present work. At any rate, for system VIII, the d_{001} spacing was not altered by washing, indicating the persistence of parathion inside the interlayer spacing. This may be due to the polar nature of the P–O and P–S groups which may strongly bond with the silicate sheets and the exchangeable cations. As expected, $CaCl_2$ did not replace the nonionic parathion.

The resistance of parathion to desorption from the interlayer spacing sheds light on the long-term (15–16 year), low-level (0.06 μg/g) persistence of parathion in soil (Voerman and Besemer, 1970; Stewart et al., 1971). Parathion apparently is difficult to displace from the interlayer spacing by infiltration of water in the natural environment. Microbial degradation of parathion will be hindered in these interlayer areas (Hirakoso, 1969; Getzin and Rosefield, 1968; Lichtenstein et al., 1968). The common microorganisms in soil such as bacteria and Actinomycetes which have dimensions of 0.5–2 μm are at least 300 times greater than the interlayer spacing. The parathion molecules are thus protected from microbial degradation but not against degradation by exoenzymes.

This report has examined the kinetics of desorption of picloram and parathion from Panoche clay and Palouse silt. The desorption kinetic reaction constants k_0' were calculated and their temperature dependence used to derive activation parameters. The merits of the thermodynamic interpretation of the behavior of pesticide in a complex system such as soil is stressed in view of the large variation in experimental conditions and methods of calculations usually employed. As conditions in soil are usually nonequilibrium and often dynamic, the separate study of the desorption and adsorption process is most useful.

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Received for review April 24, 1978. Accepted July 23, 1979.

Relation of Temperature to Ethylene Dibromide Desorption from Fumigated Wheat

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The desorption of ethylene dibromide from fumigated wheat aerated at temperatures of 0–45 °C as determined by extraction with two different solvents and by steam distillation was found to increase as the temperature decreased. The maximum amount of extractable residue was obtained with an acetone–water mixture while petroleum ether extracted only the less-tightly bound portion. Desorption of this portion seemed to be inversely related to temperature and the effect was found to be reversible. Labeled ethylene dibromide was used to substantiate the results found by chemical analysis and to determine residue rates of desorption at different relative humidities. Considerably greater desorption was found to occur at high rather than at low humidities.

Temperature has considerable influence on rate of diffusion of a fumigant into material during treatment and a corresponding effect on desorption afterward. Although more rapid diffusion and desorption might be expected as temperatures are increased, a study on halogenated fumigants by Bielorai and Alumot (1975) showed faster desorption from cereal grains at low rather than at high temperatures. The authors implied that their observations seemed to disagree with expected behavior but their results gave clear indication that this situation did occur. Other work by Scudamore and Heuser (1973) and Jagielski et al. (1978) had failed to show increased desorption at lower temperatures, and studies by Dumas and Bond (1975) on desorption of ethylene dibromide (EDBr) from apples showed reduction in desorption as the temperature was reduced.

To investigate reasons for variability in results and to establish the pattern of desorption of EDBr from wheat under laboratory conditions, residues remaining in wheat held at different temperatures and relative humidities (RH) for various time intervals were measured. Different methods of extraction were used to remove the residual fumigant and the extracts so obtained were analyzed by two GLC procedures; in addition, labeled EDBr-*1,2*-^{14}C was used for residue analysis to allow comparative assessments of data from different methods.

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0021-8561/79/1427-1206$01.00/0

MATERIALS AND METHODS

Five hundred grams of soft winter wheat, about 13% moisture content, was fumigated with EDBr in a 6-L desiccator for periods up to 72 h at 25 °C. The liquid fumigant was introduced through a 5-mm silicon rubber stopper in the top of the desiccator onto a 10 cm × 6 mm watch glass that had been preheated to 90 °C and placed on top of the wheat. Volumes of 0.05–0.5 mL of the liquid (to obtain dosages from 16 to 160 mg/L) were completely vaporized on this watch glass within 15 min. After treatment for 4–72 h the wheat was aerated 1–14 days at 0, 15, 25, and 45 °C and EDBr was extracted from 10-g samples with 20 mL of solvent after homogenizing by mixing the treated wheat. The solvents finally selected were acetone–water mixture (5:1) and petroleum ether (bp 37–54 °C) and the extraction period was 24 h for the low concentration treatment and 48 h for the high. The extract was analyzed by gas chromatography using a Bendix 2300 with 2.5 m × 3 mm stainless steel column packed with 30% didecyl phthalate liquid phase on Chromosorb W 30/60 mesh and alkali flame ionization detector. Using nitrogen as the carrier gas at a flow rate of 30 cm^3/min and a column temperature of 130 °C and 7 min retention time full-scale deflection on a 25-cm, 1-mV recorder was given by 200 ng of ethylene dibromide.

Samples were also extracted by steam distillation (Kenneth and Huelin, 1957) using 50 g of fumigated wheat and 10 mL of benzene as the extracting solvent. The extract was then analyzed by the Bendix 2300 with flame ionization detector and a 2.5 m × 3 mm stainless steel column with 25% Carbowax 20 M on Chromosorb 60/80 mesh. A flow rate of 30 cm^3/min nitrogen and a column temperature of 135 °C gave a retention time of 7.6 min and sensitivity of 1 μg for full-scale deflection. The data were calculated by a Hewlett Packard 3380 A integrator. The quantities of residual ethylene dibromide, in terms of micrograms per gram of wheat, were determined from samples held for various periods of time at the different temperatures.

To substantiate results obtained by extraction and GLC analysis and to determine possible effects of different relative humidities on desorption wheat was treated with labeled ethylene dibromide and analyzed for residual fumigant under different conditions. Ethylene dibromide (0.50 mc of EDBr-*1,2-*^{14}C) obtained from New England Nuclear was diluted to 1 mL with nonlabeled fumigant to produce a solution with a specific activity of 0.0005 mc/μL. For these experiments 100 g of wheat was fumigated with 16 mg/L of EDBr for 3 days and aerated 8 days at 3, 10, and 25 °C at 75–85% and zero humidity. The desorption at zero humidity was conducted by placing 10 g of wheat in a 6-L desiccator containing $CaCl_2$. After 8 days aeration three replicates of about 0.5 g of wheat were converted to carbon dioxide in a scintillation sample oxidizer (Intertechnique "Oxymat LN 4101") and counted in a scintillation counter (Nuclear Chicago). The radioactivity of the sample (in counts per minute) was related to the quantity of EDBr remaining as residue in the wheat. Appropriate correction was made for incomplete recovery of carbon dioxide in the "Oxymat" using standard chips containing a known quantity of ^{14}C; the recovery efficiency of the "Oxymat" was normally about 75%.

RESULTS AND DISCUSSION

For experiments where temperature was the main factor under investigation, wheat that had been fumigated for 48 h with 16 mg/L of EDBr, aerated 1–7 days, and extracted with acetone was found to contain in most cases less residue when held at zero than at 45 °C (Figure 1).

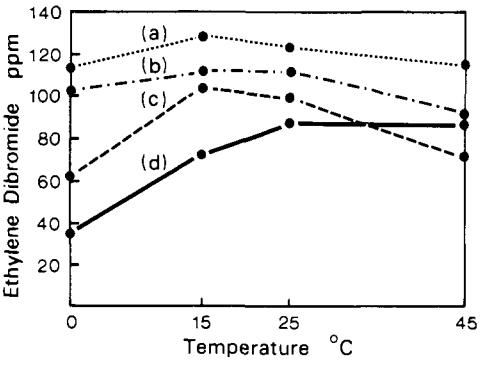

Figure 1. Ethylene dibromide residue (ppm) extracted by acetone–water from wheat treated for 48 h with 16 mg/L of EDBr and aerated for 1–7 days (a = 1 day of aeration, b = 2, c = 3, d = 7).

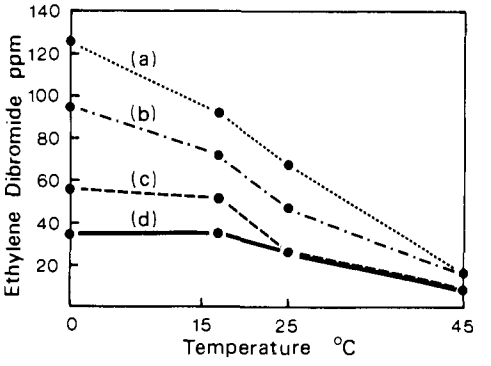

Figure 2. Ethylene dibromide residue (ppm) extracted by petroleum ether from wheat treated for 48 h with 16 mg/L of EDBr and aerated 1–7 days (a = 1 day of aeration, b = 2, c = 3, d = 7).

After 7 days of aeration the residue level in wheat held at 25 °C was more than double than at 0 °C; there was only small differences in residue extracted from wheat aired at 45 and 25 °C.

The quantities of residue found by extraction with petroleum ether were considerably different than those found in the acetone extract. Here the amounts extracted after 1–7 days of aeration were found to decrease as the temperature rose from 0–45 °C (Figure 2). When wheat was held at 45 °C only a small amount (<20 ppm) could be extracted with petroleum ether, even within the first day of aeration, while more than 120 ppm were extracted from wheat kept at 0 °C. Over the 7-day period the amount of EDBr that could be extracted by petroleum ether declined as the residual material was desorbed and, as can be seen in Figure 2, the decline was greatest at 0 °C where the extraction procedure was most effective. At the high temperature of 45 °C only a small portion could be extracted initially so that the overall decrease in 7 days of aeration was very little.

The quantity of EDBr extracted by petroleum ether from wheat held at 0 °C was approximately the same as that extracted by the acetone–water solvent while at the higher temperatures the amount extracted by the petroleum ether become progressively less with the increase in the holding temperature. When these data are compared with those from the acetone extractions it will be seen that much more residue was present in the wheat held at 45 °C but it was not extracted by the petroleum ether. Further testing showed that the remainder of this residue could be extracted with the acetone–water mixture.

The differences in extractability of residue by the two solvents can be more clearly seen when the results are

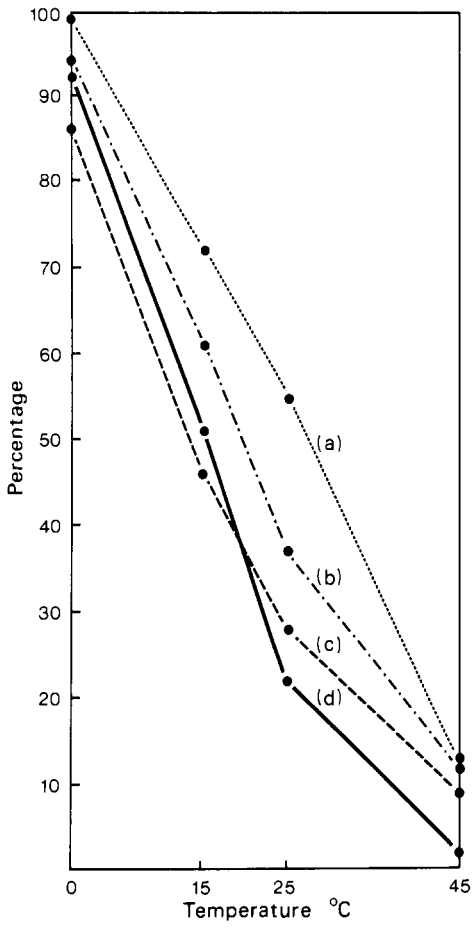

Figure 3. Percentage of ethylene dibromide extracted by petroleum ether as compared to the total extracted by the acetone–water mixture; wheat treated with 16 mg/L of EDBr for 48 h and aerated 1–7 days (a = 1 day of aeration, b = 2, c = 3, d = 7).

expressed in terms of percentages of the petroleum ether extract as compared to acetone–water extract (Figure 3). From the 0 °C wheat 85–100% was extracted; from 15 °C, 52–72%; from 25 °C, 23–55%; and from 45 °C, 5–12%. This diagram shows that EDBr was considerably more difficult to remove from its sorption sites on the wheat retained at higher than at lower temperatures as if more tightly bound, possibly by increased solubility in certain compounds of the wheat at higher temperatures, by the change in humidity due to temperature or both.

Further experiments were done to determine if this binding condition could be changed by manipulating the temperature during the aeration process. A number of petroleum ether extractions made on grain that had been aerated at the high temperature and then held for a period of time to a lower temperature all showed increased EDBr recovery. For example, when wheat that had been fumigated with 16 mg/L of EDBr for 4 h and held at 45 °C for 3 days was subsequently transferred to 0 °C for 2 h before the extraction, 10 ppm EDBr residue was recovered as compared to 0.3 ppm from the sample extracted directly after removal from 45 °C. Another example is given in Table I where extraction from wheat first held for 24 h at 25 °C and then 24 h at 0 °C gave appreciably greater recovery than wheat held at 0 °C for 24 h and then extracted after holding at 25 °C for 24 h. These data show the binding condition is reversible and is related more closely to holding temperature immediately before extraction than other temperatures to which the wheat may have been exposed previously.

Table I. Ethylene Dibromide Residue from 500 g of Wheat Fumigated with 16 mg/L for 4 h and 1 Day of Aeration

	EDBr	
temp, °C	acetone–water (5:1), ppm	petroleum ether, ppm
25	23	6
25-0[a]	25	16
0	16	14
0-25[b]	14	6

[a] Sample held 24 h at 25 °C then 24 h at 0 °C. [b] Sample held 24 h at 0 °C then 24 h at 25 °C.

Table II. Residue of Ethylene Dibromide from 500 g of Wheat Fumigated with 160 mg/L for 4 h and 7 Days of Aeration

	EDBr		
temp aeration, °C	acetone–water (5:1), ppm	petroleum ether, ppm	PE/A-W,[a] %
45	240	35	15
25	250	33	13
15	184	133	72
0	140	120	85

[a] Percentage of EDBr extracted by petroleum ether as compared to that extracted by the acetone–water mixture.

Table III. Residue of Ethylene Dibromide from 500 g of Wheat Fumigated with 160 mg/L of EDBr for 72 h after Aeration at Two Temperatures

aeration temp, °C	extraction of EDBr, ppm		
	steam distillation[a]	acetone–water[b]	petroleum ether[b]
25	1051	825	82
5	910	488	326

[a] Samples aerated 7 days, data are average of two extractions from two experiments. [b] Samples aerated 14 days, data given are average of three separate treatments.

To further confirm the observations that the fumigant desorbed more rapidly at low temperature and that it was more tightly held at higher temperatures, additional experiments were done with wheat treated with higher concentrations of EDBr. When a tenfold concentration of 160 mg/L of EDBr was used to fumigate the wheat in a 4-h exposure, the residue extracted by the acetone–water solvent was lowest from wheat held at the low temperature, thus indicating that greatest desorption occurred at the low temperature. However with petroleum ether the amounts extracted were greatest at the low temperature and declined with rise in temperature to show a direct relationship between binding power and temperature (Table II). Only a small proportion could be extracted with petroleum ether from the wheat aerated at 45 °C. The same effect was found for extractions at 3, 10, and 25 °C, also at completely dry atmosphere. As the exposure period used in the experiment was of short duration and penetration of fumigant into the kernel could be of some consequence in the subsequent desorption process, a longer exposure period of 72 h was chosen to further determine desorption at the two temperatures (Table III). Here again the EDBr residue as determined by the 48-h acetone–water extraction and a different GLC method (25% Carbowax 20 M as liquid phase and a flame ionization detector) was found to be appreciably lower in samples retained at 5 °C temperature than at 25 °C. Using a different extraction method, steam distillation and benzene solvent, with this same GLC method, the residue was

Table IV. Residue of Ethylene Dibromide from 100 g of Wheat Fumigated for 3 Days with 16 mg/L of EDBr (1,2-^{14}C) and 8 Days of Aeration[a]

aeration temp, °C	EDBr, ppm: 75–85% RH A	B	C	zero humidity A	B	C
3	50	10	4	204	228	170
10	62	10	6	230	283	216
25	20	11	8	182	244	265

[a] A, whole wheat; B, wheat ground before treatment; C, wheat ground after treatment.

similarly lower at 5 °C than at 25 °C. The residue extracted by the petroleum ether method was again lower from wheat held at the high temperature thus showing the same trend as previously demonstrated with this solvent.

Finally, the role of moisture and relative humidity in residue retention was investigated when wheat that had been fumigated with labeled ethylene dibromide was analyzed for labeled carbon. The lowest levels of residue were found in grain held at high humidity during the desorption period (Table IV). At 75–85% RH the level of residue remaining in whole wheat fumigated with 16 mg/L of EDBr-*1,2-*^{14}*C* for 3 days and aerated for 8 days was less than half that found in wheat retained over calcium chloride in a completely dry atmosphere at a temperature of 10 °C. At temperatures above and below this level at 25 and 3 °C appreciably less fumigant was found in wheat held at the high humidity. Similar results on residue levels from the fumigated wheat held at different humidities during the aeration period were found using solvent extraction and GLC analysis.

When wheat was ground either before or after fumigation, residue levels remaining after 8 days of aeration were about three–ten times below that found in the whole wheat at 75–85% humidity. In the low humidity atmosphere the amounts of residue remaining in whole and ground wheat did not differ appreciably.

In conclusion it may be said that desorption of ethylene dibromide from fumigated wheat was influenced by temperature, relative humidity, and particle size of the treated product. Undoubtedly moisture content of the grain along with temperature would affect humidity in intergranular spaces of the grain mass along with other factors involved in desorption. Similarly moisture content, humidity, and temperature might be expected to affect sorption of fumigant by the grain during treatment. Humidity appeared to be the most important factor that governed rate of desorption of the fumigant from grain, particularly when the grain had been ground to a fine particle size. Other factors may be important in the sorption and desorption processes. Further investigation is needed to fully understand the mechanism of the processes involved.

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Received for review February 26, 1979. Accepted June 29, 1979.

New Methylenedioxyphenyl Synergists for Pyrethrins

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Several new ester derivatives of alcohols derived from dillapiole have been prepared and evaluated for their synergistic efficacy toward pyrethrins against *T. castaneum* Herbst. A few of these compounds have shown comparable activity to piperonyl butoxide, a standard synergist. The relationship among the number of carbon atoms in the ester chain of these compounds, their lipophilicity, and synergistic potency is discussed.

The synergistic properties of dillapiole (2,3-dimethoxy-4,5-methylenedioxyallylbenzene, I), one of the major constituents of Indian dill (*Anethum sowa* Roxb.) seed oil, toward pyrethrins (Gulati and Parmar, 1969) and toward *N*-methylcarbamates (Tomar et al., 1978) have been described earlier. It has also been converted into a number of potent derivatives and their activities as pyrethrum synergists (Saxena et al., 1977; Tomar et al., 1979a,b) as well as toward *N*-methylcarbamates (Tomar et al., 1978; Saxena et al., 1978) have been reported. In this paper the preparation of a series of esters of two new alcohols derived from dillapiole and their synergistic properties toward pyrethrum are reported. Some of these have shown good synergism for pyrethrins against the test insect *T. castaneum* Herbst.

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METHODS AND MATERIALS

All compounds were finally purified by column chromatography on activated silica gel and purity was checked by TLC, spots being visualized by warming the dilute H_2SO_4. Infrared spectra were recorded in $CHCl_3$ on a Perkin-Elmer 457 grating spectrophotometer. NMR spectra were normally taken in CCl_4 solution, unless otherwise stated, on a Varian A-60 spectrometer using Me_4Si as internal reference; chemical shifts are given in δ values.

3-(2,3-Dimethoxy-4,5-methylenedioxyphenyl)-propan-1-ol (II). Dillapiole (I, 22.2 g) in dry dioxane (150 mL) was hydroborated and the product was oxidized with alkaline hydrogen peroxide (30%, 15 mL) in aqueous NaOH (10%, 15 mL) (Brown and SubbaRao, 1957). The

0021-8561/79/1427-1209$01.00/0