HILGARDIA

A Journal of Agricultural Science Published by the California Agricultural Experiment Station

VOLUME 14

OCTOBER, 1941

NUMBER 2

CONTENTS

CHLORATE DISTRIBUTION AND THE EFFECT OF NITRATE CONCENTRATION ON CHLORATE TOXICITY IN SOIL COLUMNS

R. S. ROSENFELS AND A. S. CRAFTS

MOVEMENT OF CARBON DISULFIDE VAPOR IN SOILS

R. M. HAGAN

UNIVERSITY OF CALIFORNIA · BERKELEY, CALIFORNIA

HILGARDIA

A Journal of Agricultural Science Published by the California Agricultural Experiment Station

Vot.	14
104.	TT

October, 1941

No. 2

CHLORATE DISTRIBUTION AND THE EFFECT OF NITRATE CONCENTRATION ON CHLORATE TOXICITY IN SOIL COLUMNS^{1,2}

R. S. ROSENFELS³ AND A. S. CRAFTS⁴

INTRODUCTION

SODIUM CHLORATE is widely used in controlling weeds. The fact that it acts most efficiently as a temporary soil sterilant $(\mathcal{3}, \mathcal{5}, \mathcal{6})^5$ emphasizes the need for accurate knowledge of its behavior in soils.

In an attempt to evaluate the effects of soil type and rainfall on the vertical distribution of sodium chlorate in soils, Crafts (2) in 1935 performed experiments on the slow percolation of sodium chlorate solutions into columns of air-dry soil. Enough solution was allowed to drip upon the soil to just wet the entire column. The column of soil was then separated into ten equal fractions, each of which was mixed and seeded with oats. The plants were grown for 30 days. In view of the fact that in some cases the oats grew normally in soil from the bottom parts of the column, but showed high toxicity in soil from the upper parts of the column, he concluded that the chlorate had been fixed in the upper layers of soil and therefore had not reached the bottom part of the column.

In 1939, experiments reported by Crafts showed that chlorate toxicity in soils is reduced roughly in proportion to the nitrate concentration of the soil solution (4, p. 655–71). This observation suggests an alternative explanation for the low toxicities occurring in some soils near the bottom of a chlorate-treated column. The percolating chlorate solution may have

¹ Received for publication May 27, 1940.

² This paper was made possible by the coöperative project on control of noxious weeds conducted by the California Agricultural Experiment Station and the Division of Cereal Crops and Diseases, Bureau of Plant Industry, United States Department of Agriculture.

³ Assistant Physiologist, Division of Cereal Crops and Diseases, Bureau of Plant Industry, United States Department of Agriculture.

⁴ Associate Professor of Botany and Associate Botanist in the Experiment Station.

⁵ Italic numbers in parentheses refer to "Literature Cited" at the end of this paper.

washed the nitrate out of the upper layers and concentrated it near the bottom. If so, the result would be the production of greater toxicity in the upper than in the lower part of the column, even though the concentration of chlorate were the same throughout the column. The present study was intended to determine whether this is the correct explanation or whether the chlorate is fixed in the upper layers, with consequent failure to reach the lower parts.

For this work, three of the four soils originally studied were chosen. In the original tests, Yolo clay loam had proved to be a soil in which toxicity was greatest in the upper parts of the column, whereas Stockton adobe clay showed uniform toxicity throughout the column. Fresno sandy loam⁶ was intermediate, with some reduction of toxicity near the bottom, but less than in Yolo clay loam.

METHODS

For experimental purposes, samples from the first 4 inches of the respective soils were taken from the field, air-dried, and thoroughly screened and mixed. Unless otherwise noted, two tubes of soil were set up for each test. After treatment with chlorate solution, one tube was used for the determination of toxicity, the other for chemical analysis.

The soil tubes and auxiliary apparatus used have been pictured and described in another paper (2, p. 470). Briefly, the tube is made by bending a sheet of celluloid 10×36 inches into a hollow cylinder about 3 inches in diameter. This is wrapped with $\frac{1}{2}$ -inch-mesh hardware cloth which is wired in place. The bottom is closed by a circle of filter paper held by a piece of hardware cloth wired to the outside of the tube. The tube, filled with soil, is secured in an upright position so that the contents of a reservoir may drip slowly upon the surface of the soil.

Table 1 gives the amount of soil used per tube for each of the three soil types represented, the volumes of sodium chlorate solution applied to each, and their respective air-dry moisture contents. The solution volumes were the amounts necessary to just moisten the columns.

In all cases $0.004 \ M$ sodium chlorate was used (426 p.p.m. NaClO₃). The contents of the reservoirs dripped upon the tops of the columns at a rate of about 12 drops per minute. About 36 hours was usually required to wet each column, and the tubes were allowed to stand 12 to 24 hours after the reservoirs were empty. The tubes were then opened, and each column of soil was cut into ten portions of equal length.

The portions from one of the duplicate columns were mixed individually, put into no. 2 cans, and seeded with Kanota oats. The details of this

⁶ The Fresno sandy loam used is designated on old soil maps as brown phase. Shaw (8) has classified this soil in the Dinuba series.

procedure have been described elsewhere (2, p. 463). The oats were grown in the greenhouse for 30 days, the crop in each can having been thinned to ten plants.

Then the fresh weight of tops and the average height of the plants were recorded. The fresh-weight yield was taken to be an inverse measure of toxicity, which in previous tests (2) was thought to result directly from the concentration of chlorate present. Fresh-weight yields of 0.1 gram or less are arbitrarily recorded as 0.1 gram and signify that for practical purposes there was no growth.

TABLE 1						
SOIL WEIGHTS, SOLUTION VOLUMES, AND MOISTURE CONTENTS OF AIR-DRY						
Soils Used in the Percolation Tests						

Soil	Weight of air-dry soil per tube	Volume of solution in each reservoir	Moisture content of air-dry soil, basis of oven-dry soil	
Yolo clay loam Stockton adobe clay Fresno sandy loam	kilos 5.0 5.0 6.5	<i>ml</i> 1,800 1,250 1,300	per cent 4.5 7.5 2.2	

The portions of the other column were also mixed individually, and the moisture content of each was determined. Samples of each were extracted with water in the ratio of one part dry soil to two parts water. The soil-water mixtures were agitated continuously for about $1\frac{1}{2}$ hours and then filtered under gravity. The extracts thus obtained were analyzed for nitrate, chlorate, and chloride. The nitrate analyses were made by the Devarda method as given by the Association of Official Agricultural Chemists (1, p. 26). As shown by preliminary tests, this method was satisfactory in the presence of chlorate, whereas the phenoldisulfonic acid colorimetric method was not.⁷

Chlorate was determined by the sulfurous acid reduction method that Rosenfels has described in another paper (7). In this method the chloride content of the extract is also determined.

Single chemical analyses and moisture determinations were made; the tests were repeated on the Yolo and Stockton soils but not on Fresno sandy loam. Results typical of the data obtained are reported.

⁷ The Devarda method can be used provided the amount of Devarda's alloy taken is sufficiently in excess of that required for reduction of nitrate present. In the work here reported the amounts of chlorate present in the 20-ml aliquots used were insufficient to necessitate an increase above the customary 3 grams of Devarda's alloy. With the phenoldisulfonic acid colorimetric method, however, even small amounts of chlorate interfere seriously by forming brownish reaction products with the phenoldisulfonic acid reagent.

TABLE 2

Chemical and Toxicity Data at Ten Levels in Columns of Soil Treated with $0.004\;M$ Sodium Chlorate

	Per cent	Composition of extract		Millimols per liter of indicated ion in extract			Yield of oats		
Portion	moisture, basis of dry soil	Wet soil, grams	Water, ml	ClO3-	NO₃-	Cl-	Fresh weight, grams	Height, cm	
Yolo clay loam									
1 2 3 5 6 7 8 9 10 Check	$\begin{array}{c} 39.4\\ 39.5\\ 40.4\\ 41.1\\ 40.6\\ 39.6\\ 39.3\\ 41.1\\ 41.9\\ 39.8\\ 4.5\end{array}$	$\begin{array}{c} 140.0\\ 140.0\\ 140.0\\ 140.0\\ 140.0\\ 140.0\\ 140.0\\ 140.0\\ 140.0\\ 140.0\\ 140.0\\ 140.5\\ \end{array}$	$\begin{array}{c} 160.0\\ 160.0\\ 160.0\\ 160.0\\ 160.0\\ 160.0\\ 160.0\\ 160.0\\ 160.0\\ 160.0\\ 160.0\\ 195.5 \end{array}$	$\begin{array}{c} 0.75\\ 0.60\\ 0.60\\ 0.67\\ 0.67\\ 0.90\\ 0.90\\ 1.02\\ 1.20\\ 0.00\\ \end{array}$	$\begin{array}{c} 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 2.00\\ 5.35\\ 6.10\\ 14.15\\ 2.90 \end{array}$	$\begin{array}{c} 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.45\\ 0.45\\ 1.42\\ 0.22 \end{array}$	0.2 0.2 0.1 0.2 0.2 0.2 0.2 0.3 2.1 4.4 5.1 5.3 5.9*	5 5 4 6 5 5 15 23 25 26 28*	
		Yolo clay lo	am (leache	d before ch	lorate appl	ied)			
1	$\begin{array}{c} 40.7\\ 41.5\\ 40.6\\ 41.6\\ 42.2\\ 41.3\\ 44.1\\ 44.5\\ 45.0\\ 45.4\\ 4.5\end{array}$	$140.0 \\ 140.0 \\ 140.0 \\ 140.0 \\ 140.0 \\ 140.0 \\ 140.0 \\ 140.0 \\ 140.0 \\ 140.0 \\ 140.0 \\ 140.5 \\ 104.5 \\ 104.5 \\ 100 \\ $	$\begin{array}{c} 160.0\\ 160.0\\ 160.0\\ 160.0\\ 160.0\\ 160.0\\ 160.0\\ 160.0\\ 160.0\\ 160.0\\ 160.0\\ 160.0\\ 195.5 \end{array}$	$\begin{array}{c} 0.70\\ 0.69\\ 0.37\\ 0.58\\ 0.69\\ 0.70\\ 0.82\\ 0.78\\ 0.75\\ 0.67\\ 0.00\\ \end{array}$	$\begin{array}{c} 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 2.90 \end{array}$	0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.0	0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1	2 2 2 2 2 2 2 2 2 3 3 4 28*	
Stockton adobe clay									
12	$\begin{array}{c} 36.1\\ 34.8\\ 34.8\\ 35.2\\ 34.3\\ 33.8\\ 35.0\\ 34.5\\ 33.9\\ 29.6\\ 7.5 \end{array}$	133.0 133.0 133.0 133.0 133.0 133.0 133.0 133.0 133.0 133.0 133.0 133.0	167.0 167.0 167.0 167.0 167.0 167.0 167.0 167.0 167.0 167.0 167.0 192.5	$\begin{array}{c} 0.64\\ 0.55\\ 0.52\\ 0.52\\ 0.52\\ 0.52\\ 0.67\\ 1.03\\ 0.90\\ 0.00\\ \end{array}$	trace trace trace trace trace 0.35 0.35 0.60 0.60 0.85 0.36	0.00 0.00 0.00 0.00 trace 1.20 1.65 1.35 0.42	0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1	3 3 3 3 3 3 3 3 3 3 21†	
Fresno sandy loam									
12 33 45 67 89 910 Check	22.0 23.1 23.5 22.9 22.6 22.0 22.3 21.5 20.6 20.3 2.2	$\begin{array}{c} 120 & 0 \\ 120 & 0 \\ 120 & 0 \\ 120 & 0 \\ 120 & 0 \\ 120 & 0 \\ 120 & 0 \\ 120 & 0 \\ 120 & 0 \\ 120 & 0 \\ 120 & 0 \\ 102 & 2 \end{array}$	180.0 180.0 180.0 180.0 180.0 180.0 180.0 180.0 180.0 180.0 180.0 180.0 197.8	$\begin{array}{c} 0.37\\ 0.39\\ 0.34\\ 0.31\\ 0.37\\ 0.37\\ 0.45\\ 0.37\\ 0.51\\ 0.45\\ 0.00\\ \end{array}$	$\begin{array}{c} 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 1.40\\ 1.55\\ 3.50\\ 0.76 \end{array}$	$\begin{array}{c} 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.33\\ 4.80\\ 8.22\\ 15.67\\ 3.81 \end{array}$	0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.8 1.3 2.4‡	3 3 3 3 3 3 3 3 10 17 22 ‡	

* Check plants grown from December 28, 1939, to January 27, 1940; experimental plants from December 6, 1939, to January 5, 1940. Experimental plants from leached column of Yolo clay loam grown December 28, 1939, to January 27, 1940.

† Check plants grown from December 28, 1939, to January 27, 1940; experimental plants from December 20, 1939, to January 19, 1940.

‡ Both check and experimental plants grown from January 5 to February 4, 1940.

RESULTS

Table 2 gives the results of the routine tests outlined above, and also those with Yolo clay loam after it had first been thoroughly leached. The leaching experiment was intended to determine the effect on toxicity produced by removal of the nitrate before applying chlorate. To accomplish this, 1,800 ml of distilled water was first permitted to drip upon each column, which just wetted the soil. Then another 1,800 ml of distilled water was added, and the soil solution in the column was permitted to drip through the filter-paper bottom. Next, 1,800 ml of 0.004 M NaClO₃ was introduced. Since chlorate began to appear in the leachate before all the chlorate solution had left the reservoir, evidently the chlorate solution was not uniformly displacing the soil solution ahead of it, but was probably in part moving along the tube walls or through channels in the soil. After the 1,800 ml of chlorate solution had left the reservoir, 1,800 ml more were added to insure complete displacement of the soil solution in the column with chlorate solution. According to tests not reported, involving only one application of 1,800 ml, the chlorate concentration was very low in the bottom portions because some of the chlorate had escaped, as described above.

In all tests the ten portions of each column were numbered from 1 to 10, beginning at the top. The portion designated "check" refers to the original untreated soil. In making extracts of the check soils, allowance was made for the air-dry moisture content, and enough water was added to give a 1:2 extract. In the ten portions of wet soil taken from the tubes the exact moisture content was not known definitely ahead of time, and each portion was extracted alike without allowance for small variations in moisture content. The approximate moisture content was of course known from the weight of soil and the volume of solution in each tube.

Each yield figure reported for the check samples is the mean of two determinations, two cans of each soil being seeded.

DISCUSSION

Clearly, according to table 2, the concentration of chlorate is not lower in the bottom portions of any column than in the top. The decrease in toxicity noted was probably caused by the downward movement of nitrate. This conclusion is further supported by the fact that in Stockton adobe clay, a soil very low in nitrate, toxicity does not decrease in the lower portions. In the tenth portion in this soil the nitrate concentration was only 0.85 millimols per liter of the extract. This quantity probably included traces of nitrogen derived from some organic constituent which underwent reduction during the Devarda distillation. Furthermore, the

preliminary removal of nitrate by leaching eliminated the decrease in toxicity in Yolo clay loam, so altering the behavior of this soil that it resembled Stockton adobe clay, a soil in which fixation had never been suspected.

The data for chloride emphasize the concentration of soluble salts in the lower portions. In Fresno sandy loam the concentration of chloride in the tenth portion was more than 0.5 per cent expressed on the basis of the soil solution at a soil moisture content of 20 per cent. The plants growing in this culture appeared to suffer from excess salt, and the yield was undoubtedly reduced by the salt concentration.

Calculations made on the data of table 2 show that all the chlorate applied remained in solution because a summation of the chlorate present in the ten fractions equals that applied. In making these calculations one assumption was necessary—namely, that each portion of a given column contains one tenth of the total amount of oven-dry soil of the column. This assumption is incorrect to the extent to which settling and lack of uniformity of packing may have caused differences in density within the soil mass. To illustrate, the calculations for the first portion of the unleached Yolo clay loam column were as follows:

The moisture content was 39.4 per cent on the basis of oven-dry soil. The amount of wet soil extracted was 140 grams. The amount of water in the wet soil, therefore, was 39.6 ml. To this was added 160 ml of distilled water, making a total of 199.6 ml of water. Since the concentration of chlorate in the extract was found by analysis to be 0.75 millimols per liter, the total amount of chlorate in this amount of soil was 0.15 millimols. The amount of oven-dry soil with which this was associated was 100.4 grams. Each portion was assumed to be one tenth of 5,000 grams of air-dry soil which contained 4.5 per cent water, expressed on the oven-dry basis, which is 478.5 grams of oven-dry soil. This quantity should have contained 0.71 millimols of chlorate which could be dissolved in water. The total quantity of chlorate found in all ten portions was 7.66 millimols for Yolo clay loam, and the amount applied (1,800 ml of 0.004 M) was 7.20. The apparent recovery, therefore, was 106 per cent. With Fresno sandy loam the recovery was 99 per cent. With Stockton adobe clay the calculation was upset because about half of the last portion was not wet by the percolating solution; and the dry soil was discarded before making the extract. Again, nevertheless, it was evident that all the chlorate applied had appeared in solution.

Besides showing that chlorate is not fixed by the soil, the data for unleached soil (table 2) show a higher concentration of chlorate in the bottom four portions of all three soils than in the top six. This is not the case with the leached soil. This fact suggests water adsorption, a phenomenon observed by others and termed negative adsorption.⁸ To check this point the following tests were made with Yolo clay loam:

Two columns of the soil were set up as before, one air-dry with 4.5 per cent moisture, dry basis, the other oven-dry. Sodium chlorate solution, approximately 0.004 M, was percolated through each column and permitted to continue on through the filter-paper bottom. Two successive 50-ml portions of each percolate were collected and then a larger third portion was collected overnight. This third portion amounted to 180 ml for the oven-dry column and to 360 ml for the air-dry soil. The six samples thus obtained and a sample of the original sodium chlorate solution were each analyzed in duplicate for chlorate. Precautions were taken to minimize evaporation during the test. The original chlorate solution proved to have a chlorate ion concentration of 4.2 millimols per liter. The first 50 ml of percolate from the oven-dry column contained 12.6 millimols per liter of chlorate; the second 50 ml, 10.0 millimols per liter; and the third portion, 7.7. The first 50 ml from the air-dry column contained 5.9; the second 50 ml, 5.9; and the third portion, 5.2. There is no doubt that the chlorate concentration was greatly increased by passage through the column of oven-dry soil and somewhat so in passing through the airdried soil.

Another test of water adsorption was also performed. In this experiment 95 grams of oven-dry soil was mixed with 75 ml of the sodium chlorate solution and the mixture was shaken several times and let stand 24 hours. The solution was then filtered off and analyzed. The chlorate ion concentration in the filtrate was 4.6 millimols per liter, whereas in the original solution it had been 4.2 millimols per liter, as before. Sufficient filtrate was obtained for only a single analysis. The test was repeated, however, with the same result—namely, the concentration of the chlorate solution was increased approximately 10 per cent by contact with the soil. The test was also repeated using air-dry soil. In this case the increase was of the order of 3 per cent in the one trial made.

Both water adsorption and the greater effectiveness of oven-dry than of air-dry soil in causing water adsorption are strikingly demonstrated by the percolation tests. In these the solution continued to invade dry soil as it passed down the column, and presumably became increasingly concentrated as it moved downward.

In view of the foregoing results, it is reasonable to expect that differential toxicity, similar to that found with Yolo clay loam, will be encountered in the use of sodium chlorate in the control of weeds on soils that

⁸ Positive adsorption is the retention of solute molecules by the soil and results in a decrease in concentration of the leachate over that of the applied solution. Negative adsorption in the above usage is the retention of water by the soil and results in an increase in solute concentration of the leachate.

contain considerable nitrate. With soils low in nitrate, the effect is likely to be reasonably uniform throughout the depth penetrated by the chlorate. The practical expedient is to increase the chlorate dosage on nitratecontaining soils.

The toxicity of the herbicide might be less altered if the application were made in the fall when absorption by plants had reduced the nitrate concentration of the soil, but if the soil temperature is still high, decomposition of the chlorate might more than offset the effect of reduced nitrate content of the soil. In summer-fallowed soils, peat, or other soils high in nitrate or other salts, the killing of deep-rooted perennials with chlorate may become impractical, in which case clean cultivation, flooding, crop competition, or some other chemical method should be used.

SUMMARY

When sodium chlorate slowly percolates through a column of soil, some of the nitrate of the soil will be washed down to the lower levels. Since concentrating the nitrate reduces the toxicity of chlorate, the killing effect on deep-rooted plants may not be so great as it is near the surface, even though the chlorate concentration is uniform throughout the depth penetrated.

In soils originally containing little or no nitrate, a reduced toxicity is not observed in the lower levels. Similarly, preliminary removal of nitrate by leaching tends to overcome inequalities in chlorate toxicity resulting from differences in nitrate distribution.

Water adsorption was clearly demonstrated in Yolo clay loam, and was apparently manifested also by the other two soils studied.

ACKNOWLEDGMENTS

The authors wish to thank Dr. J. P. Conrad and Dr. P. R. Stout for their helpful discussions of the data, and Dr. W. P. Kelley for editorial suggestions.

LITERATURE CITED

- 1. Association of Official Agricultural Chemists. 1935. Official and tentative methods of analysis. 4th ed. 710 p.
- 2. CRAFTS, A. S.
 - 1935. The toxicity of sodium arsenite and sodium chlorate in four California soils. Hilgardia 9:461-98.
- 3. CRAFTS, A. S.
 - 1935. Physiological problems connected with the use of sodium chlorate in weed control. Plant Physiol. 10:699-711.
- 4. CRAFTS, A. S.
 - 1939. The relation of nutrients to toxicity of arsenic, borax, and chlorate in soils. Jour. Agr. Research 58:637-71
- 5. LOOMIS, W. E., E. V. SMITH, RUSSELL BISSEY, and L. E. ARNOLD.
 - 1933. The absorption and movement of sodium chlorate when used as an herbicide. Jour. Amer. Soc. Agron. 25:724-39.
- 6. MUENSCHER, W. C.
 - 1932. Killing perennial weeds with chlorates during winter. New York (Cornell) Agr. Exp. Sta. Bul. 542:1-8.
- 7. ROSENFELS, R. S.
 - 1938. Determination of chlorate in soil extracts, culture solutions, and plant sap. Jour. Assoc. Off. Agr. Chem. 21:665-74.
- 8. SHAW, C. F.
 - 1927. The basis of classification and key to the soils of California. First Internatl. Cong. Soil Sci. Proc. 4:1-39.