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TOXICITY OF ARSENIC, BORAX, CHLORATE, AND THEIR COMBINATIONS IN THREE CALIFORNIA SOILS[1]

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INTRODUCTION

IN WEED CONTROL it is often desirable to apply two or more chemicals at the same time. Where, for example, both annuals and deep-rooted perennials occur, arsenic and chlorate combined may be used for complete sterilization. In such cases one must know the reciprocal effects of these reagents in order to use them with any assurance of success. This paper describes experiments designed to show the toxicity of three common herbicides used two and three at a time in three California soils.

TOXICITY STUDIES

Tests on the toxicity of sodium arsenite and sodium chlorate (*2*)[4] and sodium borate (*3*) used separately, in these soils have been published and the technique has been described. Briefly, it consists in growing indicator plants, Kanota oats in this case, in soil cultures in No. 2 cans. The chemicals being studied are added to the air-dry soil, dissolved in sufficient water to bring the soil to its field capacity. The cultures are then seeded and grown for 30 days, at which time the height and fresh weight of the indicator plants are recorded.

In the preliminary toxicity tests (*2, 3*) concentration series were used covering the complete range from 0 to 100 per cent toxic and beyond, so that cultures were included that showed no plant growth even after several croppings. In the present experiments two arbitrary growth levels were selected: the 50 per cent level at which growth was reduced to approximately one-half that of the untreated checks, and the 10 per cent level at which growth was correspondingly reduced to a low value. The concentrations used to produce growth at these two levels were derived from the original toxicity curves, the data from the first runs with the three chemicals being computed in terms of percentage of checks. Table 1 gives the values expressed as parts per million in terms of the air-dry soil. For the borax they have been converted to the hydrous form that contains 47 per cent water by weight.

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[4] Italic numbers in parentheses refer to "Literature Cited" at the end of this paper.

In these experiments the chemicals were applied in solution as the sodium salts—that is, sodium acid arsenite, $NaH_5(AsO_3)_2$; sodium tetraborate, $Na_2B_4O_7 \cdot 10H_2O$; and sodium chlorate, $NaClO_3$. These are the forms in which the chemicals are presented on the market and in which, consequently, they are most conveniently purchased for weed control. Other forms of the same toxic elements may readily be converted to this basis if their composition is known.

The letters *A, B,* and *C* are used for convenience in expressing results. *A* designates arsenic, expressed as As_2O_3 and applied as sodium acid arsenite; *B* hydrous sodium tetraborate; and *C* sodium chlorate.

TABLE 1

RATES OF APPLICATION OF ARSENIC, BORAX, AND CHLORATE GIVING 50 PER CENT AND 10 PER CENT GROWTH IN THREE CALIFORNIA SOILS

Soil type	Per cent growth	Arsenic (*A*) As_2O_3	Borax (*B*) $Na_2B_4O_7 \cdot 10H_2O$	Chlorate (*C*) $NaClO_3$
		p.p.m. in air-dry soil		
Yolo clay loam	50	300	300	100
	10	540	540	540
Fresno sandy loam	50	45	130	40
	10	140	240	200
Stockton adobe clay	50	100	700	36
	10	200	1,000	120

The plan of the experiments may best be explained in connection with the presentation of data in table 2. In addition to checks receiving only tap water, each soil at the two growth levels received each chemical in four concentrations as shown in the column headed "Rate." A value of 4 in this column represents an application equal to the whole amount required to reduce growth to the level designated. For instance, in Yolo clay loam at the 50 per cent growth level, opposite the rate 4 in the arsenic set, the crop was 16 cm in height and weighed 6.1 grams. This culture received 300 p.p.m. of As_2O_3. In Fresno sandy loam at the 10 per cent level opposite the rate 4 in the chlorate set the crop was 8 cm in height and weighed 0.3 gram. This culture received 200 p.p.m. of $NaClO_3$. The rates, 3, 2, and 1 represent dosages of ¾, 2/4, and ¼ of this basic rate respectively. In the first case cited above the dosages were 75 p.p.m., 150 p.p.m., 225 p.p.m., and 300 p.p.m. As_2O_3. Each column of cultures in each chemical set therefore represents a short concentration series consisting of an untreated check and four concentrations, the highest concentration being intended to reduce the growth in the cultures to the particular growth level under consideration.

TABLE 2

TOXICITY OF ARSENIC, BORAX, CHLORATE, AND THEIR COMBINATIONS, AS SHOWN BY GROWTH OF INDICATOR PLANTS

Application		Yolo clay loam				Fresno sandy loam				Stockton adobe clay			
		50 per cent		10 per cent		50 per cent		10 per cent		50 per cent		10 per cent	
Chemicals	Rate*	Ht.	Wt.	Ht.	Wt.	Ht.	Wt.	Ht.	Wt.	Ht.	Wt.	Ht.	Wt.
		cm	*gm*	*cm*	*gm*	*cm*	*gm*	*cm*	*gm*	*cm*	*gm*	*cm*	*gm*
Arsenic	0	15	10.5	14	9.6	28	5.4	26	5.0	15	1.5	15	1.8
	1	17	9.3	15	8.0	28	5.0	24	3.2	14	1.0	12	0.8
	2	16	7.6	13	4.6	28	4.5	15	1.2	10	0.7	10	0.6
	3	16	6.9	13	2.7	27	4.0	10	0.6	9	0.5	9	0.4
	4	16	6.1	6	0.6	25	3.3	8	0.4	9	0.5	8	0.3
Borax	0	16	9.3	14	10.0	28	5.4	27	5.2	15	1.4	14	1.6
	1	16	9.9	15	9.7	30	4.9	29	4.0	16	1.3	14	1.1
	2	17	8.9	17	7.6	30	4.3	30	3.3	15	1.1	15	1.2
	3	17	8.1	13	4.0	32	4.2	24	2.0	17	1.2	11	0.6
	4	17	6.4	6	0.9	29	3.0	17	0.7	15	0.9	4	0.1
Chlorate	0	17	10.7	15	9.6	28	5.6	27	4.9	16	1.7	15	1.7
	1	16	6.8	11	2.5	31	4.7	23	2.0	15	1.3	7	0.4
	2	17	5.7	8	1.0	28	3.2	19	1.1	9	0.6	5	0.2
	3	16	5.0	5	0.3	28	3.1	9	0.5	8	0.4	5	0.2
	4	15	4.0	5	0.2	26	2.5	8	0.3	6	0.2	4	0.1
A+*B*	4+0	16	6.1	6	0.6	25	3.3	8	0.4	9	0.5	8	0.3
	3+1	17	7.0	9	2.0	25	3.1	9	0.4	12	0.8	8	0.2
	2+2	17	7.2	14	3.7	28	3.3	9	0.4	13	0.7	8	0.2
	1+3	18	7.5	12	3.2	30	3.2	13	0.5	14	0.8	8	0.3
	0+4	17	6.4	6	0.9	29	3.0	17	0.7	15	0.9	4	0.1
A+*C*	4+0	16	6.1	6	0.6	25	3.3	8	0.4	9	0.5	8	0.3
	3+1	15	5.6	6	0.4	28	2.9	8	0.4	10	0.8	7	0.3
	2+2	16	5.0	5	0.4	27	2.5	9	0.4	10	0.6	5	0.2
	1+3	16	4.5	4	0.3	25	2.6	8	0.4	7	0.3	5	0.2
	0+4	15	4.0	5	0.2	26	2.5	8	0.3	6	0.2	4	0.1
B+*C*	4+0	17	6.4	6	0.9	29	3.0	17	0.7	15	0.9	4	0.1
	3+1	18	8.0	10	2.0	30	3.7	24	1.5	14	1.0	8	0.5
	2+2	16	7.1	13	2.4	30	4.2	23	1.7	15	1.1	9	0.7
	1+3	17	5.9	14	1.7	27	3.1	20	1.4	13	0.8	5	0.2
	0+4	15	4.0	5	0.2	26	2.5	8	0.3	6	0.2	4	0.1
A+*B*+*C*	1+2+1	17	7.3	14	3.1	32	5.2	16	1.1	14	0.8	10	0.5
	1+1+2	18	6.4	13	2.2	30	4.0	19	1.0	12	0.9	7	0.4
	2+1+1	18	6.6	14	2.7	29	3.9	11	0.6	11	0.8	9	0.4
	$\frac{4}{3}+\frac{4}{3}+\frac{4}{3}$	18	6.6	14	2.7	30	4.1	16	0.9	12	0.9	10	0.5
Checks†	0	17	10.4	15	10.1	28	5.5	27	5.1	16	1.5	16	1.7

* "Rate" is expressed in quarters of the amount of chemical necessary to produce the desired growth levels; see explanation on page 402.

† Average of 17 replicates.

In the combination sets the three chemicals were used two at a time and three at a time. They were combined in the proportions designated in the "Rate" column. These values refer strictly to the concentrations of the designated chemicals: in the $B + C$ set, $2 + 2$ means that in Yolo

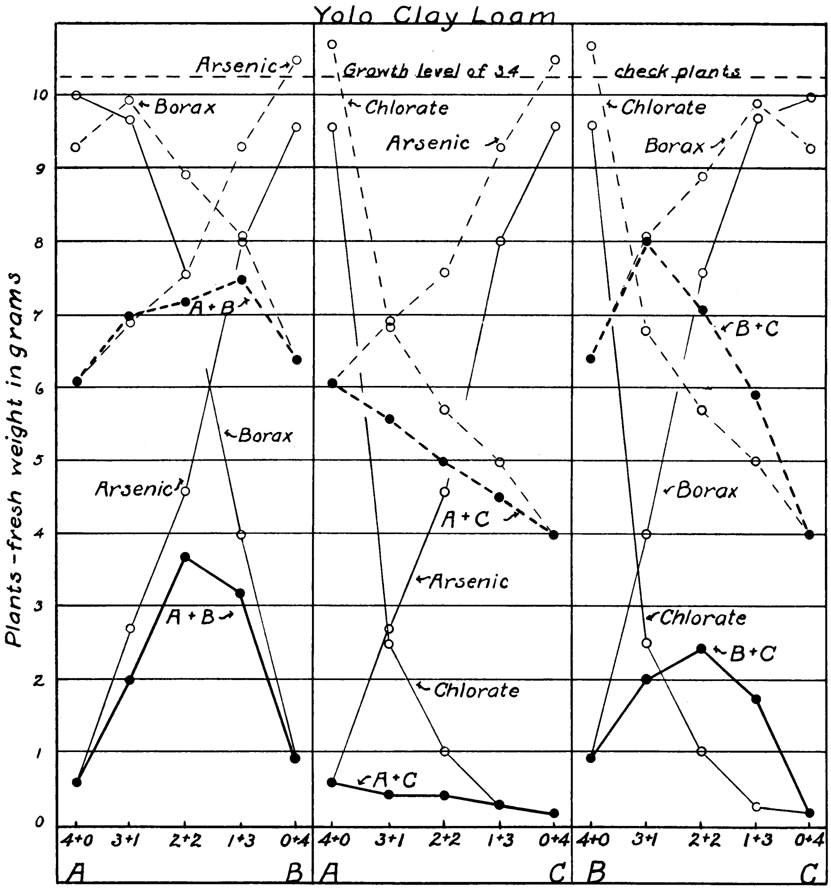

Fig. 1.—Toxicity of arsenic, borax, chlorate, and their combinations used two at a time in Yolo clay loam. Solid lines in lower part of the figure indicate the 10 per cent growth level, and dotted lines in the upper part, the 50 per cent growth level.

clay loam, for example, $\frac{2}{4}$ of 300 p.p.m. of borax (table 1) and $\frac{2}{4}$ of 100 p.p.m. of chlorate (table 1) were combined at the 50 per cent level. The dosages were therefore 150 p.p.m. of borax and 50 p.p.m. of chlorate respectively, not equal dosages of each. The same rule applied where all three chemicals were used in combination.

In each soil there were 34 different treatments, run in triplicate, and 8 checks for each growth level. The values given in table 2, except the

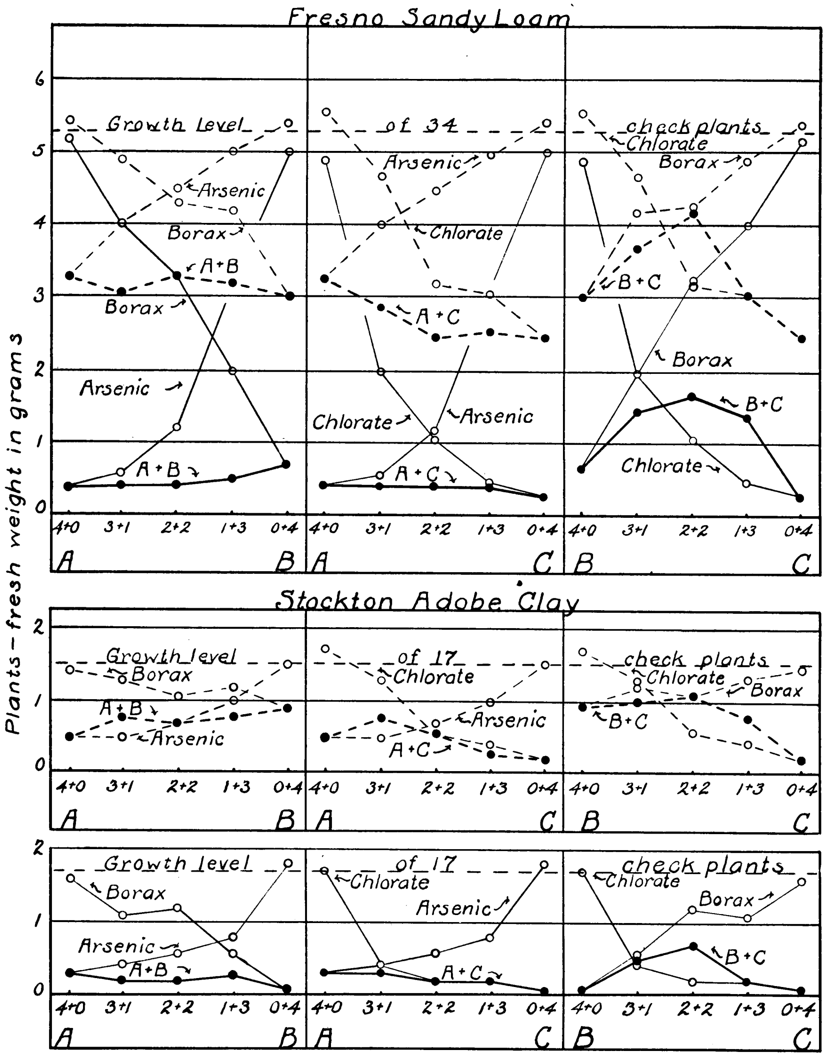

Fig. 2.—Toxicity of arsenic, borax, chlorate, and their combinations used two at a time in Fresno sandy loam and Stockton adobe clay. Solid lines in lower part of the figure indicate the 10 per cent growth level, and the dotted lines in the upper part the 50 per cent growth level.

checks at the end, represent the average of the three replicates. The values for the checks at the end of the table include the 8 unattached checks in addition to the 9 included in the single chemical sets shown above.

To facilitate the interpretation of the data figures 1, 2, and 3 have been prepared. The first two show the toxicity curves for the single chemicals and their combinations when used two at a time; figure 3 shows the relations of the chemicals used singly and used three at a time.

When herbicides are used in combination there are three possible types of response. The effects might be strictly additive. That is, at a given growth level the result of chemical treatment should be the same whether the dosage is all applied as one chemical or another, or as combinations of the two, of such amounts as to total the same in all cases. Considering, for example, the curves in figure 2 for arsenic and chlorate in Fresno sandy loam at the 10 per cent level, it made little difference whether the application was made of 4 increments of arsenic, 3 of arsenic plus 1 of chlorate, 2 of each, 1 of arsenic plus 3 of chlorate, or 4 of chlorate. In all five cases the results were essentially the same.

The second possibility is that the two chemicals might be antagonistic in their action, and the resultant reaction upon the plant might be less from mixtures than from either alone. This is the case with the chlorate-borax mixtures in all three soils.

The third possibility is that the total effect upon plants of the combination treatment might be greater than that expected on the basis of the sum of the individual effects of the two taken alone. This type of response was not observed with any of the mixtures used in these experiments.

There are three types of toxicity curves in figures 1 and 2: straight-line curves such as that for arsenic at the 50 per cent level in the Fresno sandy loam; curves that are concave as viewed from above, such as the arsenic and chlorate curves at the 10 per cent level in Fresno sandy loam; and curves that are convex when viewed from above, as the borax curves in the Yolo clay loam.

The straight-line curve indicates that all increments of a single chemical are of equal value. The concave curves indicate a high toxicity for the first increments and decreasing effectiveness as more are added. Chlorate-toxicity curves are usually of this form if the total dosage approaches the zero growth level. Convex curves indicate low toxicity in the low applications and increasing effectiveness as a lethal dosage is approached.

Evidently the combination curves in figures 1 and 2 are influenced in practically every experiment by the form of toxicity curves of the two component chemicals. In the Yolo clay loam there is antagonism between arsenic and borax at both growth levels, with toxicity much lower than would be expected on the high-borax side. In the arsenic-chlorate combinations there is in a sense no antagonism, since the curves connecting the two extremes are practically straight lines at both growth levels; but there is considerable difference in the effectiveness of the different increments of each chemical, the first of chlorate being particularly toxic in both cases.

In the borax-chlorate experiment there is distinct antagonism, the combination curve crossing that for chlorate alone, a fact indicating that the borax detracted from the effectiveness at the high-chlorate—low-borax end. This response, though related to the convex form of the borax curve, is more pronounced than would be expected from the results with those two chemicals alone.

In the Fresno sandy loam the borax is much more toxic (table 1) and in combination with arsenic shows no marked reduction in toxicity. Arsenic and chlorate also show straight-line curves for the combinations in this soil. Borax and chlorate again show antagonism with the combination curves crossing the chlorate curves. This same behavior is shown in Stockton adobe clay, where borax toxicity is extremely low. Since it occurs in all three soils it is probably related to the chemicals and relatively independent of the soil type. The arsenic-borax and arsenic-chlorate curves in the Stockton soil are essentially straight lines, a fact indicating that these combinations have little or no antagonistic action in both this and the Fresno soil.

Evidently the combinations used three at a time (fig. 3) are all less toxic than equivalent dosages of the single chemicals; and in some cases, as for example the 10 per cent growth level in Yolo clay loam, toxicities are markedly low. Since this type of mixture has only theoretical interest and is of little practical value, it will not be considered further.

One might judge from the foregoing discussion that these studies have yielded little useful information, since no mixtures of outstanding effectiveness have shown up. Such, however, is not the case. In the first place, it should be pointed out that in the future the principal use of these chemicals in combination will be in soil sterilization, a process that will gain in popularity as agricultural production comes under a higher degree of control. And very probably they will be applied dry wherever possible, for this is the least expensive method.

Among the dry chemicals used in soil sterilization, arsenic comes first in toxicity and retention in available form in the top soil (*1, 2*). In the

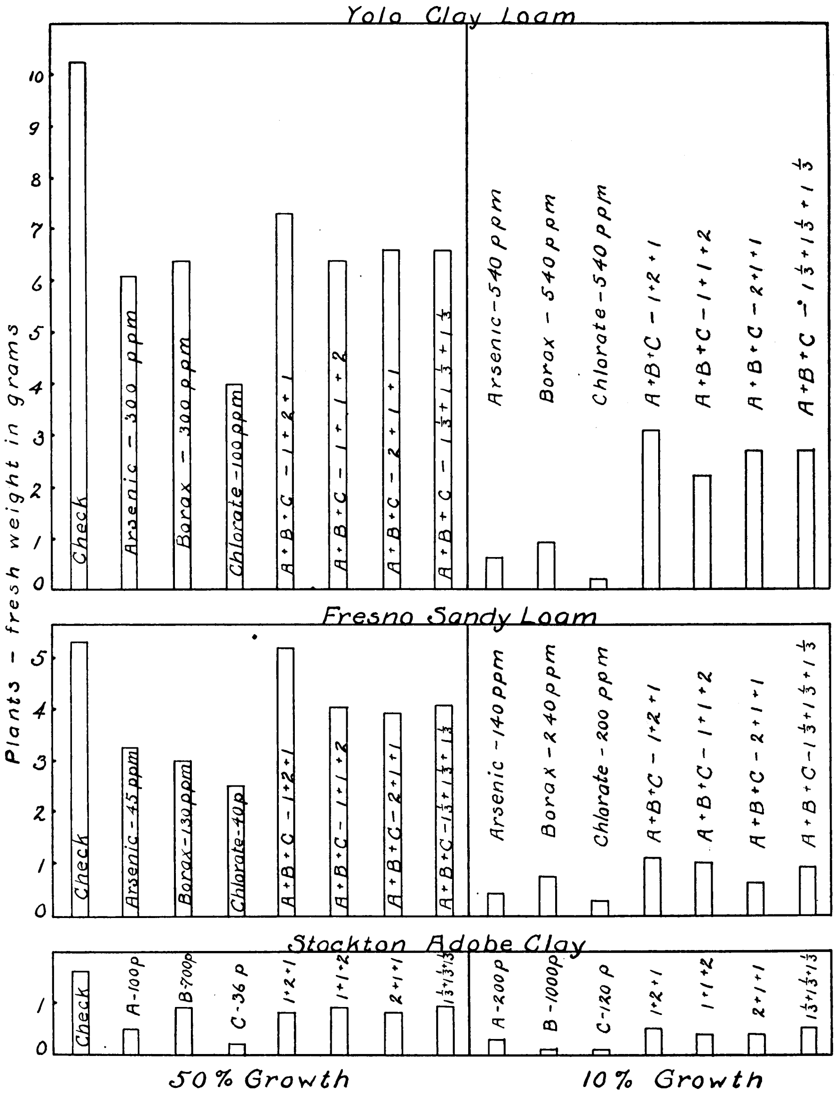

Fig. 3.—Toxicity of arsenic, borax, chlorate, and their combinations used three at a time as shown by growth of indicator plants.

form of the trioxide, however, it is only slightly soluble, and at least one season is required, under California conditions, for enough to become available to give effective sterilization. There is need for an agent that may be combined with it to kill vegetation during the year of application.

Borax, though extremely toxic to many plants when first applied to the soil, soon loses in effectiveness with time and leaching (*3*). It is more firmly retained in the top soil than chlorate and is nonpoisonous to livestock (*3*). Chlorate, being very soluble, is not held against the force of moving water in most soils. It is valuable, in consequence, for treating deep-rooted perennials and will kill annuals during the year of application in California, especially if applied in the late winter or spring.

Considering now the mixtures: arsenic and borax, both being surface sterilants, would have little or no use in combination. Though borax is nonpoisonous and might be substituted for arsenic, it is not satisfactory as a quick killer for annual weeds. In Yolo soils these chemicals are antagonistic.

Chlorate, being soluble and a quick killer, will combine with dry white arsenic to form a very desirable mixture for soil sterilization. Since they are not antagonistic in their action, these reagents may be used in any proportions; and where sufficient chlorate is incorporated, deep-rooted perennials may be eliminated in the process.

On the basis of our data the borax-chlorate combination might seem to hold little promise, since the action of these chemicals was antagonistic in all three soils. Several advantages, however, may be gained by using this mixture. Both chemicals are nonpoisonous as applied in this method; the fire hazard in the use of the chlorate would be practically eliminated; the effects would be considerably more durable than in the use of chlorate alone; and the cost could be materially reduced.

Experiments indicate that colemanite may be used as a substitute for borax (*3*). This fact would place this chemical on a cost basis of about one-tenth that of chlorate, and a very effective mixture of the two could be marketed at a nominal cost. The principal problem is to prescribe the proportions for mixing and the dosages to be used on different soils and under various climatic conditions.

The shape of the toxicity curves of borax and chlorate indicates that the most effective increments of chlorate are the first, whereas the higher applications of borax have the most pronounced effect. The combination curves indicate, furthermore, a high antagonism where little borax was combined with much chlorate. Evidently, therefore, in combining these two chemicals one should use a minimum effective dosage of chlorate and should add borax as the need is indicated by the soil type and local conditions. From table 1 little chlorate is required to reduce growth 50 per cent. In two soils less borax than chlorate is needed to lower it from 50 per cent to 10 per cent, and in the Stockton soil less than four times as much borax as chlorate is required. Considering the 1 to 10 differential in price, it seems logical to use chlorate through its range of maximum effectiveness and then to add borax enough to finish the destruction. With the added residual effect of the borax, this combination should prove economical. It is excelled only by arsenic and chlorate, a mixture which has limited use because of its poisonous nature.

DISCUSSION

The foregoing considerations indicate the use that may be made of greenhouse technique in building a body of information upon which to base an interpretation of field results. The limitations of the method should also be pointed out. As several years of experience have shown, the toxic concentrations of the various chemicals studied are not absolute but depend somewhat upon growth conditions of the indicator plants. Borax and chlorate are evidently absorbed and translocated in plants and tend to accumulate in the leaves. The toxicity of these reagents is affected, therefore, by conditions determining rates of absorption and water loss. In addition, toxicity is rapidly reduced during the initial stages of any experiment of this type; and although this loss can be shown only by comparing successive crops, it is going on from the time the first crop is planted. Since toxicity loss varies in rate with different chemicals and under different environmental conditions, comparative studies with two or more chemicals are limited in accuracy. For such reasons the concentrations required to reduce growth to certain fixed levels may not always be the same, and with the best of judgment the worker may miss the desired points. This was the case in the Yolo soil, where both the arsenic and borax concentrations used failed to bring growth to the 50 per cent level, while the chlorate concentration took it below this line. Similar discrepancies can be observed in the other two soils, which indicate the general nature of the disturbing factors. Though these discrepancies interfere somewhat with the results, the general responses are so apparent that their value is little depreciated. The convenience and adaptability of the method far outweigh its drawbacks as is indicated by the conclusions drawn.

These same factors that limit the accuracy of the greenhouse method affect the results of field applications. Chemical treatments for soil sterilization are subject not only to such obvious factors as rainfall, temperature, soil type, and species susceptibility, but to all those complex relations that determine the crop-producing power of soils and their ability to fix and retain solutes against the force of moving water. For the present the best that can be done in determining the behavior and effects of herbicides in soils is to study, by the empirical methods described, the growth of plants in the treated soils. Such studies are providing abundant information, sufficiently accurate to aid materially in the design and ultimate interpretation of field-plot studies.

SUMMARY

In the greenhouse experiments described, sodium arsenite, hydrous sodium tetraborate, and sodium chlorate are used singly and in combination to reduce growth of indicator plants.

Concentrations of these three chemicals required to reduce growth to the 50 per cent level and to the 10 per cent level in Yolo clay loam, Fresno sandy loam, and Stockton adobe clay were derived from previously published data.

In the present experiments, check series were set up in each soil, the individual chemicals being applied in increments of $\frac{1}{4}$, $\frac{2}{4}$, $\frac{3}{4}$, and $\frac{4}{4}$ of that required to reduce growth to the specified level. Each such set, constituting a short concentration series, was used as a basis for comparing the combination treatments.

In experiments combining the chemicals two at a time, they were applied in proportions of $4 + 0$, $3 + 1$, $2 + 2$, $1 + 3$, and $0 + 4$. The chemicals used three at a time were combined in the proportions of $1 + 2 + 1$, $1 + 1 + 2$, $2 + 1 + 1$, and $\frac{4}{3} + \frac{4}{3} + \frac{4}{3}$.

Arsenic and borax showed antagonistic reaction in Yolo clay loam at both the 50 per cent and the 10 per cent growth levels.

Arsenic and borax toxicities were additive in Fresno sandy loam and Stockton adobe clay.

Arsenic and chlorate toxicities were additive in all three soils at both growth levels.

Borax and chlorate showed antagonistic reactions in all three soils at both growth levels.

The combination of the chemicals used three at a time are of only theoretical interest and provide no practical information.

In the practical application of these chemicals the arsenic-borax combination would find little use.

Sodium chlorate and white arsenic applied dry, form a very useful mixture for soil sterilization. As shown by the greenhouse experiments, there is no indication of loss by antagonism in their reactions.

In the use of borax and sodium chlorate in combination for soil sterili-

zation the antagonism in their action can be reduced to a minimum by using the lowest effective dosage of chlorate and adding enough borax to complete the destruction of the vegetation.

The borax-chlorate combination for soil sterilization has the advantage of being practically nonpoisonous; and the use of the borax, besides reducing the fire hazard of the chlorate to a low level, provides a residual effect that lowers the probability of reinfestation by seedlings.

LITERATURE CITED

[1] CRAFTS, A. S.
1935. Plot tests with sodium arsenite and sodium chlorate as soil sterilants in California. California State Dept. Agr. Mo. Bul. **24**(4, 5, 6): 247–59.

[2] CRAFTS, A. S.
1935. The toxicity of sodium arsenite and sodium chlorate in four California soils. Hilgardia **9**(9):459–98.

[3] CRAFTS, A. S., and R. N. RAYNOR.
1936. The herbicidal properties of boron compounds. Hilgardia **10**(10):343–74.

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