +27.33 +19.09 - 0.82	
All values are ave RL-95 = 5% Fe Hay. L.S.D. 0.0 Boron removed, r	₂ O ₃ ; 2% each ()5 = 1212.	plicates. of B2O3, MnO2, ZnO	, CuO; and 0.1%	, MoO₃.			

^a Significant at 5% level.

L.S.D. 0.01 = 2082.