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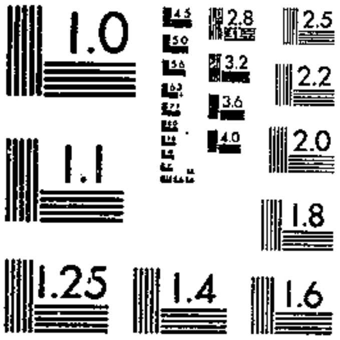

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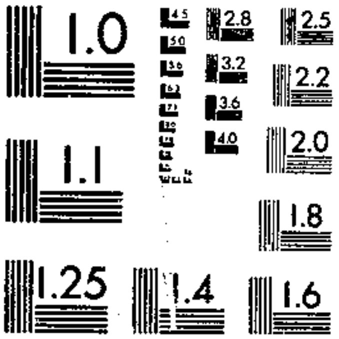

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Relation of Soil Reaction to Toxicity and Persistence of Some Herbicides in Greenhouse Plots[1]

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CONTENTS

Experimental evidence that soil reaction is a factor in the toxicity and persistence of sodium chlorate mixed into the soil was presented in a previous publication (*17*).[3] The main purpose of the investigation described in the present bulletin was to determine by greenhouse experiments whether soil reaction is also a factor in the effectiveness of other herbicides—ammonium and sodium thiocyanates, sodium arsenite, ammonium sulfamate, and borax—chlorate being used in parallel tests as a standard for comparison. Also included are the results of a study of the extent to which toxicity of residual chlorate in soil, following its use for weed control, can be reduced in soils of different reactions by applications of nitrogenous fertilizers. It is known from tests in both soil and water cultures that chlorate toxicity is influenced by the concentration of available nitrate nitrogen and that ammonium nitrogen seems to have a similar effect in soils but

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[3] Italic numbers in parentheses refer to Literature Cited, p. 30.

not in water cultures (*8*, *16*), indicating dependence of the effect on conversion of the ammonium to nitrate. Since soil reaction is known to affect the rate of nitrification (*20*, *28*), it seemed desirable to test the effects of various nitrogen compounds on the toxicity of chlorate added to acid, neutral, and alkaline soils.

SUMMARY

Sodium chlorate.—To sowings made within the first several months following its application, chlorate was most toxic in acid soil, although differences due to soil reaction were never so marked as with other herbicides. After several months this relation usually disappeared, apparently owing to relatively slow disappearance of sodium chlorate from the alkaline plots and sometimes from the strongly acid ones also.

In slightly acid or alkaline soils, chlorate toxicity was reduced by all the nitrogenous fertilizers tried—calcium and sodium nitrates, ammonium sulfate, urea, and Cyanamid, the last named being generally least effective. No appreciable difference was noted in the effects of calcium and sodium nitrates applied at rates giving equal concentrations of nitrate.

In slightly acid and alkaline soils the effects of ammonium sulfate were similar to those of nitrate from the first, but in highly acid plots (near pH 4.3) the effects of the ammonium salt were not apparent until the second crop was sown a month later. This is interpreted to mean that nitrification occurred here more slowly than in the less acid plots, ammonium nitrogen itself having been found to be without effect on chlorate toxicity. Cyanamid had no effect on chlorate toxicity in this acidified soil at any time.

Ammonium and sodium thiocyanates.—Toxicity of these two thiocyanates was markedly less in soil made alkaline with either lime or sodium bicarbonate than in an acid soil with a pH value near 5.0. Their outstanding characteristic was rapid decomposition at all soil reactions, but especially in alkaline plots, from which toxicity of an initially lethal dose sometimes disappeared in less than a month. In the strongly acid soil, toxicity was gone after about 2 or 3 months. No other herbicide added to the soil in quantity sufficient to kill or nearly kill plants sown immediately after the application lost its toxicity in so short a time. Following the initial period of toxicity, there was always a period during which successive crops of seedlings were stimulated to much better growth than the controls. Effects of equivalent applications of thiocyanate as the ammonium and sodium salts were similar.

Borax (sodium borate).—The initial toxicity of borax was less than that of chlorate and thiocyanate, four to five times as much being required for similar degrees of plant injury. Its toxicity decreased as the acidity of the soil was decreased by applications of either sodium or calcium carbonate or slaked lime. The outstanding characteristic of borax was persistence, its toxicity remaining practically unchanged for the duration of the experiments, 36 months in the longest test, whereas chlorate toxicity was practically gone from adjacent acid and neutral plots after 9 months.

Sodium arsenite.—Arsenite proved to be much less toxic than chlorate. Even after the dose was doubled less injury resulted at all soil reactions than that produced in adjacent plots by chlorate applications half as large. Toxicity was greatest in the acid plots and least in the alkaline.

Ammonium sulfamate.—Sulfamate toxicity was greatest in the acid plots. Considerable variation in the degrees of injury shown by some croppings from duplicate plots and from the same plot in successive sowings suggests that the behavior of this herbicide is responsive to small differences in some environmental factor.

METHODS

The herbicides were thoroughly mixed into the soil of greenhouse beds partitioned into small plots each containing 200 pounds of air-dry soil (fig. 1). For most of the experiments a strongly acid (approximately pH 5.0) fine sandy loam of the Plant Industry Station, Beltsville, Md., was used. It was brought to a nearly neutral reaction in some plots and to alkalinity in others by admixtures of slaked lime (calcium hydroxide) or, in one experiment, of sodium bicarbonate. For the experiments with nitrogenous fertilizers a slightly acid clay loam of Arlington Farm, Rosslyn, Va., was used. It was acidified with sulfuric acid in some plots and alkalized with slaked lime in others. The treatments were made about a week before the herbicides were applied. During this week the soil was kept well moistened and was stirred several times.

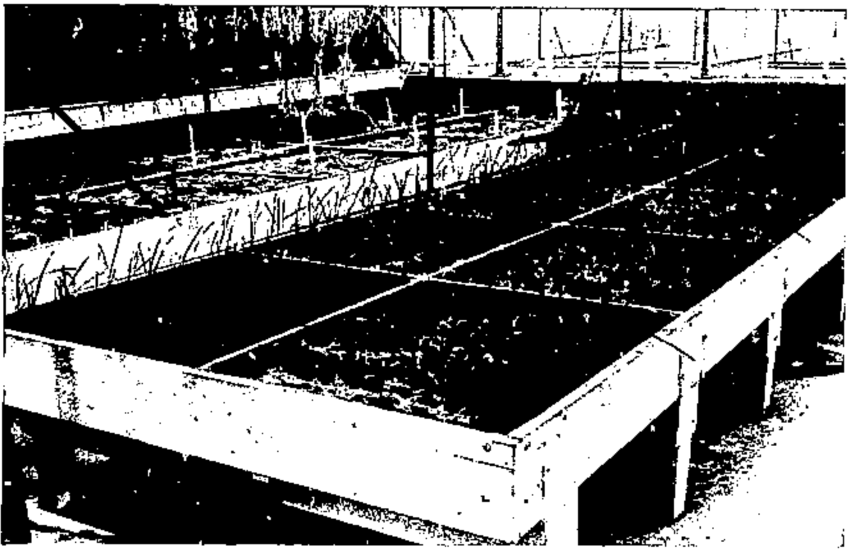

FIGURE 1.—Greenhouse plots used for herbicide tests. Borax toxicity to oats is shown in the three plots in right foreground. Corresponding control plants are in adjacent plots.

Borax was added dry, but the other herbicides were added in solution. Following their application to the surface of the plots, water was added to carry them into the soil, which then stood for several days before the final remixing.

Comparative toxicities of the herbicides in the different plots were shown by the degrees of injury sustained by test plants sown as soon as the final mixing of the soil was completed. The plants were cut and weighed after 4 to 6 weeks. Persistence of toxicity in each plot was determined by a series of such crops, with no further treatment except thorough remixing of the soil before each resowing. The seed was spaced 2 inches apart in rows 6 inches apart, six rows to a plot. As test plants, Hannchen barley, Fulghum oats, and Leoti sorgo were used.

Equal quantities of water were added to the plots by measurement throughout the experiments, except where occasional adjustments were necessary to compensate for unequal drying. The soil, with a water-holding capacity of about 35 percent, was kept moderately moist (17 to 20 percent) by frequent waterings in order to avoid intervals of increased concentration of the chemicals. As no leaching occurred, any disappearance of toxicity may be attributed to decomposition of the herbicides.

Relative degrees of injury produced by the herbicides, irrespective of effects of soil reaction, are shown by the average green weights of the plants, expressed as percentages of corresponding weights for control plants grown in soil of the same reaction without the herbicide. These "growth percentages" range from 0 where the dosage is lethal to figures near 100 where there is no herbicide injury, and higher where there is stimulation. The actual weights of the control plants grown without the herbicides are given in the tables to show the effects of soil reaction or of fertilizers on the size of the plants.

Soil reactions in the different plots were determined with a Beckmann pH meter (glass electrode) except where specified otherwise. The soil samples, taken from the level of the roots, were uniformly moistened to a soft paste. Preliminary tests demonstrated that the small variations in proportion of moisture in such samples introduced no appreciable error in the measurements. The ranges of values obtained over the periods of the experiments are given with the data in the tables.

RESULTS

EFFECTS OF SOIL REACTION ADJUSTED WITH SULFURIC ACID AND SLAKED LIME

The first experiment was a preliminary test of the effects of soil reaction on the toxicity of sodium chlorate ($NaClO_3$), ammonium thiocyanate (NH_4SCN), and ammonium sulfamate ($NH_4SO_3NH_2$) to sorgo. In some of the plots the naturally acid soil (pH 5.0) was further acidified to pH 4.4 with sulfuric acid. To 2 gallons of water in a watering can, 40 cc. of the concentrated acid was added and sprinkled on the soil. The plots were then watered to dilute the acid further, after which the soil was allowed to dry somewhat before being thoroughly mixed. Other plots were alkalized to pH 7.4 with 12 ounces of slaked lime ($Ca(OH)_2$). Seven days later the three herbicides were added, in solution, each at a rate of 5.2 gm. per plot. After 5 days, during which the soil was thoroughly mixed several

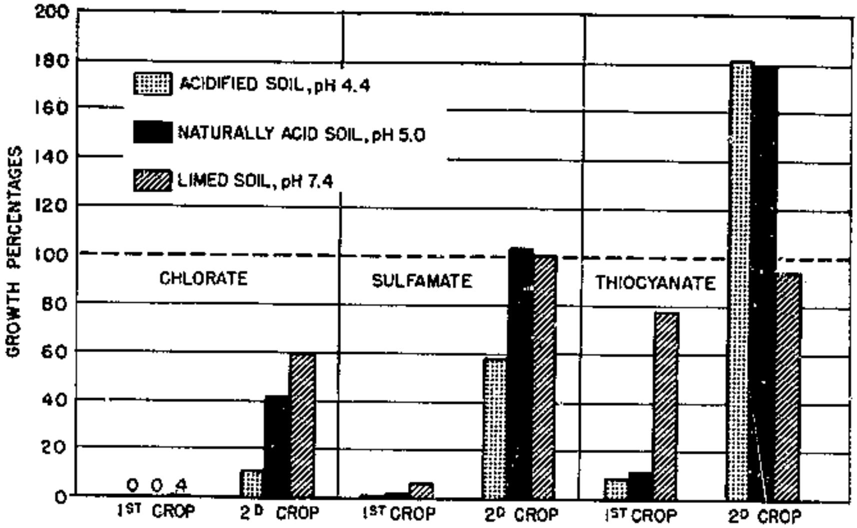

FIGURE 2.—Comparative toxicity and persistence over a 3-month period of sodium chlorate, ammonium sulfamate, and ammonium thiocyanate (5.2 gm. of each in 200 pounds of soil) to two successive crops of sorgo grown in acidified, naturally acid, and limed soils. Dotted line represents normal growth; i. e., the average green weights of control plants from plots of corresponding soil acidities not treated with a herbicide.

TABLE 1.—*Comparative toxicity and persistence of equal applications of sodium chlorate, ammonium thiocyanate, and ammonium sulfamate, as shown by growth of sorgo in soil adjusted to different reactions*

[Herbicides applied April 3, 1942]

Crop No.	Growth period (1942)	Herbicide	Growth of plants at soil reactions of—		
			pH 4.4±0.1 (acidified)	pH 5.0±0.1 (naturally acid)	pH 7.4±0.1 (limed)
			Growth percentages[1] for herbicide-treated plots		
1	Apr. 8-May 7	Chlorate	0	0	0.4
		Sulfamate	1.2	2.4	7.5
		Thiocyanate	0.5	12.2	78.1
2	June 3-July 2	Chlorate	11.1	42.0	60.0
		Sulfamate	58.5	104.0	101.8
		Thiocyanate	182.4	179.9	95.8
			Average green weights of control plants (in grams)		
1	Apr. 8-May 7	None	0.69	1.74	3.09
2	June 3-July 2	do	4.41	5.51	3.65

[1] Average green weights of about 150 plants expressed as percentages of corresponding weights for control plants from soil of the same reaction with no herbicide.

times, seed for the first crop was sown. A month later this crop was cut, and after another month a second crop was sown and grown for the same length of time. The data, summarized in table 1 and presented diagrammatically in figure 2, show definite effects of soil reaction on initial toxicities and large differences in the persistence of these toxicities over the 3-month period of the experiment.

The data for the first sowing show that the toxicity of all three herbicides decreased with decreasing soil acidity.

By the time of the second sowing, 2 months later, only sodium chlorate remained toxic at all three reactions. The trend of decreasing toxicity with decreasing soil acidity was still evident. In contrast, ammonium thiocyanate was not only gone from all the plots but at the two acid reactions it had greatly stimulated the plants, presumably in consequence of some residual nitrogen left in the soil (*3*, *13*, *27*, *32*). The sulfamate remained injurious in the most acid plot only.

Effects of Soil Reaction Adjusted With Sodium Bicarbonate

A second experiment was designed to determine the effects of soil reaction adjusted with sodium bicarbonate instead of the calcium hydroxide used in the first experiment, on the comparative toxicity and persistence of sodium chlorate, ammonium thiocyanate, and borax ($Na_2B_4O_7$).

The naturally acid soil (pH 4.8) was adjusted to pH 6.0 and 7.3 by applications of 150 and 350 gm., respectively, of sodium bicarbonate to 200-pound lots of soil. After a week, during which the soil was kept moistened and stirred several times to distribute the bicarbonate uniformly, two plots of each reaction were treated with 5 gm. of sodium chlorate, two with 25 gm. of commercial borax, two with 6.5 gm. of ammonium thiocyanate, and two were left with no herbicide, to show the effects of soil reaction alone. Each treatment was duplicated in a second bench across the aisle from the first.

Six days after application of the herbicides the first crop, barley, was sown. This crop was harvested a month later and was followed by similar crops of oats and barley, alternating; then, when summer temperatures became too high, by two crops of sorgo, followed again in the fall by barley.

Comparative degrees of injury sustained by these crops are shown by the growth percentages in table 2. Averages for the duplicate plots of the first six crops of the table are presented graphically in figure 3. The appearance of the barley plants of the second cropping is shown in figure 4.

The data show that making the soil alkaline with sodium bicarbonate reduced the toxicity of all three herbicides, just as calcium hydroxide had done in the first experiment (table 1). Therefore, the effect was correlated with the soil pH and not with the particular cation, calcium or sodium, in the alkalizing agent.

The chlorate application was lethal to the first crop at all three reactions, thiocyanate at the two acid reactions only, while borax was not lethal at any reaction, despite the larger quantity used. The

TABLE 2.—*Comparative toxicity and persistence of sodium chlorate, borax, and ammonium thiocyanate to successive crops in duplicate greenhouse plots adjusted from the natural pH 4.8 to less acid and to alkaline reactions with sodium bicarbonate*

[Herbicides applied January 20, 1943]

Crop No.	Crop [1] and herbicide application (in grams per 200 pounds of soil)	Growth at soil reactions of— pH 4.8±0.2 Plot 1	pH 4.8±0.2 Plot 2	pH 6.0±0.2 Plot 1	pH 6.0±0.2 Plot 2	pH 7.3±0.2 Plot 1	pH 7.3±0.2 Plot 2
		Growth percentages [2] for herbicide-treated plots					
	Chlorate (5 gm.):						
1	Barley	0		0		0	
2	Oats	20.9	20.0	27.3	29.4	36.4	28.2
3	Barley	8.3	12.0	37.3	28.8	49.4	44.6
4	Oats	89.9	79.3	85.7	81.9	84.6	86.2
5	Sorgo	29.3	28.5	63.2	55.6	40.9	45.7
6	do	46.0	36.8	91.3	85.7	52.8	54.8
7	Barley	95.3		128.7		79.2	
	Borax (25 gm.):						
1	Barley	5.1		7.9		47.4	
2	Oats	7.3	3.4	9.6	8.3	27.3	27.7
3	Barley	5.5	5.7	5.5	5.7	46.1	32.5
4	Oats	22.3	12.6	16.2	9.6	34.3	30.1
5	Sorgo	14.8	15.7	18.3	11.0	30.2	54.7
6	do	17.2	9.0	19.2	10.3	46.3	39.7
7	Barley	13.6	17.2	17.2	18.3	23.0	20.8
	Thiocyanate (6.5 gm.):						
1	Barley	0		0		53.5	
2	Oats	0	0	110.6	106.0	159.1	138.5
3	Barley	127.2	110.3	120.8	117.5	144.4	160.9
4	Oats	149.6	124.6	97.1	108.0	79.3	109.0
5	Sorgo	133.3	130.7	96.4	105.3	82.2	115.8
6	do	110.7	101.8	89.4	115.4	106.8	112.7
		Average green weights of control plants (in grams)					
	No herbicide:						
1	Barley	1.84		1.88		0.59	
2	Oats	1.37	1.10	1.37	1.66	.60	0.62
3	Barley	3.09	4.35	4.56	3.93	1.00	1.91
4	Oats	.95	.96	1.15	.92	.82	.44
5	Sorgo	2.86	3.23	2.90	3.12	1.45	1.33
6	do	3.89	4.65	3.55	3.81	1.66	1.73
7	Barley	2.48		2.44		2.50	

[1] The growing periods for each crop were: 1, Jan. 20 to Feb. 26, 1943; 2, Feb. 20 to Mar. 25 (the seed was sown between the rows before the first crop was cut); 3, Mar. 26 to Apr. 29; 4, May 4 to June 2; 5, June 4 to June 30; 6, July 2 to Aug. 3; 7, Oct. 21 to Dec. 3.

[2] Average green weights of about 70 plants expressed as percentages of corresponding weights for a similar number of control plants from plots of the same reaction with no herbicide.

data for the second sowing showed a different ranking, owing (1) to complete disappearance of thiocyanate toxicity at both pH 6 and 7.3 (although it was still lethal at pH 4.8) and (2) to no significant change in the toxicity of borax at any reaction. Chlorate remained very toxic but much less so than at the first sowing.

Persistence of chlorate was intermediate between that of thiocyanate and borax. Because the three crops used for the successive sowings differed greatly in susceptibility to chlorate injury, it was not possible to get a clear picture of the rate of decomposition of chlorate. Highly susceptible barley was used for the first and third

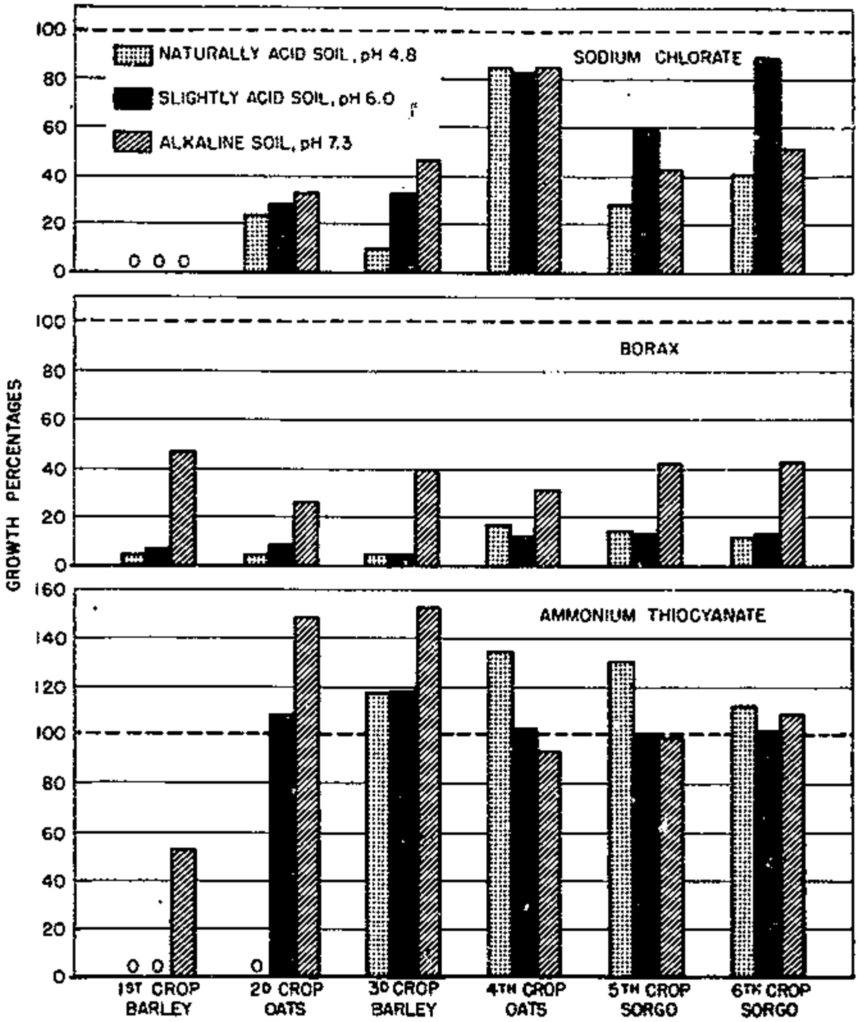

FIGURE 3.—Averages of growth percentages for duplicate plots of the first six crops summarized in table 2, showing comparative toxicity and persistence over a 10-month period of sodium chlorate (5 gm. in 200 lb. of air-dry soil), borax (25 gm.), and ammonium thiocyanate (6.5 gm.), added to a naturally acid soil (pH 4.8) and to soil adjusted to slight acidity (pH 6.0) and to alkalinity (pH 7.3) with sodium bicarbonate. The dotted lines represent weights of control plants from plots of corresponding soil acidity not treated with a herbicide.

sowings, and oats, most tolerant of the small grains (*15*), for the second and fourth. Just when the chlorate had apparently decomposed to the point of being almost nontoxic to oats, judging by the growth of the fourth crop, the advent of very warm weather made it necessary to change to sorgo for the fifth and sixth crops. Sorgo was more sensitive than oats to chlorate injury; hence the percentages for

FIGURE 4.—Borax injury to month-old barley plants grown in soil with pH values of (*A*) 4.8; (*B*) 6.0; and (*C*) 7.3.

the fifth crop dropped back, although it can be assumed that the trend of decreasing chlorate concentration in the soil continued.

Marked stimulation followed toxicity in the thiocyanate plots, as in the preceding experiment. Figure 3 brings out the rapidity with which an extremely toxic condition changed to one of stimulation with this herbicide, first in the alkaline plots, then in the acid ones, where toxicity had persisted longer. Stimulation persisted for several months, after which the plants were much like the controls, with growth percentages near 100.

Chlorate almost disappeared from all the plots subsequently (table 2), but there was no significant change in borax toxicity. In all later tests, continued for 36 months, the borax plots remained as toxic as they were initially, whereas the adjacent chlorate plots had lost their toxicity completely.

Effects of Soil Reaction Adjusted With Slaked Lime

With new soil in the plots, a similar study was made the following season (October 1943 to June 1944) of the comparative toxicity and persistence of sodium chlorate, ammonium thiocyanate, sodium arsenite, ammonium sulfamate, and borax. The soil in a third of the plots was adjusted from its naturally acid reaction (near pH 5) to nearly neutral (pH 7.1) with 150 gm. of slaked lime, and another third to an alkaline reaction (about pH 7.8) with 350 gm. Two plots of each reaction were left as controls without further treatment, and the rest, consisting of duplicates of each condition, were treated with the herbicides, thoroughly mixed into the soil 10 days later.

Rates of application of the herbicides were 5 gm. per plot of 200 pounds of soil, excepting borax, for which the rate was 20 gm. per plot. Six days after these applications barley and oats were sown in alternating rows.

Growth percentages for plants of six such sowings in succession over a 12-month period are given in table 3. The plots were so arranged that duplicates were at opposite ends of the greenhouse, and the three plots of each herbicide, in acid, neutral, and alkaline soil, respectively, were adjacent to each other. Plots numbered 1 comprised a group at the south end of the greenhouse, those numbered 2 at the north end, where there was less shading from structural elements of the greenhouse. For close comparisons, results from plots within each group are the most significant. Averages of the figures for duplicate plots are shown diagrammatically in figure 5.

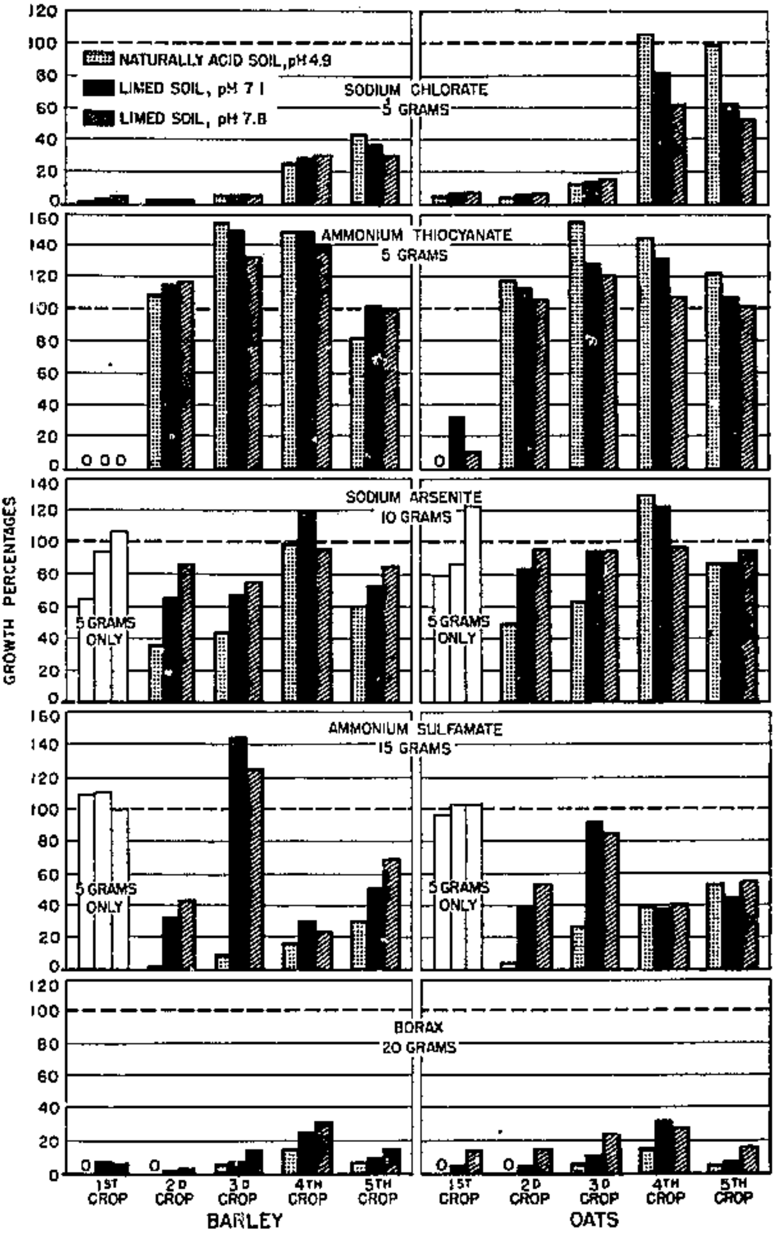

FIGURE 5.—Averages of growth percentages for duplicate plots summarized in table 3, showing comparative toxicity and persistence over an 8-month period of sodium chlorate (5 gm. in 200 lb. of air-dry soil), ammonium thiocyanate (5 gm.), sodium arsenite (5 gm. for first crop, 10 gm. thereafter), ammonium sulfamate (5 gm. for first crop, 15 gm. thereafter), and borax (20 gm.) to five successive crops each of barley and oat seedlings, in alternating rows in plots of naturally acid soil (pH 4.9), and in this soil adjusted to nearly neutral and to alkaline reactions with slaked lime. Dotted lines represent weights of control plants from plots of corresponding reactions not treated with a herbicide.

TABLE 3.—*Comparative toxicity and persistence of sodium chlorate, ammonium thiocyanate, sodium arsenite, ammonium sulfamate, and borax to six successive crops*[1] *of young plants of barley and oats in alternating rows in duplicate greenhouse soil plots adjusted from the natural pH 4.9 to nearly neutral and alkaline reactions with slaked lime*

[Herbicides applied October 15, 1943, with second applications of arsenite and sulfamate on December 12]

Herbicide and crop No.[1]	Applications (grams per 200 pounds of soil)	Barley at soil reactions of—						Oats at soil reactions of—					
		pH 4.9 ±0.3		pH 7.1 ±0.3		pH 7.8 ±0.1		pH 4.9 ±0.3		pH 7.1 ±0.3		pH 7.8 ±0.1	
		Plot 1	Plot 2	Plot 1	Plot 2	Plot 1	Plot 2	Plot 1	Plot 2	Plot 1	Plot 2	Plot 1	Plot 2
		GROWTH PERCENTAGES[2] FOR HERBICIDE-TREATED PLOTS											
Chlorate:													
1	5	[3] 2.5	0	[3] 3.0	[3] 2.3	[3] 4.1	[3] 5.5	5.2	5.8	6.2	6.7	9.7	11.0
2		[3] 2.0	[3] 1.9	[3] 1.9	[3] 2.2	1.9	2.5	5.5	5.6	6.9	6.6	7.9	7.3
3		[3] 4.3	[3] 8.2	4.6	8.3	3.6	9.7	14.1	13.0	13.8	14.9	17.5	14.3
4		25.9	25.2	22.4	35.2	23.4	37.2	109.0	100.9	83.5	77.7	69.7	53.7
5		52.7	34.7	36.1	37.2	25.7	35.7	113.0	83.0	65.7	59.9	59.9	45.2
6			65.4		73.8		55.5		108.6		97.5		73.7
Thiocyanate:													
1	5	0	0	0	0	0	0	0	0	22.5	41.3	0	22.1
2		97.5	121.2	121.0	111.0	127.0	110.1	97.1	140.3	110.4	117.1	117.8	95.3
3		159.2	152.0	149.5	151.5	120.9	145.1	146.1	165.5	128.7	128.3	116.2	124.8
4		197.2	103.1	148.5	150.6	117.3	164.0	153.8	135.1	125.1	138.7	99.1	114.8
5		92.4	70.6	100.5	102.9	102.4	96.5	123.3	121.3	110.1	105.8	106.6	96.2
6			94.8		111.8		114.6		141.8		121.9		119.0
Arsenite:													
1	5	51.3	75.2	98.9	89.5	101.3	114.2	85.3	74.3	92.5	80.8	126.0	119.8
2	5	39.7	33.1	67.7	64.0	95.0	79.9	49.0	51.4	94.1	73.6	108.9	84.7
3		45.0	43.3	74.2	60.6	78.5	73.5	67.2	59.5	97.9	93.3	100.3	91.2
4		103.7	95.6	119.2	119.4	86.6	106.8	142.1	121.2	128.7	118.8	103.1	93.0
5		74.8	46.4	85.0	62.0	94.8	77.3	121.0	56.7	108.1	68.6	120.4	70.0
6			75.0		76.9		100.9		99.3		86.0		83.0
Sulfamate:													
1	5	[3] 112.0	107.4	111.2	108.7	90.3	109.6	96.1	96.5	103.7	102.8	105.1	101.6
2	10	[3] 1.9	[3] 3.0	45.4	22.0	35.7	51.3	[3] 5.2	[3] 3.6	47.7	28.2	56.5	49.5
3		15.2	6.7	144.8	144.0	109.3	139.2	34.6	21.0	96.5	88.1	82.1	87.9
4		19.6	12.4	53.6	8.8	39.8	8.0	45.9	31.3	55.6	20.1	55.7	25.5
5		18.4	44.2	25.7	76.4	51.5	86.5	48.1	60.0	28.4	62.5	52.8	58.6
6			41.5		95.7		106.0		109.7		102.5		94.5

Borax:													
1	20	0	0	4.9	10.0	7.3	------	0	0	4.6	5.8	10.9	17.4
2	------	0	0	0	[3] 2.6	[3] 3.6	[3] 4.0	0	0	8.1	5.4	20.2	13.0
3	------	[3] 6.0	[3] 7.3	[3] 5.0	[3] 9.2	9.1	21.3	[3] 5.0	[3] 9.0	15.2	[3] 10.2	17.3	[3] 27.4
4	------	13.6	[3] 17.9	24.0	26.1	34.2	28.4	[3] 11.8	[3] 21.4	[3] 35.4	27.7	30.4	23.6
5	------	[3] 12.0	3.3	15.0	4.7	19.9	12.4	[3] 10.4	[3] 2.4	13.7	[3] 2.4	27.3	8.2
6	------	------	5.4	------	5.9	------	9.4	------	9.4	------	11.1	------	23.7
		AVERAGE GREEN WEIGHTS OF CONTROL PLANTS (IN GRAMS)											
None:													
1	------	3.08	3.26	3.57	4.46	3.92	3.94	1.77	2.02	1.87	2.13	1.77	1.87
2	------	3.26	4.11	3.81	4.92	4.03	4.83	2.10	2.43	2.22	2.69	2.14	2.75
3	------	3.03	1.90	3.08	2.81	5.00	4.22	2.32	1.90	2.88	2.70	3.02	2.88
4	------	2.45	1.79	3.70	2.40	4.03	2.47	1.87	1.50	2.84	1.91	3.03	2.27
5	------	1.51	3.60	1.91	3.82	2.37	3.53	1.00	3.00	1.35	2.77	1.37	2.90
6	------	------	5.20	------	5.77	------	4.67	------	2.67	------	2.79	------	2.53

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[1] The growing periods for each crop were: 1, Oct. 21 to Dec. 3, 1943; 2, Dec. 21 to Feb. 7, 1944; 3, Feb. 10 to Mar. 24; 4, Mar. 25 to May 6; 5, May 17 to June 19; 6, Oct. 2 to Nov. 7, 1944. A commercial fertilizer (90 gm. of 5-8-5, a surface-area rate of 1,245 pounds per acre) was added to the duplicate plots, i.e., to those numbered 2, 6 days before sowing of the fifth crop.

[2] Average green weights of about 40 plants (except where noted otherwise by footnote 3) expressed as percentages of corresponding weights of a similar number of control plants from plots with the same reaction but not treated with a herbicide.

[3] Stand much reduced; injury greater than indicated by the figures.

Ammonium thiocyanate was lethal to barley and either lethal or highly injurious to oats at all three reactions. Chlorate was similarly toxic. Sodium arsenite was much less so, producing no injury at all in the alkaline plots, and ammonium sulfamate was not toxic at any reaction, so additional applications of these two were made for the second sowings—5 gm. of the arsenite, making a total of 10 gm. in the plots, and 10 gm. of the sulfamate, making a total of 15 gm. But even with these increased dosages, the figures for the second crops show that the arsenite was still much less toxic than the chlorate remaining in nearby plots; sulfamate also was much less toxic in all but the acid plots.

By the time these second crops were sown, 2 months after the first, chlorate toxicity had not changed appreciably, whereas thiocyanate toxicity was not only gone at all three reactions but the plants were generally more vigorous than the controls. This stimulation in the thiocyanate plots was even more pronounced for the third cropping; however, by the fifth the plants were generally about the same size as the controls, presumably because the extra nitrogen was gone. Chlorate, on the other hand, remained very toxic to barley throughout the five croppings, but its concentration in the acid plots became sufficiently reduced to permit normal growth of oats, the more resistant crop. Comparison of the figures for the two crops confirms the previous finding (*15*) that barley is the more susceptible.

From the standpoint of persistence, borax was the outstanding herbicide, as in the preceding experiment. It was most toxic in the acid soil and least in the alkaline. It should be noted that these greenhouse experiments agree with field observations in indicating the necessity of an application of borax about four times that of chlorate for equal initial killing power.

The initial toxicity of ammonium sulfamate (i.e., toxicity after the dosage was increased to 15 gm. for the second cropping) was followed, in the neutral and alkaline plots, by a period of only slight toxicity (oats) or actual stimulation (barley) of the plants of the third crop. Both oats and barley of the fourth and fifth crops showed considerable injury, but by the time the sixth crop was growing there was no appreciable toxicity except to barley in the acid soil.[4]

The general tendency of the herbicides to be most injurious in acid soil and least injurious in alkaline soil is shown graphically in figure 5. Ammonium sulfamate toxicity was greatest in the acid plots and was reduced by liming the soil to alkalinity, but the nearly neutral plots were not always intermediate. This lack of regularity seemed to result from discrepancies between the degrees of injury characterizing plants in duplicate plots, suggesting a rather large difference in the toxic action of the chemical in response to differences in environment at the two ends of the greenhouse. For instance, the figures for the fourth crop, given in table 3, show much more injury

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[4] To crops of a final test, sown 4 months after the sixth cropping, i.e., 16 months after the herbicide applications, the sulfamate was no longer toxic in this soil. Plants in the chlorate plots still showed leaf-tip firing, but were not stunted. There was no significant change in the plants in the arsenite and borax plots.

in the plots of the north end of the greenhouse (numbered 2) than in the duplicates at the more shaded south end.

The growth stimulation that followed disappearance of thiocyanate toxicity was most pronounced in the acid soil and least in the alkaline.

It is noteworthy that reductions in toxicity of the herbicides were brought about in this experiment by applications of lime that benefited the barley plants, as shown by the size of the control plants, while similar effects were obtained in the preceding experiment (table 2) with applications of sodium bicarbonate that were injurious. Therefore, the correlations of herbicide injury with pH values are not attributable to effects of soil acidity on plant vigor.

The weights of the plants from some of the control plots of the third croppings dropped to such low levels as to indicate exhaustion of some of the soil nutrients. So 90 gm. of a 5–8–5 commercial fertilizer were thoroughly mixed into the 200-pound lots of soil in the duplicate plots (numbered 2), just before the fifth crop was sown. The control plants of this fifth crop (table 3) were usually at least twice as large in the fertilized as in the unfertilized plots. Increased fertility and the resulting more vigorous growth did not produce any significant effect either on the toxicity of chlorate or on that of thiocyanate. In the case of sulfamate there was less injury in the fertilized than in the unfertilized plots, shown by the appearance of the plants as well as by differences in the growth percentages, whereas borax seemed to be more toxic in the fertilized than in the unfertilized plots.

The toxicity of a new lot of sodium arsenite (Merck's reagent grade) in limed (pH 7.2) and unlimed (pH 4.9) soil, in comparison with that of sodium chlorate and the two thiocyanates (ammonium and sodium), was checked in another experiment in the spring of 1945. The applications, to 200 pounds of soil, were 5 gm. of chlorate and of the thiocyanates and 10 gm. of arsenite. Barley plants from the limed and unlimed plots, cut a month after the date of sowing, were reduced by the chlorate to 21.3 and 13.8 percent, respectively, of the size of the controls, as compared with 59.2 and 30.4 percent for the plots treated with twice as much arsenite. The plants in all the thiocyanate plots died just after emergence.

This experiment confirmed the indication of the larger experiment, that sodium arsenite is much less toxic than chlorate in this soil, and that, like chlorate, its toxicity is reduced by liming. That chlorate was so much less toxic here than in the experiment summarized in table 3 is to be attributed to much higher greenhouse temperatures, as compared with those in the winter months when the first crops of the larger experiment were grown. This effect of temperature on chlorate toxicity has been discussed previously (*15*).

COMPARATIVE EFFECTS OF AMMONIUM AND SODIUM THIOCYANATES ON PLANTS IN LIMED AND UNLIMED SOIL

To 200-pound lots of soil (pH 5.1) slaked lime was added at two rates, 125 and 350 gm., raising the pH to 6.8 and 7.7, respectively. After a 10-day period, during which the soils were kept moist and stirred several times, one plot of each reaction was treated with 5 gm. of ammonium thiocyanate, and a parallel series was treated with 5.3

gm. of sodium thiocyanate, a quantity that supplied an equal amount of SCN. Both chemicals were applied to the soil in 3 liters of solution, which was followed immediately by an additional 2 liters of water. A third series of plots was treated similarly with 5-gm. applications of sodium chlorate, and a fourth (the control plots) was made equally wet with applications of water alone. Two days after these treatments the plots were given the usual thorough mixing and sown with barley and oats in alternating rows. The growth of three successive crops of seedlings in these plots is summarized in table 4.

TABLE 4.—*Toxicity and after effects of equivalent quantities of thiocyanate as ammonium and sodium salts, in comparison with chlorate, applied to soil adjusted with slaked lime to different reactions*

[Herbicides applied November 6, 1944]

Crop	Growth period 1944-45	Herbicide	Barley at— pH 5.1	Barley at— pH 6.8	Barley at— pH 7.7	Oats at— pH 5.1	Oats at— pH 6.8	Oats at— pH 7.7
			Growth percentages[1] for herbicide-treated plots					
1	Nov. 8-Dec. 14	NH_4SCN	0	0	0	0	0	0
		NaSCN	0	0	0	0	0	0
		$NaClO_3$	0	0	0	0	0	0
2	Dec. 16-Jan. 29	NH_4SCN	0	125.3	128.1	0	152.5	110.6
		NaSCN	0	129.2	110.1	0	133.5	100.8
		$NaClO_3$	0	0	0	0	0	0
3	Feb. 1-Mar. 15	NH_4SCN	189.2	133.9	108.4	161.0	122.5	102.6
		NaSCN	184.1	110.3	105.1	146.8	108.2	104.2
		$NaClO_3$	0	0	0	6.0	8.5	9.0
			Average green weights of control plants (in grams)					
1	Nov. 8-Dec. 14	None	0.78	0.78	0.86	0.46	[illegible]	0.43
2	Dec. 16-Jan. 29	do	.79	.79	1.00	.45	.37	.53
3	Feb. 1-Mar. 15	do	1.05	2.24	2.87	2.22	2.13	3.08

[1] Average green weights of about 40 plants expressed as percentages of corresponding weights for control plants from soil of the same reaction.

Both thiocyanates killed all the plants of the first crop soon after they emerged. Sodium chlorate was similarly lethal, permitting no growth at any reaction.

Six weeks after the applications the plots were resown. This time the thiocyanates were lethal in the unlimed plots only. In the limed plots both had decomposed to such an extent that there was no sign of toxicity. In the moderately limed plots both thiocyanates had so stimulated growth that the green weights were at least 25 percent higher than those of the control plants. In the heavily limed plots there was similarly marked stimulation of barley. Sodium chlorate was still lethal at all reactions.

For the third crop, sown 3 months after the applications, there was no toxicity in any plot. The acid plots that were lethal to plants of the sowing made 6 weeks before this one had now produced plants averaging from 47 to 89 percent larger than their controls, a greater degree of stimulation than was obtained in any of the other plots. The sodium chlorate plots remained lethal to barley and highly injurious to oats.

Of special interest was the similarity in the behavior of the two thiocyanates throughout the experiment. Evidently the stimulation that so consistently follows injury in ammonium thiocyanate plots cannot be attributed to ammonium nitrogen, since similar degrees of stimulation were here obtained with the sodium salt.

Comparative Effects of Sodium and Calcium Alkalies on Borax Toxicity

The data in table 2 showed that making the soil alkaline with sodium bicarbonate reduced the toxicity of borax as effectively as did slaked lime in the experiment summarized in table 3, thus disagreeing with the observation (5) that the toxicity of boron is not reduced by sodium-containing alkalies but only by those of calcium and magnesium that could precipitate the boron as more difficultly soluble borates.

To obtain additional evidence on this point different lots of an acid borax-treated soil were given applications of calcium and sodium carbonates and of slaked lime. Into 5 kg. of air-dry soil was mixed 1 gm. of borax, then the alkalies were added dry. After being moistened with 700 cc. of water, each lot of soil was mixed again and distributed into three 6-inch pots, so that there were triplicate cultures for each treatment. Positions of the pots on the greenhouse bench were rotated according to a plan to insure similar environmental conditions for the different treatments.

The comparative effects of various alkalies on the pH of the soil and on the toxicity of the borax are shown in table 5. The data include a record of leaf symptoms and of the green weights of 7-week-old plants of barley, and of 9-week-old plants of oats sown as a second crop in the same pots after a thorough mixing and redistributing of the soil of the triplicate cultures.

TABLE 5.—*Comparative effects of sodium and calcium alkalies on borax toxicity*

FIRST SOWINGS—BARLEY

Application of alkalies to 5 kg. of soil	Borax-treated pots				Control pots—no borax		
	Condition of leaves	Green weight of 25 plants (grams)	pH Initial	pH Final	Green weight of 25 plants (grams)	pH Initial	pH Final
None	Dead	0	5.3	5.1	25.3	5.2	5.2
$Ca(OH)_2$—24 grams	Very chlorotic	2.6	7.6	7.5	22.0	7.5	7.7
$Ca(OH)_2$—12 grams	do	2.8	7.6	7.4	21.3	7.4	7.5
$CaCO_3$—24 grams	do	2.9	7.6	7.5	28.8	7.3	7.6
Na_2CO_3—12 grams	Green	2.2	8.8	8.4	0	8.6	8.4
$NaHCO_3$—12 grams	Chlorotic	3.2	8.0	7.6	17.5	8.0	7.7

SECOND SOWINGS—OATS

Application of alkalies to 5 kg. of soil	Condition of leaves	Green weight of 25 plants (grams)	pH Initial	pH Final	Green weight of 25 plants (grams)	pH Initial	pH Final
None	Dead	0	5.1	5.3	13.7	5.2	5.5
$Ca(OH)_2$—24 grams	Pale green with necrotic spots	20.1	7.5	7.0	21.4	7.7	7.0
$Ca(OH)_2$—12 grams	do	25.8	7.4	6.9	23.7	7.5	6.9
$CaCO_3$—24 grams	do	28.8	7.5	7.0	22.0	7.6	6.9
Na_2CO_3—12 grams	Green; fired leaf tips	29.0	8.4	7.0	10.9	8.4	7.0
$NaHCO_3$—12 grams	Pale green with necrotic spots	30.9	7.6	6.5	15.4	7.7	6.6

That the carbonates of sodium were as effective as the calcium alkalies in reducing the toxicity of borax, which was always lethal except where an alkali had been added, is shown in table 5 and figure 6. Sodium carbonate produced the greatest improvement in the color of the borax-injured plants of both crops. It is probably significant that this carbonate also produced the greatest degree of alkalinity in the soil. Certainly the results of this experiment give no support to the idea that increasing the soil pH reduces borax toxicity only when the alkalizing agent contains calcium or magnesium.

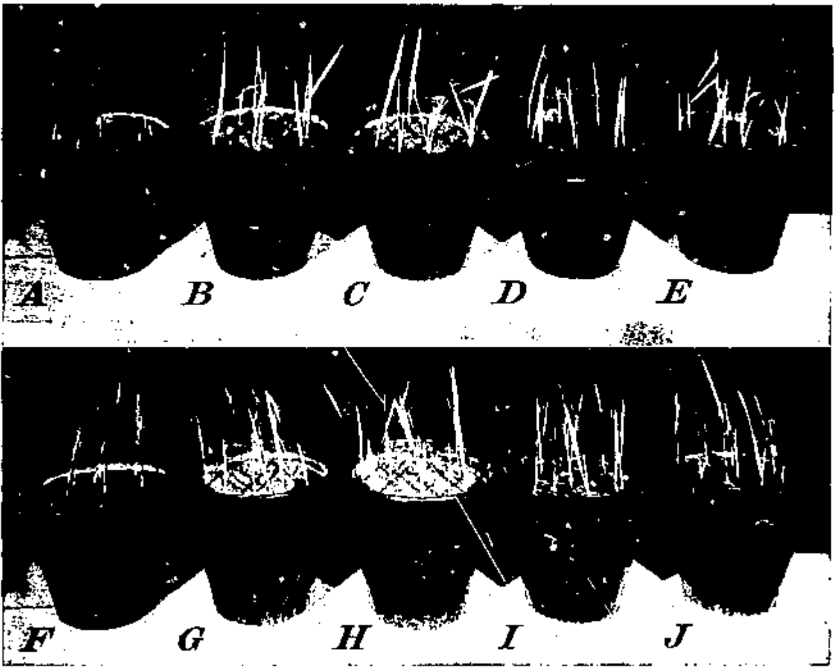

FIGURE 6.—Reductions in borax toxicity by sodium and calcium alkalies. *A* to *E*, borax-injured plants grown with: *A*, no alkali, pH 5.3; *B*, calcium hydroxide, pH 7.6; *C*, calcium carbonate, pH 7.7; *D*, sodium carbonate, pH 8.1; *E*, sodium bicarbonate, pH 7.7; *F* to *J*, control plants from corresponding alkali-treated soils without borax.

INCREASE IN BORAX TOXICITY BY ADMIXTURES OF SULFUR

The tendency of the various herbicides to be most toxic, hence most effective as weed killers, in the acid plots suggested the possibility of increasing their toxicity by admixture of sulfur as an acidifying agent. The idea was tried out with borax in the following experiment, in which the toxicity resulting from applications of borax-sulfur mixtures is compared with that of the same quantities of borax applied alone.

The soil used had been adjusted from an original pH 4.5 (soil 1) to neutrality with slaked lime 10 months previously (soil 2); and to alkalinity (soil 3) with another recent application of lime, thoroughly mixed and allowed to stand moist a week, with several turnings. The soil was then weighed into 6-inch pots, each containing 2 kg. To some was added borax alone at the rate of one-third gram per plot; to others, the same quantity of borax mixed with 5 gm. of sulfur. Controls were a third group, receiving the sulfur application alone, and a fourth group, receiving no treatment. Each treatment and each control was triplicated.

Two days after these treatments sorgo was sown (May 20). The soil was kept uniformly moist (about 19 percent) throughout the experiment. After about 3 weeks, the seedlings were cut and weighed. Comparative degrees of injury are shown by the growth percentages for two duplicate series, A and B in table 6, and illustrated by figure 7.

TABLE 6.—*Comparative toxicity of borax and a borax-sulfur mixture to sorgo in greenhouse pot cultures*

[Each figure is an average for about 20 plants from 3 pots]

Soil No.	Application	Soil pH	Growth percentages[1] for borax-treated plots				Average weights of control plants without borax	
			First cutting (June 9)		Second cutting (June 23)		First cutting (June 9)	Second cutting (June 23)
			A	B	A	B		
			Percent	*Percent*	*Percent*	*Percent*	*Grams*	*Grams*
1	Borax	4.5	28.2	25.6	20.0	13.1	0.39	1.75
2	do	7.0	62.5	56.3	40.0	33.9	.32	1.10
2a	Borax + sulfur	4.3	11.0	---------	7.2	---------	.42	1.25
3	Borax	7.7	67.7	74.2	53.8	42.4	.31	1.06
3a	Borax + sulfur	5.8	17.8	---------	8.2	---------	.45	1.82

[1] Average green weights of about 20 plants expressed as percentages of corresponding weights of the control plants in the last two columns.

No sulfur could be added to soil 1, because it was already too highly acid; however, the figures showing borax injury to the plants in this soil are included in table 6 because comparison with the data for corresponding plants in the neutral and alkaline soils without sulfur (soils 2 and 3) again demonstrated the direct relation of soil acidity to borax toxicity that appeared in the data of tables 2 and 3.

The sulfur applications greatly acidified the soil and greatly increased the toxicity of the borax (table 6). It can be assumed that there was a higher concentration of boron in the acidified soil solution as a result of less fixation of the boron (*12, p. 20*). That there was no injury from the sulfur itself nor from the acidity it produced is shown by the weights of the control plants without borax in the last two columns of table 6. In fact, these weights and the appearance of the plants (fig. 7) show that growth of the plants without borax was actually improved by the sulfur.

REDUCTION IN CHLORATE TOXICITY BY VARIOUS NITROGENOUS FERTILIZERS IN RELATION TO SOIL REACTION

Other experiments were conducted primarily to determine the extent to which the toxicity of residual chlorate, following its use for

FIGURE 7.—Increase in borax toxicity brought about by admixture of sulfur: Plants with (*A*) no treatment; (*B*) borax alone; (*C*) borax plus sulfur; (*D*) sulfur alone.

weed control, can be reduced by various nitrogenous fertilizers in soil adjusted to different reactions. It was known from tests in both soil and water cultures that chlorate toxicity is affected by the concentration of available nitrate and that ammonium nitrogen seems to have a similar action in soils but not in water cultures (*8*, *16*), indicating dependence of the effect on conversion to nitrate. Because the effect on chlorate toxicity of nitrogenous compounds other than nitrate would therefore be expected to depend on the nitrifying power of the soil, and this power to vary with the soil's acidity (*20*, *28*), it seemed desirable to compare their effects in soil adjusted to different reactions.

For the following experiments (summarized in tables 7 to 9) a lightly composted Keyport clay loam of Arlington Farm, Rosslyn, Va., with a slightly acid reaction (pH 6.5) was used.

Sodium chlorate was added in solution to the 200 pounds of soil in each plot. After it was thoroughly mixed into the entire soil mass, the nitrogen compounds, except Cyanamid, were added in solution and thoroughly mixed into the soil. Cyanamid[5] was dusted on the surface and then mixed into the entire soil mass, and water was added in quantity equal to that of the solutions applied to the other plots. For every chlorated plot there was a control plot having the same reaction and nitrogen treatment but no chlorate.

A preliminary test was made to determine the extent to which nitrate applications could be expected to reduce chlorate toxicity in this soil, which probably had a considerable nitrate content to begin with. The results showed clearly that calcium and sodium nitrate, applied at rates (21 and 20.3 gm., respectively, in 200 pounds of air-dry soil) supplying equal concentrations of nitrate, produced definite and similar effects. Where no nitrate was added, the chlorate reduced the size of the barley plants to 18.7 percent of that of the plants in corresponding plots receiving no treatment, compared with 29 percent where sodium nitrate was added with the chlorate, and 32.0 percent where calcium nitrate was used.

In a test carried out with similar applications in other chlorated plots (7.8 gm. sodium chlorate in 200 pounds of soil) sorgo plants were killed where no nitrate was added, but they were 8.4 and 6.6 percent of normal size in duplicate plots receiving sodium nitrate applications, and 6.3 and 6.7 percent in those given the calcium salt. It seems, therefore, that it is immaterial whether sodium or calcium nitrate is used, the effect on chlorate toxicity depending on the concentration of nitrate. This is in accord with a previous finding that the calcium ion has no effect on chlorate toxicity (*16*).

Effects of sodium nitrate in comparison with ammonium sulfate, urea, and Cyanamid were then tested in similar plots of this slightly acid soil that had been treated with sodium chlorate (7.8 gm. in 200 pounds of soil). Such quantities of the nitrogenous materials were used as would give equal concentrations of nitrogen, 5.4 gm. per plot. The percentages of nitrogen in sodium nitrate, ammonium sulfate, urea, and Cyanamid being 16.5, 21.2, 46.7, and 22.5, respectively, the quantities of each compound required were 32.7, 25.5, 11.6, and 24.0 gm., in the order named.

Seed of the first crop of sorgo was sown 5 days after the application of the nitrogen fertilizers to the soil. Between each of the three successive crops comprising the experiment the soil was thoroughly

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[5] Cyanamid, the commercial product, contained about 63 percent calcium cyanamide, 17 percent lime, 12 percent carbon, and 8 percent of other impurities (*22*). Calcium cyanamide is unstable and easily polymerizes in storage and in the soil to dicyanodiamide, which is not readily nitrified (*31*).

remixed in order to restore a uniform vertical distribution of the chemicals.

TABLE 7.—*Growth percentages*[1] *for month-old sorgo plants, showing comparative effects of calcium cyanamide, urea, ammonium sulfate, and sodium nitrate, supplying equal quantities of nitrogen, on the toxicity of sodium chlorate in a slightly acid soil*

Crops and dates (1941)	Bench No.	Form of nitrogen added to chlorated soil				
		None	Cyanamid	Urea	Ammonium sulfate	Sodium nitrate
		Percent	*Percent*	*Percent*	*Percent*	*Percent*
1. May 19–June 13	1	4.1	9.2	16.4	19.7	18.6
	2	4.5	9.5	17.4	18.5	19.1
2. June 13–July 11	1	26.2	46.1	56.6	61.1	53.2
	2	23.4	47.3	54.2	59.1	51.9
3. July 11–August 6	1	91.7	106.0	131.4	133.3	111.6
	2	106.2	97.2	105.6	110.8	105.5

[1] Average green weights of 80 to 90 plants, expressed as percentages of the average weights of control plants from similarly fertilized plots without chlorate.

The results, summarized in table 7, show that in the plots receiving chlorate but no added nitrogen, weights of the plants of the first crop were but 4 percent of those of the controls in the untreated plots without chlorate. Plants in the chlorated plots that had received Cyanamid, urea, ammonium sulfate, and sodium nitrate, respectively, were all less injured, improvement being least in those receiving Cyanamid. By the time the second crop was harvested toxicity was much less in all the plots, as shown by increased growth percentages, but again Cyanamid made the poorest showing as an inhibitor of the injurious effects of the chlorate. By the third sowing, only 2 months after the first, toxicity had disappeared from all the plots, as shown by growth percentages near 100, or over, and by nonappearance of leaf symptoms. The average growth percentages for the three crops are shown graphically in figure 8.

That none of the effects of nitrogen on chlorate toxicity were due to improved nutrition was shown by the weights of control plants, which throughout the experiment were slightly higher in the plots receiving no nitrogen.

It having thus been determined that all the nitrogen compounds tested would reduce chlorate toxicity in a slightly acid soil (pH 6.5), there remained the question whether acidification of the soil to a point unfavorable for the activity of nitrifying organisms would prevent or postpone the reduction in chlorate toxicity produced by such potential sources of nitrate as ammonium sulfate and Cyanamid. To acidify the soil, 400 cc. of sulfuric acid, diluted tenfold, was poured on 200 pounds of soil, followed immediately by 1 gallon of water. After the soil had dried sufficiently it was thoroughly mixed by turning at least five times. The pH value of a 1:1 water extract, determined colorimetrically, was always well below 5, the exact values being given in the tables.

Limed plots also were included to determine possible effects of alkalinity. Three-fourths of a pound of slaked lime ($Ca(OH)_2$) was added to each 200-pound lot of soil and thoroughly mixed. The pH

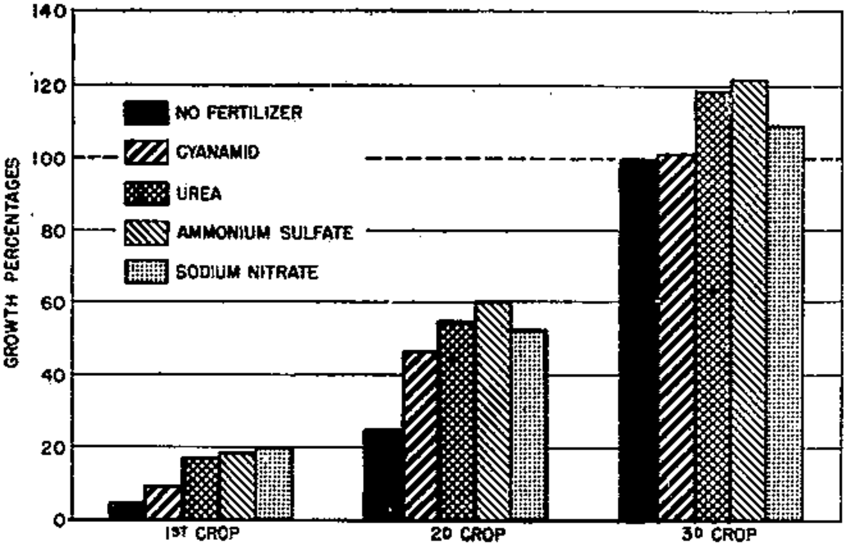

FIGURE 8.—Chlorate toxicity as affected by various nitrogenous fertilizers. Bars represent average growth percentages (from table 7), showing comparative toxicity and persistence of sodium chlorate to three successive crops of sorgo grown over a 3-month period in nearly neutral soil with and without various nitrogenous fertilizers. Dotted line represents weights of control plants from plots with the same fertilizer treatments but without chlorate.

value of a 1 : 1 water extract, determined colorimetrically, was thereby increased from near 6.5 to 7.9 in one experiment (table 8) and to 7.5 in another (table 9).

A week after these reaction adjustments, during which the soil was thoroughly stirred and restirred, sodium chlorate was added in solution at the rate of 5.2 gm. per plot. After three more days, during which the soil was again thoroughly mixed several times, the nitrogenous fertilizers were applied at the same rate as in the preceding experiment, so that each supplied 5.4 gm. of nitrogen per plot.

The growth of three successive crops of barley, each cut after 1 month, is summarized in table 8. To the plants without added nitrogen the chlorate was very toxic in the first sowing, much less so in the second, and harmful to the third in the limed plots only.

The application of sodium nitrate reduced toxicity to about the same degree at all three soil reactions, practically doubling the growth percentages, as compared with the chlorated plots not treated with sodium nitrate, in both the first and second sowings. By the third sowing the chlorate had decomposed in the acid plots, leaving them nontoxic (as shown by growth percentages of 100 or more); but in the alkaline plots, toxicity still persisted and the ameliorating effect of nitrate was still apparent.

Ammonium sulfate reduced chlorate toxicity in the slightly acid and in the alkaline soils as promptly and effectively as did sodium nitrate. Evidently at these reactions enough ammonium was nitrified within the first few days after its application to reduce chlorate toxicity

TABLE 8.—*Effects of soil reaction on reduction of chlorate toxicity to young barley plants by nitrogenous fertilizers*[1]

Nitrogenous fertilizers added to chlorate-treated soil	Soil reaction		Growth percentages[2] for chlorated plots			Average green weights of control plants without chlorate		
	Initial	Final	Crop 1	Crop 2	Crop 3	Crop 1	Crop 2	Crop 3
	pH	*pH*	*Percent*	*Percent*	*Percent*	*Grams*	*Grams*	*Grams*
None	4.3	4.5	8.8	53.6	100.5	2.76	4.50	2.70
	6.5	6.4	18.5	51.5	101.8	3.25	6.32	4.05
	7.9	7.7	10.4	20.1	43.6	3.27	6.10	4.05
$CaCN_2$	4.3	4.0	7.2	52.1	87.2	3.19	4.02	3.46
	6.5	6.4	18.9	90.9	101.0	2.78	5.21	3.47
	7.9	7.8	11.3	34.5	58.9	4.02	5.64	3.71
$(NH_4)_2SO_4$	4.3	4.5	9.6	72.0	122.8	2.83	4.00	2.59
	6.5	5.9	30.3	103.3	105.0	3.03	5.42	3.88
	7.9	7.8	24.1	44.1	61.2	2.87	5.15	3.87
$NaNO_3$	4.3	4.6	18.5	95.1	120.4	2.60	4.10	2.29
	6.5	6.4	36.2	89.2	100.5	2.94	5.40	3.65
	7.9	7.7	22.8	44.1	66.5	2.77	5.24	3.37

[1] Soil reaction adjustments were made on Feb. 3, chlorate applied on Feb. 10, nitrogen compounds on Feb. 13, and the first crop sown on Feb. 21. Growing periods for the three crops were: 1, Feb. 21 to Mar. 25; 2, Mar. 26 to Apr. 23; and 3, Apr. 23 to May 20.

[2] Average green weights of about 50 plants, expressed as percentages of the average weights of control plants from similarly treated plots without chlorate.

to the very first crop as effectively as did the nitrate applications themselves. In the very acid soil, on the other hand, the ammonium had little if any effect on the first crop, presumably because nitrification was slow here with the result that the chlorate-injured plants, harvested 6 weeks after the application, gave little if any evidence of the treatment. By the time the second crop was harvested a month later, however, enough nitrate had evidently become available in these acid plots to improve markedly the condition of the chlorated plants, for the growth percentage was increased from 53.6 to 72.0 by the sulfate; but in the adjacent acid plot, given an equivalent application of nitrate, there was practically no toxicity, as shown by the percentage 95.1. By the time of the third sowing, chlorate toxicity had disappeared from all the plots except the limed ones.

That Cyanamid had no ameliorating effect on chlorate toxicity to plants of the first sowing at any soil reaction, indicating that it did not serve as a source of nitrate under any condition in the first 6 weeks of contact with the soil, is shown in table 8. By the time of the second crop, enough nitrate had evidently become available in the slightly acid and alkaline soils to cause a reduction in chlorate injury equal to that brought about by sodium nitrate, judging from the growth percentage of 90.9, as compared with 89.2 for the nitrate. But in the very acid soil the plants were still as severely injured as in the corresponding chlorated plot that had received no nitrogen, i.e., only 52.1 percent normal, as compared with 53.6 percent for the controls without added nitrogen.

Evidently there was not enough nitrate coming from Cyanamid in this acidified soil to be detected by its effect on chlorate toxicity. The fact that ammonium sulfate was producing a positive effect on chlorate toxicity in similarly acidified plots by this time indicates that nitrification was not completely inhibited by the acidity and suggests some hindering factor in the Cyanamid plots, possibly formation of dicyanodiamide or other decomposition products that not only are unavailable as sources of nitrate but also are highly toxic to at least some of the soil microorganisms (*1, 7, 11, 18, 24*).

The data for the first two crops of table 8 are shown graphically in figure 9.

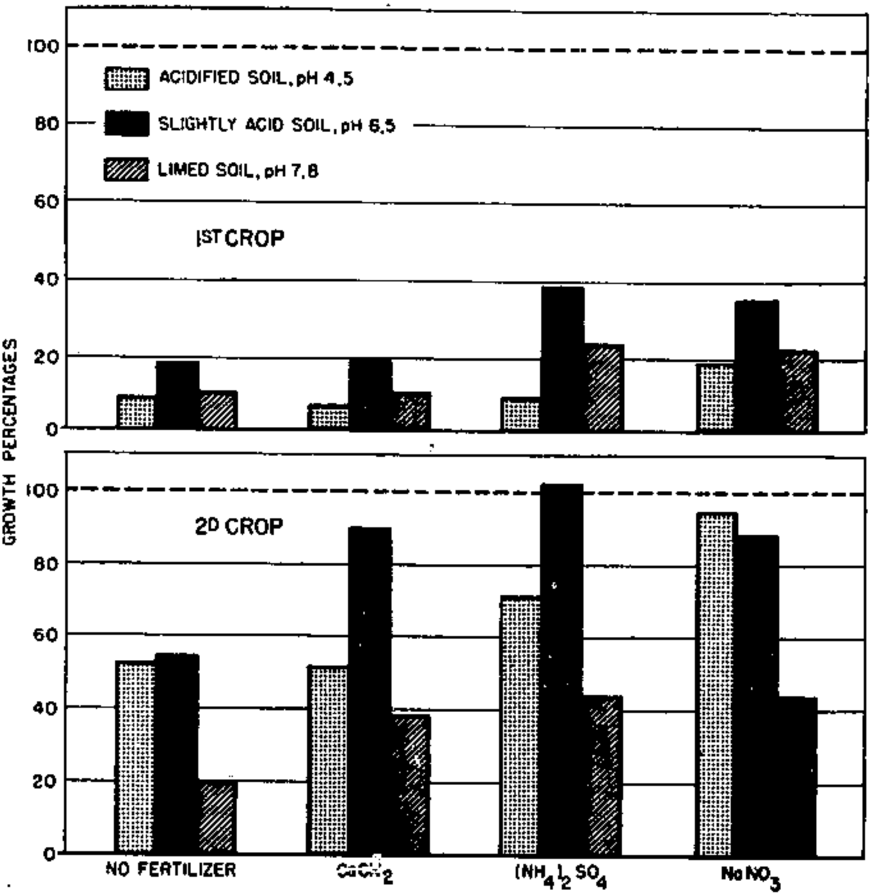

FIGURE 9.—Growth percentages of the first two crops summarized in table 8, showing effects of nitrogenous fertilizers on chlorate toxicity in acidified, naturally acid, and limed soils. Dotted line represents weights of control plants from plots of the same reactions and nitrogen applications but without chlorate.

A similar experiment with sorgo as the test plant is summarized in table 9. Chlorate was not so toxic to any of the plants here as in the preceding experiment, perhaps because of the higher temperatures prevailing at the later season.

Sodium nitrate was again effective in reducing chlorate toxicity to the first crop at all three soil reactions, while ammonium sulfate and Cyanamid were effective in the slightly acid and alkaline soils only. By the second sowing there was no evidence of chlorate toxicity in any of the plots except the limed ones, where, as before, severe injury persisted after it had disappeared elsewhere.

Presumably, presenting the weights of the chlorate-injured plants as percentages of weights of control plants from plots of the same acidity and nitrogen treatment compensates for effects of the nitrogen treatments and acidity adjustments themselves, and justifies the drawing of conclusions as to the effects of chlorate alone. But since questions may arise as to the possible effects of plant vigor on chlorate injury, absolute weights of the control plants receiving no chlorate are included in tables 8 and 9. These weights show that acidification of the untreated nearly neutral soil often reduced the size of the plants, as did liming also. In the case of barley, injury from acidity was greater than that from lime, but with sorgo this was not generally true. The sodium nitrate applications reduced the weights below those of plots of the same acidity with no added nitrogen, suggesting that the soil had a high-nitrate content initially. Had low-nitrate soil been used, effects of the nitrogen compounds on chlorate toxicity would no doubt have been greater.

TABLE 9.—*Effects of soil reaction on reduction of chlorate toxicity to young sorgo plants by nitrogenous fertilizers*[1]

Nitrogenous fertilizers added to chlorate-treated soil	Soil reaction		Growth percentages[2] for chlorate plots		Average green weights of control plants without chlorate	
	Initial	Final	Crop 1	Crop 2	Crop 1	Crop 2
	pH	*pH*	*Percent*	*Percent*	*Grams*	*Grams*
None	4.9	5.0	76.9	131.5	2.81	2.09
	6.5	6.6	70.4	133.2	3.31	2.07
	7.5	7.8	25.1	57.6	2.81	2.12
$CaCN_2$	4.9	5.2	70.0	109.5	3.07	2.18
	6.5	6.6	95.2	109.8	2.50	1.81
	7.5	7.7	51.0	70.5	2.08	1.64
$(NH_4)_2SO_4$	4.9	4.8	75.7	129.1	2.83	2.21
	6.5	6.4	90.1	102.9	2.86	2.50
	7.5	7.8	43.8	61.2	2.45	2.14
$NaNO_3$	4.9	5.1	96.2	129.5	2.26	1.83
	6.5	6.5	103.3	123.3	2.52	1.94
	7.5	7.8	50.8	58.6	2.06	1.67

[1] Soil reaction adjustments were made on Apr. 1, chlorate applied on Apr. 8, nitrogenous fertilizers on Apr. 11, and the first crop sown on Apr. 17. Growing periods for the two crops were: 1, Apr. 17 to May 15; 2, May 16 to June 17.

[2] Average green weights of about 80 plants, expressed as percentages of the average weights of control plants from similarly treated plots without chlorate.

DISCUSSION

It is recognized that such greenhouse tests as those here reported have limited applicability to field conditions because of the absence of leaching. For the same reason, however, they permit more exact determination of comparative rates of disappearance of herbicides from the treated soils through chemical and biological means, independent of mechanical removal, than would be possible in the field.

The experiments have demonstrated a general tendency for all the six herbicides tested—borax, ammonium and sodium thiocyanates, ammonium sulfamate, sodium arsenite, and sodium chlorate—to be most toxic in acid soil and least toxic in soil made alkaline with either slaked lime or sodium bicarbonate. This relation was not always so pronounced with chlorate as with the others, and in fact usually disappeared after the first few months, owing apparently to relatively slow decomposition in alkaline soil, as discussed previously (*17*), and sometimes in highly acid soil also (fig. 3).

Borax was included in the experiments because it had received some consideration as a possible herbicide (*2*, *6*, *10*, *14*, *35*). It was most toxic in the acid plots and least in the alkaline, which is in accord with the several reports indicating that boron tends to become "fixed" in limed soils. In several experiments not here described, with solution cultures adjusted and held at reactions similar to those of the soil plots, no evidence of a relation between the pH value and borax toxicity could be found, indicating dependence of the relation on a soil factor. This factor can be assumed to be the capacity of soil constituents to reduce the availability of boron to plants either by ionic exchange, molecular adsorption, or chemical precipitation, as summarized by Eaton and Wilcox (*12*). These writers, by leaf analyses and estimates of plant injury, show that the greater the boron-fixing power of the soil the less the boron intake of the plants.

There are many reports and suggested explanations of decreasing availability of boron to plants as soil acidity decreases (*5*, *12*, *19*, *21*, *23*, *25*, *29*, *30*, *34*, *36*). The only contribution of the present investigation on this point bears on the suggestion (*5*) that reduced availability of boron to plants in alkaline soil may be due to the formation of difficultly soluble borates, such as those of calcium and magnesium, a suggestion based on failure to obtain with sodium carbonate the same reduction in toxicity of borax that was obtained with calcium and magnesium carbonates. But in the present experiments, the reductions in boron toxicity brought about by sodium carbonate and bicarbonate were as marked as those obtained with calcium-containing alkalies (tables 2 and 5). Midgley and Dunklee (*21*) also have reported as much fixation of boron in soil treated with sodium as with calcium carbonate. That the nature of the base is of secondary importance is also indicated by the work of Eaton and Wilcox (*12*), who conclude that the change in boron availability following the application of lime to acid soils is a function of the change in pH value or of some variable to which hydrogen-ion measurements provide an index, a conclusion that is supported by the evidence of the present investigation.

A characteristic of the toxicity of borax that is important in considering its herbicidal value is its tendency to persist in the soil, as contrasted with the disappearance of such compounds as chlorates, and especially of thiocyanates. This tendency of borax toxicity to persist longer than that of chlorate has been noted by others also (*2*, *9*). Unless there is assurance of sufficient leaching to remove it from the root zone of crops, present evidence indicates that borax should not be applied to agricultural land in the quantities necessary for weed control. Its best use would seem to be in places where permanent soil sterility is desired—as on roadsides, railroad tracks, ditch banks, and levees.

In marked contrast, thiocyanate toxicity disappeared within 2 or 3 months from all the treated plots, and in about a month from those of neutral or alkaline reaction. In one experiment not here reported, toxicity of a treated soil, so great initially as to prevent growth of plants, disappeared after 20 days in neutral soil and 40 days in acid soil (pH 5.4). Adequate dosages for killing weeds will apparently have to be greater for limed or probably for any alkaline soil than for acid soils. Certainly the characteristics of extreme initial toxicity followed by rapid decomposition and stimulation of succeeding crops suggest outstanding advantages of the thiocyanates for some situations (*3*, *13*, *27*, *32*).

Sodium arsenite and ammonium sulfamate were much less toxic than ammonium and sodium thiocyanates and sodium chlorate. Whereas 5 gm. of thiocyanate or chlorate were generally lethal, equal applications of the arsenite were only moderately injurious in the acid plots and had no toxic effect in the alkaline plots, and the sulfamate was nontoxic at all reactions. Even when the dosages of arsenite were doubled and those of sulfamate tripled for second sowings, the soil still showed much less toxicity than that persisting from the initial applications of chlorate in adjacent plots. Both sodium arsenite and ammonium sulfamate tended to be most toxic in acid and least toxic in alkaline soil.

The experiments on inhibition of chlorate toxicity by applications of nitrogenous fertilizers show that soil reaction is a factor affecting the extent to which chlorate toxicity can be reduced by nitrogen compounds other than nitrate. Whereas nitrate was immediately effective in all the plots, ammonium sulfate was immediately effective only in the slightly acid and alkaline plots, the first evidence of its presence in the strongly acid plots appearing with second croppings sown at least a month after the applications. These findings are in accord with our knowledge that nitrate but not ammonium nitrogen reduces chlorate toxicity (*8*, *16*) and that the rate of nitrification varies directly with the pH value of the soil (*20*, *28*), being much reduced at values as low as those of the most acid plots, which were near pH 4.3 initially.

The fact that Cyanamid had no effect on chlorate toxicity in the strongly acid plots is consistent with the finding (*22*) that the nitrogen of calcium cyanamide is little used by plants when the soil is below pH 5. There is evidence that it is nitrified more slowly than urea and ammonium sulfate (*1*, *7*, *11*, *18*). Apparently its ammonification proceeds rapidly; but oxidation of the ammonia to nitrate is much slower than when the source of the ammonium is ammonium sulfate or urea (*11*), because it, or some of its decomposition products —such as dicyanodiamide, which forms by polymerization of calcium cyanamide under certain conditions—is toxic to nitrifying organisms (*1*, *7*, *11*, *18*, *24*). The formation of dicyanodiamide not only locks the nitrogen of cyanamide in less available form but inactivates nitrifying bacteria to such an extent that it may even inhibit nitrification of other sources of nitrogen in the soil.

The degree of inhibition of chlorate toxicity obtainable from nitrogenous fertilizers may be too small to be economically feasible unless the application is also needed for its fertilizer value. Perhaps it will prove to be more feasible to reduce residual chlorate by incorporating readily decomposable organic matter into the treated soil, a procedure suggested by the work of several investigators (*4*, *26*, *33*).

CONCLUSIONS

Under greenhouse conditions and in the absence of leaching, soil reaction, adjusted with sulfuric acid, slaked lime, and sodium bicarbonate, had a marked effect on the toxicity and persistence of soil applications of the herbicides tested—sodium chlorate, ammonium and sodium thiocyanates, sodium arsenite, ammonium sulfamate, and borax.

Initially all these herbicides were most toxic to plants in strongly acid soil, least toxic in alkaline soil, and intermediate in slightly acid or neutral soil. Residual toxicity to subsequent croppings did not always conform to this relation, notably in the case of chlorate, which, with the exception of one experiment, persisted longest in limed plots. In general, however, the toxicity of the herbicides persisted longest in acid soil, where their initial toxicity had been greatest.

Reduction in toxicity of sodium chlorate, ammonium thiocyanate, and borax was as marked when sodium bicarbonate was the alkalizing agent as when slaked lime was used. The bicarbonate was not tried with the other herbicides.

Sodium and calcium carbonates reduced borax injury similarly, thus demonstrating that the effect is not simply attributable to precipitation of boron as the difficultly soluble calcium borate.

Of the six compounds tested, sodium chlorate and the thiocyanates were most toxic, 5 gm. in 200 pounds of soil generally being lethal or nearly so.

Borax toxicity was the most persistent, there being no evidence of significant change after 36 months in the soil. Thiocyanates were least persistent, disappearing from all the plots within 3 months and from nonacid ones in half this time, or less.

Equivalent applications of sodium and ammonium thiocyanates were equally toxic and persistent, and their toxic and subsequent stimulating effects were similarly affected by the soil reaction.

Admixture of sulfur markedly increased borax toxicity, presumably because of the acidifying effect of sulfur on the soil.

Sodium nitrate mixed into chlorate-containing soil reduced the latter's toxicity at all soil reactions tested, i.e., from pH 4.3 to 7.9.

Ammonium sulfate reduced chlorate toxicity as promptly as did nitrates in slightly acid and in alkaline soils; but in strongly acid soils, below pH 5.0, its effect was delayed, presumably because of less rapid nitrification.

Cyanamid generally reduced chlorate toxicity fairly promptly in slightly acid and alkaline soils, but it had no effect in the strongly acid plots, even after several months.

The effect of the various nitrogen fertilizers in inhibiting chlorate toxicity, although great enough to leave no doubt as to the fact, was nevertheless too small to be of practical significance for an already fertile soil.

The results of this investigation suggest that the degree to which the various nitrogen fertilizers can inhibit chlorate toxicity depends on their ability to supply nitrogen as nitrate in the particular soil. Comparative effects of these materials at the different soil reactions were in accord with anticipated effects of soil reaction on nitrification.

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