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DEGRADATION OF 1,3-DICHLOROPROPENES IN THE SOIL

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ABSTRACT

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A review is given of the results obtained from a recent study of the fate of cis- and trans-1,3-dichloropropenes, used as nematocides, in buffer solutions and in soils. Rates of degradation and "half lives", as affected by temperature, of the parent compounds and of the chloroallyl alcohols, formed by hydrolysis, were deduced from disappearance rates and from chloride release.

The dichloropropenes disappear in sandy soils at 15—20°C (closed containers) at a rate of 2—3.5% per day. In clay-containing soils this rate is mostly considerably higher (up to about 25% per day at 20°C).

The chloroallyl alcohols are rapidly biodegraded in the soil; for the cis isomer in clay-containing soils rates were found of 20—60% per day at 15°C, for the trans isomer the rates were even about three times higher.

After an initially more rapid release of Cl^- this release slows down to about 3% per week. The available data point to some process in the soil, other than hydrolysis, which impedes degradation of part of the dichloropropene fumigant mixture.

INTRODUCTION

Fumigation of soil with 1,3-dichloropropenes, marketed in mixtures with 1,2-dichloropropane and other chlorinated C_3 hydrocarbons, is applied in The Netherlands to combat the potato cyst nematodes on more than 30 000 ha/year. This fact together with the occasional occurrence of undesirable side-effects, led to a closer investigation of the fate and persistence of these compounds and their degradation products in our soils.

The physicochemical behaviour (diffusion and sorption) in the soil of the parent compounds has been studied by Leistra (1972). We took part in the study of the chemical and biological conversions in the soil. Although we have not yet finished our experiments, it was thought worthwhile to give an interim report on the occasion of this symposium.

Fig.1 shows some structural formulae of compounds involved, together with the degradation pathway of cis- and trans-1,3-dichloropropene, considered by Castro and Belser to occur in the soil (1966, 1971). They showed that the first step, the chemical hydrolysis, does indeed take place in the soil, but it has not been proven to be the only occurring first step. They studied the metabolism of the chloroallyl alcohols in a culture solution with a *Pseudomonas* sp. isolated from the soil by an enrichment technique. Whether in soil the same process occurs and whether this is the only or main path of the degradation in soil remains to be examined.

Castro and Belser (1966) measured the chloride release from 0.01 M 1,3-dichloropropenes in buffer solutions at pH 6.9 and 7.5 and at different soil—solution ratios. They found a "half life" of 20 days corresponding with a Cl^- release rate constant of 0.034 d^{-1} — i.e. 3.4% per day — in a soil suspension. The hydrolysis rate in the buffer solutions was considerably smaller, at most with a factor 3, depending on the soil—solution ratio.

In preliminary experiments we investigated the disappearance rates of the dichloropropenes by determining the amounts remaining after different time intervals by gas chromatography. Contrary to Castro and Belser, we found that the rates of decline in buffer solutions were higher rather than lower when compared with corresponding rates in soil suspensions. We decided to perform a series of degradation studies not only in buffer solutions but also to make conversion studies in soils at their natural moisture content.

Our work was concerned primarily with the 1,3-dichloropropene isomers, but some work was also done with 1,2-dichloropropane and 2,3-dichloropropene. The concentrations applied were comparable to those occurring after a typical field application.

EXPERIMENTAL

Materials

The dichloro compounds, chloroallyl alcohols and chloroacrylic acids, mentioned in Fig.1, were kindly supplied by Shell International Research Comp.,The Hague, and the Institute for Organic Chemistry TNO, Utrecht.

The buffer solutions in which the disappearance rate of the dichloro com-

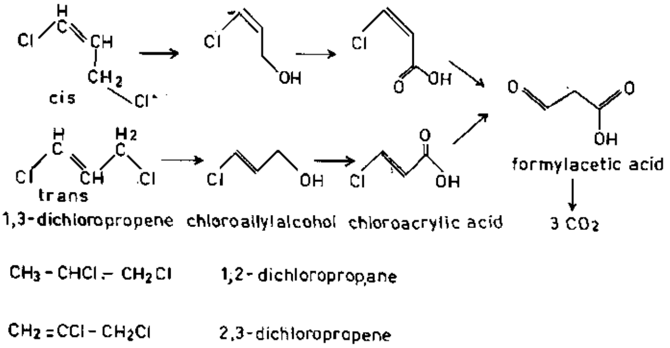

Fig.1. Main components of DD and possible path of conversion of cis- and trans-1,3-dichloropropene in the soil.

pounds was determined were citrate/phosphate buffers of pH 5.5 and 7.5.

The soils involved in the degradation studies were of two main types, namely sandy soils from the eastern part of The Netherlands, and clay-containing soils mainly from the marine clay area; one loamy brook soil from Limburg. Samples were taken from different locations in order to have varying organic matter contents (for the eastern sandy soils from 1.6 to 14.8%; for the clay-containing soils from 1.1 to 2.6%) and pH (for the first group 3.9—7.3; for the second group 6.8—7.6). The clay-containing soils varied from very sandy with a clay content of 5.2% to medium textured soils with a clay content of 19.6%.

Procedure in the degradation studies

In buffer solutions

With a hypodermic syringe a measured volume of the dichloro compound was added to buffer solutions in flasks with accurately fitting teflon-coated glass stoppers. The flasks — almost completely full — were stored at the desired temperature (2, 15, 20 or 29°C). At scheduled times flasks were taken for determination of remaining dichloro compounds. To that end the solution was transferred to a Dean and Stark apparatus and 10 ml xylene were added. Distillation was carried out for 30 min, the xylene layer separated, and part of it was dried by filtering over a layer of anhydrous sodium sulfate. This xylene solution was analysed by gas—liquid chromatography.

In soils

An amount of fresh soil, corresponding to 50 g of dry soil was weighed into a 500 ml flask. When the desired constant temperature was reached, the organic compound to be studied was added with a hypodermic syringe and the flask immediately hermetically closed. (The amount of oxygen in the flasks was sufficient to ensure aerobic conditions for several weeks.) In this way sufficient flasks were prepared and at scheduled times one was taken for analysis.

Remaining dichloro compounds were extracted by quickly adding 10 ml of xylene and 100 ml of water, immediately closing the flask afterwards and shaking for some time in order to also extract the vapour phase. Then the contents of the flask were washed into the Dean and Stark apparatus with 300 ml water and treated as described above. Applying this procedure shortly after the addition of the 1,3-dichloropropenes to the soil gave a recovery of about 90%.

In experiments with chloroallyl alcohols, residues were determined as follows: the soil was transferred into a two-necked round-bottomed flask of 250 ml, 100 ml 0.2 N sulfuric acid added, and a small piece of solid paraffin wax (anti-foam). The soil suspension, while magnetically stirred, was steam distilled until 125 ml of distillate were obtained. About halfway, the suspension was made alkaline by adding 16 ml of a 5 N NaOH solution. The distillate was analysed by gas—liquid chromatography. Applying this procedure immediately after the addition of the chloroallyl alcohols to the soil gave a recovery of more than 95% (mostly 97—98%).

Analytical methods

The concentration of dichloro compounds in the xylene extracts was determined by injecting 1 μl into a gas chromatograph (Varian 1522-3B). Column: 4 m x 3 mm, stainless steel, packed with 10% Carbowax 20M on Chromosorb W, 120°C. The carrier gas was nitrogen (40 ml/min) and the injector temperature was 150°C. The detector was an electron capture (tritium) detector, heated at 200°C.

The concentration of chloroallyl alcohols in the water extract was determined by injecting 2 μl into a stainless steel column of 2.5 m x 3 mm, packed with 15% silicon DC 550 + 0.15% Carbowax 20 M on Gas Chrom Q 80/100, heated at 100°C. The carrier gas was nitrogen (40 ml/min) and the injector temperature 150°C. Use was made of a flame ionization detector, heated at 200°C. The peaks were recorded with an integrator Hewlett—Packard 3373B.

The release of Cl^- in the soil resulting from degradation of the organochloro compounds was determined by potentiometric titration of the aqueous solution obtained by centrifugation of the soil suspensions remaining in the distillation flasks after removal of the organochloro compounds as described in the foregoing section. The titration method is essentially that described by Schwab and Tölg (1964). The values obtained were corrected for blanks obtained in the same way for samples to which no chloro compounds had been added.

RESULTS AND DISCUSSION

Disappearance rates in buffer solutions

Fig.2 summarizes some of the results obtained with cis-1,3-dichloropropene: only small differences in degradation rates at pH values of 5.5 and 7.5 were noted, but changes in temperature had a large effect. There was no effect of concentration in the range of 10—1 000 ppm.

In Table I the calculated rate constants and "half lives" are given, assuming a first-order reaction:

$$\frac{dA}{dt} = -k_r A$$

in which A is amount of compound at time t and k_r is the rate constant. Integration yields:

$$A = A_0 \cdot e^{-k_r t}$$

or:

$$k_r = \frac{-\,2.3 \log A/A_0}{t}$$

When half of the initial amount A_0 has disappeared,

$$t^{\star} \text{ (half life)} = \frac{2.3 \log 2}{k_r}$$

Table I confirms what is stated above concerning the effect of temperature and pH, and also shows that there is not much difference in the disappearance rates of the cis- and trans-1,3-dichloropropenes. The limited data available on 1,2-dichloropropane and 2,3-dichloropropene suggest that these compounds degrade more slowly.

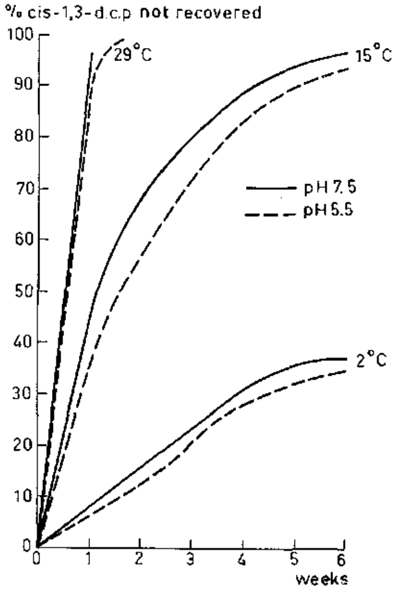

Fig. 2. Rate of conversion of cis-1,3-dichloropropene in buffer solutions of pH 5.5 and 7.5 and at different temperatures.

Disappearance rates of the 1,3-dichloropropenes in soils

In Table II the available data are given of the rate constants and half lives of cis- and trans-1,3-dichloropropene in different soils. Whether the effect of temperature on degradation rates in soils is comparable to that found for buffer solutions is still under investigation. Measurements in two samples of a sandy soil (Haren) where the disappearance rate was determined at 15 and at 20°C suggest that the temperature effect is less in soils than in the buffer solutions.

TABLE I

Disappearance rate constants (k_r) and half life (t^*; in days) of some chlorinated C_3-hydrocarbons in buffer solutions at different temperatures

	Cis-1,3-dichloro-propene			Trans-1,3-dichloro-propene			1,2-dichloro-propane	2,3-dichloro-propene	
	2°C	15°C	29°C	2°C	15°C	29°C	ca. 13°C	2°C	29°C
pH 5.5									
k_r (days^{-1})	0.008	0.062	0.36′	0.007′	0.053	0.37′	0.009	0.012′	0.025′
t^* (days)	91	11	2′	100′	13	2′	70	63′	27′
pH 7.5									
k_r (days^{-1})	0.007	0.074	0.48′	0.014	0.067	0.58′			
t^* (days)	100	9.4	1.5′	53	10.5	1.2′			

′Approximate values.

TABLE II

Disappearance rate constants (k_r; days^{-1}) and half life ($t^{\star}$; days) of cis- and trans-1,3-dichloropropene in soils

Location	Organic matter (%)	< 2 μm (%)	pH	Temperature (°C)	Cis		Trans	
					k_r	$t^{\star}$	k_r	$t^{\star}$
Eastern sandy soil								
Spier (0)	11.6			15	0.030	22		
(600)	11.1			15	0.018	37		
Haren	3.6		5.0	15	0.032'	22'	0.028	26
Haren	3.6		5.6	20	0.027'	25'	0.030	23
Borgercie.	14.8		3.9	20	0.034	20	0.034	20
Clay-containing soils								
Bant	5.5	20'	7.4	15	0.030	23	0.028	24
Wieringerwerf	1.1	5.2	6.8	20	0.24'	3'	0.22'	3'
Baexem"	1.7	14.0	7.2	20	0.20	3.5	0.24'	3'
Wieringerwerf	2.6	19.6	7.6	20	0.09	7.5	0.09	7.5
Warffum 772	1.8	13.6	7.2	20	0.08	8	0.09	8
Warffum 710	1.8	13.6	7.1	20	0.13	5	0.10	7

'Approximate values.
"Loamy brook soil.

The data in Table II point to a distinctly higher average disappearance rate in the clay-containing soils than in the sandy soils, but there was also considerable variation in degradation rate found using the same soil type. Statistical considerations suggest that the differences are larger than can be accounted for by the error of determination. There is no consistent correlation with the content of organic matter or of clay or with pH. Thus, whilst organic matter content may affect the evaporation rate due to stronger sorption (Leistra, 1972) — and hence the amount of fumigant decomposed in the soil — it does not appear to have a direct influence on the decomposition rate.

The difference between cis- and trans-1,3-dichloropropene, if significant, appeared to be very small, as was also found in buffer solutions.

Disappearance rates of the 3-chloroallyl alcohols in soils

We further determined the disappearance rates for cis- and trans-3-chloroallyl alcohol (60 ppm) added to a medium-textured clay soil, both in its natural state and after autoclaving at 120°C for 1 h. Rates were studied at 2, 15 and 29°C.

Fig.3 illustrates part of the results: there was a pronounced effect of temperature on the conversion in unsterilised soils; at 2, 15 and 29°C, the rate constants for the cis isomer were 0.12, 0.39 and 0.87 day^{-1}, respectively,

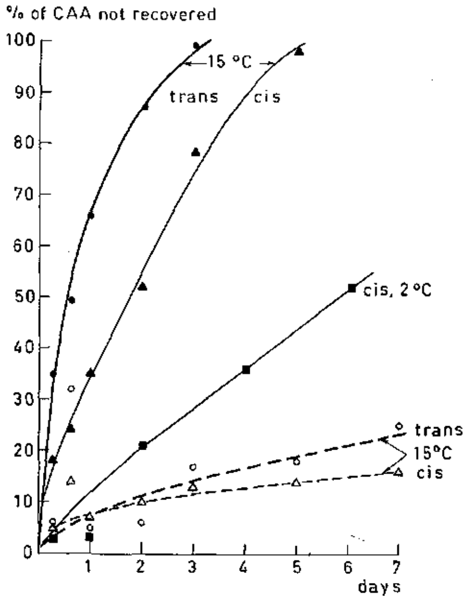

Fig. 3. Average rates of conversion of cis- and trans-3-chloroallyl alcohol (CAA) in a sandy clay soil at different temperatures (drawn curves: unsterilized soil, dotted curves: autoclaved soil).

and the corresponding half lives 142, 43 and 19 h. There was no effect of temperature and a very slow disappearance of the alcohols in sterilized soils. Thus, it seems that here a biological conversion is involved. Thirdly, we found a distinct difference between the disappearance rates of the cis and trans isomers.

We also obtained data at 15°C for three other soils with different clay content (disappearance rates in eastern sandy soils are under investigation). Table III summarizes the data obtained for the 1,3-dichloropropenes (at 20°C) and for the 3-chloroallyl alcohols (at 15°C, at 20°C the disappearance rate of the latter would presumably have been even higher). It appears that the alcohols disappear much faster than the parent dichloropropenes, about 3 to 4.5 times as fast for the cis compounds and about 6.5 to 12 times as fast for the trans compounds. The "half life" of the cis alcohol is on the average 2 days and that of the trans alcohol even less than 1 day.

If the only reaction course after adding a normal dose of DD (250 l/ha) to the soil is: 1,3-dichloropropenes → 3-chloroallyl alcohols → *X*, and the rate constants are as given in Table III, the course of the alcohol concentration can be calculated. For a ratio of rate constants of 3—4.5 for the cis compounds, the concentration of cis-3-chloroallyl alcohol in the tilth layer reaches a maximum of about 5—7 ppm after about 3—5 days. For a ratio of 6.5—12 for the trans compounds the maximum for trans-3-chloroallyl alcohol is about

TABLE III

Disappearance rate constants (k_r; days^{-1}) and half life ($t^{\star}$; days) of the 1,3-dichloropropenes (dcp) and 3-chloroallylalcohols (caa) in clay-containing soils

Organic matter (%)	< 2 µm (%)		Cis		Trans	
			dcp 20°C	caa 15°C	dcp 20°C	caa 15°C
1.1	5.2	k_r(days^{-1})		0.22		0.61
		$t^{\star}$ (days)		3.1		1.1
1.7	14.0	k_r (days^{-1})	0.20	0.59	0.24	1.60
		$t^{\star}$ (days)	3.5	1.2	3	0.4
2.6	19.6	k_r (days^{-1})	0.09	0.40	0.09	1.11
		$t^{\star}$ (days)	7.5	1.8	7.5	0.6
Average for the three soils after autoclaving		k_r (days^{-1})		0.023		0.037
		$t^{\star}$ (days)		30		18

2—4 ppm after about 1.5—2.5 days. At lower temperatures the rate constants will be lower. If the ratio remains constant, the maximum will be the same, only the time at which this maximum is reached will be later, the lower the rate constant of the first step of the reaction. Since in field application 15—80% of the fumigant decomposes — depending on soil type and moisture content (Leistra, 1972) — the maximum level of the chloroallyl alcohols could amount to about 8 ppm. However, so far we have failed to detect any accumulation of chloroallyl alcohols after field application of DD (the detection limit of the method employed is about 1 ppm).

Cl^- release in soils

In later experiments with sandy soils and clay-containing soils we also determined the rate of release of Cl^- in the soil, separately from cis-1,3-dichloropropene; trans-1,3-dichloropropene; 1,2-dichloropropane; 2,3-dichloropropene; cis-3-chloroallyl alcohol; trans-3-chloroallyl alcohol; cis-3-chloroacrylic acid and trans-3-chloroacrylic acid. The temperature was 20°C. Part of the results is shown in Fig.4.

The upper two curves show the rate of disappearance of the 1,3-dichloropropenes in the clay-containing and in the sandy soils (the points represent average values for the cis and trans isomers). The lower two curves show the Cl^--release accompanied by the disappearance of the dichloropropenes. In the first week there is a rapid release of Cl^- (although not so rapid as the disappearance of the dichloropropenes) and in the clay-containing soils the Cl^--release was faster than in the sandy soils. After 1 week the Cl^--release rate lags more and more behind the disappearance rate of the parent compounds and

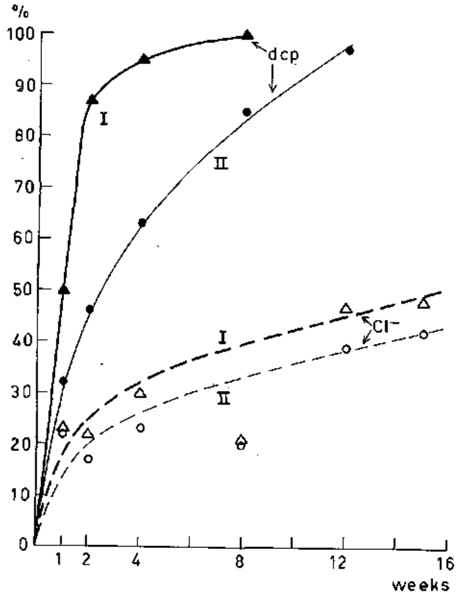

Fig.4. Rates of disappearance of 1,3-dichloropropenes (dcp; drawn curves) and of Cl$^-$-release (dotted curves), in clay-containing soils (I) and in sandy soils (II), when incubated at 20°C.

TABLE IV

Average rate of Cl$^-$ -release from a number of organochloro compounds in soil incubated at 20°C, in percents of initially added amount of organochlorine

Chloro compound	ppm added	Number of soils	Period of incubation in weeks							k_r Cl$^-$*
			1	2	4	8	12	15/16	20	
Cis-1,3-dichloropropene	73	4	22	17	26	19	37	44		0.03
Trans-1,3-dichloropropene	73	4	22	26	26	22?	49	46		0.03
1,2-dichloropropane	69	4	27	26	17	21	41	38		0.02
2,3-dichloropropene	72	3	17	18	23	25	48	37		0.03
Cis-3-chloroallylalcohol	70	6	27	36	41	48	53		66	0.04
Trans-3-chloroallylalcohol	70	6	24	38	42	43	49		63	0.04
Cis-3-chloroacrylic acid	60	6	35	58	55	66	63		86	0.03
Trans-3-chloroacrylic acid	60	6	32	68	48	55	58		86	0.03

*k_r Cl$^-$ is the estimated rate constant for Cl$^-$-release from the second week, expressed in weeks^{-1}

the rate constant is then only about 3% per week. The data obtained suggest that the dichloropropenes are subject in the soil to two relatively fast primary processes, namely a hydrolysis to the corresponding chloroallyl alcohols (a rapid release of Cl^-) and another process leading to a state or to compounds from which the chlorine is released very slowly. It may be mentioned here that Martin (1966) also found a very slow Cl^--release after fumigation of a loam soil with DD. Even after 35 weeks he still found a slowly continuing Cl^--release. This means that results of Cl^--release studies, carried out in soil suspensions as done by Castro and Belser (1966), cannot be transferred to soils in a field situation. (Castro and Belser found a completed Cl^--release in about 7 weeks.)

With regard to Cl^--release, all compounds investigated showed essentially the same behaviour in all soils. An account is given in Table IV. With the chloroallyl alcohols and -acrylic acids (containing no easily hydrolyzable chlorine atoms) the rapid Cl^--release lasted almost 2 weeks before it slowed down to about 3% per week. The course of Cl^--release clearly merits further work aimed at confirming that it is typical and, if so, determining its significance.

The data presented offer a possible explanation for the fact that side-effects of soil fumigation are observed long after the original components have become undetectable by the extraction procedure employed. It is difficult to conclude that chloroallyl alcohols or chloroacrylic acids are responsible, as they degrade so rapidly.

SUMMARY OF THE MOST IMPORTANT CONCLUSIONS

(1) The 1,3-dichloropropenes disappear in sandy soils at 15—20°C (closed containers) at a rate of 2—3.5% per day (an average "half life" of 24 days). In clay-containing soils the disappearance rate is mostly considerably higher (up to about 25% per day at 20°C). There is no marked difference between the two isomers.

(2) The chloroallyl alcohols — assumed hydrolysates of the 1,3-dichloropropenes — are rapidly biodegraded at 15°C in the soil; the cis isomer less rapidly than the trans (average "half lives" in clay-containing soils of about 2 days and less than 1 day, respectively). This explains why so far no accumulation of chloroallyl alcohols has been found after field application of DD.

(3) After an initially more rapid release of Cl^-, this release slows down to about 3% per week. The available data point to some process in the soil, other than hydrolysis, which impedes complete degradation of part of the dichloropropene fumigant mixture to CO_2 and Cl^-.

REFERENCES

Belser, N.O. and Castro, C.E., 1971. Biodehalogenation — The metabolism of the nematocides cis- and trans-3-chloroallyl alcohol by a bacterium isolated from soil. J. Agric. Fd Chem., 19: 23—26

Castro, C.E. and Belser, N.O., 1966. Hydrolysis of cis- and trans-1,3-dichloropropene in wet soil. J. Agric. Fd Chem., 14: 69—70

Leistra, M., 1972. Diffusion and adsorption of the nematocide 1,3-dichloropropene in soil. Thesis Agricultural University, Wageningen, 105 pp. Also: Agric. Res. Rep. (Wageningen), 769: 105 pp.

Martin, J.P., 1966. Influence of pesticides on soil microbes and soil properties. In: Pesticides and Their Effects on Soils and Water. Am. Soc. Agron. Spec. Publ., 8: 95—108

Schwab, G. and Tölg, G., 1964. Beiträge zur Ultramikro-Spurenanalyse organischer Stoffe IV. Z. Anal. Chem., 205: 29—40