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Distribution and Sorption of Liquid Fumigants Applied to Wheat by Recirculation[1]

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ABSTRACT

Laboratory fumigation experiments with wheat at 12.2% moisture and 77° F. were conducted in recirculators using a liquid formulation of 76.5% carbon tetrachloride (CCl_4), 3.5% ethylene dibromide (EDB), 10% carbon disulfide (CS_2), and 10% ethylene dichloride (EDC), by weight, to study the sorption and vertical distribution of each component. Gas samples were taken at five levels and five times during fumigation and were analyzed by mass spectrometry and by thermal conductivity. A small amount of EDB reached the bottom, but nearly all the EDB apparently was sorbed in the upper levels during the 30 minutes of recirculation. The other components were fairly evenly distributed but showed a slight tendency to settle downward during the longer exposures. Selective sorption occurred and the decreasing order of sorption was EDB, EDC, CS_2, CCl_4. Based on pounds of fumigant per 1000 cubic feet, the average composition in gas samples taken from interstitial space after 24 hours of exposure was 86.56% CCl_4, 0.00% EDB, 7.15% CS_2, 1.26% EDC, and 5.24% CO_2. Of the total formulation about 65% and 85% were sorbed during ½ and 24 hours, respectively.

The recirculation method of fumigating bulk-stored grain offers many advantages over the conventional methods, which utilize the forces of nature to distribute the fumigant vapors in a grain mass. Phillips (1957) was among the first in this country to report the practicality of applying liquid fumigants by recirculation. Considerable information is available concerning the insecticidal performance of liquid fumigants, but relatively little is known about the distribution and sorption of each chemical component. Kenaga (1956) reported on the gravity distribution of the components of liquid fumigants in a column of grain. The present paper presents the results of experiments conducted to determine the distribution and sorption of four chemical compounds in a liquid formulation when applied by the recirculation method.

METHODS AND MATERIALS.—Serafume®[4], a fumigant formulation containing 76.5% carbon tetrachloride (CCl_4), 3.5% ethylene dibromide (EDB), 10% carbon disulfide (CS_2), and 10% ethylene dichloride (EDC), by weight, was selected because it provided an opportunity to observe four of the commonly used components of commerical mixtures in one experiment. Duplicate fumigations were conducted on two different dates, making a total of four replicates. The average fumigation temperature was 77° F. (74° to 80°).

Each recirculator (Fig. 1) was 6 feet tall and 8 inches in diameter and was filled with 100 pounds of Hard Red Winter Wheat having a moisture content of 12.2%. The total volume of each recirculator, including the blower and duct, was 2.47 cubic feet. Copper gas sampling tubes were located at the 3-, 18-, 36-, 54-, and 72-inch levels, from the top downward. After filling the recirculators with wheat and sealing them with plastic tape, a neoprene stopper was removed from the top of each and the fumi-

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[4] Trademark of the Dow Chemical Company. The use of trade names in this paper is for identification purposes only and does not constitute an endorsement of the products by the United States Department of Agriculture.

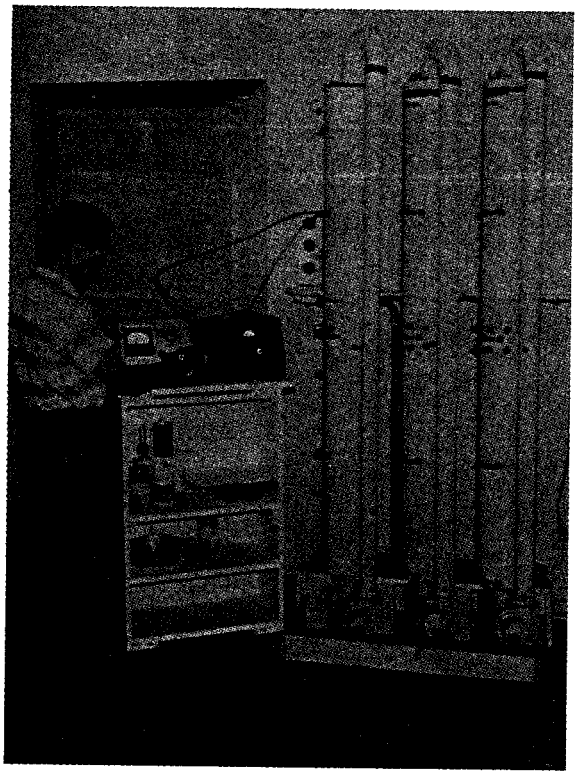

FIG. 1.—Recirculation tests were conducted in these three cylinders which are equipped with blowers to move air downward through the larger column and return it upward through the smaller pipe.

gant was applied to the wheat surface by means of a hypodermic syringe. The dosage rate was 2 gallons per 1000 bushels. When calculated on the basis of the pounds of each component per 1000 cubic feet of free space the dosages were: CCl_4, 22.74 lbs.; EDB, 1.04 lbs.; EDC, 2.97 lbs.; and CS_2, 2.97 lbs. Immediately after application of the fumigant, the stopper was replaced and the recirculation started. Each fan moved air at the rate of 0.82 cubic feet per minute per bushel and was operated for 30 minutes. This movement made a total of about 30 air changes in the wheat.

Gas samples were drawn and analyzed by a Gow-Mac, 4-filament, air reference, thermal conductivity (T/C) gas analyzer and returned to the same level from which they were drawn. Samples were taken 30 minutes, 1 hour, 4 hours, 8 hours, and 24 hours after the beginning of the tests. In addition to the Gow-Mac analyses, an additional 125-ml. gas sample was taken from each level at each of the time intervals for mass spectrometric analyses by the Dow Chemical Company. Special care was taken so that the samples were not diluted by air in the sample lines. The sensitivities, or error limits, for measurement of air-fumigant mixtures analyzed by mass spectrometry were as follows:

Compound	*Molar per cent*	*Pounds per 1000 cu. ft.*
Ethylene dichloride	0.005	0.014
Ethylene dibromide	0.005	0.026
Carbon disulfide	0.002	0.004
Carbon tetrachloride	0.005	0.021

With ethylene dibromide, the lower sensitivity limit is within the range of toxicity to insects. The sensitivity of the Gow-Mac T/C unit was estimated to be 0.05 pounds per 1000 cubic feet for CCl_4, EDC, and CS_2. The T/C unit is very slow to respond to EDB and has very wide limits of error, which were estimated to be in the range of 0.1 to 0.2 pounds/1000 cubic feet.

RESULTS AND DISCUSSION.—Table 1 lists the average concentrations for each combination of time and location. Mean concentrations were also calculated and recorded for all locations combined and each time interval. The sorption and vertical distribution of the components are shown in this table. A small amount of EDB reached the bottom, as indicated in the 30-minute samples, but apparently the bulk of it was sorbed in the upper levels. The amounts of EDB not held by sorption after 1 hour were too small to be measured by this method. The analyses indicated that the other components were fairly evenly distributed by the 30 minutes' recirculation. A slight degree of settling was observed during 24 hours' exposure, probably because the vapors were heavier than air.

It is obvious from this table that the T/C readings gave a more consistent measurement of the total gas concentration than the mass spectrometer totals. However, the T/C readings did not indicate how much of each compound was present. On the average, the T/C readings were 1.4 times the total mass spectrometer readings.

Table 1.—Gas concentrations in wheat-filled recirculators after application of 22.74 lbs. CCl_4, 1.04 lbs. EDB, 2.97 lbs. CS_2, and 2.97 lbs. EDC per 1000 cubic feet free space.

TIME INTERVAL AND DEPTH OF SAMPLE IN INCHES	POUNDS PER 1000 CUBIC FEET[a]						
	Mass Spectrometer						T/C
	CCl_4	EDB[b]	CS_2	EDC[c]	CO_2	Total	Total
30 Minutes							
3	8.98	0.02	0.80	0.28	0.15	10.23	13.29
18	8.52	.01	.72	.26	.15	9.65	12.93
36	9.13	.01	.78	.26	.14	10.32	12.91
54	8.81	.01	.73	.38	.20	10.13	12.84
71	7.24	< .01	.68	.18	.20	8.30	12.81
Mean[d]	8.53	.01	.74	.27	.17	9.72	12.96
1 Hour							
3	6.38	0.00	0.53	0.14	0.18	7.23	11.56
18	5.98	< .01	.56	.14	.18	6.86	11.38
36	6.21	< .01	.49	.12	.18	7.00	11.06
54	6.32	.00	.52	.12	.17	7.13	11.00
71	7.04	.00	.63	.15	.18	8.00	11.87
Mean[d]	6.59	< .01	.55	.13	.18	7.45	11.38
4 Hours							
3	5.50	0.00	0.45	0.11	0.19	6.25	8.66
18	5.70	.00	.44	.09	.17	6.40	8.50
36	4.48	.00	.37	.08	.19	5.12	8.41
54	5.55	.00	.45	.08	.13	6.26	8.78
71	5.08	.00	.47	.10	.18	5.83	9.91
Mean[d]	5.26	.00	.43	.09	.18	5.96	8.85
8 Hours							
3	4.44	0.00	0.33	0.07	0.19	5.03	7.39
18	4.76	.00	.36	.07	.20	5.39	7.13
36	3.32	.00	.30	.04	.20	3.86	7.22
54	5.43	.00	.45	.09	.18	6.15	7.80
71	4.98	.00	.40	.09	.17	5.64	8.63
Mean[d]	4.58	.00	.37	.07	.19	5.21	7.63
24 Hours							
3	3.25	0.00	0.26	0.05	0.20	3.76	5.45
18	3.45	.00	.29	.05	.22	4.01	5.45
36	3.25	.00	.29	.05	.22	3.81	5.59
54	4.00	.00	.32	.05	.22	4.59	5.74
71	4.00	.00	.32	.06	.22	4.60	5.90
Mean[d]	3.59	.00	.29	.05	.21	4.14	5.71

[a] Average of 4 replicates.
[b] Ethylene dibromide.
[c] Ethylene dichloride.
[d] Average of individual samples from all locations at each time interval.

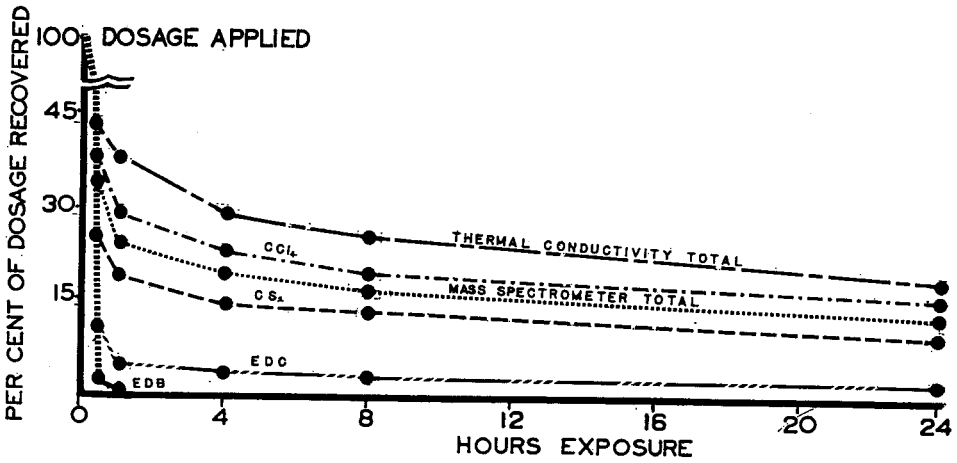

FIG. 2.—Fumigant sorption curves based on amounts recovered from interstitial space in wheat.

Table 2.—Composition of gas samples taken from wheat during fumigation with Serafume.

TIME INTERVAL AND DEPTH OF SAMPLE IN INCHES	PER CENT BY WEIGHT[a]				
	CCl_4	EDB[b]	CS_2	EDC[c]	CO_2
30 Minutes					
3	88.13	0.15	7.85	2.75	1.47
18	88.11	.13	7.45	2.69	1.55
36	89.07	.12	7.61	2.54	1.37
54	88.45	.08	7.33	3.82	2.01
71	87.12	.06	8.18	2.17	2.41
Mean	88.17	.11	7.68	2.79	1.76
1 Hour					
3	88.73	0.00	7.37	1.95	2.50
18	88.86	.06	8.32	2.08	2.67
36	88.71	.04	7.00	1.71	2.57
54	88.64	.00	7.29	1.68	2.38
71	88.11	.00	7.88	1.88	2.25
Mean	88.61	.02	7.57	1.86	2.47
4 Hours					
3	88.85	0.00	7.27	1.78	3.07
18	88.92	.00	6.86	1.40	2.65
36	87.67	.00	7.24	1.57	3.72
54	88.80	.00	7.20	1.28	2.88
71	87.29	.00	8.08	1.72	3.09
Mean	88.31	.00	7.33	1.55	3.08
8 Hours					
3	88.27	0.00	6.56	1.39	3.78
18	88.15	.00	6.67	1.30	3.70
36	86.01	.00	7.77	1.04	5.18
54	88.29	.00	7.32	1.46	2.93
71	88.45	.00	7.10	1.60	3.02
Mean	87.83	.00	7.08	1.36	3.72
24 Hours					
3	86.21	0.00	6.90	1.33	5.30
18	86.03	.00	7.23	1.25	5.49
36	85.30	.00	7.61	1.31	5.77
54	87.72	.00	7.02	1.10	4.82
71	87.53	.00	7.00	1.31	4.81
Mean	87.56	.00	7.15	1.26	5.24

[a] Mass spectrometer.
[b] Ethylene dibromide.
[c] Ethylene dichloride.

This relationship ranged from 0.8 to 2.8. The variations did not indicate any kind of trend which could be correlated with the small degree of selective sorption which occurred after the first 30 minutes and changed the ratios of the components in the interstitial gas.

Table 2 shows the fumigant composition of gas samples taken in each of the different time and location intervals. These data present further evidence of selective sorption in that EDB was sorbed most rapidly and to the greatest extent, followed in order by EDC, CS_2, and CCl_4. The percentage of carbon dioxide was recorded because it produces a T/C signal approximately equal to that of CCl_4. The amount of CO_2 actually remained fairly constant, but as shown in table 2, its relative concentration increased because of the sorption of the fumigant compounds. The selective sorption was very rapid and much of it occurred during the first 30 minutes.

Figure 2 illustrates the relative soption rates of the four components and of the mixture as a whole. Each of the points on the curves was calculated by dividing the average mass spectrometer or T/C reading by the theoretical dosage applied. Again, it is apparent that much of the fumigant (60% to 70%) was sorbed during the first 30 minutes. About 85% of the total applied dosage was sorbed during 24 hours' exposure.

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