to have 0.021 and 0.004 p.p.m. of phosphine present, respectively.

A second baking experiment was carried out using a 3-kg. sample of commercial flour to which 120.4 mg. of powdered Phostoxin tablet had been added. This, theoretically, represents 13.4 p.p.m. of phosphine, but analysis showed only 4.95 p.p.m. This is to be expected because of losses of phosphine during mixing. Two loaves of bread were made, and analysis indicated that 0.029 p.p.m. of apparent phosphine was present. On comparison with the control values obtained above, however, no phosphine appeared.

Discussion

The analytical method as described above is extremely sensitive. The limiting factor, as is true in most residue analyses, is the extent of separation of the compound of interest from interfering materials. In the present case, this refers to the phosphorus content of the reagents, especially the water, used in the reactions. To determine quantities in the range of parts per billion, the concentration of phosphorus in the reagents must be below this range. Reference should also be made to the results obtained in the baking studies with control flour and bread. The cause of this apparent phosphine in the control samples is not known, though it may be due to particles of flour being carried over from the reaction flask, as flour is very difficult to wet. However, this is not true of the bread and an appreciable blank value was present in this case also. These results point out the necessity of always running control or blank samples with any analysis.

The results of experiments with grain indicate the residues that may be expected on fumigation with Phostoxin under a wide variety or circumstances. The original recommendation by the manufacturer to treat with ten tablets of Phostoxin per ton of grain has since been changed to six tablets per ton.

The rate of application in laboratory experiments was considerably in excess of the recommended rates, and the results of these studies should be interpreted in terms of maximum residues to be expected. The field experiments were carried out using the now recommended dosages of Phostoxin. The maximum residue found was 0.046 p.p.m. of phosphine and this decreased to 0.006 p.p.m. after aerating.

Aeration proved very effective in removing any residues present, as shown in the results of both laboratory and field experiments. Laboratory experiment 8 indicates this effect very clearly with a decrease in phosphine content from 3.03 to 0.004 p.p.m. after simple exposure to air and is confirmed in other laboratory and field experiments.

No consistent relation was found between dosage and residue in field experiments, nor with time after exposure, as there appears to be under laboratory conditions. All residues in samples received from field conditions were very small, possibly because of sampling conditions, although every precaution was taken to prevent loss of phosphine.

The results of the baking studies indicate that no phosphine should be expected in baked products from Phostoxin-treated wheat; even when Phostoxin was added to flour immediately before baking, no residue was found.

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SOIL FUMIGANTS

Diffusion and Pest Control by Methyl Bromide and Chloropicrin Applied to Covered Soil

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Methyl bromide and chloropicrin have frequently been used to fumigate soils covered with plastic film for the control of weed seeds, fungi, and nematodes. The influence of temperature, moisture, air space, organic matter, depth of injection, and other factors on depth of control by these fumigants is not sufficiently understood and is the subject of this investigation.

Materials and Methods

The soil used was a Hanford fine sandy loam from Orange County, California. It was composed of 58.0% sand, 27.0% silt, and 15.0% clay (*1*). The pH was 8.1 and the organic carbon content 0.2 % (*6*). Moisture content was determined by drying soil in an oven at 221° F. and the porosity of soil was considered to be the per cent of its volume occupied by gases (*2*).

Infestation of the soil with seeds was accomplished by mixing commercial oats (*Avena* sp.) with soil that had been previously fumigated with methyl bromide to eliminate damping-off organisms and then thoroughly aerated. Per cent reduction in germination of seeds was recorded for each experiment and was considered to be an index of relative pest control.

Two experimental methods were used. Elimination of rate of diffusion as a factor influencing control was accomplished by injecting the fumigants into the center of 650-ml. capacity Ball freezer jars completely filled with loosely packed soil containing seed. Methyl bromide was applied as a gas and chloropicrin as a liquid dissolved in acetone. The amounts of acetone used (less than 0.2 ml. per jar) did not influence the apparent toxicity of chloropicrin to the seeds. The jars were tightly sealed, incubated for the required period of time, and uncapped, and germination in comparison to check treatments was determined.

The toxicity of the two fumigants to the oats in the above-mentioned type of test was determined for temperatures of

The factors influencing diffusion and pest control by methyl bromide and chloropicrin applied to covered soil were investigated. Reduction in germination of oats in treated soil was considered an index of the relative degree of diffusion and pest control by the fumigants. Factors that tend to increase rate of diffusion of chloropicrin through soil increase depth of pest control; the reverse is generally true for methyl bromide. Effect of the soil or environmental situation on basic toxicity of the fumigant sometimes negated and sometimes enhanced the result of its effect on rate of diffusion of the fumigant. The optimum fumigation situation for chloropicrin applied under a soil cover appears to be moist, highly porous, warm soil low in organic matter. With methyl bromide, the soil should also be warm, moist, and low in organic matter, but compact instead of highly porous.

Table I. Rates, Method of Application, and Experimental Conditions Used in Studying Degree and Depth of Control of Oat Seed Germination by Methyl Bromide and Chloropicrin in Soil

Experimental Information	*Figure number* 1	2	3	4	5	6	7	8	9		10
									Organic Matter		
Factor Being Investigated	*Gravity*	*Application rate*	*Sealing period*	*Interval between injection and sealing*	*Injection depth and location of seal*	*Location of impermeable barrier*	*Air space*	*Moisture*	*Steer manure*	*Peat moss*	*Temp.*
Length of soil column, inches	60	30	30	30	30	6 to 30	30	30	30	30	30
Sealing period, hours	Not sealed	48	0.5 to 48	48	48	48	48	48	48	48	48
Interval between injection and sealing, minutes	....	None	None	0 to 15	None	None	None	None	None	None	None
Injection depth, inches	30	0	0	0 to 6	0 to 12	0	0	0	0	0	0
Location of seal	....	Soil surface	Soil surface	Soil surface	Soil surface and 12 inches above	Soil surface	Soil surface	Soil surface	Soil surface	Soil surface	Soil surface
Depth of barrier, inches	None	None	None	None	None	6–24, none	None	None	None	None	None
Temperature, °F.	70	60	70	60	60	60	60	60	60	60	40 to 90
Organic matter added											
Steer manure, %	None	None	None	None	None	None	None	None	0 to 2	None	None
Peat moss, %	None	None	None	None	None	None	None	None	None	0 to 4	None
For methyl bromide											
Pounds/acre	600	25 to 800	400	400	400	600	400	400	400	400	400
Air space/%	24	38	24	24	40	27	26 to 53	40	26	39	26
Moisture/%	11.6	6.7	11.6	14.4	7.5	12.0	12.3	5.0 to 14.0	12.0	10.0	12.8
For chloropicrin											
Pounds/acre	400	25 to 800	200	500	400	400	300	300	100	100	200
Air space, %	35	38	24	35	40	38	24 to 52	40	37	39	37
Moisture, %	11.6	6.7	11.6	14.4	7.5	12.0	12.3	5.0 to 14.0	12.0	10.0	12.8

Table II. Toxicity of Methyl Bromide and Chloropicrin to Oat Seeds in Sealed Containers for Various Temperatures, Exposure Periods, Moisture, and Organic Matter Levels

				% Reduction in Germination of Oat Seeds for Indicated Chemical and Dosage, Pounds/Acre												
				Methyl Bromide						*Chloropicrin*						
Temp., °F.	*Exposure Period, Hours*	*Moisture*[a]	*Manure Added, %*	*25*	*50*	*100*	*200*	*400*	*800*	*12.5*	*25*	*50*	*100*	*200*	*400*	*800*
40	48	High	0	0	0	97	100	100	100	0	0	0	100	100	100	100
60	48	High	0	93	75	100	100	100	100	0	66	100	100	100	100	100
80	48	High	0	0	80	100	100	100	100	16	100	100	100	100	100	100
60	4	High	0	0	0	0	100	100	100	0	0	0	100	100	100	100
60	48	Low	0	0	0	33	87	100	100	0	0	0	0	0	90	100
60	48	High	10	60	70	100	93	100	100	0	0	0	0	99	100	100

[a] Low moisture was 1% for methyl bromide and 1.5% for chloropicrin; high moisture was 8.7% for methyl bromide and 9.9% for chloropicrin.

Table III. Some Physical Properties of Methyl Bromide and Chloropicrin

Chemical	Molecular Weight	B. P.,[a] 760 Mm. Hg Pressure, °C.	Vapor[a] Pressure, 20° C., Mm. Hg	Solubility in Water at 20° C., P.P.M.	Weight Ratio[b] of Fumigant in Water to Fumigant in Air at 20° C.	Estimated[c] Diffusion Coefficient in Air at 20° C., D_0
Methyl bromide	94.95	3.6	1380	16,000[d] (at 760 mm. vapor pressure)	4.06	0.097
Chloropicrin	164.39	111.9	20	1,950[e]	10.82	0.069

[a] (5).
[b] Ratio of weights of fumigant in equal volumes of water and air estimated from their solubilities in water and vapor pressures at equilibrium.
[c] (4).
[d] (3).
[e] Determined by Main Analytical Laboratory, The Dow Chemical Co., Midland, Mich.

40°, 60°, and 80° F., exposure periods of 4 and 48 hours, organic matter (steer manure) additions to the soil of 0 and 10.0%, and soil moisture contents of 1.0 and 8.7% for methyl bromide and 1.5 and 8.7% for chloropicrin.

Simulation of the field application of fumigants under plastic film was accomplished as follows: Saran (vinylidene chloride copolymer) pipe $1^{7}/_{16}$ inches in I. D., $1\ ^{14}/_{16}$ inches in O. D., and 30 inches long was split lengthwise and then fastened together on the inside with adhesive 7-mil poly(vinyl chloride) tape. Longer tubes were prepared by fastening together two of the tubes described above with adhesive tape. The tubes were filled with soil containing seed and, except for the gravity experiment, sealed with rubber stoppers covered with 2-mil polyethylene film. The bottoms of the tubes were not ordinarily sealed, but in one experiment, barriers to diffusion of fumigants through soil (such as a water-soaked or very compact soil layer) were simulated at different depths by inserting tightly fitting rubber stoppers.

For convenience, methyl bromide was applied as a gas and chloropicrin as a liquid dissolved in acetone (less than 0.1 ml. of acetone per tube). Unreported experiments showed that essentially similar results were obtained whether chemicals were applied undiluted or diluted to potential use levels in acetone or xylene. After fumigant application, and vertical incubation of the tubes for 7 days, the containers were slit lengthwise and opened up, and control was determined in 3-inch increments with respect to depth. Once germination increased to above the 50% level, it almost always increased to 100% within the next 3-inch increment of depth, and thus degrees of oat seed control less than 50% are not presented.

Experimental conditions, chemical rates, and methods of application used in studying the effects of various factors on depth of control by the two fumigants are shown in Table I.

Results and Discussion

The toxicity of methyl bromide and chloropicrin to oat seeds in sealed containers (Table II) increased with increased temperature, increased moisture, increased exposure period, and decreased organic matter.

Some of the physical properties of the fumigants are shown in Table III. Chloropicrin, because of its lower vapor pressure, higher distribution ratio of fumigant in water to that in air, and lower diffusion coefficient through air, would be expected to vaporize and diffuse through soil much more slowly than methyl bromide.

Figure 1 illustrates that gravity had little or no effect on diffusion of both chloropicrin and methyl bromide, since in both instances reduction in seed germination above and below the point of injection was approximately equal. Fumigants, presumably, move through soil by random molecular diffusion rather than mass flow of vapor.

Progressive increase in depth of control with increasing rates of application of

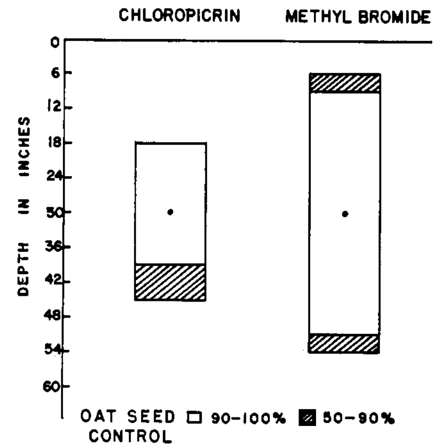


Figure 1. Control of oat seeds by chloropicrin and methyl bromide as related to the possible effect of gravity on movement of fumigant through soil

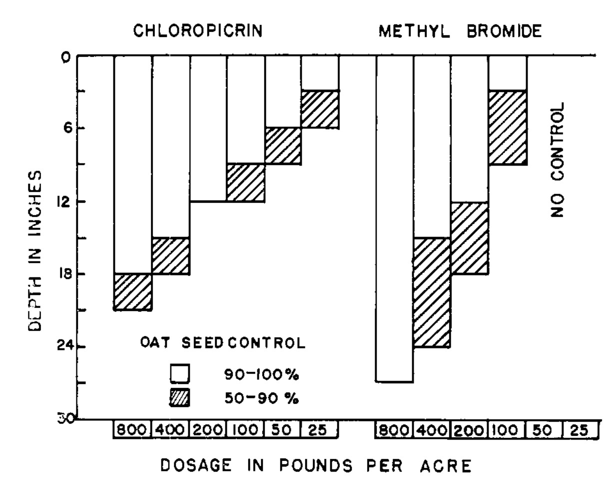


Figure 2. Control of oat seeds with various dosages of chloropicrin and methyl bromide

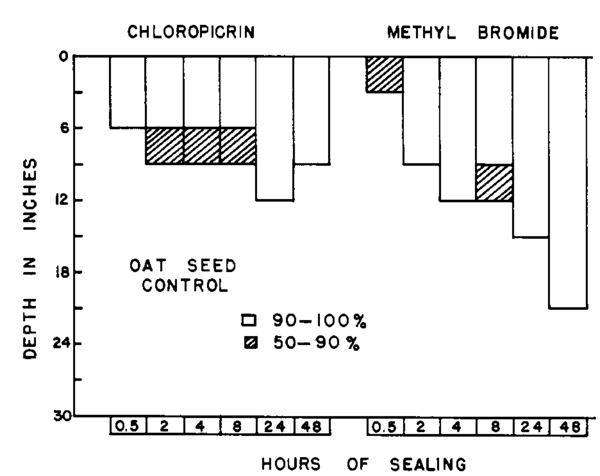
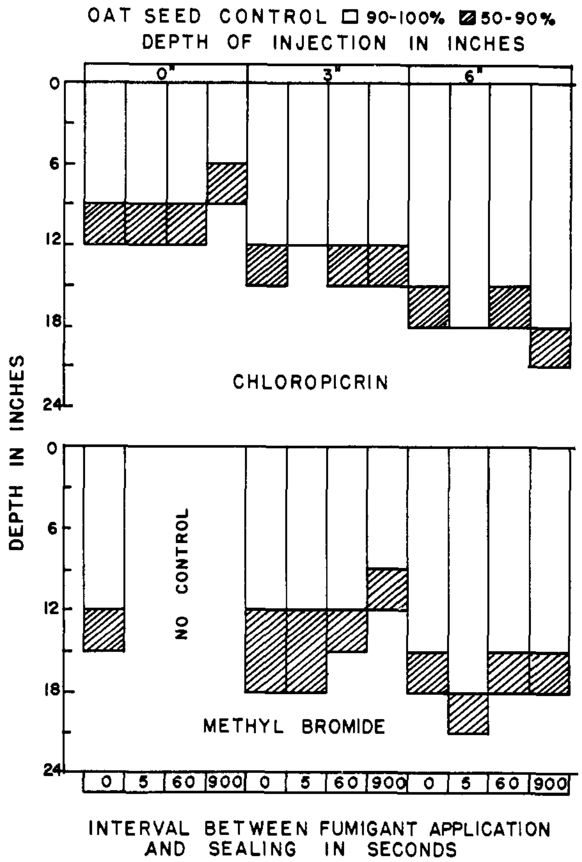


Figure 3. Control of oat seeds by chloropicrin and methyl bromide with various sealing periods



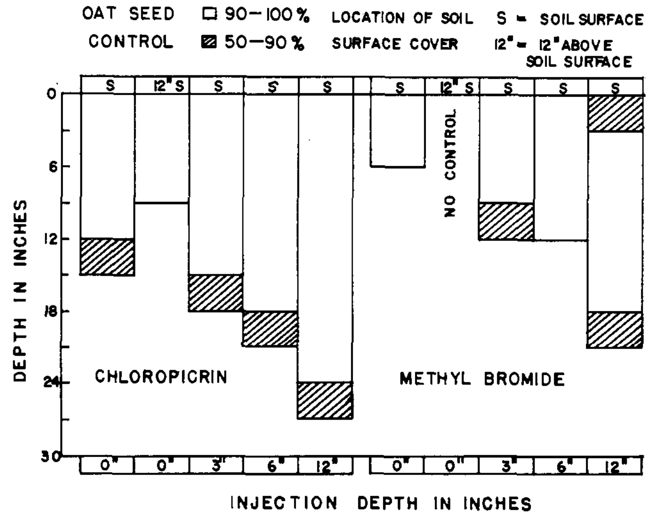


Figure 5. Control of oat seeds by methyl bromide and chloropicrin applied at various depths in the soil

◀ Figure 4. Control of oat seeds by chloropicrin and methyl bromide with various intervals between fumigant application and sealing

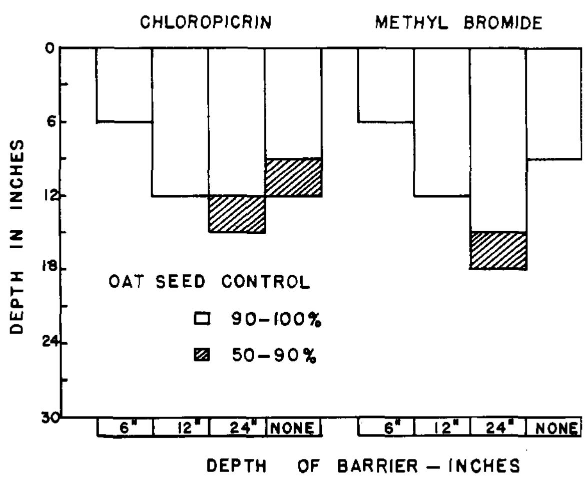


Figure 6. Control of oat seeds by chloropicrin and methyl bromide with impermeable barriers placed at various depths in the soil

fumigant is shown in Figure 2. The rate of increase of depth of control with increasing rate of application was more gradual with chloropicrin than with methyl bromide. Presumably, rate of diffusion through soil is a more important factor limiting depth of control with chloropicrin than with methyl bromide.

The effect of sealing period on depth of control is shown in Figure 3. With both chloropicrin and methyl bromide, increased depth of control was obtained with increased sealing period, the effect being more pronounced with the latter than the former. Unreported tests at different rates of fumigant application illustrated that increased rates of fumigant application can compensate for decreased sealing period as far as achieving control to a desired depth is concerned.

Figure 4 illustrates the effect of the interval between injection and sealing in relation to injection depth. It is evident that with methyl bromide applied at the surface of the soil, no interval between injection and sealing can be tolerated, but that with injection at as shallow a depth as 3 inches, an interval of 1 minute between injection and sealing can be tolerated and even an interval of 15 minutes does not result in a drastic reduction in depth of control. With an injection depth of 6 inches, an interval of as much as 15 minutes between treating and sealing can be tolerated. With the much less volatile chloropicrin, even with application of the material to the surface of the soil, a waiting period of between 1 and 15 minutes prior to sealing can be tolerated without resulting in substantial reduction in depth of control.

The effect of location of the seal in relation to injection depth is shown in Figure 5. It is obvious that with both methyl bromide and chloropicrin, better control is obtained if the seal is placed at the surface of the soil than at 12 inches above the soil. Better depth of control was obtained with increasing injection depth, except that with a 12-inch injection depth, poor control was obtained at the soil surface with methyl bromide. Presumably, a higher rate of application or a longer sealing period would have ensured control at the surface even with an injection depth of 12 inches. It seems reasonable to conclude that increasing injection depth will always increase the control zone although injection at too great a depth may result in lack of control at the soil surface. Since control at the soil surface is mandatory, it becomes a matter of selecting an optimum depth of injection for any given dosage and sealing period so that maximum depth of control is obtained without sacrificing control at the soil surface.

Figure 6 shows the effect of impermeable barriers at various depths on control by methyl bromide and chloropicrin. It is evident that with the more slowly diffusing chloropicrin, barriers do little or nothing to enhance the action of the fumigant. However, with the more rapidly diffusing methyl bromide (es-

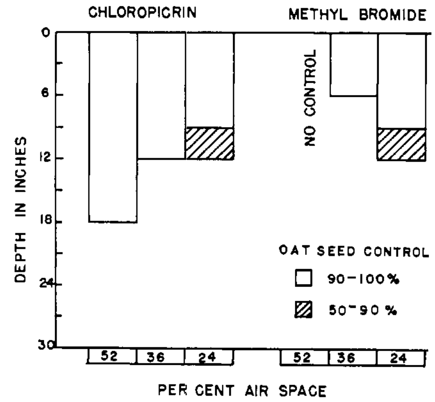


Figure 7. Control of oat seeds by chloropicrin and methyl bromide at different soil air space percentages

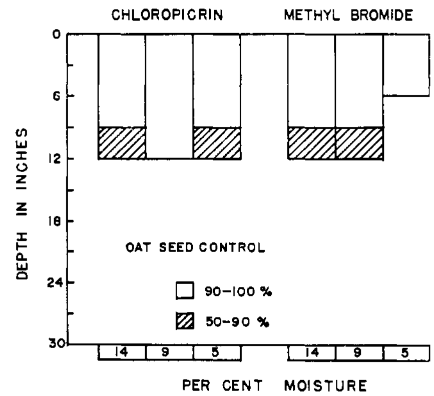


Figure 8. Control of oat seeds by chloropicrin and methyl bromide at different soil moisture percentages

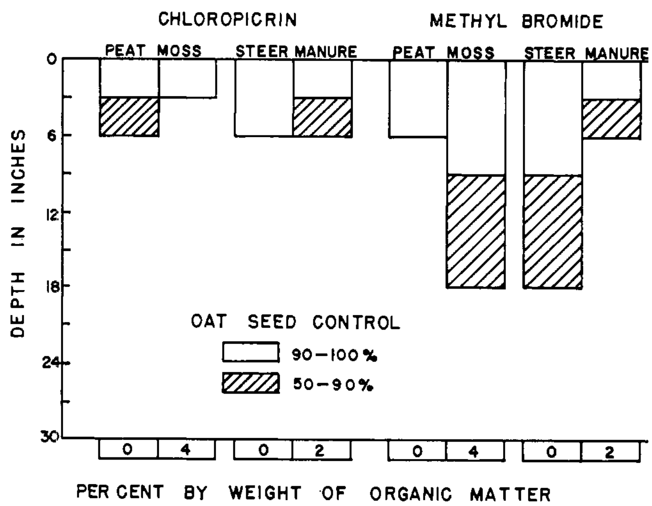


Figure 9. Control of oat seeds by chloropicrin and methyl bromide in soil mixed with peat moss and steer manure

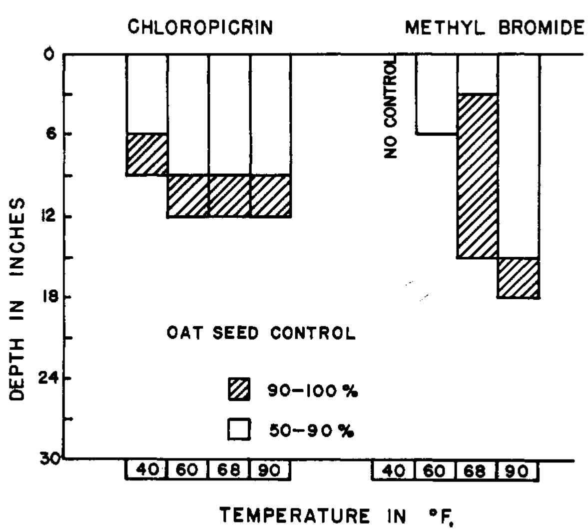


Figure 10. Control of oat seeds by chloropicrin and methyl bromide at various soil temperatures

pecially in a rather loose soil), a barrier at an appropriate depth can do much to enhance control in the upper layers of soil in comparison to having no barrier at all.

The effect of per cent air space on depth of control by fumigants is shown in Figure 7. The more slowly diffusing chloropicrin gives increased depth of control with increased air space, while exactly the reverse was true for the more rapidly diffusing methyl bromide. Thus, optimum air space for use of chloropicrin is much higher than for methyl bromide.

Figure 8 shows the effect of per cent moisture in the soil on depth of control by fumigants. It was expected that with increasing soil moisture, methyl bromide would be more effective because the toxicity of fumigant to the seeds would increase (Table II) and the resistance of the soil to diffusion and thus the exposure period of the seeds to the fumigant would increase. The results obtained confirmed this supposition. With chloropicrin, however, the decreased rate of diffusion associated with increased moisture might decrease depth of control and counterbalance the value of increased soil moisture in increasing the toxicity of fumigant to the seeds. This appears to have happened and results show relatively uniform depth of control over a wide range of soil moisture levels.

The effect of organic matter on depth of control is shown in Figure 9. Largely because of the sorption of slowly diffusing chloropicrin by organic matter, addition of both peat moss and steer manure to the soil decreased depth of control by chloropicrin. However, with methyl bromide, addition of steer manure decreased control, but addition of peat moss enhanced depth of control. It would seem that the decreased rate of diffusion of the fumigant through the soil in the presence of added organic matter sometimes, as in the case of peat moss, increases its effectiveness so as to more than counterbalance decreased effectiveness due to sorption and reaction of the fumigant with the added organic matter.

Figure 10 illustrates the effect of temperature on depth of control by fumigants. With both fumigants, depth of control decreased with decreasing temperature, more with methyl bromide than with chloropicrin. This would be expected for chloropicrin, since decreasing temperature decreases both the basic toxicity of fumigant to seeds and its rate of diffusion. With methyl bromide, its decreased basic toxicity at lower temperatures must have more than counterbalanced the increased effectiveness due to slower diffusion through soil.

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