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THE USE OF ARSENICAL COMPOUNDS IN THE CONTROL OF DEEP-ROOTED PERENNIAL WEEDS[1]

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INTRODUCTION

As chemical weed control becomes more generally practiced, the limitations as well as the possibilities of the various methods become more evident. The effectiveness of these methods depends upon certain factors which must be carefully considered if consistent results are to be obtained. Many of the factors may be controlled by the operator. It is, therefore, essential to the successful practice of any new method that a descriptive study of the more readily controlled factors be made; for only when we understand the underlying principles may we obtain the best results.

This preliminary report describes the preparation and use of an arsenical solution recently employed with considerable success in controlling deep-rooted perennial weeds. It discusses the mechanism involved in the movement of the arsenical solution into the roots of plants, and submits data for comparing and evaluating the factors that tend to limit its action. It discusses also the conditions essential to successful practice and gives certain precautions for the handling of the reagents.

One should understand at the outset that the arsenical herbicide described in the following pages will not completely eradicate perennial weeds. Such results cannot be expected of any chemical weed killer. This herbicide has, however, proved very satisfactory when prepared properly and applied under optimum conditions.

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Arsenicals have long been utilized in the destruction of undesirable vegetation. Sodium arsenite is the active ingredient in many proprietary herbicides. Although other chemicals have recently been widely used against the more noxious perennial weeds, certain arsenic compounds are cheaper and may be more effective.

In 1917 Gray[2] reported that, under some conditions, sodium arsenite solution, applied to the foliage of morning-glory plants, was absorbed and carried into the roots. In 1927 Kennedy and Crafts[4] suggested a mechanism which they thought to be responsible for this movement of arsenic compounds within the plant. In 1930[1] they gave additional data on their work, citing evidence to confirm their theory. Morgan[5] has recently proposed the same mechanism to explain the translocation of arsenic acid in his experiments with hoary cress.

The work presented here further strengthens the theory; and, though the limitations of the method are definitely described, the possibility of developing an efficient control practice seems nearer realization than was apparent in these earlier reports.

The mechanism responsible for the rapid translocation of arsenic compounds into the roots of morning-glory after application to the leaves may be briefly described as follows. When the plant has been transpiring freely for some time, water loss from the leaves exceeds intake by the roots. As the pressure within the xylem becomes subatmospheric, a water deficit develops in all living cells. When a plant in this condition is sprayed with a solution of a strong acid or base, the living cells of the leaves and stems are killed and rendered permeable. The pressure gradient becomes immediately effective and all moisture free to move is forced into the xylem and carried down into the roots. If soluble arsenic compounds are present in the spray solution, they will diffuse into the tissues, will become mixed with the vacuolar sap, and, as the cells collapse, will be carried downward along with any unevaporated spray solution. When destruction of the foliage is complete, the tissues become dry, the downward movement in the xylem stops, and the arsenic compounds slowly diffuse from the vessels, killing all living cells of the root. The various factors limiting the action of this mechanism have been described elsewhere in detail[4, 1].

EXPERIMENTAL RESULTS

Little has been published on the effective concentrations of arsenic compounds and of acids in herbicidal solutions. Gray[2] used approximately a 0.5 per cent solution of As_2O_3, and a previous publication[1] mentioned $\frac{M}{20}$ (approximately 1 per cent) as the optimum concentration.

Tables 1, 2, and 3 present experimental evidence relative to the critical concentrations of these reagents. The plots used were all one square rod in area and were densely infested with morning-glory (*Convolvulus arvensis* L.).

TABLE 1

EFFECTS OF CONCENTRATION EXPRESSED AS PER CENT As_2O_3 ON RESULTS OF SPRAYING MORNING-GLORY WITH ACID ARSENICAL SPRAYS

Per cent As_2O_3	Number of plots	Average percentage resprouts two months after spraying
4.00	6	9.1
2.00	18	7.2
1.00	18	8.2
0.50	12	8.4
0.25	12	15.8

It is apparent from the data in table 1 that 0.5 per cent As_2O_3 is the lowest effective arsenic concentration under the conditions of the experiment and may be considered a lower limit for sprays in field practice.

TABLE 2

RESULTS OF SPRAYING WITH ARSENICAL SOLUTIONS DIFFERING IN ACID CONCENTRATION

Normality of acid, H_2SO_4	Number of plots	Average percentage resprouts two months after spraying
0.50	25	49.0
1.00	25	9.9
1.50	16	6.1
2.00	25	11.1

As indicated in previous publications,[1, 3] a spray of acid reaction is more effective than an alkaline one. The data in table 2 show the relation between acid concentration and effectiveness of the spray.

These figures (table 2) may be compared with some laboratory data (table 3) on the time required for killing morning-glory tissues with acid solutions of differing concentrations. The times of killing were found by allowing leaf sections to stand in acid solutions of determined pH values until death occurred. The pH values in the table were taken from a titration curve on ground morning-glory tissue.

TABLE 3

TIME REQUIRED FOR KILLING MORNING-GLORY TISSUE WITH ACID OF DIFFERENT NORMALITIES

Normality of acid H_2SO_4	pH attained	Time required for killing, hours
0.41	4.00	48.0
0.50	3.70	16.7
0.75	3.00	4.8
1.00	2.40	1.2
1.25	2.00	0.8
1.50	1.90	0.7
1.75	1.85	0.6
2.00	1.80	0.6

Tables 2 and 3 indicate that the use of a solution sufficiently high in acidity to cause rapid killing of the sprayed foliage is essential in this method of applying arsenicals as herbicides. They further indicate that the acid concentration should be at least 1.0 N to give satisfactory results in the field.

Because the volume of solution available for translocation into the roots is definitely limited by the amount of evaporation of the spray solution occurring after it is applied, the time element in the killing process is necessarily of prime importance. Evaporation being conditioned by temperature and humidity, which are both subject to diurnal variation, certain hours should be best for applying these sprays. Commercial operators have long favored night spraying, the benefits of which have been demonstrated time and again in the field. The data in table 4 offer further substantiation. They are not given as complete proof, but merely to show the magnitude of differences to be expected.

Although the factors affecting evaporation also condition transpiration and thus the water deficit in the plant, water is absorbed only slowly by the roots, especially from soils that are low in moisture; and the deficit remains high for several hours after sundown.

TABLE 4

INFLUENCE OF TIME OF DAY UPON RESULTS OF SPRAYING WITH ACID ARSENICAL*

Plot No.	Date of application	Time of application	Percentage resprouts two months after spraying
1	Sept. 8	8:00 p.m.	5
2	Sept. 9	8:30 a.m.	20
3	Sept. 9	11:00 a.m.	15
4	Sept. 9	1:30 p.m.	10
5	Sept. 9	4:00 p.m.	10
6	Sept. 9	6:30 p.m.	5
7	Sept. 9	9:00 p.m.	5

* Solution containing H_2SO_4 of 1.0 N concentration and 1 per cent As_2O_3.

Plant physiologists generally agree that considerable energy is used in absorbing moisture from soils, especially when the moisure content approaches the permanent wilting percentage. This competition between the soil and the plant for water is reflected in the water content of the plant and also in the effectiveness of acid arsenical sprays as related to tension in the xylem vessels. The results of the following experiment (table 5) indicate that distribution of arsenical compounds is not effective in plants too abundantly supplied with moisture. Eight plots, located in an orchard, were used. Four had been recently irrigated, so that the soil was still very damp. The plants were making rapid growth and had formed a dense mat of foliage. The other four plots had not been irrigated for six weeks. Though the plants had an abundance of foliage, end growth had practically ceased, and their appearance evidenced the lack of available moisture.

Here again (table 5) the data are given as a confirmation of results observed many times in the field. As the author has already pointed out,(1) Gray's recommendation of fall spraying has probably more bearing on soil moisture conditions than on movement of organic foods in the plant. The figures in table 5 indicate that little is accomplished by spraying plants which are growing in a soil saturated with moisture. If top growth is cut off until the soil becomes drier, however, too little foliage may be subsequently produced, and poor results will follow. One should, apparently, allow a maximum growth of tops to develop and then depend upon this large leaf surface to deplete the soil moisture until a high deficit is produced. Only where an ample amount of foliage exists is this type of treatment satisfactory.

The spray solution applied to the plots mentioned above (table 5) was low in acidity (approximately 0.5 N), a condition which, because of its effect upon penetration, tended to emphasize the differences between treatments on wet and dry soils. The effects of diurnal variation in evaporation rate upon distribution of the arsenical solution are also shown.

TABLE 5

INFLUENCE OF SOIL MOISTURE ON RESULTS OF SPRAYING WITH ACID ARSENICALS

Soil dry			Soil moist, recently irrigated		
Plot No.	Time of application	Percentage resprouts two months after spraying	Plot No.	Time of application	Percentage resprouts two months after spraying
1	2:00 p.m.	75	5	2:30 p.m.	100
2	3:00 p.m.	50	6	3:30 p.m.	100
3	4:00 p.m.	10	7	4:30 p.m.	100
4	7:30 p.m.	5	8	8:00 p.m.	75

When the foliage of sprayed plants has become completely killed and all free moisture has moved down into the roots, rapid mass flow of the arsenical solution ceases; the effectiveness of the application is fixed by the extent of distribution at this time. If more moisture is applied to the tops of the plants before the water columns of the xylem become disrupted, downward flow should be resumed, and distribution of the arsenic compounds should become more extensive. Plots 3 and 7 in table 5 were sprayed with several light applications of water soon after treatment with the chemical solution and plots 4 and 8 were sprayed with water early on the following morning. This procedure, in addition to the favorable time of application, probably explains the excellent results obtained on the dry plots with this particular spray solution.

TABLE 6

THE EFFECTS OF ADDED APPLICATIONS OF WATER UPON THE RESULTS OF APPLYING ACID ARSENICALS

Number of applications of water	Series 1		Series 2		Series 3	
	Number of plots	Average percentage resprouts two months after spraying	Number of plots	Average percentage resprouts two months after spryaing	Number of plots	Average percentage resprouts two months after spraying
0	6	19.1	12	6.3	12	14.6
1	6	8.3	....	....	....	....
2	6	5.0	....	....	....	....
3	....	....	12	3.0	12	11.6

The results of the practice are further illustrated in table 6. Three series of plots received the acid arsenical spray in the evening. In the first series 6 plots were sprayed twice with water on the following morning, 6 plots received one application, and 6 plots were untreated. In the second and third series, 12 plots in each received three applications on the following morning, while 12 received no water.

Although these three series of plots differed considerably in their general results, because of differences in time and manner of application, all showed consistently less resprouting where water was applied to the dead tops on the morning after the original spraying. Application of water seems, therefore, to be a cheap and easy method of increasing the effectiveness of spraying with acid arsenicals.

DISCUSSION

Though the data presented on some phases of this work are not extensive, and many experiments are still in progress, a few essential points seem well established. A simple, workable method for preparing an acid arsenical solution in the field is described in the next section. Experiments now going on indicate that little can be hoped for in the improvement of this basic formula, at least until the chemistry of the solutions has been more thoroughly studied.

The field trials emphasize the importance of temperature, incident radiation, humidity, and air velocity on evaporation, and consequently upon the action of the mechanism involved. Once a given solution has been applied to the foliage of the plants, the volume of liquid that carries arsenical compounds into the roots depends directly upon the rate of penetration and translocation and is inversely proportional to the amount of evaporation occurring. When the application is made before sundown during the summer in the central valleys of California, the temperature is usually high, the incident energy intense, and the relative humidity low. Though the high temperature causes rapid penetration, all three of these factors favor a high rate of evaporation. Plot tests and field trials show that at this time of day insufficient solution reaches the roots to provide for a thorough distribution.

After dark the temperature drops, radiation is practically eliminated, and relative humidity goes up. Evaporation, in consequence, is very much reduced; and though penetration is less rapid, the acidity of the solution can be adjusted to keep it optimum. The total volume of liquid, including the vacuolar sap of the plant cells, which is available for translocation, is greater. The xylem tissues of the root system therefore become completely filled with arsenical solution, and injury is much more general. Strong winds at any time increase evaporation rate and lower the effectiveness of the treatment.

The foregoing discussion indicates the complexity of the relation existing between the composition of the spray solution, the temperature, and those factors primarily influencing evaporation. The latter factors have not been accurately measured and evaluated. The only way in which they have been given consideration here has been in delaying the application until after sundown. An accurate determination of their influence is needed if more consistent results are to be obtained. These determinations constitute a part of the work which is in progress.

Though the method which has been described for killing deep-rooted perennial weeds with an acid arsenical solution has been developed to such a degree that one is reasonably sure of satisfactory results provided all controlling factors are carefully considered, it should be emphasized that complete eradication is seldom, if ever, accomplished. Not all plants in a field can be in the proper condition at any one time. Those in the centers of heavily infested areas will have less water available than those bordering on uninfested regions. Often lateral roots extending into uninfested soil will be killed for some distance from the main root, but, becoming independent, will send up shoots and establish themselves as new plants. Morning-glory roots are often cut by gophers at various depths, from which they are able to send up new shoots and reestablish themselves. Insect injury often leads to a premature drying of foliar organs, and these plants are little affected by the spray solution.

One should further note that the problem of eradicating an old, established stand of almost any perennial weed involves more than the elimination of existing plants. Ridding the land of seeds remains as the most vital step if reinfestation is to be avoided. Experiments in progress indicate that a stand of morning-glory may, with proper handling, be sufficiently matured for effective treatment before viable seeds have been produced. Seeds which are green at the time of treatment are apparently killed by the arsenic compounds and fail to germinate.

Almost all stands of morning-glory, however, have a thorough infestation of the soil with seed from previous years, which must be germinated and killed before the danger is eliminated. Probably the best method for controlling the seedlings and the few old plants that come back after spraying is to cultivate thoroughly and weed-cut about twice after each irrigation, or each spring on unirrigated land. On the other hand, the plants may be allowed to mature and then sprayed; but this method is more expensive and less certain than weed cutting. Further work must be done on this phase of the problem before definite recommendations can be made.

Because of the abundance of wild morning-glory (*Convolvulus arvensis*), the experiments described in this paper have been performed on that plant. A few tests on other weeds indicate that at least two more, alkali mallow (*Sida hederacea* Dougl.) and Russian knapweed (*Centaurea repens* L.), are equally susceptible to this type of treatment, if not more so. There is little hope of controlling the perennial grasses by this spray, for it is practically impossible to wet them with an aqueous solution and get the necessary intimate contact with the plant. Other flat-leaved plants that develop late enough in the season to deplete the soil moisture should lend themselves, however, to this treatment.

One need fear no permanent injury to the soil from the use of this type of spray. The small amount of arsenic trioxide used is insignificant in comparison with the mass of soil involved and seems to stimulate rather than inhibit the growth of subsequent crops. Experiments in soil sterilization indicate that applications of two hundred to three hundred pounds of sodium arsenite per acre have little effect upon subsequent crop growth. Evidently, then, many applications of the acid arsenical described above would be necessary to cause any permanent harm.

PREPARATION OF THE SPRAY SOLUTION

For practical field use one must have a convenient method of preparing the spray solution. Few methods have been described [3, 5, 6] for the preparation of an acid arsenical solution for herbicidal purposes; and those few entail the use of arsenic pentoxide or arsenic acid, less toxic and more expensive forms than the common trioxide. During the experimental work just presented, a simple, practical method was developed which should prove useful for almost any scale of operation.

Arsenic trioxide is amphoteric and will react according to the following equations:

$$(1)\quad As_2O_3 + 6\,HCl = 2\,AsCl_3 + 3\,H_2O$$
$$(2)\quad As_2O_3 + 2\,NaOH + H_2O = 2\,NaH_2\,AsO_3$$

A solution may be made according to the first reaction by refluxing the arsenic trioxide in concentrated hydrochloric acid. The second reaction, being exothermic, goes very rapidly when only a small quantity of water is used.

As the spray solution should have an acid reaction, it would seem illogical to use alkali as an agent in dissolving the arsenic (equation 2). Probably for this reason, acid arsenicals previously made from arsenic trioxide have been produced by the costly process of refluxing with acid (equation 1). When one considers the problem quantitatively, however, and determines the cost of the chemicals used, it is obvious that the acidification of the alkaline solution, after it has been diluted to field strength, is by far the more practical method.

Because the alkali used in dissolving the arsenic must be neutralized in the final solution, it should be kept at a minimum in preparing the stock solution. A series of empirical tests with the commercial chemicals has shown that a solution containing 4 parts by weight of arsenic trioxide, 1 part by weight of sodium hydroxide, and 3 parts by weight of water is permanent and convenient to use as a stock solution. This forms a solution of sodium acid arsenite, in which the amount of sodium hydroxide is small; hence but little sulfuric acid is wasted in its neutralization. Five hundred gallons of spray solution containing 0.5 per cent arsenic trioxide would contain only 5 pounds of caustic soda, and about an equal quantity of sulfuric acid is required to neutralize it. The cost of these is negligible. Laboratory tests have shown that the small amount of sodium sulfate formed is entirely inert and in no way affects the action of the acid or arsenical. This quantity of sodium arsenite solution suffices for one acre of morning-glory, and previous data (table 2) indicate that if sulfuric acid to a concentration of 1.0 N (approximately 5 per cent by weight) is incorporated an effective herbicide will be produced.

Where only a few acres are to be sprayed, the necessary solution can be made up and handled with the equipment available on most farms. The stock solution of the arsenical does not affect iron containers; and though 1.0 N sulfuric acid is very corrosive to metal, when mixed with the necessary sodium arsenite it reacts only slowly with iron. Equipment designed to handle this solution in large quantities and over extended periods of time should be made of bronze or brass. Wooden tanks are not injured.

Nozzles throwing a flat, fan-shaped spray have given good results; the pressure should not exceed 100 pounds per square inch. An effort should be made to build up an excess of the solution on the foliage since the extent of distribution within the plant depends largely upon the volume of solution available.

As arsenic compounds are extremely poisonous, neither the dry arsenic trioxide dust nor the fumes from the stock solution or spray mist should be inhaled. The hands, the face, and, especially, the eyes should be protected from both arsenicals and sulfuric acid; and livestock must be kept away from the chemicals, the solutions, and the sprayed vegetation. Sulfuric acid should be handled only by persons familiar with its properties. A bucket containing saturated bicarbonate of soda solution should be available at all times for washing the face or hands in case of an accident during the mixing or application of the spray solution.

SUMMARY

A mechanism, dependent upon a water deficit in the plant, has been described to account for the movement of arsenicals from the sprayed foliage into the underground root system.

The most dilute arsenical solution giving effective control in field plots contained 0.5 per cent As_2O_3 by weight. Higher concentrations up to 4 per cent seemed not significantly more effective.

An arsenical spray solution of acid reaction seems most effective in the field. The lowest effective concentration of the acid was apparently 1.0 N.

From late afternoon until midnight has been advocated as the best time to use this type of spray. The data given confirm this recommendation.

For best results the soil in which the plants are growing should not be excessively moist. There should be a full development of foliage.

Application of water to the dead foliage on the morning after spraying increased the percentage of plants killed.

The stock arsenical solution is prepared by mixing dry 4 parts by weight of As_2O_3 and 1 part by weight of NaOH, adding 3 parts by weight of water and stirring until dissolved.

The spray solution is made by diluting 1 part by weight of the stock arsenical solution with 100 parts by weight of water, mixing thoroughly, and then adding, with constant stirring, 5 parts by weight of concentrated H_2SO_4.

About 500 gallons of this spray solution will be needed in treating an acre of morning-glory. Weeds having more abundant top growth require more solution.

A nozzle giving a fan-shaped spray, operating at 100 pounds pressure, has proved satisfactory.

The seedlings which come up after irrigation or during the spring after spraying on unirrigated land should be killed by cultivation or spraying.

No permanent injury to the soil results from this type of treatment.

The arsenious oxide and concentrated sulfuric acid used in the preparation of the spray solution should be handled with great caution.

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