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COPPER AND ZINC AS ANTAGONISTIC AGENTS TO THE "ALKALI" SALTS IN SOILS

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Since the appearance of Osterhout's pointed reply[1] to Loew's criticism of the conception of antagonistic salt effects and physiologically balanced solutions for plants, no one has seriously questioned the validity of accepting as well-founded the aforementioned conception. Indeed the antagonistic salt effect is now regarded as one of the established facts in plant physiology, as it has been in animal physiology since 1900, when Loeb[2] first suggested the idea of the ion-proteid compounds and the mechanism of toxic and antagonistic salt effects. In the large amount of work which has been accomplished on the antagonistic effects of salts during the last fifteen years, the heavy metals have received very little attention, while the alkali and alkali-earth metals have been tested out in a number of ways and with a variety of media.

In the experiments on animals, which we have cited above, it was found by Loeb[3] that for the development of the eggs of marine fish (Fundulus) in NaCl solution of the same osmotic pressure as sea water, copper and mercury were powerless to antagonize the toxic effects of common salt. Zinc and cobalt, on the other hand, manifested a marked antagonism to NaCl in the direction indicated, and lead, nickel, and uranium showed slight but definite antagonistic powers under similar circumstances. Experiments involving antagonistic

[1] Osterhout, W. J. V. The Nature of Balanced Solutions. Bot. Gaz. 47: 48. 1909.

[2] Loeb, J. On Ion-Proteid Compounds and their Rôle in the Mechanics of Life Phenomena. The Poisonous Character of a Pure NaCl Solution. Amer. Journ. Physiol. 3: 327. 1900.

[3] Loeb and Gies, Pflüger's Arch. 93: 246. 1902.

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powers of copper and zinc ions to the toxic properties of other ions have been few and the results obtained rather fragmentary. They have dealt chiefly with animal material. Indirectly, however, a small amount of data has been obtained in experiments with plant or fungus organisms as regards antagonistic powers of copper and zinc. We use the term *indirectly* advisedly, since, unlike our experiments, those in question have attempted to antagonize the toxic properties of copper and zinc by adding the less toxic or non-toxic metals to a given medium for the growth of the organism tested, whereas we have attempted to use copper and zinc to antagonize the toxic concentrations of what are known as "alkali" salts in soils. The indirect evidence is very important, however, and deserves mention here. Clark[4] was able to diminish markedly the toxic effects of $CuSO_4$ and $CuCl_2$ for germination of spores of *Oedocephalum albidum* and *Rhizopus nigricans* by the addition of various ammonium, sodium, and potassium salts. Among other heavy metals, Le Renard[5] found that copper and zinc could be rendered much less toxic in culture media for Penicillium by the addition of various salts of ammonium, potassium and magnesium. True and Gies[6] demonstrated that the toxicity of copper and zinc, as well as that of mercury in various salts for *Lupinus albus*, could be considerably reduced by the addition of calcium to the medium of growth. Szücs,[7] working with *Cucurbita pepo* and using the responsiveness of the root to a geotropic stimulus as a criterion, found that $AlCl_3$ in certain concentrations possessed the property of inhibiting the toxic effects of $CuSO_4$. More recently, Hawkins[8] has shown to exist certain cases of undoubted inhibition of the toxic effects, on fungus spores, of heavy metals, including copper and zinc, by the presence of calcium, magnesium, or potassium nitrates. It will be noted that only two experiments with higher plants are cited among the investigations just reviewed. Moreover, Szücs used a very unusual and less convincing criterion for antagonism effects, and True and Gies used calcium to antagonize copper, but did not try the antagonistic properties of copper against the alkali or alkali earth metals or their ions.

On the other hand, Lillie[9] found that copper, as well as several

[4] Clark, J. F. Bot. Gaz. **33**: 26–48. 1902.

[5] Le Renard, Alf. Ann. Sci. Nat. Bot. IX. **16**: 276–336. 1912.

[6] True & Gies, Bull. Torrey Club **30**: 390–402. 1903.

[7] Szücs, Jos. Jahrb. Wiss. Bot. **52**: 85–143. 1912.

[8] Hawkins, L. A. Physiol. Res. **1**: 57–92. 1913.

[9] Lillie, R. S. Amer. Journ. Physiol. **10**: 419. 1904.

other toxic metals, possesses definite powers of antagonizing the toxic effects of NaCl on the normal existence and activation of cilia in the larvae of a marine annelid (Arenicola). With the exception of uranium, however, copper was the most feeble antagonistic agent to the action of NaCl just mentioned of thirteen metals tested.

In view of the negative results obtained with copper by Loeb, and the entire lack of data, in so far as the more important functions of plants are concerned, on the antagonistic action of that metal to the alkalies, we deemed it wise, among the different series of antagonism experiments carried out in our laboratory, to test the action of copper as an antagonistic agent to "alkali" salts in soils. This seemed particularly important in view of certain marked stimulating effects obtained by us[10] through the presence in the soil of copper, zinc and other metals, in the growth of barley in soil cultures. Owing to many similarities between the stimulating effects of copper and zinc in the studies just referred to, we decided to study the antagonistic powers of zinc, as well as those of copper, in the new experiments. The latter have now been completed and the results have, in many ways, been so striking as to justify their publication at this time. Our data constitute the first evidence, so far as we are aware, of the antagonistic action of copper and zinc to the toxic effects of "alkali" salts as regards the living cells of higher plants.[11]

Methods Employed in the Experiment

The plants used as indicators of the salt effects here studied were a selected strain of the Beldi variety of barley (*Hordeum vulgare*). They were grown in soil in 8-inch earthenware pots which were paraffined prior to the introduction of the soil. Twenty seeds were planted in every pot and the plants were later thinned to six plants per pot. As nearly as possible, optimum and uniform moisture conditions were maintained in all the soils. Some of the common salts of alkali soils, viz, NaCl, Na_2SO_4, and Na_2CO_4, were employed as toxic agents and were added on a percentage basis of the dry weight of the soils. The antagonistic agents were $CuSO_4$, $ZnSO_4$, $CuCl_2$, $ZnCl_2$ and $CuCO_3$, and were added to the salt-treated soils on the basis of parts per million of

[10] Lipman and Gericke, Univ. Cal. Publ. Agr. Sci. 1: 495–587.

[11] Hibbard, R. P., has shown that $CuSO_4$ and chloral hydrate antagonize each other, but such an instance of antagonism is not comparable with those which we furnish in this paper since chloral hydrate is an organic compound.

the dry weight of the soil. The toxic salt in every case was used in uniform concentration throughout a given series, whereas the antagonistic salt was used in varying concentrations. Except as otherwise stated below, all salts were mixed with the soils a few days prior to planting the seeds.

Two types of soil were employed, the Oakley blow sand and the Berkeley clay adobe. Both of these soils have frequently been described in papers issued from our laboratory.[12] It should be added that different lots of one and the same type of soil were used and these varied in producing power without treatment due to field conditions which need no discussion here. In any one series, however, soils from different lots were never mixed. Seven series of cultures in duplicate were grown on each soil type. The plants were grown to maturity, harvested, dried at 100° C., and weighed. The dry weights of both tops and roots were determined in every case, and in the case of the tops, separate determinations were also made of the dry weight of the straw and the grain. The results are given in the tables. For the sake of clearness, it is deemed best to consider briefly each series by itself.

Series I

$CuSO_4$ versus Na_2SO_4—Adobe Soil

Na_2SO_4 .5 percent constant—$CuSO_4$ varying

Three consecutive crops were grown in this series, the second crop being planted shortly after the first was harvested. The salt applications were, of course, made only once, namely, prior to the planting of the first crop. The results obtained with regard to yields of straw, grain, and roots are given in Tables I, II and III.

Straw Production.—Straw yields are evidently not very markedly influenced by the antagonistic effects of $CuSO_4$ to Na_2SO_4. This seems to be true especially in the first two crops. In the third crop, the effect is a little more marked in the direction indicated. On the other hand, the lack of agreement, which is noted between some of the duplicate cultures, is more marked in the third crop than in the other two. It should be observed that the lack of toxicity manifested by Na_2SO_4 alone in the second crop is doubtless due to a loss of some of the salt, since Na_2SO_4 is characterized by a tendency to crystallize from the soil and to creep to and over the edges of the pots. Moreover,

[12] Univ. Cal. Publ. Agr. Sci. 1: 495–587.

any spots on the pot from which the paraffine has disappeared in one way or another always become centers of absorption for Na_2SO_4, which then readily disintegrates the pottery. In spite of these disturbing elements in the experiment, there can be no question that $CuSO_4$ has

Table I

Antagonism Between $CuSO_4$ and Na_2SO_4 For Barley—Adobe Soil, First Crop

No.	% Na_2SO_4 Added	$CuSO_4$ in Parts per Million	Wt. of Straw	Wt. of Grain	Wt. Dry Matter Above Surface	Wt. of Roots	Wt. of Total Dry Matter
			g.	g.	g.	g.	g.
1	.5%	100	6.98	8.02	15.00	1.80	16.80
2	.5%	100	5.73	2.27	8.00	1.30	9.30
3	.5%	200	8.50	4.50	13.00	2.70	15.70
4	.5%	200	6.90	4.10	11.00	2.00	13.00
5	.5%	300	7.25	5.95	13.20	1.70	14.90
6	.5%	300	7.70	4.30	12.00	1.00	13.00
7	.5%	400	8.85	5.15	14.00	1.50	15.50
8	.5%	400	9.20	3.60	12.80	2.80	15.60
9	.5%	500	11.60	5.50	17.10	2.30	19.40
10	.5%	500	8.30	5.20	13.50	2.00	15.50
11	.5%	600	8.23	5.27	13.50	2.00	15.50
12	.5%	600	9.15	3.35	12.50	2.50	15.00
13	.5%	700	9.25	5.15	14.40	2.40	16.80
14	.5%	700	6.40	3.60	10.00	1.40	11.40
15	.5%	800	9.20	5.30	14.50	1.90	16.40
16	.5%	800	7.55	3.95	11.50	1.20	12.70
17	.5%	—	7.13	2.17	9.30	.85	10.15
18	.5%	—	7.33	1.07	8.40	1.50	9.90
19	—	—	10.70	—	10.70	2.50	13.20
20	—	—	14.00	4.30	18.30	2.00	20.30
21	—	—	12.05	1.75	14.80	1.40	16.20

exercised a definitely antagonistic effect to the toxicity of Na_2SO_4. Concentrations no greater than 500 parts per million $CuSO_4$ were sufficient in all cases to give the maximum antagonism to .5 percent of Na_2SO_4, and in the second and third crops, which are probably more reliable criteria than the first crop, 100 and 200 parts per million were fully as efficacious, if not more so than the larger amounts. These considerations would seem to indicate that amounts of $CuSO_4$ equivalent to from one tenth to one fiftieth of the amount of Na_2SO_4 present are sufficient to antagonize the latter salt when it is present in soil at concentrations of about .5 percent.

As regards grain yields, the antagonism of $CuSO_4$ to Na_2SO_4 is much more marked than in the case of straw yields. This is particularly so for the first and second crop of the series. In the third crop,

TABLE II

Antagonism Between $CuSO_4$ and Na_2SO_4 For Barley—Adobe Soil, Second Crop

No.	% Na_2SO_4 Added	$CuSO_4$ in Parts per Million	Wt. of Straw.	Wt. of Grain	Wt. Dry Matter Above Surface	Wt. of Roots	Wt. of Total Dry Matter
			g.	g.	g.	g.	g.
1	.5%	100	2.58	1.00	3.58	.50	4.08
2	.5%	100	2.75	.55	3.30	.55	3.85
3	.5%	200	3.66	1.04	4.70	.52	5.22
4	.5%	200	2.35	.65	3.00	.65	3.65
5	.5%	300	2.70	.80	3.50	.50	4.00
6	.5%	300	2.56	.88	3.44	.38	3.82
7	.5%	400	2.62	.60	3.22	.40	3.62
8	.5%	400	3.77	.75	4.52	.75	5.27
9	.5%	500					
10	.5%	500	2.55	.40	2.95	.60	3.55
11	.5%	600	2.05	.75	2.80	.50	3.30
12	.5%	600	2.25	.45	2.70	.95	3.65
13	.5%	700	3.10	.20	3.30	1.00	4.30
14	.5%	700	3.00	1.00	4.00	.80	4.80
15	.5%	800	2.50	.50	3.00	.50	3.50
16	.5%	800	2.65	.40	3.05	.40	3.45
17	.5%	——	2.61	.35	2.96	.55	3.31
18	.5%	——	2.00	.30	2.30	.70	3.00
19	——	——	2.75	.25	3.00	.25	3.25
20	——	——	2.15	.25	2.40		2.40

TABLE III

Antagonism Between $CuSO_4$ and Na_2SO_4 For Barley—Adobe Soil, Third Crop

No.	% Na_2SO_4 Added	$CuSO_4$ in Parts per Million	Wt. of Straw	Wt. of Grain	Wt. Dry Matter Above Surface	Wt. of Roots	Wt. of Total Dry Matter
			g.	g.	g.	g.	g.
1	.5%	100	18.90	2.10	21.00	2.00	23.00
2	.5%	100	4.90	1.60	6.50	.40	6.90
3	.5%	200	7.60	3.40	11.00	1.24	12.24
4	.5%	200	10.00	2.00	12.00	1.05	13.05
5	.5%	300	13.30	1.80	15.10	.85	15.95
6	.5%	300	5.40	2.60	8.00	.80	8.80
7	.5%	400	4.80	3.80	8.60	1.10	9.70
8	.5%	400	5.70	2.30	8.00	1.16	9.16
9	.5%	500	12.20	3.20	15.40	1.20	16.60
10	.5%	500	7.40	1.60	9.00	1.50	10.50
11	.5%	600	4.30	3.70	8.00	.94	8.94
12	.5%	600	6.10	1.90	8.00	1.00	9.00
13	.5%	700	5.50	3.30	8.80	1.50	10.30
14	.5%	700	5.55	3.50	9.05	.95	10.00
15	.5%	800	6.10	2.80	8.90	1.00	9.90
16	.5%	800	6.00	3.00	9.00	.70	9.70
17	.5%	——	4.40	2.00	6.40	.64	7.04
18	.5%	——	4.00	3.00	7.00	.90	7.90
19	——	——	7.50	2.50	10.00	1.56	11.56
20	——	——	12.70	1.30	14.00	1.87	15.87

the effect is relatively slight. The antagonism is most marked in the first and third crops at concentrations of $CuSO_4$ in excess of 300 parts per million, while in the second crop it is just as marked at 100 parts per million as at 200 and 300 parts per million and much more marked than at the higher concentrations.

Root yields seem to have been definitely improved by the antagonistic influence of $CuSO_4$ to Na_2SO_4 in the first crop. In the second crop, the effect was barely perceptible at the higher concentrations of $CuSO_4$ employed, but it was again clearly evident in the third crop, despite the poor agreement between some of the yields of the duplicate pots.

Series II

$CuCl_2$ versus NaCl—Adobe Soil.

NaCl .3 percent constant—$CuCl_2$ varying.

As was the case in Series I, three consecutive crops were grown and harvested in this series. The antagonism between Cu and Na seem to be very much more marked, however, in Series II than in Series I. The results obtained are given in Tables IV, V, and VI, for the first, second, and third crops, respectively.

As regards straw production in the first crop, increases in yield, due to the antagonistic effect of $CuCl_2$ to NaCl, rise to a maximum of 75 percent over that obtained in the pots treated with NaCl alone. Small additions of 50 to 100 parts per million of $CuCl_2$ seem to have just as strong an antagonizing influence as larger applications of that salt. Additions of $CuCl_2$, equivalent to 300 or 350 parts per million, still show as high antagonizing powers as the smaller amounts. Additions of larger concentrations of $CuCl_2$, however, do not show an antagonizing power; but, even up to and including concentrations of 500 parts per million $CuCl_2$, they do not increase the toxicity of .3 per cent. NaCl. Higher concentrations of $CuCl_2$ than 500 parts per million were not tested. In the second crop, straw production, owing to the unfavorable conditions for growth at the time, was unsatisfactory, but shows clearly enough the antagonism between $CuCl_2$ and NaCl at nearly all concentrations used. This was true, moreover, despite the fact that the toxicity of .3 percent NaCl was scarcely manifest, due apparently to the general poor growing conditions for the crop. In the third crop, the antagonism as regards the straw yields is very marked. The toxicity of NaCl, as shown in Table VI, reduces the yield of barley below that in the untreated control by approximately 60 percent. But concentrations of $CuCl_2$ with .3 percent NaCl increase the yields again to a point only about 30 percent below the yield of the control plants. Again, as in the first series, all the concentrations of $CuCl_2$ used exhibit antagonizing powers to NaCl, and the smallest concentrations are as effective as the larger ones, if not more so.

Table IV

Antagonism Between $CuCl_2$ and NaCl For Barley—Adobe Soil, First Crop

No.	% NaCl Added	$CuCl_2$ Added in Parts per Million	Wt. of Straw	Wt. of Grain	Wt. Dry Matter Above Surface	Wt. of Roots	Wt. of Total Dry Matter
			g.	g.	g.	g.	g.
1	.3%	50	6.28	1.12	7.40	1.75	9.15
2	.3%	50	4.87	2.13	7.00	1.00	8.00
3	.3%	100	7.68	4.32	12.00	1.30	13.30
4	.3%	100	8.00	3.50	11.50	1.00	12.50
5	.3%	150	6.22	3.78	10.00	1.20	11.20
6	.3%	150	6.00	1.80	7.80	.70	8.50
7	.3%	200	6.63	3.37	10.00	1.50	11.50
8	.3%	200	7.40	3.40	10.80	1.70	12.50
9	.3%	250	6.18	2.82	9.00	1.20	10.20
10	.3%	250	6.08	2.52	8.60	2.00	10.60
11	.3%	300	5.98	3.82	9.80	1.40	11.20
12	.3%	300	6.07	1.93	8.00	.40	8.40
13	—	—	—	—	—	—	—
14	.3%	350	6.38	1.82	8.20	.60	8.80
15	.3%	400	5.28	2.22	7.50	1.00	8.50
16	.3%	400	4.20	4.30	8.50	1.20	9.70
17	.3%	450	5.60	1.80	7.40	.70	8.10
18	.3%	450	4.88	2.62	7.50	.40	7.90
19	.3%	500	4.76	2.64	7.40	.70	8.10
20	.3%	500	4.26	3.04	7.30	.65	7.95
21	.3%	—	5.23	.37	5.60	.81	6.41
22	.3%	—	4.08	.92	5.00	.40	5.40
23	—	—	10.70	—	10.70	2.50	13.20
24	—	—	14.00	4.30	18.30	2.00	20.30
25	—	—	12.05	1.75	14.80	1.40	16.20

Very much more marked, however, than the antagonism which characterizes the three series as regards straw yields, is that concerned with the grain yields. In the first crop, the grain yields are from three to six times as great in the copper-treated cultures as in those receiving only NaCl, and equal, and in certain instances surpass, in quantity, the yields of the untreated control soils. In the second crop, the grain yields are only slightly increased through the instrumentality of the antagonism in question. In the third crop, the yields of grain in the antagonism cultures are doubled and even trebled when compared with those obtained from the cultures treated with NaCl alone and in many instances are equivalent to those obtained from the untreated soil. It is to be noted again that the smaller applications of the copper salt appear to be as effective antagonistic agents as the largest applications.

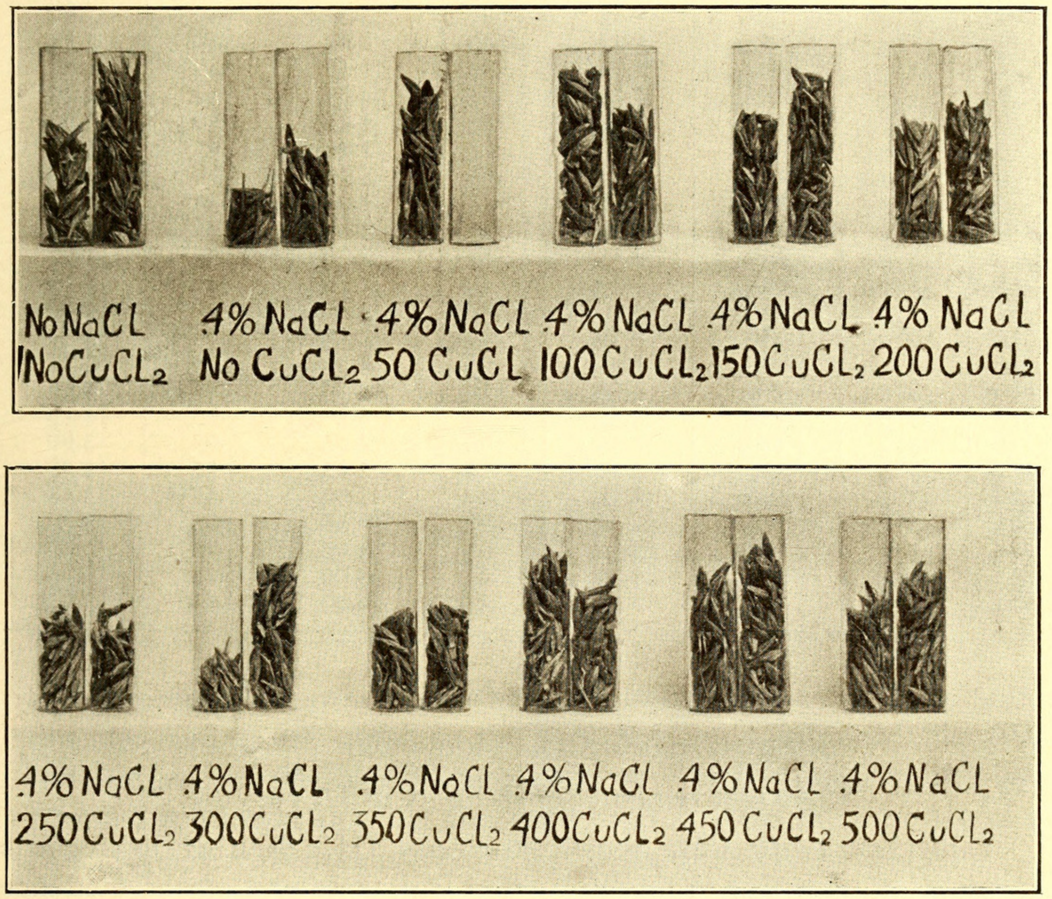

FIG. 1. $CuCl_2$ *vs.* NaCl. Showing the marked antagonism between the two salts for barley grain yields on the Berkeley adobe soil even to the third crop after one treatment. The yield from one of the duplicate pots in the third pair was lost as shown by the empty vial in the photograph.

The root yields are very markedly improved in the cultures by addition of $CuCl_2$ to the NaCl in all three crops and particularly so in the cases of the smaller additions of the copper salt.

TABLE V

Antagonism Between $CuCl_2$ and NaCl For Barley—Adobe Soil, Second Crop

No.	% NaCl Added	$CuCl_2$ in Parts per Million	Wt. of Straw	Wt. of Grain	Wt. Dry Matter Above Surface	Wt. of Roots	Wt. of Total Dry Matter
			g.	g.	g.	g.	g.
1	.3%	50	2.88	.88	3.76	.88	4.64
2	.3%	50	2.84	.46	3.30	.50	3.80
3	.3%	100	2.44	.40	2.84	.40	3.24
4	.3%	100	2.13	.45	2.58	.45	3.03
5	.3%	150	3.70	.35	4.05	.44	4.49
6	.3%	150	2.82	.58	3.40	.50	3.90
7	.3%	200	3.75	.65	4.40	.85	5.25
8	.3%	200	3.10	.60	3.70	.60	4.30
9	.3%	250	2.18	.42	2.60	.42	3.02
10	.3%	250	2.65	.95	3.60	.95	4.55
11	.3%	300	2.13	.57	2.70	.27	2.97
12	.3%	300	2.30	.40	2.70	.40	3.10
13	.3%	350	3.00	.80	3.80	.20	4.00
14	.3%	350	2.49	.66	3.15	.66	3.81
15	.3%	400	1.93	.65	2.58	.65	3.23
16	.3%	400	3.72	.18	3.90	.18	4.08
17	.3%	450	2.85	.65	3.50	.65	4.15
18	.3%	450	2.30	.65	2.95	.65	3.60
19	.3%	500	3.10	.85	3.95	.25	4.20
20	.3%	500	2.55	.45	3.00	.45	3.45
21	.3%	——	2.50	.05	2.55	.65	3.20
22	.3%	——	3.10	.95	4.05	.45	4.50
23	——	——	2.75	.25	3.00	.25	3.25
24	——	——	2.15	.25	2.40	.25	2.65

Series III

$CuCO_3$ versus Na_2CO_3—Adobe Soil

Na_2CO_3 .3 percent constant—$CuCO_3$ varying

Only two crops were grown in Series III. Neither as regards straw production nor grain production was there any strong evidence of antagonism between Na_2CO_3 and $CuCO_3$. It did seem, however, that the larger applications of the copper salt used showed a distinct tendency to antagonize the toxic properties of .3 percent Na_2CO_3 in the soil. Contrary to the behavior of the foregoing series, the one here under consideration showed the small amounts of the copper salt to be much less effective than the larger amounts and the evidence seems even to point to an increase of toxicity when the copper salt in low concentrations is added to the sodium salt. These observations hold for the second as well as for the first crop, though the second crop cannot be seriously considered, for the same reasons that made the

TABLE VI

Antagonism Between $CuCl_2$ and NaCl For Barley—Adobe Soil, Third Crop

No.	% NaCl Added	$CuCl_2$ in Parts per Million	Wt. of Straw	Wt. of Grain	Wt. Dry Matter Above Surface	Wt. of Roots	Wt. of Total Dry Matter
			g.	g.	g.	g.	g.
1	.3%	50	6.30	2.70	9.00	1.16	10.16
2	.3%	50	4.50	1.70	6.20	1.40	7.60
3	.3%	100	5.10	2.70	7.80	.74	8.54
4	.3%	100	5.75	1.65	7.40	.40	7.80
5	.3%	150	3.50	2.10	5.60	.25	5.85
6	.3%	150	7.20	2.40	9.60	.50	10.10
7	.3%	200	6.14	1.46	7.60	.40	8.00
8	.3%	200	5.32	2.08	7.40	.62	8.02
9	.3%	250	3.35	1.25	4.60	.58	5.18
10	.3%	250	4.70	1.30	6.00	.36	6.36
11	.3%	300	4.90	.50	5.40	.60	6.00
12	.3%	300	5.50	2.30	7.80	Lost	7.80
13	.3%	350	4.32	1.28	5.60	.20	5.80
14	.3%	350	5.00	1.20	6.20	Lost	6.20
15	.3%	400	4.00	2.00	6.00	Lost	6.00
16	.3%	400	4.20	1.80	6.00	.20	6.20
17	.3%	450	4.40	2.00	6.40	.35	6.75
18	.3%	450	4.50	2.50	7.00	.31	7.31
19	.3%	500	3.60	1.40	5.00	.38	5.38
20	.3%	500	3.85	2.35	6.20	.28	6.48
21	.3%	—	4.10	.60	4.70	.65	5.35
22	.3%	—	3.04	1.16	4.20	.22	4.42
23	—	—	7.50	2.50	10.00	1.56	11.56
24	—	—	12.70	1.30	14.00	1.87	15.87

second crop in the other series an uncertain factor. Root yields were not obtained at all, owing to the bad physical condition of the adobe soil, induced by the Na_2CO_3 applications. Unfortunately, this series was not continued through the third crop as were the others and the conclusions are, consequently, of less value than the foregoing.

Series IV

$ZnSO_4$ versus Na_2SO_4—Adobe Soil

Na_2SO_4 .6 percent constant—$ZnSO_4$ varying

Owing to the difficulty encountered with the creeping of Na_2SO_4 up and out of the pots employed in these experiments, it was decided to try one series with zinc and sodium sulphates in large wide-mouth bottles. The results obtained with this series, which obviated the loss of Na_2SO_4 from the soil, together with the general arrangement of the cultures are given in Table VII. Control cultures in bottles with no salt treatment were inadvertently omitted from the series. This omission in the experiment is regrettable, but owing to the definiteness of the toxic effects of Na_2SO_4 obtained and to the equally definite evidences of antagonism between zinc and sodium, it does not militate seriously against the usefulness and significance of the results.

TABLE VII

Antagonism Between $ZnSo_4$ and Na_2SO_4 For Barley—Adobe Soil, One Crop

No.	% Na_2SO_4 Added	$ZnSO_4$ in Parts per Million	Wt. of Straw	Wt. of Grain	Wt. Dry Matter Above Surface	Wt. of Roots
			g.	g.	g.	
1	.6%	——	5.30	2.10	7.40	Did not harvest roots. Could not get them out of bottles.
2	.6%	——	5.60	2.00	7.60	
3	.6%	100	5.20	4.00	9.20	
4	.6%	100	5.80	2.80	8.60	
5	.6%	300	7.10	4.90	12.00	
6	.6%	300	5.40	2.20	7.60	
7	.6%	500	6.00	4.00	10.40	
8	.6%	500	7.30	3.30	10.60	
9	.6%	700	11.30	4.50	15.80	
10	.6%	700	7.70	3.80	11.50	
11	.6%	1,000	12.60	2.80	15.40	
12	.6%	1,000	12.50	4.30	16.80	

The straw yields are clearly influenced for the better by the applications of $ZnSO_4$ to the Na_2SO_4-treated soil. Particularly is this true of cultures receiving the larger applications of $ZnSO_4$. There can be no doubt of the definite antagonism indicated in these data. In the case of the grain yields likewise, the evidences of antagonism are very clear, but the smaller concentrations of $ZnSO_4$ appear to have been as effective in antagonism as regards grain production as the larger concentrations of that salt. It was found impossible to remove the soil from the bottles at the end of the experiment in such a fashion as to permit of the determination of root yields. Hence the latter are not given in the table. It is to be noted in connection with Series IV that the agreement between duplicate cultures is much better in bottles as containers than in pots. Particularly when alkali salts are involved, the use of bottles or similar glass containers would seem to deserve preference over even paraffined pots. Whether or not the ordinary glazed crocks now employed by us will combine the advantages of the glass with the advantages of earthenware pots will, we hop bee, soon determined.

Series V

$ZnCl_2$ versus NaCl—Adobe Soil

NaCl .4 percent constant—$ZnCl_2$ varying

Table VIII shows the arrangement of the cultures in this series and gives the concentrations of salts used. Despite poor agreement between the yields of duplicate pots, it is clearly shown in the table that $ZnCl_2$ exercises a powerful antagonistic effect to the toxic properties of NaCl, in so far as the production of total dry matter of barley plants is concerned. As regards grain and root production, the antagonistic effect mentioned is not so marked, but is distinct and great enough to satisfy the most critical of its existence and potency. The poor agreement between the yields of duplicate pots, which has been referred to above, does not permit of an exact appraisal of the relative efficiencies of small and large amounts of $ZnCl_2$ as antagonistic agents to the toxic effects of .4 percent of NaCl. Moreover, 50 parts per million $ZnCl_2$, the lowest concentration of that salt employed, seems to be of high potency in the direction indicated. Nevertheless, concentrations of 300 parts per million $ZnCl_2$ seem to be considerably more efficacious than either smaller or larger concentrations of that salt. Only one crop was grown in the pots of this series.

TABLE VIII

Antagonism Between $ZnCl_2$ and NaCl For Barley—Adobe Soil, One Crop

No.	% NaCl Added	$ZnCl_2$ in Parts per Million	Wt. of Straw	Wt. of Grain	Wt. Dry Matter Above Surface	Wt. of Roots	Wt. of Total Dry Matter
			g.	g.	g.	g.	g.
1	.4%	50	4.50	2.30	6.80	.40	7.20
2	.4%	50	7.30	3.70	11.00	.60	11.60
3	.4%	100	6.70	2.90	9.60	1.20	10.80
4	.4%	100	6.82	2.18	9.00	.75	9.75
5	.4%	300	9.20	4.80	14.00	.75	14.75
6	.4%	300	7.92	4.48	12.40	.80	13.20
7	.4%	500	6.70	3.70	10.40	1.00	11.40
8	.4%	500	7.16	2.34	9.50	.96	10.46
9	.4%	700	6.24	3.16	9.40	1.34	10.74
10	.4%	700	5.75	2.75	8.50	.46	8.96
11	.4%	—	5.00	1.90	6.90	.40	7.30
12	.4%	—	4.70	2.30	7.00	.55	7.55
13	.4%	—	5.75	.75	6.50	.45	6.95
14	—	—	12.20	5.30	17.50	2.50	20.00
15	—	—	8.44	4.56	13.00	3.40	16.40

Series VI

$ZnSO_4$ versus NaCl—Adobe Soil

NaCl .4 percent constant—$ZnSO_4$ varying

This series brings into play four ions instead of three, as in the series in which the antagonizing salts possess the same anion. The results are given in Table IX, together with the usual explanatory data. Once again, we see the marked evidences of the toxic properties of .4 percent NaCl to barley in the adobe soil and the equally marked

TABLE IX

Antagonism Between $ZnSO_4$ and NaCl For Barley—Adobe Soil, One Crop

No.	% NaCl Added	$ZnSO_4$ in Parts per Million	Wt. of Straw	Wt. of Grain	Wt. Dry Matter Above Surface	Wt. of Roots	Wt. of Total Dry Matter
			g.	g.	g.	g.	g.
1	.4%	50	5.88	3.72	9.60	.65	10.25
2	.4%	50	7.90	3.80	11.70	.65	12.35
3	.4%	100	8.90	3.70	12.60	1.10	13.70
4	.4%	100	9.96	4.24	14.20	1.14	15.34
5	.4%	300	8.80	5.00	13.80	.40	14.20
6	.4%	300	9.04	4.56	13.60	.75	.75
7	.4%	500	5.24	4.16	9.40	.84	10.24
8	.4%	500	6.10	3.50	9.60	.70	10.30
9	.4%	700	7.30	4.50	11.80	1.00	12.80
10	.4%	700	7.30	2.70	10.00	.55	10.55
11	.4%	1,000	8.15	3.85	12.00	.80	12.80
12	.4%	1,000	6.30	3.70	10.00	1.20	11.20
13	.4%	——	5.00	1.90	6.90	.40	7.30
14	.4%	——	4.70	2.30	7.00	.55	7.55
15	.4%	——	5.75	.75	6.50	.45	6.95
16	——	——	12.20	5.30	17.50	2.50	20.00
17	——	——	8.44	4.56	13.00	3.40	16.40

antagonizing properties thereto of another salt. As triplicate pots show clearly, less than half the yield of barley is obtained in the NaCl-treated soils of that produced in the control pots. The addition to the NaCl, however, of 50 parts per million of $ZnSO_4$ very largely overcomes the toxic effect in question, and the addition of 100, or 300 parts per million of $ZnSO_4$ almost entirely obliterates it. The addition of larger quantities of $ZnSO_4$ seems to be less effective than the last two named, but about as effective as 50 parts per million up to and including the largest quantity used, viz., 1,000 parts per million. Again, the effects of antagonism are marked with respect to grain and straw production, as well as with respect to root yields, though perhaps least striking in the latter case.

Series VII

$CuSO_4$ versus Na_3SO_4—Oakley Soil

Na_2SO_4 .5 percent constant—$CuSO_4$ varying

Two errors were made in this series. The first consisted in the omission of control untreated pots from the experiment. The second was the addition of equal amounts of ammonium nitrate to all pots in order to obtain better absolute yields. The reasons for referring to these as errors are obvious. Nevertheless, the data in Table X are interesting, inasmuch as they do indicate, in spite of the presence of ammonium nitrate in the pots, distinct antagonism between Na_2SO_4 and $CuSO_4$.

TABLE X*

Antagonism Between $CuSO_4$ and Na_2SO_4 For Barley—Oakley Soil, One Crop

No.	% Na_2SO_4 Added	$CuSO_4$ in Parts per Million	Wt. of Straw	Wt. of Grain	Wt. Dry Matter Above Surface	Wt. of Roots	Wt. of Total Dry Matter
			g.	g.	g.	g.	g.
1	.5%	100	8.00	2.00	10.00	.55	10.55
2	.5%	100	8.38	3.62	12.00	.67	12.67
3	.5%	200	10.45	2.55	13.00	.50	13.50
4	.5%	200	9.27	3.43	12.70	.80	13.50
5	.5%	300	8.50	2.00	10.50	.55	11.05
6	.5%	300	10.62	5.18	15.80	.50	16.30
7	.5%	400	7.80	2.70	10.50	.50	11.00
8	.5%	400	6.60	1.40	8.00	.23	8.23
9	.5%	—	6.05	2.95	9.00	.58	9.58
10	.5%	—	7.90	2.10	10.00	.90	10.90

* 1 g. NH_4NO_3 added to each pot 1 month after plants were up.

Series VIII

$ZnCl_2$ versus NaCl—Oakley Soil

NaCl .4 percent constant—$ZnCl_2$ varying

Despite the errors of the two series just described, evidence on the existence of antagonism between the heavy metals and the alkali salts in the Oakley soil is to be found in Table XI of Series VIII, in which, moreover, the larger concentration of NaCl employed made possible the bringing into stronger relief the antagonisms in question. The data in Table XI speak largely for themselves. It remains but to mention that the higher concentration of $ZnCl_2$ used inhibited the growth of barley entirely in this series and that grain was produced only in the cultures in which the most marked antagonism occurred.

TABLE XI

Antagonism Between $ZnCl_2$ and NaCl For Barley—Oakley Soil, One Crop

No.	% NaCl Added	$ZnCl_2$ in Parts per Million	Wt of Straw	Wt. of Grain	Wt. Dry Matter Above Surface	Wt. of Roots	Wt. of Total Dry Matter
			g.	g.	g.	g.	g.
1	.4%	100	3.85	.05	3.90	.23	4.30
2	.4%	100	2.10	—	2.10	.17	2.27
3	.4%	200	4.80	.65	5.45	.32	5.77
4	.4%	200	2.50	.50	3.00	.60	3.60
5	.4%	300	2.05	—	2.05	.35	2.40
6	.4%	300	1.55	—	1.55	.15	1.70
7	.4%	400	1.10	—	1.10	.08	1.18
8	.4%	400	—	—	—	—	—
9	.4%	500	—	—	—	—	—
10	.4%	500	—	—	—	—	—
11	.4%	1,000	—	—	—	—	—
12	.4%	1,000	—	—	—	—	—
13	.4%	—	1.60	—	1.60	.17	1.77
14	.4%	—	1.65	—	1.65	.24	1.89
15	—	—	3.25	—	3.25	.32	3.57
16	—	—	2.97	—	2.97	.24	3.14

TABLE XII

Antagonism Between $CuSO_4$ and NaCl For Barley—Oakley Soil, One Crop

No.	% NaCl Added	$CuSO_4$ in Parts per Million	Wt. of Straw	Wt. of Grain	Wt. Dry Matter Above Surface	Wt. of Roots	Wt. of Total Dry Matter
			g.	g.	g.	g.	g.
1	.4%	50	24.60	4.20	28.80	.78	29.58
2	.4%	50	13.90	6.10	20.00	.80	20.80
3	.4%	100	20.90	2.10	23.00	.90	23.90
4	.4%	100	18.80	1.20	20.00	.76	20.76
5	.4%	200	20.40	2.40	22.80	.40	23.20
6	.4%	200	13.00	3.20	16.20	Lost	16.20
7	.4%	300	29.40	1.00	30.40	.80	31.20
8	.4%	300	13.40	1.60	15.00	—	15.00
9	.4%	400	16.50	1.00	17.50	.40	17.90
10	.4%	400	9.80	3.20	13.00	1.56	14.56
11	.4%	500	15.30	1.70	17.00	.52	17.52
12	.4%	500	11.90	1.30	13.20	.40	13.60
13	.4%	—	8.10	1.90	10.00	.16	10.16
14	.4%	—	12.20	2.80	15.00	.40	15.40
15	—	—	20.40	2.40	22.80	2.60	25.40
16	—	—	24.00	2.00	26.00	1.00	27.00
17	—	—	12.80	4.20	17.00	1.20	18.20

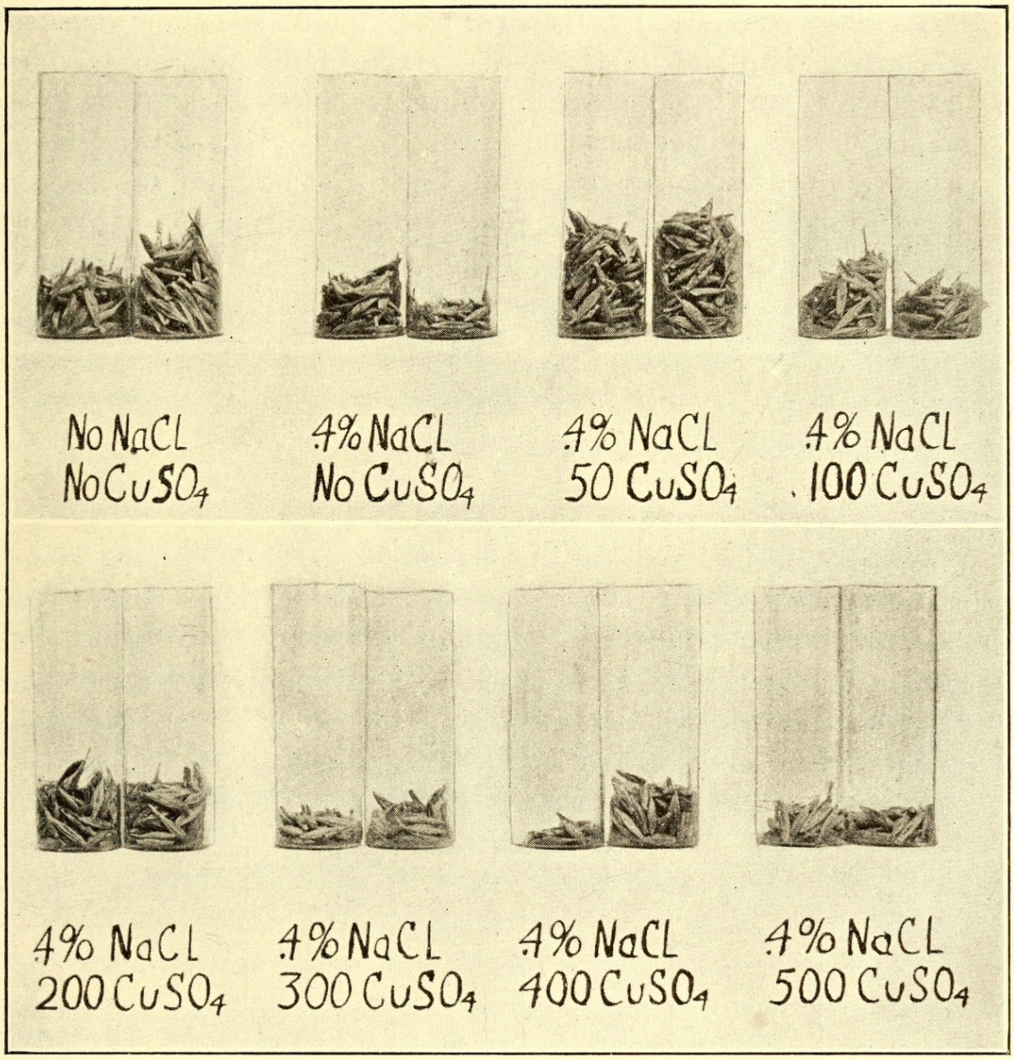

FIG. 2. $CuSO_4$ *vs.* NaCl. Showing yields of grain from Oakley soil, first crop with and without different salt treatment. The duplicate vials represent the yields of duplicate pots and give an idea of the individual variability in plant production. The antagonism obtaining here is clearly very marked.

Series IX

$CuSO_4$ versus NaCl—Oakley Soil

NaCl .4 percent constant—$CuSO_4$ varying

Table XII gives the results obtained and other necessary data in regard to Series IX. The Oakley soil used in this case was different from any of the lots used in the other series described in this paper and hence gave very different yields in all the pots. The figures submitted show, as clearly as any obtained with the adobe soil, how markedly $CuSO_4$ antagonizes NaCl. Even 50 parts per million of $CuSO_4$ added to .4 percent NaCl is sufficient to obliterate entirely the toxic effects of the last-named salt and perhaps even to go beyond in the direction of stimulation. Large quantities of $CuSO_4$ as high as 400 and 500 parts per million are also very effective in antagonizing .4 percent NaCl. There would seem to be much promise in the data obtained for application to alkali conditions in the field, like those obtaining in the Imperial Valley.

Series X

$ZnSO_4$ versus NaCl—Oakley Soil

NaCl .4 percent constant—$ZnSO_4$ varying

While the absolute yields in this series were small, the data in Table XIII show clearly that $ZnSO_4$ has a definite power of antagonizing NaCl when the latter is used at the toxic concentration of .4 percent. At high concentrations of $ZnSO_4$ plus .4 percent NaCl, no growth was obtained.

TABLE XIII

Antagonism Between $ZnSO_4$ and NaCl For Barley—Oakley Soil, First Crop

No.	% NaCl Added	$ZnSO_4$ in Parts per Million	Wt. of Straw	Wt. of Grain	Wt. Dry Matter Above Surface	Wt. of Roots	Wt. of Total Dry Matter
			g.	g.	g.	g.	g.
1	.4%	100	1.73	.17	1.90	.20	2.10
2	.4%	100	3.85	—	3.85	.70	4.55
3	.4%	200	2.40	.30	2.70	.52	3.22
4	.4%	200	2.42	.18	2.60	.70	3.30
5	.4%	300	3.70	—	3.70	.45	4.15
6	.4%	300	1.95	.05	2.00	.40	2.40
7	.4%	400	2.15	—	2.15	.35	2.50
8	.4%	400	1.90	.10	2.00	.34	2.34
9	.4%	500	3.35	—	3.35	.48	3.83
10	.4%	500	1.67	.08	1.75	.22	1.97
11	.4%	1,000	Trace	—	Trace	—	—
12	.4%	1,000	Trace	—	Trace	—	—
13	.4%	2,000	—	—	—	—	—
14	.4%	2,000	—	—	—	—	—
15	.4%	3,000	—	—	—	—	—
16	.4%	3,000	—	—	—	—	—
17	.4%	—	.72	—	.72	.06	.78
18	.4%	—	1.05	—	1.05	.10	1.15
19	.4%	—	.75	—	.75	.05	.80
20	—	—	4.70	—	4.70	.25	4.95
21	—	—	3.30	—	3.30	.32	3.62

General Discussion

It may be stated without qualification that the data submitted above are evidence of the antagonistic action of the heavy metals to alkali salts for crop plants grown in pots. Moreover, our evidence appears to be the first of the kind ever published. If, as now seems likely, the principles thus adduced may be applied to field conditions, a new factor of safety may be introduced into alkali problems which may possess major importance in competent hands. From the scientific standpoint, on the other hand, the facts which we have obtained are equally interesting and important and indicate a field of investigation of great promise with regard to the mechanism of the antagonistic action which we have noted.

That the effects noted are, in a sense, certainly not ephemeral ones may be gleaned from the data submitted for the adobe soil in which three crops were grown in succession in some of the series and antagonism was shown to obtain in all cases. It is unfortunate that similar results were not obtained for the Oakley soil which could be submitted in this paper, but the results of certain series which were not complete and therefore could not be given here indicate, as one would expect, that the facts adduced in the case of the adobe soil are of equal cogency in their application to the Oakley soil.

Other general features of our experiments, which may demand special attention here, are the following: The small quantities of the metals which are sufficient to antagonize large quantities of alkali salts render the economics of the applications of the scientific principles involved fairly simple. If it should prove possible to employ refuse from metallic ores for the purpose, the task of antagonizing the alkali salts in soils should prove particularly simple. The fact, also, that zinc is nearly as effective as copper in the direction noted may be indicative of possibilities in the same line with other and cheaper metals, a point which we shall hope to determine in future experiments.

The reproductions of photographs of some of the grain yields in vials as containers will serve to emphasize the data for the yields which are given in the tables.

In the discussions given herewith, the authors have been fully cognizant of the differences which obtain between the amounts of salts applied to the soil and those which remain actively in solution in the soil water. We have not attempted, therefore, to give in the tables any idea as to the actual amounts of interacting salts in the antagonisms noted. For one thing, this would be impossible with the methods now possessed by soil investigators. Besides, we do not consider our results as applying to any phase of the problem except that of the actual conditions which exist in soils when certain amounts of the alkali salts are present, and when their effects are more or less modified by the addition of other salts. In view of these considerations, it appears that the question raised by us, in anticipation of its being brought forward by others, is of little pertinence in so far as our main thesis is concerned.

Summary

Experiments bearing on the antagonism between salts of the heavy metals, Cu and Zn, and the common alkali salts of soils have been carried out as follows: Plants were grown in pots and two different soils were tested. NaCl, Na_2SO_4 and Na_2CO_3 were used in toxic and constant quantities, the salts of the heavy metals varying in quantity within a given series. Barley was the plant grown. Briefly, the following results were obtained:

1. Copper and zinc antagonize NaCl, Na_2SO_4 and Na_2CO_3 in the Berkeley adobe soil, and the antagonism is evident even if three successive crops are used as criteria, and when only the metallic ions vary.

2. When four ions are introduced, for example, as in the case of $CuSO_4$ versus NaCl, fully as much and even more antagonism is manifest between the heavy metals and the alkali salts.

3. Although only one crop was grown on the Oakley sand, similar evidences of marked antagonism between the heavy metals and the alkali salts were noted. The evidence in this case was, however, particularly striking in the case of $CuSO_4$ versus NaCl.

4. These findings should possess considerable significance in the field reclamation of alkali lands, and particularly in the case of those which do not contain large enough quantities of salts to render them unfit for plant growth by reasons of high osmotic pressures in their soil solutions.