

Dissipation Rates in Soil of 1,2-Dichloropropane and 1,3- and 2,3-Dichloropropenes^a

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The rates of dissipation in soil and chloride-ion release, of the main components of dichloropropane–dichloropropene mixtures used as nematicides, were studied in sealed glass containers at different temperatures and moisture conditions. Half-lives of (*Z*)- and (*E*)-1,3-dichloropropenes at 20°C in soils were found to vary from 3 to 25 days; those of 1,2-dichloropropane and 2,3-dichloropropene were about four times and twice as long, respectively. The dissipation rates changed by a factor of about 2 per 10°C change in temperature. Judging from the release rates of water-extractable inorganic chloride in the soil (0–4% per week), the total degradation of all components applied at normal field rates was extremely slow. This indicated the formation of residues containing covalently bound chlorine. Only in 'enrichment cultures' was complete degradation indicated.

1. Introduction

Soil fumigation with commercial formulations of dichloropropane–dichloropropene mixtures, such as 'D-D' and 'Telone', in order to combat nematodes, is practiced on a large scale in the Netherlands, particularly on sandy soils used for starch potato cropping.

Leistra¹ studied the diffusion and adsorption of the 1,3-dichloropropene (1,3-D) isomers in soil. In Table 1 his estimation is given of the relative contribution of the various routes by which (*Z*)-1,3-D was dissipated from the upper soil layer at 12°C after field application. The contribution of 'decomposition' to the dissipation appears to be variable, depending partly on the type of soil and its moisture content; decomposition was not proven directly but was measured only as the decrease in the percentage recovery of the added compounds in the course of time. Non-recovery may be due partly to the forming of bound residues of the parent compounds, and in this paper, the more general term dissipation is used.

In a previous paper,² dissipation rates and half-lives were calculated from the results of a study in a closed system of the fate of (*Z*)- and (*E*)-1,3-D in buffer solutions and in soils. Preliminary data were also given in that paper for the chloride-ion release rate from these compounds in the soil. This study has now been completed by determining the temperature and moisture dependency of the dissipation rates of the two isomers in soil. A similar study was made of 1,2-dichloropropane (1,2-D) and, less extensively, of 2,3-dichloropropene (2,3-D), which are other components of the mixture used in practice.

2. Experimental

2.1. Materials and general methods

Materials, procedures for the dissipation studies in soils, and analytical methods were described in detail previously;² residues of the parent dichloro compounds in the soils were extracted by codistil-

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Table 1. Estimation of the relative contribution of the various routes of dissipation of field-applied (*Z*)-1,3-dichloropropene, at 12°C, from the upper soil layer (after Leistra¹)

Soil type	Moisture condition ^a	Volatilisation (%)	Diffusion into deeper layers (%)	Decomposition (?) (%)
Sand soil	pF 3	75	10	15
	pF 2	60	5	35
Sandy loam	pF 3	55	5	40
	pF 2	20	1	80

^a pF = 10-logarithm of the moisture tension expressed in cm of water.

lation with xylene and water, and determined by gas-liquid chromatography. The soils used in the present experiments were two sandy soils [locations Spier and Wageningen; organic matter content 7.7 and 1.9%; pH (potassium chloride) 4.3 and 5.0, respectively] and two clay-containing soils [locations Lelystad and Eenrum; organic matter content 1.5 and 1.8%; clay content 7.9 and 17.4%; pH (potassium chloride) 7.7 and 7.6, respectively]. The soils had never been fumigated. Dissipation rates in fresh soils at about field capacity (pF 2; pF = 10-logarithm of the moisture tension expressed in cm of water) for (*Z*)- and (*E*)-1,3-D were measured at 2, 15, 20, and 29°C; for 1,2-D' at 2, 15, and 29°C, and for 2,3-D at 15 and 29°C. For (*Z*)-1,3-D, the dissipation rates were also determined in air-dry and in water-saturated soil.

2.2. Concentration of 1,2-D' in the gas phase and its distribution over the gas, water and solid phases

Pure 1,2-D', contained in a 120-ml sealed glass bottle, was left to equilibrate with its gas phase for 24 h at 2°C and at 23°C. Samples (50 μ l) were then taken from the gas phase with a gas-tight syringe which was emptied into xylene (1 ml) contained in small glass tubes. From the concentration of 1,2-D' in this xylene solution, determined by gas chromatography (g.c.), the concentration in the gas phase was calculated. In the same way the concentration of 1,2-D' in the gas phase was determined at 15°C and at 29°C, after 50 ml of distilled water to which 5 μ l of 1,2-D' was added, and 15.0 g of moist moss peat, containing 11.0 g of water and 3.8 g of organic matter, to which 15 μ l of 1,2-D' was added, were left to equilibrate with the gas phase. After taking the gas samples, the rest of the 1,2-D' in the bottles was extracted by adding 10 ml of xylene, shaking, and washing the mixture with water into a Dean and Stark apparatus. Distillation was then carried out for 30 min. The xylene layer was separated and dried by filtering over a layer of anhydrous sodium sulphate. This xylene solution was also analysed by g.c. All determinations were made in duplicate. From the data obtained, the distribution ratios for 1,2-D' in the water and gas phases ($K_{w/g}$), in the organic matter and gas phases ($K_{om/g}$) and in the organic matter and water phases ($K_{om/w}$) were calculated.

2.3. Chloride-ion titration

The chloride-ion content of aqueous soil extracts was estimated by a voltametric titration with 0.01M-silver nitrate after adjusting the pH to 5-6 with diluted chlorine-free nitric acid, this method being more precise than the potentiometric titration method used previously.

Extraction from soil with 0.1M-potassium nitrate solution gave somewhat higher values for chloride ion but the increase was the same for soils treated with the organochlorine compounds as for untreated soils.

To obtain clear extracts by centrifugation or filtration, some chlorine-free calcium sulphate was added to the soil suspensions.

2.4. Total chlorine in soil

Total chlorine was determined in soil samples obtained by courtesy of the Plant Protection Service in Wageningen. The samples were taken from the upper 20 cm of an experimental field of sandy

soil at Wageningen (see section 2.1) where, over a period of 9 years, different plots had received 0, 100, 200, 300 or 400 litres 'D-D' ha⁻¹ every year, every 2 years, or every 3 years. For the previous 5 years before sampling in November 1973, 7 months or more after the last 'D-D' application, only carrots had been grown as a crop. Total chlorine was also determined in soil samples of two similar experimental fields of the Plant Protection Service (locations Spier and Lelystad) where, however, a crop rotation was used.

Total chlorine was also determined in 'enrichment cultures', in sandy soil, of microorganisms capable of decomposing certain organochlorine compounds. These cultures were obtained by adding normal doses of 'D-D', 'Telone', (Z), and (E)-1,3-D, 1,2-D', and 3-chloroallyl alcohol every 2 weeks, nine times in succession. Thereafter two maintenance doses were given after 2 and 6 months. The doses were applied to 11 kg of soil, contained in large glass jars. The jars were kept closed until 3 days before the next dose was given. During these 3 days the soil was aerated by forcing a stream of moist air through the soil. Twenty-seven months after the last dose, soil samples were analysed for water-extractable chloride (in duplicate) and for total chlorine (in triplicate). Total chlorine in soil was determined essentially as described by Agazzi *et al.*³ Soil (10–15 g) contained in a ceramic boat was combusted in a quartz tube, connected by Teflon tubing (rubber tubing should be avoided) to a small gas scrubber, charged with a 5% sodium carbonate solution. The inlet of the quartz tube had a ground inner joint fitted with a ground outer joint connected with a cylinder containing pure oxygen. Heating at 1000°C was by an electrically heated movable furnace.

After combustion, the contents of the gas scrubber and of the ceramic boat were transferred to a glass beaker (the quartz tube was also rinsed with water), dilute nitric acid was added and carbon dioxide was removed by boiling. Chloride was determined by voltametric titration with 0.01M-silver nitrate. The deviation between replicates was rather large, presumably due mainly to varying amounts of plant roots, which were found to contain up to 2% by weight of total chlorine, based on dry weight.

3. Results and discussion

3.1. Comparison of dissipation rates and half-lives of (Z)- and (E)-1,3-D, 1,2-D' and 2,3-D at 15°C

Table 2 gives the dissipation rate constants and half-lives of these compounds at 15°C in fresh soil (closed system), derived by assuming first-order reactions to be responsible for their disappearance (disappearance was assumed following non-recovery by extraction). In accordance with their sensitivity to hydrolysis, the persistence of 1,2-D' and 2,3-D was higher than that of (Z)- or (E)-1,3-D; for 1,2-D', it was on average four times that of (Z)-1,3-D and more than six times that of (E)-1,3-D.

Complementary to the study by Leistra¹ of the physicochemical behaviour of (Z)- and (E)-1,3-D in the soil, some similar measurements were made for 1,2-D'. For the pure compound

Table 2. Dissipation rate constants (k_r) and half-lives ($t_{1/2}$) of (Z)- and (E)-1,3-dichloropropene, 1,2-dichloropropane, and 2,3-dichloropropene at 15°C in a closed system and fresh soil

Location	(Z)-1,3-D		(E)-1,3-D		1,2-D'		2,3-D	
	k_r (day ⁻¹)	$t_{1/2}$ (days)	k_r (day ⁻¹)	$t_{1/2}$ (days)	k_r (day ⁻¹)	$t_{1/2}$ (days)	k_r (day ⁻¹)	$t_{1/2}$ (days)
Spier	0.037	19	0.055	13	0.010	69	0.018	38
Wageningen	0.055	13	0.154	4.5	0.017	41	0.026	26
Lelystad	0.055	13	0.164	4	0.012	58	0.034	20
Eenrum	0.105	7	0.120	6	0.016	43	0.037	19
Mean ^a	0.051	13	0.088	8	0.013	52	0.026	26

^a Calculated from the mean amounts of parent compounds, recovered from the four soils after various time intervals.

Table 3. The distribution ratios for 1,2-D' in the water and gas phases ($K_{w/g}$), in the organic matter and gas phases ($K_{om/g}$), and in the organic matter and water phases ($K_{om/w}$), respectively, compared with the ratios for (Z)- and (E)-1,3-D (taken from Leistra¹)

Temperature (°C)	$K_{w/g}^a$			$K_{om/g}^b$			$K_{om/w}^c$
	1,2-D'	(Z)-1,3-D	(E)-1,3-D	1,2-D'	(Z)-1,3-D	(E)-1,3-D	1,2-D'
15	13			134			11
20	11	18	26	118	240	420	11
29	7			79			11

^a ($\mu\text{g ml}^{-1}$ of water)/($\mu\text{g ml}^{-1}$ of gas).

^b ($\mu\text{g g}^{-1}$ of dry organic matter)/($\mu\text{g ml}^{-1}$ of gas).

^c ($\mu\text{g g}^{-1}$ of dry organic matter)/($\mu\text{g ml}^{-1}$ of water).

at normal pressure, a concentration in the gas phase was found of 53 and 118 $\mu\text{g cm}^{-3}$ at 2°C and 23°C, respectively. These values are of the same magnitude as found by Leistra for (Z)- and (E)-1,3-D; their volatilities are therefore roughly comparable. Table 3 gives information on the distribution over the gas, water, and solid phases. The data for $K_{w/g}$ fit in very well with those reported by McKenry and Thomason.⁴ In order to compare the data obtained with those of Leistra determined at other temperatures, data for 20°C were inferred by interpolation. It appeared that the solubility of 1,2-D' in water as well as the sorption by organic matter was considerably lower than for (Z)-1,3-D, which in turn showed lower solubility and sorption than (E)-1,3-D. Thus, after field application of a mixture, 1,2-D' disappears faster than 1,3-D from soil by volatilisation.

These measurements, however, do not exclude the possibility that part of the added 1,2-D' adhered strongly to the organic matter; the same holds for (Z)- and (E)-1,3-D. An indication that

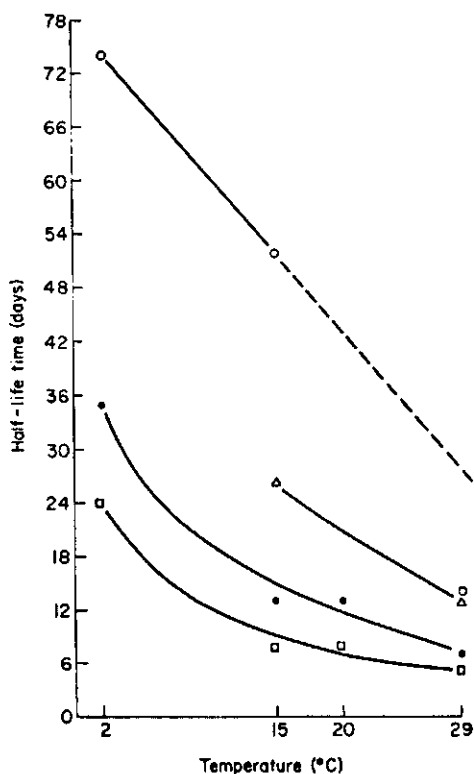


Figure 1. Relation between the temperature and half-life times of: ○, 1,2-dichloropropane; □, (E)-1,3-dichloropropane; ●, (Z)-1,3-dichloropropane; and △, 2,3-dichloropropane, in soil in closed containers.

some 1,2-D' is bound in the soil is that ear malformation occasionally occurs in some winter wheat varieties, even in the second and third year after soil fumigation with 'D-D' or 'Telone'. This ear malformation appears to be caused by 1,2-D', of which these formulations contain about 20% and 15%, respectively.⁵

3.2. Effect of temperature and moisture content on soil dissipation rates

The effect of temperature on the dissipation rates for (*Z*)- and (*E*)-1,3-D, for 1,2-D', and for 2,3-D is shown in Figure 1. The dissipation rates changed by a factor of about 2 for every 10°C change in temperature in the important region from 2 to 20°C. This is a normal effect for many chemical and biological reactions. Dutch farmers sometimes postpone soil fumigation until very late in the autumn. It is important to realise that the risk of undesirable side-effects is then disproportionately enlarged, because at that time soils are often wetter and colder, which also suppresses volatilisation (see Table 1).

An impression of the effect of the moisture content of the soil on the dissipation, in a closed system where there was no loss by volatilisation, can be obtained from Table 4. The dissipation

Table 4. Effect of moisture condition on the dissipation rate constants (k_r) and half-lives ($t_{1/2}$) of (*Z*)-1,3-dichloropropene in the soil at 20°C in a closed system

Location	Air-dry soil			Moist soil (pF 2)			Water-saturated soil		
	Water content (%)	k_r (day ⁻¹)	$t_{1/2}$ (days)	Water content (%)	k_r (day ⁻¹)	$t_{1/2}$ (days)	Water content (%)	k_r (day ⁻¹)	$t_{1/2}$ (days)
Spier	1.6	0.026	27	18.9	0.042	16	25.6	0.050	14
Wageningen	1.1	0.021	32	12.8	0.061	11	19.4	0.060	12
Lelystad	1.1	0.019	37	17.6	0.065	11	24.1	0.053	13
Eenrum	2.0	0.022	32	18.8	0.094	7	30.7	0.115	6
Mean ^a		0.020	35		0.054	13		0.056	12

^a See note under Table 2.

rates of (*Z*)-1,3-D in soil at field capacity and in water-saturated soil were not significantly different. In air-dry soil the rate constant was much smaller but not zero; the half-life at 20°C (35 days) was on average equal to that in the moist soils at 2°C. McKenry and Thomason⁴ report a high sorption capacity of air-dry soil, deduced from the decrease of the concentration in the gas phase; this may be mainly physical adsorption. It should be emphasised that, in the present experiments, the disappearance of the compounds was measured as the amount non-distillable after adding water and xylene to the soil. Physically adsorbed 1,3-D is considered to be extracted under these circumstances.

3.3. The effect of differences between soil types on the dissipation of the 1,3-D isomers

The present results, together with those previously obtained² for (*Z*)- and (*E*)-1,3-D at 20°C with Dutch soils, of which four were acid sandy soils and nine were neutral clay containing soils, are summarised in Table 5. It is quite evident ($P < 5\%$) that the dissipation rate in both soil types was different when volatilisation was prevented. The true cause of this difference is not clear. There is no consistent correlation with organic matter or clay content, and in buffer solutions of pH 5.5 and 7.5 (without soil) the dissipation rates were not significantly different.²

Under field application conditions this tendency toward a higher persistence in sandy soils would be counterbalanced by a higher loss through volatilisation (Table 1). Taking both dissipation routes into account, the parent compounds should be classified as pesticides of low persistence in the soil.

It has not yet been possible to establish whether the difference in half-life times of (*Z*)- and (*E*)-1,3-D is statistically significant, because of the scarcity of data, particularly for sandy soils. A lower persistence of the (*E*)-isomer, added to a smaller rate of volatilisation after field applications,

Table 5. Average half-lives for (*Z*)- and (*E*)-1,3-D at 20°C in Dutch acid sandy soils and neutral clay-containing soils in closed systems

Type of soil	Number of samples	Organic matter (%)	Clay (< 2 μm) (%)	pH (potassium chloride)	<i>t</i> _{1/2} (days)	
					(<i>Z</i>)-1,3-D	(<i>E</i>)-1,3-D
Sandy	4	7.3 (1.9-14.8)		4.6 (3.9-5.3)	19 (11.25)	15 (5-23)
Clay-containing	9	1.8 (1.1-2.6)	13.0 (5.2-19.6)	7.3 (6.8-7.7)	6½ (3-11)	5½ (3-8)

Figures in parentheses show the range of the results.

would mean that larger amounts of the degradation products of (*E*)-1,3-D could be expected in the soil, than of the (*Z*)-isomer.

3.4. Chloride-ion release in soils

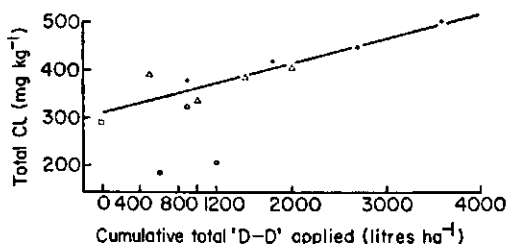
A preliminary conclusion of previous experiments² was that the various organochlorine compounds that were tested seemed initially to undergo a rapid loss of chlorine, which slowed down after 1 or 2 weeks to a more or less constant rate of about 3% per week. This chloride-ion release was deduced from the increase of water-extractable chloride in the soil, assuming that the latter was constant when no organochlorine compounds had been added.

Later it was discovered that the total amount of chlorine in the soils is normally much higher (often ten-fold or more) than the amount extractable with water and also much higher than the 75 mg chlorine kg⁻¹ added in the form of a normal field application of 'D-D' (250 litres ha⁻¹). The non-extractable chlorine in untreated soils is presumably present mainly in cells of plant roots and microbes. As noted earlier, a total chlorine content of up to 2%, based on dry weight, was found for plant roots. To correct for a possible natural chlorine mineralisation in soils in the series of measurements with the four soils and the four compounds discussed above, plus (*EZ*)-3-chloroallyl alcohol, the untreated soils were therefore also incubated at the same temperatures and sampled at the same dates. The surprising result was that in the first days, in all cases, about the same increase of water-extractable chloride ion was found. After some days, in the untreated soils this increase slowed down to practically zero. Except when 1,2-D' was added, a slow but continuous release of chloride ion occurred, at a rate of up to 4% per week at 15-20°C. This was apparently due to decomposition of the added organochlorine compounds. This release was found to be temperature-dependent and was almost zero at 2°C. From 1,2-D', also at 15°C and at 29°C, no significant chloride release could be established in 14 weeks, although in that time more than half of the added 1,2-D' had disappeared despite prevention of volatilisation.

This means that the earlier conclusion,² that some process in the soil impedes complete degradation of part of the fumigant mixture to carbon dioxide and chloride ion, has probably to be extended to all the fumigant when applied at field application level. In contrast to the findings of Castro and Belser,⁶ there is no evidence from the present observations for the assumption, also made by McKenry and Thomason,⁴ that the relatively rapid disappearance of 1,3-D in closed containers with soil, and hydrolysis to 3-chloroallyl alcohol, occur at the same rate. Castro and Belser, however, used levels of (*Z*)- or (*E*)-1,3-D five times as high, or even higher, when expressed per gram of soil, and worked with extremely wet soil or soil suspensions.

Assuming a first-order process leading to the observed average chloride-ion release rate constant of 2% per week, then in 1 year, about 65% of the field-applied organic chlorine which is not volatilised should have been released as water-extractable (leachable) chloride. Theoretically it would take about 4.5 years before 99% of the added organic chlorine was released. In other words, fumigation more often than is usually practised (once every 4 years) might result in an accumulation of compounds containing covalently bound chlorine. In Figure 2, the total amounts of chlorine

Figure 2. Relation between the total chlorine in soil, November 1973, from an experimental field at Wageningen and the total amount of 'D-D' applied in the course of 9 years; □, no 'D-D' applied; ●, application every year of 100, 200, 300 and 400 litres ha⁻¹ (final application in April 1973); △, the same amounts applied every 2 years (final application in April 1973); and ○, the same amounts applied every 3 years (final application in April 1971).



found in the soil samples of the experimental field at Wageningen, described in section 2.4, are plotted against the total amount of 'D-D' applied in 9 years. Water-extractable chloride ion accounted for only a few per cent of the total chlorine content of the soil. The equation for the straight line drawn is $y = 0.05x + 312$, suggesting that 5% of the added organic chlorine is still in the soil as covalently bound chlorine. This is about 20% of all the organic chlorine added in the form of 'D-D' in 9 years. According to Leistra (see Table 1), 65–85% of the added 'D-D' disappears from sandy soil by volatilisation and diffusion to deeper layers. Thus, most of the remaining organic chlorine may still have been present. In view of the fact that the upward trend of the line in Figure 2 is caused mainly by the data of the plots where 'D-D' is applied each year, and because of the considerable experimental scatter, a definite conclusion cannot be drawn. It may be mentioned, however, that Roberts and Stoydin,⁷ in a field experiment with ¹⁴C-labelled 'D-D', found that after 1 year the soil still contained 5% of the applied radioactivity.

No consistent relation between the total chlorine in the soil and the amount of 'D-D' applied was found for the two similar experimental fields at Spier and Lelystad, as noted in section 2.4. This may, however, be due to the fact that in those cases a crop rotation was used, leading to different amounts of roots (with a high chlorine content) in the different plots.

An indication that, once released from the organic compounds, chloride does indeed become water-extractable is obtained from the 'enrichment cultures' also described in section 2.4. The results of the soil analyses are given in Table 6. The conclusion is that the increase of total chlorine in the treated soils was roughly equal (taking into account that the standard deviation for total chlorine was 88 mg kg⁻¹) to the increase of water-extractable chloride. Thus, at least in these 'enrichment cultures', the organochlorine compounds that were not volatilised during the aeration period could be assumed to be completely decomposed to carbon dioxide and chloride ion.

Table 6. Total and water-extractable chlorine after application, to a moist sandy soil, of organochlorine compounds at field application level, at a frequency of once every 2 weeks and a total of 11 applications, the soil then being stored for 27 months at room temperature

Organic chlorine applied		Chlorine contents after 27 months				Increase of organic Cl over added Cl (%)
		Total Cl ^a		Water-extractable Cl ^b		
Compound	(mg kg ⁻¹)	Content (mg kg ⁻¹)	Increase (mg kg ⁻¹)	Content (mg kg ⁻¹)	Increase (mg kg ⁻¹)	
Control	0	274		26		
'D-D'	1110	497	223	314	288	26
'Telone'	850	575	301	340	314	37
(Z)-1,3-D	345	462	188	206	180	52
(E)-1,3-D	345	466	192	256	230	67
1,2-D'	320	249	-25	106	80	25
(EZ)-CAA ^c	200	371	97	224	198	100

^a Triplicates; standard deviation was 88 mg kg⁻¹.

^b Duplicates; standard deviation was 11 mg kg⁻¹.

^c (EZ)-3-Chloroallyl alcohol.

Another interesting point is that 1,2-D', which was shown to have a higher half-life in the soil, appears to be degraded to the same extent as 'D-D' (see last column of Table 6). The data in this column for (*Z*)- and (*E*)-1,3-D reflect the faster volatilisation of the (*Z*)-isomer, as established by Leistra.¹

As a final conclusion it may be stated that the pathway of the degradation of these organochlorine compounds, after applying normal doses at long intervals (1 year or more), should be investigated more closely in view of the fact that the disappearance rate is much higher than the rate of chloride release. This might best, perhaps only, be accomplished by using radiolabelled chlorine as well as radiolabelled carbon compounds.⁷

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